Brett Kaufman · Clyde L. Briant *Editors*

Metallurgical Design and Industry

Prehistory to the Space Age

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Editors
Brett Kaufman
Department of the Classics
University of Illinois at Urbana-Champaign
Urbana, IL, USA

Clyde L. Briant
School of Engineering
Brown University
Providence, RI, USA

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Preface

This volume was conceived by a metallurgical engineer (Briant) and a metallurgical archaeologist (Kaufman) following many conversations and joint lectures given to students. We felt that there exists a conceptual arc of connectivity between metallurgical innovations since prehistory, which can best be described as a design process that evolves, grows, and changes from generation to generation of smiths and engineers. The material and physical constraints for metal manufacture that both confound technological advancements and, once their principles are discovered through experimentation, allow for the next wave of innovations are a part of the design process just as much as the cultural and societal tastes and taboos that guide and limit designers as they seek an audience and market for their products.

The chapters herein examine cutting-edge metallurgical technologies and their places in societies through the centuries and millennia. Specific but broad case studies authored by scientists with first-hand industry and/or academic experience make up a major portion of the book. A primary reason for including these studies is to guide materials scientists and engineers to understand the importance of designing their research and inventions with broad societal impacts in mind. The contributions of leading scholars in the world of modern and ancient metallurgy illustrates how innovative engineering design is best constructed through creative materials science and engineering applications that are based on the knowledge of both material properties and economic analysis, while simultaneously envisioning their concepts in their cultural and communal contexts. As a result, the book encourages a design process that emphasizes the anticipation of social tastes and, as such, enriches the historical and anthropological understanding of human technological behavior, while assisting scientists in conceptualizing the relevance and potential acceptance of their discoveries in industry and by society.

Humans are dependent on physical materials to execute their visions of culture and society. More than other material types, innovations in the realm of metallic alloys have set the pace both for human interrelationships and the manipulation of their environments for thousands of years. The exploitation of raw mineral resources and fabrication of engineered alloys embody and symbolize the technological acumen that humans have evolved to possess. Individuals and cultures depend on metals of all types for the functioning of society, from lubricating the gears of economy with metal coinage and surplus, to increasing the speed of mobility through terrestrial and aerospace applications and the speed of information through electricity and electronics.

The following chapters therefore offer technical explanations for the designs and products of a variety of industries, while historic portraits of the major players and innovators offer a lens into the personal sides of some of the most ambitious engineering endeavors, all situated within a societal context. Kaufman draws from economic anthropology, design theory, and archaeometallurgy to provide a survey of non-ferrous, precious, and ferrous metallurgical traditions, from prehistory to the nineteenth century. He synthesizes the physical and aesthetic properties of alloys within their social use contexts in the Old and New Worlds, commonalities between prehistoric, historic, and modern industrial development, and the risks to public health and ecological fallout. Walley introduces the historical context of heavy armour and ballistics before engaging with the experimentation and utility of these technologies in naval warfare. He concludes with the legacy of armament proliferation leading into the era of the World Wars. Gordon offers an extensive look into the recent history of mining and economic geology. He highlights the legacy and ever-growing risks of metallurgical pollution – disasters and mass destruction are becoming more commonplace at both old and active mining sites, and innovations are needed to contain this hazardous waste, in addition to heightened social and corporate responsibility. The intersection of railroad, settlement expansion, and resource acquisition in the American nineteenth and twentieth centuries is interwoven within economic and design contexts to explain the modern (and future) global market of metal commodities. Ono fuses Chinese, Japanese, and English language scholarship to track structural metallurgy from the perspective of bridge building in an overarching technological-historical perspective ranging from the earliest bridges until the mega-bridges of today. Technical appraisals of catastrophic bridge failures attest to the ongoing fragility of the industrial endeavor. Kumar and Padture outline the history of aviation before engaging with specifications of the jet engine, propulsion systems, and other aircraft components. They present the development and capacities of aluminum and titanium alloys as well as nickel-based superalloys and polymer matrix composites used for aerospace applications. They also point out the important role that coatings have played in allowing aircraft engines to run at higher and higher temperatures. Briant focuses on the catastrophic failure of alloyed steel steam turbines that generate electricity for the grid. He illustrates how what may seem to be an obvious solution to a technical problem may later be shown not to have been the root cause of the problem at all. To describe the process by which a solution is reached, he details the concept of technology interaction spheres which facilitate communication and knowledge-sharing mechanisms that tap into market forces, professional organizations, communities of specialists, workers, etc. that can be used to come up with solutions to fundamental technological problems. He also mentions the importance of archiving information, lest it be lost once a problem is solved. In turn, this volume in part serves to attempt the preservation of technological and metallurgical knowledge from various eras and in specific applications, at least as much as is possible via the written word as opposed to physical practice.

Of course, there are many other metallurgy applications not covered in much detail – biomedical and dental applications, furnace structure, nanometallurgy, and infrastructure of biomass and nuclear plants; the list could go on to touch on almost any industrial or artistic field. Metallurgy is one of the most permeating technologies, and research is constantly developing, while the global centers of metallurgical industry and personnel are constantly shifting based on regional production, resources, and demands. What remains constant are the properties of the metals themselves, which is a materials science issue, as well as the design principles underpinning production and industry, which is a social process.

Some chapters contain an acknowledgments section that the authors have used to give thanks where it is due. However, this book itself would not have been possible without the concerted and patient efforts of the publishing team at Springer. Specifically, the editors wish to extend sincere thanks to Brinda Megasyamalan, Brian Halm, Anita Lekhwani, Faith Pilacik, Ania Levinson, Sharmila Sasikumar, and Charles Glaser.

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Providence, RI, USA Clyde L. Briant

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About the Authors

Clyde L. Briant is a professor in the School of Engineering at Brown University. From 1976 to 1994, he was a staff metallurgist at the General Electric Company Corporate Research and Development Center in Schenectady, New York. He joined Brown in 1994. He was dean of engineering at Brown from 2003 to 2006 and vice president for research from 2006 to 2013. His primary research activities have been in the field of mechanical properties and microstructures of metallic materials, and he is currently studying the history of technology, particularly the development of the steam turbine industry. He is a fellow of both ASM International and TMS and is a member of the National Academy of Engineering.

Robert Gordon is senior research scientist and professor emeritus at Yale University, where he taught courses on mineral physics and on energy, water, and mineral resources. While regents' fellow at the Smithsonian Institution, he began a study of historical metallurgy that led to his book, *American Iron*, to field work at smelting sites in the Adirondacks, and in the laboratory, to exploration of the physics and chemistry of traditional smelting processes, the techniques used by metalworking artisans in pre-Hispanic Peru and ancient Nubia, and the metallurgical innovators in the early American republic. He collaborated with colleagues in geology and economics in assessing the consequences of the declining grade of ore minerals and with Thomas Graedel and his industrial ecology students modeling the flow of metals from ore through use and on to recycling or landfill.

Brett Kaufman is an assistant professor in the Department of the Classics at the University of Illinois at Urbana-Champaign, joining the faculty in 2018. He graduated with a PhD in archaeology from the University of California, Los Angeles, before holding a postdoctoral fellowship at Brown University, and an assistant professorship at the University of Science and Technology Beijing where he maintains an affiliation. His research focuses primarily on ancient, historic, and prehistoric science and engineering with a particular specialty in metallurgy (archaeometallurgy), the archaeology and history of the Mediterranean and Near East, and reconstructing the management strategies of past societies facing environmental change and resource shortages. His research has been supported by the National Science Foundation, the National Geographic Society, and the National Natural Science Foundation of China.

Sharvan Kumar is professor in the School of Engineering at Brown University. He received his bachelor of technology degree in metallurgy from the Indian Institute of Technology Madras (1979) and his MS and PhD in materials science and engineering from Drexel University (1981, 1984). He worked at Martin Marietta Laboratories in Baltimore, Maryland (1985–1994), focusing on aerospace materials, including coinventing a family of aluminum-copper-lithium alloys used to construct the external fuel tanks for the US space shuttles. He joined Brown University in 1995 and has since pursued his research interests in structural materials including intermetallic compounds, high-strength steels, refractory alloys, and shape memory alloys. His contributions have earned him the Maryland Distinguished Young Scientist Award (1994), Best Symposium Paper Award twice (1993, 2001) at the First and Third International Symposium on Structural Intermetallics, fellow of the American Society for Materials International (2003), the Japan Society for the Promotion of Science Fellowship (2009), and the Alexander von Humboldt Award (2015).

Kanji Ono received a BE from Tokyo Institute of Technology, and a PhD in materials science from Northwestern University. After a year of postdoctoral research at Northwestern, he joined the faculty of the University of California, Los Angeles, where he became professor of engineering in 1976 and professor emeritus in 2005. He was awarded the HM Howe Medal by ASM International, the Achievement Award by ASNT, the Gold Medal Award by AEWG, and the Kishinoue Award by JSNDI. He is the author of more than 250 publications in materials science, acoustic emission, and non-destructive testing and was the founding editor of *Journal of Acoustic Emission*. His areas of research have included physical metallurgy, strength and fracture of metallic and composite materials, non-destructive testing, and physical acoustics.

Nitin P. Padture is the Otis E. Randall university professor of engineering and director of the Institute for Molecular and Nanoscale Innovation at Brown University. He received his BTech in metallurgical engineering from the Indian Institute of Technology Bombay (1985), MS in ceramic engineering from Alfred University (1987), and PhD in materials science and engineering from Lehigh University (1991). Prior to joining Brown University in 2012, he was College of Engineering distinguished professor and founding director of the NSF-funded Materials Research Science & Engineering Center at the Ohio State University. Padture's research interests are in the broad areas of advanced structural ceramics/coatings/composites and functional nanomaterials/devices, with applications ranging from jet engines to nanoelectronics to solar cells. He is author or coauthor of over 200 publications, which have been cited widely. A fellow of the American Association for the

Advancement of Science and the American Ceramic Society, Padture is editor of the international journals *Acta Materialia* and *Scripta Materialia*.

Stephen M. Walley graduated with a PhD from the University of Cambridge in 1983. He then worked as a research associate at the Cavendish Laboratory. Although retiring in 2014, he is still professionally active in the SMF Fracture and Shock Physics at the Cavendish Laboratory. Over the years, he has coauthored about 100 papers on the solid particle erosion of polymers, ballistic impact on glass/polymer laminates, the ignition mechanisms of propellants and explosives, and the high strain rate mechanical properties of polymers, metals, and energetic materials. He is minutes secretary of the Governing Board of the DYMAT Association. In retirement, he is writing papers and book chapters of a more historical nature, as well as writing up for publication studies performed in recent years by members of the Fracture and Shock Physics Group.

Chapter 1
Anthropology of Metallurgical Design: A Survey of Metallurgical Traditions from Hominin Evolution to the Industrial Revolution

Brett Kaufman

Introduction

A pillar of the human ability to withstand the entropy of nature is found in the harnessing of metals and metallurgical technology. The cumulative ambitions and rituals of metallurgical engineers and smiths since the Holocene (~12,000 years ago–today) have resulted in a planet covered in skyscrapers, bridges, automobiles, trains, and planes. Biomedical implants keep hearts beating and hips functioning, such intricate and profoundly helpful devices that it is worthwhile to piece together the thousands of years of prerequisite efforts that went into making them as well as many other human-made metallic artifacts. Archaeologists picture the first innovators realizing that the eye-catching green malachite and blue azurite copper mineral ores they used for jewelry were somehow related to the native (pure) copper metal deposits associated with the ore. Their early experiments also enabled the concept of currency thousands of years later. In other words, early metallurgy began the long path toward money. Long before coinage, metal came to symbolize surplus and wealth in New World and Old World cultures, independently from each other. It was much more convenient to trade tons of grain via a mutually valued, compact, recyclable, fungible metal than it was to move the intended product. Here, the biological need for sustenance is abstracted into a cultural standard of value, lubricating the economy and increasing speed and ease of market transactions.

Beyond jewelry that symbolized wealth, and ingots that standardized it, some of the first bronze forms to be adopted ubiquitously across Eurasia were weapons (Begemann et al. 2008; Matteoli and Storti 1982; Philip 1989; Tallon 1987). Metals represented wealth, and were also the means to protect and at times to violently acquire it. Metals are both a tool of destruction that has enabled our species to wreak havoc on each other at proportions exponential to what was possible before alloys

B. Kaufman (✉)
Department of the Classics, University of Illinois at Urbana-Champaign, Urbana, IL, USA
e-mail: bsk@illinois.edu

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of war, and a flexible medium to actualize artistic visions. Like other technologies, metallurgy is a compounded science, with incremental successes occurring over thousands of years leading to today's array of metallurgical capabilities.

Remarkably, without cultural transfer, the order of adoption of non-ferrous alloys of the Near Eastern Early Bronze Age (ca. 3500–2000 BC) paralleled that of the Andean Moche and Middle Horizon (AD 100–1000)—pure copper to arsenical copper to tin bronze (Lechtman 2014; Muhly 1973). This is a case of convergent cultural evolution. The thousands of years separating these two traditions are not to be seen as a puzzling gap in time, but rather an astounding convergence as these few millennia are a small fraction of time when considered within the context of the emergence of *Homo sapiens* and the cognitive advances of the species throughout the Middle Paleolithic (Adler et al. 2014; Mithen 1994, 1998; Renfrew and Zubrow 1994; Richerson and Boyd 1989). As discussed below, the invention of lost-wax casting is another example of convergent practices that cultures from both hemispheres share in common without knowledge transfer.

The ancient designers of the Antikythera mechanism, a bronze computational device dated to the second century BC that calculated astronomical and calendrical positions, are unknown to us (de Solla Price 1974; Freeth et al. 2006, 2008). Few personalities responsible for the "eureka moments" of innovation can be identified, with the notable exceptions of more recent inventors such as Henry Cort and Sir Henry Bessemer. The royal coppersmith Hiram, of mixed Phoenician and Israelite descent, is lauded in biblical texts as "filled with wisdom, capacity, and knowledge to make all copper wares. He came to King Solomon and made all his wares" (1 Kings 7:14; Kaufman forthcoming). The goldsmith Amenemhat of New Kingdom Egypt was considered important enough to be buried in a rich tomb, recently discovered (Daley 2017). Carthaginian master smiths, ironsmiths, bronze casters, and goldsmiths were stratified in a hierarchy of technical specialties and ranks, some of them often wealthy enough to commission their own dedicatory inscriptions in stone to their goddess Tanit and god Ba'al Hammon (Kaufman 2014). But the lack of historical records for the vast majority of ancient nameless geniuses of metallurgical science is inversely correlated to the profound respect reserved for them and their work, personified in mythical inventors and/or fictional alloys with unearthly properties from Orichalcum of Atlantis (Caley 1964; Eaton and McKerrell 1976, 184) to Mithril of *Lord of the Rings* (Tolkien 1954), to the *Valyrian* steel of *Game of Thrones* (Martin 2003), and to Rearden Metal of *Atlas Shrugged* (Rand 1957).

There are several excellent syntheses and seminal works of the metallurgical past much greater in detail than this chapter but which inform it fundamentally (*for general*, Bachmann 1982; Craddock 1995; Craddock and Hughes 1985; Craddock and Lang 2003; Killick and Fenn 2012; Mei and Rehren 2009; Rehren and Pernicka 2008; Roberts et al. 2009; Roberts and Thornton 2014; Scott 1991; Shilstein and Shalev 2011; Smith 1981; Tylecote 1962; Wertime 1973; Young et al. 1999; *for non-ferrous*, Craddock 1998, 2017; Muhly 1973, 1985; Scott 2010; *For ferrous*: Hošek et al. 2000; Humphris and Rehren 2011; La Niece et al. 2007; Scott 2013; Soulignac 2017; Wagner 2008; Wertime and Muhly 1980; *for precious*, McEwan 2000; Morteani and Northover 1995; Ramage and Craddock 2000; *for surface treatments*, La Niece and Craddock 1993). In this volume, we broach the humbling task of tying ancient and historical metallurgy to modern advances, uniting the discipline via the theoretical and applied concepts of design.

The design process is inextricably and intrinsically linked to culture, political economy, and environment. Teasing out the social science and humanistic aspects of the engineering process through design concepts is a stimulating methodological challenge with the conceptual and physical remnants of past technological systems deeply embedded in artifacts. Anthropological and historical studies of technology and materials science conceptualization of societal taste can benefit mutually through theoretical and applied design. In an overarching sense, design begins with a *concept* that is influenced by societal tastes, market or gift exchange forces, available technology, investment climate and socioeconomic organization, previous artistic or industrial design, and emotions and aesthetics. Once these are formalized, *development* begins, which includes *experimentation*, materials selection, risk assessment, sketching and modeling, and in some contexts environmental testing and sustainability. Finally, the details are specified, a prototype is generated, and *production* commences. Design is an assembly of choices made by the smith and user or engineer and client within a "system of technology," with a final product reflecting a palimpsest of individual and cultural tastes and demands (see Briant chapter, this volume; Ashby and Johnson 2014; Dym et al. 2014; Kingery 2001; Radivojević 2015; Roberts 2014, 435; Roberts and Radivojević 2015; Schiffer and Skibo 1987; Whiteley 2004). Viewing ancient artifacts in their social, economic, and technological contexts—or trying to understand why cultures made what they made and consumed what they consumed—is greatly aided by design theory.

Toward a goal of seeking methods to identify the behavioral underpinnings of object design, in this chapter the intention is to set the chronological framework for metallurgical benchmarks worldwide using comparative data acquired from anthropological methods of archaeology and ethnography, and historical and epigraphic texts. Archaeologists often debate as to the exact calendar dates and ranges for archaeologically attested cultures. The dates provided below reflect the most recent or consensus dating schemes of which I am aware. Following an anthropological treatment of human behavior and technology through materiality, surplus, and sociopolitical organization and hierarchy, pre-modern metallurgy is presented through the properties, culture and design requirements, production specifications, and details of manufacture of alloys in both New and Old World contexts, concluding with the ecology of mining, industry, and resource management.

The result is a semi-encyclopedic archaeometallurgy referential survey within technological and behavioral contexts. Focus is kept mostly on design or the interface between cultural choice and technological capability, with expanded discussion of case studies that highlight the experiments and adoptions of alloys and production techniques that resulted in specific properties and outcomes. Of course, much is left out in the way of examples, and technical explanations of thermochemical processes and specifications of furnace designs are limited. Extractive metallurgy and smelting technologies are superficially covered here. Not discussed in any detail is metallography, phase diagrams, isotopic provenience, or experimental analysis—in short, the methodologies of metallurgical epistemology. For more detailed information, the reader can turn to other chapters in this volume, as well as the references cited section, within which is found a great diversity of comparative metallurgical traditions as well as archaeometallurgical methods. In writing such a survey, there is always a risk of being so broad as to cover nothing in a meaningful way, but I hope that in any case the reader may find kernels of relevant synthesized information below that inform both practical design processes and anthropological engagements with technology.

Behavioral Metallurgy: Materiality, Surplus, Sociopolitical Hierarchy

There are an infinite number of potential alloys. Based on elemental composition, they can often be grouped into distinct categories, for example, a true tin bronze is 10–14 wt% tin and the remainder copper; steel contains less than 2.1 wt% carbon and the remainder iron and often other alloying elements. More broadly lumped together, with compositional flexibility, are brass (zinc and copper), pewter (tin with lead or antimony), *paktong* (copper, nickel, zinc), electrum (gold and silver), *tumbaga* (gold and copper), stainless steel (steel with varying constituents including chromium, molybdenum, nickel, manganese, aluminum, and titanium), and superalloys (cobalt and nickel based), and the list goes on and necessarily exceeds the limits of this chapter. There are tens of thousands of industry-certified standard alloys as designated by entities such as AISI, SAE International, and ASM International, in addition to proprietary alloys and treatments of private companies and militaries that are sometimes later made public (Doig 1998; Kiser et al. 2005; Shoemaker and Crum 2000). Categorization of metals is useful because with these names are associated the various properties that make these alloys important to various communities and individuals. Salient properties include mechanical (strength, malleability, weldability, ductility, hardness, tensility, sharpness), aesthetic (luster, appears like gold or silver), acoustic (ring, resonance, bass), thermodynamic (fuel efficiency), and electrical (resistivity and conductivity).

Materiality and Early Experimentation

In anthropological studies of technology, there is often a struggle with the idea of functionality (Ingold 2012; Yener 2000, 9). A general dichotomy is perceived between luxury/ritual and useful/functional applications of material types. But for metals (and probably other material types), it is impossible to assign alloys as either ritual or functional, since these terms do not really convey the intricate ways in which metal-using cultures have employed them in daily customs. As Trigger (2003,

67) points out, artifacts and economic behaviors "acquire their functional significance from the manner in which they are related to social organization." Objects must meet a need, and there is a risk that a reliance on traditional ritual versus functional categories prevents fleshing out multi-dimensional interpretations of human behavior. Materials often serve to facilitate social transactions (currency, jewelry, abstracted value) and are therefore functional, even if they are not used to plow and fight, or for mechanical or high-stress purposes (Dobres 2001; Dobres and Hoffman 1994). In a bid to change this ritual versus functional construct and make room for interpretive nuance, there is a latent trend in the social sciences to explore the agency or agentive powers of materials (Dobres and Robb 2000; Hodder 2012; Meskell 2005). Although materials do have their own thermodynamic, aesthetic, acoustic, and mechanical properties which thereby influence or limit human behavioral options, they are not socially cognizant, and therefore all the power they possess is given to them by humans for use in human society.

Material things are imbibed with value and become symbols of social processes (Papadopoulos and Urton 2012). Mineral resources such as precious metals are then used to reinforce and communicate the hierarchical relationships that would have existed even without the possession of gold and silver. However, any claim that things themselves have some sort of conscious agency implies the ability for active strategy, and subsequently serves as a distraction from developing models to understand the cultural creation of value by different peoples and communities. In other words, focusing too intently on or giving materials too much of their own agency strips individual agency from those same people who made the artifacts, even while the specific properties and availability of the artifacts or raw materials provide constraints and feedback to human behaviors.

In tandem, the industrial or technological ambitions of prehistoric or modern, ethnographically documented cultures are sometimes seen by scholars as of secondary importance to their cultural and religious identity, or at best as separate and unintegrated. This Western scholarly bias, common over the past few decades, may come from a good-intentioned effort to make up for a colonial attitude that marginalized other cultures and imposed a Western standard of capitalistic industriousness. But, as Skibo and Schiffer (2008, 23) rightly state, the belief that traditional ethnographic or ancient societies are so different from the modern world that logic, cost, or profit is frequently or always less important to them than social and ideological factors *is* essentially a Western colonialist view, which has tended to see non-industrial cultures as primitive and superstitious. For example, rituals are employed by some African blacksmiths during a smelt in order to succeed in the creation of a good steel (Childs 2000, 221–222; see also Iles and Childs 2014 and van der Merwe and Avery 1987 for discussions of the "science versus magic" paradigm). Here, spirituality and industry cannot be separated, and there are other examples of how culture is shaped through industry (Mrozowski 2006; Schmidt 1997a, b).

For the purpose of metals, materials science terminological categorization of alloys based on their properties is descriptive and useful in an anthropological behavioral approach—namely, what properties a metal has and how this impacts human use of the objects across cultures, and across species. An appropriate first property to discuss is that of aesthetics, as the neurobiological attraction to shiny native metal and colorful ores marked the deep time commencement of metallurgical science.

The ability that humans have to see the luster and diverse colors of metallic objects is the synaptic underpinning for the value that our species places on metals, giving this shiny, colorful material-type "cultural potential" (Tuniz et al. 2014, 33). The sociobiological propensity of some hominins to recognize and use shiny objects is an area that is relatively understudied, but *Homo sapiens* is not the only primate species to differentiate colors. The evolution of trichromacy is not limited to *Homo sapiens* and helps explain the archaeological evidence left by phylogenetically related species (Neanderthals, *erectus*) that used metallic minerals presumably for their color properties (Prescott 2006). In other words, the biologically selected ability to discern between colors of potential food, specifically frugivory (fruit eating) (Osorio and Vorobyev 1996), resulted in an unintended cultural attraction to red, green, blue, and other polychromatic mineral ores and native metals (Nathans et al. 1986). Furthermore, gemstones such as rubies, emeralds, and amethyst are chromatically differentiated from similar mineral crystallizations through metallic impurities such as chromium, vanadium, aluminum, and iron.

It is important to note that early attraction to metallic materials and their manipulation by primates is not technically considered metallurgy, which is defined by the extractive processes of metals from their ores, and including such practices as cold- and hot-working, annealing, folding, and decorative shaping of native metals. The examples given here are rather intended to introduce the optic capabilities of hominins to identify metals and the cultural choice to keep them. The earliest evidence for intentional hominin collection of metal-bearing colored minerals may be the Makapansgat pebble, a reddish-brown jasperite or banded ironstone (Bednarik 1998). Although this artifact was not recovered in controlled archaeological excavations, it was thought to be associated with the remains of *Australopithecus africanus* making it about three million years old (Dart 1955). There are always methodological problems that come with basing conclusions on a single artifact.

There is much more widespread evidence for the use of red ocher by *Homo ergaster* and *Homo erectus* in tandem with Acheulean chronology—it is not certain what these pigments were used for, but *ergaster/erectus* certainly distinguished this mineral from other, more workable minerals used to make tools (Oakley 1981; Schmandt-Besserat 1980; Wreschner et al. 1980). *Homo neanderthalensis* used red and black hematite, goethite, and manganese dioxide ores, typically smearing or storing red pigments in shells in what was likely a symbolic act (Boyd and Silk 2012, 295; Oakley 1981), although Duarte (2014) argues for a health benefit in mixing iron with seafood. The early evidence for *Homo sapiens* using ocher dates to around 160 kya (thousand years ago) (Duarte 2014). Red ocher is today considered by the Kenyan Maasai Moran as having lion-repellent properties (Paul Meiliara, personal communication).

As archaeological evidence is preserved in a temporal bottleneck—meaning recent finds are better preserved than older ones—it is not known just to what extent the earliest utilization of metallic minerals was commonplace. The proliferation of the cultural value placed on metals is seen increasing throughout the Holocene (since ~12 kya) at sites such as Shanidar Cave and Zawi Chemi in Iraq, Hallan Çemi in Turkey, and Rosh Horesha in Israel. Ores such as the copper-bearing mineral malachite, as well as ocher, were cultivated for jewelry, pendants, and pigment (Bar-Yosef 1992, 29; Killick 2009, 2014, 19; Lehner and Yener 2014, 538; Roberts et al. 2009, 1013). Greenstone beads and powdered copper minerals such as malachite, azurite, and chrysocolla were used for cosmetic and decorative purposes across a wide swath of Eurasia during the Pre-Pottery Neolithic (eighth/seventh millennia BC), including Southwest Asia and the Balkans (Bar-Yosef Mayer and Porat 2008; Golden et al. 2001; Hauptmann et al. 1992).

By 5000 BC metal-bearing minerals were being smelted, the earliest current evidence coming from the Balkans via copper-smelting residues (Radivojević and Rehren 2016; Radivojević et al. 2010). With early native copper working and later smelting, mechanical properties were now added to the aesthetic concerns that originally brought metal-bearing minerals to the attention of humans. Due to the inexhaustible number of potential alloys, experimentation has always played a major role in metallurgical design and innovation, and this holds true for the first smelters of the mid-Holocene. The occurrence of other metals is discussed below, but for copper, the metal in its native (pure) form is often geologically associated with its mineralized ore deposits (Craddock 1995, 94; Killick 2014, 19–20).

It is reasonable to surmise that a piece of malachite jewelry was intentionally or accidentally dropped into an open-fire pit, the smelted product recovered and seen to be all but identical to the same native coppers found with those minerals. This realization is the first theoretical cognitive leap toward extractive metallurgy. Pre-Pottery Neolithic lime plaster production would also have provided the necessary pyrotechnological backdrop for early smelting experiments (Hauptmann et al. 1992). The archaeological record shows us decades, centuries, and millennia of the alloys that wound up being chosen for their properties—much rarer is to recover remains of what must have been the feverish days, weeks, months, and years of experimentation of any available minerals that might yield metal upon a smelt (Roberts and Radivojević 2015; Thornton 2014, 669; Yener 2000, 29). From a behavioral design standpoint, experimentation is akin to “spurts of invention” that result in a “cascade” of production and its corollary cultural acceptance, and later archaeological ubiquity (Skibo and Schiffer 2008, 3).

Surplus

Nineteenth- and early-twentieth centuries interpretations of the development of statecraft and sociopolitical complexity frequently conceived of evolutionary adaptation as a linear process trending toward a modern Western level of sophistication, with metallurgy seen as a hallmark of civilization along with such endeavors as agriculture, writing, urbanism, and monumental architecture (Childe 1944, 1951; Engels 1884; Morgan 1877; for Herbert Spencer see Perrin 1976). In today's (ideally) more scientifically rigorous and (relatively) more culturally sensitive anthropological archaeology, the development of cultures and their individual traits is not seen as linear and progressive or as a contest between moral codes, but rather as reflecting diverse adaptive mechanisms that communities practiced to survive and fluoresce according to their unique environmental and/or cultural circumstances (Brumfiel and Earle 1987; Earle et al. 2015; O'Brien and Holland 1992; Shennan 2002; Stanish 2004). In the Old World, extractive metallurgy preceded urban-based political complexity, or states, by several millennia (Lehner and Yener 2014, 530; Radivojević et al. 2010), showing metallurgical practice does not necessarily require hierarchical society to function (Erb-Satullo et al. 2017). Conversely in the Andes, innovations in copper smelting were achieved under the archaic Moche state (Lechtman 2014, 376). In the American Pacific Northwest, complex hunter-gatherers relied on worked coppers for a myriad of social and economic functions (Boas 1966), discussed below. On the other hand, there are several examples of material-exchange-based cultural organization in which metals did not play an emic role. In turn, metallurgy is not a prerequisite harbinger of civilization, but it may be argued that the adoption of metal in pre-state societies was a factor in the promotion of hierarchy, market liquidity, and speed of information via efficient communication of value that eventually facilitated state formation. Although every culture is differentiated by its particular emic (internally developed) and etic (externally imposed) circumstances, some behaviors are universal and can be witnessed within every culture, such as surplus hoarding.

Surplus hoarding behaviors have evolved to be so common to every individual that groups must sanction them through cultural mechanisms of reward or taboo (Lee 1990, 1992, 39–40). Surplus or differential wealth accumulation may be considered a universal behavior in all societies. Theoretically, it is explainable as a cultural response to risk and uncertainty, or to an evolved psychology that enhanced human fitness in the Middle to Upper Paleolithic. Regardless of the causes, such accumulation that violates the norms of egalitarianism in hunter-gatherer societies requires a response. Some groups glorify it; others discourage it (Brooks et al. 1984, 299; Hayden 2011), showing that it is a behavior that has clearly been selected for since the Middle Paleolithic. Heterarchical and hierarchical groups create taboos or leveling devices (cultural overrides) that sanction how surplus is to be acquired and distributed.

Surplus comes in two broad conceptual categories, subsistence surplus versus abstracted surplus. Subsistence surplus allows survival, by stockpiling nutritional or protective resources, or "social storage" (Halstead and O'Shea 1982), akin to animal hoarding or "practical storage" (Ingold 1987; Sutton and Anderson 2014). One example of communally protected surplus in an urban societal context is that of cows in India. There is ideologically strong stigma and penalty associated toward interfering with this renewable subsistence resource (Harris 1966; Sutton and

Anderson 2014, 28). For some ethnographically documented hunter-gatherer communities, ostentatious displays of individual prowess are so taboo that sometimes the successful hunter is barred from a share of the meat (Hayden 2011, 103). As societies become hierarchical, subsistence surplus is used as "staple finance" to exert control over commoners, the value of the staple eventually represented abstractly as "wealth finance" (Earle 1997, 74).

Abstracted surplus or symbolic, "convertible" wealth (wealth finance) allows a market economy characterized by rapidity of transactions and liquid assets, gift exchange, and barter (Knapp 2013). Abstracted surplus is a prerequisite condition for social hierarchical splintering and the formation of inequality, as wealth is used by archaic leaders and managerial elites to finance a political economy transitioning from egalitarian or communitarian to indebted and productive (Earle 1997, 93; Saitta and Keene 1990; Stanish 2004, 2010). Metal is arguably the most materially ubiquitous type of abstracted surplus, but this has also been expressed through many other material forms, for example, whale teeth in Fiji (Sahlins 2013), Iroquois wampum beads (Graber 2001), and Channel Island shell bead currency (Arnold et al. 2016; Arnold 1993).

In many cultures of varying sociopolitical organization, metal is an essential component to the functioning of a surplus economy. Since many cultures disconnected in space and time share the trait of metal use, and since alloys in their inanimateness possess identical properties no matter who made them, metal as a surplus wealth symbol is therefore a useful proxy in the attempt to understand comparatively the intricacies of cultural choice as it is expressed through technology, economy, ritual, and art. Trigger (2003, 48–49) rightly points out that metals are "an abstract concept of wealth to replace control of land or crop surpluses" and made investment in other endeavors easier—essentially metals grant a certain speed of transmission that is prerequisite to a market economy.

Metals are a convenient and practical way to symbolize—or monetize—surplus that can find a nutritional parallel in agricultural surplus (see Morehart 2014 and Morehart and De Lucia 2015 for recent discussions and intellectual history of surplus in general, and agricultural surplus in particular). Some examples of pre-coinage metal standardization and monetization are found in Early Bronze Age copper ingots of the Levant (Hauptmann et al. 2015), the copper *Ösenringe* of the European Bronze Age (Earle 1997, 26; Krause and Pernicka 1998; Vandkilde 2003), the oxhide ingot trade of the Mediterranean Late Bronze Age (Lo Schiavo 2009), the epigraphic equivalencies of silver shekels to various foodstuffs in Ur III Mesopotamia (Englund 2012), and the arsenical copper axe-monies widely distributed from the Andes up through Ecuador and Mexico (Hosler et al. 1990). These examples are characterized by the standardization and at times fungibility of the metal objects, which enabled fluid transactions of wealth over long distances. One of the most striking examples of a pre-coinage metal-based economy, known to scholars due to extensive ethnographic, archaeological, and archaeometallurgical documentation, is that of the Pacific Northwest phenomenon of coppers or copper shields.

Wealth Finance and Sociopolitical Hierarchy in the Pacific Northwest

The cultural system of the American Pacific Northwest has been the one of the singular foci of anthropological research since the field was founded, due in part to the work of pioneering anthropologist Franz Boas mostly among the Kwakwaka'wakw (Kwakiutl; Boas 1966). The sociopolitical organization and hierarchical structuring of the regional cultures as witnessed by early researchers are today characterized as that of "complex hunter-gatherers" or "affluent foragers" (Arnold et al. 2016; Arnold 1996; Moss 2011). These characterizations stem from the fact that state-level society did not form in the region, and neither did agricultural intensification. Instead, a complex system of clans and chiefdoms thrived from Oregon to Alaska, with material correlates to surplus storage and hierarchy formation beginning around 1500–1000 BC (Ames 1994, 216). Abundant natural resources were harvested through hunting and gathering, with salmon being the most important and ubiquitous, but supplemented by a diverse basket of other marine and terrestrial mammals (seals, sea lions), other types of fish, and shellfish through clam garden mariculture (Cannon and Yang 2006; Lepofsky et al. 2015). By 1000 BC, village life became more common with evidence of fish weirs at mouths of salmon streams, and by around AD 1 at the settlement of Marpole, early evidence of hereditary social inequality is seen through status and wealth items including differential house size (Coupland et al. 2009; Matson and Coupland 1995).

The Pacific Northwest cultural complex demonstrates that it is not agriculture in particular which drives complexity and hierarchy formation, but surplus and the competition over it, in this case salmon and the ability to smoke and preserve it (Ames and Maschner 1999, 13; Hayden 1990). Complex hunter-gatherers of the Northwest Coast were largely arranged in hierarchies divided between slaves (mostly war captives) and free people. At the highest rung were chiefs, followed by chiefly supporters or other title-holding individuals, followed by commoners or people without titles (Ames 1981; Ames and Maschner 1999). The economic system that underpinned social hierarchy was comprised of financial mechanisms that facilitated complex society, reflected dramatically in the potlatch, or the conspicuous consumption of surplus wealth through feasting and destruction in fire at communally sanctioned events. The potlatch, banned by the Canadian government from 1885 to 1951, was an essential element in the social organization of Northwest Coast societies. It was the means through which individuals could demonstrate their influence and ability to acquire possessions, or failure to do so (Smith 2015). The fungible unit of value among the Kwakwaka'wakw was a blanket, traded by the thousands. Through systems of interest and indebtedness, individuals could lose or amass fortunes, the latter a necessary criterion to rise in rank and influence.

Leaders who sought to outdo one another, either to gain followers for labor or warfare, would burn at the potlatch surplus goods such as oil, coppers, or other items in order to display the depth of their wealth, converting it into prestige (Suttles 1968, 67). The potlatch involved consumption of resources through two means: feasting and destruction. The feasting served to indicate how much food wealth could be provided to dependents. The destruction was meant to indicate how much wealth in general the individual had. The competition was stiff—chiefs had to prove their prowess for accumulating wealth, because due to close sanguine relatedness people could choose to follow several different chiefs with whom they had equal ties of kinship (Sutton and Anderson 2014, 181–182).

The maintenance of a surplus economy was spurred by the potlatch, because the amount of goods one property owner was willing to destroy was a signal to other property owners as to how much property the potlatcher had, meaning they could get an idea of what percentage of property another was willing to destroy and how much property the destroyer believed himself capable of generating (Boas 1966). This enabled competition and continued productivity. With so many fresh and preserved subsistence surplus resources available, the people of the region adopted a metal-based wealth finance economy transacted through the trading of coppers (Fig. 1.1). The copper or copper shield was the most highly valued item of symbolic or abstracted wealth in relation to size and frequency, not gold. Coppers were so

Fig. 1.1 Tlingit copper with hawk iconography, dating to sometime before 1876. The t-shape with flared/axe-form upper section is typical of Pacific Northwest coppers: length 94 cm, width 56.52 cm, and height 0.15 cm. (Smithsonian 20778; Boas 1897; Jopling 1989, figs. 4, 56; Ames and Maschner 1999, fig. 37; line drawing by Katelyn Jo Bishop)

fundamental to the observed ethnographic socioeconomic transactions that defining the ways that they were used provides a lens into the societal mechanisms of the region. Copper sheets were hammered into iconographic shapes and intricately decorated, folded, annealed, and hot-worked (Jopling 1989). Each copper had its own unique tradition which in part determined its value in blankets (which required labor to produce, this labor converted into wealth symbolized by a copper), sometimes numbering in the thousands (Boas 1966). Reconstruction of the Pacific Northwest financial system and the transactive mechanisms executed through coppers is greatly benefited from descriptive ethnohistoric accounts.

Blankets, canoes, coppers, and eulachon fish oil ("grease feast") would be burnt and destroyed in the potlatch. Coppers played an integral role in the potlatch and facilitated competitive displays of prestige and shaming. An intricate system of rivalry underlay the potlatch, which gave individuals opportunities to one-up other chiefs. If a copper was broken and a piece given to a rival, the rival must pay for it, or else break his own copper and throw them both into the sea. If a chief perceived his grease feast was greater than his rival, he could refuse a spoon of grease and run out to get a copper to attempt to emasculate the other chief, who can prevent this by tying his own coppers to house posts.

Boas (1966) relates several other social interactions facilitated through coppers not during a potlatch. Coppers would only appreciate in value, and even if coppers were broken, they could represent partial value. If the pieces were reunited to a whole, then the copper would be worth much more than ever before. With every trade the value of the copper increased, meaning that more blankets would be produced by the lower levels of the clan or tribe. Coppers were loaned out to be repaid with interest. Young boys were expected to raise capital through coppers, a type of economic initiation rite. Coppers were buried under houses thereby increasing the value of a house. Quick sales could be transacted for half price, thereby increasing market liquidity. Coppers could be used as promissory notes for later feasting. A chief could never refuse to buy a copper if a sale was offered; otherwise he would lose face. If he was the seller, out of modesty, he could not negotiate for a better deal (i.e. more blankets for the copper), but his friends could bargain on his behalf. Beyond these specific economic functions, copper in various forms had immense spiritual value as well, and was known for its healing properties (Acheson 2003, 224–227; Cooper 2012).

There have been debates as to whether coppers are an indigenous economic tradition or whether they were introduced or greatly increased due to European trade copper (Jopling 1989; Keddie 1990). This follows from a broader skepticism as to whether or not the social interactions Boas witnessed were relatively new and caused by the appearance of Europeans, as opposed to being related to pre-contact societal mechanisms (see Lightfoot et al. 1998, 202 for relevant theoretical discussion). Ethnographic observations can only be applied in the interpretation of past practices using archaeological data in specific circumstances (Lane 2005; Whiteley

2004; Wylie 1985). For the purposes of the current discussion, it is necessary to remember that studying adaptive cultural practices necessitates an understanding that identities and behaviors are never static. For example, it is possible that trade in iron and other metal goods crossing over the Bering Strait into Alaska from Siberia or China has occurred intermittently for thousands of years (Cooper et al. 2016; Keddie 2006). Clearly this arctic network is a different socioeconomic case than historical European contact, but it does show that innovations in technology that we see in the archaeological record are a result of a design process that incorporates feedback from dynamic and hybrid cultural and technological processes (van Dommelen 1997).

For the specific case of coppers, although the availability of copper to peoples of the Pacific Northwest seems to have greatly increased following trade with Europeans in the form of copper sheet or scrap from copper ship sheathing, the copper tradition is known to stem from pre-contact antiquity evidenced by descriptions in oral histories such as that of the Tsimshian legend of Tsauda and Halus reported by Boas (1916; Staniforth 1985; Wayman et al. 1992, 5). More recently, archaeological evidence has also shown that the use of native copper has a great antiquity in the Pacific Northwest, far preceding European contact, copper material being used as a status symbol for at least 2000 years but likely even longer (Acheson 2003; Burley 1980, 27–28; Cooper 2006, 63, 2011; Cooper et al. 2008, 2015; Cybulski et al. 1992, 63; Franklin et al. 1981; MacDonald 1981; Wayman et al. 1992). In any case, the introduction of European metal syncretized quite well with indigenous metallurgical traditions and usage, and a great demand for iron and copper characterized trade between coastal peoples and European traders from the eighteenth century AD (Beals 1980; Cole and Darling 1990; King 1981; Lang and Meeks 1981; Wayman 1993; Wayman et al. 1992, 4). If what Boas was observing was a society at the extreme edge of disorder due to European encroachment, then the coppers are symbolic of the adaptation of pre-contact value to a new economy through a traditional medium.

The case of the coppers of the Pacific Northwest is a graphic example of how metals can take on extremely high societal and economic significance. The abstracted surplus unit of value in the copper was not truly fungible in this case, but was infused with unique histories that made each object so highly valued that market transactions, labor costs, and the hierarchy system itself were pegged to coppers and expressed by them. In most ancient and historical case studies, we see abandoned foundries, tombs filled with metals, factories, etc., and may not consider the dynamic design process behind the objects. A case study such as the Pacific Northwest informs theoretical models as to how metal has come to represent symbolic wealth across numerous cultures, how the conception of wealth in the form of copper remained constant despite radical and grave sociopolitical upheaval, while serving as a reminder that excavated metallurgical debris and hoards were once saturated with intricate socioeconomic and cultural processes and values.

Non-Ferrous Alloys

The aesthetic and cultural properties of metals were introduced in the previous section. Now a fuller treatment of the physical properties and cultural values of metals is presented with emphasis on chronology and regional variation. The following sections interweave discussions of alloy type, geological occurrence, regional scale technological innovation and adoption, culturally derived design constraints and audience/market desires for alloys and objects, production processes, and chronology, with non-exhaustive comparison of metallurgical traditions from both Old and New Worlds. To begin, the non-ferrous metals considered are copper, tin, arsenical copper, lead, and zinc, and alloys thereof.

Reduction Principles

The process wherein metals are smelted from ores is called extractive metallurgy. Much of the difficulty in ancient smelting was not so much an inability to achieve high temperatures, which were often possible. Challenges involved (1) maintaining constant heat for long periods of time and (2) achieving a reducing environment (carbon monoxide-rich environment) in the furnace in order to reduce oxide from the metal.

In addition to metals such as iron, copper, tin, lead, silver, etc., metalliferous ores contain other materials called gangue. Gangue is an all-encompassing term that includes any unwanted mineralization that must be removed during the smelt, including, for example, calcium if the ore is derived from a limestone formation, silica if the ore occurs with quartz, sulfides, chlorides, and, quite commonly, carbonates and oxides. Sulfur-rich ores are often roasted before the smelt. The sulfur content is vaporized, leaving a more manageable oxide with fewer impurities introduced into the alloy. Calcium and silicon gangue are often extracted via the use of a flux, and the unwanted waste is tapped off in the form of slag (Iles 2014; Killick and Miller 2014). In the case of mineral oxides, it is essential to create a reducing atmosphere in the furnace so that the metal is deoxidized. This is achieved through the formation of carbon monoxide from the charcoal in the furnace (Craddock 2000a, b). These reduction principles are to a certain extent applicable to both ferrous and non-ferrous ores, while some metal-dependent specifics of smelting and reduction are presented below when relevant.

Pure Copper

Copper is extremely rare in the Earth's crust, relative to the levels exploitable by humans for most of their existence (Killick 2014; Table 2.1). Copper is usually deposited in various layers of sulfides and oxides/carbonates, and also occurs as a native metal. In North America, Lake Superior and specifically the Upper Peninsula of Michigan maintain some of the highest concentrations of native copper and copper ore on the planet. In fact, this is the reason why smelting was never developed on the continent—there is such an abundance of native copper that it was never tapped out like it was elsewhere in the world, necessitating the adoption of smelting technologies for continued copper supply. This is a case of environment or geology determining cultural adaptations and technological outcomes. Among North American cultures, it would have been a waste of energy and time, labor, and fuel to smelt copper ores.

The beginnings of the North American tradition are traced to the Old Copper Complex (or Culture) dating from around 4000 to 1000 BC, spread across the Great Lakes (Ehrhardt 2014, 312, fig. 13.1). Comprised of several distinct mobile hunter-gatherer groups, they also shared a common metallurgical tradition of cold-working technology and artifact style. There was no casting, melting, or smelting, but the production process involved fabricating directly from copper nuggets, which were hammered, flattened, and repeatedly folded over and bent into plates, sheets, and blanks. Sharp edges were hammered out and annealed. Desired were relatively large, utilitarian artifacts. This stood in contrast to Hopewell forms (100 BC–AD 400) which saw a proliferation of copper being used for ornaments and jewelry, traded as a raw material or a finished product, and hammered into stock. Iron and native silver were incorporated as overlay, and high arsenic native copper was purposefully selected (Ehrhardt 2014, 317; Wayman et al. 1992). Now a prestige good possibly manufactured by full-time specialists, the display of wealth copper is another line of evidence for the emergent hierarchies characteristic to this period and the Mississippian (AD 900–European contact; Childs 1994; Ehrhardt 2014, 314–318; Pauketat 2007).

In light of the earlier case study of the metallurgy of the Pacific Northwest, it is clear that North America had at least one center, if not multiple centers of metallurgical innovation, which either slowly spread across the continent, or otherwise due to the widespread abundance of native copper, several different groups adopted this material type independently. This metallurgy is characterized by extensive deformation and shaping through cold-work, and finishing with annealing. The tedious and exacting cold-working and annealing metallurgy of North America continuously developed over thousands of years, often sharing iconographic themes, and in the later settled complex societies of eastern North America, the long-standing ritual importance of copper material is seen in its proliferation as buried offerings in earthworks (Trevelyan 2004, 2).

Native copper can occur as small workable lumps, but also as massive boulder-like objects weighing several tons (Maddin et al. 1980, 212). Ores, or mineralized metals, are defined based on a sliding scale of how economical it is to extract the metal, meaning that what is called an ore this year may not technically be an ore next year (Killick 2014). Copper sulfides are at times enriched in other minerals such as arsenic and are found in the deeper levels of ore deposits, which are capped at the surface by a gossan of iron oxides, weathered and oxidized copper carbonates, and native copper (Killick 2014, 19). Oxidation and weathering to produce coppers in native, oxide, and carbonate forms mostly occur through the uppermost level of minerals interacting with water, but also as the result of bacteria known as *Thiobacillus ferrooxidans* (Charles 1980, 159). Leaching from the surface that trickles down into the rest of the deposit can cause secondary sulfide enrichment which results in the formation of different types of mineral compounds.

Early metallurgical use of copper was practiced on native or pure copper nuggets that would be cold-worked and deformed into shape, often hammered to give a sharp edge, annealed, and even melted down and cast. Some examples of early ore jewelry are given above, but here the focus is primarily on the early working of copper. There has been a running debate as to whether the earliest copper artifacts are from the work of native coppers, or if people began smelting almost immediately once copper was recognized as a valued material (Coghlan 1940; Killick 2014, 20; Maddin et al. 1980; Thornton et al. 2009b; Tylecote 1962, 27). The resolution of this argument is important for the study of early pyrotechnology, but for the purposes of mechanical properties of the copper, it does not really matter.

The main risk for pure copper objects is having different impurities in the alloy matrix, such as sulfides or slag stringers, which will make it susceptible to a higher rate of failure under mechanical stresses than a highly pure copper. An unworked, hammered, or annealed native copper piece can have upward of 99.9 wt% copper (Cooper 2012, 565). However, chemical purity of copper is not a definitive criterion for distinguishing between native and smelted copper, especially since native coppers could be melted down and therefore take on impurities from the crucible, pit, or furnace environment. Likewise, smelting a copper oxide or carbonate can yield a highly pure copper (Maddin et al. 1980, 214). Sometimes it is quite clear when copper objects are the result of a smelt, due to the vast amount of impurities remnant from the ore body (Pernicka et al. 1997; Segal et al. 1996–1997), or the presence of slag and non-metallic inclusions (Wayman et al. 1992, 14, but see Maddin et al. 1980, 214–215). Impurities are not always undesired in a copper alloy for pre-modern applications where high-grade purity is not necessary (in contrast to the pureness needed for electricity grade copper wiring; also see Schiffer 2006). For example, lead increases castability, and nickel can increase strength, hardness, and corrosion resistance in a copper alloy matrix.

Early copper smelting was conducted in simple open pits, crucibles (Fig. 1.2), or furnaces (Thornton et al. 2009a, b; Tylecote 1982), the delivery of air to increase temperature often aided by tuyères and bellows (Donnan 1998). With early high-purity oxide and carbonate mineral ores, the smelt was often "slag-free," although later utilization of sulfidic and lower-grade ores required a slagging process to remove the unwanted gangue material (Bourgarit 2007; Craddock 2000a, b; Killick 1991, 49, 2015, 313; Roberts 2014, 430). Once smelted, molten copper was poured into open (single) or closed (double) stone or ceramic molds to create objects, or cast as ingots into open sand pits or limestone molds (Craddock et al. 1997; Hauptmann et al. 2002; La Niece 2016). The utilization of ingots represents one of the earliest forms of commodity standardization for the trade of surplus metals, and is seen across cultures in the Mediterranean oxhide, bar, bun, and plano-convex ingots, and the Andean *naipes* and axe-money ingots (Hauptmann et al. 2015; Hosler et al. 1990; Lechtman 2014; Yahalom-Mack et al. 2014).

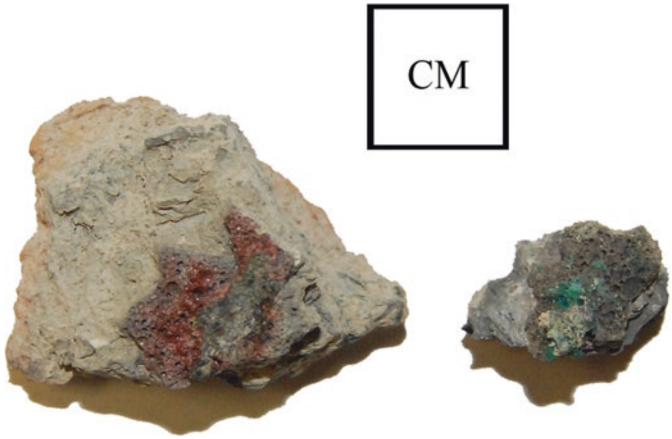

Fig. 1.2 Crucible fragments with remnant bronze slag or dross (oxide waste) from a melting/recycling operation in the Iron Age construction layers of the earliest Israelite monumental architecture in the City of David, Jerusalem (~1000 BC; from excavations conducted by Eilat Mazar in 2006–2007; Kaufman forthcoming; photograph by the author)

The earliest known copper artifacts in the Old World come from Neolithic Anatolia, where from the ninth to seventh millennia BC, people worked native copper into ornaments in an early display of wealth-based social stratification (Lehner and Yener 2014, 538; Schoop 1995). By the late eighth millennium BC, copper use is seen spreading out from the core area of Anatolia (Roberts et al. 2009, 1013). A major debate in the field of archaeometallurgy is whether or not there is one center of innovation for the development of metallurgy followed by technological diffusion, or rather that there were multiple groups that either conceived of metallurgical extraction on their own, or heard about it and experimented themselves until successful replication (Roberts 2014). This issue is not addressed here, but the reader can consult the references cited for robust discussions.

Precluding identification of a single culture as the inventors of metallurgy, it is clear that metallurgy in the Old World emerges from some place or places in the Balkan-Anatolian-northern Mesopotamian region (with some scholars arguing for an independent invention in the Iberian Peninsula as well, see Renfrew 1967, 1973; Ruiz-Taboada and Montero-Ruiz 1999). Knowledge of native copper working appears to move out of this zone eastward to the Iranian Plateau, where early finds such as a rolled native copper bead date to eighth to seventh millennia SW Iran (Hole 2000; Smith 1969; Thornton 2009). Despite very minimal evidence such as the native copper bead from Tell Ramad in Syria (Golden 2009, 286; Roberts et al. 2009, 1013), smelting technologies soon spread rapidly, and the artifacts that are mostly undisputed as native copper are relegated to the very early stages of metal use. The current earliest evidence for copper smelting comes from the Balkans around 5000 BC (Radivojević et al. 2010). In the southern Levant, with no native copper sources, the earliest evidence for metallurgy is extractive and dates to around 4200 BC during a period known as the Chalcolithic (~4500–3500 BC) (Golden 2009; Golden et al. 2001).

Arsenical Copper

Arsenic and copper occur frequently together in nature, and this is likely the reason that humans stumbled upon the first copper alloy (Heskel and Lamberg-Karlovsky 1980; Lamberg-Karlovsky 1972; Thornton et al. 2002). In addition to arsenic, copper ores often contain varying degrees of impurities such as nickel, zinc, silver, and lead, which in large enough amounts conferred unique properties to the alloys, often unintentionally (MacFarlane and Lechtman 2016).

Although pure copper in either native or smelted form is useful and beautiful, it does not necessarily have greater mechanical properties when compared to other material types available to Neolithic, Chalcolithic, and Bronze Age peoples such as wood, obsidian, bone, flint, ceramics, etc. (Roberts et al. 2009, 1012). With the advent of smelting technologies, several cultures sought greater material traits in their metals, and became aware of the ability to improve copper through alloying with the metalloid arsenic. It is important to emphasize that arsenic is a metalloid and does not exist in the native form, but because it does often co-occur in geological deposits with copper and other metals, it enables production of so-called bi- or polymetallic alloys. This meant that early smelters did not distinguish between copper and arsenic, but likely conceived of available ores as different grades of copper, for example, those with arsenic being more desirable (see Eaton and McKerrell 1976). Anatolia is rich in polymetallic ores, and in turn is a central location to witness a highly diverse experimentation and adoption of alloy classes from the fifth millennium BC, with desirable impurities of antimony, arsenic, and tin very common (Lehner and Yener 2014, 539).

Arsenical copper was the first bronze alloy developed by people, often called a natural or unintentional alloy. This mixture persisted as the alloy of choice for at least an entire millennium in the southwestern Iberian Peninsula before tin bronze was adopted (Valério et al. 2014). Arsenic content of between 2 and 6 wt% conferred beneficial mechanical properties to the alloy, including increased hardness, strength, and reduced viscosity when compared to pure copper allowing for more intricate castings. In quantities around and above 8 wt%, the alloy takes on a silvery sheen which adds an extra aesthetic appeal, but at this range, the matrix becomes embrittled and can fail (Budd and Ottaway 1991; Kuijpers 2017; Radivojević et al. 2018).

This early alloy became highly desired as knowledge of its properties spread. Evidence for down-the-line trade comes from the arsenical copper repertoire of the Irish and British Early Bronze Age, the end of the third millennium BC. Most of the raw arsenical copper originated from Ross Island. Beginning with arsenic-rich alloys, items were traded and melted down so that each culture that received the metal could recast it into their own culturally appropriate shapes, forms, and typologies. Since arsenic is volatile, with every recasting, arsenic content was lost. As the alloys were traded further and further away, arsenic was lost each time, demonstrating a decrease in arsenic content as a function of geographic distribution (Bray and Pollard 2012; see also McKerrell and Tylecote 1972). However, arsenic loss is non-linear, and there are several mitigating factors, such as the presence of nickel, which has affinity for arsenic and can assist in its retention (Mödlinger et al. 2017; Sabatini 2015).

One of the most spectacular examples of the castings made possible by arsenical coppers is that of the Nahal Mishmar Hoard of the southern Levant, discovered in the Judean Desert and dating to the Chalcolithic in the first part of the fourth millennium BC (Goren 2008; Tadmor et al. 1995). Hundreds of pieces stashed away in a cave include maceheads, standards, crowns, and tools, frequently taking zoomorphic forms. The arsenical copper alloys were often antimony and nickel rich, with impurities of bismuth, lead, and silver. Although an origin of the ores or raw materials may be found in Anatolia or elsewhere in metal-rich regions of Transcaucasia, production of the objects likely occurred locally. Contemporary sites such as Shiqmim had remains of alloys, crucibles, ore, and slag (Shalev and Northover 1987, 1993). This shows that by the Chalcolithic era, long distance trade and specialized metallurgical knowledge was widespread, although the latter may have been rooted in village rather than regional traditions (Golden 2009, 285). At least some objects from the hoard were produced by lost-wax casting over a stone core. So specialized was the metallurgy of arsenical copper in the southern Levant, that during the several hundred years of societal reorganization leading into the Early Bronze Age, either the technological knowhow was lost or the trade routes allowing access to arsenic-rich ores dried up (Kaufman 2013). The period in between that of the Nahal Mishmar Hoard and the adoption of tin bronze, the Early Bronze Age I–III (~3500–2300 BC), has provided archaeological evidence of only pure copper objects, with the coming of tin bronze (and a renewal of arsenical coppers) beginning in the Early Bronze Age IV (~2300–1900 BC). A brief detour from alloy types to fundamental production techniques relating to casting technology and object design is appropriate as alloying copper with arsenic, lead, and tin went hand in hand with mold fabrication in the ability to manufacture complex shapes.

Lost-Wax Casting and Piece-Mold Casting

A fundamental aspect of casting technology is that of lost-wax casting (*cire perdue*). The ability to execute intricate designs in metal form was made convenient and possible with the invention of this technique, alongside alloying copper with arsenic, lead, and tin which decreased viscosity of the molten metal as it traveled through the spaces and creases of the mold (Hunt 1980). Instead of relying on relatively crude carvings in stone or clay molds to achieve forms, a three-dimensional model of the casting could be made in perishable, workable material.

Like all casting technologies, there are numerous ways to achieve the desired outcome, often specific to an artisan or smith. But the basic principles of lost-wax casting can be divided into the two major types, direct lost-wax casting and indirect lost-wax casting. If the model is used only once (consumed in the process), this is direct lost-wax casting. If the model is recovered for reuse and additional casting of replicas, this is indirect lost-wax casting (Stone 1981). For both types, an original model is carved, engraved, or otherwise designed out of some material that is to be replicated in metal. Models are made from wax, beeswax, clay, plaster, wood, another metal object to be imitated (aftercasts), and at times even actual animals (Stone 1981, 2001, 2006). The artisan invests or packs refractory material such as clay or plaster of paris around the model. Hollow sprues and gates are constructed that will deliver the molten metal to the interior. Once the clay investment dries, the wax model is melted out (direct), and the molten metal is poured in, or the investment can be cut in parts and the model removed (indirect). Through slushing and core pouring, the object can be cast in hollow form, and to prevent the core from moving during the cast, chaplets or armature will be necessary to hold the core in place (Stone 1981). Following the casting, core materials are dug out, but are often left behind to some degree (Mugnaini et al. 2014). Chasing and working are employed to remove deformities and irregularities, sprue marks, etc.

The origin of this technique is also the subject of debate and uncertainty within the field of archaeometallurgy, although the earliest known current evidence dates to fifth millennium BC Pakistan at two separate sites, as well as one in Bulgaria (Craddock 2015; Davey 2009; Leusch et al. 2014; Mille et al. 2004; Thoury et al. 2016). Some of the earliest pieces made by lost-wax casting were zoomorphic cylinder seals in Mesopotamia in the fourth millennium BC, in addition to the exquisite Chalcolithic hoard from Nahal Mishmar discussed above (Goren 2008; Hunt 1980). Bronze and gold artifacts of the Early Dynastic (ED) Sumerians (~2600 BC) demonstrate a tradition of the lost-wax process. The ED III Sumerians were early innovators of metallurgy—they were also the first culture to adopt tin bronze for widespread use (Moorey 1994). Whether there were one or multiple centers of discovery of the lost-wax technique, by the second half of the third and into the second millennia BC, the technology was being used from the Indus to Greece. An Old Babylonian inscription dated to 1789 BC during the reign of Hammurabi represents the earliest textual attestation of the process (Hunt 1980, 65–67). An Elamite statue dating to the fourteenth century BC was cast with a nearly pure copper alloy, a tin bronze core, and weighed 1750 kg (Meyers 2000). The Egyptian state during the Third Intermediate Period (1070–664 BC) commissioned a wide array of statues of gods and kings made via lost-wax casting (Schorsch 2014, 295).

The process of lost-wax casting requires extensive technical knowledge, and therefore depending on the availability of craftspeople, the ubiquity of the technique and quality of the pieces is differential over time. Inspired by Greco-Roman statuary (Lombardi and Vidale 1998), the Renaissance masters revived and engaged intensively in the art of lost-wax casting, and much of what we know of the practice is derived from the *De la Pirotechnica* of Biringuccio, published in 1540 (Biringuccio 1540, translated by Smith and Gnudi; Stone 1981; for lost-wax casting in modern aerospace applications, see Kumar and Padture, Chap. 5, this volume).

Like the aforementioned alloy progression from copper to arsenical copper to tin bronze, lost-wax casting is another example of convergent cultural evolution between the Old and New Worlds. The center of innovation of South American lost-wax casting is currently considered to be in modern Colombia, where gold was the preferred medium for the castings. In what has been argued to be a highly ritualized process wherein wax, molds, and metal were symbolically charged with connotations of fertility, social order, protection, and health, goldsmiths in the first millennium BC employed several techniques including the use of multiple cores in a single casting, and the casting on of metal for repairs (Martinón-Torres and Uribe-Villegas 2015; Perea et al. 2013). Lost-wax cast bronze bells were made in Colombia and Costa Rica by AD 100, spreading northward to West Mexico centuries later (Hosler 2014, 334–335). Here, the acoustic properties of the bells mattered, meaning the design details involved a variety of shapes, sizes, colors, and tones that were culturally desired. Using lost-wax casting of alloys with relatively high amounts of tin and arsenic constituents, artisans could ensure the fluid casting needed to produce large, hollow bells. Of further benefit, the high tin objects had golden luster (Fang and McDonnell 2011; Radivojević et al. 2018), and high arsenic ones looked silvery, representing the solar and lunar deities (Hosler 2014, 342; for bronze musical instruments in Archaic and Classical Greece, see Papadopoulos 2017).

Lost-wax casting always involves extensive post-casting modifications. Scraping, cutting, patching, and chasing were common ways to file down and polish sprues, gates, and other deformities created during the casting. Perhaps in part due to a cultural or economic preference to avoid post-casting finishing, the earliest bronze castings in Erlitou and Shang China were done using the piece-mold technique, in the Central Plain during the third millennium BC. It is still debated when exactly lost-wax casting was adopted in China, perhaps during the Spring and Autumn (771–475 BC) or Warring States periods (475–221 BC) (Meyers 1988). Elsewhere in East Asia, such as Thailand where lost-wax casting was employed, the pieces were usually left as cast without additional working (White and Hamilton 2009, 2014).

Piece-mold casting involves making a model, impressing it onto clay molds or simply carving a design onto molds, and marking registrations and cutting the molds into three or more pieces (Liu et al. 2013 and citations therein; Meyers 1988). The pieces would then be reassembled for the cast. For a hollow piece, the model or something like the model should be shaved down to make a core that is spaced away from the mold impressions, leaving room for the cast metal. Massive and intricate castings of pieces weighing over 800 kg attest to a highly specialized and constantly shifting tradition of piece-mold bronze casting in China that lasted for millennia (Liu 2009; Liu et al. 2013, 2402–2403).

Although piece-mold casting was also practiced extensively in the Central Andes and not exclusive to China (Lechtman 1988), mold production was its own specialized, labor-intensive endeavor that was an indispensable part of the ancient Chinese metallurgical industry. Evidence from the Eastern Zhou period (770–221 BC) attests to the details of this skill. High sand/clay ratio of the molds provided elevated silica content, which would have conferred positive physical properties for firing such as minimal shrinkage during drying and firing (necessary to maintain the morphology of the cast object, as well as the impressions and carved relief of the decorations). High porosity in the ceramic microstructure of the mold allowed for venting of vapors, thereby decreasing the formation and freezing of holes in the cast metal product. High porosity also lessened the risk of fractures and failure from thermal shock because porous voids can limit the expansion of cracks during the firing (Liu et al. 2013, 240–241).

These advances in technical ceramics were combined with careful alloying practices, with smiths choosing a great diversity of constituent elements for their copper that increased the fluidity of the molten metal (reduction in viscosity), allowing for the casting of intricate shapes (Chen et al. 2009, 2017). It is especially important to increase the fluidity of the alloy for piece-mold casting as opposed to lost-wax casting, as the former does not have as intricate a system of sprues and gates to deliver metal evenly before it cools as in the latter. This is likely the chief reason explaining the preference in ancient China for leaded alloys. Molten pure copper alone is often too sticky to cast anything that requires complexity in the mold form. Alloying with arsenic, tin, and especially lead will vastly improve the casting process. Leaded tin bronzes were highly common in the earliest Chinese bronze metallurgy of the Shang Dynasty (Mei et al. 2009), while other standard alloy classes included arsenical copper, antimonial copper, and a ternary copper-nickel-arsenic (Chen et al. 2009).

Tin Bronze

Intentional alloying of copper with tin to form bronze began in the Near East by the end of the fourth millennium BC but only became widespread in the mid-third millennium BC (Lehner 2014; Moorey 1994; Thornton 2014). Bronze Age Near Eastern trade in tin is directly attested in Old Assyrian textual records (Larsen 1982), as well as by tin ingots such as those recovered from the Uluburun shipwreck off the coast of Turkey (Pulak 1998). Tin oxides, in the form of cassiterite or stannite, are found often in alluvial lodes or veins (Deer et al. 1992, 534–535) that were tapped and followed by ancient smiths for experimentation and later consistent utilization. Tin nuggets, called stream, alluvial, or placer tin, would sink to the bottom of streams and could be panned or picked out there, much like gold, and indeed these two metals frequently occur together in placer deposits (Craddock 1995, 111; Muhly 1973, 248).

The co-smelting or mixing of tin with copper required a cognitive leap wherein smiths intentionally alloyed these two metals that rarely occur together geologically. The spectacularly useful and attractive tin bronze was the result, and it became one of the most widespread and enduring copper alloys. Its use has continued in many parts of the world uninterrupted since around the mid-third millennium BC until today. Hard, strong, corrosion-resistant, and with a golden sheen, tin contents of between 10 and 14 wt% are referred to as “true bronze” (in opposition to the “natural bronze” or As+Cu alloy).

Some of the earliest breakthroughs in the invention of tin bronze alloys come from Anatolia around 3000 BC, where polymetallic ore veins and lodes are ubiquitous, making experimentation easier through geological availability (Lehner and Yener 2014, 545; Yener et al. 2015; Yener and Vandiver 1993). Further south, the Sumerians became aware of this technology by the Early Dynastic III, and by

Fig. 1.3 Tin bronze dagger (86Cu13.5Sn0.6Pb) from a tomb at ‘Enot Shuni in the southern Levant, Middle Bronze Age IIA–C (~2000–1530 BC; excavations carried out by Martin Peilstöcker and the Israel Antiquities Authority in 2001; corrosion removed; modified from Kaufman 2013, fig. 5; photograph by the author)

2500 BC, tin bronze was popularly adopted in Mesopotamia (Moorey 1994). From there it spread west to the Levant, and was adopted by Levantine cultures during the collapse of urban society in the Early Bronze Age IV (2300 BC), in part due to the fuel efficiency of tin during a period of record timber shortages (Kaufman 2013; Kaufman and Scott 2015; Philip 1989, 1991). The mobility of the semi-nomadic pastoral lifestyle of the Amorites/Canaanites facilitated cultural exchange over vast areas and played a factor in the transmission of bronze technology (Fig. 1.3).

By around 2000 BC, bronze metallurgy continued down the Fertile Crescent, entering the Egyptian technological repertoire, although knowledge about early Egyptian metallurgy has been relatively limited until recent work and is still much less well-understood than neighboring regions (Odler 2016; Rademakers et al. 2017; Rehren and Pernicka 2014). It is possible that the Levantine Amorites (Hyksos) which conquered Egypt in the Second Intermediate Period were largely responsible for the importation of tin bronze metallurgy (both implements and knowhow) to the Nile Delta. It is also in the beginning of the second millennium BC that bronze spread firmly into the western reaches of Europe, although some advocate a late third millennium BC independent innovation in the British Isles (Dolfini 2014; Kienlin 2014, 454–455), as well as to East Asia where a diversity of bronze alloys and forms proliferated under the Shang Dynasty (Chen et al. 2009).

Perhaps the longest-running question that has confounded Near Eastern archaeometallurgists is “where did the tin come from?” Pioneering methodologies in lead isotope analysis over the past few decades have incorporated established lead isotope signatures in regional geological deposits with the lead isotope signatures of copper artifacts in the attempt to find matches, and therefore determine the ore source of the alloys (Stos-Gale and Gale 2009 and citations therein). There has been much speculation as to where the earliest tin sources were tapped for bronze production, ranging from Afghanistan to Cornwall (Begemann et al. 1999; Lehner et al. 2013; Muhly 1985; Stech and Pigott 1986). The question is still open, in part due to the difficulties encountered from ancient recycling of alloys which often resulted in the mixing of metals that had been derived from geologically distant and diverse ore occurrences (Pollard et al. 2017). Furthermore, the lead isotopes are most often those associated with the copper ore, not tin. In addition to lead isotopy, the isotopes of tin are being researched for possible provenance applications (Haustein et al. 2010; Mason et al. 2016; Nessel et al. 2015).

There are at least two distinct metallurgical traditions in the New World, one originating in North America that focused on unsmelted pure copper (discussed above), and the other in South America which began with pure copper but later included a vast range of smelted alloys including tin bronze.

Smelting was first developed in the Peruvian Andes around 2000 years ago and spread northward to Mexico by sea around AD 600, with further down-the-line trade of alloys such as copper bells reaching as far as the American Southwest (Hosler 2013; Lechtman 1980; Simmons and Shugar 2013; Watson et al. 2015). Plastic deformation through hammering and the creation of metal foil were common technological styles used to adorn artifacts that were used as status symbols before the advent of state-level hierarchies. In the Andes, the working of native gold predominated early metal assemblages dated to the third millennium BC, but native copper was also worked down through the second and first millennia BC well before smelted copper (discussed below; Aldenderfer et al. 2008; Burger and Gordon 1998; Hosler 2013; Lechtman 2014, 369). Therefore, a deep metallurgical tradition was present in the Andes before the invention of bronze metallurgy. It is during the Moche civilization that the proliferation of extractive copper metallurgy became widespread, with copper richly adorning elite burials and being a symbol of the wealthiest individuals, particularly powerful women (Donnan and Castillo 1992; Lechtman 2007, 317, 2014, 376). Moche metallurgy thrived beginning around the early years AD, while the years AD 600–1000 saw the true fluorescence of bronze (Lechtman 2014, 381).

The central and south-central Andean zones contain one of the world's most concentrated and largest deposits of copper ore, along with arsenic and antimony mineralizations that were amenable to alloying. The cassiterite (tin oxide) lodes of the Bolivian *Altiplano* allowed for the production of tin bronze during the Middle Horizon, Late Intermediate Period, and finally in great quantities during the Inka state (or around AD 700–sixteenth century; Lechtman 2014, 365–366, fig. 15.4). Gold and silver were also abundant, but more localized than the massive copper deposits.

The hallmark of the Andean metallurgical tradition is defined by Lechtman as the "three-component system." In the early centuries AD, the Andean Early Intermediate Period, Andean smiths developed what Lechtman calls a metallurgical "ideal" based on the three-component materials of copper, silver, and gold (Lechtman 2014, 369). The addition of copper to various percentages of silver and gold improved the strength and toughness of the alloys, while allowing for precious metal surface enrichment of the base metal. These specialty-alloying practices also enabled color transformation of metals across a range of desired hues, transformations that symbolized gender, political, and cosmological ideals (Lechtman 2007, 318–319, 322).

Brass and Gunmetal

For most of its history, brass, an alloy of copper and zinc, has been desired by people due to its aesthetic appeal—it is a yellow metal resembling gold when zinc contents range about 10–20 wt%. The addition of zinc can also yield improved hardness and strength akin to arsenical or tin bronzes (Scott 2010, 191). Brass was viewed as a useful alloy for coinage in several cultural contexts including Roman (Caley 1964; Carter et al. 1978), Chinese (Craddock 2009), and remains widespread in hard currency today (Shilstein and Shalev 2011). Furthermore, due to the fact that zinc is a volatile metal, zinc oxide (calamine) would condense inside of the furnace during zinc or brass production. This would be scraped off and used for medicinal purposes, and it is likely that zinc metal was heated and vaporized to treat wounds as well (Craddock 1998, 5; Craddock et al. 1998a, b, 27).

Although arsenic and tin are the oldest alloying constituents for copper in both the Old and New World, in the Old World zinc was also added to the repertoire resulting in brass metallurgy. Brass usually is relegated to the back burner in discussions of metallurgical contributions to the development of civilization. But as Thornton (2007) suggests, the several occurrences of prehistoric brass that are depositionally linked to bronze artifacts may indicate that brass was an intentional if not ubiquitous alloy. Important for this argument is the mid-third millennium BC metal assemblage from Kalmikya in Russia with distinct separation of arsenic and zinc alloys, displaying intentionality of production (Thornton 2007, 128). The other possibility is that zinc-rich ores were accidentally smelted in the quest for bronze, and that brass finds from the third millennium until the last half of the first millennium BC may then represent accidental production/experimentation. Accidental zinc-copper alloys are unlikely to have a zinc content greater than 6–7 wt%, and there are very few examples of weapons with contents below this range from third to second millennium BC Mediterranean and Near Eastern contexts (Pollard et al. 2017, Chapter 6; Thornton 2007, 124). There are around 30 artifacts from prehistoric Bronze Age Southwest Asia that contain over 8 wt% zinc, so even if these alloys were intentional, they were not common. During the second millennium BC, copper-zinc alloys appear sporadically across the Iranian Plateau, and it is possible that the origins of brass metallurgy are to be found in Central Asia (Frame 2010; Thornton and Ehlers 2003; Thornton et al. 2002, 1459).

It is during the first millennium BC that zinc production becomes codified into the metallurgical repertoire in both India and the Hellenistic world, becoming commonplace by the fourth century BC (Craddock 2017; Craddock et al. 1998a, b, 27; Thornton 2007, 125). As mentioned above, the geographic origins of brass have not been conclusively determined. Although India is a likely candidate, the evolution of brass technology is today conceived similarly to bronze in that it is unclear if localized experimentation with various mineralizations spurred multiple centers of innovation, or if it was diffused from a central source (Killick 2014, 36; Rehren 1999).

The ability to pinpoint the earliest historical recognition by metalworkers of zinc and brass in India is not due to textual paucity as there is a great deal of documentation in the first millennium BC, but rather the inability to date the texts satisfactorily (Craddock et al. 1998a, b, 27). Brass is the accepted designation for the Greek alloy *oreichalkos*, meaning "copper of the mountain." This latter terminology was also used in eighth to seventh centuries BC Neo-Assyrian cuneiform tablets likely denoting brass (Bayley 1998, 8). The alloy consistently rose out of obscurity, and was commonly found in parts of the Roman world during their transition to empire in the first century BC (Bayley 1998, 7; Rehren 1999). Dated to around this time, hundreds of ceramic crucibles specially designed for the cementation of zinc ores were recovered in Germania Inferior (Rehren 1999).

Throughout the Late Antique in the Mediterranean, tin became scarce, and this may be a primary factor in the growing ubiquity of copper-zinc alloying (Craddock et al. 1998b, 73). Although a repertoire of brass artifacts have been dated to the Late Neolithic Yangshao culture of China, the context is dubious as is the appearance of brass in a culture without any other metallurgy (Fan et al. 2012; Scott 2010, 193; Thornton 2007, 125). However, intriguingly, some other Neolithic brasses have recently been discovered at various sites, lending credence to those suggesting a preference and perhaps ability to smelt brasses as the earliest metallurgical tradition in China (Ma and Li 2010). Securely, brass production was adopted in China during the late Tang Dynasty, around AD 900 (Scott 2010, 193). It was written about and produced in the Islamic world throughout the Medieval Period (Craddock et al. 1998a, b). Brass comes and goes in some regions, such as in Britain where it is seen during the Roman occupation, and then disappears until a reintroduction by Saxons and Vikings (Bayley 1998, 20). Due to improvements in the ability to control volatile zinc metal via distillation (discussed below), by the Late Medieval through the Renaissance, brass was widespread throughout the Old World (Day 1998; Scott 2010, 194). Zinc is often found as a constituent in metalliferous ores, and the accidental production of natural brasses through co-smelting is known in pre-Columbian Argentina (Craddock 1995, 293; Gonzales 1979).

The zinc-copper alloy of brass can be produced through cementation or distillation processes. In the cementation process, zinc ores and copper ores are smelted together so that zinc metal is absorbed into the copper during the reduction process before it can evaporate (Scott 1991, 19). The upper limit of zinc content achievable through cementation is around 28 wt%, whereas the solubility limit of zinc in copper is 30 wt% (Davis 2001, 4; Scott 2010, 194). Zinc is highly volatile—remelting of a brass alloy can cause a loss of up to 10% zinc (Thornton 2007, 124). To achieve higher zinc concentrations, the process of distillation was developed: zinc ores were smelted in highly reducing conditions in ascending ceramic retorts where zinc vapors would cool in pots, condense, and be collected (Craddock 2009; Zhou et al. 2014). Once zinc metal is obtained, it can also be added directly to molten copper (Craddock et al. 1998a, b, 27). Zinc distillation was practiced on an industrial scale by the mid-nineteenth century AD (Bourgarit and Bauchau 2010; Bourgarit and Thomas 2011).

Zinc alloys can corrode badly in a process called dezincification, but the use of certain alloying constituents can counter this, and over the past several centuries, many new alloys have sprung up with zinc. From the seventeenth to twenty-first centuries AD, zinc has been employed in the creation of several brass alloy categories for numerous functions including corrosion-resistant applications and ordnance (Scott 2010, 198–210). Of notable mechanical use is naval brass (nearly 40 wt% zinc, <1 wt% tin, remainder copper) which finds many applications for its corrosion resistance and strength properties in marine applications. Although due to brittleness alloys with >50 wt% zinc are usually avoided, they are known to occur (Scott 1991, 19–20).

Gunmetal is an alloy of copper-tin-zinc, also conferring a golden hue to the object. Prehistoric examples of this alloy seem to be intentional, rather than as recycled scrap of tin bronze and brass. This is reasoned because zinc and tin rarely occur together geologically which makes accidental co-smelting unlikely, because tin inhibits zinc solubility in copper, and because there is little evidence for copper-arsenic-zinc or copper-antimony-zinc alloys which would be expected with random scrapping. Like brass, gunmetal alloys are present by the second millennium BC in the Mediterranean (Killick 2014, 36; Thornton 2007, 130–131).

Lead and Pewter

Lead metal on its own does not well withstand mechanical stresses, but its geological abundance and alloying properties make it useful in a range of applications (Craddock 1995, 205). The ease with which it is smelted, melted, and cast into complicated forms, as well as its heavy weight, has been found to be highly relevant for specific functions. Pure lead was used for standard weights, net sinkers, and loom weights, and it was also cast into sheet, cast into bronze molds to recreate the clay mold, and in the Roman period used extensively for pipe systems (Tylecote 1962, 94–95). Due to the drastic reduction of radioactivity in lead over time, Roman lead is highly sought after for use today as shielding in subnuclear and particle physics experiments (Alessandrello et al. 1991; Moskowitz 2013).

Pure lead has a remarkable property in that it recrystallizes at −12 °C, below room temperature. Therefore, lead can be manipulated, hammered, and bent into shapes like piping without embrittlement (Scott 1991, 9). The downside is the detriments of the metal on human health, and its historical prevalence in piping and paint before health concerns were recognized left a legacy of toxicity that had to be dealt with in the past few decades (Shugar and Mass 2013). Modern regulations such as the Safe Drinking Water Act of the United States mandate stringent lead contents for piping, although as is discussed below regulation does not always mean implementation of lead reduction, as seen in the case of Flint, Michigan (Ingraham 2017).

Lead ores such as galena (lead sulfide), cerussite (lead carbonate), and lead oxides (few found today but these were perhaps more prevalent in antiquity) are easy to smelt under mildly reducing conditions (Craddock 1995, 205). Lead can be smelted and melted in simple open hearths or fires (Rhead 1935).

The addition of lead to bronzes decreased the viscosity of the alloy allowing for more successful castings, and Bronze Age smiths made use of this alloying constituent frequently and in several cultural contexts. A good example is that of Bronze Age China, where large and intricate castings as well as hand mirrors were frequently made of leaded high-tin bronze from the Shang period onward (Chen et al. 2016; Scott 2010, 174–189).

Lead-tin alloys melt at very low temperatures, often below 200 °C, and were therefore useful as soft solders and, among other applications, were employed to join together piping in Roman aqueducts (Price 1977, 258; Scott 1991, 144). Lead-tin or antimony-tin objects also make up the class of alloys referred to as pewter, and these were commonly used for utensils until the dangers of lead became clear. Roman tableware has been found to contain 20–30 wt% lead, and sometimes as high as 50 wt% lead (Tylecote 1962, 69). Lead was cheap, abundant, and in certain amounts increased alloy hardness. Modern pewter objects now use the antimony-tin system instead, although antimony is also not without health detriments (Scott 1991, 142).

Another highly valued property of lead is its affinity for the precious metals of gold and silver (Liu et al. 2015, 153–154). Gold and silver ores would be smelted together with lead, forming a bullion of the metals, from which the precious metals could be later extracted through various beneficiation and cupellation processes.

Precious Metals

Metals have taken on a number of roles in human evolution, broadly summarized as either relationships of *conductivity* or *dependence*. Mostly metals are used as a conduit, lubricating the gears of economy with metal coinage and currency, exponentially increasing speed of transportation through railroad tracks, locomotives, or airplanes, and literally conducting electricity through pure copper wiring thereby increasing the speed of information. Dependence on metals is seen in such cases as biomedical titanium hip or ventricular implants. Sometimes it is hard to differentiate between dependent or conductive paths, such as when a culture inherits a valuation of gold as its most precious commodity. Do the hierarchical relationships that form according to how much gold each family or social unit possesses make the community members dependent on the metal for the functioning of social order? Or is the precious metal simply the symbolic conduit that communicates ranked levels of inequality that would exist anyway had gold never been valued in the first place? The answer is likely some of both, intrinsic attraction to the luster and properties combined with the inertia of cultural traditions that favor certain material types. In this section, some of the basic aesthetic and mechanical properties are discussed within a context of the regional and temporal spread of precious metals.

Gold

Gold, silver, and platinum are among the most coveted materials. Of the mechanically useful alloys listed above, both tin bronze and brass are valued for their gold aesthetic. Several historical economies have been backed by a precious metal standard, infusing paper currency with symbolic precious metal value. Today, abstracted gold and silver—not even the real materials—are valued as safe haven assets for investors who take comfort in owning the metals financially though exchange traded funds during times of market panic (Cowan 2016). In other words, metals like gold and silver represent real, intrinsic value to certain cultures. Why is this? For gold, it may be simply stated that its value is a function of rarity and properties. Gold is exceedingly rare in the Earth's crust at 0.004 ppm (Ag is 0.08 ppm and Cu is 68 ppm), and along with 22 other trace elements together forming 0.0003% of total elements in the Earth's crust (Morteani 1995, 100). When gold does occur, it is often in the native form, or gold nugget, often making extractive metallurgy unnecessary. Gold is soft and ductile, meaning it can be hammered into shape without cracking (Raub 1995). Pure gold is chemically passive making it resistant to corrosion unless alloyed with other metals (Möller 1995) or, in a symbolic sense, evoking eternity through its lack of deterioration.

Gold is most frequently extracted from placer deposits, which form when moving water washes out weathered primary veins and carries the gold where it concentrates at the stream bottom due to gravity (Craddock 1995, 110). Here, it is known to join with other dense metals such as tin and platinum group elements (PGE) which also have washed out from their primary formations. Gold can also occur in pyrite or arsenopyrite ores, and can be extracted via smelting with silica flux or with mercury treatments (Craddock 1995, 110). Silver in varying degrees is almost always present in native gold, the natural electrum alloy, and the refining of this alloy has been recorded in Sumerian and Egyptian records dating to the third millennium BC. Predynastic Egyptians of the fourth millennium BC exploited the rich local gold mines of the Eastern Desert and Nubia, and employed a different terminology for gold mined from veins vis-à-vis placer gold (Gouda et al. 2007, 14). Over the millennia, many electrochemical and extractive processes have been developed to refine gold, with some of the earliest and well-known dating to the gold and silver coinage of the Lydians before and during the time of King Croesus in the seventh to sixth centuries BC (Craddock 1995, 115–119; Ramage and Craddock 2000; Rehren and Nixon 2014).

Some cultures did not value gold before it was introduced via external colonial or economic contact, such as in pre-contact North America and Sub-Saharan Africa before the thirteenth century AD (Killick 2009, 15). Gold was sparsely used as an item of value in the Central Plain of China until the Western Zhou period (1046–771 BC), and silver became popular later yet during the Warring States period (475–221 BC) (Liu 2015, 46). By the time of the Western Han Dynasty (206 BC– AD 9), gold was used as a therapeutic and medicinal treatment, thought to confer beneficial health properties, but which in excess quantities may have caused harm (Zhao and Ning 2001).

Still, many other cultures independently coveted gold for its intrinsic aesthetic and working properties. Gradually, although not all cultures began with a taste for gold, by today it has become arguably the basic standard of universal value. News of new gold deposits has sparked massive global migrations. The first recorded placer gold rush occurred in the mid-fifth millennium BC on the shores of the Black Sea (Chernykh 1992; Killick 2014, 23), and the settlement of the American West as we know it today finds its roots in the search for this metal during the 1849 California Gold Rush (Brands 2003).

Gold and native copper were the first metals to attract the attention of Andean hunter-gatherers who hammered small pieces to make jewelry around 2000 BC. The first millennium BC Chavín culture developed a taste that favored gold nearly to the exclusion of all other metals (Lechtman 2014, 369–371). Not long after the emergence of agricultural society on Cuba, gold and gold alloys were gathered and worked, and this eventually became a major focal point for the interaction between the indigenous Taíno peoples and Columbus when he landed on the island, as well as the colonial Europeans who followed (Martinón-Torres et al. 2007). It was this lust for gold by European populations which spurred much of the colonial enterprise, and which also has left little archaeological evidence due to the booty being sent back to the Spanish Crown. The Inka state employed gold in monumental proportions, and Spanish accounts relay Inka palaces and temples clad in gold and silver, life-sized gold and silver statues of people and animals, and expert Andean precious metal smiths. An unknown, massive amount of Late Horizon gold- and silverworks were destroyed by Spanish melting and export campaigns in the sixteenth century AD (Lechtman 2007, 313–314), with Seville tax lists documenting the import of ~155 tons of gold and 17,000 tons of silver between AD 1531 and 1660 (Rehren 2011, 77). For ancient Egyptians, the moon and bones of gods were made of silver, and the flesh of gods was made of gold, and both are frequently found in archaeological contexts in varying degrees (Gouda et al. 2007).

Currently, the earliest known gold metallurgy is from the Varna I cemetery in Bulgaria, with the expertise of the goldsmiths indicating not experimentation but a fully developed technical mastery by 4550–4450 BC (Leusch et al. 2015). This Chalcolithic society utilized multiple geological deposits of gold, and had a paleo-industrial technological organization that required numerous people with expert knowledge that produced over 3000 recovered gold and gold alloy objects for burial deposition (Leusch et al. 2015, 353, 362). Gold metallurgy was not known to the neighboring regions, and all evidence points toward a diffusion of this practice out of the Balkans, first through trade and later through technological transmission (Renfrew and Slater 2005, 314–316).

Gold both accelerated and enabled the formation of early hierarchies and societal inequality, due to its compactness, durability, and visual appeal. In the mid-third millennium BC Iberian Peninsula, the earliest hierarchies coincide with the earliest gold manufactories (Nocete et al. 2014). By around 3000 BC, the people of Early Bronze Age Crete were importing gold (Legarra Herrero 2014). The trade in precious metals was the driving force behind Bronze Age international trade between Europe and the Near East (Sherratt 1993). In the Iron Age Near Eastern commodity trade system, although silver was the predominant metal of value, spectacular gold and gem work executed by the Phoenicians served as a medium through which to express their cosmopolitan character. Fusing Egyptian, Mesopotamian, and their own Levantine iconographies, the Phoenicians adorned Neo-Assyrian royalty with jewelry that the most skilled craftspeople today would be hard-pressed to reproduce (Hussein 2011; Hussein and Benzel 2014).

Silver

Silver is to a certain extent similar to gold in its cultural valuation, in that the aesthetic attraction is in part derived from the relatively high resistance to oxidation (continued luster), and some cultures preferred silver over gold. This is true in various periods of Mesopotamian and Persian history—in Ur III Sumer (2100–2000 BC), a shekel of silver (8.33 g) bought 300 l of barley, 30 l of fish oil, 10 l of butter, or a sheep (Englund 2012, 427). The antiquity of worked native silver can be traced at least as far back as the mid-sixth millennium BC from Domuztepe in Anatolia (Lehner and Yener 2014, 538). Late Chalcolithic smelters (late fourth millennium BC, Late Uruk) from the Iranian Plateau and eastern Anatolia were the first to refine silver from argentiferous lead ore through cupellation, and the earliest intentional alloy cast by eastern Anatolian smiths was silver-copper as seen at the Late Chalcolithic-Early Bronze Age "royal" tomb at Arslantepe (Lehner and Yener 2014, 538, 542; Nezafati and Pernicka 2012; Palmieri et al. 2002; Pernicka et al. 1998). In Early Bronze Age I Jordan (fourth to third millennia BC), a piece of silver was alloyed with copper and gold, cast into sheet, hammered, and annealed, and this find is one of hundreds of other silver alloys recovered from contemporary contexts in Egypt and the Levant (Philip and Rehren 1996).

Silver has been heavily mined out since antiquity, so European smiths of the recent past would consider a galena ore with 10 ppm silver a viable source. The argentiferous lead ore galena was the most common source for silver in antiquity, with silver content usually ranging from 0.1 to 0.5 wt% (Xie and Rehren 2009). Silver is found in its native form, in native electrum, and in a variety of other mineral formations including silver chlorides, silver sulfides, argentiferous lead-, antimony-, and arsenic-bearing ores, jarosite ores, and pyrite ores (Craddock 1995, 211–212). Depending on the ore type, different extractive methods often requiring several steps were employed to win silver from argentiferous ores.

One of the more widespread extractive practices involving lead-silver ores was *cupellation*. Here, the argentiferous lead ore would be smelted at high temperatures under reducing conditions which led to molten silver and lead mixed together. The high temperature would ensure that much lead was lost to evaporation (some of which would condense in the furnace that could be collected depending on the furnace design), and the remaining lead would now have a higher percentage of silver concentrated within it. This smelted metal product known as bullion, including silver, lead, and other impurities, would be heated in a cupel or cupellation hearth with oxidizing conditions, thereby creating lead oxide, or litharge. The litharge would absorb the other impurities, and through capillary action, much of it would itself be absorbed into the walls of the cupel which were made of materials specifically selected for this purpose, such as bone ash, wood ash, or clay (Craddock 1995, 214–228; Martinón-Torres et al. 2008). A button of molten silver would collect in the cupel and could then be recovered, and special care was taken to avoid the silver also being absorbed into the cupellation hearth lining (Rehren and Kraus 1999). The cupel could be crushed and smelted to recover the lead (Scott 1991: 139), with the lead metal by-product being more than 100 times the amount of silver (Xie and Rehren 2009).

The cupellation process is known to have been carried out in Mesopotamia as early as ~3300 BC at the Late Uruk site of Habuba Kabira (Pernicka et al. 1998). So strong is the affinity of silver for lead, that lead would often be added to a molten bath of other metals such as copper to alloy with silver impurities, followed by heat treatments that caused the silvered lead to be melted out; finally the silver separated through cupellation. This process, known as liquation, was utilized commonly in Medieval China and Europe, as recounted historically by Su Sung, Biringuccio, and Agricola (Craddock 1995, 232 and citations therein).

As mentioned above, silver became a hallmark of global trade throughout the Bronze Age in western Eurasia, silver being shipped in ingot form by the third millennium BC at Troy (Murillo-Barroso et al. 2015, 257). An Early–Middle Bronze Age (~2000 BC) Canaanite warrior at Shuni was buried with a stunning silver-copper duckbill axe that depicted the semi-nomadic pastoralist lifestyle of that society, with the iconography of a shepherd dog on one side of the blade and a sheep/goat on the other (Caspi et al. 2009; Philip 1995). The Phoenician colonization of the Iberian Peninsula had as its driving factor the search for silver, and the indigenous coastal settlement patterns and hierarchical structure were altered permanently following these Iron Age mining and cupellation ventures (Renzi and Rovira Llorens 2015). By the eleventh to thirteenth centuries AD, gold and silver had become so highly valued that the Song emperors often had to prohibit common melting of these precious metals to ensure supply for official purposes (Liu 2015, 47). Twelfth century AD trade for English cattle and grain in exchange for German silver codified the "sterling" coinage of 92 wt% silver and 8 wt% copper (Scott 2010, 55).

Silver played an important role in Andean ritual. Ethnohistoric accounts as well as spatial analysis of excavated Moche tombs at Sipán indicate that gold and silver were associated with masculine and feminine aspects of the human body, with silver representing the moon and femininity (Lechtman 2007, 314–315; Zori and Tropper 2013). Inka custom dictated that only the elite were permitted to use silver (Rehren 2011; Zori and Tropper 2013). The oldest known silver smelting in South America was being carried out ca. 40 BC– AD 120 at the northern Lake Titicaca Basin, before the formation of the Tiwanaku state, the earliest state-level complex society in the southern Andes (Schultze et al. 2009; Stanish 2002, 190).

Electrum

It is common for gold and silver to occur together geologically, often in alloy form, and in specific percentages this alloy is called electrum. There is almost always some silver content in native gold, ranging from 5 to 50 wt% (Craddock 1995, 111). The higher range has been attested in jewelry from Phoenician Cádiz (46Au51Ag4Cu), although in this case it is not clear if the alloy is artificial or natural (Ortega-Feliu et al. 2007). Ancient peoples recognized this natural affinity of the metals—Pliny categorized electrum as over 20% silver and the remainder gold (Gouda et al. 2007, 15). The Egyptians obtained the natural alloy from surrounding regions including Nubia, and over time differentiated precious metals linguistically from just a single word to gold, silver ("white gold"), and electrum, the latter—which is attested hieroglyphically and iconographically—being hammered in sheets (Gouda et al. 2007, 15–16; Schorsch 2014, 277). As coinage was innovated and developed into the most cost-effective way to transmit wealth, electrum was used for the earliest coins in seventh century BC Lydia-Ionia. After 561 BC, King Croesus initiated a reform wherein gold and silver coinage was divided into separate mints, and in the fifth century BC, copper alloys as well began to be used as coins (Bürger 1995, 35–36).

Separation of gold from silver in the electrum alloy was not a simple matter, usually requiring the solid-state cementation of silver with chlorides, sulfates, or nitrates. Evidence for one process comes from Sardis. Either electrum grains or hammered electrum coins were packed in a slurry of salt and brick dust, and placed in a coarse ceramic vessel. This was put in a furnace and heated until the silver converted into silver chloride via solid-state processes and was absorbed into the cement mixture. The gold would be removed, and the silver cupelled out from the cement (Craddock 1995, 117–118, 2000a, b).

Platinum

Platinum can occur in native form (Killick 2014, 29), and with a melting temperature of 1768 °C, it stands as the only metal of antiquity that was not melted and cast into shape (Scott 2014, 75). Platinum group elements (PGE: platinum, palladium, rhodium, iridium, osmium, ruthenium) are found as impurities in ancient gold objects, such as in the third millennium BC Sumerian Early Dynastic royal tombs at Ur (Jansen et al. 2016; Meeks and Tite 1980; Ogden 1977). Although PGE were often considered bothersome impurities in placer gold, pre-Columbian smiths in the Colombian and Ecuadoran Andes developed methods to fabricate objects out of platinum, to sinter platinum granules with gold producing bimetallic objects, and to clad artifacts with platinum (Craddock 1995, 119–121; Scott and Bray 1980, 1994). Platinum metal was used in early scientific instruments due to its coefficient of expansion being similar to soda-lime glass (Scott 1991, 143), and its catalytic properties were utilized for the first lamp to be ignited without need for sparks from a tinder box in the early nineteenth century (Turner 1983, 127).

Surface Treatments

Now that non-ferrous metals and the special subclass of precious metals have been summarized, it is fitting to conclude these sections with a brief overview of surface treatments and plating techniques. There are several kinds of natural surface alterations, such as corrosion due to years and centuries of weathering either in open air or buried in archaeological deposits, inverse segregation when metals of different melting points separate during cooling, and patination that grows and then becomes inert to form a natural protective shield around certain alloys such as tin bronzes. There are also a host of artificial surface treatments that metalworkers have developed, often with the goal of creating an external aesthetic such as a golden hue plated over a cheaper bulk alloy. Even artificial corrosion and patination are common, dating at least to second millennium BC Mycenaean Greece and New Kingdom Egypt with the appearance of artificial purple-black patina over copper-gold alloys (Craddock and Giumlia-Mair 1993; Hughes 1993). There are so many types of plating techniques, often requiring complex electrochemical processes, that this survey is necessarily partial and covers only some of the more common design practices (see La Niece and Craddock 1993 for the authoritative, extensive treatment; for niello see Northover and La Niece 2009; for mechanical joining and soldering, see Lechtman et al. 1975; for experimentation with chemical solutions, see Benzonelli et al. 2017).

Manual, electrochemical, and depletion plating practices are known historically, with recipes for chemical modifications of gilded plating attested in Medieval texts (Crabbé et al. 2016). The *Book of Kings* relays that Solomon made it a frequent practice to gild architectural and decorative elements of the First Temple, and recent excavations in the City of David have yielded a piece of decorative sheet or ornament with low-tin copper bulk and silvered/gilded plating (Kaufman forthcoming). The archaeological record is full of examples of the design achievements of ancient smiths. In the New World, the gold-copper alloy known as *tumbaga* was manufactured through the practice of *depletion gilding*, for example, when gold is alloyed along with base metals such as copper, and the surface is depleted of those base metals causing precious metal surface enrichment (Lechtman 1973; Scott 1983). In the Andes, Moche smiths added copper to gold and/or silver (resulting in binary or ternary alloys), subjecting the alloy to repeated cycles of hammering, annealing, and pickling that would deplete copper from the surface of the sheet. This left a tough and stiff bulk alloy to shape with a golden or silver surface luster—the desired effect (Lechtman 2007, 318–319, 2014, 379). However, depletion gilding could also occur unintentionally during hammering and annealing, and was not always the desired outcome when the pink hue of the gold-copper bulk alloy was the goal (Sáenz-Samper and Martinón-Torres 2017). *Tumbaga* alloys were used to create a variety of object types, including musical pan pipes dating from the eighth to tenth centuries AD (Scott 1991, Appendix F).

In contrast to depletion gilding, it was also possible to plate base metals with precious metals when none of the latter were alloyed in the bulk to begin with. For example, ancient Ecuadoran smiths employed *wash* or *fusion gilding* in which a heated copper object was brought into contact with molten *tumbaga*. The gold-copper plate would fuse over the object, and could then be worked and pickled to enhance the golden surface further (Scott 1986). Simple dipping into a molten bath was also practiced, and this was often practiced in the Old World with metallic molten tin (*dip tinning*, Scott 2014, 81).

Before the advent of electricity, with the corollary ability to use electrical charge for electroplating of metals, metal artisans in both the Old and New Worlds utilized *electrochemical replacement plating* or *displacement plating*. In this process, the smith again begins with a base metal such as copper. An aqueous bath of corrosive minerals is mixed with gold and heated, salt is added to bring the solution from acidic to alkaline, and the copper is immersed into the solute paste. The gold from the solution then plates onto the copper, even into the tiniest angles and cracks that mechanically plated foil could not reach. The gilded copper object is then removed and heated, causing the gold plate and copper substrate to bond (Bray 1993; Lechtman 1984). Base metals could also be subjected to *mercury amalgam gilding*, in which mercury and gold are mixed and applied to the surface of the object (mercury can also form an amalgam with silver, tin, zinc, lead, and copper; Anheuser 2000; Scott 1991). The mercury evaporates when heated, leaving the gold behind on the surface. This technique was practiced in China as early as the Warring States period (Jett 1993).

Iron and Steel

The earliest use of metals and metallurgy was an inertial point of no return for human technological development. With the commencement of the Eastern Mediterranean Iron Age around 1200 BC, ferrous metals now received the close attention of both smiths and communities (Sherratt 1994). By the tenth century BC in the Near East, iron and steel implements surpassed copper alloys as the most utilized metal (Curtis et al. 1979; Dezsö and Curtis 1991; Waldbaum 1980, 1989). For the first time in thousands of years, the primary position of bronze was displaced by ferrous alloys in the metallurgical repertoire. However, bronze was not replaced, still occupying an important role in Near Eastern and European metallurgy due to the key factor that at this stage iron could not be cast. Due to its castability over iron, copper alloys continued to be employed in this period for intricate designs, armor, and helmets alongside steel weapons (Blyth 1993, 25). It was only in the later Middle Ages that cast iron began to be produced in Europe. In China, cast iron was invented in the early first millennium BC and achieved widespread use by around 400 BC (Rubin and Ko 1995; Wagner 2008, 104, 115). Therefore, ferrous metallurgy in China versus the rest of Eurasia developed on two different trajectories. Furthermore, Sub-Saharan Africa may have been another node of independent ferrous metallurgical innovation.

Chronology and Metallurgical Principles

Iron makes up about 5% of the Earth's crust, and the core of the Earth is an iron-nickel mass which gives it magnetic properties and helps keep it in orbit. There are two kinds of native iron. Telluric iron is native iron that has formed terrestrially with nickel content defined to be under 5 wt% (Craddock 1995). Meteoritic iron finds its origins extraterrestrially and arrived to Earth via meteorites. It is distinguished from telluric iron in two principal ways: (1) it has a nickel content of between 5 and 20 wt%, and (2) this causes it to have a characteristic Widmänstatten microstructure (overlapping crystalline nickel-iron lamellae, which however can also occur in human-produced nickel-iron alloys; see Hermelin et al. 1979). Ancient, pre-Iron Age humans knew that iron could come from meteors, as is evidenced textually. Egyptians called it "iron from heaven," and the Hittites—famous for their iron work—called it AN.BAR, or "black metal from the sky" (Waldbaum 1980). Punjab blacksmiths referred to it as "lightning iron" (Larsen et al. 2011). However, most iron must be smelted from ores (hematite, magnetite, goethite, limonite, etc.), and iron smelting most certainly was discovered as an accidental by-product of copper smelting, as is discussed in the next section.

There are several types of ferrous alloys when discussed within the context of antiquity. Most common is wrought iron, which is pure iron with little (0.02 wt%) to no carbon content. This metal has a characteristic α-ferrite microstructure. The presence of carbon in amounts less than 2.1 wt% in iron makes it a steel. There are several categories of steel microstructures depending on the carbon content and cooling rate (Scott 2013). Austenite is stable only in the temperature range of approximately 750–900 °C. If austenite is quenched from high temperature, martensite is formed at the quenched surface which is very hard and can hold a sharp edge, but is brittle and must be tempered for the optimal properties of tools and weaponry. When cooled in air, austenite breaks down into the ferrite-pearlite microstructure. Pearlite, or "natural steel," is a lamellar combination of ferrite and cementite. Ancient smiths and ironmongers from Japanese tatara specialists to Viking sword makers commonly combined these phases through folding, laminating, quenching, welding, case hardening, twisting, and hammering to optimize sharpness, hardness, toughness, and pattern welding in the fabrication of the best and most visually appealing pieces (Buchwald and Wivel 1998, 83, 94; Craddock 1995, 236–237; Ghiara et al. 2014; Godfrey and van Nie 2004; Lang 2017; Pleiner 1980; Scott 1991, 2013; Tylecote 1962, 295; Tylecote and Gilmour 1986, 15; Williams 2009).

Cast iron outside of China begins in the Late Antique to Middle Ages, most commonly produced following the introduction of the blast furnace, reaching Britain around AD 1500 (Disser et al. 2014; Lang 2017; Tylecote 1962, 300). The major difficulty with casting iron is not only about reaching high heat or reducing conditions, but also controlling the carbon content (Scott 2013, 120). Cast iron typically contains between 2 and 5 wt% carbon, making the product hard and brittle. The carbon will manifest microstructurally in three forms, being ferrite, cementite, and graphite (Craddock 1995, 236). An iron with free graphite is known as gray cast iron, with cementite as white cast iron, and with a mix of graphite and cementite as mottled cast iron. In ancient China, high-purity wrought iron smelted from the bloomery (direct) process would be alloyed with high-carbon cast iron to achieve a proper steel carbon content of between 0.8 and 1.2 wt%, a process known as co-fusion (Han 1998; Scott 2013, 119; Wagner 2007). The inevitable impurities in an iron alloy, including silicon, phosphorous, sulfur, manganese, nickel, and chromium, will confer varying properties (Scott 2013, 120). As seen in traditional African smelting furnaces, it is possible to obtain cast iron, wrought iron, and steel products all within one smelt. A single smelt could take place over the order of many hours or days of full-time effort by the smithing team (David et al. 1989). Comparative historical accounts confirm the great lengths of time that smiths would have to work the bellows. Farmhands employed by Viking ironsmith Skallagrim Kveldulfsson complained about how early they had to wake up to assist him in his forge, prompting him to recite a verse (translation by Scudder 2005):

> The wielder of iron must rise
> early to earn wealth from his bellows,
> From that sack that sucks in
> the sea's brother, the wind.
> I let my hammer ring down
> on precious metal of fire,
> the hot iron, while the bag
> wheezes greedy for wind.

It is likely that for most of antiquity iron and steel were thought to be two distinct elements. In 1774, Swedish chemist Tobern Bergman undertook chemical assaying experiments with wootz steel and identified that wrought iron, cast iron, and steel were differentiated by their carbon contents, although only later was carbon discovered as a unique element (at the time it was referred to as plumbago; Ranganathan and Srinivasan 2006, 69). Wootz or Damascus steel is a high-carbon cast steel with around 1–1.3 wt% carbon, traditionally developed in India from the second century AD and famed for its beautiful crystalline structures (Bronson 1986; Craddock 1995, 275; Maugh 1982; Perttula 2004; Scott 2013, 118; Smith 1982; Verhoeven et al. 1993; Verhoeven and Pendray 1993; Wadsworth and Sherby 1982). Sword blades of wootz were commonly made in the Islamic Middle East, forged famously in Damascus but also in Persia. Special small crucibles would be packed with wrought iron, cast iron, perhaps small amounts of silver, and organic materials such as wood, leaves, fruit skins, and some slag, then sealed, and packed down in a furnace to be fired at high temperatures with charcoal or coal for several hours or days (Craddock 1995, 275–277; Scott 2013, 118; Wagner 2008, 266). The steel would melt and solidify into a wootz cake which could then be forged and worked (Scott 2013, 117). Recent research on a Damascus steel blade has shown that part of the excellent properties may be due to carbon nanotubes and cementite nanowires formed during the production (Reibold et al. 2006). The fascination with wootz steel and attempts to recreate this lost technology have been a consistent hallmark in modern metallurgy. Michael Faraday futilely attempted to replicate wootz steel, but in the process, his experimentations in adding alloying elements to iron and steel helped revolutionize steel metallurgy (Ranganathan and Srinivasan 2006, 70–71).

Innovations in the Near East, China, and Africa

There are three regions where innovations in the earliest ferrous metallurgy blossomed, to a certain extent independently: the Near East, Sub-Saharan Africa, and China. In the Near East and Sub-Saharan Africa, iron and steel were acquired through the bloomery or the direct process (Buchwald and Wivel 1998). In China, cast iron extracted through a blast furnace (indirect process) was independently innovated (Han and Chen 2013). There are several possible mechanisms by which iron metallurgy was innovated, mostly considered to be a by-product of copper metallurgy. After the development of bronze metallurgy around 3000–2000 BC across Eurasia, the technological knowledge existed to experiment with various alloys, and this eventually resulted in the discovery and utilization of iron.

Three mechanisms are likely responsible for innovations in ferrous metallurgy and the transition to ferrous metallurgy from bronze metallurgy: (1) iron ore flux was used to reduce copper oxides and carbonates, and the smiths saw that iron blooms were accidentally created (Wertime 1980; Wheeler and Maddin 1980); (2) once the oxidized gossan of copper surface deposits was fully exploited, smiths used the remaining iron-rich sulfidic ores to smelt copper, and the smelts would result in unmelted iron and matte (Craddock 1995, 149–153); (3) to produce the world's first alloy—arsenical copper—sometimes an iron arsenide ore (*speiss*) was melted or co-smelted with copper, which would leave behind an iron by-product for the smith (Rehren et al. 2012; Thornton et al. 2009b). It was these early pioneering efforts in copper metallurgy that ultimately resulted in the recognition of the iron by-product and its utility. These are the several proposed mechanisms and paths through which copper metallurgy led to the discovery of iron metallurgy. However, in sub-Saharan Africa, current evidence does not rule out the independent invention of iron and steel without an earlier expertise in non-ferrous metallurgy (Killick 2009, 2015).

Iron, steel, and ferrous technology accompanied widespread sociocultural changes across Eurasia during the Iron Age. The combined advent of steel and the alphabet was particularly instrumental for the formation of Levantine Northwest Semitic secondary states such as those of the Phoenicians developed at Tyre, Sidon, and Byblos, and those that the Israelites formed at Jerusalem and Samaria (Joffe 2002; Price 1978). Phoenicians were some of the earliest adopters of ferrous technology, employing it for both weapons and tools by around 1000 BC (Dayagi-Mendels 2002; Gal and Alexandre 2000). They were the expert sailors and industrialists of their time, and profited greatly by introducing iron to communities across the Mediterranean. They traded iron for silver with communities in the Iberian Peninsula, which were unaware of ferrous metallurgy and iron products until the arrival of the Phoenicians (Aubet Semmler 2002a; Craddock and Meeks

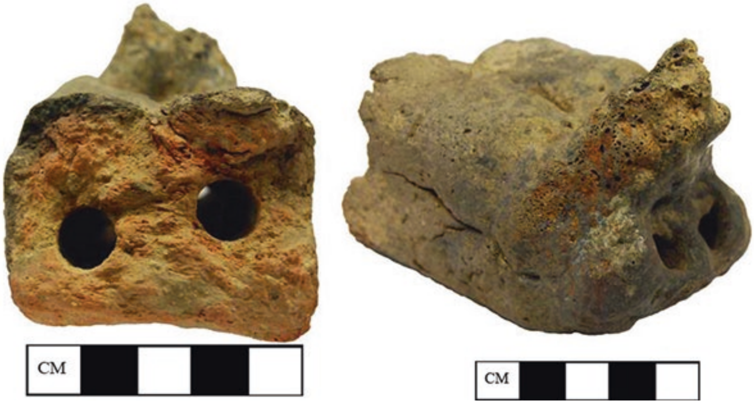

Fig. 1.4 Double-barreled ceramic tuyère with iron slag hood from an iron workshop at Phoenician Carthage (700–500 BC). The holes were poked into the slag when it was molten to facilitate air flow. Internal (left) and front and side (right) aspects shown (From the Bir Massouda 2000–2001 excavations carried out by the University of Amsterdam, courtesy of Roald Docter; see Kaufman et al. 2016, fig. 4; photograph by the author)

1987; Sanmartí 2009). By around 800 BC, the Phoenicians settled in North Africa in their colony of Carthage. They immediately began transmitting iron metallurgical knowledge to indigenous North Africans, a Neolithic culture unfamiliar with metallurgical technologies (Sanmartí et al. 2012). From 650–400 BC, the Phoenician colony of Carthage practiced intensive iron smithing and forging, likely trading the exotic new iron implements for agricultural products and other goods with the indigenous communities in and around Cape Bon (Fig. 1.4; Kaufman et al. 2016).

Blooomery iron technology began to be developed in China around 1000 BC, with some open questions regarding whether or not this invention was completely independent, or whether some cultural influences from the steppes sent iron down into the Central Plain through northwestern regions such as Xinjiang (Mei et al. 2015, 226; Wagner 2008, 88). From a technological standpoint as discussed above, it is reasonable to propose that iron metallurgy could have been invented independently in areas where bronze working was already prevalent (Han and Chen 2013, 171; Thornton et al. 2009b; Wertime 1980). Furthermore, debris of bloomery ironworking dating to the fourteenth century BC indicates a relatively early experimentation with iron smelting in China (Liu et al. 2014, 56).

Early first millennium BC ferrous metallurgy was characterized by the bloomery process, but by the fifth century BC, the world's earliest cast iron technology was invented (Han and Chen 2013), likely stemming from south Shanxi and west Henan and radiating out to other regions (Mei et al. 2015, 226). Although the earliest evidences of Chinese cast iron using a blast furnace are few in number and at times come from uncertain contexts, they demonstrate that by 800 BC, this technology was likely employed (Wagner 2008, 104), and after 400 BC (during the transition from Spring and Autumn to Warring States periods), cast iron production became widespread and conducted with expert knowledge (Lam 2014, 518; Needham 1964;

Wagner 2008, 115). Cast iron was used to make molds, and at times decarburized and puddled to render agricultural implements and weapons. Artifacts from the site of Dongheishan dating mostly to the Warring States and Han Dynasty display a high degree of technical mastery and include cast iron, decarburized cast iron, decarburized steel, puddled steel, malleable cast iron, and maybe co-fusion steel (Liu et al. 2014, 60). Chinese achievements in mass production of iron metallurgy are well-documented during the Western Han period (Han and Chen 2013, 176; Wagner 2001). Blast furnaces were invented in China by the fifth century BC and from there spread slowly, eventually to the Islamic world and all the way to Northern Europe, but only reached sub-Saharan Africa during European colonization (Huang et al. 2015; Killick 2015, 312).

Unlike the Near East and China, where the progression of extractive metallurgy went from pure copper, to arsenical copper, to tin bronze, to iron and steel, African metallurgists focused first on ferrous metallurgy (Bisson 2000, 84; de Barros 2000, 147–148). This technology brought with it rapid changes in sociopolitical organization, since the ability to control ironmaking gave power to certain specialist groups, whereas the incumbent lithic production was more ubiquitous and not as easily controlled. From an economic and mineral resource perspective, this meant that technology moved directly from the Stone Age to the Iron Age, much as in North Africa. Distortions in the geological record make radiocarbon dates unreliable from 800 to 400 BC, but it was broadly during this time when African smiths either invented or innovated imported technologies resulting in a diverse array of ferrous metallurgical traditions.

East Africa is home to some of the oldest potential iron metallurgy in Sub-Saharan Africa, and by 400 BC archaeological evidence demonstrates several types of smelting furnaces (Killick 2009, 2015, 312). Extensive ethnographic documentation of traditional African mining and smelting has provided a great deal of information on many technological aspects of pre-modern ferrous metallurgy, as well as social processes surrounding the practices. Pre-colonial ferrous metallurgical technological processes are highly variable in Africa (Rehren et al. 2007), with the most successful smelting systems simultaneously producing wrought iron, cast iron, and steel from a single smelt (David et al. 1989). The smelt is often conducted during the rainy season, perhaps due to cool temperatures (de Barros 2000, 153) but also because furnace conditions may benefit from increased moisture content. Until metal markets were flooded with cheap European steel (from Britain in the case of the Kenyan and Tanzanian Maasai), traditional smelting was a widespread practice that granted its practitioners economic power (Sumra and Katabaro 2016). Much about African metallurgy is known through ethnographic documentation of traditional African smiths, but very few of these traditions have survived European colonization (for examples of ethnographic documentation of traditional African ferrous metallurgy, see Avery et al. 1988; Brown 1995; Childs 1991; David et al. 1989; Humphris and Iles 2013; Nkirote 2013; Rehren et al. 2007; Schmidt 2009; Soulignac and Serneels 2013).

Still, despite the introduction of commercial metals, survival of this prehistoric technology in various locations allows for a synthesis of traditional African metallurgical practice, albeit particular practices and resources diverged from region to region. Magnetite-rich sands were processed to win the ore, often aided by natural hydraulic action (Larick 1986, 169). Charcoal for the furnace charge was made with acacia timber where available. Differential forest management practices are witnessed as in some places timber stands were devastated due to metallurgical fuel acquisition (de Barros 2000, 148; Håkansson et al. 2008, 378), whereas in others healthy forests survived indicating either low-level manufacture or successful timber management strategies (Eichhorn et al. 2013; Killick 2009; Lyaya 2013). Metallurgical ceramics such as tuyères and crucibles would have to be prepared, tempering clays in such a way that they would not crack under thermal stress. This was often achieved by including chaff or other organic materials that could burn off.

The furnaces themselves ranged from small slag-pit shaft furnaces, to several-meters-tall shaft furnaces with many tuyères, to natural draft furnaces with no bellow action depending wholly on wind delivery (Killick 2015, 312). The furnace would be preheated before being charged to reduce thermal shock and increase efficiency of the smelt, usually with valveless bellows (Avery and Schmidt 1996, contra Killick 1991). A differentiation in isotherms and reducing conditions through heat loss and variable furnace design made smelting an unpredictable activity, and the elaborate rituals often witnessed before, during, and after the smelt were seen as a way to mitigate smelting failures (Childs 2000, 221–222; Schmidt 1997a, b). Sub-Saharan African smiths used the bloomery process, delivering air into the charge creating a reducing atmosphere, temporarily tapping slag and removing blooms which would then be forged and smithed into final products improved by annealing and quenching (Killick 2015, 312). At times, pits would be dug under the shaft furnace and padded with plant matter to catch the slag in its hollows while allowing the reduction reaction to take place above (Iles 2009).

Industrial Revolution

The Chemical Revolution and Industrial Revolution brought about exponential changes in the development of metallurgical technologies (Eddy et al. 2014). One of the pillars of this rapid change was the ability to cast huge amounts of steel. As mentioned above, most of the great smiths and metallurgical innovators throughout the ages are nameless to us, having left their technical legacies alone. In the modern age, our reverence for inventors (and our ability to record great amounts of information beginning with the printing press, as well as perhaps changing attitudes on individualism) has led to some recognition, and in the eighteenth and nineteenth centuries, two names stand out in particular, Henry Cort and Henry Bessemer. Students, of technology are also much indebted to John Percy's prolific treatises and writings. Cort patented a new kind of puddling system, whereby desiliconized cast or pig iron (high carbon metal with impurities) would be decarburized into wrought iron (King 2005, see Ono, Chap. 4, this volume). Iron was melted in a separate puddling bed where the carbon and slag oxidized, leaving the pure metal. The ingenuity of Cort's system over previous methods was that it isolated the iron from the fuel, in this case mineral coal, thereby freeing the final pure, wrought iron product from deleterious sulfur impurities usually associated with coal fuels (Wagner 2008, 32–34).

One of the great difficulties in the traditional bloomery process is to keep temperatures constant, not letting the furnace get too hot, thereby creating cast iron that is useless without additional treatments such as remelting, decarburization through puddling, or co-fusion (Wagner 2008, 105). Henry Bessemer solved this problem. In Bessemer's own words (Bessemer 1905, 138), state-of-the-art metallurgy before his process was characterized by there being:

> no steel suitable for structural purposes. Ships, bridges, railway rails, tyres and axles were constructed of wrought iron, while the use of steel was confined to cutlery, tools, springs, and the smaller parts of machinery. This steel was manufactured by heating bars of Swedish wrought iron for a period of some six weeks in contact with charcoal, during which period a part of the carbon was transferred to the iron. The bars were then broken into small pieces, and melted in crucibles holding not more than 60 lb. each. The process was long and costly, and the maximum size of ingot which could be produced was determined by the number of crucibles a given works could deal with simultaneously. Such steel when rolled into bars was sold at £50 to £60 a ton. The wrought iron bars from which the steel was made were manufactured from pig-iron, as was all wrought iron, by the process known as 'puddling.' Naturally, such a process was costly; puddling demands great strength and endurance on the part of the workmen, combined with much skill.

Bessemer goes on to explain how his metallurgical contemporaries experimented with fusion of malleable scrap with pig iron and coke "to improve cast iron" but which resulted in the unfortunate product of white cast iron with high sulfur impurities (Bessemer 1905, 138–139). During a series of experiments in fusing steel in a pig or cast iron bath using a reverberatory furnace that he designed and for which he filed a patent in 1855, an unintended "incident" occurred which due to his "impulsive nature, and intense desire to follow up every new problem that presented itself" sent him on a course to revolutionize ferrous metallurgy and usher in a new era of structural materials (Bessemer 1905, 140–141). It is worthwhile to recount this process in some detail, as it is rare to have the experimentation component of the design process so described by the inventor (although some claimed the American William Kelly to be the inventor, reminding us that litigation and competing claims over patents can also be a common part of the technology process (Skrabec 2006, 63–64)). Bessemer noticed that "atmospheric air alone was capable of wholly decarburising gray pig iron, and converting it into malleable iron without puddling or any other manipulation" (Bessemer 1905, 142). Essentially, by directing a blast of oxygen directly into the molten bath, a combustion process occurred by which the carbon and silicon content of the molten iron was vaporized or expelled as slag out of the mouth of the converter. The process also requires a heat above the melting temperature of iron, so that it does not freeze while it is being poured out. A great deal of fuel was needed to maintain this temperature, which apparently was difficult to provide during the reaction process and would also increase the cost of the procedure.

In turn, Bessemer realized that by bringing the bath to a high heat and bombarding it with oxygen via tuyères, the combustion process became so violent and explosive that the reaction became self-heating. To Bessemer's great surprise, the first experiments in fact resulted in such unexpected combustive power that a series of "mild explosions, throwing molten slags and splashes of metal high up into the air" resulted in a "veritable volcano in a state of active eruption." The workers could not approach the reaction area and the building almost burned down. After 10 min, the product was able to be tapped, and it was found to be "wholly decarburised malleable iron" (Bessemer 1905, 144). Later, this wrought iron could be melted and fused with iron of various carbon contents, allowing for the total control of carbon content and the casting of steels. With these principles established, Bessemer focused his efforts on perfecting furnace design to accommodate the combustion reactions, and his patented process began to spread across the industrializing world (such as Davis 1929).

Ecology and Environmental Impacts

The previous sections have offered an outline of metallurgical traditions, the design specifications for many ancient and historical alloys, and the various properties they offer. The production of all of these types of metals is a labor-, resource-, and energy-intensive endeavor, and no discussion about metallurgical design or metallurgy in society is complete without considering these factors. Fallout from metallurgical activity affects human health and environments. Ecology, or the interplay between environment and society, is impacted by industrial activities and has been for millennia.

Mining

A discussion of mining can be framed in two distinct ways, the productive and the destructive. Productive mining is the need to acquire metallic minerals so they can be smelted, cast, and used by individuals, governments, corporations, and other entities. However, mining necessarily is coupled with the destructive process, in which sediment and accompanying ecosystems are heavily disturbed, waterways diverted for sluicing, and waste such as heavy metal contaminants and slag left or released into natural environments.

A brief overview of the types of mining in the productive sense is now detailed (see Gordon, this volume, for an extensive treatment of recent mining innovations). There are many methods to remove metalliferous ores from the veins, lodes, alluvial, and colluvial deposits that carry them. Bronze Age miners would dig open pit mine shafts (Rothenberg and Blanco-Freijeiro 1981), and tunnel shaft-and-gallery mines (Rothenberg 1999). Veins and deposits inside mines would be burnt, called firesetting, to loosen the walls to make it easier for miners to break up the ore. Hauling mechanisms up from the pit or gallery could be installed by leaving rock walls intact (Rothenberg and Blanco-Freijeiro 1981, fig. 25, or through the construction of a haulage-way (Book V, Agricola's *De Re Metallica*, translated by

Hoover and Hoover 1950). Hydraulic mechanisms were often employed to beneficiate ores or win gold. Hydrological engineering at the Hellenistic Laurion silver mines employed recycled water for the mining operations (van Liefferinge et al. 2014). Gold prospectors of the American West innovated hydraulic mining or sluicing, blasting water through a deposit to win gold with such force that entire hilltops could be taken down (Brands 2003; Craddock 1995; Lynch 2002).

Mining camps and settlements have been a consistent feature of human mineral exploitation, and often subsist on the fringes of society (Knapp et al. 1998; Knapp and Pigott 1997). Mining camps in frontier zones in the historical period are commonly, paradoxically home to the moral liminal spaces of society while being key strategic outposts for the expansive political economies of colonial states, such as in the American West (Hardesty 1988, 1998).

Mining and resource acquisition enterprises of colonial states can share spatial similarities across time. Sociopolitical design is expressed architecturally in hierarchical settlement layouts established by corporate owners and colonial administrators to separate themselves from laborers, seen in both archaeological and historical records (Lightfoot et al. 1998; Skibo and Schiffer 2008, 31–34). Frequently, there is a mining node, then a warehouse, then export (Hardesty 1998, 89). This pattern is seen in the American West, but it finds parallels with Phoenician mineral exploitation and extractive metallurgy in the Iberian Peninsula during the Iron Age (Aubet Semmler 2002b; Niemeyer 2002; Ruiz Mata 2002). Based in the major urban center of Tyre, the Phoenicians developed a strategy to maintain their autonomy from the region's Neo-Assyrian overlords through being the indispensable procurers of luxury goods, exotica, and precious metals. The establishment of far-flung warehousing centers could only be commercially viable for the Tyrian state if high returns on their investment into colonial and mercantile infrastructure could be obtained, the likes of which could only be derived from precious metals, especially silver (Johnston 2013; Murillo-Barroso et al. 2016; Renzi and Rovira Llorens 2015). Phoenician traders were the agents of this mercantile cooperative network that enfranchised local elites through the provision of otherwise unobtainable luxury commodities, mostly in exchange for rights to silver mines, silver, and establishment of warehousing colonies (Johnston and Kaufman forthcoming). Today, we maintain this legacy of mining, warehousing surplus, and export with exponentially greater amounts of metal at depots such as the London Metal Exchange. Transportation is a major factor here, with corporate control by state or economic actors playing an inextricable part.

Waste and Heavy Metal Pollution

Metallurgy is a dirty industry, with destructive pollutive dumping of slag and tailings being a major downside to the practice. Metallurgical landscapes of pollution are common, but much if not all of the waste is tucked and dammed away. However, the infrastructure to prevent fallout does not always hold, and disasters have become commonplace. Cleanup and safety efforts seem to be increasing, but it remains to be seen if current investment is sufficient (see Gordon, this volume). Metallurgical pollution can be broadly conceived of in two ways: atmospheric and localized.

Pollution of copper, lead, zinc, antimony, arsenic, and mercury, as recorded in such relatively chemically passive deposits as Greenland ice (Hong et al. 1994, 1996; Nriagu 1996), ombrotrophic peat bogs (Mighall et al. 2009; Shotyk et al. 1996), and lake and lagoon sediments (Hillman et al. 2015; Manteca et al. 2017; Pyatt et al. 2000), has peaked and troughed corresponding to changes in industrial capacity since the Bronze Age, with greatly accelerated global heavy metal contamination since the Industrial Revolution. Annual copper emissions into the atmosphere were measured as high as ~2100 to 2300 metric tons at the peak of the Roman Empire around 2000 years ago, as well as during the Northern Song Dynasty in China around 1000 years ago. These outputs were even higher than copper emissions for the mid-eighteenth and nineteenth centuries, and up to around 10% of modern emissions (Hong et al. 1996: 248, fig. 2). These global emissions are the result of cumulative local ecologies, where numerous mining, smelting, forging, and melting operations altogether result in local ecosystem pollution.

The by-product of metallurgical production—slag—as well as tailings from the mines, and abandoned mining and beneficiation infrastructure, has been left behind when mines fail or nearby settlements are deserted. There are veritable mountains of slag in Cyprus due to the long history of copper exploitation on that island (Kassianidou 2012). A single site within the ancient mining region of Wadi Faynan in Jordan has some 15,000 tons of slag (Ben-Yosef and Levy 2014). Slag is by weight and volume the most common archaeometallurgical remain, due to its durability, chemical passivity, as well as the fact that so much of it was produced. Metallurgical waste and dumping impact local soils and sediments, and heavy metal pollution cycles through the environment for millennia, prompting a need for identification and remediation which is often costly and complex (Brooks 1998; Grattan et al. 2014; Knabb et al. 2016; Monna et al. 2004; Pontevedra-Pombal et al. 2013; Rascio and Navari-Izzo 2011; Vigliotti et al. 2003; Zhang et al. 2017).

In 2015, mismanagement of the old Gold King mine in Colorado resulted in a spill of nearly a million pounds of toxic metals into natural waterways. This mine is but one of 160,000 abandoned hard rock mines in the western United States, 33,000 of which pollute water sources and have arsenic-laced tailings (Frosch and Harder 2015). Also in 2015, the Fundão dam in Brazil—holding back 55 million cubic meters of sludgy tailings—burst, causing the destruction of villages, the deaths of at least 17 people, and a trail of pollution 400 miles long as the toxic deluge traveled to the Atlantic Ocean (Kiernan 2016). Designing and refurbishing dams that will hold against the test of time, and against the digging of ever deeper mines as well as the containment of historical tailings, are challenges that will grow increasingly more urgent.

Detriments to Human Health

Health detriments to individuals from mining and metallurgy are widely recognized today, with downstream pollution neglected by governments and corporations constituting an abuse of human rights (Ballard and Banks 2003; Townsend 2009, 45–52). Even in developed countries that have passed regulation to protect their citizenries from heavy metal toxicity such as the Safe Drinking Water Act in the United States, recent events such as lead poisoning in Flint, Michigan, highlights the difficulties in confronting legacy infrastructure in tandem with inadequate monitoring, lack of regulation, and minimal or no investment in improvements (Ingraham 2017).

Metallurgical design is not restricted to the product specifications of an object. The engineering of down-the-line sustainable and safe planning is a design process that must factor in human contact with contaminants from the ore source, to the consumer, to waste treatment and management (see Gordon, this volume, for more extensive discussion of mining design).

Poisoning and health detriments from metallurgy and metal products or infrastructure are not a new phenomenon (Linduff 1977). Metalworking can be hazardous, and without well-developed safety protocols, carries high risk of acute injury and accident as well as long-term health problems to miners, smiths, and inventors. In the mid-sixteenth century, Agricola in his treatise *De Re Metallica* relayed (translation by Hoover and Hoover 1950):

> The critics say further that mining is a perilous occupation to pursue, because the miners are sometimes killed by the pestilential air which they breathe; sometimes their lungs rot away; sometimes the men perish by being crushed in masses of rock; sometimes, falling from the ladders into the shafts, they break their arms, legs, or necks; and it is added there is no compensation which should be thought great enough to equalize the extreme dangers to safety and life.

Around AD 600, a copper miner in Chile (Chuquicamata) died and was naturally mummified in a mine along with his mining equipment and a basket of ore (Bird 1979; Craddock 1995, 42–47; Weisgerber 1992). Some mining communities work down ore deposits over several generations, and an intimate portrait of the life and living conditions of tenth century BC miners at Timna in southern Israel can be found in Ben-Yosef et al. (2017). Conditions could be extremely difficult in this desert region. North of Timna in Faynan, both sites situated in the Aravah Valley copper deposit, Roman prisoners were “condemned to the mines” where they were subjected to severe physical conditions in the desert heat, copper and lead poisoning, and exposure to radon gas (Grattan et al. 2002, 2004; Najjar and Levy 2011).

In addition to health hazards due to mining conditions and accidents, heavy metal poisoning can be another concern for metallurgical practitioners (Martin et al. 2005; Özdemir et al. 2010; Pyatt et al. 2005; Stuart-Macadam 1991, 103–104). Of course, arsenic has been used nefariously for intentional harm (Wolfsperger et al. 1993), but the interest here is rather the unintentional detrimental side effects faced by metallurgical practitioners and people in close contact with toxins. The hair of glacier mummy Ötzi “the Iceman” was found to have elevated levels of arsenic and copper, showing he was either directly involved or in close proximity to the incipient copper working technology of the Alps in the fourth millennium BC (Bolt 2012; Brothwell and Grime 2002). Furthermore, heavy metal and metalloid residues have played a toxic role in non-metallurgical environments. Despite attempts for the repatriation of cultural artifacts to Native American tribes via the Native American Graves Protection and Repatriation Act (NAGPRA) to be a seen as a wholly positive experience, many objects stored in museums and returned to the tribes are coated in old arsenic and cyanide pesticide treatments, creating a toxic health burden for the receiving institutions and personnel for which they are not equipped or trained to manage (Nash and Colwell-Chanthaphonh 2010). Arsenical dyes and pigments were popularly used for the brilliant greens, yellows, and blues of Victorian era wallpaper, until reported cases of rotted flesh, death, and an incident where Queen Victoria responded to the ailment of a visiting dignitary by stripping Buckingham Palace of all its green wallpaper prompted a change to arsenic-free papers (Ball 2003; Hawksley 2016; Meier 2016). Preservation of the health and safety of mining professionals and the populace usually must be enacted via regulation based on societal demand, at the sociopolitical organizational level of state or empire, especially when infrastructure or industrial methods are the source of the ailment.

Finally, just what defines an elevated level of contamination is a cultural determination based on biological risk. Plants hyperaccumulate certain kinds of metals and can remediate polluted environments through several known processes. As one example, phytovolatilization is when toxins such as mercury, selenium, and arsenic are absorbed into plant roots and converted into non-toxic forms, which are then released harmlessly back into the atmosphere (Brooks 1998; Favas et al. 2014). In humans, metals are necessary for several biological functions, and in certain conditions inhibit a variety of pathologies (Jomova and Valko 2011). An argument has recently been made that *Homo* species have evolved a physiological adaptation to tolerate certain levels of heavy metal contaminants, as introduced into their cave habitats by bat guano and the combustion by-products from the use of fire (Monge et al. 2015).

Fuel

Although this is the final section of this survey, it is one of the most important topics to be covered. Without fuel for smelting, melting and recycling, heat treatments, firesetting the mines, firing technical ceramics like crucibles, etc., there is no metallurgy. The metallurgists of antiquity procured fuel from the dung of domesticated animals, wood and timber charcoal, coal, and peat (Dodson et al. 2014; Rehder 2000; Wertime 1983). One major paleoecological limiting factor in paleoindustrial metal production is that of fuel availability and proximity to the ore source (Li et al. 2011; Wagner 2008, 145).

Timber management in particular has been an integral part of metallurgical production, as timber charcoal was the major source of fuel in antiquity (see Kaufman

2011 and citations therein for a more complete survey of sustainable timber management practices in metallurgy since prehistory; Kaufman and Scott 2015). All forest stands on the island of Cyprus were repeatedly stripped and regenerated at least 16 times to fuel metallurgical furnaces over the course of three millennia (Constantinou 1982). Timber as an essential commodity for metal production has driven the price of metals. In a deforested region such as the Late Medieval Middle East where local timber resources were precious, imported wrought iron from forested areas of India could fetch a high enough price to make it worth shipping iron cargo across the Indian Ocean (Craddock 2003, 243).

In the first centuries of Spanish occupation of the Andes, three distinct types of silver production were being carried out simultaneously: the indigenous *huayrachinas*, or furnaces which were designed to be fuel efficient but with an incomplete metal yield, the European dragon furnace with higher metal yield but which consumed more fuel, and the amalgamation patio process. The utilization of indigenous fuel-efficient furnaces in South America at the expense of metal yield is economical in this context due to the limited timber resources but abundant raw mineral wealth. The European dragon furnace was designed to maximize short-term profit in silver gain without concern for the long-term sustainability of rare forest stands (Rehren 2011).

Concluding Remarks

The chronologies of incremental and sudden alloy innovations differ from region to region, but the design principles remain the same. The touch, feel, look, sound, and use of metal alloys, objects, and structures must satisfy aesthetic, mechanical, and acoustic properties, financial demands to increase economic liquidity and facilitate hierarchical social interactions through surplus wealth, and cultural taboo. Metallurgy, like any technology, is about the combination of choices. These choices are driven by particular tastes of the audience or society, as well as the individual agent, consumer, or designer. This survey details design constraints and innovations based on metalliferous minerals and metallurgical practice, from the attraction of hominins to ores and pigments, to the birth of co-smelting and tin bronze in the Bronze Age, to the ability to cast iron and steel in massive quantities in the Industrial Revolution. Within a context of particular cultural choices, the common threads found throughout millennia of metallurgical practice are all dictated by the design process: concept, experimentation, and production. These three spheres of design are not necessarily developed linearly or in a vacuum, and can be seen as a dynamic feedback process wherein experimentation can lead to new concepts, and production begets further experimentation.

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Chapter 2
The Beginnings of the Use of Iron and Steel in Heavy Armour

Stephen M. Walley

Historical Introduction[1]

The use of serious amounts of iron and steel in armour began in 1859 with the development of ironclad warships by France and Britain (Fig. 2.1). By this date, iron ships had been around for some time. The first one we know about made its maiden voyage to Birmingham, England, on a canal on July 28, 1787 (Grantham 1868). The first iron warship (really a floating artillery battery) was built in 1839 for the East India Company and was used in 1842 on the Pearl River in the First Opium War with China (Grantham 1868). This allowed a direct (and mostly favourable) comparison with wooden ships of which the rest of the fleet was formed, although there was some concern about whether the danger from shot holes might be greater for an iron as compared to a wooden ship.

Ironclads (Fig. 2.2) famously had a role in the American Civil War (1861–1865). Note the similarity in outwards appearance to the wooden battering ships used by the Spanish in the siege of Gibraltar in 1782 (Fig. 2.3). One of the major visible differences between the 1782 and 1861 ships was the change from wind to steam propulsion.

In 1921 Robertson wrote a chapter in his book *The Evolution of Naval Armament* about the introduction of explosive shells to European navies. Robertson pointed out that for many centuries of land warfare, guns were not very efficient at "battery", namely, the destruction of an opponent's defences. Thus "endeavour was made to

[1] *Note on imperial units of measurement:* Some quotes in this chapter are taken from British and American sources where imperial units of length and weight were used. For those unfamiliar with these units, the (approximate) conversion factors to the metric system are as follows: 1 inch is 25 mm, 1 foot (= 12 inches) is 305 mm, 1 yard (= 3 feet or 36 inches) is 0.9 m, 1 mile (= 1760 yards) is 1.6 km, 1 pound (abbreviation lb.) is 0.45 kg), and 1 (British) hundredweight (abbreviation cwt.) (= 112 lbs.; don't ask) is 51 kg.

S. M. Walley (✉)
SMF Fracture and Shock Physics Group, Cavendish Laboratory, Cambridge, UK
e-mail: smw14@cam.ac.uk

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Fig. 2.1 *HMS Warrior*, launched 1860. Now moored at Portsmouth Historic Dockyard. (Photographed by the author on March 16, 2017)

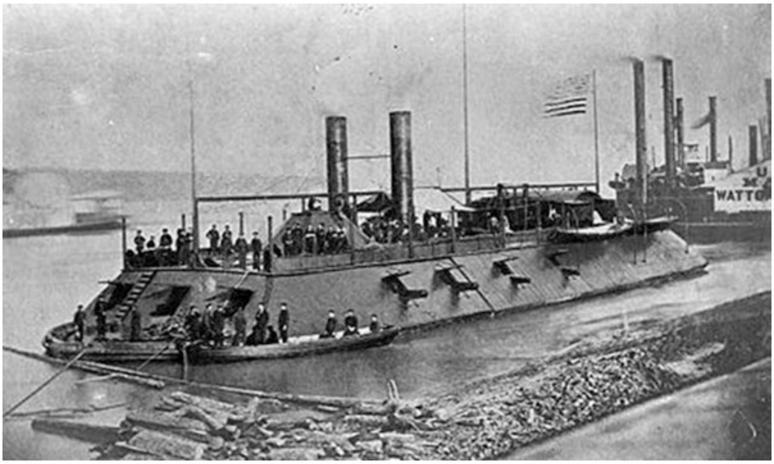


Fig. 2.2 City-class ironclad floating battery, *USS Cairo*. According to Bearss (1966), this is the only known photograph of this ship taken between its launch sometime in 1861 and its sinking on December 12, 1862. (Photographer unknown)

substitute incendiarism or explosion for the relatively ineffective method of impact" (Robertson 1921a, 160). He then continued: "In sea warfare the solid cannon ball remained the orthodox missile; the use of explosive or incendiary shells was deemed so dangerous a practice as to forbid its acceptance by the great maritime powers, save in exceptional cases, until the nineteenth century" (Robertson 1921a, 161). However,

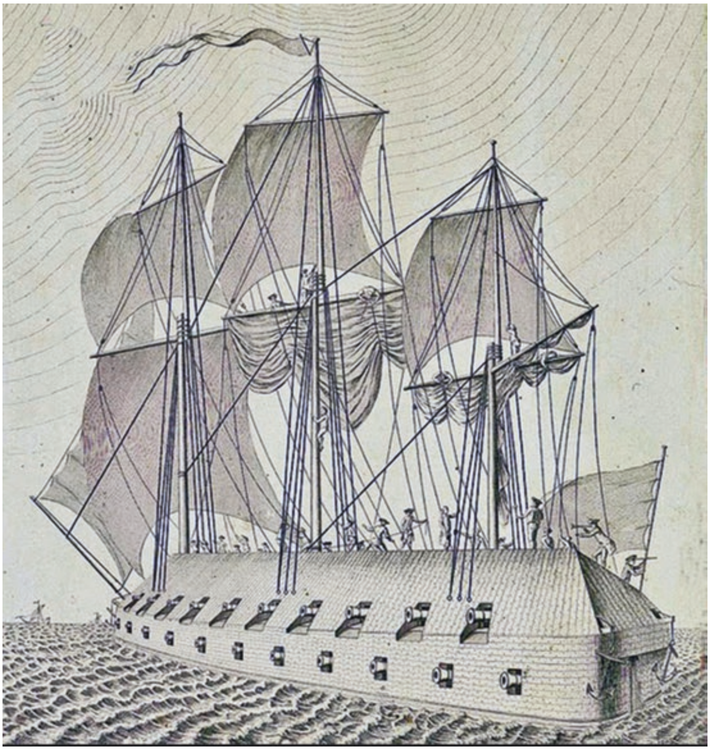


Fig. 2.3 *Pastora*, one of ten wooden battering ships used by the Spanish in the siege of Gibraltar in 1782

the decision of the French military authorities in 1837 to the general installation on board ships of guns that could fire explosive shells (*canons-à-bombes*) (Robertson 1921a, 175–176) quickly led to Britain doing the same. Solid shot was retained, however, as it had greater range and penetrating power (Robertson 1921a, 176).

The main technical reason why several navies (most notably the French, British, American, and Russian) eventually replaced all-wood ships by wooden ships protected by iron plates was the development by Henri-Joseph Paixhans in France of explosive shells that could be fired horizontally from guns towards a ship's broadside (Anon 1828; Morgan and Creuze 1829; Paixhans 1822a, 1825, 1827, 1838; Simmons 1837, 1839). For if such shells lodge within the timbers of a wooden ship, they are almost impossible to remove before they set the ship on fire. Paixhans saw that this would lead eventually to ships having to be protected by iron armour: "Une autre influence de ce cannon-à-bombes, qui brise et incendie si vivement les vaisseaux de bois, ce sera tôt ou tard l'adoption de vaisseaux en fer, ou recouverts d'une armure suffisante contre l'artillerie" ("Another consequence of shell-firing guns, which shatter and burn wooden ships so effectively, will sooner or later either be the introduction of iron ships or ships covered with sufficient armor to resist this type of artillery").

The reader may be asking why it took more than 30 years to initiate the change. This matter was thoroughly researched by Baxter in1933 and later by Sondhaus (2001). The main technical reasons for being cautious about armouring wooden ships by cladding them with iron were as follows: (i) the cast iron that was available at the time was too brittle (Holley 1865a); (ii) for electrochemical reasons, iron (unlike wood) cannot be protected by copper sheets against fouling by plant and animal life (Brown 1990a; Fincham 1851b; Mallet 1847); and (iii) the magnetic nature of iron which was known to make compasses useless (Bennett 1827), although a method was quickly developed to compensate compasses for the magnetic effect of iron whether in the hull or the masts (Airy 1840; Hays 1845).

Paixhans was not the inventor of explosive shells. For as he himself pointed out, hollow shells had been in use since at least 1434 to deliver fire to an enemy (Paixhans 1822b). Initially this was achieved by simply throwing firepots at the opposing troops (Fig. 2.4).

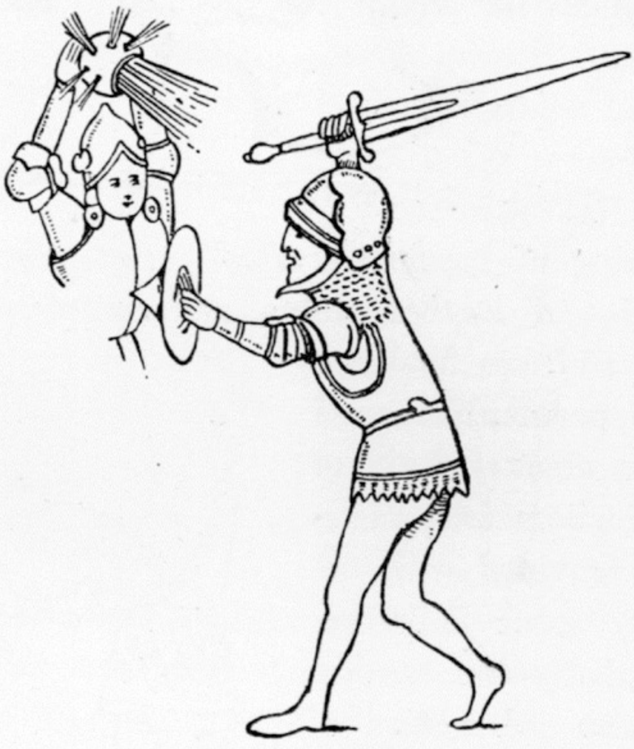


FIG. 337.—Petardier and swordsman, fifteenth century. (Roy. MS. 18, E. V.)

Fig. 2.4 Fifteenth-century petardier (with firepot) and swordsman. (From Ashdown 1909)

However, the ability to make shells that could both survive being fired and also explode when and where required was a long time coming. As Hogg pointed out in 1963 (pp 51):

> Our ancestors were not insensible to the advantages of a shower of small particles over that of a single missile when engaging an enemy in combat and the concept of a projectile breaking up during flight was amongst the early dreams of artillerymen. Shells were therefore fired on rare occasions during the infancy of artillery technique. Shot, however, were considered to be more efficacious and the reason is not far to seek. Man's thoughts had outrun his manufacturing ability, and the absence of an efficient fuze until the middle of the nineteenth century damped the ardour of the shell protagonist in the shell versus shot controversy of earlier centuries.

As hinted at by Hogg, from time to time, there were attempts at firing shells out of guns. For example, as early as 1674 (pp 21), Anderson wrote a section in his book *The Genuine Use and Effects of the Gunne* headed: "Concerning the shooting of granados out of long gunnes, as suppose a cannon and a demy-cannon, &c". Anderson's book is very theoretical, consisting of a set of mathematical "propositions" linking the diameter of the bore of the gun, the length of the gun barrel, and the weight of the shot to the range. Ten years later Mallet published a drawing of a spherical shell containing a fuse in volume 3 of his work *Les Travaux de Mars* (Fig. 2.5).

Before Paixhans' studies, the most famous case of explosive shells being successfully fired from guns occurred during the siege of Gibraltar in 1781. In Drinkwater's account, *A History of the Late Siege of Gibraltar* (1793, 63), we read:

> Our firing was still continued; but their parties were at too considerable a distance (being near a mile) to be materially annoyed by our shot; and the works being surrounded by sand, the large shells sunk so deep, that the splinters seldom rose to the surface. An experiment was therefore recommended by Captain Mercier, namely to fire out of guns, five and a half inch shells, with short fuses; which were tried on the 25th [September], and found to answer extremely well. These small shells, according to Capt. Mercier's method, were dispatched with such precision, and the fuses calculated to such exactness, that the shell ofen [sic] burst over their heads, and wounded them before they could get under cover.

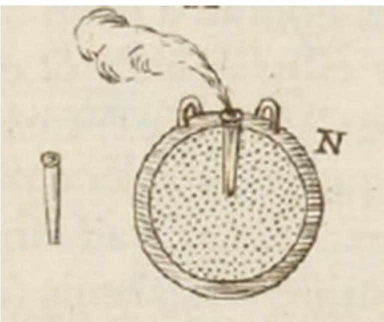


Fig. 2.5 Mallet's design for a fused exploding shell shown in fig. 19 of his book *Les Travaux de Mars. Vol. 3* published in 1684

Fig. 2.6 Portrait by F. Arrowsmith of Henry Scrope Shrapnel (1761–1842). (Reproduced by kind permission of the Royal Artillery Institution)

Another English officer present at the siege of Gibraltar was Henry Scrope Shrapnel (Fig. 2.6). He was inspired by what he saw to develop a variable duration fuse for hollow shells that were not only filled with explosive but also with shot (Fig. 2.7). The charge of explosive was just sufficient to break the casing of the shell in flight resulting in the enemy troops being showered by high velocity pieces of metal. In 1852, his surname became the official name for this type of exploding shell (McGuffie 1965, 78) and subsequently for any fragment thrown out by an explosion.

Those who made and supplied body armour must have carried out tests to see if it worked, but surviving reports of systematic studies on terminal ballistics are rare before the seventeenth century (Anon 1667; de Gaya 1678). One of the few ancient records that does survive dates from the eleventh century AD in China. It was written by Shen Gua (1031–1095) and has recently been published in English translation by Wagner (2008):

> In Zhenrong Military Prefecture there is a suit of iron armor which is carefully preserved and handed down as an heirloom. When Han Wei-gong was serving as Military Commissioner of Jingyuan he took it out and tested it. At a distance of fifty paces he shot at it with a strong crossbow and was unable to penetrate it. One arrow did penetrate an armor scale: this one hit a drill-hole, and was pared down by the drill-hole, all of the iron curling back. Such was its hardness.

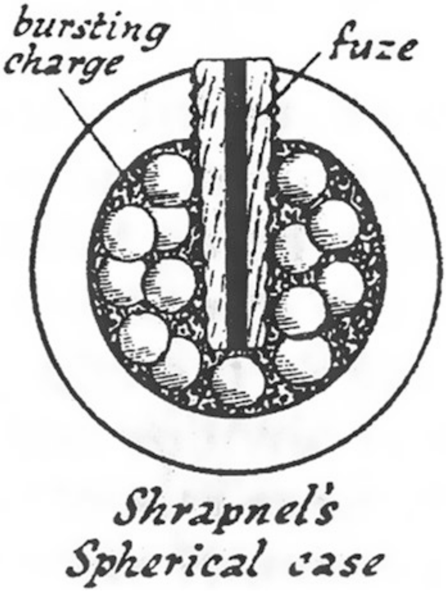


Fig. 2.7 Schematic diagram of Shrapnel's design for a shell ignited by a slow-burning fuse. Note the similarities to Mallet's design, except that it contains shot. (From Wilson 1944a, 1945. Reproduced by kind permission of the Royal Artillery Institution and the Royal Artillery Journal)

However, the account does not appear to report part of a systematic study of the penetration of body armour by arrows but rather describes a provincial governor abusing his authority.

Until the invention of gunpowder, soldiers commonly either threw or shot sharp-pointed things such as javelins, lances, and arrows (Fig. 2.8; Hurley 1975) or used slings (Grose 1786; Hirsch et al. 1995; Keeley et al. 2007; Scoffern 1858a), ballistas (Fig. 2.9; Rossi 2012; Rossi and Pagano 2013), and trebuchets (Fig. 2.10; Chevedden et al. 1995; Hannam 2009; Tarver 1995) to hurl hard round things such as rocks and stones at their enemies. For example, the following account reports events around Jerusalem from the eighth century BC: "And [Uzziah] made in Jerusalem engines, invented by cunning men, to be on the towers and upon the bulwarks, to shoot arrows and great stones" (2 Chronicles 26:15, King James Translation).

Although hand-held guns were invented early on (Fig. 2.11), bows and arrows continued to be used for centuries after the invention of the gun for the reasons given in the following quote from Smythe in 1590: "I think there is no man of any experience in the aforenamed weapons, that will denie, but that Archers are able to discharge foure or fiue arrows apeece, before the Harquebuziers shall bee readie to discharge one bullet". Smythe goes on to list a number of other advantages arrows have over guns. The main role of guns, therefore, for a long time was as artillery pieces (Figs. 2.12 and 2.13), replacing the trebuchet as a means of firing projectiles over city walls (DeVries 1995).

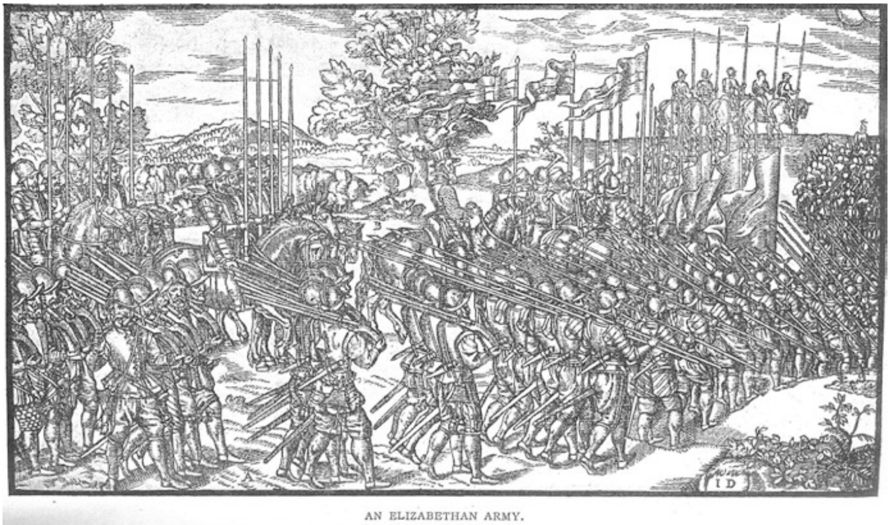


Fig. 2.8 An Elizabethan army on the march carrying a mixture of lances and guns. (From Holden 1903. Woodcut originally published by John Derricke in 1581)

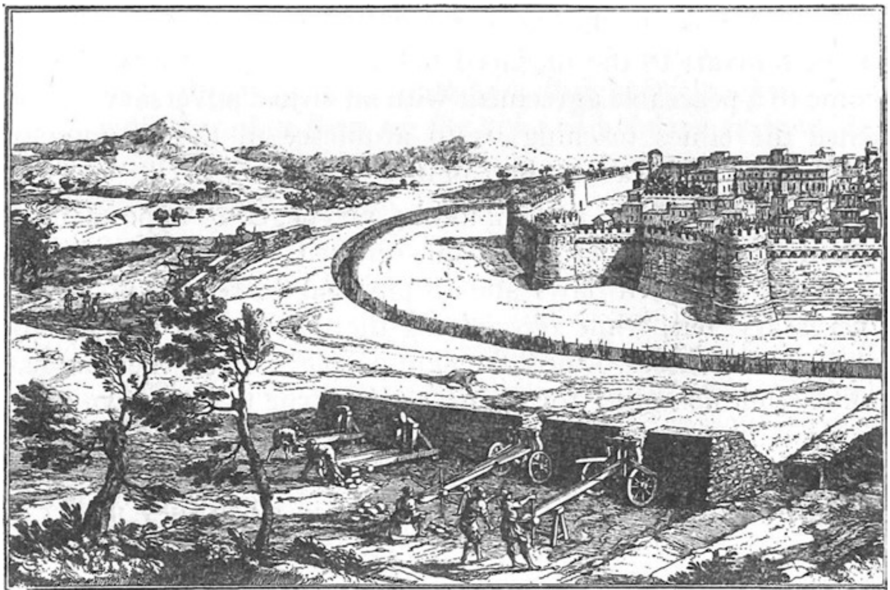


Fig. 2.9 Drawing of use of ballistas to assault a walled town

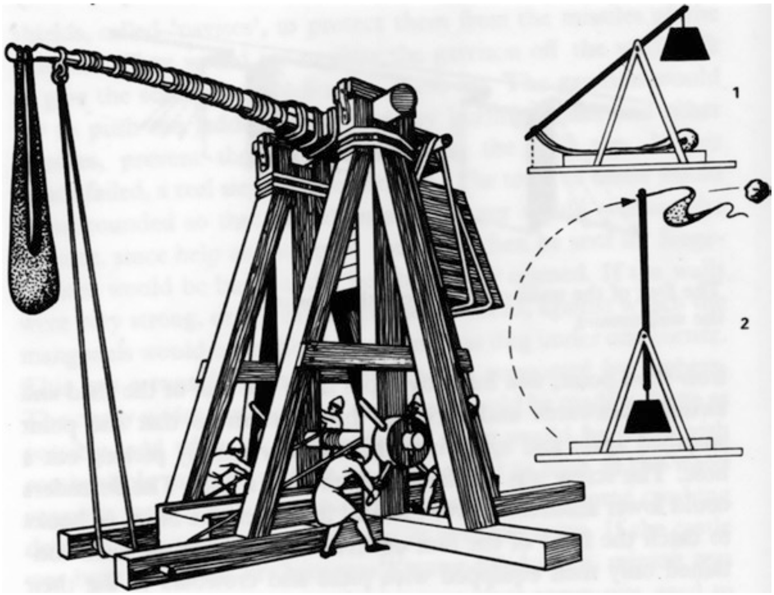


Fig. 2.10 Drawing of trebuchet and schematics of it in action. (From Norman and Pottinger 1966. Image used with permission of Weidenfield and Nicholson, Orion Publishing Group)

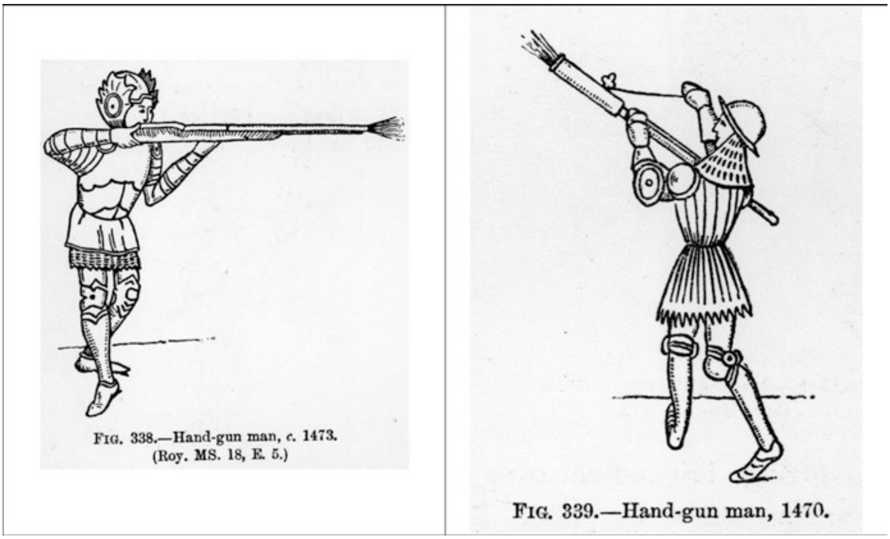


Fig. 2.11 Hand gunmen in the 1470s. (From Ashdown 1909)

Fig. 2.12 Cannonier, fifteenth century. (From Ashdown 1909)

Theory of Projectile Motion

In 1849, Louis Napoleon Bonaparte (nephew of the Emperor Napoleon) asserted that cannons were first mentioned in the records of Italian and French towns early in the fourteenth century and that the English used them at the Battle of Crécy in 1346 (Bonaparte 1849). Before that time, it was not necessary for archers or their commanders to understand the theory of projectile motion. All that was necessary was many hundreds of hours of practice (Hurley 1975). The invention of gunpowder changed all that (Andrade 2016; Kelly 2004; Lindsay 1974), as it allowed the projection of hard tough iron or granite spheres (cannonballs) or small metal shot at much greater speeds than previously possible (Bourne 1587; Charbonnier 1928; de Gaya 1678; Hogg 1963; Scoffern 1858a).

One unintended consequence of the invention of gunpowder was the breaking of the link between bodily effort and the outcome that was desired, which fundamentally altered the human labour and energy calculations of warfare. This link had been weakening since the invention of the trebuchet (Chevedden 1995; Chevedden et al. 1995; Hannam 2009; Tarver 1995). So it became necessary to have some understanding of how to achieve the range required to, for example, fire a projectile over a city wall (Fig. 2.13). As late as 1695, Edmund Halley commented on the lack of understanding of how to achieve a desired outcome with a gun:

> It was formerly the opinion of those concerned in artillery, that there was a certain requisite of powder for each gun, and that in mortars, where the distance was to be varied, it must be done by giving a greater or lesser elevation to the piece. But now our later experience has taught us that the same thing may be more certainly and readily performed by increasing and diminishing the quantity of powder, whether regard be had to the execution to be done, or to the charge of doing it. For when bombs are discharged with great elevations of the mortar, they fall too perpendicular, and bury themselves too deep in the ground, to do all that damage they might, if they came more oblique, and broke upon or near the surface of the earth; which is a thing acknowledged by the besieged in all towns, who unpave their streets, to let the bombs bury themselves, and thereby stifle the force of their splinters.

Fig. 2.13 Typical use of a mortar in the seventeenth century to fire over a city wall. (From Mallet 1684)

So what theory of projectile motion was available to the first gunners? One clue may be found in a diagram (Fig. 2.14) included in a set of handbooks (or magazines) published in 1669 to help English sea captains do their job. At first sight, the trajectories appear qualitatively what a modern calculation that takes air drag into account would predict (Fig. 2.15). However, closer inspection of the uppermost trajectory in Fig. 2.14 reveals the motion is split into three distinct sections separated in the diagram by tick marks. From right to left, the initial, straight part is labelled "The violent motion". The second, curved part is labelled "The mixt or crooked motion". The third, vertically straight downwards part is labelled "The naturall motion".

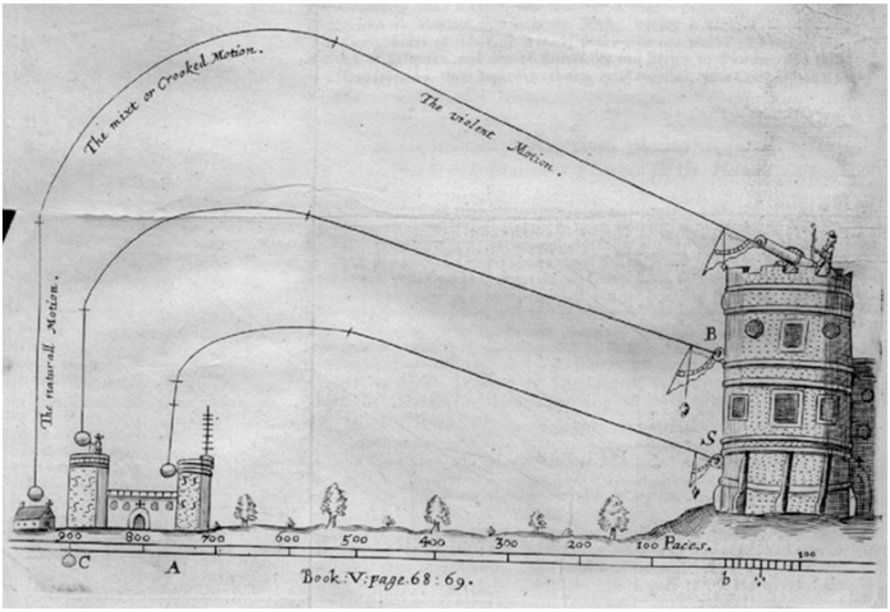


Fig. 2.14 Diagram of projectile motion in Samuel Sturmy's "The Mariners Magazine. 5: Mathematical and Practical Arts" published in 1669

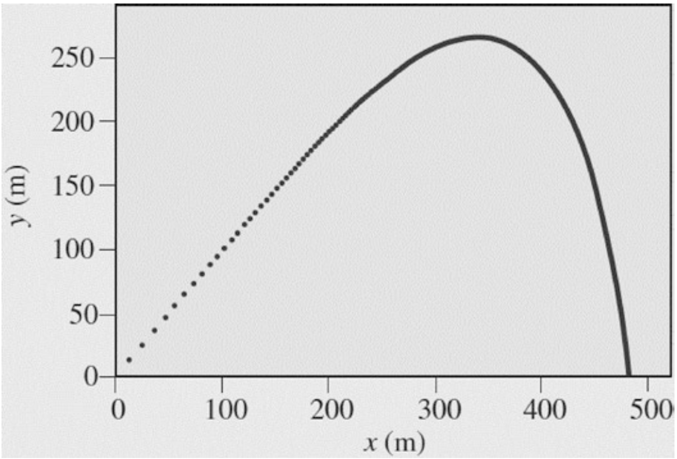


Fig. 2.15 Simulated trajectory of a cannonball assuming air drag force proportional to the square of the velocity. Initial speed 400 m/s, launch angle 45°. (From La Rocca and Riggi 2009. Image used with permission of IOP Publishing)

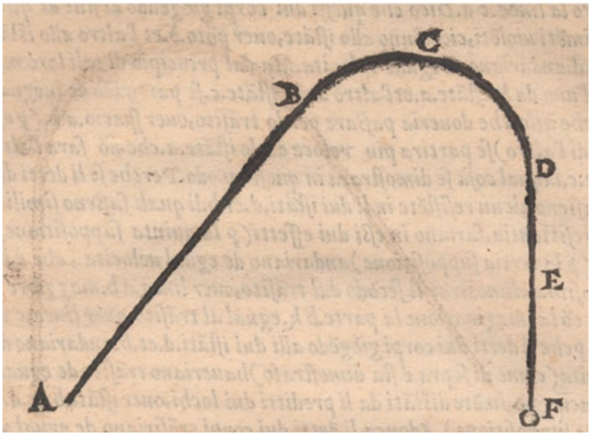


Fig. 2.16 Diagram of projectile motion as drawn by Tartaglia in 1537 (first published in English in 1588). AB is so-called violent motion, BCD is "mixed motion", and DEF is "natural motion". Tartaglia's book was republished (with commentary) in a modern English translation by Valleriani (2013)

The first known representation of what a projectile does when it is fired out of a cannon (Fig. 2.16) appeared in a book entitled *Nova Scientia* written by the Venetian Niccolo Fontana (usually known by his nickname Tartaglia) and first published in 1537. Tartaglia was credited by Hall as being the founder of the theory of gunnery (Hall 1952).

The physical theory behind Tartaglia's deceptively simple drawing is not that of Isaac Newton, who published his ideas 150 years later in 1687 (Motte and Cohen 1968; Newton 1687). Rather it has its origin in the writings of Aristotle (384–322 BC), namely, *Physics* (books 7 and 8) and *On the Heavens* (Grant 1996; Hankinson 1995), albeit modified by two men (John Philoponus, AD 490–570, and John Buridan, AD 1295–1363) who came up with the idea of impetus. The issues that Aristotle raised and that his successors grappled with have recently been reviewed by Yavetz (2015). Suffice it to say that Aristotle's theory of projectile motion, originally developed in the context of javelins and arrows, led to the astonishing cartoon first published in 1561 (Fig. 2.17) in which a cannonball fired from a gun is shown moving in a perfectly straight line to some point and then dropping vertically downwards.

In 2009, Hannam made the following comment concerning this diagram:

> Historians have long been puzzled how anyone could believe that a projectile could travel in a straight line and then drop out of the sky. After all, experience should have taught otherwise. But experience can be misleading. Bowmen were well aware that they could shoot straight at a target for maximum accuracy or fire into the air for maximum range. Those under a hail of arrows would have noted that they came from above and, under the circumstances, no one would have bothered to measure the exact angle of incidence. The trebuchet also propelled its rock into the air and, by the time this landed, it had lost a good deal of its forward momentum to air resistance. It would have appeared to those under attack that the projectiles were coming from above.

Note also that Figs. 2.13 and 2.14 show that a major interest of gunners was the delivery of projectiles over city walls rather than to batter them down, although they did that as well (DeVries 1995).

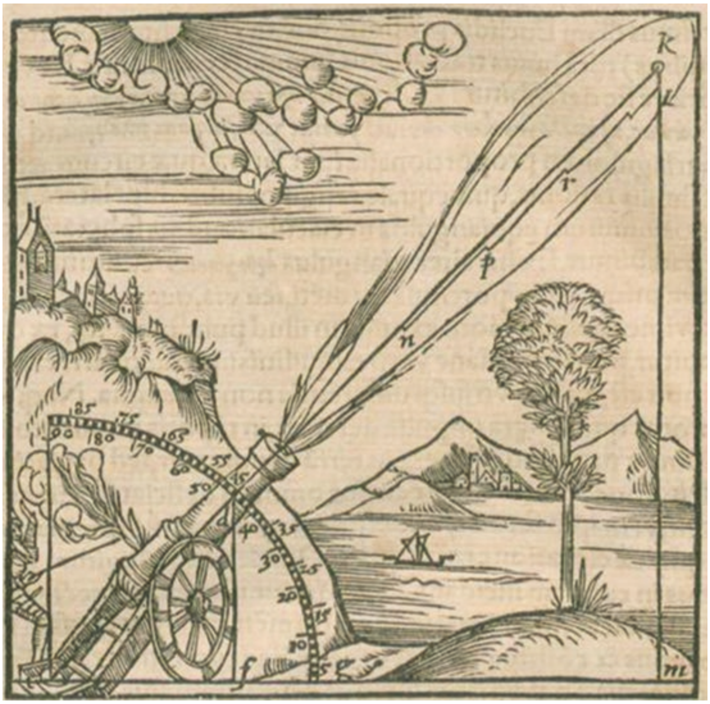


Fig. 2.17 Drawing by Daniel Santbech in 1561 of Aristotle's theory of projectile motion applied to a cannonball. (Santbech 1561)

It is clear from the frontispiece to his book *Nova Scientia* (Fig. 2.18a) that Tartaglia was aware that the trajectory of projectiles fired upwards from a mortar was curved along its entire length. Indeed the curve first published in 1537 looks suspiciously like a parabola. This cartoon was drawn about 100 years before Galileo published his proof in *Two New Sciences* that ballistic trajectories are parabolic (Drake 1974). Note also in Fig. 2.18b a cannon to the right of the mortar is shown firing horizontally. It is clear that Tartaglia knew that the shot does not hit the ground vertically. This observation is made even clearer in a book he published in 1538 (Fig. 2.19).

What Technical Developments Occurred in Ballistics and Armour Between the Seventeenth and Nineteenth Centuries?

A Century of Little Progress?

In 1952 (pp 21), Hall asserted that the art of gunnery had fallen behind scientific understanding by the mid-eighteenth century, despite a promising start in the mid-seventeenth century. For example, from the very foundation of the Royal Society

(a)

(b)

Fig. 2.18 Tartaglia's (1588) drawings from the frontispiece of his *Nova Scientia* of (**a**) the trajectory of a projectile fired upwards and (**b**) horizontally

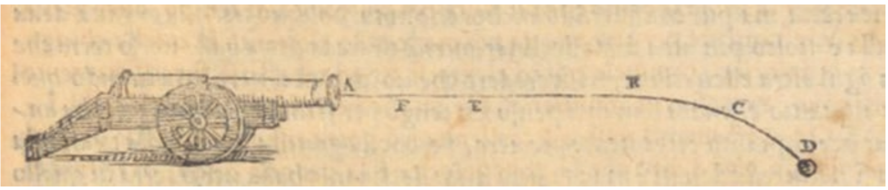


Fig. 2.19 Tartaglia's revised idea about projectile trajectories as set out in his 1538 publication *Quesiti et Inventioni Diverse. 1*

(1660), military matters were discussed at its meetings (e.g. Birch 1756a, b, c, 1757a, b, c, d) although very few papers on explosives and ballistics were actually published in its transactions (Anon 1667; Greaves 1685; Halley 1695). There appears to have been a revival of interest in gunnery (Anon 1742; Robins 1743) and rockets (Ellicott 1750; Robins 1749) among Fellows of the Royal Society during the 1740s. But as far as I can tell, only two papers on gunpowder (Hutton and Horsley 1778; Thompson 1781) and one on gunnery were published in the *Transactions of the Royal Society* in the succeeding century (Miller 1827).

Hall's opinion would appear to be backed up by an anonymous article published in 1862: "During the great European war at the beginning of the present century [i.e. the 19th], there took place no improvements whatever in the fabrication of arms; and it was lucky for the success of the French Empire that it was so; for with all his wonderful genius for military affairs, the first Napoleon was singularly deficient in mechanical knowledge, and in the application of the effects of mechanical skill" (Anon 1862).

However, an alternative view was expressed by Duffy in 1985 (pp 154) who said that improvements of up to 50% were made in ordnance during the eighteenth century, which increased the advantage of attack over defence. Particularly valuable researches were performed by Bernard Forest de Bélidor (who oversaw a series of experiments at the La Fère artillery school). These resulted in revised tables of charges and elevations, published in *Le Bombardier François* in 1731. By 1740, he was able to state that it was useless to load a cannon with a charge heavier than one third of the weight of the shot: greater charges merely threw unburnt powder out of the muzzle. At the time, the regulations said the charge should be one half the weight of the shot. The subtitle of Bélidor's book was *Nouvelle Méthode de Jetter les Bombes avec Précision*. This is probably a reference back to a book by Blondel published in 1683 entitled *L'Art de Jetter les Bombes*. The frontispiece of Blondel's book (Fig. 2.20) contains a drawing of the archetypal bomb, an image used in many cartoons during the twentieth century.

Rifling

One of the major developments in guns since the time of Tartaglia was rifling. This consists of cutting either straight or spiral grooves on the inside of a barrel. Litchfield, writing in 1880, said: "The first discovery that the cutting of spiral grooves upon the inner surface of gun barrels gave largely increased accuracy to projectiles is attributed to the accident of a gunmaker in Vienna, during the latter part of the fifteenth century". However, Litchfield did not say from where he obtained this information.

Robertson, writing in 1921b, said it was not known when or where rifling was developed. One suggestion that is often made is that rifling may have been invented to make guns easier to clean between firings as traditional gunpowder (Table 2.1) leaves behind a considerable quantity of solid residue after reaction. Holley asserted

L'ART
DE JETTER
LES BOMBES.
PAR MONSIEUR BLONDEL MARECHAL de Camp aux Armées du Roy, & cy-devant Maître de Mathematique de Monseigneur le Dauphin.

POTENTIS FULMINEO ICTU

BIBLIOTHECÆ REGIÆ

A Paris.
Chez L'AUTHEUR au Faux-bourg S. Germain ruë Jacob, au coin de celle de S. Benoist.
Et NICOLAS LANGLOIS ruë S. Jaques à la Victoire.

M. DC. LXXXIII.
AVEC PRIVILEGE DU ROY.

Fig. 2.20 Shell in the frontispiece of Blondel's *The Art of Throwing Bombs*, 1683. Cartoonists in later centuries used similar drawings to represent bombs. (From Blondel 1683a)

Table 2.1 Proportion by weight of the different ingredients for making gunpowder by the different European powers

	England	France	Sweden	Poland	Italy	Russia
Saltpetre	75	75	75	80	76.5	70
Sulphur	10	9.5	9	8	11	11.5
Charcoal	15	15.5	16	12	12.5	18.5

Taken from an American publication entitled "Practical Marine Gunnery", published in 1822 (Marshall 1822). Note that even at that late date, there was no agreement about the ratios of the ingredients nor even about why all three components were necessary

(1865b, 431) that the first set of experiments on rifled cannon was performed in Russia in 1836 using guns designed by Montigny, a Belgian. Over two thousand firings were carried out over a few days: an impressive feat for the time. However, according to Holley these trials led to the rejection of Montigny's design by both Russia and Britain.

Robins pointed out in 1742 (pp 338) that changing the shape of spinning projectiles from spherical to egg-shaped would stabilize them in flight, a principle he said was well-known from archery where archers arrange the feathers on arrow shafts to cause them to rotate. This idea was first picked up by Norton in England around 1830 (Anon 1830; Anon 1831; Greener 1835), but not adopted until 1849 when Minié in France invented the so-called Minié ball (Fig. 2.21). After this date, bullets rapidly changed shape from spherical ("bullet" is derived from a French word meaning "little ball") to the cylindro-conoidal shape we are familiar with today so that in 1858b Scoffern could say "the era of rifle-balls has departed, never to be revived". Minié's design was to ensure that the base of the bullet engaged with the rifling in order to impart spin, something that is now achieved using an exterior driving band (a band of soft metal, nowadays often a polymer) on the outside of a shell that engages with the rifling on the inside of the barrel so as to impart a torque to the shell to spin it up (see Fig. 2.22; Hartman and Stirbis 1973; Montgomery 1975; Veblen and Alger 1919).

Scoffern wrote the following about rifles and cylindrical bullets in 1858b: "The rifle gun is an ingenious contrivance for converting the undefined and irregular motion of fire-arm projectiles into one predetermined and regular; by imparting, in point of fact, a spinning-top like motion to the bullet, and thus insuring its continuance in a vertical trajectory curve. It is strange, however, that although the rifle principle is founded on the idea of a spinning-top; yet, until very recently, the spinning motion was imparted to a round bullet merely; and not to projectiles fashioned like a top".

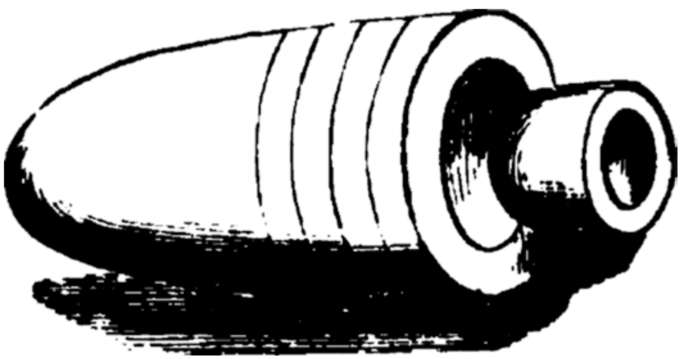


Fig. 2.21 Minié bullet consisting of a soft cylindro-conical projectile with a hard iron thimble at the base. The iron thimble is driven into the smaller cavity in the base of the projectile, thereby expanding it and forcing it to engage with the rifling of the barrel. (From Scoffern 1858b)

Fig. 2.22 Photograph of a driving band from a 6-inch shell that has been fired. (From Veblen and Alger 1919)

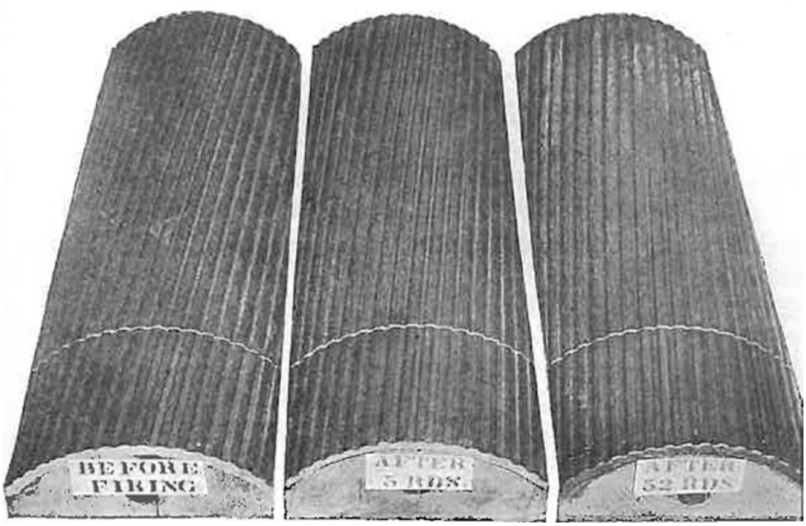


Fig. 2.23 Photographs of impressions made using rubber of interior rifling of a 10-inch gun showing effects of erosion. From left to right: original grooves; grooves after 5 firings; grooves after 52 firings. (From Birnie 1907)

A fairly gentle spiral is all that is required to achieve sufficient stabilizing spin (Fig. 2.23): Scoffern said one turn in 40 diameters. He pointed out that "the engraving of these long spirals is a matter of great delicacy; and that if these spirals be not absolutely parallel one with another, the object for which they were made will have been lost". Rifling grooves are subject to quite severe wear in service as Fig. 2.23 also shows. So low-wear alternatives were explored in which rotation was imparted by the hot gases from the driving charge being channelled into grooves on the projectile (Fig. 2.24). One advantage of this design is that it makes use of some of the energy of the propellant that would otherwise be wasted (windage).

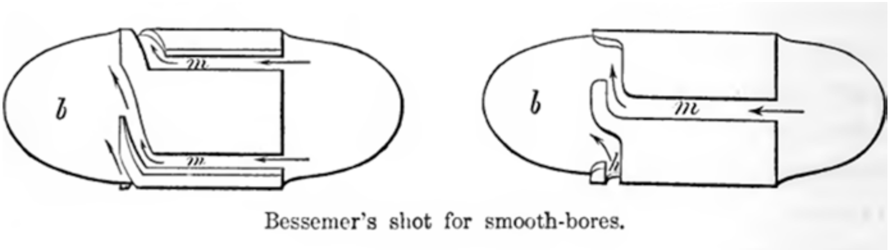


Fig. 2.24 Design of projectile for producing stabilizing rotation of a projectile using a smooth-bore gun. (From Holley 1865b, 572)

Fig. 2.25 Use of an ox as a rifle rest when shooting deer. (From de Espinar 1644, 445)

Another reason that was often advanced for the stability of spinning projectiles in flight was the evening out of the interaction of a bullet with the air. Thus Fremantle, writing in 1901 (pp 3) stated: "The flight of a bullet spinning on itself on an axis in the direction of its line of motion develops two useful features: it maintains its position very nearly in line (so far as gravity will permit), if it have any irregularities of form or density it present them on all sides successively as it revolves to the air obstructing it. Thus any tendencies to deviate in one particular direction, such as may arise from unsymmetrical form or weight, are made to cancel themselves by being converted into tendencies to deviate equally in all directions".

One major disadvantage of rifles is that the rate at which they can be fired is much lower than smooth-bore guns (such as muskets) since rifles take much more time to reload. Hence for a long time, they tended to be used only by hunters (Fig. 2.25) and concealed sharpshooters or snipers (Fig. 2.26). Note in Fig. 2.25 the

Fig. 2.26 One from a set of colored etchings of a rifleman published in 1804. (From Baker 1804)

chain attached to the huntsman's foot allowing him to change the orientation of the ox's head. The ox also concealed the hunter from his prey.

Projectile Velocity Measurements

Prony stated in 1805 that the first measurements of projectile velocity were performed by Robins using a ballistic pendulum (Fig. 2.27; Robins 1742, 1743). According to Prony, Hutton had earlier made use of this technique, but Hutton had also estimated initial projectile velocity by measuring how high cannonballs could be fired (Hutton and Horsley 1778). Note that there was both a minimum and a maximum velocity that Robins' pendulum device could measure. The minimum, 400–500 ft s^{-1} (or 120–150 m s^{-1}), was set by the requirement that the bullet be absorbed by the wood facing on the pendulum bob (GKIH in Fig. 2.27). The maximum was set by the requirement that the bullet does not penetrate right through the wood to the iron backing.

The most sophisticated measurements of projectile velocity at the time Prony wrote in 1805 had recently been made by Grobert. These experiments involved firing a shot through two spinning discs a known distance apart and which had also been engraved with lines at fixed angular spacings (Fig. 2.28). All that was required was to know how fast the discs were spinning.

A summary of Prony's description of how Grobert used the apparatus shown schematically in Fig. 2.28 is given as follows. The discs were mounted a known distance apart (11 feet) on a rod and set spinning using a falling weight attached to a cord passing through a pulley. The pulley was connected to the rod via a chain and a wheel in the middle of the rod and on its axis (see Fig. 2.28). The rate of rotation of the discs was measured using a stopwatch when the rate of rotation had become constant, which was also when the gun was fired parallel to the rod and through the

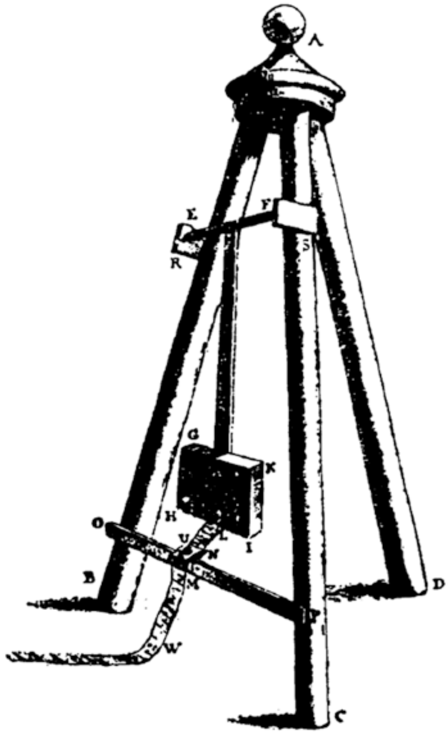


Fig. 2.27 Drawing of Robins' ballistic pendulum, used to make the first (indirect) measurements of projectile velocity. (From Robins 1742)

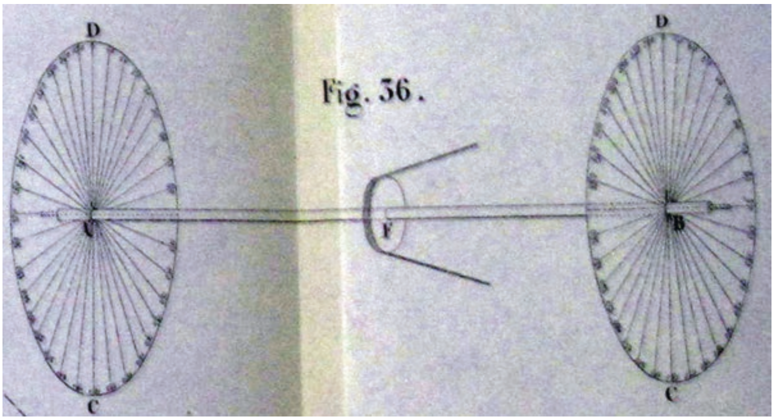


Fig. 2.28 Drawing of Grobert's spinning disc method of measuring projectile velocity directly. (From Didion 1860)

spinning discs. The velocity V of the shot was calculated using the following formula:

$$V = \frac{2\pi n}{kt} \cdot \frac{r}{a} b$$

where k was the ratio between the turns made by the wheel and axle and the arbor of the discs; t the time employed by the wheel and axle to make a number of turns n; r the distance of the hole in the second disc from the center; a the arc described by this hole, while the ball passes from one disc to the other; and b the distance between the discs. The mean velocity deduced from ten experiments with a carbine was 1269.5 feet per second and that from experiments with a musket was 1397 feet per second.

Prony goes on to describe other experiments performed by Grobert where the charge size was reduced, the effect of air resistance quantified, and modifications made for performing experiments at various elevations up to 45°. Prony reckoned the apparatus could be enlarged to perform similar measurements for cannonballs, though how large the apparatus would have to be he said would have to be determined by trial. Grobert also apparently had automated the apparatus "to prevent any mistake from want of attention in the persons employed", but Prony drily remarks that "…complicated machinery is always liable to get out of order, and it may be dispensed with here, if the observers be ever so little expert and attentive".

About 90 years later, it was possible to measure the velocity of a rifle bullet as it travelled up a barrel and for the first few meters of its travel using a dropweight, a tuning fork, some wires, and a piece of smoked glass mounted on a spring-loaded carriage (Fig. 2.29a). The tuning fork provided a measurement of the time, accurate to 0.1 ms. The three needles below the tuning fork were caused to jump to new positions using electromagnets incorporated in three electric circuits. These three circuits each contained a wire at various locations along the range that was broken by the passage of the shot. The first wire was at the muzzle of the gun. The spring-loaded carriage on which the glass plate was mounted was set in motion by the same mechanism that triggered the firing of the gun. A set of traces from 15 separate experiments is given in fig. 2.29b. These are probably the most sophisticated measurements of interior and exterior ballistics that were possible before the invention of the cathode ray oscilloscope.

The Contributions of Robins to Exterior and Interior Ballistics

In 1950, Corner credited Benjamin Robins (1707–1751) in the frontispiece of his book *Theory of the Interior Ballistics of Guns* as being the founder of the study of interior ballistics (the motion of a projectile up a gun barrel). Robins also studied exterior ballistics (the motion of a projectile between firing and impact) of rockets and guns. An assessment of Benjamin Robins' investigations was published by

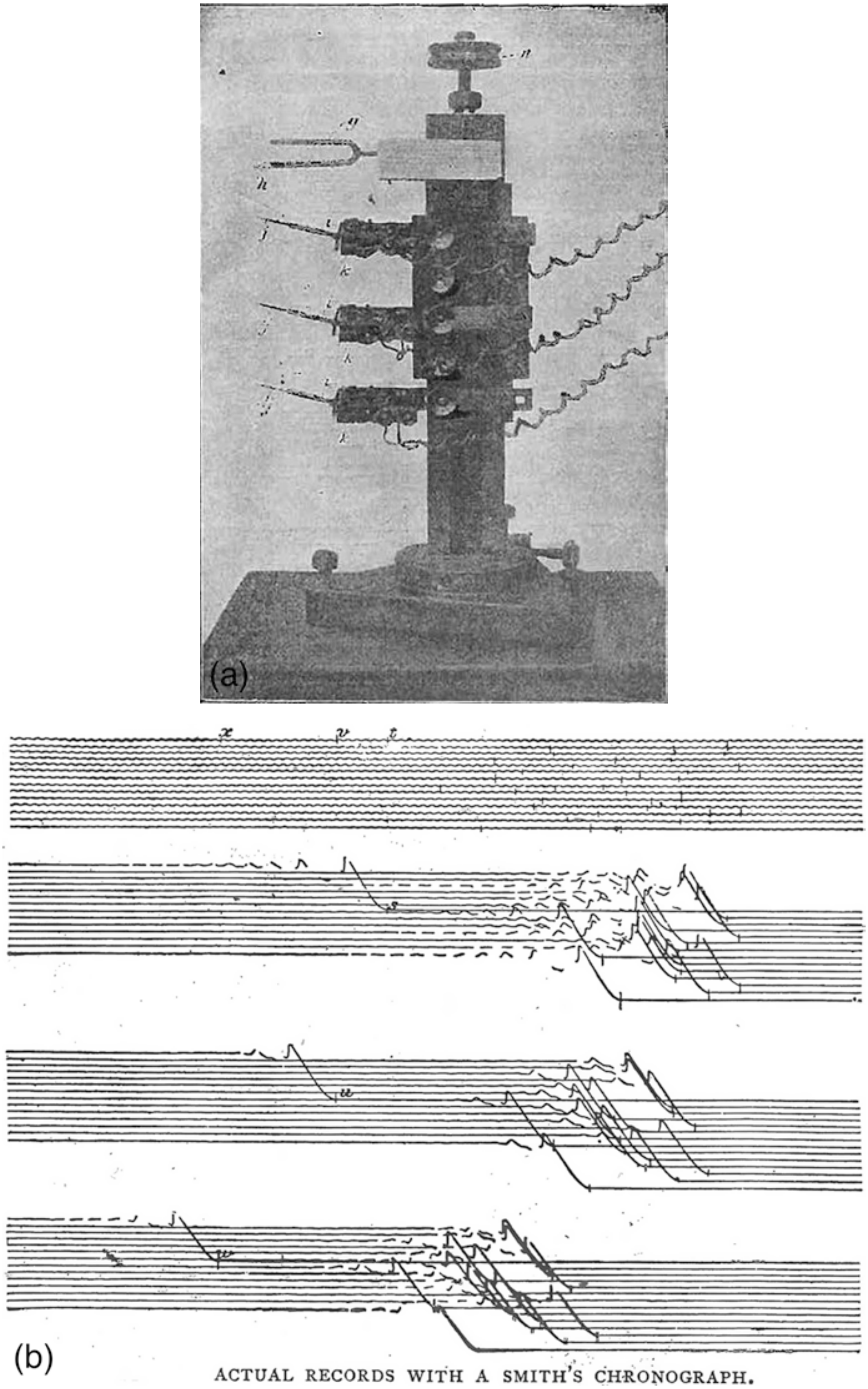


Fig. 2.29 Late nineteenth-century method of measuring times sufficiently accurately so as to determine the velocity of a rifle bullet during firing. (**a**) Photograph of the chronograph showing the tuning fork, g, at the top with one "scratching point", h, and three other needles below each labelled "i"; (**b**) set of traces obtained using this apparatus from 15 separate experiments with a gun. (From Griffith 1897)

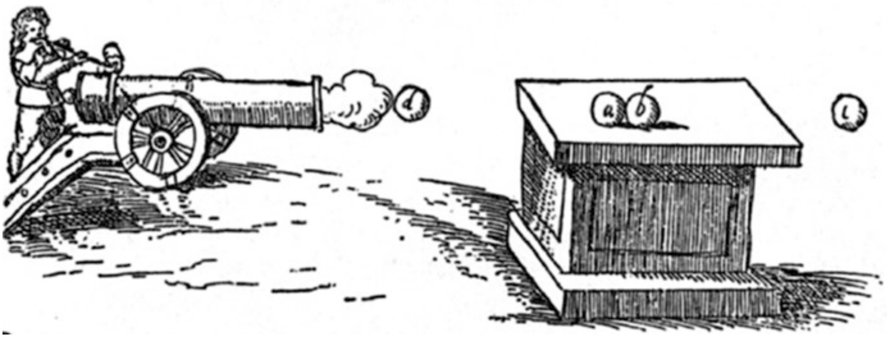


Fig. 2.30 Drawing showing the principle of transfer of momentum from one cannonball to another. (From Marci 1639)

Johnson in four papers (Johnson 1986, 1990, 1992a, b). Johnson's 1990 paper set Robins' studies within the historical context of the development of the understanding of mechanics. One of the most remarkable illustrations that Johnson found dates from 1639 which shows a precursor of what is now called "Newton's pendulum", the main differences being that cannonballs were used and the target ball rested on a table rather than being suspended by strings (Fig. 2.30).

An assessment of the state of the art of gunnery before Robins began his investigations was published by Robertson in 1921 in his book entitled *The Evolution of Naval Armament* (Robertson 1921c). Robertson observed (1921c, 114) that before Robins published his book *New Principles of Gunnery* in 1742, the gunner was "primed with a false theory of the trajectory" (i.e. that due to Aristotle, discussed earlier in this chapter). In addition, balls in flight were believed to be affected by passing over water or over valleys. Furthermore, guns were imperfectly bored meaning that cannonballs were a loose fit so that they often "issued from the muzzle in a direction often wildly divergent from that in which the piece had been laid; on land it attained its effects by virtue of the size of the target attacked or by use of the *ricochet*".

Robertson continued (1921c, 115–116) that: "The records of actual firing results were almost non-existent. Practitioners and mathematicians, searching for the law which would give the true trajectories of cannon balls, found that the results of their own experience would not square with any tried combination of mathematical curves":

> For thoughtful men of all ages… the flight of bodies through the air had had an absorbing interest. The subject was one of perennial disputation. The vagaries of projectiles, the laws governing the discharge of balls from cannon, could not fail to arouse the curiosity of an enthusiast like Robins… Perusal of such books as had been written on the subject soon convinced him of the shallowness of existing theories. Of the English authors scarcely any two agreed with one another, and all of them carped at Tartaglia, the Italian scientist who in the classic book of the sixteenth century tried to uphold Galileo's theory of parabolic motion as applied to military projectiles. But what struck Robins most forcibly about all

> their writings was the almost entire absence of trial and experiment by which to confirm their dogmatical assertions. This absence of any appeal to experiment was certainly not confined to treatises on gunnery; it was a conspicuous feature of most of the classical attempts to advance the knowledge of physical science. Yet the flight of projectiles was a problem which lent itself with ease to that inductive method of discovering its laws through a careful accumulation of facts. This work had not been done.

According to Robertson (1921c, 117–118), this state of affairs began to change when Robins (1743) presented the findings of his book *New Principles of Gunnery* to the Royal Society in London:

> In 1743 Robins' *New Principles of Gunnery* was read before the Royal Society. In a short but comprehensive paper which dealt with both internal and external ballistics, with the operation of the propellant in the gun and with the subsequent flight of the projectile, the author enunciated a series of propositions which, founded on known laws of physics and sustained by actual experiment, reduced to simple and calculable phenomena the mysteries and anomalies of the art of shooting with great guns. He showed the nature of the combustion of gunpowder, and how to measure the force of the elastic fluid derived from it. He showed, by a curve drawn with the gun axis as a base, the variation of pressure in the gun as the fluid expanded, and the work done on the ball thereby. Producing his ballistic pendulum he showed how, by firing a bullet of known weight into a pendulum of known weight, the velocity of impact could be directly ascertained.

Robins found that his theory (presented graphically in Fig. 2.31) agreed with his ballistic pendulum experiments to within about 5%.

Robins then went to report possibly the first measurements of air resistance to the motion of shot. He did this by firing a shot through a series of thin screens in order to determine the paths they followed. He found that the resistance of the air was not negligible, as was commonly believed at the time. For example, he calculated from the experimentally measured trajectories that the initial resistance of the air to a

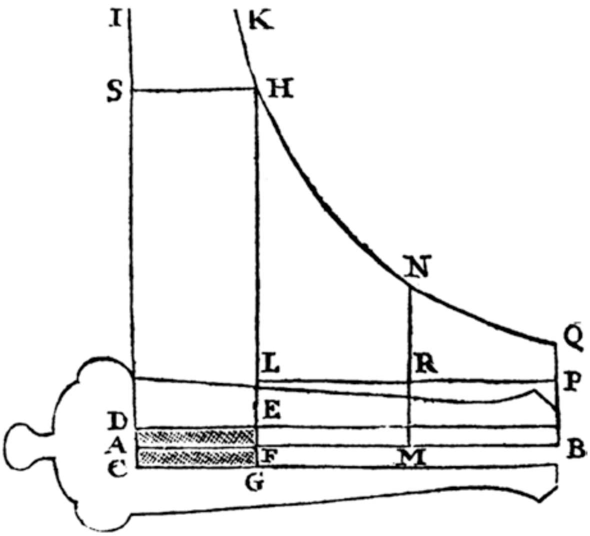


Fig. 2.31 Robins' 1742 graph of the variation of pressure in a cannon as the hot gases produced by the gunpowder push the shot along the barrel. The letters in this figure allowed Robins to refer in his text to various parts of the gun and its workings. For example, "A" was the breech, "B" the muzzle, "DEGC" the powder, and so forth. (From Robins 1742)

24-pound cannonball, fired using 16 pounds of powder, was about 24 times the ball's weight.

His experiments also showed that the paths that the shot takes through the air are neither parabolas nor some other planar curve. In fact the balls usually followed trajectories with a double curvature, sometimes curving to the right and sometimes to the left of the direction of fire. He attributed this additional deviation to the spin imparted to the ball as it rolled along the barrel of the gun (shot in those days was a very loose fit to the barrel). He dramatically demonstrated this by bending the end of a musket to the left and firing it while it was firmly held in a vice. The expectation of the onlookers was that the shot would go to the left. In fact, the shot curved to the right. These experiments by Robins were also discussed in an article published in 1830 (Anon 1830).

In 1812 (pp 90–91), Simmons wrote the following: "…when the resistance of the air is also considered, which is enormously great, and which very much impedes the projectile velocity, the path deviates greatly from the parabola, and the determination of the circumstances of its motion becomes one of the most complex and difficult problems in nature". He also refers (1812, 91) to a calculation by Bernoulli that air resistance is sufficient to reduce the height to which a cannonball might ascend from 58,750 feet (17,920 m) to 7819 feet (2380 m).

Another remarkable discovery that Robins made was the sudden large increase in air resistance when the shot is fired at around the speed of sound in air, known at that time to be just under 1100 feet per second.

Robins also performed investigations of the possible use of rockets to increase the speed of harpoon-like projectiles (Robins 1749), but there is little evidence that these studies resulted in a change to the traditional use of rockets to carry fire over city walls (Hume 1811; Johnson 1992c; Johnson 1993a, b), something for which mortars were also used (Wilson 1944a, b).

Ricochet

Robertson wrote the following about ricochet in 1921a, 160–161: "the howitzer… was greatly enhanced by the discovery by Marshall Vauban at the end of the seventeenth century, of the efficacy of the *ricochet*. Under this system the fuzed bomb or grenade, instead of being projected from a mortar set at a high elevation, to describe a lofty and almost parabolic trajectory, was discharged from a howitzer at a sufficiently low elevation to cause it to strike the ground some distance short of its objective, whence it proceeded, leaping and finally rolling along the ground till it came to its target, where it exploded".

About ricochet, Muller wrote in 1746 (pp 22): "The greatest improvement made in the art of attacking happened in the year 1697, when M. Vauban made first use of ricochet firing at the siege of Ath, whereby the besieged, placed behind the parapets, were as much exposed to the fire of the besiegers, as if there had been none; whereas before, they had been secure as long as the parapet was not demolished: and the worst is, that there can be no remedy found to prevent this enfilading, without

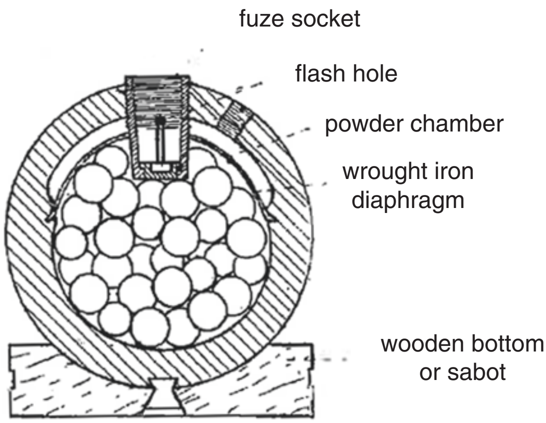


Fig. 2.32 Boxer's 1852 modification of Shrapnel's 1784 shell design. (From Marshall 1919)

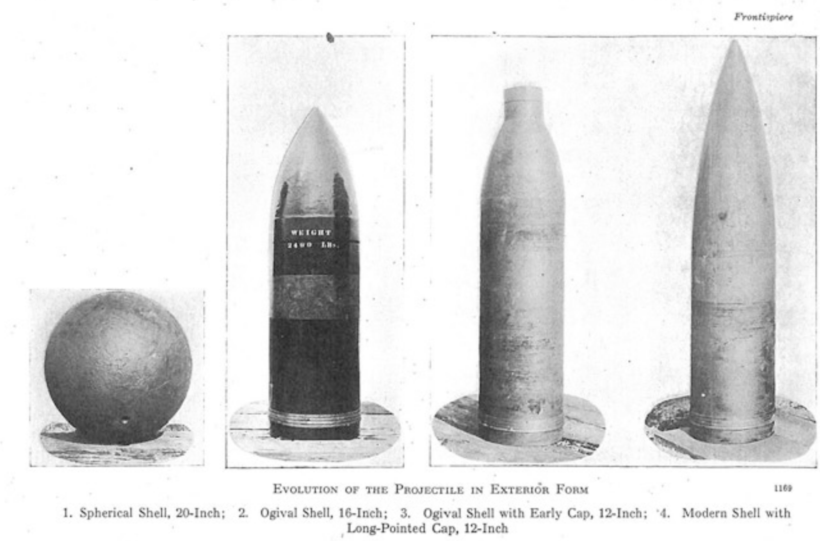


Fig. 2.33 Photograph published in 1912 showing the evolution of the shape of artillery shells during the nineteenth century. From Anon (1912)

falling into inconveniences almost as bad as those which we endeavour to avoid". Paixhans devoted a complete chapter of his 1822c book *Nouvelle Force Maritime* to ricochet.

Shrapnel's airburst shells largely replaced ricochet fire during the nineteenth century (Duffy 1985, 164–165) and carried on being developed (Fig. 2.32) until replaced later that century by cylindrical shells fired from rifled guns (Fig. 2.33). Note in Fig. 2.32 that wooden plates were used to transmit the driving force from the hot propellant gases to the shell. These plates were called sabots, the French word for the one-piece carved wooden clogs worn by the poor. This name is still in use to this day (Huang et al. 2014).

In 1856, Dahlgren wrote a discussion of fuses in his book *Shells and Shell-Guns* (Dahlgren 1856a). The basic design was a hollow tube filled with gunpowder. These were ignited by the hot gases produced by the main firing charge of the gun. As the first fuses were made from wood, on firing the spherical shell had to be oriented so that the fuse was on the axis of the bore of the gun but pointing away from the main propellant charge. That way they could mechanically withstand the acceleration (circa 200,000 m s^{-2} in a modern gun (Church et al. 2001)), avoid being thermally destroyed by the explosion of the gunpowder, and yet be ignited by the hot gases flowing around the shell. When Dahlgren wrote, fuses with metallic casings were increasingly being used. These had the advantages that they could be held in place in the shell by a screw thread and were not so easily broken by inertial forces. It was therefore not so critical that the fuse was aligned with the axis on firing. However, metal-cased fuses were more prone to extinction than wooden ones due to metal being a better conductor of heat.

Differences Between Using Guns on Ships as Opposed to Land

Ricochet was harder to use successfully on water than on land. For example, in 1855b Howard Douglas reported that four out of five naval shells that were ricocheted off water failed due to extinguishing of their fuses. The second main cause of failure (one in three) was plugging of the fuse by fragments of timber on impact.

The first book I have been able to find which teaches the principles of naval gunnery was written by Robert Simmons and published in London in 1812. It is both a textbook outlining the theory of internal and external ballistics, some mathematics and geometry, as well as being a handbook on how to manage ordnance on-board a ship. Ten years later (1822), an American, George Marshall, published a very detailed handbook on the same topic. He left out all the mathematics and ballistic theory saying "the science and correctness of [Mr. Simmons] principles are unintelligible to most of our gunners". Even so, Marshall's own book goes into great detail about a wide range of topics including stores, procedures, etc. even describing how to blow up a ship and how to avoid gunpowder getting into nooks and crannies, a possible cause of accidents when ships were taken into dock to be refitted or repaired by carpenters.

The Beginnings of Systematic Experimental Studies of Terminal Ballistics: Early Studies of Ballistic Impact Against Earth Banks, Masonry, and Wood

The first systematic investigations of the mechanics of the ballistic penetration of solids were reported in 1810 by Moore (who worked at Woolwich Arsenal, England) on wood, in 1836 by Piobert (who worked at Metz, France) in the 1820s–1830s on wood, and in 1848 by Isidore Didion (also of Metz) on earth, masonry, and wood in 1834–1835. However, there were earlier isolated reports such as the one by Greaves in 1685 published in the *Philosophical Transactions of the Royal Society of London* concerning some experiments performed in 1651 at Woolwich on oak butts and by Robins in 1742 and 1747 of a few experiments he had performed on the ballistic resistance of wood. Simmons (1812, 99) credited Robins with finding that the depth of penetration of wood scaled with the square of the velocity of impact.

Although Robins' studies of the ballistic penetration of wood by cannonballs were not systematic (Robins 1742, 1747), he reported the following important observation (in a discussion of the optimum amount of gunpowder that should be used for a shot of a given weight), namely: "It is Matter of Experiment, that a Bullet, which can but just pass through a Piece of Timber, and loses almost all its Motion thereby, has a much better Chance of rending and fracturing it, than if is passed through it with a much greater velocity" (Robins 1747). Note that the only experiments on penetration that Simmons (writing in 1812) knew of were those by Robins on wood.

In 1848 in a book entitled *Traité de Balistique*, Didion published the following formula for the penetration E of wood by a spherical projectile impacting at a velocity V (these studies were performed at Metz in 1834–1835 and first published by Piobert, Morin, and Didion in 1837):

$$E = \frac{2RD}{3g\beta} 2.3026 \log\left(1 + \frac{\beta}{\alpha} V^2\right) \tag{2.1}$$

where R is the radius of the projectile, D is its density, g is its weight, and α and β are "quantities that depend on the nature of the medium" which he defined by the following equation:

$$\rho = \pi R^2 \left(\alpha + \beta v^2\right) \tag{2.2}$$

where ρ is the resistance of the medium and v is the velocity at any given instant. The separation of density and weight in Eq. (2.1) allows comparisons to be made between shells and solid shot of the same diameter. This is the first time that anyone had published a relationship between the ballistic resistance of a solid medium and the impact velocity.

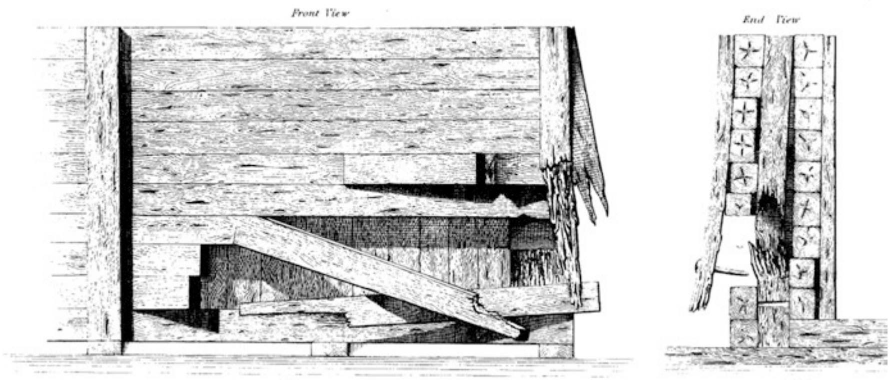
Didion's book is remarkable for two other things: (i) his thorough survey of previous analyses of round and oblong projectile motion in vacuum and air (see also Didion 1856, 1857) and (ii) his observations on the effect of moisture content on the penetration resistance of earth (1848, 241–242), a subject that is still an active area of research (Perry 2017). A second edition of this book was published in 1860.

As may be seen from the following table, a few years later (1856b, 176), Dahlgren found good agreement between Didion's theory and his own experiments even at a distance of 1300 yards (1170 m), a range sufficiently great that air resistance has a large effect and has to be taken into account (Table 2.2).

Table 2.2 Comparison of Didion's penetration formulas with experiments on wood

			Penetration at 1300 yds.	
Class of Gun.	Chge. of Gun.	Projectile.	Computed.	Actual.
32-pdr. of 57 cwt.	9 lbs.	Shot	21 in..13	21 in..0
8-inch of 55 cwt.	7 lbs.	Shell	16 in..16	15 in..58

From Dahlgren 1856b, 176



(a) (b)

Fig. 2.34 Effects of the explosion of a heavy shell that was fired at an oak target. (**a**) Front view; (**b**) end view. (From Dahlgren 1856c, opposite page 227)

As Dahlgren pointed out in 1856 in his book *Shells and Shell-Guns*:

> There is no similarity in the action which shot and shells are designed to exert on timber. The shot is to pierce and separate the wood by the force of penetration alone, crushing and rending the fibres, tearing asunder the several parts bolted together, and driving off splinters large and small with great violence from the further surface. The shell is intended to explode while lodged in the mass of the ship, disuniting its structure, and driving out more or less of the material in fragments.

Drawings from his book that demonstrate the effects of an exploding shell on a wooden target are presented in Fig. 2.34. He quoted Sir Howard Douglas to the effect that shells that lodge in the side of a wooden ship may be compared in their effects to mines.

However, as Dahlgren (1856b) pointed out earlier in his book, at the time of writing "…the probable effects of artillery on ships, require no little patience and ingenuity to resolve, even when the practice is conducted experimentally, and therefore with power to determine many of the conditions under which it shall occur: but in action, these are not only beyond control, but most frequently beyond conjecture, and the results are liable to the whole possible combination of effects, due to unequal force and to unequal resistance". He noticed that there were differences between "the results of practice upon ships and upon the solid wood of targets". He

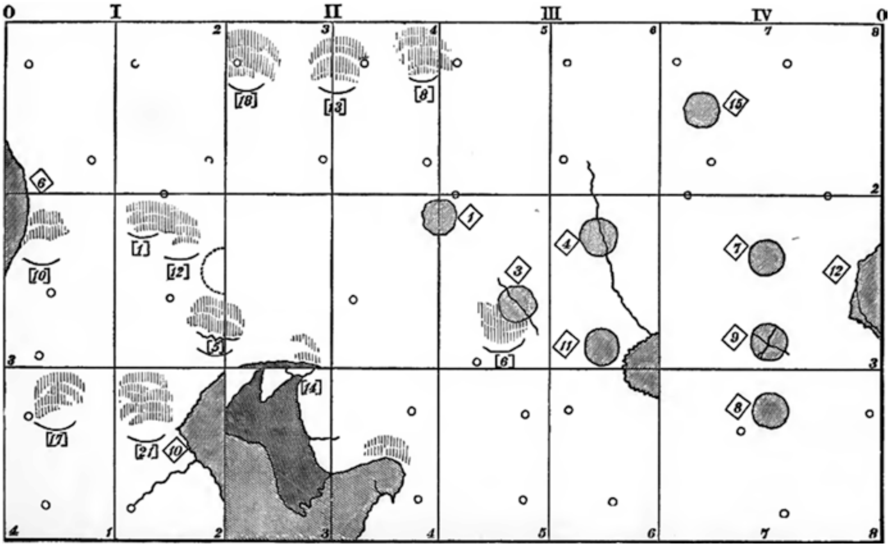


Fig. 2.35 Drawing of results of impacts of elongated solid cast iron shot against a 7-foot-long, 3-feet-wide timber-backed wrought iron plate 4.5 inches thick inclined at 51° to the vertical. Experiments performed in 1861. For more details of the various impact sites, see the descriptions given in Tables 117 and 118 in Holley 1865b, 640–642

recommended that the innermost part of the sides of a ship be made of "softer and less fibrous materials" that will produce fewer fast moving splinters since it is these that produce "the chief damage… to the personal [sic] of a ship".

Holley (1865b, 623) asserted that the first authenticated experiments of the effect of artillery upon metal armour were conducted in the United States during the war with the British Empire in 1812. A few years later (1827), experiments were performed at Woolwich, England, on masonry covered by iron.

In one set of experiments performed at Portsmouth in 1861, angling of timber-backed targets was found to have a significant effect on penetration depth. For example, the depth of penetration of cast iron shot into wrought iron plates inclined at 51° to the vertical (Fig. 2.35) was found to be about half that for the same plates mounted normal to the gun. Also damage to the wood backing of these plates was "very slight" and the cast iron shot usually shattered on impact. However, experiments performed around the same time on unbacked plates found no effect of angle of inclination on penetration (Holley 1865b, 665–666). At the time of writing (1865b), Holley had no explanation for the different outcomes of these experiments. Terminal ballistic experiments on brickwork faced by iron plates were also performed (Holley 1865b, 654–665).

In 1861 in Britain, a "special committee on iron" was appointed by the Secretary of State for War. The work entrusted to them was to investigate the application of iron to defensive purposes in war. This committee operated for 3 years, their second (and final) report being published in 1864 (Hay et al. 1864).

Their main findings were as follows:

(i) Of all the types of iron and its alloys (steel) available at the time, "wrought iron of the softest and toughest quality is the best material for Armour plates".
(ii) The static properties of iron are no sure guide to its response to impact by shot.
(iii) Steel shells are "by far the most damaging projectiles for use against armour-plated vessels".
(iv) As far as fastening armour plates to ships was concerned, "great advantage is derived from the use of elastic washers under the nuts".
(v) "The great number of splinters of wood shows how untenable wooden ships must be when penetrated by heavy artillery, without the protection afforded by an iron skin".
(vi) "For plates of equal quality, large area is an advantage as the plates are decidedly weaker towards the edges than in the middle".
(vii) When they performed a literature review at the start of their work (1861), they found "that although sufficient trials had been made to lead to a belief that iron was capable of forming a good protection against artillery, still very little practical knowledge had been acquired either as to the quality of material most efficient for the purpose, or the most advantageous mode in which the material should be applied".
(viii) Rolling as opposed to hammering was found to be the best way of manufacturing armour plates as it produces a softer, more uniform product.
(ix) By inviting the ironmasters to see the experiments, a "great improvement in the manufacture of heavy iron plates" had taken place between 1861 and 1864.
(x) "Plates of French manufacture have been tried; but although the iron used for their manufacture is of very superior quality, being remarkably free from injurious impurities, yet the plates at first all more or less failed in the manufacture, particularly in respects the welding, which was exceedingly imperfect".
(xi) After investigating more than 400 designs of various structures suggested by "certain eminent engineers and ship-builders…we have arrived at the simple result, that the best application of the material is a single plate of uniform thickness, with the surface perfectly plane".
(xii) The ballistic resistance of plates was found to be approximately proportional to the square of the thickness, but they say this rule should not be relied upon.
(xiii) Joining plates together by "grooving and tongueing", as was done for the *Warrior*, was a mistake and had now been "abandoned in all vessels built subsequently to our [first] Report".
(xiv) After having performed elaborate experiments to see if wood backing could be dispensed with, they found that wood "appears to have important functions for which no thoroughly efficient substitute has yet been found".

In 1863, some rather unusual experiments were performed in the United States on hog's hair targets and in the United Kingdom (1864) on targets made of wool. For the hog's hair experiments, Holley (1865a, 774) quoted from the *Scientific American* of October 10, 1863 that "…all the bales were pierced, and the projectiles not having been found, it was not possible to ascertain which offered the greatest resistance". Similar results were reported for the British wool experiments: "The shot, on examination, were found to have passed through the 11 feet of wool, the bottom of the iron caisson, and buried themselves in 12 feet of solid earth" (Holley 1865a, 772).

Prosser reported in 1840 a proposal by the Spaniard Don Juan Costigin in 1810 to armour forts using iron (Fig. 2.36). Prosser wrote that Paixhans had performed some small-scale experiments in France as early as 1809 that yielded mixed results. Positively, the projectiles were fragmented on striking iron plates. However, negatively the fragments of iron that were formed by the impact were highly likely to be dangerous to the defenders. Also the cast iron target plates broke. Thus the commissioners who paid for the study said that "the use of cast

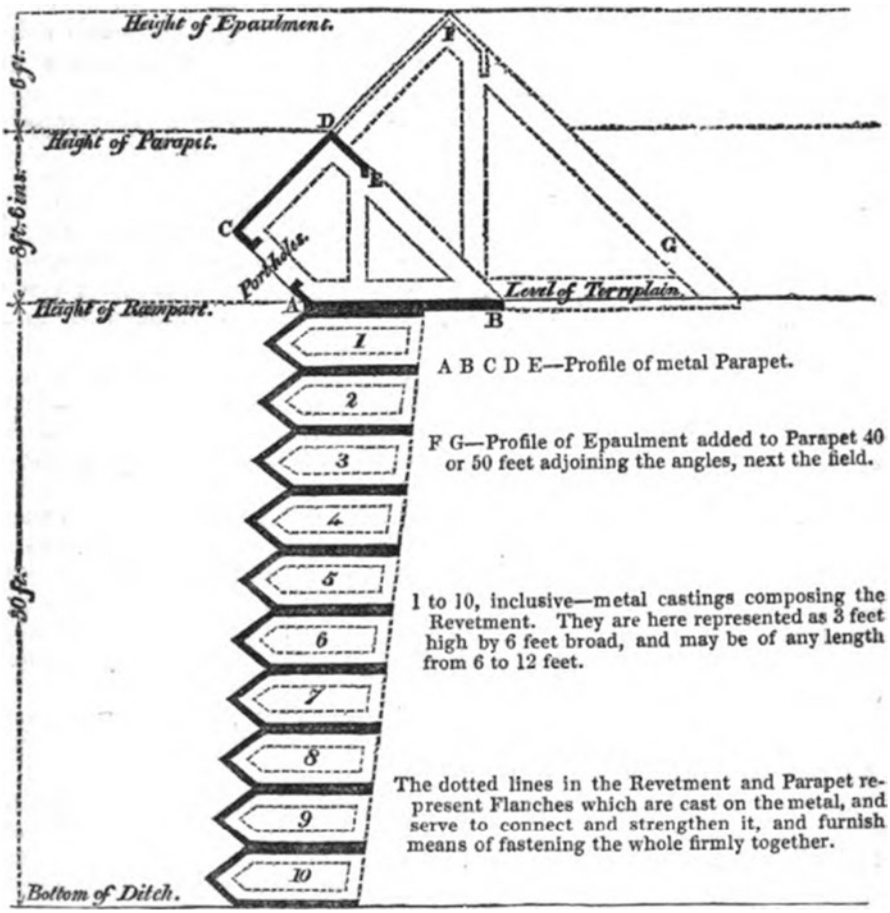


Fig. 2.36 Proposal by Costigin in 1810 for the armouring of fortress walls with iron (reported in English by Prosser in 1840). Behind the metal castings, Costigin said there would, as usual, be a wall of solid masonry to which the castings would be bonded, the whole being cemented using grout.

iron…to revet the cheeks of embrasures…is far from offering the advantages imagined by some persons…".

Totten reported in 1857 that several hundred experiments had been carried out at West Point, New York, between 1852 and 1855 on the effect of firing heavy ordnance against fixed targets made from granite, concrete, and brick (Totten 1857). The effect of armouring the targets using wrought and cast iron plates was also investigated. Cast iron was found to be useless (for the reason shown in Fig. 2.37), the result of some tests reported 8 years later by Holley in 1865b (pp 305), but wrought iron afforded some measure of protection.

Totten reported that granite walls were able to shatter cannonballs fired at them. He reported that drawings and sketches had been made of the "many and beautiful photographs" of the impacted specimens, but these do not appear to have been reproduced in his report.

In 1865b (pp 300), Holley quoted the following result from a report he had written 5 years earlier in 1860. He found that the dynamic tensile strength of an iron cannon burst using gunpowder was 75,684 lbs per square inch, whereas its strength

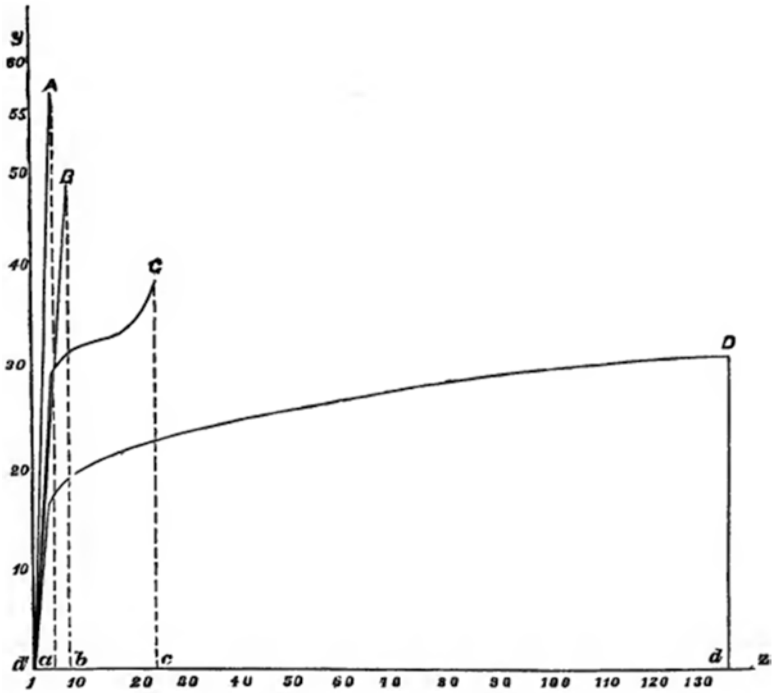


Fig. 2.37 Load-extension plots showing the ductility of various irons and steels. Experiments reported in 1865. Curve A was for cast steel. Curve B was for "harsh, strong wrought iron". Curve C was for "soft strong iron". Curve D was for "extremely ductile but not very strong iron". (From Holley 1865b, 305)

measured using a "testing machine" was only 26,866 lbs per square inch. I believe this is the first time anyone had reported the quantitative difference between the dynamic and static tensile strengths of any material.

In support of the assertion I have just made, Cox wrote the following in 1849: "The dynamical strength of beams, or their capability of sustaining weights moving rapidly over them, has never been satisfactorily discussed. There does not appear to be extant a single theoretical investigation of this subject – and the deficiency is due to two causes: it occurs partly because the subject has but comparatively recently grown into importance; partly because of its excessive and insuperable difficulties when investigated by the exact methods of theoretical mechanics". As may be deduced from the quote just given, Cox's article was theoretical rather than experimental, so he did not report any measurements of the difference between the quasi-static (i.e. in slow deformation) and dynamic (i.e. rapid deformation) strengths of iron girders. Rather he identified mechanical inertia and the work done by the steam engine as important parameters to consider when thinking about this novel problem.

Cox's interest in this problem was due to increasing concern about the novel use of iron in railway bridges (see Ono, Chap. 4, this volume). This concern can be seen in the following quote that Cox gave from the minutes of a meeting held in June 1847 of a government commission (The Commissioners of the Railways) which expresses doubt as to "whether the experimental data and the theoretical principles at present known are adequate for the designing of iron bridges, when these are to be traversed by loads of extraordinary weight at great velocities".

Another man with a professional interest in iron bridges and probably the first to publish articles on experimental investigations into the dynamic properties of materials (in the 1830s) was Hodgkinson (1831a, 1832b, 1834, 1836, 1838, 1839; Rawson 1865). He was also the first person to publish drawings of the X-shaped fracture produced by the dynamic upsetting of metal cylinders (Hodgkinson 1838, 1839), a phenomenon we now call adiabatic shear banding (Bai and Dodd 1992; Dodd and Bai 2012).

In 1866a, 294–295, Watts gave a description of the effect of armour on cast iron shot and the effect of shot on armour plate. He also made an estimate of the energy imparted by the impact of shot:

> When the shot strikes the armour-plate, a further waste of energy takes place through the disfigurement of the shot itself. It has been shown by Sir W.G. Armstrong, and corroborated by the experiments of the Iron Plate Committee, as quoted by Mr. Fairbairn, that when the shot is of cast-iron, it flies to pieces on striking the armour-plate; and that in producing that effect about half its energy is wasted. If of wrought iron or soft steel it is compressed and flattened, and about a fifth of its energy is wasted. In designing ships' armour, provision must be made for the case of the enemy using the most efficient material for projectiles; hence it is safest to estimate the energy of the blow at from 144,000 to 192,000 foot-lbs per pound of powder, without deduction…The first effect of a shot striking an armour-plate is to produce an indentation, in the neighbourhood of which the iron is compressed. The compression is transmitted both forwards and sideways, diminishing in intensity as it is spread over layers of iron of gradually increasing area, and accompanied by tension in a transverse direction. The energy of the shot is expended in producing that strained condition of the iron. The *dynamic resistance*, or power of the plate to resist the blow, is equal to the quantity of mechanical work required to bring the plate into the most highly strained condition which it can bear without rupture. Should that quantity of work be greater than the energy of the shot, the plate withstands the blow; should it

> be less, the plate gives way, either by the formation of a number of radiating cracks, spreading from a point opposite the shot on the inner side of the plate, or by the punching out of a piece of a roughly conical figure, spreading from the indentation at the outer side, or by making a hole surrounded by a burr. The first mode of giving way, by cracking or bursting, is held to be an inferior quality of materials or of workmanship; the second, by punching, of a better quality; the last, by a burred hole, of the toughest and best.

Watts was also clear-sighted about the lack of knowledge of the dynamic strength of materials at the time: "Besides the quality of the iron, the dynamic resistance of a plate of a given thickness depends on the volume of metal put into a strained condition by the blow of the shot, and on the distribution of the stress in that metal. Owing to the imperfect state of our experimental knowledge, there does not yet exist any complete and exact theory of the laws of the dynamic resistance of plates to shot; but from such investigations as are possible in the current state of knowledge, it is clear, that for a plate of a given thickness *there is a certain diameter of indentation for which the dynamic resistance is a minimum*; becoming greater for a larger indentation, because of the increased volume throughout which the stress acts; and greater also for a smaller indentation, because of the way the stress is distributed" (Watts' italics).

Watts reported that the backing of armour plates by a number of materials, but mostly wood, was an active area of investigation: "Backing composed wholly of timber (as when armour-plates are simply bolted upon a wooden ship) adds little to the power of an armour-plate to resist penetration, its principal use being to stop shot and shell after they have passed through the armour-plate, and to diminish the vibration communicated to the hull of a ship by a blow; and for that purpose it should be made as thick as possible, by filling in the spaces between the frames with solid wood. It is otherwise when the wooden backing has a rigidly framed iron skin behind it; for then the compression of the wood between the armour-plate and the iron skin takes up a considerable part of the energy of the blow; so that the backing not only serves to stop shot that may penetrate through the armour-plate, and to deaden vibration, but adds to the dynamic resistance that must be overcome before the plate can be penetrated".

Backing, of course, does not have to be made from a single material. Wood-iron laminates were found to be effective. In the following quote, "compound backing" consisted of:

> alternate layers of timber and plate-iron, in the proportion of $4\frac{1}{2}$ inches of timber to $\frac{1}{2}$ inch of iron, or nearly so, set with their edges outwards, and fastened together with bolts. It is placed between the outer armour-plate and an inner armour-plate of about one-fourth of the thickness of the outer armour-plate. Between the inner armour-plate and the skin of the ship is a second backing of wood alone; the whole bolted to the ship with through bolts, and the ship's skin being stiffened as already mentioned with longitudinal outside stringers… An armour-plate backed with three times its thickness of compound backing (including an inner armour-plate of about one-fourth of the thickness of the outer), and with a second backing of wood of about half the thickness of the first backing, over a properly framed iron skin, is equivalent to an unbacked plate of about 1.6 times the thickness of the outer plate.

A selection of engraved drawings of the results of ballistic experiments performed in the 1850s and 1860s on specimens made of wood and iron is presented in Figs. 2.38, 2.39, 2.40 and 2.41.

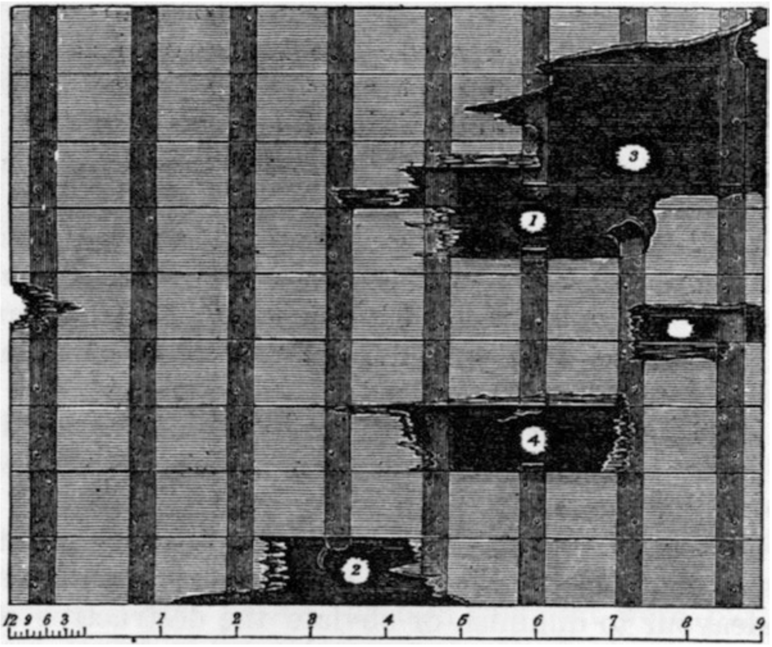
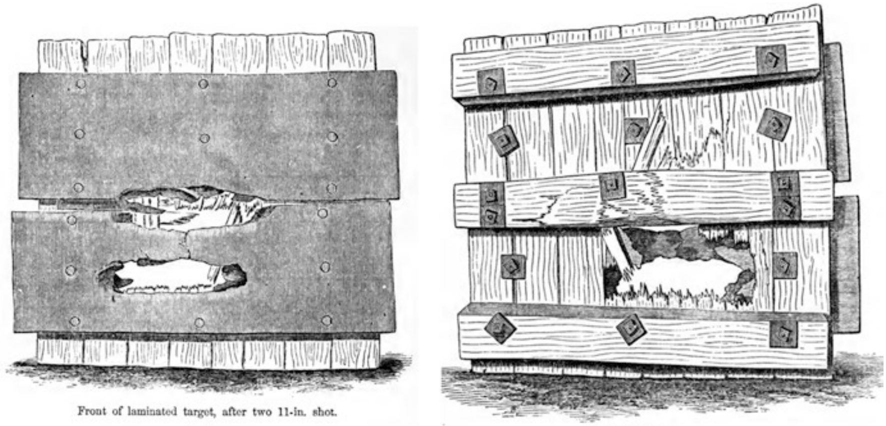


Fig. 2.38 Results of firing various types of shot against a wood and iron specimen representing a section of the *HMS Simoom*. Scale bar below the drawing is in feet. The construction and dimensions of the specimen were as follows: ribs of $\frac{5}{8}$-inch iron, 4.5 inches wide, 11.5 inches apart, covered with a 5-inch teak planking on the outside and 2 inch on the inside. The breadth of the 5-inch planking was 10.5 inches, and the breadth of the 2 inch planking was $9\frac{2}{3}$ inches. The whole specimen (10 feet long by 8 inches in depth) was placed 450 yards from the guns with the outside face towards the guns. (From Douglas 1855c, 140)

When Did Ships Start to Be Made from Iron?

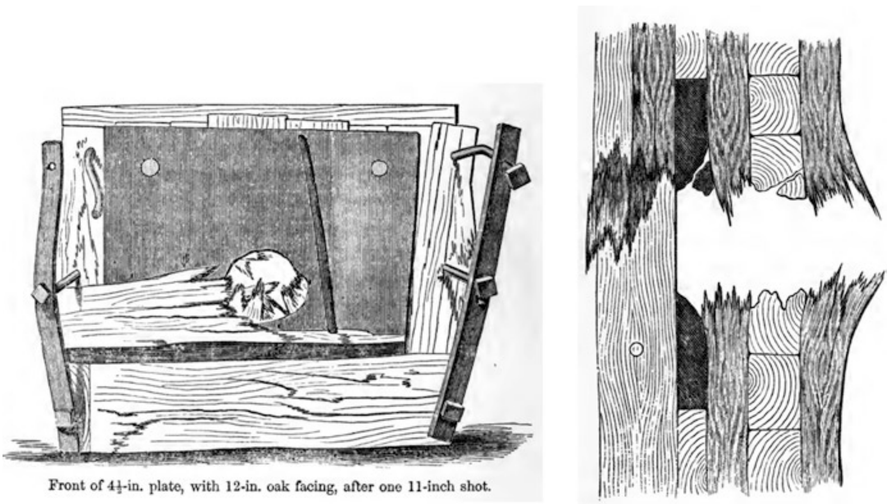
In 1851a, Fincham published a magisterial work entitled *A History of Naval Architecture*. This was reprinted in 1979. Near the end of his book, Fincham discussed the use of iron in shipbuilding, the beginning of which he said “lies within the limits of one’s memory”. He stated: “Iron boats were first built for the navigation of canals; and the origin of them belongs, by general consent, to about the beginning of this century. A considerable period elapsed before any more important use was made of them; for, though iron vessels were used as steamers, before they were used with sail-power, it was not until 1821 that a steam-engine was employed as the motive power to an iron vessel”.

Fincham was, however, mistaken. In the introduction to his book *Iron Ship-Building*, Grantham (1868) quoted from a publication dated July 28, 1787 (which unfortunately he did not name but which Brown writing in 1990 believed to be a Birmingham newspaper (Brown 1990b, 73)) to the effect that the first iron boat



(a) (b)

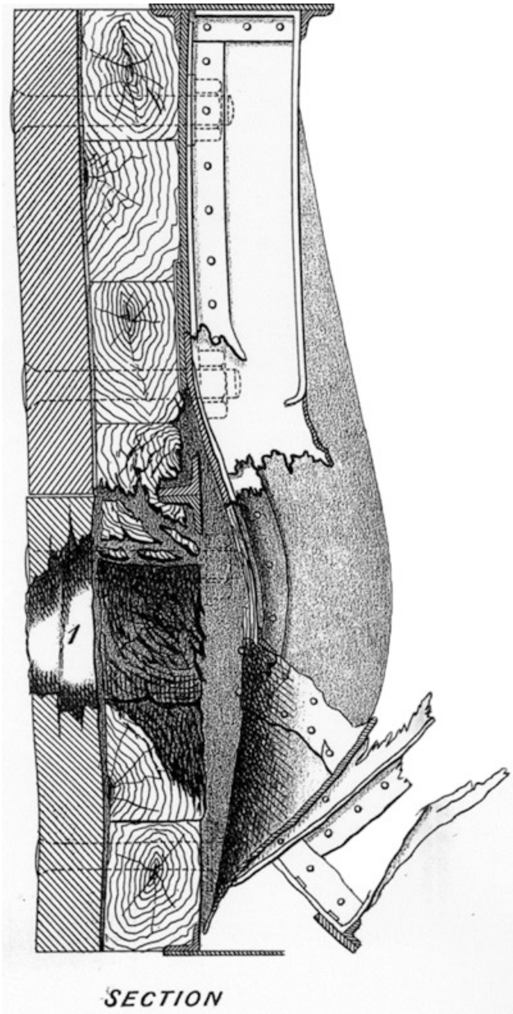
Fig. 2.39 (**a**) Front of a laminated target inclined 15° from the line of fire and backed by India rubber and timber after the impact of two 11-inch shots; (**b**) back view of the same target. Experiment performed September 4, 1862. (From Holley 1865b, 726)



(a) (b)

Fig. 2.40 (**a**) Back view of a 4.5-inch-thick iron plate faced with a 12-inch oak and backed by 20 inches of oak after the impact of a one 11-inch shot; (**b**) cross section of wood from the same target. (From Holley 1865b, 754–755)

Fig. 2.41 Drawing of a cross section through an iron and wood target (representing a section of the sides of *HMS Agincourt*) after being struck by a shell fired from an 8-inch Mackay gun at 200 yards. (From Morgan and Creuze 1865)



was built for canal use in that year: "A few days ago, a boat built of English iron by J. Wilkinson, Esq., of Bradley Forge, came up our canal to this town [Birmingham], loaded with 22 tons and 15 hundredweight of its own metal, &c". Note that Grantham's 1868 book is a revision of a pamphlet entitled *Iron as a Material for Shipbuilding* which he wrote to accompany a lecture he gave in 1842 to The Polytechnic Society of Liverpool. On page 6 of this pamphlet, he stated that one motivation for starting to make ships out of iron was the scarcity of suitably curved wood at that time in Britain.

In due course, iron boats started to make sea journeys. For example, an account of the first steam-driven iron vessel to make the journey from London to Paris was published in *Le Constitutionnel* of June 13, 1822 (quote taken from *Iron as a Material for Shipbuilding* (Grantham 1842, 6–7)):

> Le bateau à vapeur en fer, l'Aaron Manby, Capt. Anglais Napier, est. arrivé hier, Lundi, à huit heures du soir au Port St. Nicholas, avec un chargement de graine de tréfle, qu'il avait pris à Rouen, et de quelques pièces de fonte et de mecaniques, venant d'Angleterre. Le bateau Français à vapeur, Le Duc de Bordeaux, arrivé de Rouen samedi au soir, avec un chargement complet qu'il n'avait pu mettre à terre en entier, était parti du port à quatre heures du soir pour aller à la rencontre du bateau Anglais qu'il a atteint à la hauteur de Saint Cloud, en face des cascades. Ils sont partis ensemble, de la pointe de L'Isle Seguin, et le bateau Français, dont la manoeuvre est. visiblement supérieure, est. arrivé au Port St. Nicholas quarante minutes avant l'Anglais. Les curieux ont été, pendant, toute la journée, visiter les deux bateaux.

My translation of the above is as follows:

> The iron steam ship, the Aaron Manby, captained by Napier, an Englishman, arrived yesterday (Monday) at Port St. Nicholas at eight o'clock in the evening, with a cargo of clover seed from Rouen, along with some castings and machines from England. The French steam ship, The Duke of Bordeaux, which had arrived in Rouen Saturday evening with a cargo which it had not been possible to fully unload, had gone to the port at four o'clock in the evening to meet the English boat. The meeting occurred near Saint-Cloud in front of the Cascades. They left together, from the tip of Seguin Island, and the French boat whose manoeuverability was visibly superior, arrived at Port St. Nicholas forty minutes before the English. The curious, meanwhile, visited the two boats all day.

According to Grantham it would be another 30 years before a second boat travelled all the way from London to Paris. Brown said this was due to French navigation laws forbidding direct voyages from London to Paris (Brown 1990c). Grantham outlined in his book *Iron Ship-Building* (Grantham 1868, 86–97) the superior strength-to-weight properties of iron as compared to wood. He also discussed iron's superior mouldability, resistance to damage from collision with both rocks and ice, and durability in both salt and fresh water. The "last great enemy" of iron ships that remained in 1868 was the fouling problem (Grantham 1868, 237–240).

Fincham went on to list a number of advantages (and some disadvantages) of iron vessels compared to wooden ones: "The advantages of iron vessels consist, generally, in their durability, strength and safety, capacity for storage, economy and salubrity". Iron vessels had also proved more resistant to damage by collision: "… the security must be in such proportion as a ship is capable of enduring, unhurt, the casualties of tempests, rocks, and shores. …Experience has shown that unless the concussion takes place with great violence, mere indentation of the metal is generally the greatest injury sustained". Other factors that he listed in favour of iron vessels over wood included the fact that they were cheaper to build and to maintain. He states that even the highest quality wooden ships lasted no more than 30 years in service, although he goes on to say that it was not yet known how long iron ships would last. This observation on the life expectancy of wooden boats may go some way to explain why Fincham thought in 1851 that the origin of iron boats was more recent than was actually the case as the replacement of commercial wooden ships by those constructed out of iron would have been a slow and gradual process due to the cost of doing so.

At the time when Fincham wrote, ballistic experiments had been performed at Woolwich and Portsmouth on iron plates riveted together both with and without a lining of an intimate mixture of cork and rubber termed "kamptulicon". These experiments proved "unfavourable to the employment of iron ships in warlike operations". However, Fincham noted that if the problem of "the internal effect of shot" could be solved, the relative abundance of iron would make "the building of iron vessels more expeditious than that of wood". In addition he believed they would be cheaper to maintain.

In 1839, the British government started building steam-powered iron packet boats for river exploration and for transporting mail and other supplies. Steam-powered iron vessels of war started to be built in 1843, but as Fincham remarked, their paddle-wheel propulsion "interfered with the freedom of armament". This problem began to be overcome the following year (1844) by the introduction in naval ships of screw (propeller) propulsion, some 9 years after the first full-scale experiments on steam-driven screw propulsion had been performed. Also around this time, two famous iron-hulled sea-going passenger ships were designed and built by Isambard Kingdom Brunel: the *SS Great Britain* (launched 1845) and the *SS Great Eastern* (launched 1859).

The main perceived disadvantages of iron vessels compared to wooden ones were (i) their susceptibility to corrosion (Anon 1900; Mallet 1842), (ii) their fouling by plant and animal life (Anon 1900; Mallet 1847), and (iii) their magnetic properties which rendered compasses useless (Bennett 1827). However, ways were soon found that made it possible to use compasses on iron ships (Airy 1840; Hays 1845).

Concerning fouling, Fincham wrote:

> Prior to experience, it was apprehended that the saline property of the sea-water would have a strong corrosive effect on the iron; and that this material would be rapidly destroyed. But experience has shown that the effect of salt-water on *iron alone* is so small as hardly to bear a comparison with that which it has upon iron in connection with wood. And this remarkable difference of effect has been shown in iron vessels in which timber was used for the keel: for the bolts which had been driven through the keel to form its proper connections, have been acted upon with a rapidity almost to destroy them, before the iron plates forming the external parts of the hull had become perceptibly diminished in thickness by the same agency;– an important condition being, that the vessel should be kept in use, rather than lie up unemployed. Vessels which were built in the earliest stage of this art, subsequent to that of building mere canal-boats, bore the service many years, needing but little repair; and remained in a perfectly good condition to a later period than that to which the durability of wooden vessels ordinarily, and under similar circumstances, extends. Since the inner surface of the iron plates may be almost wholly protected from oxidation, the external wear is nearly all that is to be apprehended. The outer surface of the metal might also be protected in a great measure from corrosion; but yet the vessels were subject to the great disadvantage of having their speed diminished, after a very short period of service, by the adhesion and growth of animal and vegetable matter.

He goes on to say that a coating of red lead had no effect on the growth of animal and vegetable life but that recent experiments (by a Mr. Hay, the chemical lecturer at Portsmouth dockyard) had shown that a coating containing copper oxide served both to protect iron from corrosion by seawater and also prevented the adhesion of "animal and vegetable substances". Wooden naval ships had been protected by copper sheets against fouling by algae and damage by wood-boring animals since the middle of the eighteenth century (Davy 1824a, b; Harris 1966). This is how the phrase "copper-bottomed" arose. But copper plates cannot be used to protect iron against biological fouling in water as such a system forms an electrical cell leading to rapid corrosion of the iron (Brown 1990a).

Russell, writing some 10 years after Fincham (Russell 1861, 52), agreed with him about the superior resistance to decay of iron vessels as opposed to wooden ones:

> An iron ship never decays if well cared for. At least, I have not lived long enough to know how long an iron ship, built of good material, on right principles, will last. There are vessels twenty years old, showing no symptoms of general decay, even though hard worked in every climate all these years: all the hulls want is paint and care…The bane of the wooden navy is dry rot. You build a magnificent ship of the line; you launch her in time of peace; you lay her up for five years in the harbour of Portsmouth; and one fine morning, on a threat of war, a telegraphic message is sent that this new ship is to be put in commission. She is brought into dock to be overhauled and put forward, and lords are informed that her timbers are so much decayed, that she will require a thorough repair at an unknown cost of time and money, and that, therefore, some other ship must be put forward…In an iron fleet there is no such disease as dry rot, nor anything analogous to it. The durability of an iron fleet laid up in ordinary, is certain. An iron man of war, anchored in the Hamoze for twenty years, receiving a decent coat of paint when required, will be as fit for service any day in twenty years as it is the first day. For this purpose it is necessary that it should be wholly of iron, or at least, that wood should to the utmost possible be kept out of the construction.

Why Were Ironclad Naval Ships Developed?

The political and technical reasons why several navies (most notably the French, British, American, and Russian) replaced all-wood ships (such as *HMS Victory*, Fig. 2.42) by wooden ships armoured with iron plates (such as *HMS Warrior*, Fig. 2.1) were thoroughly researched by Baxter in 1933 and later by Sondhaus (2001). The main technical reason for the change was (as discussed earlier) the development in the early 1820s in France by Henri-Joseph Paixhans of explosive shells that could be fired horizontally from guns.

One previous method of setting wooden ships on fire was to fire red-hot solid shot. There was, however, a risk of the cannon exploding if the firing of the gun was delayed due to the heating of the gun barrel in contact with the shot causing expansion of the metal and hence contraction of the gun bore (Fig. 2.43).

Paixhans started his research in 1809 during the Napoleonic Wars (Paixhans 1822a, 33). His motive, expressed in many places in his writings, was to gain an advantage over the English. For example, in his book *Expériences Faites par la Marine Française* (1825, 27), he wrote: "Les Anglais (toujours je les cite, puisqu'ils sont, en paix et en guerre, nos rivaux les plus redoutables), les Anglais auront, comme nous, des canons-à-bombes. Mais si les canons-à-bombes détruisent la marine actuelle, nous n'avons que 160 bâtimens à perdre, et l'Angleterre en a près de 500", which being translated reads, "The English (always I refer to them, because they are, in peace as in war, our most redoubtable rivals), will have, like us, cannons that can fire shells. But if such weapons destroy both existing navies, we have only 160 ships to lose, whereas England has nearly 500" (a translation into English of the introduction to his book was pub-

Fig. 2.42 *HMS Victory* launched in 1765 and now in dry dock at Portsmouth Historic Dockyard. (Photographed by the author on March 16, 2017)

lished 2 years later in 1827 and most of the rest of the book was published in the United States in English in 1838).

The perception of the French establishment that its navy was inferior to that of England was a strong driving force for technical innovation within that country. Thus Paixhans wrote the following in 1825 when discussing the introduction of shell-firing guns onto naval ships: "Ils seront donc moins défavorables à la France que les vaisseaux de ligne actuels, avec lesquels il y aura toujours plus d'avantage pour l'Angleterre que pour nous, parce que les Anglais sont plus riches, et qu'ayant plus que nous leurs habitudes et leurs intérêts sur la mer, ils y auront toujours une certaine supériorité d'expérience" ("They will therefore be more favourable to France than the present ships of the line for which the advantage always lies with England because the English are richer than we are, and also since their interests lie on the seas to which they are more accustomed than us, they will always have more experience to draw on") (Paixhans 1825, 23).

In support of this, Robertson wrote the following in 1921d: "Up to [June 1859] the initiative, in the slow evolution of naval material, had rested mainly with France". There was also a sentimental attachment in England to the "wooden walls" that had defended it against attack for several centuries (see, e.g. the series of 11 articles that Allen wrote for the *United Service Magazine* from 1839 to 1844, the first being about *The Agamemnon* (Allen 1839), the last being about *The Defiance* (Allen 1844a, b)). Despite the sentimentality of these articles, there were good technical reasons for being cautious about the armouring of wooden ships by cladding them

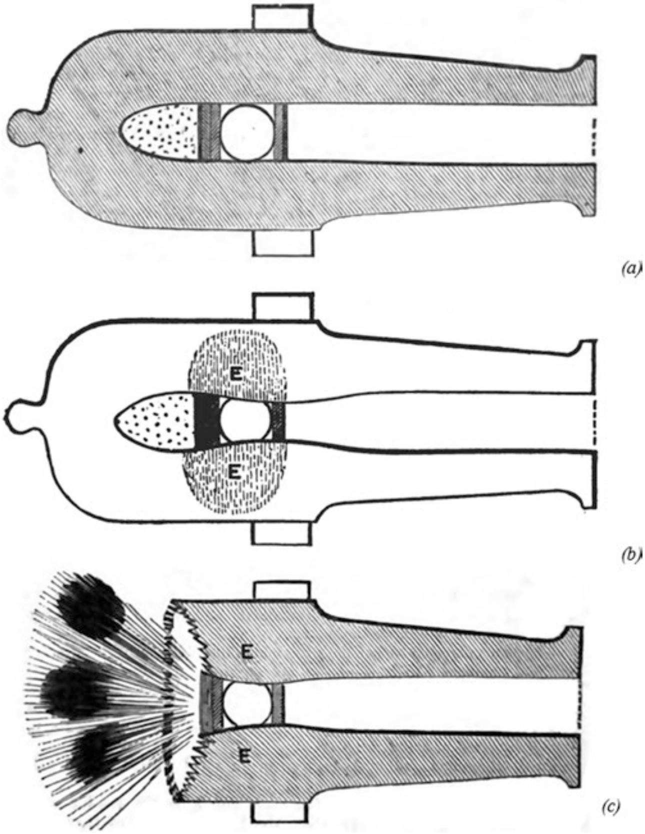


Fig. 2.43 Effect of heated shot on the bore of a cannon. (**a**) Cannon just loaded with shot and powder; (**b**) contraction of bore of cannon due to expansion of the metal in contact with the heated shot for a few minutes; (**c**) catastrophic bursting of cannon when subsequently fired. (From Gearing 1854)

with iron. Although the iron that was available at the time was a good defence against explosive shells, which were relatively light and therefore bounced off (Barnaby 1860), cast iron was shown time and time again to be useless against solid shot, being much too brittle (Fig. 2.37; Holley 1865a; Robertson 1921d; Totten 1857). Also experience with making guns out of cast iron had shown that it was of very variable quality. Some guns made of cast iron exploded after only a few shots, while others survived being fired several thousand times (Holley 1865b, 322). So the cladding of wooden fighting ships by iron only started to happen some 30 years or so after Paixhans' studies (Anon 1865).

The Battle of Sinope (1853) between the Russian and Ottoman Empires was pivotal to this process as it was widely believed at the time that the main reason why the Russian fleet prevailed against that of the Ottomans was because the Russians used explosive shells (Douglas 1855a; Paixhans 1855). Thus Sondhaus wrote in

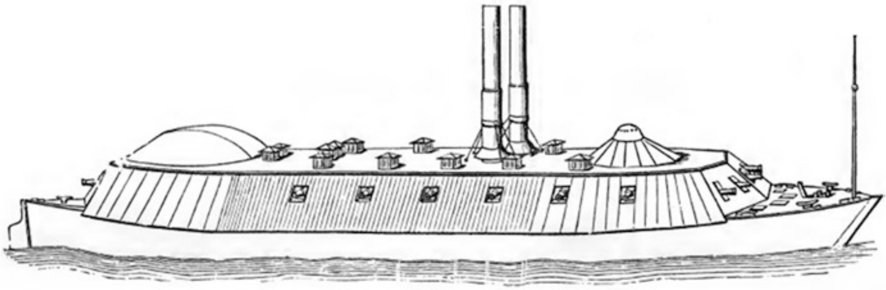


Fig. 2.44 Drawing of the Mississippi Ironclad "Benton". (From Holley 1865b, xii)

2001 (pp 58): "Many contemporary experts considered the outcome of Sinope a triumph of the shell gun, and there is evidence that the battle sowed the seeds of Napoleon III's doubts about the survivability of wooden warships against the latest heavy artillery". However, Sondhaus went to say: "But in order to draw such 'lessons' one had to ignore that it took six hours for Nakhimov to destroy the Turco-Egyptian squadron, despite the facts that he had six ships of the line with over 600 guns and that Osman Pasha's largest warships were frigates. Competent gunnery using solid shot alone would have been decisive at Sinope".

The first engagement between steam-powered ironclad naval ships occurred in 1862 during the American Civil War. Battles took place both on the sea and on the rivers. Note the similarity in the shape of the armoured vessels (shown in Figs. 2.2 and 2.44) with the all-wood battering ships used earlier in the siege of Gibraltar (Fig. 2.3).

The 1860s saw several books published in English on the art of building ships out of iron (Fairbairn 1865; Grantham 1868; Reed 1869; Russell 1865; Watts et al. 1866b). Reed acknowledges his debt to Grantham, Scott Russell, Fairbairn, and Rankine. Rankine (Fig. 2.45) was an amazingly productive Scottish academic engineer who wrote two substantial textbooks for students and practitioners of both mechanical and civil engineering (Rankine 1858, 1862). A collection of Rankine's papers was published in 1881 by Millar. In the field of impact and shock, Rankine is perhaps best known for first publishing the equations that describe the propagation of shock waves through gases (Rankine 1870). His equations can also be applied to condensed matter.

It should be noted that around this time (1860), analytical techniques were sufficiently developed that Longridge could show theoretically why making a gun barrel out of a set of nested tubes of graded hardness and ductility (high hardness but low ductility on the inside and low hardness but high ductility on the outside; Fig. 2.46) was better than making one out of a single homogeneous tube (Fig. 2.47). This combination of cast iron on the inside and wrought iron on the outside had previously been suggested for artillery by Thiéry in 1834 (see also Thiéry 1840) and subsequently implemented in steam engine boilers (Holley 1865b).

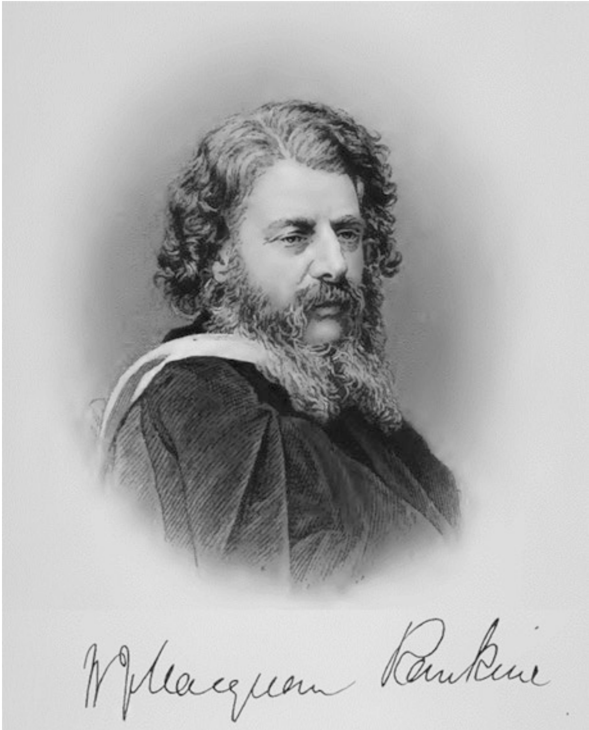


Fig. 2.45 Photograph of William John Macquorn Rankine. (From Millar 1881)

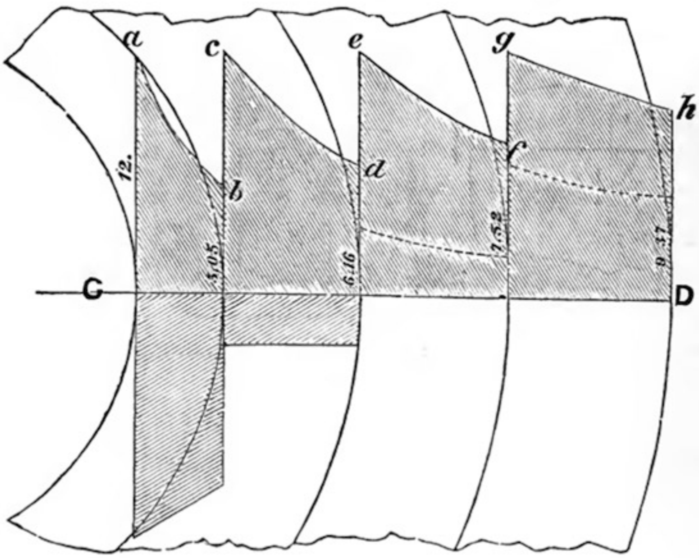


Fig. 2.46 Hoop strain field in a gun made of nested tubes. The superimposed graphs show schematically the work done in each hoop during the firing of the gun. (From Longridge 1860)

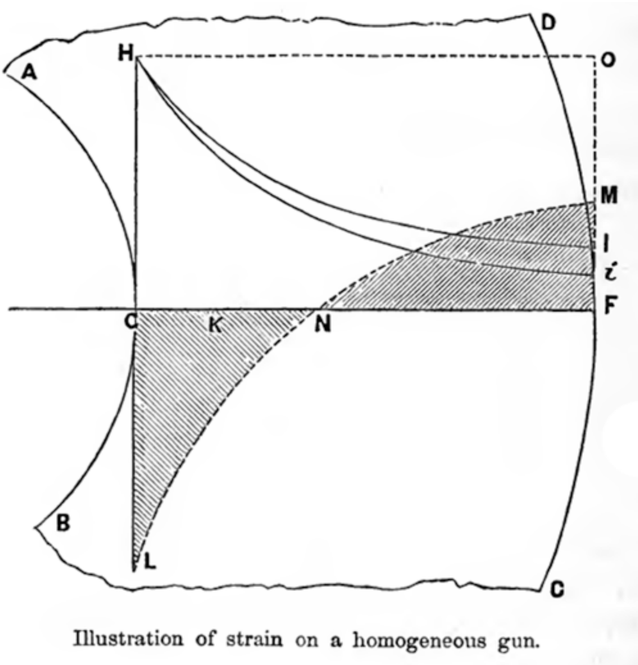


Fig. 2.47 Hoop strain field in a homogeneous gun barrel during firing. (From Longridge 1860)

The most famous and long-running argument about whether naval ships should be clad with iron armour was between Scott Russell (who was in favor) and Howard Douglas (who was against; Douglas 1860, 1861a, b; Russell 1861, 1863, 1865). This dispute at a high level within the British Establishment was summarized by Robertson in 1921d, 257–258. The bitterness of the argument may be gauged by the following quote from the preface that Russell wrote to his magnificent and beautifully produced work *The Modern System of Naval Architecture* published by the Queen's printer in three huge volumes in 1865, 4 years after Douglas' death (sadly these volumes have not yet been scanned and hence made available online): "The introduction of iron ships into the war navy of England has been the result of a long struggle of truth and common sense against perverse, obstinate prejudice. Ill-educated, disqualified persons, by obtaining seats at the Board of Admiralty, have been enabled to perpetuate the construction of inflammable wooden ships, long after they had in their possession irresistible proofs of the plain fact, that the modern shell, and shell gun, rendered wooden men-of-war utterly untenable, and so they succeeded in wasting precious time, and the treasure of the country, in expenditure, which they knew to be worthless; and were content to take no other precaution for the future safety of the nation, than the childish expedient of shutting their eyes".

Russell had earlier said what he thought on this matter at greater length in a pamphlet entitled *The Fleet of the Future: Iron or Wood?* published in 1861. The following quotes from this publication give the flavor of it:

It is well known that for some twelve or fifteen years, distinguished men, in the navy and out of it, have been gradually coming, by a course of practical experience and careful observation, to the belief that iron ships possess many advantages over wooden ships for purposes of war… Some twelve years ago I built some iron vessels of war which possessed the advantage of carrying heavier armament, drawing less water, and steaming faster than any wooden vessels of war the same size, and they afterwards did good service in the Sea of Azof. But the capture of Kinburn in the Crimea seems to have been the turning point in this question, as the effects of shot on the iron-plated vessels of the Emperor Napoleon satisfied him of the comparative invulnerability of iron sides, and decided his policy for the future in favour of iron defences. Encouraged by his example, the advocates of iron war ships in England have continued to urge their views with increased energy and tardy success. At this moment it is believed that France has gained material advantages by her willing and ready adoption of iron-coated ships, and that we have lost much by our tardy and reluctant adoption of the new element of defence.

Russell's main arguments in favour of protecting ships with iron plates were (1861, 1–2):

(i) "it was found [fifteen years ago] that in action iron vessels presented the advantages of turning aside shot fired obliquely; of being more easily repaired when damaged; and of being less easily set on fire than wooden ships"; (ii) "…on the skin of an iron ship these shells are broken to pieces, the powder flies out like so much dust, and therefore THE SHELLS NEVER EXPLODE. The fragments of iron do no more mischief than if they had never formed any part of a shell, and are just as much or as little innocuous as any other fragments of iron would be. It was the discovery of molten shells [author's note: a method of setting wooden ships on fire before explosive shells were approved for use on board ships was to heat cannonballs to red heat or even to fill hollow shells with liquid iron (hence 'molten shells')] that put an end to wooden walls; but the discovery that shells were shattered to pieces by iron, and their explosive power taken out of them, was the crowning fact which made the victory of iron complete. Shells are therefore the chief missiles of modern warfare, and a battery engaging a wooden ship of any size would, as a matter of course, pour into her broadsides of molten iron and explosive shells. It is believed that one round of molten iron and one round of percussion shells well delivered into a first-rate wooden man-of-war would destroy her; that the action would probably last three minutes (not more), and that in five minutes she would be a blazing and sinking hull. Such would be the victory of artillery over wooden walls. Iron has restored the equilibrium between attack and defence. It has done more than that. It has turned the scale against artillery; for shells cannot effectively penetrate the sides of iron ship, and shells are by far the most destructive missiles of war". (Russell 1861, 29–30)

In the year of his death, Douglas is recorded as being reconciled to the idea of the armouring of naval ships but only because the French had started building them. He still issued a warning that it would not end well, and he remained totally opposed to the idea of all-iron ships of war as this quote makes clear: "…vessels formed wholly of iron are utterly unfit for all the purposes and contingencies of war. I ground that opinion upon the incontestable fact, that a plate of wrought-iron of the best quality, 6 feet square and 8 inches thick, leaning upon, but not in contact with, immense slabs of granite by which it was supported, was penetrated, cracked, and broken up by 68-pounder shot at 600 and 400 yards' distance, with a charge of 16 lbs" (Douglas 1861a).

Around this time, the effect of various backings (cast iron, granite, various woods) was studied on the penetration mechanics of wrought iron plates. Rigid backings were found to be better than elastic backings (Holley 1865b, 668). Rubber facings were also investigated (Holley 1865b, 744).

Mid-Nineteenth-Century Terminal Ballistic Experiments

In 1933 Baxter listed the places he knew of where ballistic experiments had been performed in the years leading up to the introduction of ironclad naval ships (pp 56):

> Experiments in firing against iron armour intended for use in fortifications were conducted at Waalsdorp in Holland in 1843, at Turin [Italy] by Cavalli in 1845, at Woolwich [UK] between 1846 and 1850, at West Point [USA] by General Totten in the years 1853 and 1855, and by Brialmont and others in Belgium in the 1850s. With a view to cuirassing their warships on the Danube the Austrians, in the summer of 1855, fired 6- and 18-pounder field pieces against both vertical and inclined targets faced with iron. The most interesting experiments of this period, however, were those conducted by French researchers at Gavres between 1843 and 1845.

Despite the hundreds, possibly even thousands, of ballistic experiments that were being performed in various countries around this time, there was an awareness of how little was actually understood. Thus, in 1865 Holley gave the following summary of the state of the art of terminal ballistics (Holley 1865b, 133–134):

> The great problem remains unsolved. Indeed, engineers are looking for its solution in diverse or opposite directions. Seeing that the results of experiments, and especially of warfare, in testing guns against armour are developing new features of strength and weakness every day; that these results are still somewhat uncertain, and that time enough has not elapsed to enable the profession at large to collect and digest what facts there are, few if any *first principles* are universally recognized. This is still more the case since, from motives of gain, pride, or official conservatism, many persons have taken advantage of the limited knowledge on the subject to establish their own schemes, by arranging experiments to show their favourable side and to conceal the other, or by publishing one class of facts and ignoring those of a conflicting character (footnote: The readers of British scientific journals, for instance, will observe the number and general fairness of these complaints). Or sometimes reticence and a show of mystery are maintained, ostensibly to withhold information from foreign governments, when it is very well known that *governments* find means of acquainting themselves with each other's practice. The real loser is the government that, in concealing the truth, withholds it from its *own* people – from the great mass of ingenious and skilful men in civil life who would turn it to good account.

In the last decade of the nineteenth century, Garrison reviewed the progress that had been made in iron and steel armour during that century (Garrison 1892a, b). He wrote the following about cast iron: "Chilled cast iron is one of the hardest substances known in the arts, but what iron gains in hardness when in this form it loses in other qualities such as elasticity, ductility, etc. In order to possess a maximum of ballistic resistance an armour-plate must be not only very hard, but also elastic and ductile; these fundamental conditions have been thoroughly demonstrated by several trials of chilled cast-iron armour".

Garrison also reported that the effect of the angle of impact had been investigated as well:

> The results of trials several years later [after 1884], however, led to both of these firms [St. Chamond (in France) and Gruson (of Bruckau)] abandoning cast iron for armour-plate. It appears from the total results of the trials, that for land defences (glacis armour chiefly), where the conditions were such that the angle of incidence of the projectile was not great, chilled cast-iron plates made a good defence. In almost every case the projectiles were

> broken up. The penetration was very slight, the surface at the points of impact being chipped off, and, as would be expected, the general destructive effect upon the shield was to crack it in various directions. When iron is in a crystalline state its tendency to crack under the impact of a projectile is intensified when the latter strikes at a glancing angle, for under these conditions a second blow is delivered by the base of the projectile whilst the molecules of the iron are yet in violent vibration, caused by the impact of the point or ogival. On the other hand, these plates can be made cheaply and of great thickness for land defences, and owing to their hardness, rigidity and the rapidity with which they transmit shocks throughout their entire mass, they must be broken up bodily to be destroyed.

A particular problem that steam-powered ships had that land-based fortifications did not is the need to protect boilers against damage by shot. Coal bunkers were located in order to have a dual function. They were not just a store of fuel for the steam boilers but were positioned between the boilers and the hull of the ship to give some extra ballistic protection to the boilers. This was important because if a shell or a cannonball managed to strike the steam boilers, the effect would be catastrophic. Hence the interest in investigating the ballistic impact resistance of coal.

One idea first proposed to the *Conseil des Travaux* in France in 1834 (Baxter 1933, 28) was to incorporate as part of the armour the coal bunkers that steamships need in order to function. Watts et al. writing in 1866a, 296 wrote that this idea appears to have been widely implemented: "Armour specially for the protection of magazines, engines, and boilers, consists in general of armour-plate transverse bulkheads, or of shell-proof decks and platforms. The coal-bunkers are often so arranged as to give additional protection to engines and boilers against shot or shells which may penetrate through the side armour of the ship".

However, coal itself is not very effective at stopping a shot as this summary by Baxter of experiments carried out in France in 1843 shows (Baxter 1933, 58):

> In a long series of experiments on the beach at Gavres, near Lorient, the targets were generally larger, heavier, and more firmly planted than those used in England. The ordinary French target, to which iron plates were screwed, was of solid oak, six meters high by twelves meters broad, formed of heavy posts bolted together, set down into the sand, and firmly buttressed. The firing tests which began July 27, 1843, showed that no ordinary coal bunkers could give adequate protection. Solid shot fired from a long 30-pounder with five kilograms of powder at 10 meters range penetrated 3.43 meters of coal. Similar shot pierced 59 cm. of oak plus 2.79 meters of coal, as well as 59 cm. of oak, plus 11 mm. sheet iron, plus 2.83 meters of coal. When 27 cm. shells with a bursting charge of 3.2 kilograms were fired at an oak wall 59 cm. thick, backed by two meters of coal plus a bulkhead of 12 mm. sheet iron, the projectiles or their fragments never reached the sheet iron, but were found in the coal at a depth of never more than 1.4 meters. Shells generally exploded when passing through the outer wall of oak.

French researchers also investigated layering or laminating oak, iron, and coal as this quote from Baxter shows (1933, 59) (note that a given mass of iron was shown to be more effective as armour than the same mass of oak):

> At the request of the Prince de Joinville, a new series of tests of nine targets of oak, of iron, and of different combinations of oak and coal, of iron and coal, and of oak, iron and coal, began at Gavres in August, 1844. By using 30-pounder solid shot striking the targets at only 10 meters range with a velocity of 450 meters per second, the commission gave to the guns an advantage which it frankly admitted would be extremely rare in actual warfare. Armor which proved inadequate under these drastic tests, the commission observed, might well be

impenetrable under ordinary battle conditions. A thickness of 1.8 meters of solid oak, or three times the thickness of the sides of a steam frigate of 540 horse power, was required to stop the shot. The 30-pounder shot always broke up when it struck armour made up of eight, ten, or twelve layers of 12 mm. sheet iron. The fragments traversed eight layers, and some of them pierced ten, but none passed through armour of twelve layers. Even that maximum protection, however, was so badly damaged by the test as to afford no security. Per square meter of surface, this target of twelve sheets of iron weighed 1120 kilograms, as compared with about 1800 for the minimum impenetrable wall of oak, and with even heavier weights to such of the combination targets as resisted shot.

Wrought iron's superiority to cast iron was demonstrated in some tests performed at Portsmouth, UK, in 1858 (Baxter 1933, 124):

Tests of 68-pounder shot at ranges of 400, 200, and 100 yards against plates fastened to the side of the *Alfred* at Portsmouth in August showed the superiority of wrought-iron plates to those of homogeneous metal and of steel, as then manufactured. Slabs of vulcanized india rubber, much vaunted as armour then and later by inventors of 'shot-proof' ships failed utterly. Captain Hewlett reported that no shot that struck the wrought-iron plates actually penetrated the ship's side, even at 100 yards. In one spot three feet in length by two feet broad, eight projectiles struck close together, fracturing the armour but failing to penetrate the backing. "On the inside, in a line with that spot, no very great injury is done to the ship's side, and possibly not a man would have been wounded.' Pointing out that so concentrated a fire would have knocked an unarmoured ship to pieces, he concluded that the experiments: 'tend to shew to immense advantage ships clothed with wrought iron have over one not so protected; it puts a vessel with a few heavy guns more than on a par with the *heaviest 3-decker* supposing she has more speed, and… under such circumstances…the issue of an action could not long remain doubtful.

Wide variability in the ballistic resistance of wrought iron "made by the same manufacturers under apparently similar circumstances" was a problem, but Hewlett (quoted by Baxter) hoped that continued experiments might explain why this was so. The conclusion of these studies was "that 4-inch plates of common wrought iron 'appear to afford a reasonable amount of protection,' but that no decision as to building armoured vessels could be reached until it was ascertained whether such plates could resist the elongated shot fired by Whitworth's rifled guns, which he thought would probably be found to have much greater penetrating power both above and under water".

According to Baxter, the effects of rifled ordnance against armour were first studied by British researchers in 1858 (Baxter 1933, 125–127). The experiments were performed at Portsmouth in October of that year:

against 4-inch iron plates attached to the side of the *Alfred*. Three cast-iron shot from a Whitworth 68-pounder at 350 and 400 yards cracked the plates and started the bolts fastening them to the hull, but caused indentations of only $\frac{5}{8}$ to $1\frac{1}{8}$ inches. The only wrought-iron shot that struck the armour before the gun burst right through the plate and the ship's side, which here measured 6 or 7 inches of oak planking.

Further experiments that same month demonstrated the importance of weight in projectiles destined to attack armour. A single 68-pounder shot did almost as much injury to the armour and more damage to the woodwork and frame of the target ship than five 32-pounder shot that struck close together. Comparing these results with a confidential report from Colonel Claremont, the British military attaché at Paris, on the French armour tests, Captain Hewlett noted the superior penetration of wrought-iron shot from the British 68-pounders as compared with that of steel shot from the French 50-pounders. The results of the tests, however, gave great encouragement to the advocates of armour. Wrought-iron plates 4 inches thick resisted perfectly both cast-iron 68-pounder shot and wrought-iron shot weighing 72 pounds, fired with full service charges at 400 yards range. At 200 and 100 yards the projectiles had greater effect, but none passed completely through, save those striking in holes previously made. Even at twenty yards the cast-iron shot failed to penetrate, but the wrought-iron shot passed through the ship's side, showering the deck with splinters and fragments of iron. Hewlett believed these experiments were 'sufficiently conclusive as to the almost invulnerability of the common wrought iron plates at the shortest distances,' and predicted that a fast ironclad, carrying a few heavy guns, would have 'an immeasurable advantage of Ships of any size not so clothed.' If she were to be supplied with Martin's shells, filled with molten iron heated in a cupola installed on board, he thought it impossible to say what havoc she might work among an enemy's fleet.

Experimental firing against the floating batteries *Erebus* and *Meteor* in October and November demonstrated the importance of heavy wooden backing for the plates. Those of the *Erebus*, backed only by 5 or 6 inches of oak and the $5/8$ -inch iron skin of the vessel, suffered much more damage than those of the *Meteor*, a wooden-hulled battery on the French model, with 25 inches of oak behind the armour. At no time during the firing at the *Meteor* did it appear that the inconsequential damage inboard would have caused any inconvenience to the men working her guns.

Holley also gave a possible explanation as to why a 66-lb shot travelling at 1422 ft/s had far greater penetrating power than a 200-lb shot travelling at 780 ft/s, despite the calculated work done on impact being almost the same (Holley 1865b, 136), namely, that the faster, lighter shot "does its work *in much less time than the other*. This explains the whole matter". He had previously pointed out in a footnote on page 135 of his book that rate/velocity effects were well-known in the slate industry: "The punching of clean, small holes in roofing-slate, by a rapid stroke, when a lighter and slower stroke would smash the whole mass; and many other every-day experiments and processes illustrate the fact, that the element of *time* essentially modifies the effects of moving forces". He gave an explanation for the effect of duration of impact as follows (Holley 1865b, 135):

> In the case of the high velocity, the effect was wholly *local*, because the surrounding material had not time to propagate the vibrations throughout the mass. In other words, the cohesion of the material was not sufficient, in the time allowed, to overcome the inertia of the surrounding mass. The *distribution* of the effect, in the other case, was due to the low velocity. In both cases, the work done might have been the same.

Confirmation of this idea has been achieved in recent decades through the study of impacts on plates using modern optical techniques (e.g. Moore et al. 2009).

In the context of trying to understand the differences between low and high velocity impact on plates, Holley made the first mention that I know of concerning elastic/shock wave effects: "if the plate is 100 times heavier than the shot, and the shot has a velocity of 1000 feet per second, the plate will be moved bodily at the rate of 10 feet per second. But before this occurs, the whole force of the shot will have

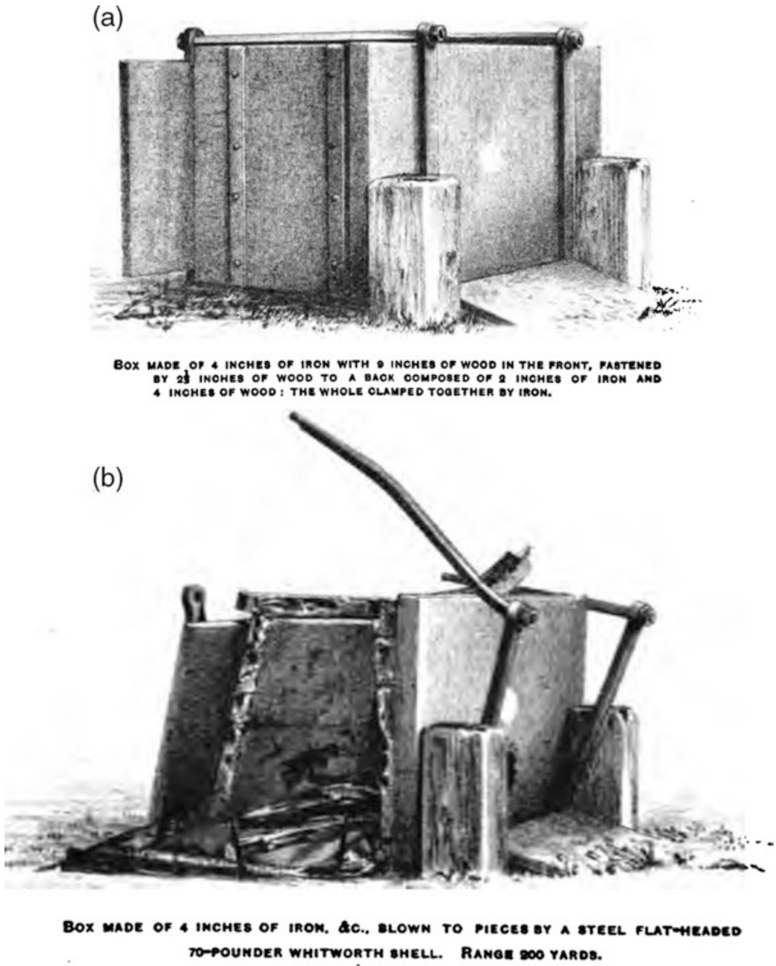


Fig. 2.48 Example of the effect of a shell on the iron bolts holding an ironclad box together. (From Whitworth 1873, 44–45)

been communicated through the mass from one layer to the other, by a wave moving at about the velocity of sound" (Holley 1865b, 280–281).

One weakness of the ironclad system from an engineering point of view is that the iron plates have to be fastened somehow to the wooden ship they are supposed to be protecting. So even a shot that does not penetrate can do a substantial amount of damage by bending the armour plate that it hits and thus deforming or breaking the bolts that hold it onto the ship (Holley 1865b, 152). An example of what can happen is given in Fig. 2.48. This makes the point that the structure of an armour system is just as important as the properties of the materials it is made from, if not more so.

Holley has a very interesting discussion in which he compares laminated with solid armour plate. He compared the action of a shot with that produced by a punch

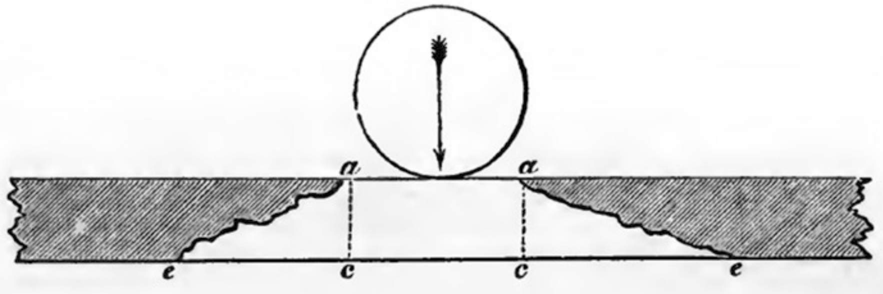


Fig. 2.49 An early example of a Hertzian cone crack in solid plate. (From Holley 1865b, 158)

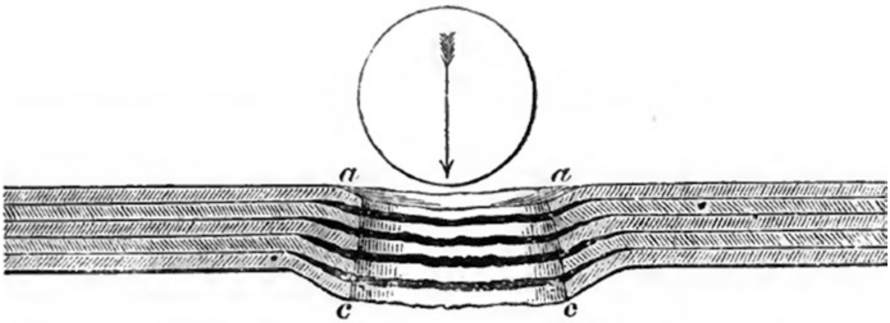


Fig. 2.50 Mechanism of damage produced in a laminated armour. (From Holley 1865b, 158)

in a workshop. In a workshop a plate rests upon a die with a hole of a certain diameter shown as *a c* in Fig. 2.49. No such die exists when a shot impacts an armour plate. Thus the diameter of the rear of the hole produced is much greater (*a e*) meaning that the load is distributed over a much larger area. The effect of lamination is to substantially reduce the area within the fracture zone (Fig. 2.50). In Holley's own words (1865b, 156–157):

> The reason why laminated armour is more easily pierced than solid armour, is thus explained: In a punching machine, the resistance of a plate to punching is directly as the fractured area, that is to say, directly as the thickness of the plate, for a given diameter of hole. But the resistance of a plate to punching-*shot* is found to be about as the square of its thickness. Now, in a machine there is a die under the plate, which prevents the metal around the punch from breaking down. Under an armour-plate there is no such die; the metal under the punch carries the adjacent metal with it, and the hole at the back is very much larger than the hole at the front. So that, while in a machine the fractured area (Fig. 2.49) would be *a e*, or at least so much larger than the united fractured areas of the thin plates forming the laminated armour (Fig. 2.50) as to account for the superior resistance of solid plates.

An example of the result of impact on a set of thin plates backed up by wood is given in Fig. 2.51. The shot can be seen to punch cleanly through and, according to Holley, "passed on some 100 yards to the rear".

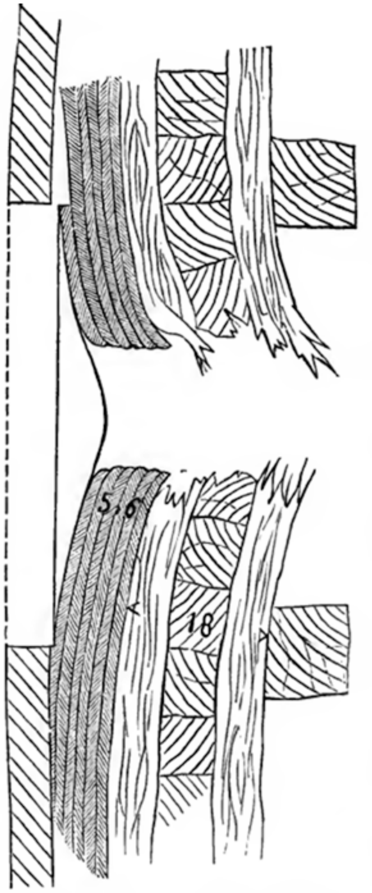


Fig. 2.51 Drawing of the result of firing a 10-inch diameter, 130-lb. cast iron spherical shot through a target composed of six 1-inch iron plates backed by 18 inches of oak. The target was 15 feet square. (From Holley 1865b, 156)

I believe that Fig. 2.49 may be the first published drawing of what later became known as "Hertzian fracture" after the German scientist who first analysed the elastic stress field under a spherical indenter and showed qualitatively that the lines of maximum shear stress form a cone (Hertz 1896; Walley 2012). The idea that the cone produced by Hertzian fracture spreads the load in hard-faced body armour (and thus reduces injury to the wearer) was proposed in 1989 by Field et al. (1989; Walley 2014).

One disadvantage that spherical has over cylindrical shot that Holley identified is shear fracture (Fig. 2.52). He comments that when a sphere strikes a plate, "the mass *c* is directly arrested and supported; but the overhanging mass *a a*, having no support, often breaks away, and having failed to impart its momentum to *c*, strikes a large area of the plate, in a salvo of small pieces, with greatly diminished velocity and effect" (Holley 1865b, 198–199). Thus around this time, Whitworth (among others) developed cylindrical shot (Fig. 2.53) which proved very effective against the new armoured ironclad ships (Whitworth 1870). Many years later particle frag-

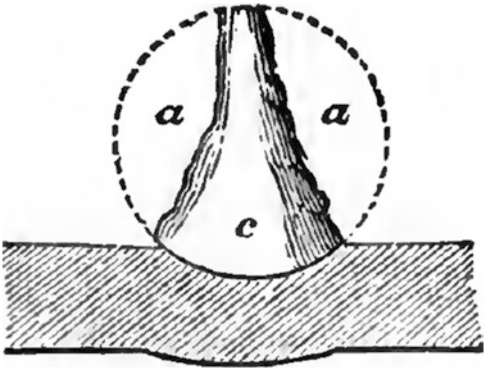


Fig. 2.52 Fracture of a spherical shot caused by impacting armour. (From Holley 1865b, 198)

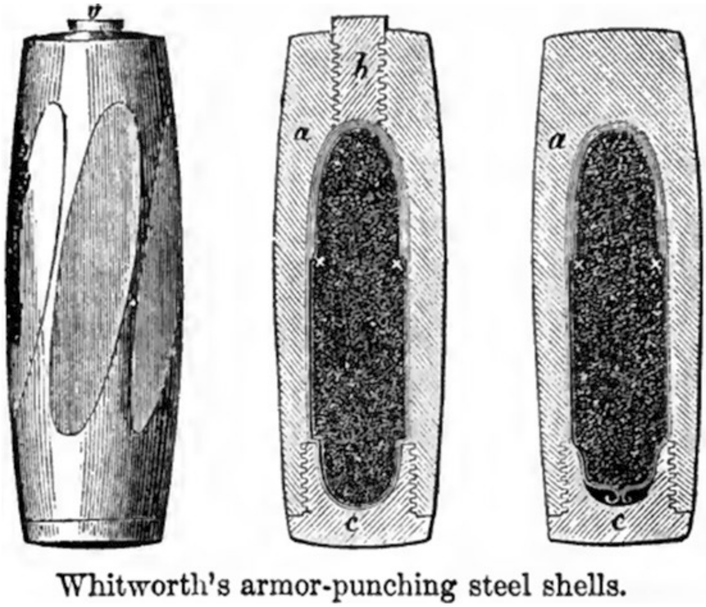


Fig. 2.53 Whitworth's rifled armour-punching steel shells. (From Holley 1865b, 182)

mentation was proposed as making a contribution to material removal in solid particle erosion, and high-speed photographic sequences were taken of this phenomenon (Fig. 2.54; Tilly 1973).

These were the sort of experiments that were performed in the years just before the decision was taken in France, Britain, and the United States to start building ironclad warships. No optical diagnostics, stress, or strain gauges were available at the time. All the military researchers could do was to construct targets representing sections of proposed armour systems and fire at them (Holley 1865b, 143 ff.; see also, e.g. Fig. 2.41). This was expensive, but still cheaper than firing at complete

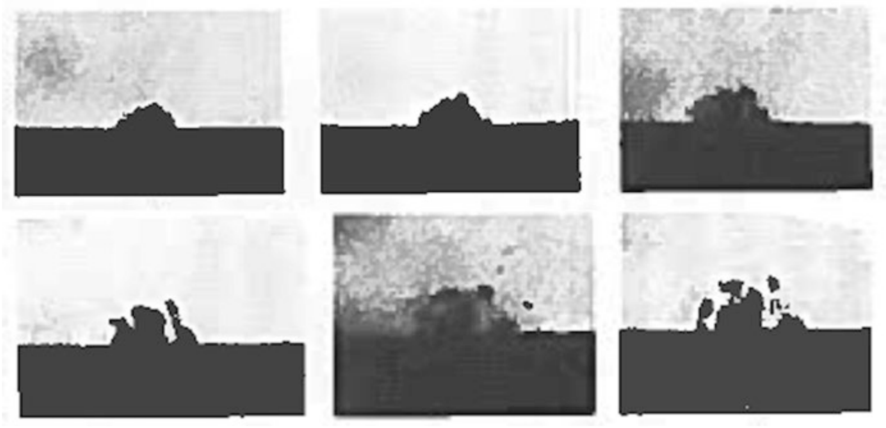


Fig. 2.54 Selected frames from the high speed photographic sequence of the disintegration of a 0.5 mm quartz sphere that has impacted a steel surface normally at 900 ft/sec (275 m/s). (From Tilly 1973. Image used with permission of Elsevier)

ships or fortifications. However, there were issues around about how large to make the targets as Hewlett noted that projectiles that struck near the edge of a plate did the most damage (Baxter 1933, 124).

In the absence of diagnostics, all the investigators could do was describe the damage done to a target. There are many hundreds, if not thousands, of such descriptions in the military literature of the second half of the nineteenth century. For example, the following report of an extraordinary test was given by Batcheller, an American who had been invited to spend several months at Shoeburyness, England, in 1891 (Batcheller 1892):

> One very interesting experiment was made at Shoeburyness while I was there, showing the effect upon armor plating of a shot from one of the largest guns in the English Navy. It was a 110 ton gun, taken from one of the ironclads, having a calibre of a little more than sixteen inches. The projectile used was one of the armor piercing type having a very hard point. The target consisted of two compound armor plates of iron and steel, having a combined thickness of twenty-eight inches. They were supported in heavy wrought-iron frames, and were backed with twelve-inch oak timbers twenty feet deep. Back of the oak stood a brick wall faced with granite, probably six or eight feet thick. The projectile passed through the twenty-eight inches of iron and steel, breaking the plates and bending out of shape the massive frames that held them; then it passed through the twenty feet of oak, crushing and displacing the timbers in all directions and turned up sideways against the brick wall in almost as good condition as before being fired. While it failed to pierce the wall it cracked it in all directions, and displaced some of the granite blocks on the face farthest from the gun. It was hard to realize that so much work could be done by a single shot from any gun. At the Naval Exhibition held in London during the past summer, this experiment was illustrated by a full size drawing.

Although it would be some time after the invention of photography before it became possible to trigger a camera accurately enough to capture the moment of impact, people quickly understood its potential to obtain information about ballistic events (Boys 1893; see also Fig. 2.55). Even as early as 1866, it proved possible to

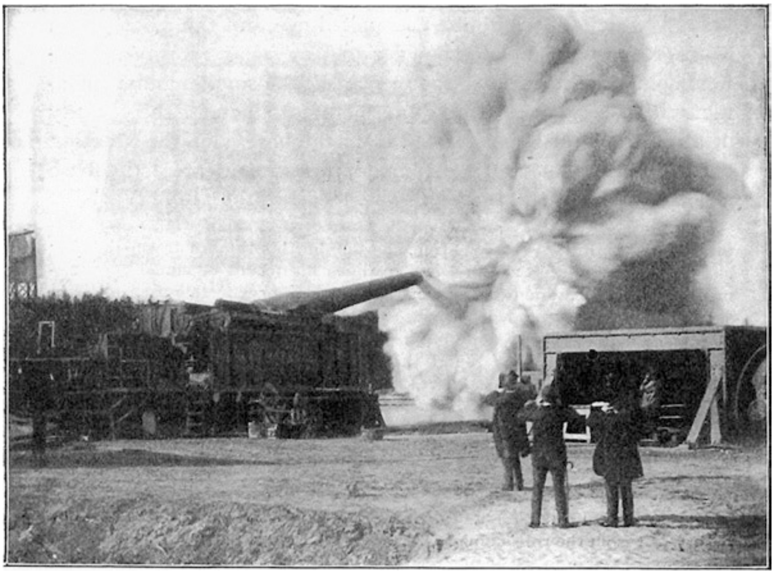


Fig. 2.55 Photograph of a gun being fired in 1899. The image showed that the projectile could continue to be accelerated after leaving the muzzle by the gas escaping from the gun. (From Farley 1899)

capture "freeze-frame" images of cannonballs emerging from guns as the following quote makes clear (Anon 1866): "Some months ago, when on a visit to Woolwich Arsenal, we were shown by Mr. McKinlay, Proof Master, some photographs taken of guns while being fired. So rapid had been the exposure, and so well had the proper moment for the exposure been seized, that the projectile could be seen protruding from the cannon's mouth while in the act of proceeding on its distant mission". The method used at Woolwich to freeze the motion was a spinning disc technique (McKinley 1866). Sadly the author of that report did not arrange for engravings to be made of the images, and I have not been able to determine whether the photographic plates still exist.

Advantages of Pointed Bullets and Shells over Round Shot

Holley reminded his readers that Isaac Newton had said in his *Principia* that a pointed body "would, in passing through a fluid, experience less resistance than a body of any other shape" (Holley 1865b, 536). Holley commented that the shape that Newton drew "is very similar to the ogival" (Fig. 2.56), although in fact the curves that Newton drew were parabolas rather than circles (Fig. 2.57).

Newton also seems to have been the first to try and estimate the depth of penetration produced by ballistic impact (Gaite 2017), but since he did not know (and had no way

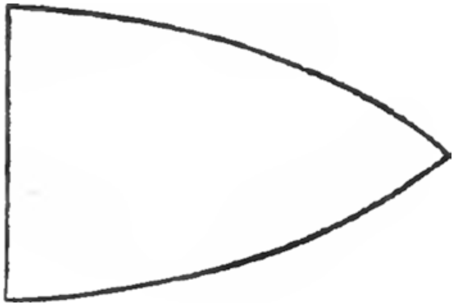


Fig. 2.56 Shape of body that Newton said would experience less resistance to passing through a fluid than any other shape. (From Holley 1865b, 536)

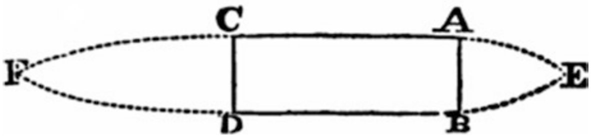


Fig. 2.57 Newton's method of modifying a cylinder (ABCD) in order to reduce its resistance to motion "from F towards E" through a fluid. (See Cohen and Whitman 1999, 745)

of determining) the flow stress of materials, his calculation was based on the distance required to transfer the momentum of the projectile to an equal mass of the target material. For a cylindrical projectile, Newton's method gives the penetration depth as the length of the rod multiplied by the relative density of the projectile to the target material. This calculation is approximately true only for impact velocities very much greater than were achievable by gunners in Newton's day (and indeed for many years afterwards).

The superior penetrative power of pointed shot was recognized by 1866 (Fig. 2.58), such shapes having long been used in solid bullets (Scoffern 1858b). As manufacturing techniques improved, these became the standard design for shells (Whitworth 1870; see also Fig. 2.33). Then, of course, the apparently endless cycle of improvements to defence and attack began again: the response to the development of pointed shells was to make armour plates harder on the impact side (face-hardening). The shells were later (1897) made more penetrating using a soft metal cap, sometimes including lubricant (Fig. 2.59).

Weaver made the following observation in 1892:

> For more than thirty years the contest between guns and armour has been going on. At times the gun has been the acknowledged victor, and again the plate has been first. So regular indeed has been the pendulum like swing of advantage from the one to the other that an existing supremacy of either has seemed enough to initiate a corresponding advance of the other. Only a few years ago it seemed that the gun had fairly conquered the plate, and it was supposed that, in view of the improvements made in projectiles, it would, this time, retain its vantage ground for a longer period than usual. But, following the lead of Schneider and Company, of France, plate makers have, step by step, been able to give armour a position farther in advance of the gun and projectile than ever before. Were it not for the teachings

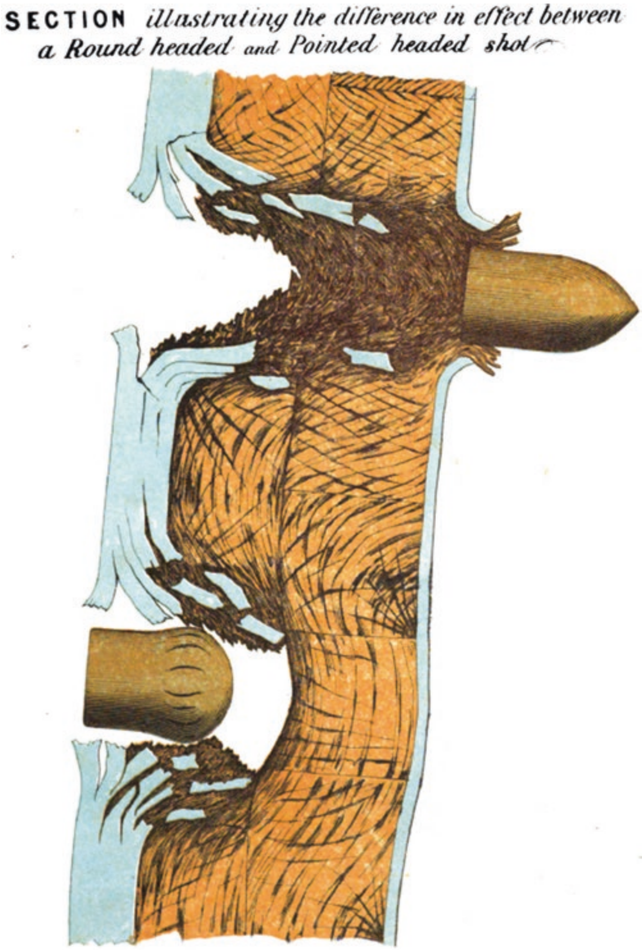


Fig. 2.58 First known illustration of advantage of pointed-head shot. (From Noble 1866)

of the past one might look for little material alteration in the present relations of gun and plate. It remains for the gun and projectile makers to meet the conditions established by the Annapolis trials of 1890 and the Indian Head trials of 1891. Until they do, the plates must be considered to have gained an advantage over both the gun and projectile.

The process, of course, continued so that in 1918 Crossman commented:

From the day the horrified jackies of our old navy watched their round shot bounce off the armored sides of the *Merrimac*, ballistic sharks and armour experts have striven assiduously to produce the fabled condition of an irresistible force meeting an immovable body. From that hour to this, and with the end not in sight, projectile maker has gone armour manufacturer one better, only to have the other 'see and raise' him, with the process repeated in wearisome iteration. And now the argument has been transferred to land, becoming the case of the rifle and machine gun versus the steel shell for men, cars, planes and tanks.

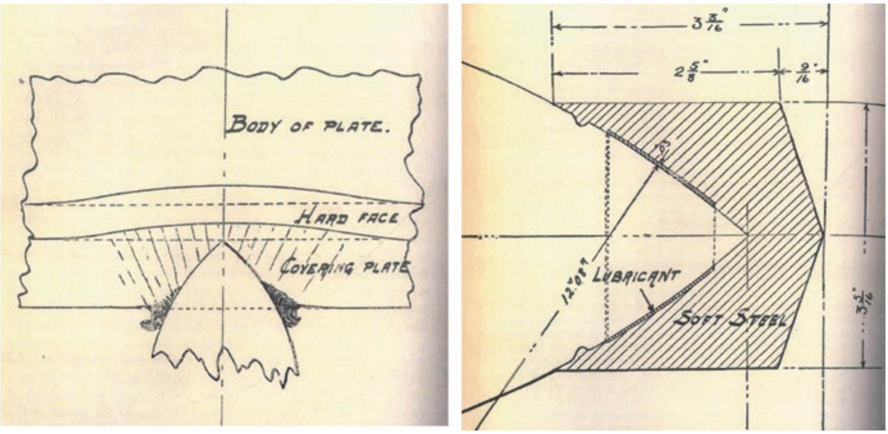


Fig. 2.59 Diagrams explaining why a shell with a soft metal cap performs better than one that is uncapped against face-hardened armour. (From Davis 1897)

Machine Guns

I will not give here a detailed history of the invention and development of the machine gun as there have been a number of books published on the topic from the First World War onwards (e.g. Hogg 1979; Keller 2009; Longstaff 1917; Popenker and Williams 2011; Smith 2002). Instead I will reproduce a few quotes to give an impression of the impact this new weapon made and the motivations of the people involved.

The precursor to the machine gun was a multitubular gun called the mitrailleur (Fosbery 1869; Gatling 1870; Owen 1874; Rogers 1871). As the following quote from 1869 makes clear, many people were not impressed with it as a weapon (Anon 1869): "At a time when we are grappling with a stern question of armament, it seems odd that there should be brought under discussion a contrivance which, in the present advanced state of gunnery and musketry, can only be classed among the toys of science." …. "In conclusion, without doubting the possible utility of mitrailleurs for many important purposes in war, if the weapons can be brought to the suggested perfection, we submit that they cannot at present uphold the expectations held forth for them by their enthusiastic inventors".

However, Rogers' writing in 1871 said that one aim of developing such a potentially terrible weapon had been, believe it or not, humanitarian: He was quoting from a lecture given at the School of Musketry in 1853 concerning "mitrailleuses" (Rogers 1871): "…the practical philosopher… will endeavour to render war as terrible as possible, well knowing that so soon as certain death awaits two rival armies, princes must fight their own battles or war must cease. Therefore, however paradoxical it may appear at first sight, whoever increases the power of destruction is engaged in the cause of humanity".

However, this apparently noble aim was not realized as Crossman commented in 1918 (Crossman 1918):

> It is doubtful that even today armor would be revived as it has been, were it not for the many things of lighter penetration than bullets which are flying about our battlefields: shrapnel, shell splinters, grenade fragments, bayonet points. These things made light protection for the head very desirable; this, extended to the body in the form of a light cuirass affair, was then, because of the comparative immobility of the troops, thickened into protection against the bullets themselves, despite the weight this added. At the present time, therefore, we find a second coming of armor for man, gasoline horse, and flying machine not equalled since the Middle Ages. The armored tank waddles imperturbably astride of machine gun positions and cleans out the operators therein, it saunters down street in the face of cracking infantry fire. Armor coats the engines and most of the crew of airplanes, it surrounds light motor cars, it covers the head of every soldier of the fighting nations outside of Russia. It has been tentatively taken up as body covering in the form of layers of canvas and steel or of woven steel links. In thickness merely enough to stop the plain infantry bullet, it forms the shield and the apron of every field gun. Most of these things are practicable only while the forces are in a state of relative deadlock; their weight would hamper troops on the march… Special armor-piercing bullets were not new when war broke out, but the occasion for them had been limited to getting through the shields of field artillery, and infantry didn't often get close enough to field guns to make this need an urgent one. But after the first year of the war, when snipers began to ensconce themselves behind armor shields and armored cars began to reinforce infantry at threatened points of the line, while airplanes demonstrated surprising immunity to machine gun fire, the ordnance experts began to take a keener interest in bullets that would not be so easily discouraged on meeting a stubborn steel plate… The one general objection to all these armor-piercing bullets is that, after completing penetration, they are all reduced to tiny steel shot of 0.218 to 0.24 caliber; the remainder of the bullet disappears into thin air on impact with the steel. … But in spite of these, these bullets will greatly reduce the enthusiasm to steel bullet stoppers; even a 0.218 hole in one's anatomy is more discouraging than none at all.

Although body-armour was not widely available during World War I, Crossman reproduced a couple of photographs of attempts by the Italians and Germans at devising steel armour that gave some measure of protection against machine gun fire (Figs. 2.60 and 2.61).

Machine-gunners were, of course, themselves vulnerable to return fire from their opponents. As steel armour is heavy, one ingenious solution that was devised in the 1880s to the problem of transporting it to the battlefield was to make the wheels of the gun carriage out of armour steel plate (Fig. 2.62).

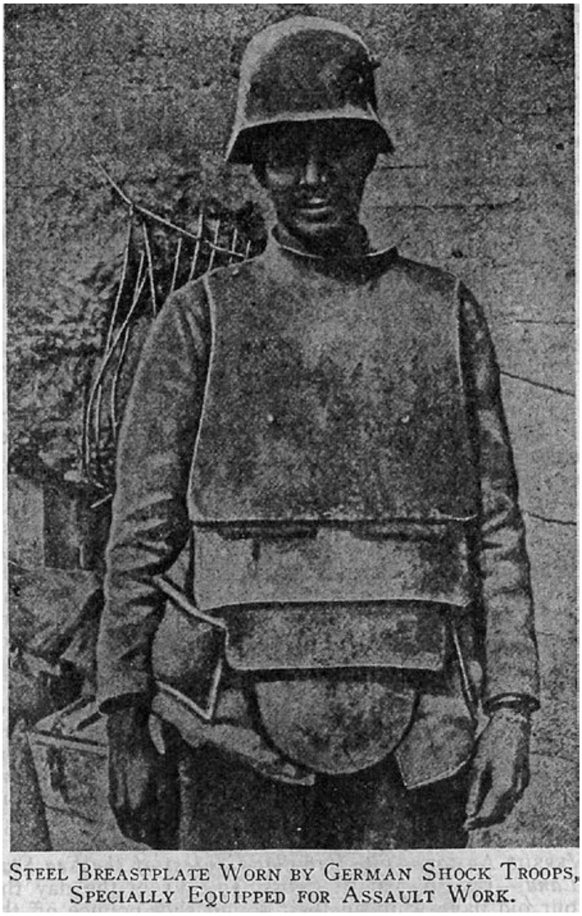
Angled Armour

As mentioned earlier in this chapter, it had long been known that, generally speaking, fortifications were more effective at defeating projectiles if the impact took place at an angle. This must have been observed many times after star forts were developed in the 1520s in Italy in response to the invention of the cannon (Fig. 2.63; Blondel 1683b; Sparavigna 2015).

It should be noted, however, that the move away from the traditional design of a castle (Fig. 2.64) was based on geometrical arguments about eliminating blind spots on the part of the defenders rather than deflecting cannonballs. After initial successes with the design, the idea seems to have been oversold, and the designs

Fig. 2.60 Italian soldiers, carrying pieces of tank armour, advancing against machine gun fire in World War I. (From Crossman 1918)

Fig. 2.61 Steel breastplate worn by German shock troops during World War I. (From Crossman 1918)



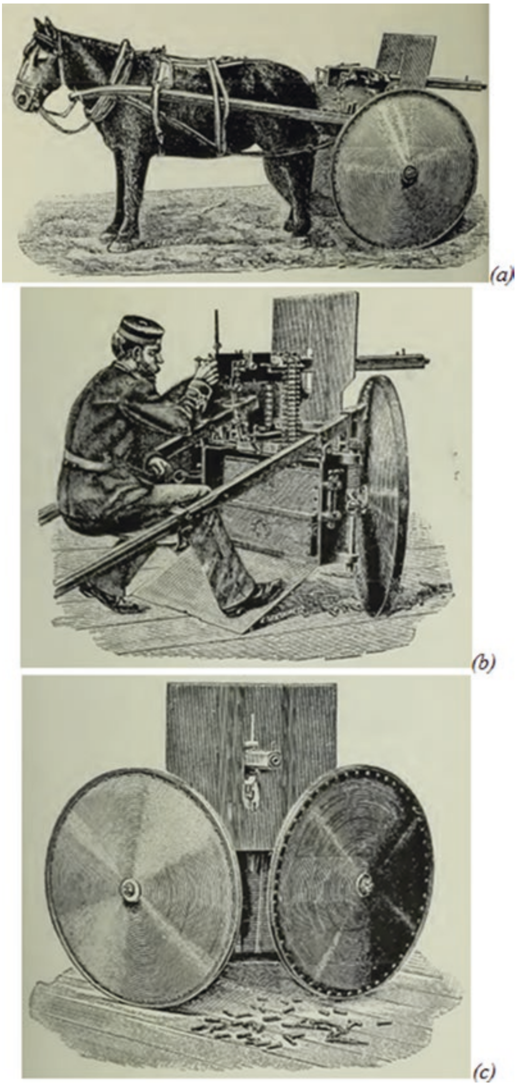


Fig. 2.62 (**a**) Machine gun armour shields that double up as carriage wheels; (**b**) man operating machine gun from behind armour plates; (**c**) front view of an armoured machine gun. Maxim ARCM design from around 1887. Figures originally published in *Scientific American*. (From Longstaff 1917)

became ever more elaborate (Fig. 2.65). Muller commented in 1746 (pp 22): "Notwithstanding all the improvements which have been made in the art of fortifying since the invention of gunpowder, that of attacking is still superior to it. Engineers have tried in vain to render the advantages of a fortification equal to those of the attack; the superiority of the besiegers fire, together with the greater number of men, obliges generally, sooner or later, the besieged to submit". Ten years later, Maurice de Saxe was particularly scathing (de Saxe 1756, 141): "Je ne suis pas bien savant, mais la grande réputation des Messieurs de Vauban & Coehoorn ne m'en a jamais imposée. Ils ont fortifiées des places avec des dépenses immenses & ne les ont pas rendues plus fortes". Or in English translation (Duffy

Fig. 2.63 Fort George, Inverness. A rare example of a bastion fort in the British Isles

Fig. 2.64 Carnarvon Castle, North Wales

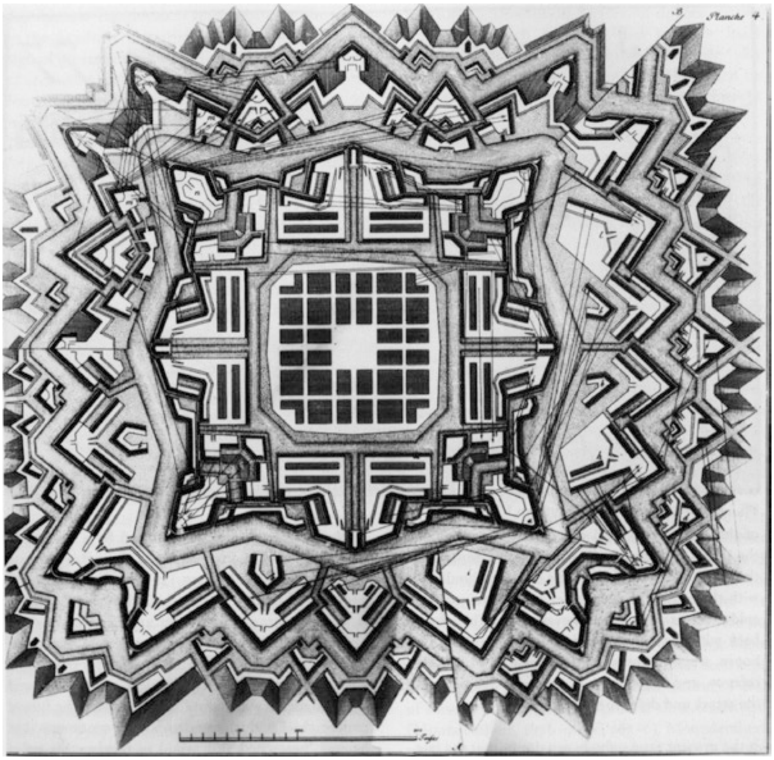


Fig. 2.65 Over-elaborate bastion design. (From Duffy 1985, 155)

1985, 154): “I am not much of a student, but I have never been overawed by the reputation of Vauban and Coehoorn. They fortified towns at immense expense without making them any stronger” (Vauban and Coehoorn were designers and promoters of so-called star forts; see Figs. 2.63 and 2.65).

Iron armour was also found to resist penetration better if the impact occurred obliquely (Garrison 1892a, b; Russell 1861), although there had been some evidence to the contrary (Holley 1865a). In the late 1860s, Whitworth performed some studies of the effectiveness of his new cylindrical shells at much shallower angles of impact against ship armour than in previous studies (Fig. 2.66).

Another relevant comment was made by Weaver in 1892:

> If a projectile do not strike the plate at right angles to the face of the plate, only a fractional part of the projectile’s energy will be expended normally, and it is, of course, only that energy due to the *normal* component of velocity that is efficient in overcoming the resistance offered by the plate. It is precisely in connection with this question of oblique impact that it has been the custom to overlook, and to fail to credit to armour one of the most important advantages it has over the gun and projectile. If we call to mind the actual conditions of attack, it appears at once very clear that normal impact must of necessity be an exceptional occurrence. The motion and direction of the ship, the curved shapes given to armour, the angle of fall of the projectile, all operate to make normal impact a rare event. From this the following principle may be enunciated: that whereas the gun never realized

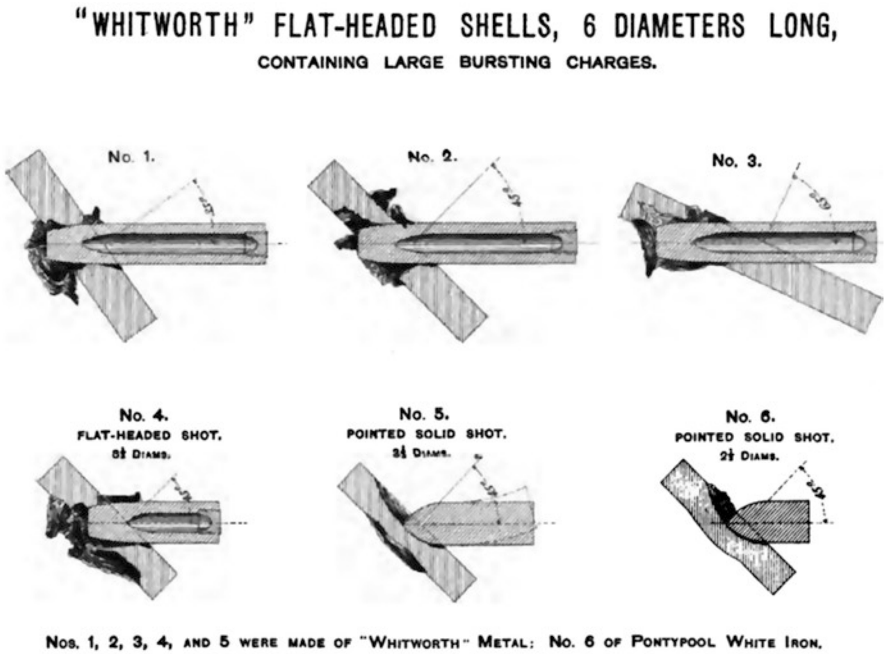


Fig. 2.66 From Whitworth 1873, 48

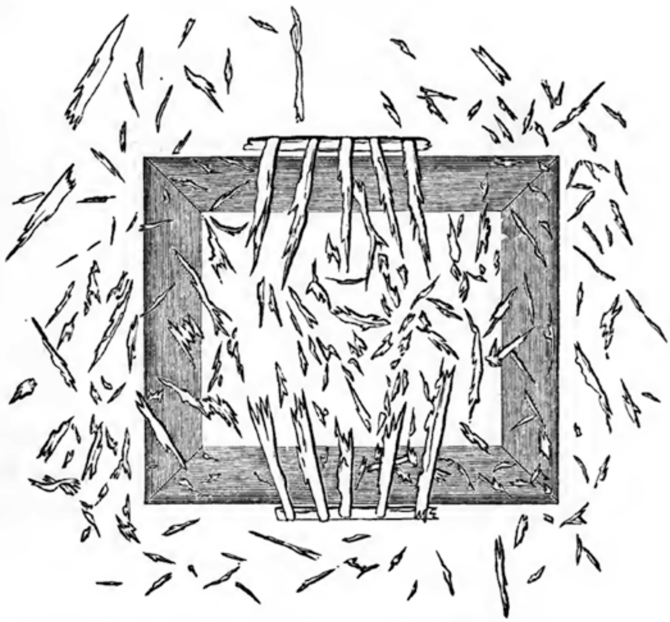
> in full the advantages it has on the testing-ground, the plate, reciprocally, is never so much at a disadvantage as on the testing-ground; the plate will not lose a foot-pound of its resisting capacity, and the chances are it will gain greatly by the actual conditions of combat.

Weaver then went to describe experiments conducted in England, France, Denmark, and the United States on oblique impact. He concluded that: "it is thought that steel armor will deflect all projectiles that strike under an angle greater than 60° with the normal".

Blast

Armour and fortifications are also subject to attack by blast. Although guncotton, a detonating explosive, now known as nitrocellulose, was invented in the 1840s (Ransome 1847); it was not until the 1860s that it was introduced into service when ways of making and handling it safely had been developed (Abel 1865; Lenk 1864). Its effect on wooden structures such as bridges (Fig. 2.67), ships (Fig. 2.68), and palisades (Fig. 2.69) was devastating.

Figure 2.70 shows the result of a trial performed in 1887 of the sequential impact of three 122-lb shells each filled with 2.3 lbs of dynamite. The target was a 14-inch wall consisting of two thicknesses of wrought iron, on top of which was a 3-inch roof. The first shot blew the roof off. The conclusion was that a combination of



Bridge of oak, shattered to atoms by a box of 25 lbs. of gun-cotton.

Fig. 2.67 Effect of 25lbs of guncotton on an oak bridge. (From Holley 1865b, 795)

impact and blast could eventually overcome an armoured fort that otherwise would withstand ballistic impact indefinitely. An understanding of the effects of explosive loading of iron plates would have to wait until 1914 when Bertram Hopkinson (Fig. 2.71) used elastic wave theory to explain why scabs of metal were thrown off the inside of a metal plate at high speed by the detonation of guncotton on the outside (Fig. 2.72; Hopkinson 1914), a phenomenon later called "Hopkinson fracture" by Kolsky and Shi in 1958.

Thus began a more intensively theoretical approach to ballistics and impact as opposed to just experimentation. From that time on, researchers had both the theoretical and experimental tools to understand, measure, and explain the phenomena that their predecessors had observed but struggled to explain. No longer would it be adequate simply to fire a gun at a target and describe what happened.

Concluding Remarks

The developments in armour and ballistics that took place between 1860 and 1914 were just the beginning of the story of heavy armour. For just when someone creates an armour system they think cannot be defeated, someone else develops a new weapon that is able to breach it. Right back at the start of this process in 1860, Barnaby wrote: "[A] ship may be cased with armour which today is shot-proof; but

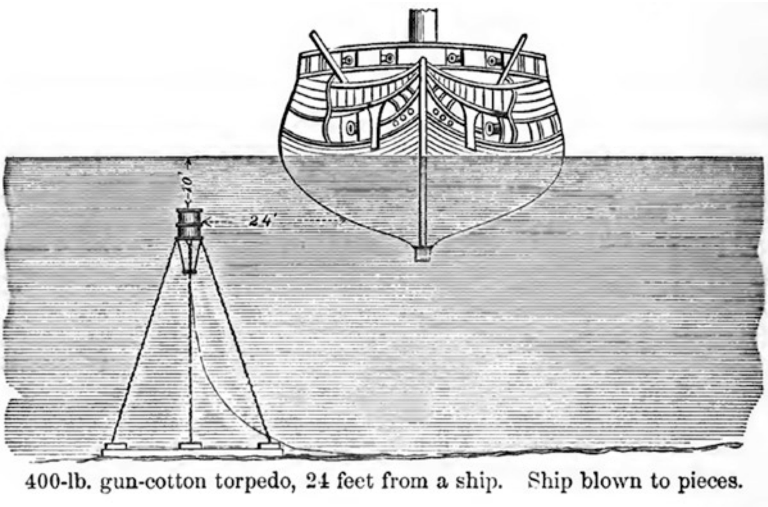


Fig. 2.68 Study of effect of underwater explosion of guncotton on a wooden ship. (From Holley 1865b, 796)

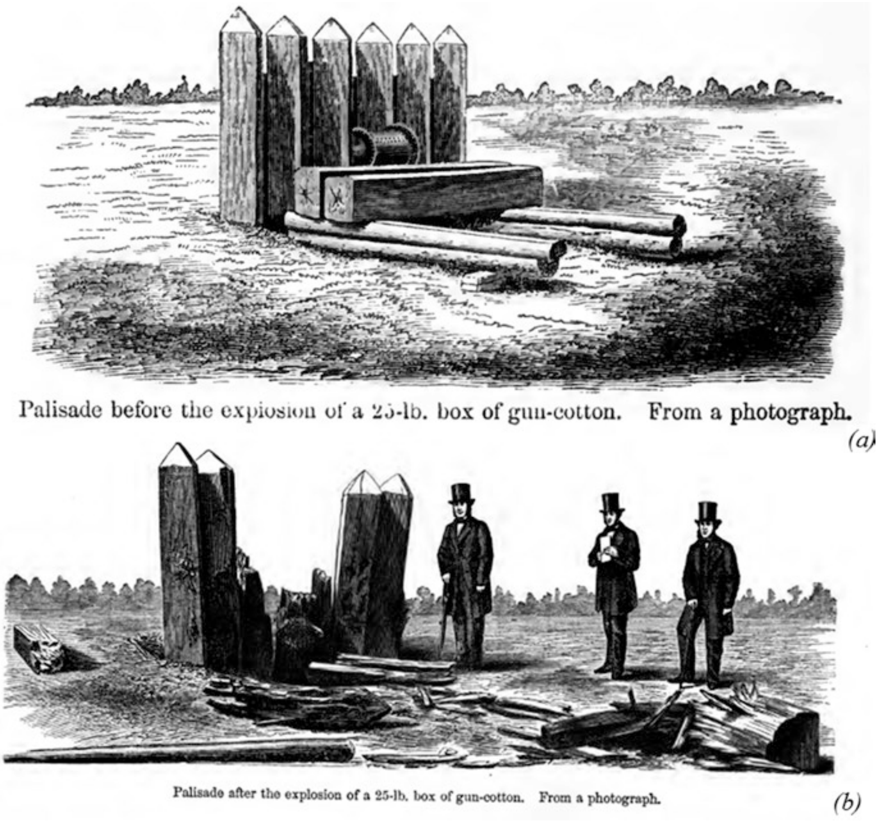


Fig. 2.69 Engravings of photographs of the effect of 25lbs of guncotton on a wooden palisade. (**a**) Before explosion. (**b**) After explosion. (From Holley 1865b, 830–831)

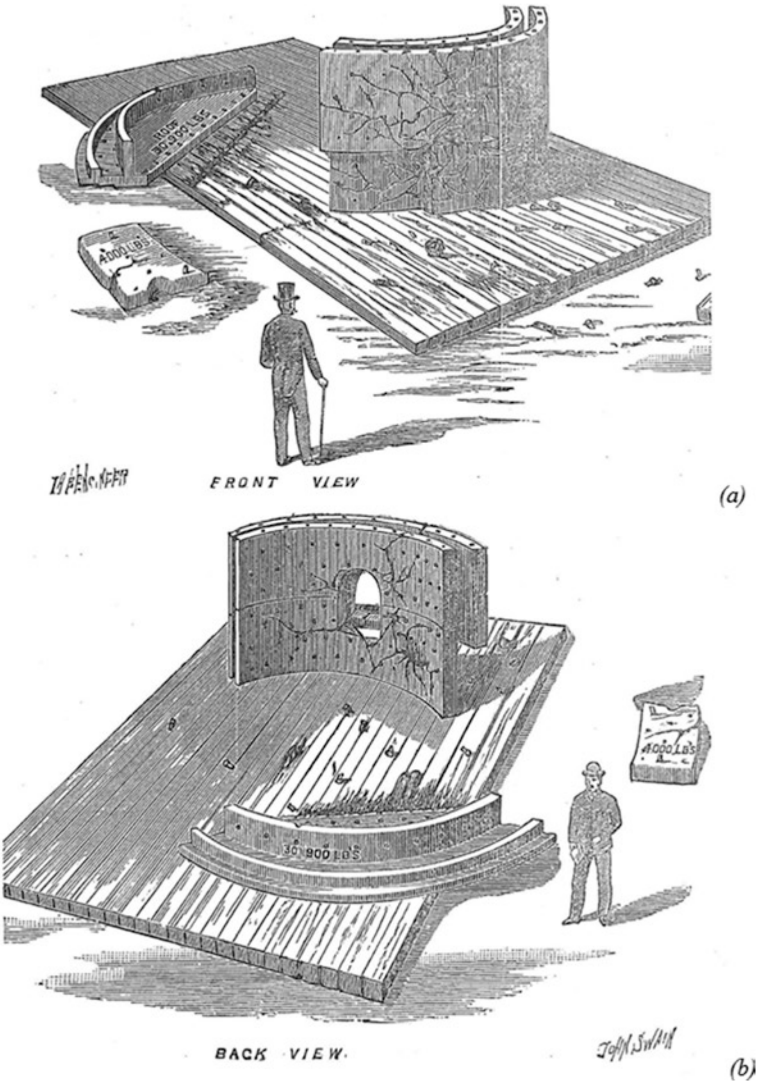


Fig. 2.70 Result of an American experiment on the combined effect of blast and impact due to the explosion after impact of a dynamite-filled shell on wrought-iron armour. (From Browne 1893)

tomorrow it may be pierced with ease by shot or shell thrown by some new iron monster". Thus shortly after the *HMS Warrior* was launched in 1860, shells were developed by Whitworth (Fig. 2.53) and also Armstrong that could punch through its armour. This process continues right up to the present day. A recent example demonstrates this in action, namely, explosive reactive armour (ERA). This was developed to combat the threat from shaped charges (Held 1999a; Held et al. 1998). However, almost simultaneously a weapon system (tandem-shaped charges) that

Fig. 2.71 Photograph of Bertram Hopkinson sitting at his desk in 1904. (From Hopkinson 1928)

Fig. 2.72 Incipient spall produced in a 1.25-inch-thick mild steel plate by the detonation of a slab of guncotton on the underside. (From Hopkinson 1914)

had been patented some years before (Kintish and Marcus 1973) was suggested by some of the same people involved in the development of ERA as a method of overcoming it (Held 1999b; Iyer 1999).

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Appendix A: List of Nineteenth-Century Military, Engineering, and Scientific Journals Containing Information Relevant to This Review

Note that due to constraints of time and difficulty of access, the author was not able to consult the non-English literature in the original languages. However, many articles of interest were translated at the time and republished in both British and American journals. The journals are listed here for the benefit of future researchers.

American Journal of Science (still published)
Arms and Explosives (UK journal, published 1893–1920)
Army Quarterly (UK journal; now Army Quarterly Defence Journal)
Artilleriskii Journal (in Russian)
Artilleristische Monatshefte
Baumaterialenkunde (started 1896)
Bulletin Belge Sciences Militaires
Bulletin Renseignements Artillerie
Bulletin Des Sciences Militaires
Bulletin de la Société d'Encouragement pour l'Industrie Nationale
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences
Dingler's Polytechnische Journal
Engineering
Giornale di'Artiglieria e Genio
Journal of the American Society of Naval Engineers
Journal of the Franklin Institute (started 1826 and still published)
Journal of Natural Philosophy, Chemistry, and the Arts (Nicholson's Journal; pulished 1797–1814, when it was merged with *The Philosophical Magazine*)
Journal des Sciences Militaires
Journal Royal United Services Institute (started 1857)
Journal of the United Services Institute of India
Journal of the United States Artillery (published 1892–1922)
Kriegstechnische Zeitschrift
Kynoch Journal
Memoirs of the American Academy of Arts and Sciences
Memoirs of the Manchester Literary and Philosophical Society
Mémorial de l'Artillerie Française
Mémorial de l'Artillerie Marine
Memorial de Artilleria
Mémorial des Poudres Et Salpêtres
Militär-Wochenblatt
Minutes and Proceedings of the Institute of Civil Engineers (started 1837)

Minutes and Proceedings of the Royal Artillery Institute
Mitteilungen über Gegenstände des Artillerie- und Geniewesens
Nuovo Cimento (started 1855)
Philosophical Magazine (started 1798)
Philosophical Transactions of the Royal Society of London (started 1665)
Proceedings of the American Philosophical Society
Proceedings of United States Naval Institute
Professional Papers of the Corps of Royal Engineers (started 1837)
Reports of the British Association for the Advancement of Science
Rivista di Artiglieria e Genio
Revista Cientifico-Militar
Revue Armée Belge
Revue Artillerie
Revue du Génie Militaire
Revue Maritime
Revue Militaire des Armées Etrangères
Revue Militaire Française
Revue Militaire Suisse
Scientific American (still published)
Stahl und Eisen (started 1881)
The Engineer
The Military Engineer
The Military Review
The Royal Engineers Journal (started 1870)
Transactions of the American Society of Mechanical Engineers (started 1880)
Transactions of the Institute of Engineers and Shipbuilders of Scotland
Transactions of the Institute of Naval Architects
Transactions of the North East Coast Institute of Engineers and Shipbuilders
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Chapter 3
Transformative Innovation in Mining and Metallurgy

Robert Gordon

Introduction

As the USA entered the last third of the nineteenth century, a huge expansion of industry was underway that required iron, copper, and other metals in quantities never before seen. The existing methods of finding and evaluating ore deposits (Fig. 3.1) or mining them (Fig. 3.2) no longer sufficed. Only with transformative innovations could the new demand be met. By the early twentieth century, these were in place. Mining ever-lower-grade ores in ever-larger quantities meant generating more wastes (Fig. 3.3), but these tailings could be left in the mining districts, while the benefits of cheap, abundant metals were enjoyed elsewhere. Then, in the mid-twentieth century came the realization that metal resources just might not be inexhaustible, and that waste repositories might have finite capacity. A new discipline, life cycle analysis, traced the size and location of metal stocks and wastes. The news was not good, emphasized by disasters from toxic emissions and failures of waste-containing dams. Here were challenges to technology as great as those of metal abundance. Unresolved social and environmental consequences of mineral extraction became more of a threat to continued economic growth than possible resource scarcity.

Transfer of knowledge and experience from other areas of technology and commerce through diverse individuals and routes was a primary source of the innovations that made an order-of-magnitude increase in metal production. The free flow and exchange of ideas and techniques was essential and was accomplished by people who came from diverse backgrounds and trades and as immigrants from other countries. New printing and papermaking methods distributed knowledge of innovations through journals, trade papers, and manufacturers' catalogs (Newell 1986).

R. Gordon (✉)
Department of Geology and Geophysics, Yale University, New Haven, CT, USA
e-mail: robert.gordon@yale.edu

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Fig. 3.1 Exploring for ore circa 1880. Ore samples are being extracted from a test shaft in the Tri-State lead-zinc district (Missouri, Kansas, Oklahoma)

Mining engineering and economic geology were in the first stages of becoming professions, but would be well established by the turn of the century.

Physics and chemistry contributed directly to some innovations, as in electrowinning and refining. But other problems that needed guidance from science were neglected because of their complexity or the absence of basic research yet to be done. The surface chemistry and hydrodynamics of bubble motion in the fluid-solid grain mixtures used for mineral separation by flotation were developed only after the process was perfected through trial and error experimentation. None of the innovations could have been realized without capitalists to assemble the requisite finance and managers to create backward integration from metal producers to ore sources.

Mining

Aside from copper obtained from a few small mines in the East, the USA had depended on imported copper until Michigan was admitted to the Union in 1837. Reports from its newly established geological survey directed by Douglass Houghton on the mineral wealth of the Upper Peninsula attracted prospectors and

Fig. 3.2 Mining circa 1880. Collapse of underground workings of a lead-zinc mine formed this pit here being examined by the mine staff

speculators in search of native copper, which they could pick up in stream beds and trace back to its sources. They soon flooded the area with claims. Mining was a different matter; there was little experience with hard-rock mining on a large scale in the USA. Miners from Cornwall, England, brought the requisite skills and innovations to Michigan. These miners had generations of experience and of up-to-date methods. By the mid-nineteenth century, declining ore resources and the increasing costs of working at ever-greater depths had forced their industry into decline. Rather than host unemployed miners, Cornish parishes often paid passage money for them to immigrate to America, where their skills were immediately applicable in the deep, hard-rock copper mines of the newly opened Lake Superior district and from there throughout the American West (Lankton 1991; Rule 1998).

Extracting ore by hand-jacking shot holes and blasting with black powder, the traditional technique much celebrated in folk song, was labor intensive and unable to achieve production on the scale needed in Michigan or at the new, much larger western mines. Boring the 5000-ft long Hoosac railway tunnel through a mountain of hard rock in northwestern Massachusetts (Fig. 3.4) became a stimulus and test bed for innovations immediately applicable to mining. The tunnel builders got off to a grand start in 1853 with a novel, purpose-built boring machine, but it expired after advancing only a few yards. After a hiatus during the Civil War, Jonathan Couch and Joseph Fowle tried steam-powered drills, with little success. Charles Burleigh, a

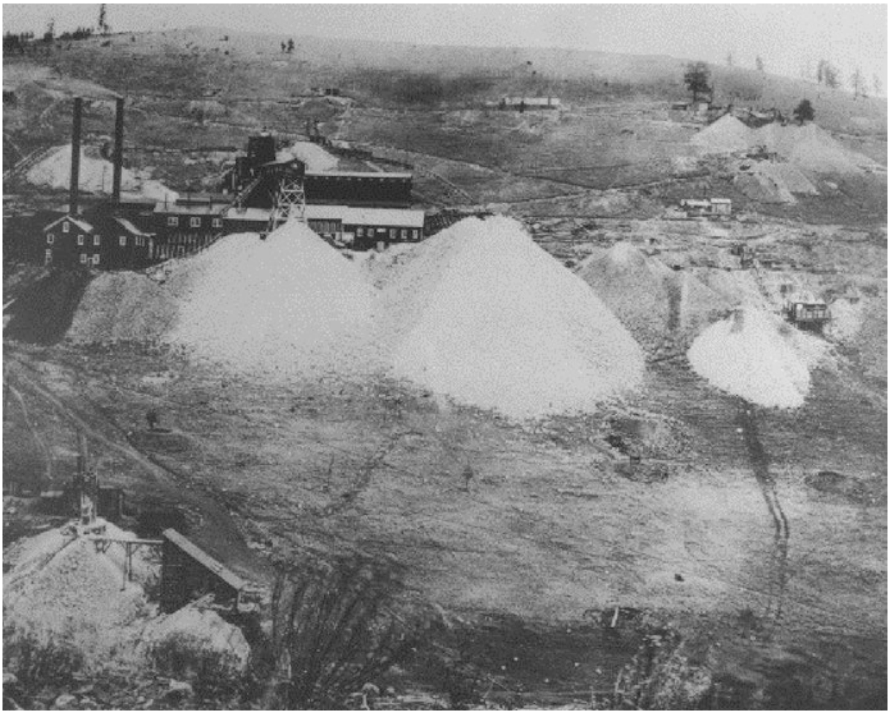

Fig. 3.3 Milling circa 1880. Stamp mills in Colorado discharged ever-increasing wastes without recovering much metal. What became of them was someone else's problem

42-year-old mechanic from Waterville, Maine, worked at the Putnam Machine Works in Fitchburg, Massachusetts, when in 1866 Couch and Fowle recruited him to help with their steam-powered drills. Burleigh abandoned steam and designed an entirely new rock drill mechanism that rotated and advanced the drill bit as it was repeatedly driven forward with compressed air. Exhaust air absorbed the recoil of the drill bit after it struck the rock face. His mechanism had interchangeable parts to facilitate rapid repair. With Burleigh drills at work, rapid progress was made on the Hoosac. Development of rock drills was going on in Europe as well, and there was a regular trans-Atlantic exchange of patents and descriptions. Nevertheless Burleigh worked independently; his drill was an American original (Schexnayder 2015).

As soon as news of the success of the Burleigh drills on the Hoosac reached managers of northern Michigan copper mines, they adopted them. The Burleighs drilled far faster than was possible by hand jacking, and had the added advantage that the air exhaust helped with mine ventilation. But its mountings were too big and heavy to handle in most mine adits. A.C. Rand and other artisan inventors entered the field with smaller, lighter drills from 1871 onward (Fig. 3.5; Lankton 1991; Newell 1986).

Finding iron in upper Michigan was more difficult than finding copper because it was buried under drift left by the Laurentide Ice Sheet. Houghton's deputy, William Burt, had learned that running survey lines by magnetic compass was unre-

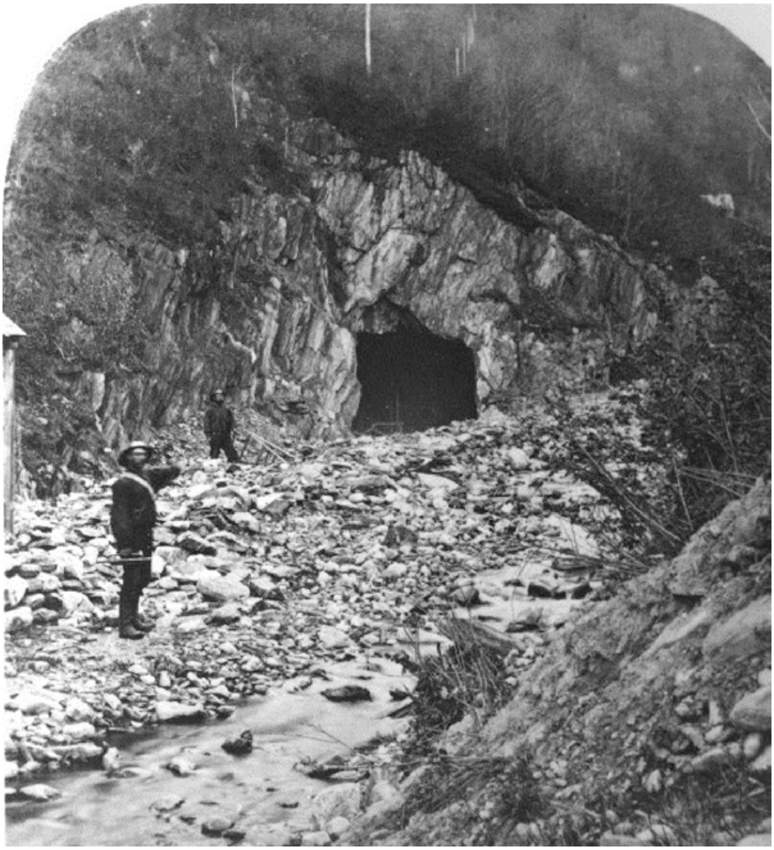

Fig. 3.4 Excavation of the mile-long Hoosac Tunnel in western Massachusetts served as a test bed for new drilling and blasting methods in hard-rock mining. (Mowbray photograph)

liable, and designed an attachment for determining true direction from the sun's azimuth.[1] He then used magnetic compass deviation as a geophysical prospecting technique to detect iron ore near Negaunee, the first of the ore bodies of the Marquette Range (Walker 1979).[2] Established mining methods sufficed here until discovery of soft ore on the Mesabi Range in Minnesota (Lankford et al. 1985).

[1] Using the sun's azimuth for direction required that the surveyor know time accurately, usually with the aid of a chronometer. We don't know if Burt had a chronometer.

[2] Since there was no iron smelting in upper Michigan, the newly mined ore had to be sent to blast furnaces on the lower lakes. A steam-powered vessel had been brought in pieces and erected on Lake Superior in 1845, but sending ore to the lower lakes proved uneconomic since it had to be offloaded, carried, and reloaded at Sault Sainte Marie. Upper Michigan entrepreneurs, who had abundant wood fuel at hand, then built charcoal-fired blast furnaces near the mines. Since they clear-cut the forest and sold off the cleared land to immigrant farmers, their wood supply gave out. It was then cheaper to ship ore south to the fuel rather than mineral coal north to the ore (LaFayette 1990). Once the Soo Canal was completed in 1855, the transition to use of lake ore in Pittsburgh,

Fig. 3.5 Rock drills driven by compressed air replaced hand-jacking for drilling shot holes, here in an underground mine

The Merritt brothers, adventurer entrepreneurs, explored the as yet unmined Mesabi with dip needles and small, exploratory shafts.[3] In 1887, these methods led them to rich, soft hematite under the glacial overburden. They began extracting it with shaft mines to avoid the cost of removing the overburden and shipped out samples of Mesabi soft ore for trial (Evans 1942; Lankford et al. 1985). Blast furnace operators found that the powerful air blast they used for their more refractory ore blew the fine Mesabi ore out of the furnace before it could react with the carbon

Cleveland, and other steelmaking centers near coking coal was underway (Evans 1942, Reynolds 2012). Erroneous carbon 14 dates are a curious consequence of this trade. Some steelmakers used mixtures of charcoal-smelted and coke-smelted pig in their Bessemer converters. In one example excavated iron artifacts claimed to have been made in pre-colonial America on the basis of their radiocarbon dates were actually fragments of barbed wire made of steel converted from mixed pig.

[3] Lewis H. Merritt, from Chautauqua County, New York, joined explorers for mineral resources in northern Minnesota by 1855 and convinced himself that there must be large iron resources west of the Vermilion and other early Lake Superior iron mines, but now buried under a cover of glacial deposits. He passed his enthusiasm on to his five sons. They prospected whenever time and money allowed from 1874 onward, using a dip needle as an indicator of buried ore, thereby ignoring the prevalent belief that nonmagnetic ore would have no magnetic signature. When in 1889 the Minnesota legislature authorized the sale of leases on state land, Leonidas Merritt, the senior brother, got 31 leases that would require royalty payment of 25 cent/ton. In November 1890 the brothers followed up a magnetic anomaly, test pits, and drilling with their Missabe mine. They raised enough capital to get a rail connection in place and commenced mining (Evans 1942). A mining boom on the Mesabi Range followed, and the Merritt's Missabe would eventually be the largest mine on the range.

monoxide reducing gas. Once they understood that the fine ore reacted faster and lowered their blast pressure, they wanted all the soft ore they could get. Ramping up the scale of production on the Mesabi then took transfer of a novel technique from an unlikely source, a tide-power project in Boston.

Boston industries operated on tide power created by a system of dams in basins built in its Back Bay from 1821 until 1855, when new land was needed more than tide power. Filling the no longer needed basins was an enormous earth-moving project made possible by two Massachusetts innovations, William Otis's steam shovel (Stueland 1994) and Goss and Munson's dedicated earth-moving system (Newman and Holton 2008). The shovel excavated glacial sand and gravel from kames, kame terraces, and eskers in Needham and loaded it on purpose-built dumping rail cars that were hauled nine miles to the Back Bay (Fig. 3.6). Trains arrived on a 45-min schedule throughout the day, year in and year out until the filling was completed in 1890. The Mesabi entrepreneurs copied this technique exactly in 1893: steam shovels dug out the soft ore and loaded it in specially designed rail cars. Ore trains took the cars to Duluth, Minnesota, or Superior, Wisconsin, to dump ore directly into the holds of ships at the ore docks. With the mining problem solved, the remaining task was to organize and finance a large, steady flow of ore from the upper lakes to the furnaces along the lower lakes.

Initially getting lake ore to smelters, convincing blast furnace men to use this unfamiliar product, and then organizing a system to provide a reliable supply were undertaken by independent agents, most operating out of Cleveland, Ohio, for the M. A. Hanna Company. They served as conduits for information that miners needed

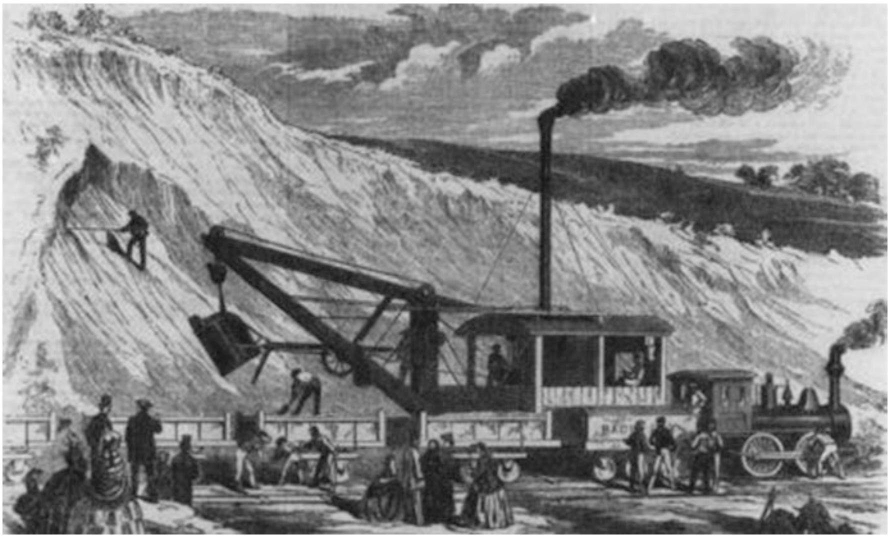

Fig. 3.6 The system of earth moving with steam shovels and trains of dumping cars running on a regular schedule developed for filling the Back Bay in Boston was applied directly to open-pit mining of the soft Mesabi ore (*Ballou's Pictorial*, October 1858)

about markets and demand for steel and iron. They also acted as shipping agents arranging charters for the independently owned lake ore carriers (Reynolds 2012). Integrating ore production from the Mesabi into a reliable supply chain required a new scale of financial resources. Henry Oliver, who began his career selling nuts and bolts, owned a mid-size steelworks, and by 1892 was looking for a new endeavor that he found with Leonidas Merritt. Oliver raised the capital to buy the Merritts' Missabe mine and undertook shipping and selling the ore, while the Merritt brothers went on to open other mines. Unfortunately for them they raised money by borrowing from J. D. Rockefeller who, when they were unable to repay, took over the Merritt mines, ending their pioneering work on the Mesabi (Evans 1942). When Oliver found that he needed more money, he enlisted Henry C. Frick of Carnegie Steel Company. Then financial distress in the mining industry during the 1893 economic depression allowed Oliver and others to sell out to the financiers who were assembling the fully integrated US Steel Company (Reynolds 2012). With centralized management the integrated system from mine to finished steel was in place.

Production of copper in upper Michigan was entering decline just as rapidly expanding use of electric power accelerated demand for copper. Help was on the way when in 1881 miners digging for silver in Butte, Montana, unexpectedly encountered rich chalcocite at the bottom of a 600-ft deep shaft. George Hearst (father of the newspaper mogul) raised capital to finance large-scale underground mining, a smelter at the purpose-built town of Anaconda, and a connecting railway. Within 3 years Montana produced nearly half of the copper used in the USA. Over the next decades, Anaconda advanced deep, hard-rock, underground mining to its fullest development in the USA (Hyde 1998; LeCain 2009).

Meanwhile in Arizona explorers found outcrops of rich copper ore directly after the Gadsden Purchase made the territory part of the USA. Banditry, hostility from local inhabitants, and the absence of a railroad limited the initial mining ventures. Morenci was typical. Mining began there shortly after the 1870 discovery of outcrops of ore containing 15–35% copper. Miners dug it out by driving drifts into hillsides. A smelter was built, a railway connection made, and a mill completed that used gravity separation to process ore containing 6.5% copper into concentrate containing 23% copper. But the Morenci miners soon ran through the initially found, rich oxide ore. The porphyry ore containing 1–4% copper below the worked-out surface enrichment zone was too lean to work with existing technology. Other Arizona mines followed this same path to what would have been a dead end except for Daniel Jackling (Cleland 1952; Hyde 1998).

Daniel C. Jackling (1869–1956) had a job evaluating small silver and gold mines in Utah that took him to the Bingham Canyon in 1898, where he noticed indications of porphyry copper at depth, and confirmed it with test holes. Profitable mining of the abundant but very low-grade ore would have to be by a large open pit that could deliver more ore at lower cost than heretofore attained by mines anywhere. Jackling went to the Mesabi to see the high-throughput, low-cost mining that made direct-shipping iron ore hugely profitable. With financing by the Guggenheim brothers, he transferred the Mesabi technique to Utah. Since the porphyry ore was neither soft nor continuous, Jackling added exploratory drilling to the Mesabi technique.

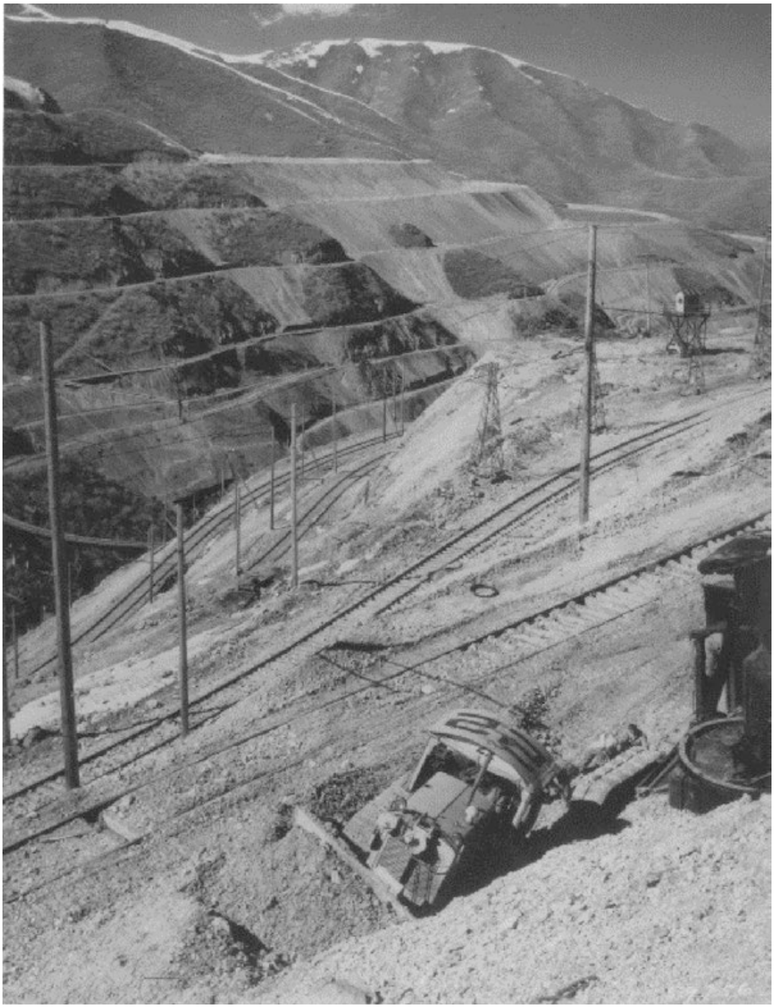

Fig. 3.7 Miners at the Bingham pit in Utah took out ore on rail cars running on tracks laid on benches built on the steep sides of the excavation

Additionally, the hard porphyry ore had to be loosened and pulverized by explosives set in drilled holes before it could be shoveled into rail cars for transport to the mill. With electric power he eliminated the nuisance of hauling coal to steam shovels within the mine. Then with new shovels that could rotate through a full arc, the Bingham mine extracted ore at a speed never before seen. Today the Bingham (Fig. 3.7) is the world's largest man-made excavation.[4]

[4] Jackling's Bingham and other ventures gained him wealth enough to build an elegant Spanish Colonial Revival mansion in Woodside, an affluent community near San Francisco, in 1926. His house gained notoriety when Steve Jobs purchased it as a teardown, only to be stymied by preservationists (LeCain 2009).

Jackson benefited from another innovation developed at the Hoosac Tunnel project. Black powder was relatively slow burning, which was suitable for use in rifles where the long barrel allowed the full propulsive force of the expanding gas to accelerate a bullet. It did not provide the shock needed to properly spread cracks through hard rock. Nitroglycerine, first made in 1846 by Ascanio Sobrero, could do that but was so overly sensitive that at first its only use was as a remedy for heart attacks. George Mowbray, who described himself as an operative chemist, undertook the rock-blasting challenge (Mowbray 1872). Mowbray was in business in Titusville, Pennsylvania, providing nitroglycerine, known there as blasting oil, for shooting oil wells. He saw opportunity in the Hoosac Tunnel project, moved east, and built a nitroglycerine works near the west portal of the tunnel (Fig. 3.8). Mowbray believed that attaining good purity would make the blasting oil safer to handle but discovered the essential safety key by chance. When detonation of black

Fig. 3.8 Mowbray built his blasting-oil works at the western end of the Hoosac tunnel adjacent to its spoil piles, seen here in the background of the picture. (Mowbray photograph)

powder failed to break a dangerous ice jam on the Deerfield River, Mowbray offered some of his product. It was January, and cold, and it was accepted that nitroglycerine was even more unstable when frozen. So he packed shipment in warmed straw covered with fur robes for the sleigh trip to the river. Alas, it arrived frozen. But then it refused to detonate until thawed. Thereafter Mowbray always sent his blasting oil to the tunnel, winter or summer, chilled, and accidents declined to near nil. A remarkable feature of Mowbray's operation at the Hoosac was the extent to which he had to make nearly everything he needed. There was no off-the-shelf procurement. To make nitroglycerine he used a mixture of sodium nitrate and sulfuric acid dribbled into glycerin with the heat of reaction carried off by running water. His homemade apparatus is shown in Fig. 3.9.

Wider adoption of blasting oil was impeded by numerous users ignoring Mowbray's safety precautions, to the regret of their families and friends. This problem was solved when diatomaceous earth was impregnated with blasting oil to make dynamite in 1877, at the California Powder Works. Jackling used it to pulverize the Bingham ore so that it could be shoveled into dump cars.

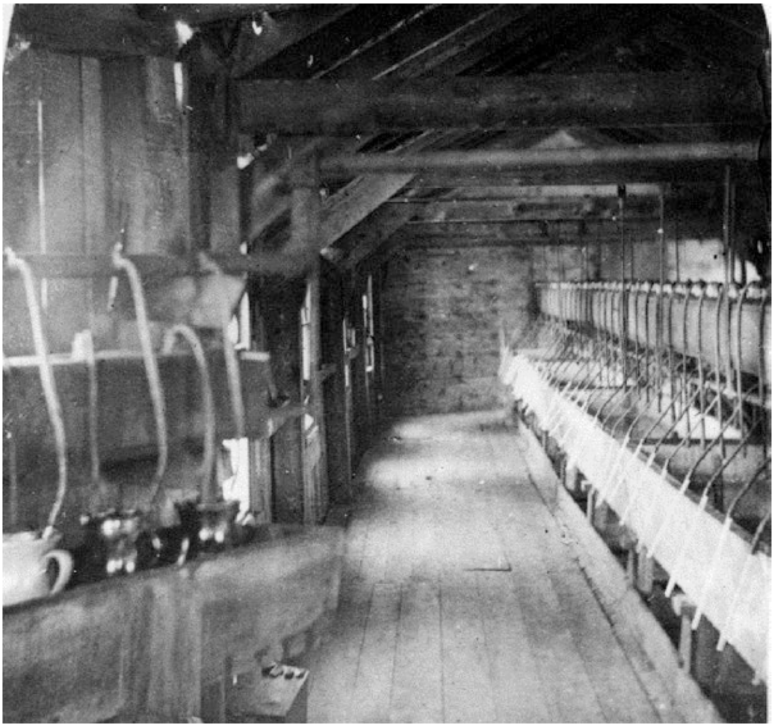

Fig. 3.9 Mowbray built his own equipment for combining nitric acid and glycerin while carrying off the heat of reaction with running water, and had very few accidents. (Mowbray photograph)

Milling

Metals in the lithosphere are in solid solution in silicate minerals. Only rarely have ore-forming processes concentrated them into oxides or sulfides, as in the sample of zinc ore from Franklin, New Jersey (Fig. 3.10; Skinner 1977). The first step in milling is to break the ore into pieces at least as small as the metal-bearing mineral grains. The Blake ore crusher, patented in 1858 by Eli Whitney Blake (Eli the first's nephew), was the first innovation to replace traditional comminution, and is still a mainstay in the mineral industry. Nevertheless, comminution remains energy intensive and, unlike subsequent separation processes, has resisted transformative innovation.[5] After comminution the valuable mineral, the heads, has to be separated from the much larger amount of gangue, the tails. Tailings today are a major environmental problem, discussed below.

At the time Jackling opened the Bingham pit, the available separation techniques relied on gravity separation, James Colquhoun's vanner (an ore-dressing device that separates heavy ore constituents from light ones by placing finely ground ore on an inclined, laterally vibrated, moving belt upon which a countercurrent flow of water washes the lighter constituents off the belt) invented at Morenci, and Redman Wilfley's shaking table invented in Leadville. Neither achieved good recovery from low-grade, porphyry ore. Jackling's venture was saved by the single most important innovation in modern large-scale metal production, the froth flotation process.

Fig. 3.10 Museum-quality specimen of ore from the Franklin Mine in New Jersey. The ore minerals are franklinite (black) and willemite (red) in a matrix of gangue. (Photograph by B. J. Skinner)

[5]Although the fracture toughness of rock can be reduced by stress corrosion, the large friction losses in grinding remain.

Froth flotation attaches sulfides or other metal-bearing minerals to air bubbles that float them, while the quartz and other gangue minerals are not bonded and sink to the bottom of the flotation cell. The method depends on specific mineral surface properties, on modification of those properties by adsorbed reagents, and on control of the surface tension of the flotation medium. A bubble will attach to an ore grain only if there is a decrease in free energy $\Delta G = \gamma_{sg} - (\gamma_{sl} + \gamma_{lg}) < 0$. Here the γs are the surface energies of the solid-gas, liquid-solid, and liquid-gas interfaces. To make the flotation process work, the solid-gas and solid-liquid interfacial energies have to be manipulated with adsorbed reagents to make bubbles in the flotation medium attach only to grains of the valuable mineral while simultaneously keeping the liquid-gas surface energy low enough to assure that ascending bubbles carrying their loads of selected grains do not burst, and thereby drop the attached load of valuable mineral before it could be collected.[6]

It took innovators over 50 years of trial and experimentation to figure out how to use the different interactions of metal-bearing and gangue mineral with fluids in a separation process. They had no guidance from science since the requisite surface chemistry and fluid mechanics did not exist (Rao 2004). The search began in 1860 when William Haynes, in England, observed that sulfides would bond with coal tar in a way that might facilitate their separation from the silicate gangue minerals. How to do it was a task undertaken by diverse artisans and experimenters in the USA, Italy, Great Britain, and Australia. First was Carrie Everson, widowed wife of a medical doctor who had lost all his money through investment in the Denver's Golden Age Mining Company. Everson made systematic experiments with oils and acids and in 1878 achieved preferential bonding and separation. Her 1885 US patent 348,157 explained that when a mixture of cotton seed or other oils and sulfuric acid was mixed into ground-up ore, the addition of water could flush out the quartz gangue. The often-repeated stories that she made her discovery while washing out her husband's oily socks, or in another version, the sample bags in an assay office, originated with nineteenth-century authors who had trouble with the notion that women could, or should, do engineering. Everson was, in fact, a competent experimenter who knew chemistry.

Some experimenters thought it would be best to sink the ore grains once they were attached to a fluid. At a small mine in Llanelltyd, North Wales, in 1894, Frank Elmore and his brother Stanley managed to get separation, but in a nasty oily mess. Then, in 1901 Alcide Froment, an engineer at the Traversella mine in Italy found that by reducing the amount of oil and adding acid that reacted with the carbonate in the ore to produce bubbles, the sulfide grains adhered to the bubbles, which carried the valuable mineral to the surface of the separation cell. Following this discovery, the possibilities of the large financial gain that could accrue to successful inventors brought scores of experimenters and entrepreneurs into the search. In Australia, Charles Potter at the Broken Hill Proprietary mine in 1902 also observed how bubbles formed by reaction of acid with carbonates in their lead-zinc ore levi-

[6] Achieving selective adsorption of additives to get the needed surface energies on the sulfides was complicated by their surface structure sensitivity. This is illustrated by the search on the surface of a galena crystal with a cat's whisker needed to make a crystal radio work.

tated the metal-bearing sulfides. But his patent failed to adequately explain how this worked, and it added to the growing confusion among experimenters about separation mechanisms. Many experimenters now made incremental improvements in the mechanics of the flotation and collection and the reagents that controlled surface properties. They created swarms of patents that in turn spawned the multiplicity of lawsuits and court testimony that makes the subsequent history of flotation nearly impenetrable. The fully developed process, in place by 1915, used collectors, surfactants that adsorb on the desired mineral to make them hydrophobic, frothers to form the necessary bubbles, activators or depressants for selective flotation, pH regulators, and sometimes flocculants, in quantities that range from 0.2 to 35 ppm. The technique was developed largely through empirical testing at industrial mills but also by A. F. Taggart at the Columbia School of Mines and A. M. Gaudin at MIT (Lynch et al. 2007; Rickard and Ralston 1917). By the 1950s, the flotation process achieved recovery as high as 96% of the copper in porphyry ores in the USA, but it then began to decline as flotation improvement did not keep up with declining ore grade (Gordon 2002).

Froth flotation was the single greatest innovation that has made possible expanded metal extraction from the increasingly lower-grade ores available for mining. It also found application in the beneficiation of coal. Without froth flotation the copper needed for the electrical age could not have been supplied.

Metallurgy: Smelting and Refining

Copper smelters could not attain the purity needed for high electrical conductivity by pyrometallurgy because they could not remove the trace amounts of arsenic that ruin conductivity. This problem was solved by an innovation that originated in pure science but reached practice by way of the decorative arts.

As news of Alessandro Volta's current-producing pile spread in 1800, investigators throughout Europe gave over experimenting with static electricity in favor of electric currents. In 1804, W. Hisinger and J. J. Berzelius showed that salt solutions were electrical conductors and could be decomposed by flowing current. Faraday's experiments in 1830 led to his laws of electrolysis. Popular interest in electricity was on the rise. John Wright (1808–1844), a surgeon in Birmingham who experimented with electrochemistry in his spare time, collaborated with his neighbor George Elkington, maker of high-end silver tableware. Elkington (1801–1865) had apprenticed in his uncle's silver plating business in 1815, became its owner, and brought his cousin Henry into the enterprise. At that time silver plate was made by hot rolling thin strips of silver to a copper substrate. The product, called Sheffield plate, had quality control problems (Fig. 3.11). Elkington paid Wright £500 for the privilege of applying for a patent on their joint work. (Wright got another £500 when British patent 8447 was issued in 1840.) He perfected silver electroplating (British patent 8,447, 1840) and with it achieved closer control over plate thickness and uniformity (Fig. 3.12; Gore 1890; Ulke 1903).

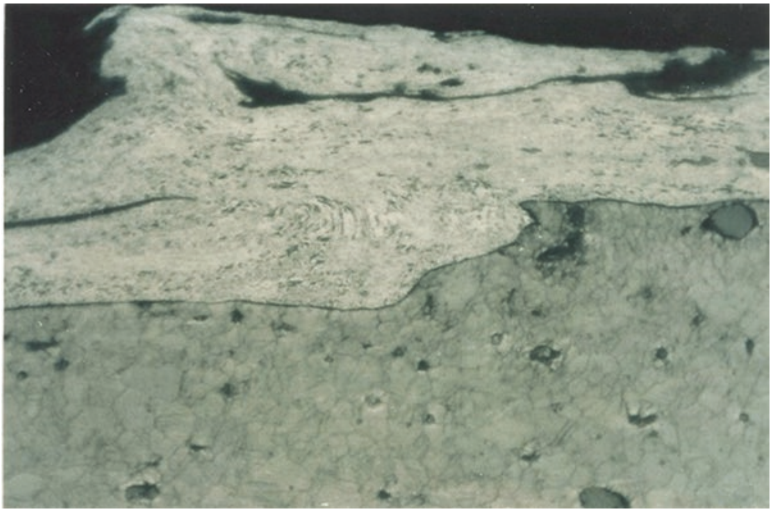

Fig. 3.11 Optical micrograph of Sheffield plate. Specimen is a mid-nineteenth-century table fork excavated at the Glebe House, Woodbury, Connecticut. An alloy of silver with 32% copper was roll-bonded to a base metal substrate. The average thickness of the plate where uniform is 0.06 mm. Length of section in the image is 0.17 mm

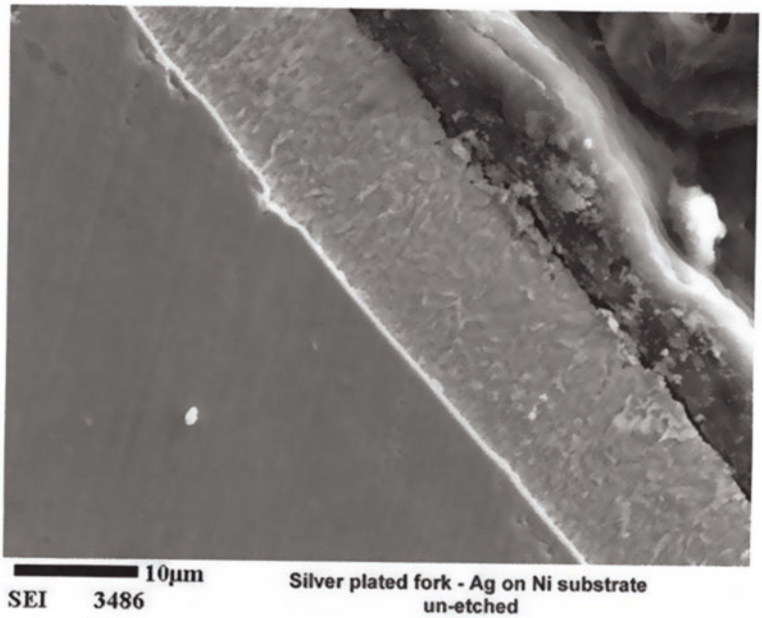

Fig. 3.12 Scanning electron microscope image of electroplated silverware

George's son James made the next step to industrial technology in 1865, when he used an electric current to dissolve impure copper from an anode and, with close control of voltage applied to the cell, deposited copper with the purity needed to be a good conductor on a cathode starting sheet. He patented the process in 1869 and obtained a US patent in 1870. That same year he set up a custom refining works in Pembrey, Wales (Gore 1890). Americans were slow to adopt the process. Only in 1882 did Edward Balbach and F. A. Thum set up the first American commercial refinery, in Newark, New Jersey. By 1895 there were 16 more, most on the east coast but also in Montana, at Anaconda and Great Falls.

From electrolytic refining it was not a big step to electrowinning. Copper leached out of low-grade ore or old mine tailings with dilute acid could be used as the electrolyte in a cell with an inert anode and a copper starting-sheet cathode. Passing current through the cell deposited copper from the leachate on the cathode. Electrowinning could also be applied to production of zinc. A commercial process was patented in France as early as 1883, but the first commercial production was not until 1916, probably because electrowinning zinc is more energy intensive than almost any other electrolytic process in metallurgy (Gore 1890; MacKinnon 1984).

The path from pure chemistry to solvent extraction led through medicine rather than the decorative arts or industry. Gold occurs as small particles in massive amounts of gangue (Fig. 3.13). As mining moved to ever-lower-grade ore, the efficacy of mechanical extraction processes diminished to near nothing. Hydrometallurgy solved this problem. John S. MacArthur, a chemist, collaborating with medical doctors Robert and William Forrest in the basement of the Forrests' Glasgow clinic, found that a very dilute solution of NaCN (0.01–0.1%) dissolves gold and that higher concentrations of cyanide do not speed the process. Adding zinc shaving to the solution precipitated the gold. (See MacArthur's October 1887 British patent 14174 19. Electrowinning the gold is possible but has not proved useful.) Within 2 years cyanidation was in commercial use and was responsible for doubling world gold production in the next decades (Habashi 1987). At that time it was not necessary to know how the process worked. It was 60 years later, in 1947, that P. F. Thompson in Australia showed that the solution of gold is a corrosion process in which cathodic and anodic processes form on the surface of the gold in the presence of oxygen (Thompson 1947). A consequence of the adoption of the cyanide process was a large drop in demand for mercury (as amalgamation was less effective and more expensive than the cyanide process, although still remained in limited use for onboard gold dredges) and the resulting closure of mercury mining in California, which eliminated both a source of pollution and the destruction of vegetation on hillsides by smelter fumes from mercury smelters (Johnston 2013). The cyanide process was an early step away from extraction of metals by mechanical concentration processes (Hovis and Mouat 1996). Solvent extraction was soon applied to other metals, when James Colquhoun in 1893 designed a plant to recover copper being lost in mill tailings (Hyde 1998). The tailings were leached with sulfuric acid and the copper so dissolved was then precipitated on scrap iron. In the modern version of the process, electrowinning substitutes for the precipitation on scrap iron.

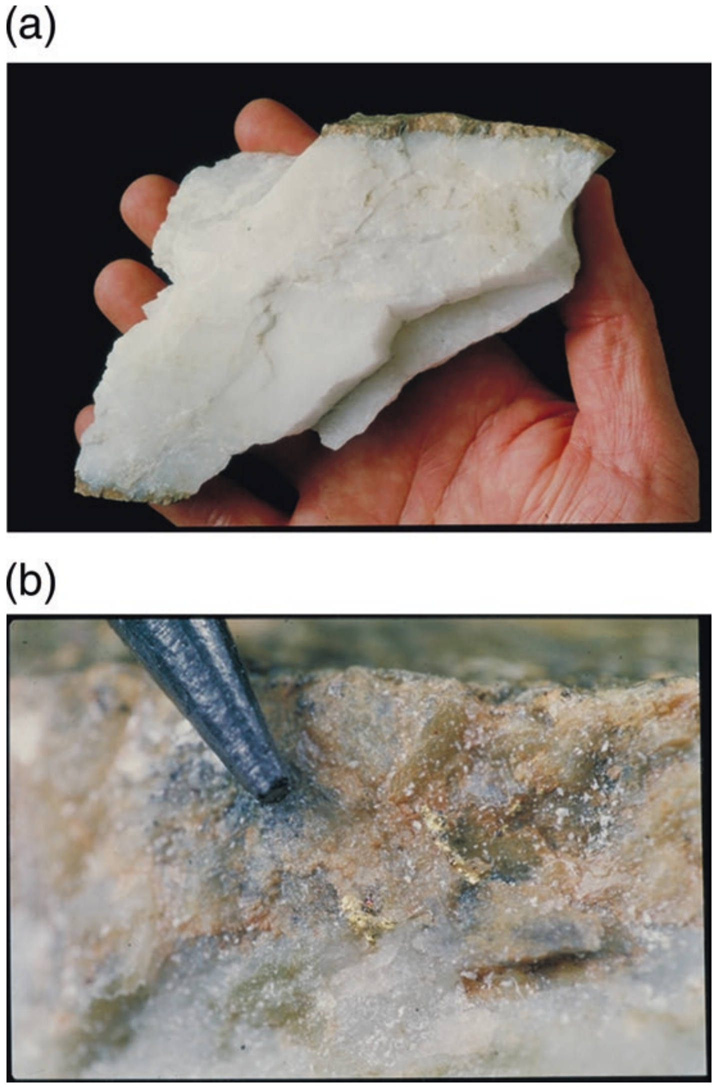

Fig. 3.13 Gold ore from Alaska. (**a**) Hand specimen. (**b**) Enlarged view to reveal the gold, seen just beyond the pencil point. Today this is considered to be rich ore. (Photographs by Christopher Barton)

The path from physics and chemistry to electrolytic aluminum smelting was direct rather than via the arts. Both Hall in Ohio and Héroult in France were intrigued with the then novel metal aluminum through reading semi-popular articles. Both launched their searches for a reduction method with boosts from their chemistry professors, and both were aided by women family members, Hall by his sister and Héroult by his mother. But their temperaments could not have been more different. Hall, the serious-minded son of a minister, lived at home in Oberlin, where the college of that name had a strong tradition of training missionaries. Héroult was the mischievous young man dismissed from the École des Mines at the end of his first year (Bickrert 1986; Craig 1986).

Commercial aluminum also depended on an Austrian chemist and the textile and dyestuff industry. Pierre Berthier discovered bauxite, a mixture of hydrated aluminum oxides with silica and iron impurities, in 1821 near the French village of Les Baux (hence the name). He mistakenly thought it could be an iron ore because of its red color. As a source of aluminum, the iron and silica must be removed since they are more easily reduced than aluminum. Louis Le Chatelier (son of Henri of equilibrium principle fame) developed a method of making alumina from bauxite by a three-step process that involved reaction with sodium carbonate, leaching, and precipitating aluminum hydroxide with carbon dioxide. But the recovery attained was small and its application limited.

Karl J. Bayer (1847–1904) invented the two steps used to get pure alumina by solution of bauxite in hot Na(OH) under pressure followed by precipitation of pure, crystalline Al_2O_3 but in reverse order. Bayer grew up in Silesia, then a part of the Austrian Empire but now in Poland, studied chemistry in Germany, and returned to Austria to a teaching job. Then in 1885 he joined the Tentelev Chemical Works near St. Petersburg in Russia that was using the Le Chatelier process to make the aluminum hydroxide used as a mordant for dyeing cloth. Bayer's problem was to find a way to precipitate crystalline $Al(OH)_3$ instead of gelatinous oxide. In 1888 he found that aluminum hydroxide could be precipitated from a sodium aluminate solution with a seed of freshly prepared aluminum hydroxide. This made a pure, crystalline product.

Bayer made his second discovery in 1892 at the Elabuga dye works in the Tatarstan. He found that the alumina in bauxite could be selectively dissolved by heating it in a solution of Na(OH) under pressure in an autoclave. The impurities in bauxite were rejected, and pure aluminum hydroxide could then be recovered from the sodium aluminate solution. He adapted the pressure technology from techniques then in use in making organic intermediates for dyestuffs. The process of pressure leaching and controlled precipitation is used today much as it was by Bayer, albeit scaled up with sophisticated quality control. Since gallium is now an important component of electronic devices instead of a curiosity, an advantage of the Bayer process today is that the gallium in bauxite is recovered (Habashi 1983).

Mining and Metallurgical Engineers

Mining engineers do not appear among the innovators above. They only established themselves as a profession with the American Institute of Mining Engineers (AIME) in 1873, when their primary task was evaluating the economic potential of mineral discoveries. Promotors used their reports to enlist investment by financiers, who counted on the accuracy of the engineers' work to protect them from fraud arising through stock manipulation or salting of prospects. Henry Janin, graduate of Yale and the Freiberg mining academy in Germany, was building a growing reputation for integrity and reliability in 1872 when he was enlisted to investigate a claim of diamond deposits in Arizona. He was taken by the promotors on a long, circuitous journey while blindfolded. In a brief inspection of the site, he recovered gems later appraised by Tiffany as genuine and valuable. A speculative frenzy followed. By chance, geologist Clarence King spotted the promotors emerging from a railroad train and by tracing their rail travels backward found the putative gem mine site, in Wyoming, not Arizona. He and Janin then found it liberally salted. The fraud created a sensation. Janin salvaged his reputation only by a quick retraction of his preliminary report (Grossman 2014). Nevertheless there were great opportunities for mining engineers to make profitable investments. Several universities benefited handsomely, as by Henry Krumb's bequest to the Columbia School of Mines, and John Hays Hammond's and Alan Batemen's generosity to Yale.

The AIME created a code of ethics to help establish mining engineering as a proper profession. Further steps toward professionalism came with the founding of the Columbia School of Mines and a mining engineering program at MIT in 1876. By 1892 16 US schools were graduating mining engineers. Of 871 mining engineers graduated between 1867 and 1892, Columbia produced 402 and MIT 126 (Newell 1986).

Edward W. Davis represents the more mature work of mining engineers that also required participation in politics. At the Minnesota School of Mines, Davis recognized the eventual exhaustion of the easily mined Minnesota iron ores and turned in 1911 to research on beneficiation, picking up where Edison had left off with his failed magnetic separation venture by adding beneficiation by flotation (Manuel 2013). Daniel Jackling returned to Minnesota for a collaboration with Davis. Their Mesabi Iron Company produced ore pellets that contained 60% iron. This development was premature. The pellets had a higher silica content than blast furnace operators were used to, and actual exhaustion of the rich Mesabi ore was still a distant prospect. Davis turned to advocacy to assure the future of iron mining in Minnesota. His work illustrates the range of tasks that an engineer might need to undertake including mining, industrial, economic, and policy-making endeavors. A problem with taconite, the low-grade, hard iron ore, was that once ore was discovered, it was taxed regardless of grade until mined, a strong disincentive to exploration. Davis worked to get the tax code changed. When by the 1950s exhaustion of the high-grade, soft Mesabi ore was at hand rather than a distant prospect, taconite reserves had been located. This enabled the Reserve Mining Company to commence beneficiation of taconite to produce iron pellets that made excellent blast furnace feed, thereby enabling Minnesota to remain a producer of iron ore and avoid the regional economic hardship that typically faced regions with worked-out mines.

A Problem Revealed

The miners and entrepreneurs who facilitated the ever-increasing production of metals were following the ancient principle or the moral duty enunciated by Vannoccio Biringuccio (1540):

> For by mining such ore it might happen one day, even in a single hour, without any danger to themselves, but only to their hirelings, and without so many inconveniences, annoying outrages, or other things, they would become very wealthy…For this reason I say and conclude that the gifts of such copious blessings conceded by heaven should not be left to our descendants in future centuries…For this we should denounce them and severely reprove them in the same terms that farmers would deserve if, when the fruits of the earth ripen, instead of gathering them, we should leave them to rot and waste in the fields.

For centuries mines were opened, worked to exhaustion, and their place taken by new ones. Foster Hewitt in 1929 showed how mines typically passed through stages of discovery, expanding, peak, and declining production to abandonment (Hewitt 1929). At the Great Copper Mountain (Stora Kopparberg) in Falun, Sweden, mining began before AD 1080, peaked in 1650, and declined to an end in 1980. The huge pit formed by collapse of its underground workings in the eighteenth century is now a tourist attraction (Rydberg 1979).

Only in the Industrial Revolution did the possibility that mineral exhaustion might actually happen attract attention. Jevons in 1866 warned how depletion of Britain's mineable coal would terminate its economic growth (Jevons 1866).[7] Six years later J. S. Mill broached the then radical idea that prosperity could be attained in a steady state rather than a growing economy (Mill 1872). Thereafter little more was heard of either issue outside of scholarly circles.[8]

Dependence on tungsten imported from China needed for high-speed steel cutting tools caused some inconvenience during WWI, but was resolved by substitution of molybdenum, which could be mined in the USA. Commodity supply problems received little further attention until WWII stopped imports of rubber and tin from East Asia. Concern about strategic metals led the federal government to assemble a group of leading scientists—the Paley Commission—in 1952 to assess the natural resources available within the USA (President's 1952). Two years later Harrison Brown, a distinguished geochemist, addressed mineral exhaustion in his book *The Challenge of Man's Future* (Brown 1954). Both the Commission and Brown reached an alarmist conclusion: many metal resources would be exhausted within a few decades.

These predictions were wrong. The Commission determined the nation's copper resource available for future use to be 25 Mt. Twenty five years later that much copper had been produced in the USA, and a new estimate of the resource available for

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[7] Jevons saw coal consumption dependent on population and intensity of use. He noted that since 1800 the population of Britain had doubled but that coal consumption had increased eightfold. He expected that with this rate of growth, the coal supply would be exhausted because of the difficulty of mining at greater depths. His text was written to attract popular attention, which it did. His later work in economics was on a sounder basis (Keynes 1936).

[8] Mill's argument is primarily about population rather than constraints arising from finite resources. He asserted that previous economists believed sustained growth was needed to avert universal poverty arising from population growth. Mill saw stable population as essential to avoiding widespread poverty, advocated a more uniform distribution of wealth, and limits on inherited wealth. He felt that population was already large enough that people need opportunities for solitude, the presence of wildlife, and some land left uncultivated. Only in 1973 did Herman Daly revive the steady-state, sustainable economic model.

Table 3.1 Metal depletion times (years)

	1992	2000	2007
Copper	66	50	60
Zinc	45	54	46
Lead	41	44	48
Nickel	120	122	90

future use then stood at 35 Mt. More than enough new resource had been found to cover both the metal extracted in the intervening 25 years and create a bigger reserve for future use. The Commission and Brown went astray by misunderstanding the difference between reserves and resources. They arrived at depletion times by dividing the reserves of a metal by the current rate of extraction, both assumed to be constant. They are not (Table 3.1). Reserves are metal in the ground that can be mined profitably at current prices. That means that a price increase can expand reserves just as discovery of new resources would. (Resource is a physical quantity, the amount of ore in the accessible earth.)

The prevailing view of mineral resources through the 1960s is on display in *Scarcity and Growth*, where economists Barnett and Morse showed that despite a large increase in demand, mineral prices remained constant or fell since 1870 because of decreased extraction costs and the enlargement of reserves (Barnett and Morse 1964). They questioned any need for natural resource conservation. Nevertheless doubts were stirring, stimulated by publication of Garrett Hardin's 1968 essay on the tragedy of the commons (Hardin 1968). That and the subsequent well-publicized collapse of the Grand Banks cod fishery (Pilkey and Pilkey-Jarvis 2007) prepared the way for the enthusiastic reception of *The Limits of Growth* in 1972, where Meadows and colleagues warned that unrestrained flow of natural resources into wastes via consumption of food and material goods was a path to social and economic collapse (Meadows et al. 1972). Archaeological evidence of vanished societies showed that collapse can happen. That the doomsday predictions were made with computer models added verisimilitude. Thus *Limits* had an immediate appeal in the early 1970s that led to the sale of 9 million copies printed in 29 languages.

While the predictions of imminent collapse soon proved unfounded, the real significance of *Limits* was raising awareness and introducing computer modeling as a tool for exploration of the consequences of unbounded economic growth.[9] Some economists were now ready to explore resource use more critically. In *Scarcity and Growth Reconsidered* (Smith 1979), essays by Georgescu-Roegen (1979) and Herman Daly (1979) challenged the established economic doctrine that, for example, assumed when a product reached end of life, the materials in it simply vanished. The launch of spaceship earth was underway (Rome 2016), as evidenced by numerous new journals (Table 3.2).

[9]The predicted collapse was rescheduled for a later date in the *Limits to Growth, the 30-Year Update* (Meadows et al. 2004).

Table 3.2 Initial dates of mineral resource journals through 2000

1871	Transactions AIME
1905	Economic Geology
1949	Journal of Metals
1967	Environmental Science & Technology
1972	Science of the Total Environment
1974	Resources Policy
1977	Conservation and Recycling
1981	Resource and Conservation
1988	Resources, Conservation and Recycling (formed by merger)
1989	Ecological Economics
1993	Journal of Cleaner Production
1997	Journal of Industrial Ecology
1999	Journal of Materials Cycles and Waste Management

Geologists expanded the scope of their research in ways that would not have been thought of a few years earlier. Techniques of underwater observation allowed geologists to watch previously inferred processes of ore formation in action. The hydrothermal mid-Atlantic vent field "TAG" has been making an ore deposit for the past 50–100 ky and now has upward of 4×10^6 t of ore containing 1–5% copper. In a new economic insight, deWit showed that the thermal energy derived from the Earth's internal heat used to form this deposit gives its copper an endowed energy content with a current dollar value 10–20 times the value of copper that we extract from existing ore. This is embodied energy we harvest and do not have to pay for when we extract copper from ore rather than ordinary rock, an insight that gave us a new way of valuing ore deposits (deWit 2005).

Interdisciplinary collaborations blossomed. One originated in geologist Brian Skinner's suggestion that if the ore of a metal were exhausted, the metal content of ordinary crustal rock could be a backstop resource (Skinner 1977). An econometric model with inputs from economics, geology, and engineering tested this possibility for copper. This linear programming exercise begins with the grade-tonnage relationship for copper ores and the cost of mining and smelting as ore grade diminishes to the backstop level. It assigns discounted costs to each component of copper use, the substitution of alternative materials, and recycling the stock in use. It then computes the path that yields the lowest cost of providing copper services. The results showed that use of the backstop resource would not be a significant drag on the industrial economy when ordinary ore resources were exhausted (Gordon et al. 2006). However, an econometric model does not deal with factors for which monetary values are not assigned, such as displacement of people from new mine sites or destruction of habitats.

New Concepts and Disciplines

That resource depletion and waste accumulation are actually serious problems led to questioning long-accepted assumptions. The ZPG (zero population growth) movement attracted attention. Thomas Princen (2005) and Giles Slade (2006) revisited the consequences of consumer culture. M. King Hubbert showed how fuel resources could be depleted and unresolved waste disposal could limit nuclear power (Inman 2016). Emergence of health problems arising from severe air pollution visible as smog in large cities was a stimulus to action. The enormity of the issues raised by the catastrophists called for broadened scope in materials and environmental research. Metals had to be seen as cycling from extraction through use to discard and reuse. This was not a new idea. In 1762 Jared Eliot explained it in his *Essay on Iron*:

> Water which is raised from the Seas, Lakes, Ponds and Rivers, and carried in Clouds over the Land, is let fall in Dews and rains, and returns by Rills, Brooks, and Rivers, to the Places prepared to receive it; and as Water continues its circular Motion and Rounds, so I conceive it is with Iron; by the Water the Particles of Iron are carried to a proper Bed or Receptacle, thence it is taken and wrought for the Use of Man, and is worn out in his Service; or contracts to Rust and is consumed when it is worn away, as by the Earth in plowing, or from Horses Shoes in traveling, or from Iron Shod Wheels in carting, or by grinding with a grind Stone: The Iron by these means returns to earth again: When it is corrupted by Rust; this is much as when a Tree rots, or a man dies, they Each return to Mother earth again; these same particles of Iron then worn away, are not annihilated or lost, but being joined with Sulphur, and those other materials that constitute Iron Ore, it proceeds and takes the same Journey round till it comes to the Smith's Forge again: Under all these changes and Revolutions there is no Addition; the same Quantity as there was at first, there remains the same still, and no more.[10]

Now it had to be made quantitative. A beginning was made by Kneese, Ayres, and d'Arge in their *Economics and the Environment: A Materials Balance Approach*. They initiated research that, expanded by many others, matured as life cycle analysis (LCA). Components of metal production and use, formerly studied individually, are incorporated into cycles: metal flows from sources through use providing services onward to reuse or to sinks. In the past recycling was seen as just a way of reducing a metal shortage or, less likely, as a way to reduce dependence on landfills; now it and the accumulation of metals in waste repositories are made full components of metal cycles.

Understanding metal cycles and their consequences depended on knowing the size and location of metal stocks in use and in wastes as well as flows between these stocks. Material flow analysis (MFA), undertaken initially in the 1970s and greatly expanded in the 1990s, accomplished this (Fischer-Kowalski and Hüttler 1998). By 2004, when Brunner and Rechberger published their handbook of MFA, the methods

[10] Jared Eliot, minister and doctor in colonial Connecticut, invested in iron mines and with his son, Aaron, was building a cementation steelworks. He had noticed that magnetite was separated from glacial sands by running water, collected it, and made iron from it. The essay reports on this successful experiment (Gordon and Raber 2007).

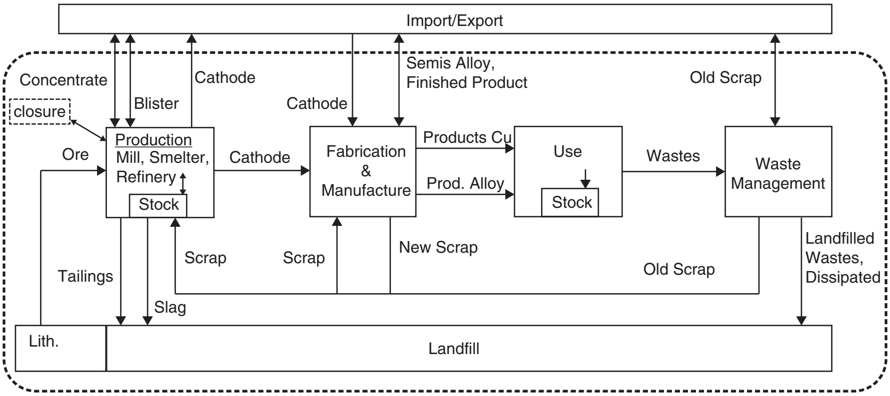

Fig. 3.14 A basic MFA diagram, illustrated for copper in North America. Stocks of metal are represented by the boxes and the flows by arrows

and techniques had fully matured (Brunner and Rechberger 2004). In the MFA diagram in Fig. 3.14, boxes show metal stocks and arrows the flows between them. Production incorporates all the processes of mining, milling, smelting, and refining to make primary metal. Newly made metal passes through fabrication and manufacturing into use in products, with some recycling of scrap within manufacturing. The size of the stock of metal in use providing services depends on the balance between inflow of metal contained in new products and outflow of end-of-life products passed to waste management. Here the metal content of the discards divides between recycling and waste repositories, such as landfills. The requirement of a mass balance imposes discipline on the analysis, something lacking in earlier studies of individual flows or stocks. When stocks and flows are determined for a region, nation, or continent, allowance for cross boundary flows originating in trade networks is needed, and can create difficulties in applying mass balance, except for a whole-world cycle. A MFA study is typically done for a specified time interval without establishing initial stocks. When these are wanted, the bottom-up method described below is used.

The flow into stocks in use to replace end-of-life products and addition of new products drives metal production and manufacture. Product lifetimes determine the flow into waste management. Consumerism has forced product lifetimes downward since the 1930s (Princen 2005; Slade 2006). It is now accelerated by the increasingly rapid turnover of electronic devices.

The new perspectives on metal supply and use from MFA is illustrated by a study of copper in North America through the twentieth century. Through these 100 years, 160 Mt of copper was extracted from ores and entered use and formed two new stocks, 70 Mt providing services while 85 Mt were confined to landfills from end-of-life products, wastes from primary metal production in tailings, and slags (Spatari et al. 2005). The results reveal the large losses to waste repositories relative to the metal that continues to provide services. Data on copper production show that 14% of the copper in the ore mined in the USA in the twentieth century was lost in tailings and slag during milling and smelting. A large increase in the price of copper might trigger recovery of some of this lost metal, if new innovations were to provide the means. Recovery of the metal now residing in tailings and slags would supply 10 years of US copper demand. However, 13,000 Mt of copper tailings would still be with us, creating an unresolved environmental hazard (Gordon 2002).

In the study by Spatari et al., changes in stocks were determined from inflows and outflows. This is the "top-down" method. The location and use of stocks can be found by the "bottom-up" method. Applied to New Haven, Connecticut, for example, it shows that a per capita stock of 9200 kg/c (kilograms per capita) of iron and 144 kg/c of copper in buildings, infrastructure, transportation systems, and equipment are used to sustain the population of the city. If this intensity of copper use were extended to less-developed countries, it would require consumption of all presently identified copper reserves (Drakonakis et al. 2007).

These and other studies by MFA show increased pressure on copper resources is expected from economic growth and increased population in coming decades. Providing the needed new metal will depend on the rate of discovery of new sources relative to the rate of extraction. These rates are compared in Fig. 3.15, which shows the cumulative extraction of copper and the cumulative copper resources discovered worldwide since the onset of industrialization began early in the eighteenth century. At first, large copper sources were found as ever-larger parts of the Earth's surface were explored; the amounts extracted were relatively small. Over successive decades copper extraction converged with copper discovery, suggesting that discovery may not keep up with demand in the future. Offsetting this is the expectation that as basic infrastructure is built and technology finds more efficient ways to use metal, the

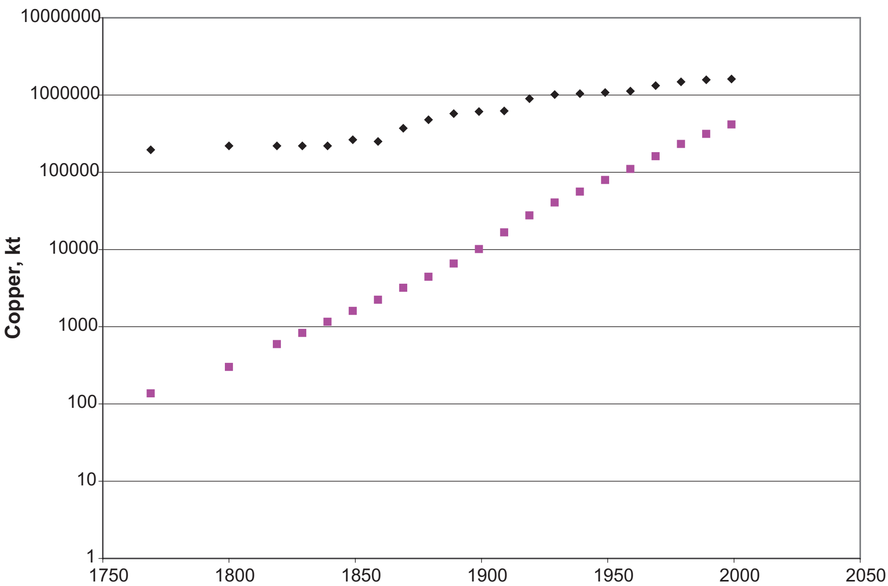

Fig. 3.15 Cumulative amounts of copper discovered (black) and copper extracted (red) worldwide

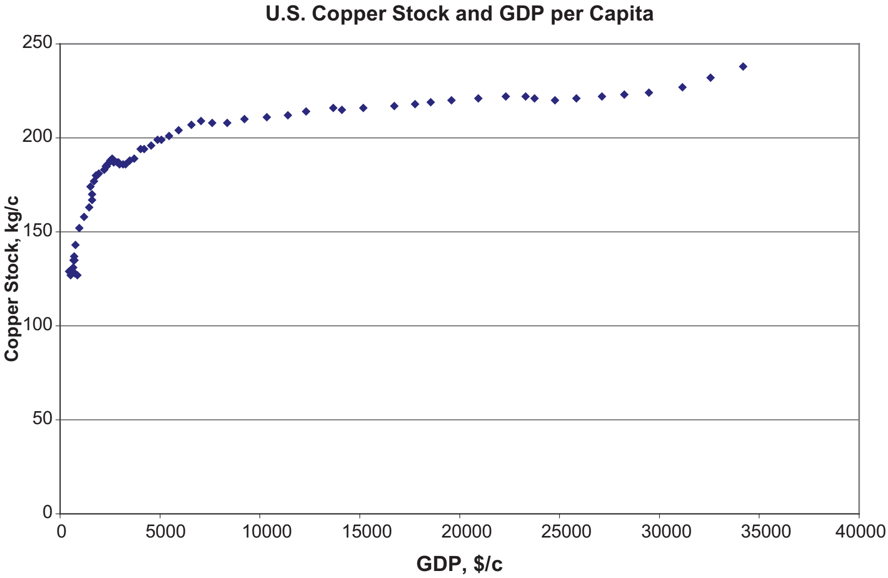

Fig. 3.16 Copper stock in use providing services per capita vs. GDP per capita in the USA

intensity of metal use relative to GDP will decline. The data in Fig. 3.16 show that this has not yet happened for copper (Gordon et al. 2006).

The MFA technique can be used with alternative economic development scenarios to make projections of future metal demand. Elshkaki et al. (2016) found that copper demand will increase by over 200% by 2050. Meeting this demand would require extracting copper from all of the copper reserves, the reserve base, and up to 80% of the ultimately recoverable resource, confirming the indication in Fig. 3.15. The resulting decrease in ore grade will lead to a rapid increase in the energy used in mining and milling and a close approach to the need to use the backstop resource (Elshkaki et al. 2016).

Copper and iron as still-essential metals in the future are now joined by the rare metals, essential components of electronic devices and renewable energy sources (Abraham 2015; Veronese 2015). Graedel and colleagues use MFA to investigate issues arising with their production and add a series of new concerns under the heading of criticality, an inventory of all the factors that can complicate their supply (Graedel et al. 2015). Nuss and Eckelman (2014) in an expanded MFA analysis assembled cradle-to-grave environmental burdens for 63 metals that include energy used in extraction, warming potential from greenhouse gas emissions during winning from ore, health issues, and environmental damage. On a per kilogram basis, the greatest impact arises from the platinum group metals and gold since these are recovered from very low-grade ores.[11]

[11] Predictions of metal scarcity arising from exhaustion of metal resources were made by individuals and by government committees in the first part of the twentieth century. They were joined by non-government, not-for-profit organizations. Now in the twenty-first century, a worldwide

The problems of using lower-grade resources with accompanying increased energy demand and creation of greater quantities of ever-more toxic wastes suggest that the concerns of the catastrophists, while distant, may be in view. In the meantime urgent, unresolved issues with the environmental and social costs of metal use await innovation that so far has not been forthcoming.

Environment

"'Death … more desirable than life?' The human skeleton record and toxicological implications of ancient copper mining in Wadi Faynan." So begins a paper on heavy metals ingested by miners at the notorious Roman copper mines of Phaeno in the early-Christian era (Grattan et al. 2002). Mining's long-established reputation as dangerous and polluting is abundantly documented by archaeological and physical evidence (see Kaufman, Chap. 1, this volume) including the "copper man," the ancient miner found with his tools preserved by the copper-rich fluids in the mine shaft in which he was trapped in Chile (Bird 1979).[12] The Phaeno mine remains a health hazard today (Grattan et al. 2003), as do other former mine sites worldwide. They are numerous because whenever mines became unprofitable to work through exhaustion or were too deep for existing techniques, they and their mess were simply abandoned in favor of new sources elsewhere.

Mining districts ancient to modern are littered with mine shafts and waste dumps, plagued by release of toxic drainage, and marked by the remains of formerly prosperous communities that testify to social as well as environmental demise. A horrific event just 50 years ago triggered us to get serious about remediation. At 0910 on 21 October 1966, a pile of mine waste on the slope of the hill above Aberfan, Wales, that had been creeping downward for about an hour liquefied and at 30 km/h crashed into the town's elementary school to kill 144 children.[13]

The new, transformative techniques of mass mining adopted in the late nineteenth century, with their accompanying milling and smelting industries, created equally massive environmental problems which mine operators did their best to ignore until forced to confront them by lawsuits and legislation. Finding solutions to messes left by mining is today a greater challenge to technology than creating new methods of mining. The failure of innovation to solve these problems is responsible for growing resistance to new mine ventures and a greater threat to the supply of metals than actual resource scarcity.

organization, the International Resource Panel, has taken up the task (Ali et al. 2017). Economic drag due to exhaustion of metal-bearing mineral sources has yet to emerge. Identification of more potential resources continues apace (Kessler and Wilkinson 2008).

[12] A "petrified miner" was also recovered in 1719 in Sweden's Falun copper mine and identified as Fat Matts, who disappeared in the mine in 1677 (Rydberg 1979).

[13] The flow resulted from liquefaction due to pore pressure rise in water-saturated slate fines. See also K. T. Ericson on the 1972 Buffalo Creek flood that caused 125 deaths and destroyed 507 homes in West Virginia (Erickson 1976).

Successful Innovations

There have been some successes, as in control of atmospheric emissions from smelting. There was a powerful incentive to reduce emissions since otherwise lawsuits would have closed large, profitable non-ferrous metal mines and mills in the late nineteenth and early twentieth centuries.

The processing of sulfide ores, the most abundant sources of copper, lead, and zinc, was the primary culprit in the release of noxious emissions. Industrial copper smelting first concentrated in Swansea, Wales, where it blanketed the city with copper smoke, a mixture of sulfur dioxide and metal-containing particulates. Lawsuits, legislation, and a search for remedies by distinguished scientists including Davy and Faraday achieved little and left building taller stacks to better disperse the smoke as the only alternative. Only closure of the smelters as the industry moved elsewhere finally relieved Swansea of the smoke nuisance (Newell 1997).

The USA avoided copper smoke until the late nineteenth century since it imported copper from Swansea, or mined native copper in upper Michigan. The problem arrived in 1890, when smelters in Tennessee's Ducktown district, having exhausted their oxide ores, began heap roasting sulfides. Sulfur-rich smoke drifting into neighboring Georgia provoked farmers' lawsuits that the US Supreme Court decided in the farmers' favor in 1907. The Ducktown smelters tried three fixes, a high stack, a sulfuric acid plant, and blast furnace smelting of unroasted ore. A market for the acid nearby at a fertilizer works coupled with low arsenic content in the ore made these fixes technically and economically possible and allowed smelting to continue for several decades (Morin 2013; Quinn 1993).[14]

Copper production at Butte, Montana, was on an altogether larger scale with correspondingly larger problems, particularly at the Washoe smelter in Anaconda. Its emissions shriveled farmers' crops and killed ranchers' cattle. Lawsuits followed. As at Swansea and Ducktown, the copper company built a tall stack and then another that, though now disused, remains the world's largest free-standing masonry structure. It diluted the smoke that reached the ground while spreading the pollution further. Next an innovation based on laboratory science made continued copper production possible. Frederick Cottrell, a student of Wilhelm Ostwald and chemistry instructor at UC Berkeley, following up on earlier experiments by Sir Oliver Lodge in 1907 precipitated smoke particles with an electric field. His Western Pacific Precipitation Company was helped by financial backing from DuPont, which had emission problems of its own at its California lead smelter. It had the precipitation process ready to scale up when AS&R called for help at the Garfield smelter that processed ore from Jackling's Bingham mine. The Cottrell precipitator saved Garfield from closure and was thereafter widely adopted. Cottrell used income from his invention to found the non-profit Research Corporation that continues to advance science through grant programs (LeCain 2009).

[14] Local hotel proprietors made the most of a bad situation by advertising the health benefits to be had from the sulfur-rich local air (Quinn 1993).

Fig. 3.17 In the Belgian retort furnace, zinc ore is reduced to metal vapor that is collected in condensers. The residual carbon monoxide reducing gas burns at the condenser mouths

Emissions from zinc smelting caused the notorious Donora, Pennsylvania, killer smog in 1948. An atmospheric inversion in October of that year trapped emissions from neighboring zinc works that over several days killed 20 and sickened half the town's people. The zinc was made by the traditional Belgian retort technique (Fig. 3.17). Electrowinning was a partial solution to this smelter smoke problem. It had been used commercially to make zinc since 1916 (Fig. 3.18), but its widespread use was delayed because it is energy intensive and mineral fuel was cheaper in places that did not have access to inexpensive hydropower. However, sulfide ore still had to be roasted, as the flue and stack seen in Fig. 3.18 show. The last horizontal zinc works in the USA closed in 1976 due in part to emission and health issues. Thereafter all zinc production was by electrowinning (Dutrizac 1983).

Innovations Needed

Milling ever-lower-grade ores made huge quantities of tailings that are now wet slurries carrying unrecovered sulfides and frothing agents. The stuff is dangerous and unstable. What to do with it is a huge, unresolved problem urgently in need of innovative solutions.

Tailings generate no revenue, so the incentive is to get them out of sight and out of mind in the cheapest way possible. At first a popular solution was to dump them

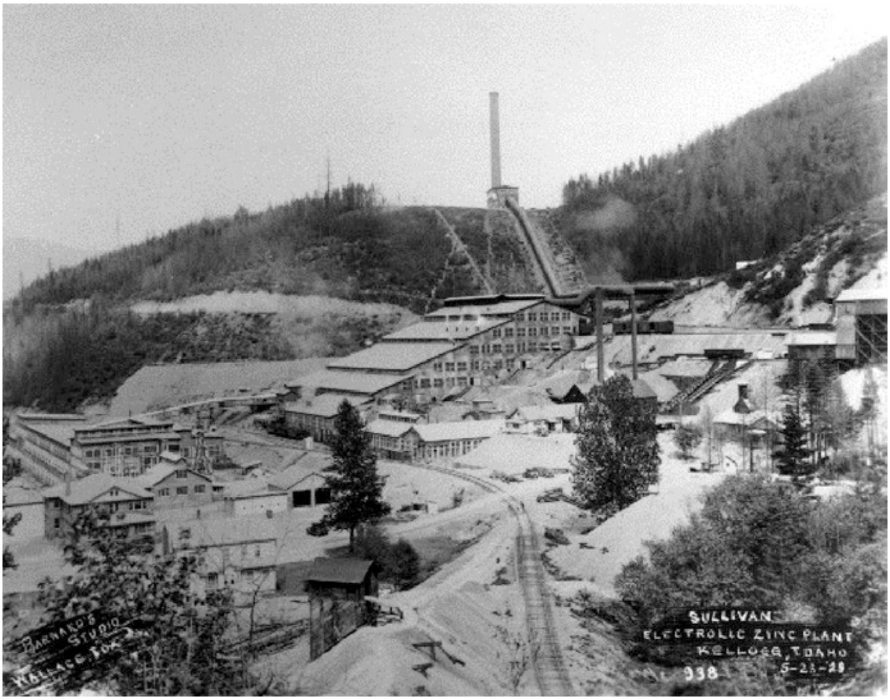

Fig. 3.18 At this electrolytic zinc works in Idaho the fumes from the preliminary roasting of the ore are released by the stack seen on the hilltop

into a lake if one were handy (Fig. 3.19). Miners on the Keweenaw Peninsula, Michigan, used Torch Lake. Tailings had advanced the lake's shoreline by 600 m before mining ended. Years later, with the mines and mills long gone, fishers found that Torch Lake fish had lesions, presumably caused by the flotation agents retained in the tailings. Excavating and reburying the waste was a public responsibility that cost over $12 million (Gordon and Malone 1994). It was a minor prelude to things to come.

The concern about exhaustion of direct-shipping ores from the Mesabi that had been premature in 1911 was no longer at the end of WWII. ARMCO and Republic Steel revived the 1911 Davis-Jackling plan for beneficiating taconite with the Reserve mill they built in 1951. It could make 6×10^6 t/year of enriched pellets, ideal blast furnace feed. Reserve used a 1948 state regulatory approval to place its tailings in Lake Superior. Years later a new pollution control agency in Minnesota found the fibrous mineral cummingtonite in water samples taken near Duluth, and assumed that the source was the Reserve tailings, and that cummingtonite was an asbestos-form mineral, which it is not. At this time it was easy to find medical doctors with slight knowledge of mineralogy willing to be expert witnesses. With their aid a lawsuit stopped tailings disposal in the lake although no health hazard was proved (Bartlett 1980). Placing tailings from taconite in Lake Superior was a poor idea for aesthetic reasons, but it didn't lead to disasters. The story is different for the

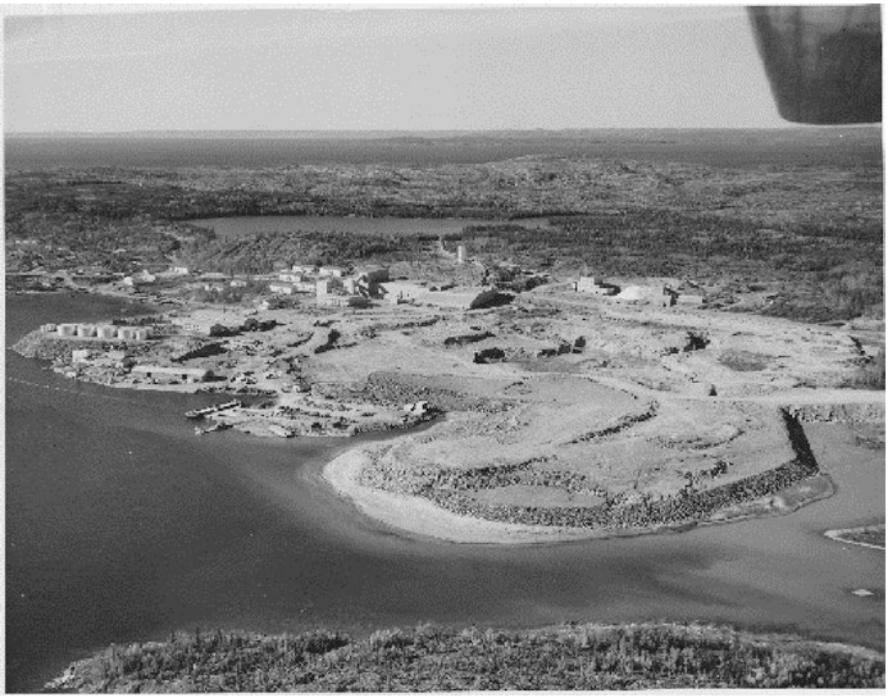

Fig. 3.19 Mine waste and tailings disposal at the Gunnar uranium mine in Saskatchewan

non-ferrous metals. The residue from the leaching step of the Bayer process is red mud, a mixture of iron oxide with rutile, ilmenite, quartz, and hydrated aluminum silicates. Each ton of alumina is typically accompanied by a ton of red mud. Its disposal is a problem. At Ajka, Hungary, failure of a retaining dam in 2010 released 10^6 m^3 of red mud stored in ponds at an aluminum production facility. The neighboring town was flooded with it; there were 10 deaths and over 150 persons injured, many with sever chemical burns since the mud was highly basic, with pH = 13. The toxic mud reached the Danube River (Enserink 2010).

Mineral separation by flotation, the key innovation that made production of copper, lead, and zinc from low-grade high-volume ore possible, also produced a wet, semi-fluid slurry of finely ground rock with residual sulfides that can flow like a liquid. There is a lot of it, even from 0.5% copper ore, which is high grade today. Backfilling a mine is not an option because the volume of the waste is greater than the volume of the ore excavated, and its fluid content would have to be contained. Even where land is nearly valueless, the tailings cannot be just spread around; they have to be confined in ponds by dams, and some of these are the world's largest (Table 3.3). Tailings dams are made of the lowest-cost material at hand, usually tailings themselves or other mine wastes, and thus are vulnerable to all the problems of earth-fill dams, notorious for failure when penetrated by seeping water.[15] Since tailings

[15] The infamous Johnstown Flood among others originated in the failure of an earth-fill dam.

Table 3.3 The world's largest dams by volume

Tailings:	Syncrude tailings, Canada	540,000 m^3
	New Cornelia tailings, USA	209,500
River:	Fort Peck	96,050
	Aswan High	44,300

dams generate no revenue, they receive the smallest possible care. Failure can release a flood of slurry bearing toxic chemicals.

Southern Spain has been host to mining of sulfide minerals for copper, zinc, and mercury since before and during Phoenician and Roman times (see Kaufman, Chap. 1, this volume), in the region that gave one of the world's largest mining enterprises its name, Rio Tinto. The largest pollution event in Spanish history occurred when the tailings dam at the Aznalcóllar mine collapsed in April 1998. The dam, constructed of mine waste, had been started in 1978, when production of zinc, lead, and copper concentrates began, and was built higher year by year to contain a tailings pond 2 km long and 1 km wide. It had reached a height of 25 m and was being raised at the rate of 1 m per year when seepage so weakened it that on 25 April 1998 wind-driven waves initiated rapid disintegration that released 4×10^6 m^3 of acidic water and 2×10^6 m^3 of slurry into Doñana National Park, the largest reserve for bird species in Europe (Grimalt et al. 1999). Then, just 2 years later, a tailings dam retaining waste from gold production failed in Maramureş County, NW Romania. It released waste containing 100 tons of cyanide into tributaries of the Tasa River, itself a major tributary of the Danube. Cyanide pollution spread through Hungary, Yugoslavia, and Bulgaria.

The long catalog of catastrophic tailings dam failures continued year by year to 5 November 2015, when a dam retaining waste from iron mining in Brazil collapsed and flooded the town Bento Rodrigues with at least 17 killed. The list will continue.

Dry tailings do not pose the same catastrophic flood problem, but create equally intractable hazards. The Picher mining field in northeastern Oklahoma from 1900 into the 1970s produced lead and zinc from sulfide minerals found in limestone. Here 1000 hectares are underlain by mines that when active pumped out 5×10^4 m^3 of water a day. Milling created solid waste, known as chat; 12×10^6 t of it are stacked in piles (Fig. 3.20). Residents of Picher and nearby towns accepted the piles of white chat as part of their landscape; children played on them, and adults rode dirt bikes over them (Fig. 3.21). Only years later did a high school teacher notice the growing proportion of children in Picher with learning disabilities. Investigation revealed that the chat piles are a source of lead-bearing dust in particles less than 0.4 mm in size. Returning the chat to mines is impractical because it would displace the contaminated mine water, even if there were enough space for it. Absent a technological fix, the people of Picher had no alternative but to leave; their relatively modern community is now a ghost town like those in the Old West but without the romantic ambience that attracts tourists. The Pitcher district is the nation's largest Superfund site (Stewart and Fields 2016).

Finding a use for tailings has been tried; as aggregate in concrete, they made houses in Mineville, NY, the center of the Adirondack iron mining district. This was possible since the mineral mined here is magnetite rather than a sulfide. Sulfide tail-

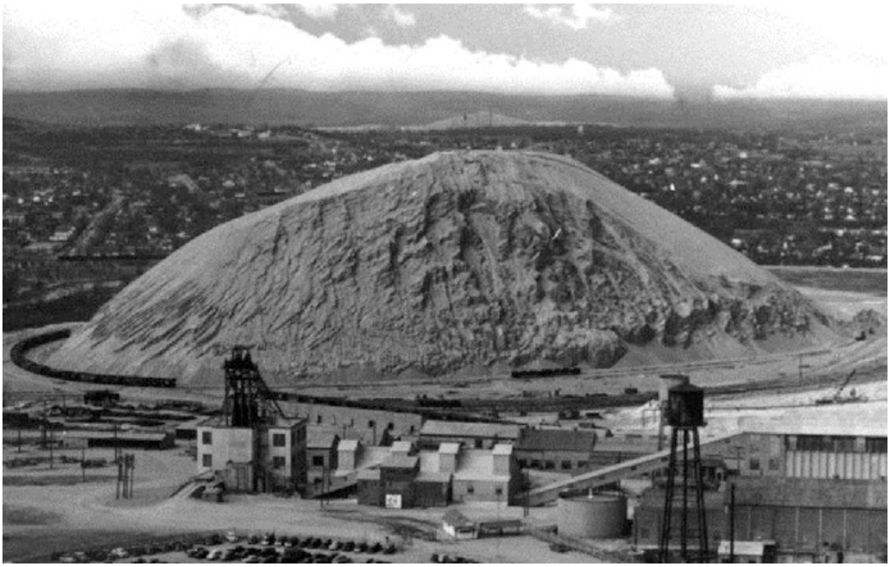

Fig. 3.20 Massive piles of chat are a prominent landscape feature of the US Tri-State lead district landscape

Fig. 3.21 The dark line at the base of this chat pile is the trail left by a rider on a dirt bike headed for the top of the pile. Until people realized that chat had a dangerous lead content, they saw the piles as a recreational resource. (Photograph by Patrick Malone)

ings aggregate went into concrete for the Wallace, Idaho, county courthouse (Quivik 2013). But the quantities so used are minute. The innovation needed to deal with tailings has not been forthcoming.

Festering Problems

On 7 December 2016, 25,000 snow geese perished when they landed in what appeared to them to be a promising overnight resting place on their annual migration south. It was the Berkeley Pit in Butte, Montana.

Digging the pit began in 1955, when Anaconda switched from underground to surface mining. By 1980 it was 1.5 miles wide and 1800 ft deep. The pit was dewatered through abandoned underground mine working to a sump at the 3600 ft level established by Anaconda in 1901. As pumping continued a cone of depression formed in the surrounding groundwater. When the Atlantic Richfield Company, in what must be one of the worst business decisions ever made, bought out Anaconda in 1977, with the idea of diversifying from oil to copper, it acquired the Berkeley pit. Working it was a money loser. ARCO stopped mining in 1982 and shut off the dewatering pumps (LeCain 2009; Pilkey and Pilkey-Jarvis 2007). The pit is filling with water that in its epilimnion has a pH of 2.5 and abundant heavy metal content. It will reach the level of the regional ground water in about 2020. A pumping and water treatment plant may delay this, but no saving innovation is yet in sight.

Numerous additions could be made to the already long list of environmental and social consequences of metal production awaiting innovative solutions. Begin with waste from electronic devices (Abraham 2015; Stahel 2016; Veronese 2015; Zang and Guan 2016). Add the radioactive waste from power reactors now stored in holding ponds but mandated by law to be placed in impenetrable, permanent, secure isolation where no one would think of drilling for water during the next 10,000 years. (Ten thousand years? What a fantasy.)

Conclusion

In 1880 the USA was on the threshold of the expansion that would make it the world's largest industrial economy. The innovations that supplied the metals to make this happen were made by diverse individuals including artisans, ingenious mechanics, entrepreneurial adventurers, and some scientists and engineers. Free, open, and easy communication facilitated by low-cost paper and printing contributed. Financial rewards were a powerful incentive, and the externalities could be left for the future. That future is now here.

Seventy years ago professors at mining schools talked of mining without mines. Next there was the idea of transferring mining to the sea floor. These things did not happen. Instead ore is still extracted, milled, and smelted in mining districts, now usually in less-developed countries, and the metal transported to use elsewhere, where the wastes and social disruption of its production are someone else's problem. This is unsustainable. Here is today's need for transformative innovation.

Acknowledgments I thank Brian Skinner for many insights on mineral resources, Barbara Reck for an update on her most recent research in life cycle analysis, Dennis Meadows for the diagrams that illustrate his current thinking on the *Limits of Growth*, and Margaret Anex for a critical reading of the manuscript. Patrick Malone shared the story and pictures of his explorations of the Tri-State lead-zinc district.

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Chapter 4
Structural Materials: Metallurgy of Bridges

Kanji Ono

Introduction

This chapter considers metallurgical developments that are related to bridge design and construction. Bridges are naturally of large scale, and iron and steels have been used as the principal components since antiquity. Common knowledge for engineers and historians includes the famous Iron Bridge in England, completed in 1779 (see Fig. 4.1, reproduced from Nicholson 1829). It seems certain that this is the oldest iron arch bridge (Kostof 1985). Some argue that the completion of this bridge was the critical event for the Industrial Revolution, while others contend that Watt's steam engine in 1784 was the main impetus. Perhaps both contributed in tandem, multiplying their influence synergistically. From the metallurgical side, Abraham Darby's use of coke for pig iron production in 1709 represents an important step forward in allowing the construction of the Iron Bridge and for the rapid rise of the British steel industry (Cossons and Trinder 1979). The British Isles did not have an adequate supply of charcoal even in the eighteenth century, for example, 70 % of its iron was imported from Russia and Sweden in 1770 (Ågren 1998). Yet, British iron production started to accelerate around 1780 (blue arrow), as shown in Fig. 4.2 (data from Birch 1967 and Swank 1888).

The history of iron bridges, however, takes us first to ancient times, long before the Industrial Revolution. A natural first place to examine the ancient metallurgy that enabled iron bridge building is in Asia, with a long tradition of constructing bridges. More recently, by the 1990s, wires of ultrahigh-strength steels have been developed, making it possible to build long-span bridges. Advanced microstructural design at the nanoscale and modern fabrication methods are the keys to discover how we progressed from the Brooklyn Bridge to the Akashi Kaikyo Bridge.

K. Ono (✉)
Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, CA, USA
e-mail: ono@ucla.edu

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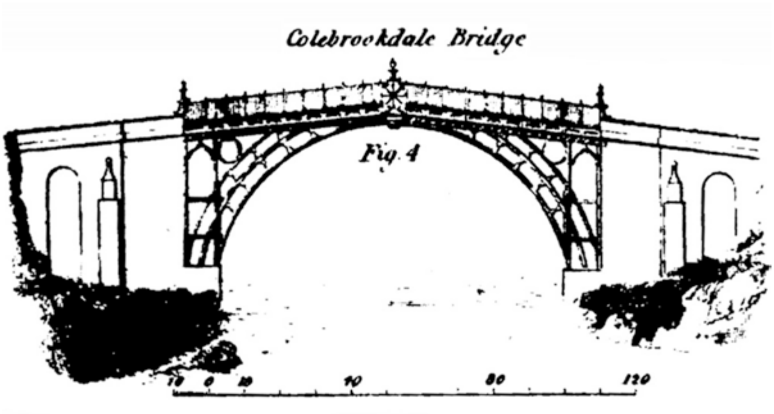


Fig. 4.1 Drawing of the Iron Bridge at Coalbrookdale (Nicholson 1829, 983). The scale shown is in feet

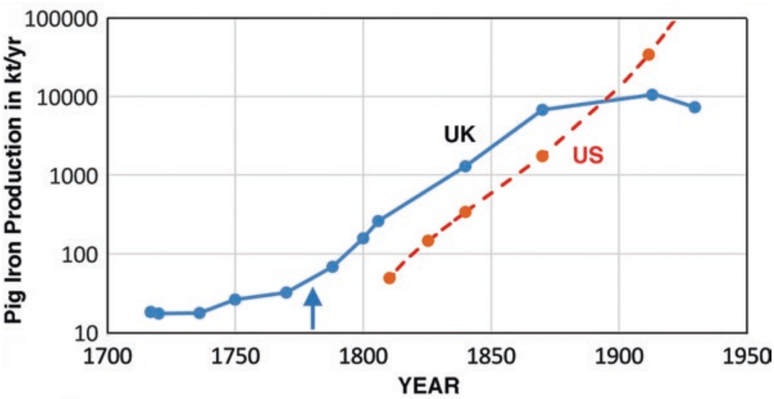


Fig. 4.2 Annual pig iron production in the UK and USA in the eighteenth and nineteenth centuries (in kt = 1000 t). (Data from Birch (1967) and Swank (1888)). The arrow indicates the start of a rapid rise in 1780. Also note that 1913 was the peak year for UK production

Bridges are essential in our modern life, but their utility has served human society since prehistoric times. Among numerous books on bridges, Plowden (1974) covers the historical development of bridges well with fabulous photographs (albeit with an emphasis on the USA). A more recent book by Fernández (2003) provides a global coverage with technical details. Since Fernández himself has designed and built many bridges, his book offers unique perspectives.

Several basic terms need to be introduced before proceeding. These are on the type of bridges: beam, truss, arch, suspension, and cable-stayed (White 2015; Wright 2015a). A beam bridge is a long bar or beam (it tends to be referred to as a girder) supported at each end. Figure 4.3a shows a curved girder bridge of I-beams and a deck (road surface). This type is the simplest, but can only be used for a short span

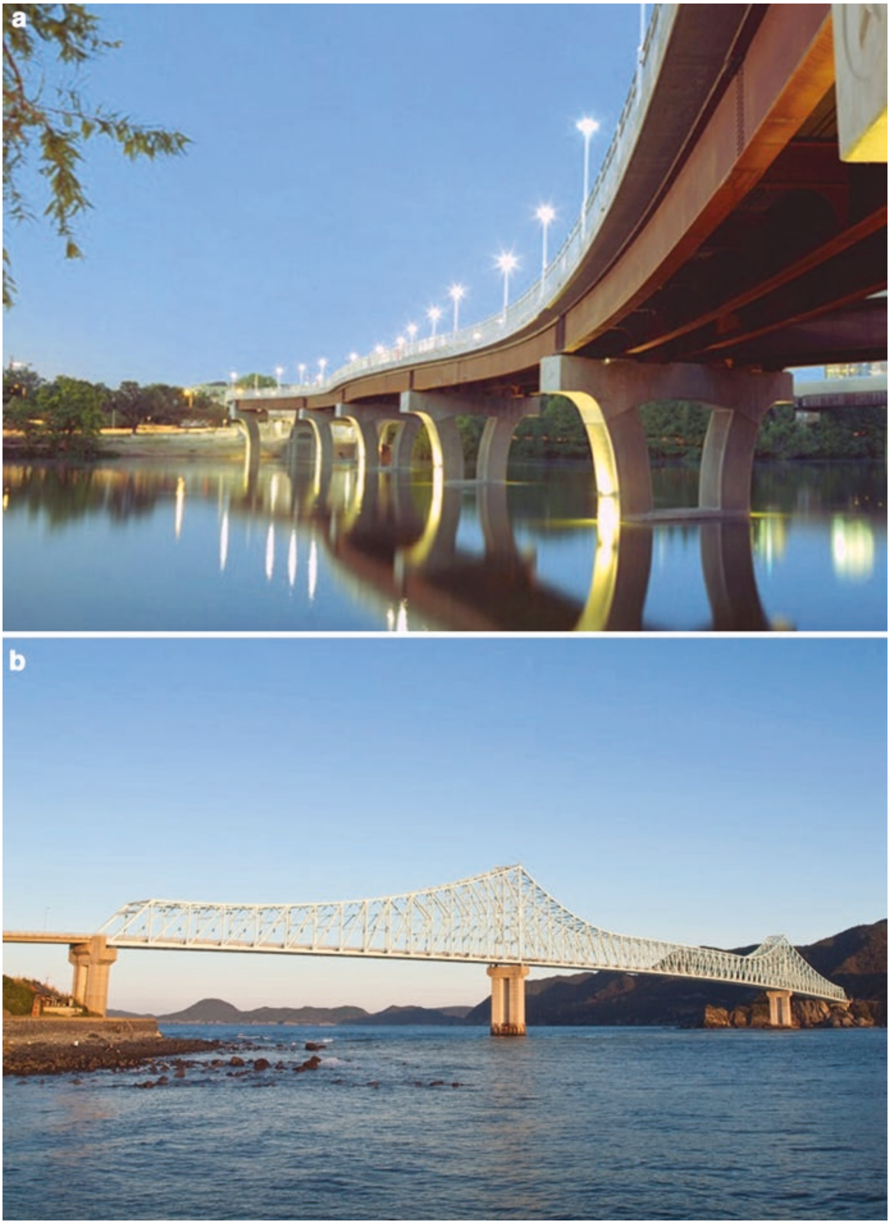


Fig. 4.3 Five main types of bridge. (**a**) Beam or girder bridge. (**b**) Truss bridge. Ikitsuki Ohashi, Nagasaki, Japan, longest-span continuous truss bridge. 400 m main span. (**c**) Arch bridge. New River Gorge Bridge, Fayetteville, West Virginia. With a 518 m arch length, it is the third longest today. (**d**) Suspension bridge. Golden Gate Bridge, San Francisco, CA. 1280 m main span. (©2017 Kwan M, used with permission). (**e**) Cable-stayed bridge. Normandy Bridge, Le Havre, France. 856 m main span. (Photographs (**a–c**) and (**e**) are from FHWA-HIF-16-002. (White 2015; Wright 2015a))

Fig. 4.3 (continued)

Fig. 4.3 (continued)

(or with multiple piers) as the bottom part of the girder is stressed in tension. This tensile stress usually limits the span length and maximum bridge load since most materials are weaker in tension (only fiber composites are stronger in tension). A truss bridge (Fig. 4.3b) distributes the tensile stress to other structural elements, allowing more efficient uses of materials. This type was most popular in early modern bridges but is still used. An arch bridge (Fig. 4.3c) redistributes the tensile stress on a beam into compressive stresses on the arch under the beam (here, a truss is also incorporated). Stone arch bridges had been built since Greek and Roman times, and their refined descendants built with concrete are still used today. Suspension bridges like the Golden Gate Bridge are typically spectacular as they span large distances over wide straits and deep valleys. When support structures cannot be built to shorten the span, this is the only choice (Fig. 4.3d). Cable-stayed (suspension) bridges are becoming popular as this form allows broader latitude to designers (Fig. 4.3e). The availability of high-strength steel cables is indispensable for the last two types.

In this chapter, we begin with ancient iron bridges and associated ironmaking technology. Next, cast iron and its bridge uses are discussed, followed by wrought iron and steel bridges including their metallurgical attributes. Particular attention is given to the development of wire ropes and cables, which have been critical in the advancement of bridge structures. When technical terms are used, explanations are provided when necessary. Bridge-specific terms are explained in Wright (2015b), including lists of steels being used today. Many things historical had to be discovered anew as these are usually not dealt with in the field of materials engineering, but the design principles underlying ancient engineering feats may find relevance in modern applications. Basic information on bridges discussed is tabulated in Appendix A in the order they appear in the text.

Iron Bridges in China and India

In order to frame the metallurgical history of bridge construction, it is necessary to detail the known technological developments and milestones in various times and places. In this section, historical and travelers' accounts are synthesized to present known data about the earliest recognized iron bridges.

Plowden (1974) mentioned (without any references) that an iron bridge was built in Ancient China (AD 56 in the Eastern Han era, the Jihong Bridge) and also noted that another was possibly built around 200 BC. The latter was unspecified but was presumably the bridge located on Pan Ho 樊河 (now called Xijiang 西江, north of Hanzhong 漢中). In *Shiji* by Sima Qian (the first-century BC historian), it was recorded that a bridge was built by Fan Kuai 樊噲 in 206 BC between May and August. However, there is no mention of the use of iron. Some authors (Huang and Luo 2013; Mao 1987) hinted that *Shiji* pointed to the beginning of iron bridge construction, but no archaeological or textual evidence has been discovered. Actually, this bridge building was a part of diversionary tactics in the taking of Guanzhong, still 4 years before the biggest battle (the Battle of Gaixia) for the succession of the Qin dynasty between Liu Bang of Han and Xiang Yu of Chu. All resources presumably had to be devoted to the war effort, and it may have been too great a challenge to build a new type of iron bridge when the fate of the dynasty was still uncertain, considering the ubiquity and sturdiness of the incumbent technology using wooden planks. Actually, Liu's forces had to rebuild a road along Bao River (褒河) leading to Guanzhong, not just a bridge. This road, known as Baoxie Road (褒斜道), consisted of many bridges and about 200 km of plank road (栈道: roadway is supported by horizontal beams (栈阁), which were inserted into holes bored on the cliff side).

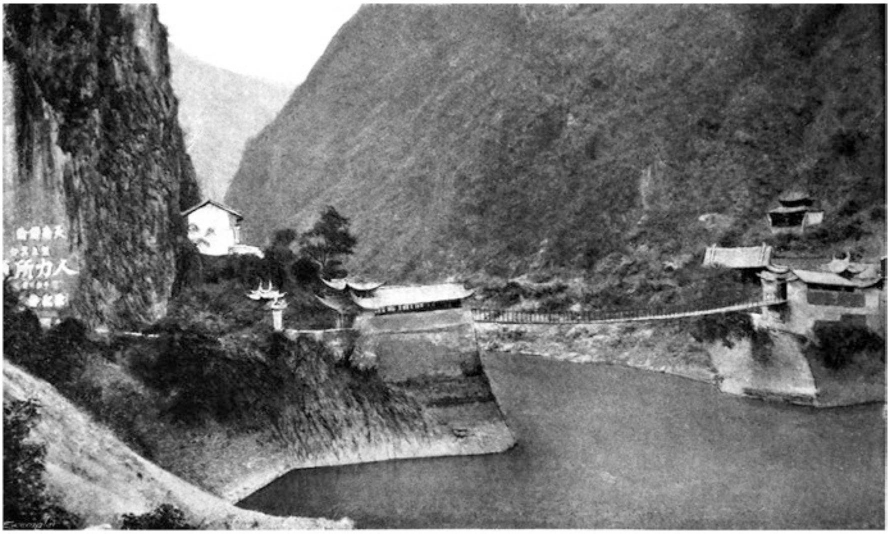
In 1979, the remains of three substantial bridges were discovered along this ancient route. The road was originally built in 314 BC and Liu's forces burnt the plank road down earlier in 206 BC (Tang 2000a). In the eighteenth century, Du Halde (1741) traveled to the Pan Ho Bridge and described it in his book, *The General History of China*. By this time of observation, the bridge was made of iron. He noted that the river "is a torrent, which is not wide, but very deep." On the bridge, he saw two stone piers that were 2 m wide, on each of which four chains hung by the support of large rings. The chains were tied together, forming a mesh. Wooden planks were fastened over the chain mesh forming a walkway. He was told of additional bridges in existence in the neighboring regions with the same design, the most famous of which was over the Jinsha River 金沙江 at Lijiang in Yunnan. According to Tang (2000a, 499) the Pan Ho Bridge was rebuilt as an iron bridge in the 1530s and multiple times since due to flood damage. Although it is not mentioned if the old bridge was an iron bridge, historical texts imply it had been used for many centuries, so it is likely that the bridge was upgraded to iron before the Ming era rebuilding.

Plowden's mention of the AD 56 iron bridge has no reference and is questionable (Plowden 1974). Since Kircher (1667) put the year as AD 65, Plowden perhaps transposed the digits to 56 (before Emperor Ming started his reign in AD 58). The bridge in this case was known as the Lanjin Bridge in Yong Ping Prefecture, Yunnan.

A well-known bridge historian, Pan Hong-Xuan, investigated the site in 1980 and concluded that this is actually identical to the Jihong Bridge 霁虹桥 at Lanjin (Pan 1981). This crossing of the Lancang River (upstream of Mekong) was first achieved by ferry in AD 69, and eventually a suspension bridge was built and rebuilt using bamboo ropes (AD 220–280 and AD 860–870). In 1295, a wooden bridge was built and named as Jihong. It was rebuilt by a monk, Le Ran 了然, as an iron bridge in 1475. During the Qing period, several repairs were made, first during 1644–1661 (Tang 2000a, 501). This bridge was destroyed in 1986 by a huge flash flood due to a landslide at the site. This bridge had a span of 57.3 m, the total length being 113.4 m, and with 16 foundation chains and 2 handrail chains, but only 14 + 1 chains remained in May 1980 (Pan 1981, 1985). The chains consisted of 176 elliptical rings of 2.5–2.8 cm in diameter, 30–40 cm in length, and 8–12 cm width. The bridge width was 3.7 m at its base. These details agree reasonably well with Kircher's description of a length of 300 palms (~20 cm for 1 palm), and 20 chains (Kircher 1667). However, serious doubts must be raised on his account. Kircher's source of information, Father Grueber, was sent to China in 1656. He returned from Beijing to Rome, initially with Father d'Orville. Their itinerary of 1661, given in Grueber and Braumann (1985) and Gerner (2007), indicates that the pair journeyed through Lining, Xining, Lake Qinghai (Kokonor), the Transhimalaya Mountains, the Reting Monastery, and Lhasa. After a month at Lhasa, they crossed to Nepal by the 5100 m-high Kuti Pass route in November, continuing to India and Persia, then to Rome. They did not go to Yunnan. Gerner believes they must have crossed two iron cable bridges in Tibet. In particular, Rinchen Chakzam is close to the Reting Monastery (Gerner 2007, 77). Thus, Kircher's bridge information is either concerning a different bridge or from some unknown sources. Besides, Grueber had to walk from Beijing to the Levant, the last part by himself, so most of the information must be from memory. At this time, it is most prudent not to depend on Kircher's account.

An American traveler, Geil (1904), crossed the Jihong Bridge in 1903 on his way from Shanghai to Burma. His photographs are shown in Fig. 4.4. At the time, it had all the planks intact (all were gone in 1980) and also had iron side-guards with handrail chains. This Jihong Bridge was an important crossing point of the Lancang River since the Eastern Han era, as this was on the southern route of the Silk Road. Ethnic Han people emigrated to this area starting during the reign of Emperor Wu (140–86 BC) and attempted to trade with Indians, but this was initially blocked by the Burmese. At the time, the Xiongnu people were strong and the northern trade route was unreliable (Nagasawa 1993). By the mid-first century AD, a magistrate was stationed at Yongjing (today's Baoshan) as the Han territory covered a large area west of the Nu River (which is to the west of the Lancang). Thus, although it is now lost, the Jihong was the oldest iron bridge with credible written records. Note that these two (Jihong and Lancang) were sometimes treated as separate bridges, e.g., Needham (1971), but a recent compilation of ancient bridges no longer lists the Lancang Bridge (Tang 2000a).

It is interesting that the southern Silk Road was the likely trade route by which the *paktong* (or *baiting*) alloy (of copper-nickel-zinc with a silvery look) was traded with the Hellenistic kingdom at Taxila (present-day Pakistan) in the second century BC (Widemann 2009). Earlier, *paktong* was traded to people of the Punjab region,



(a)

(b)

Fig. 4.4 (**a**) Jihong Bridge in 1903. (**b**) Inside the Jihong Bridge. Handrail chains were extant, though mostly hidden. (Both photographs are from Geil, *A Yankee on the Yangtze* (1904)) who presented 2.5 t of this alloy to Alexander the Great in the fourth century BC. The mine was at Huili, Sichuan, near Kunming, so it is most natural to cross the Lancang and Nu Rivers and reach Burma and India even from the early times (Widemann 2009). In the Eastern Han era, the Yongchang Road was maintained for trading with India. Some ancient gates and ruins are still standing along the old Silk Road route (Yongchang Road Remains 2004).

Another bridge noted by Du Halde is the iron bridge over the Jinsha River. This was probably built by Tibetan people during the Zui era of AD 581–600, who controlled this region at that time. This is known as Shenchuan Iron Bridge 神川铁桥 (or 塔城铁桥). Another source attributed this to bridge builders of the Naxi people 纳西族 in AD 680 in the early Tang era (Shenchuan Iron Bridge 2017). A Tibetan king also built Iron Bridge Castle on the north shore for its protection, which remains as a place name of Tachenzheng on Lapuhe, a tributary of Jinsha in Yunnan. This bridge was destroyed in AD 793 when the Nanzhou 南诏 people of Naxi rebelled against the Tibetan ruler, desiring to return their lands to the Tang Empire. It was referred to as “Iron Bridge” in New Tang History (新唐書, AD 1050) and Nanzhou History (南诏野史, AD 1260), and this was used as a place name even over a century after its destruction. A Qing history book of the seventeenth century (读史方舆纪要) mentioned the existence of the bridge ruin with holes in the rocks and iron chain remnants. It was further stated that one could see ancient iron rings at the bottom of the river when water became clear in the winter months. All traces have disappeared presently, however. At this time, this bridge was the first recorded iron bridge within the Central Plain of China.

A recent article examined the military applications of iron cable bridges during the period between the Han and Tang era, or the third to seventh centuries AD (Huang and Luo 2013). This was one of the most unstable periods in China characterized by widespread warfare, especially in the Central Plain with territorial disputes over the Three Gorges area. Throughout the Han era and following its collapse, it seems that control of iron bridges was considered strategically important, enough so that there are records of battles being fought over them. Contemporary records are rare in such periods of strife. Most references for this study are unavailable in the USA and cannot be evaluated at this time. Later chronicles that mention fighting over iron cable bridges are the primary sources, albeit removed in time. For example, a battle in AD 549 for an iron bridge at the entrance to the West Ridge (Xiling Gap) is based on the Qing history book (读史方舆纪要) cited above, but this account was written a millennium after the events. The authors’ acceptance of Mao’s “diagnosis” that iron cable bridges were built in the second century BC in Southwestern China and Tibet (Mao 1987) does not suffice as historical evidence. Thus, the idea of a third-century cable bridge across the Yangtze is unrealistic and needs factual verification. Actually, a chapter by Mao in another book never mentioned Han era iron bridges (Mao 1986).

Another useful route to pursue information on early iron bridges is the examination of travelers’ accounts. The most famous traveler in the Tang era is Xuanzang 玄奘, who traveled to India seeking Buddhist sutras and wrote *Great Tang Records on the Western Regions* (Xuanzang AD 646). While crossing the Hindu Kush mountains following the Indus River, he needed to hang on to iron chains, but no explicit mention of iron bridges was recorded despite reference to this book by Needham and others (Needham 1971). However, a ten-volume biography (*Biography of the Tripitaka Master of Dacien Temple* 大慈恩寺三蔵法師伝; Hui AD 688) did include a passage mentioning an iron bridge in Vol. 2: 又東南登危險度鐵橋行千餘里至迦濕彌羅國: "Then I climbed to the Southeast, where the road was full of danger, high and steep, crossing an iron bridge, and after more than 500 km I reached Kashmir." The first part of his travels was after leaving Taxila to the north, then going to Urasa (today's Hazara, Pakistan). The next segment going from Urasa to Kashmir was where the iron bridge appeared. Thus, Xuan apparently did travel on an iron bridge. Over a century earlier in AD 518, Zong Yun (accompanied by Hui Sheng) also ventured to India and had a similarly difficult travel through the Pamir Plain. His experience was archived in *Laoyang Temple Records* 洛陽伽藍記 (Zong AD 547). "Passing through an iron chain bridge (銕鎖為橋), hanging in mid-air, over a deep canyon with no bottom in sight, with nothing to grab if one falls." In addition, a note added to an earlier passage of Vol. 5 specifically mentions an iron bridge by the Chilin Shan (today's Sun Moon Mountain, in Qinghai) on the way to Gandhara (Kandahar, Afghanistan) in December, AD 518. They clearly went over an iron chain bridge before reaching India. Though not connected to iron bridges, Zong mentioned the sighting of two iron pillars, one 26 m tall, three and a half times higher than the Delhi pillar. Both missions returned to China with many volumes of sutras (170 for Zong and 657 for Xuan before the age of paper in India), so porters must have accompanied them and the expeditions perhaps avoided steep ways.

Over a century earlier in AD 399–413, Faxian traveled to India through the Pamir Mountains (Faxian AD 414). His route passed Darel where he visited a large temple at Pouguch in AD 401, and the next passage he encountered was the most dangerous along the right bank of the Indus River (Tsuchiya 1993, 2010). This was where Faxian trekked through footpaths cut on the sides of cliffs (昔人有鑿石通路), and the remains of such a footpath are still visible along the Karakoram Highway. He also crossed a river by a cable bridge (度梯已躡懸絚過河), but without mentioning iron usage. Thus, we find that cable bridges and iron chain technology existed in the fourth- to sixth-centuries Central Asia and India as well. Since ironmaking was well developed in India by that time, it is natural to attribute the technology to India, but the question remains as to where iron chains were manufactured. In fact, Marshall (1951) reported on 221 ancient iron artifacts discovered in the 1920s at Taxila (about 250 km south of Darel). These were dated to the third century BC and included three high carbon steels (carbon, C, between 0.7 and 1.7 wt% (from now on %)) as well as 108 wrought iron bars of 0.6–1.8 kg each. Comparable iron pieces have been found elsewhere in India and fully characterized, giving support for the Taxila dating (Park and Shinde 2013). Hadfield (1912) examined fifth century AD ferrous objects, a steel chisel, an iron nail, and an iron tool from the Colombo Museum (Sri Lanka). He found the chisel surface-hardened by adding carbon to the wrought iron core and by subsequent heat treatment through quenching. The iron nail and tool had only traces of carbon, but had 0.3% phosphorous. Hadfield also conducted chemical analyses of Taxila iron and steel (Marshall 1951). These and more recently excavated ferrous materials amply demonstrate the high technical levels reached in ancient South Asia which in part enabled production of structural materials.

Similar records of iron bridges may exist for travel accounts through southwestern China, but this must wait for future discoveries. There was a famous traveler, Xu Xiake 徐霞客, who toured this region and wrote a travelogue, but his accounts are late, from the seventeenth century (Tang 2000a). The abundance of iron in Central Asia at the time, in particular at Shue 疏勒国 (now Kashgar, Xinjiang, China), was also recorded in Vol. 102 of Weishu 魏書 (AD 554–559) along with rice, copper, tin, cotton, etc. Xuan also recorded his travels through this country, especially focusing on the many Buddhist temples he witnessed.

Of the remaining old iron bridges relevant to this discussion, Luding Bridge is the most famous. For one, this was built in 1706 with an imperial decree and may be the oldest extant iron bridge today. It is situated on the Dadu River, 250 km SW of Chengdu. It has a span of 101.6 m with a 2.8 m width at its base, with nine foundation chains and four side chains. The fame of this bridge in China arose from the fighting over its control during the Long March in 1935. As for other bridges, according to a list published in 1986 (Mao 1986), at least five bridges were built during the Ming era, that is, before 1644. It is unclear if these still exist today.

Another group of old iron bridges has received much less attention. In 2000, ten bridges with two cables are listed in Tang (2000a, 520), though details of most are absent. These are fifteenth-century iron bridges in the Himalayan region, Tibet, and Bhutan, in particular. By tradition, Thangtong Gyalpo, a religious leader and bridge builder, was credited for building 58 iron bridges, starting in 1430. Three articles (Clarke 2006; Epprecht 1979; Peters 1987) and two books (Gerner 2007; Stearns 2007) discuss this topic. Gerner (2007, 70) listed six old iron chain bridges still existing in Tibet (at least in parts). He attributed the Chung Riwoche Chakzam Bridge to the artisan engineer Thangtong, with a photograph and chain link dimensions. The bridge span was given as wide (60 m) and short (35 m), but the chain length is unknown. The source of the Thangtong attribution is a history book in the Tibetan language (Tshedwang 1994), but it is unknown if any supporting evidence exists. Clarke (2006) provided a historical background of iron metallurgy in Tibet and Central Asia. While its technical history remains essentially unknown, Tibetan iron technology unquestionably existed in the 1400s at the level required for chain production. Clarke (2006) identified the sources of iron from iron ores in eastern Tibet and noted that Thangtong had 18 blacksmiths working for him, making chains. How ironmaking functioned was not discussed. Pope (1811) gave a drawing of one of Bhutan's bridges, Chuka-cha-zum, reproduced as Fig. 4.5. It was in Chukha district and had a span of 44 m with the mid-span 10 m above the river level in the dry season. As shown in Fig. 4.5, five foundation chains and two side chains were used. Bamboo mats formed the passageway, 2.4 m wide.

Epprecht (1979) conducted metallurgical studies on an iron ring part from Bhutan, probably of fifteenth-century origin. Unfortunately, the provenance of the tested ring is only given as Bhutan, not a particular source, so his results cannot be linked to a specific bridge. The iron ring contained low levels of carbon and sulfur and high phosphorus and was smelted with charcoal. That is, the chain was made of

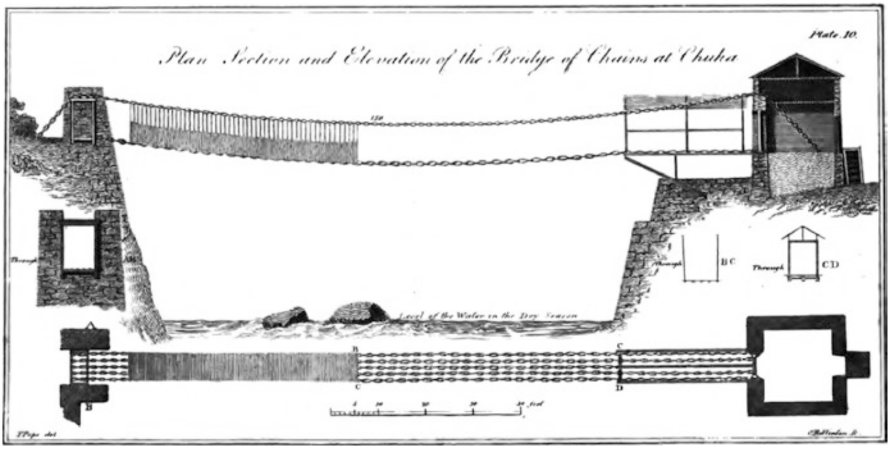


Fig. 4.5 Nineteenth-century drawing of Chuka-cha-zum chain bridge in Bhutan. (Pope 1811)

wrought iron with a high phosphorous content, smelted using charcoal, a result common to Indian iron, e.g., the Delhi iron pillar. The chemical composition was 0.012 C, 0.004 S, 0.049 P, 0.07 Si, 0.007 Cu, <0.001 Mn and Cr, 0.001 Al, 0.01 Zn, and 0.007 As. This evidence favors local ironmaking because of the high phosphorous content. Epprecht's work also contains micrographs of the iron ring, indicative of good iron quality. Thangtong's ambitious projects required huge resources and fundraising, and these appear to be his main contribution. Regardless of his exact role(s), the existence of many iron bridges attributed to his construction activities is indisputable. When the Qing army went to Tibet in 1792 to repel Nepalese invaders, they recorded many sightings of iron bridges. No exact number was given, however. Many observations and photographs by travelers since have appeared in print, including Needham (1971) and Gerner (2007). It appears, however, that none of the original bridges in Bhutan attributed to Thangtong exist any longer, with the exception of one renovated bridge. Two were moved by the Indian Army in 1969, and three were destroyed in 1968, 1969, and 2004. One was rebuilt recently at Tachog Lakhang near Paro, but apparently at a higher location nearby using some bridge chains from Docsum and Tashigang (Wood 2013).

Ancient Iron and Steel Metallurgy

In order to frame bridge making within its metallurgical context, a detailed chronological and technical survey of ancient and historic ferrous metallurgy is presented here with a focus on the following: the possible routes of diffusion of iron and steel technologies, alloy classes useful for bridge building, and wiredrawing useful for the manufacture of suspension cables.

While native metals and meteoric iron were used from early times, the technology of extracting metals from ores (smelting) and of shaping them to useful products (metalworking) traces back to the sixth millennium BC based on our current evidence (Radivojević and Rehren 2015; Radivojević et al. 2010; see Kaufman Chap. 1, this volume). Bronze artifacts unearthed at Nahal Mishmar in Israel included arsenic bronze castings (by pouring molten bronze into mold cavities) and are an early example of lost-wax casting. In the following two millennia, bronze technology developed and advanced in multiple regions, either independently or by diffusion. By the mid-second millennium BC, copper, tin, and lead extraction was practiced and bronze objects were cast at numerous sites across Eurasia (Tylecote 1992). It has been proposed that Hittites may have been the first to start intensive iron extraction in the mid-second millennium BC in Anatolia with this technology then diffusing out to neighboring regions; however, much is still unknown about the transition to ferrous metallurgy in the Near East (Bryce 2006). By the first millennium BC, the technology had spread widely, including to the European ironmaking cultures of Hallstatt and La Téne, but any meaningful discussion of the paths of technological diffusion requires its own dedicated consideration and is beyond the scope of this chapter. Figure 4.6 shows an iron sword from Hallstatt, Austria, from the first millennium BC period. Advances in ferrous technology continued throughout antiquity; see Tylecote and Gilmour (1986) and Lang (1988) for metallographic examinations of Roman swords.

With recent discoveries, the actual starting date of Anatolian ironmaking may go back to 2000 BC or earlier. A bar-like iron object was found in 2006 from stratum IV (twenty-second–twentieth centuries BC) at the Japanese excavations that have been in progress at Kaman-Kalehöyük. While it is heavily corroded, Akanuma's chemical analysis gives 93.2% Fe, 3.68% Si, 1.47% Al, 0.82% Ca, and 0.003% Ni (excluding gaseous elements). The very low Ni implies this iron was not of meteoric origin, while high Si and Al are probably of slag origin. Backscattered electron images show a mostly ferrite matrix with some iron carbides, as shown in Fig. 4.7

Fig. 4.6 Iron sword with ivory pommel from Grave 507 at Hallstatt, Austria, ca. 800 BC, displayed at Hallstatt Museum, Austria. Identification by H. Reschreiter, Vienna Natural History Museum. (Photographed by the author, 2000)

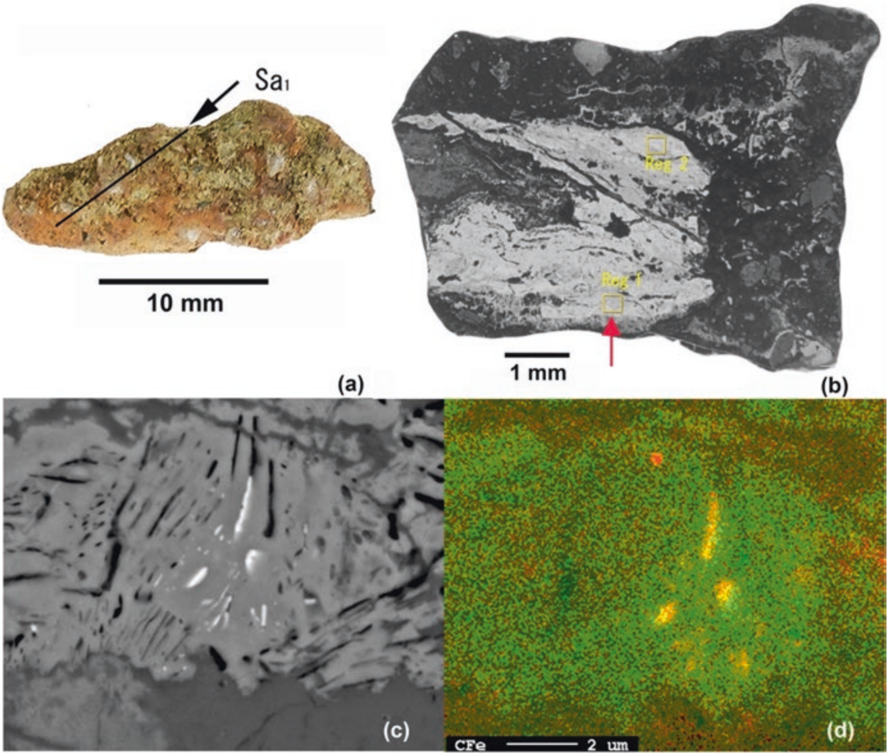


Fig. 4.7 Bar-like iron sample from Anatolia. (**a**) Photograph of the sample. Sa_1 indicates the line of sectioning. (**b**) Macrophotograph of the section. White zone showed metallic luster. Red arrow indicates the position of microanalysis. (**c**) Backscattered electron image. Light gray is metallic, white is iron carbide, and black areas are lacking iron carbide. (**d**) Wavelength-dispersive chemical element mapping. Green = iron, yellow = iron carbide, red = carbon. Note the correspondence between white areas in (**c**) and yellow areas in (**d**), indicating coarse lamellar structures. (Rearranged from the original files of Akanuma (2008, fig. 1). ©2008, Japanese Institute of Anatolian Archaeology, used with permission)

(Akanuma 2008). The C content for the imaged region was estimated as 0.1–0.3%. (Note that ferrite is pure iron with a small amount of C, less than 0.01%.) Three more iron objects from stratum III (twentieth–eighteenth centuries BC or Assyrian Colony period) had 0.1–0.3% C. From stratum II (tenth–fifth centuries BC), 17 more samples with utilitarian shapes were analyzed with comparable results (Akanuma 2006). More recently, two more iron objects were excavated from the layer below the 2006 piece and are being evaluated. These have higher C contents than the 2006 bar sample (Akanuma, personal communication, 2017). Recent excavations such as those conducted by Akanuma's team provide excellent knowledge for early iron innovations. Still, examples of smelted iron across Mesopotamia and Anatolia date as early as the third millennium BC, and much is currently lacking in the way of conclusively determining the earliest origins and spread of this technology (Waldbaum 1980; Yahalom-Mack and Eliyahu-Behar 2015).

In this regard, the question of whether Near Eastern ironmaking technology influenced ironmaking in the South and East Asian regions has attracted much interest. Tewari provided ^{14}C dates pushing back Indian ironmaking to the nineteenth century BC (Tewari 2003). Tripathi (2015) summarized various iron objects from ^{14}C-dated sites in India during the second millennium BC. Specific reference of Indian iron objects, however, only goes back to the twelfth century BC, while many iron weapons, tools, and utensils were discovered at sites dated before the sixth century BC (Tripathi 2015). The earliest date for Chinese iron objects has now been established as the fourteenth century BC (Chen 2014; Mei et al. 2015). Two iron objects were discovered at a well-preserved tomb in Chen Qí-Mó Gou (CQMG), and an improved ^{14}C dating method was used. This ^{14}C date is derived from accelerator mass spectrometry (AMS) dating, requiring a much smaller sampling size and faster analysis capability, incidentally also used for dating the aforementioned Anatolian strata. The CQMG iron pieces were of wrought iron with 0.1–0.2% C and fine-grained ferrite-pearlite structure with aligned iron-oxide inclusions. (Here, pearlite refers to a lamellar mixture of ferrite and iron carbide.) These pieces were produced by a direct reduction process. With current evidence from across Eurasia, an independent Chinese origin for ferrous technological innovation and perhaps invention is still favored by consensus.

A word should be said here about the actual process of obtaining iron. Iron was obtained from iron ores containing iron oxides of various types: hematite, magnetite, goethite, etc. The reduction process that strips oxygen from these oxides occurs when the ores are heated to above 1200 °C with charcoal or mineral coal by the action of carbon monoxide gas. Since early times, cylindrical furnaces, called bloomeries, were mostly utilized, and this name also is used for the entire process, in which no melting of iron occurred. The resulting mix of porous iron and oxide slags is called a bloom, which was consolidated with subsequent heating and hammering, resulting in wrought iron (Gordon 1996; Wagner 2008). An eighteenth-century version of the bloomery, or direct process, is shown in Fig. 4.8. This type has an integrated air inlet and is known as a Catalan forge (Overman 1865).

Let us continue now and focus on the first millennium BC in China. For the Central Plain of China, this millennium started under the (Western) Zhou. As the Zhou dynasty began to break up by the early eighth century BC, iron objects started to appear at multiple locations (Chen 2014; Mei et al. 2015). Two wrought iron objects were unearthed from the Tianma-Qucun site in the 1980s, dated to the eighth century BC. Also found there was a round piece of pig iron containing 4.5% C. Currently, this is treated as the first discovery of white cast iron in China and is a symbol of national pride as it proves the Chinese invention of cast iron. However, it can more properly be called pig iron because it was not cast into a mold. Pig iron typically contains 2–4% C and melts below 1200 °C. It acquired this name from the way it was cast in a series of small lumps, resembling feeding piglets. The terminology

Fig. 4.8 Remains of a Catalan forge at Mission San Juan Capistrano, CA. These bloomery furnaces were built in 1797 and supplied wrought iron for making tools at the mission. These are the oldest metalworking structures in California. (Photograph by W. Hsieh, 2015, used under Creative Commons License Non-Commercial 2.0. www.flickr.com/photos/whsieh78/24266319841/)

of "white" cast iron is due to the broken face of the alloy appearing shiny, in contrast to gray cast iron showing grayish rough fracture surfaces. Regardless of the intent of the ancient ironmaker or current naming, technically, this is a significant departure from the direct reduction (bloomery) ironmaking method, in which no melting occurs. The pig iron (or high C iron) piece had to be solidified from the molten metallic state. Although this is a revolutionary accomplishment, in terms of the technical level of Chinese metallurgists of the eighth century BC, who were using a 1200 °C pouring temperature for bronze casting for several centuries, this was not as difficult an obstacle as one might imagine. Thus, one anticipates more discoveries of iron and ironmaking remains from even earlier times.

Further west in Xinjiang, many more iron artifacts were discovered that could be from the tenth century BC, but problems of accurate dating persist at these sites, and Chen (2014) places the tentative date to be during the ninth–eighth centuries BC. Most of the artifacts were wrought iron, but several sword remnants had steel microstructures derived from the absorption of carbon. Carbon content is estimated to range up to 0.4% with ferrite-pearlite structures. (During the early period, it was believed that wrought iron was made, though clear ironmaking sites are yet to be identified. This can be expected as early ironmaking sites that were later developed into more advanced ironmaking technology workshops may leave behind little of the earlier traces.) These were followed by numerous iron objects, and by the sixth century BC, white cast iron products started to appear. This implies that bloomery smelting was replaced by the more productive blast furnace, and casting practice commenced. In the next 300–400 years to the beginning of the Han period (206 BC), substantial progress occurred in iron metallurgy, and details of where, how, and when various products emerged are being clarified through careful studies, specific to particular regions. (See Chen (2014), who provided the timelines for iron object discoveries in several different regions with details of AMS ^{14}C-dating and metallographic results.)

High-temperature furnaces required higher-capacity bellows. In combination with tubular ceramic tuyères, air injection devices converted a shaft furnace into a blast furnace of increasing capacity. This blast furnace technology produced pig iron more and more efficiently. By casting into a mold, white cast iron objects were mass produced from the pig iron. From the size of excavated remains of multiple Han era blast furnaces (some with large solidified iron pieces remaining), the height of such furnaces reached 5–6 m with a volume of 50 m^3. Because of accidental shutdown of blast furnaces, a few 5–20 t scrapped iron lumps are known in Sichuan, giving one village a ferrous toponym, Iron Ox (Chen 2014, 272). At least one 20 t lump was found at Guxingzhen, Henan (Seki 2008).

With increasing temperature in the blast furnace, Si starts to be reduced as well and an increasing amount of Si is dissolved in pig iron to about 0.3%. This Si addition is still below the level needed to make gray cast iron (>1%) under usual contemporary sand casting conditions (i.e., pouring into a cavity made in compacted sand molds). Silicon is needed in gray cast iron to stabilize ferrite, destabilize carbide, and promote flaky graphite formation. Metallurgical differences between white and gray cast irons come from the phases produced: for white cast iron, pearlite and iron carbide are formed, and for gray cast iron, ferrite and graphite are formed. Both of them are brittle and cannot be worked by hammering, for example. White cast iron is harder and more brittle but is useable for many applications, especially for agriculture and for many tools and utensils. Some white cast iron products were heated for a long time, imparting ductility and rendering the alloy into malleable iron. Gray cast iron also is brittle but is much softer (Chen 2014; Davis 1996; Scott 1991).

Pig iron, becoming plentiful by the fourth century BC, was also converted to low carbon steels by fining (抄钢法) (Bronson 1999; Chen 2014; Liu 2002; Wagner 2008), a replacement of bloomery iron. Initially, carbon was removed from pig iron (decarburization) by reheating it for days, exposing iron to air and burning off carbon. This process was aided by casting pig iron into thin plates (板生鉄), as illustrated many centuries later in the *Tiangong Kaiwu* of 1637 (Wagner 2008, 340–342). The same process converted brittle white cast iron pieces to useable products. This decarburization process appears to require a large amount of fuel. However, Rostoker (1988) reproduced the decarburization process over 5 days of heating at 800 °C. He concluded that, “It could have been done by submerging the castings in a deep bed of ashes kept hot by a slow fire above.” He continued that a 6 mm-thick cast iron plate can similarly be converted to a steel. This process was studied earlier (Burke et al. 1960) and was attributed to the diffusion of C in austenite, a high-temperature phase of iron. The diffusivities of C in the solid and liquid states of iron are known (Morgan and Kitchener 1954; Tibbetts 1980), and the thickness of decarburization can be calculated using the diffusion distance given by $\sqrt{Dt}$, where D is the temperature- and concentration-dependent diffusivity and t is the time of heating (Shewmon 1989). For solid iron with $C = 1.5\%$ at 1000 °C, $D = 9.5 \times 10^{-5}$ mm²/s and one finds that $\sqrt{Dt} = 2.9$ mm for a 1-day-long heating ($t = 8.64 \times 10^4$ s), decreasing heating time by a factor of 5 compared to Rostoker's result above. Note that decarburization proceeds on both surfaces, doubling the thickness to 5.8 mm. For liquid iron at 1560 °C, D increases to 1.4×10^{-2} mm²/s, but still 600 s are needed to get the same diffusion distance (without stirring), thus demonstrating the importance of direct contact with air in a fining operation.

In the Chinese fining process, C in molten pig iron was oxidized by manually stirring it with long rods and by adding irons and or crushed iron ores. Chen (2014, 305) described this fining process (抄钢法) as consisting of the following: (a) raising the pig iron temperature so that the material was in a partially molten pasty state; (b) stirring with long rods to increase exposure to air to raise its temperature; (c) burning off C, Si, and Mn; and (d) burning off C completely to get iron, or partially to get medium or high C steels. This process was also started from molten pig iron according to Liu (ed) (2002) and the *Tian Gong Kai Wu* cited above. Liu (ed) (2002, 77) specifically describes adding a process of blowing air through the liquid (通过鼓风) which may be considered as a precursor to the Bessemer process (see Kaufman Chap. 1, this volume). The partially molten state corresponds to a mixture of liquid and solid iron that occurs in a binary Fe-C alloy above 1147 °C and at a C concentration of less than 4.3%. Since Chinese fining was conducted starting from liquid pig iron with a shallow hearth of about 15 cm in depth and 40 cm in diameter (Wagner 2008, 243), it may be more descriptive to call it a wet fining process. This process was clearly illustrated in the *Tiangong Kaiwu* from the seventeenth century with molten pig iron being stirred with long rods where the hearth was about 1 m by 1 m (Wagner 2008, fig. 133). This differed from the European fining practice without a pool of molten pig iron or dry fining. In European fining, an end of a pig iron bar was melted, dripping into a pool of molten slag and becoming a part of pasty iron mass. The pasty iron was further oxidized and started to solidify, indicating the end of the fining process (Tylecote 1992 102).

Higher carbon steels were also produced in several different ways. One way is to heat white cast iron in an oxidizing condition without melting, so that C is reduced by oxidation. This applies to thin sections or to surface layers only. The addition of C to wrought iron (cementation, known today as carburization) was also possible by heating with carbon sources in a sealed pot or by dipping it into molten pig iron. The last method, from the mid-sixth century, is called 灌钢法 in Chinese (Liu (2002, 80–81), although a different method had the same name in the seventeenth century (Wagner 2008). Additionally, various heat treatment processes were introduced for imparting higher hardness and strength. Wagner (2008) presented a detailed chronology of technical achievements in China, although newer archaeological finds will no doubt rewrite what is known today. With such technical evolution, Chinese iron production reached 15,000 t annually by the second century BC or early Han era (Arai 1991). These were primarily cast iron objects, but steels and iron were also widely used. This estimate was based on the daily production of 0.5 t at the He-1 (河一) iron office (at Guxingzhen, Henan) along with 48 other offices under the state monopoly. The estimated capacity is conservative since a blast furnace with an estimated volume of about 50 m^3 with 1 t daily production capacity was found at He-1 (Seki 2008). In the same period, Arai also estimated Roman iron production of 3000 t/year based on the amount of leftover slag. Often cited Roman production estimates of 82,500 t/year are arbitrary using a baseless per capita consumption of 1.5 kg/year (Healy 1978) and should therefore be treated with caution. (See Krauss (2015) and Scott (1991) for a better understanding of micrographs and steel products.)

The abundance of Chinese iron can be attested by iron objects found in a neighboring country, Japan. Iron pieces started to appear there from the fourth century BC or when the cultivation of rice as well as bronze items arrived from China (Fujio 2014; Nojima 2014). In 2012, a low C steel block was unearthed at Fukuoka with little effect of corrosion even though it was buried at the layer dated to the first century BC to first century AD. It had 0.26% C, 0.51% Mn, 0.01% Si, 0.06% P, 0.048% S, and 0.22% Cu (Ohmura 2013). Since local ironmaking was absent, this was most likely imported from China. The Fukuoka iron is also of interest for its chemistry. High Mn, P, and Cu levels may reflect their ore sources. However, it is puzzling to find high S and very low Si, as the block was highly corrosion resistant.

Dozens of imported iron bars have also been excavated from several western Japanese sites (Nojima 2014). Many weapons are known to exist from historical records, the material all coming from China and later from the Korean peninsula since domestic ironmaking only started in the fifth century AD or later. An example is an ancient sword made from imported iron. Kitada (2009) analyzed this sword dated from the second to sixth centuries AD and found a multi-layered structure of low C ferrite (0.05–0.1%) and medium C steel (0.35–0.45% C) with a ferrite-pearlite structure. A large inclusion was seen in his micrograph, but this was from forge welding of different steel pieces. Also shown were micron-sized iron-oxide inclusions in the ferrite matrix. From this micrograph, the inclusion content was quantitatively measured as 1.4%, which is comparable to a mid-twentieth-century wrought iron. Such metallographic examination is rare due to the scarcity of ancient iron objects in Japan. Similar iron and steel micrographs in Chen (2014) also lead to the same observation of low inclusion contents in Chinese fined iron. For the sake of cross-cultural comparison regarding impurity levels, two Roman steel and wrought iron micrographs were similarly examined (Lang 2017, fig. 1; Scott 1991, fig. 100). Their microstructures were not homogeneous, and their inclusion contents varied: 9.5–27% for steel and 4.5–32% for iron. American wrought iron micrographs (Gordon 1996, figs. A3 and A4) had more uniform inclusion distributions, with an older iron (1680–1710) showing 26% and an 1849 Wheeling iron giving 9.0%. An iron sample from an 1824 footbridge yielded a 11.6% inclusion content (de Bouw and Wouters 2005, fig. 8). Obviously, more samples must be examined for a quantitative comparison between divergent methods, but these examples may be helpful in understanding the results and pitfalls of various ironmaking techniques.

Precursor technologies leading to the capability to build iron and steel bridges also include techniques in wire and chain production. Lewis (1919, 1952) and Newberry and Notis (2004) provided historical accounts of wire-making. Gold wire chains were used in jewelry since 2500 BC in Mesopotamia (Cartwright 2014; Lewis 1952). Wiredrawing in Europe was definitely practiced by the Viking Age (Thomsen and Thomsen 1974). Chinese bronze wares used chains for decorative purpose from similarly ancient times and many 30–50 cm-tall bowls with chains are extant (Tang 2000a, 498). Uses of mechanical chains are credited to the Greek engineer, Philo Mechanicus, in the third century BC (Rance 2013). Actual use of iron chains for anchors was witnessed by Caesar in the first century BC during his Gallic campaign (Caesar 51 BC). Caesar also mentioned their use for detaining prisoners. (Caesar 51 BC Book 5, Ch. 27). Some Roman chains have survived, providing archaeological corroboration (Vickers 1992). Han era books also noted the use of iron chains for holding prisoners or criminals (Tang 2000a). For the case cited, there were over 100,000 money counterfeiters, who were shackled and chained, requiring more than 100 km of chains for this use alone. But historical numbers are sometimes exaggerated and the actual length may have been much less. Still, the conditions for using iron chains for suspension bridges were satisfied by Han era China since iron chains were already being made in large quantities.

Iron metallurgy was similarly advanced in India (Balasubramaniam et al. 2015) as the metallurgists there mastered bloomery iron from the twelfth century BC and started wootz steel production by the third century BC, gaining fame in the Middle East and Roman Europe (Giumlia-Mair et al. 2009). Thus, it is expected that they, too, had chain-making technology before the Common Era. Due to geographical proximity, Indian iron technology was most likely transmitted to the north side of the Pamir Plain, allowing them to bridge with iron chains across deep valleys in the Hindu Kush Mountains. While the mountain crossing was never easy, the army of Alexander the Great made a round trip a few centuries earlier, so pilgrims, engineers, and traders could have trekked as well. As mentioned in the previous section, this is the crossing where Chinese monks utilized the Central Asian iron chains and chain bridges, making these the oldest iron bridges in recorded history.

Cast Iron

In this section, we begin a discussion of different types of iron alloys and their use in bridge construction. Cast iron is historically the generic name for products made by casting molten iron into a mold and has traditionally represented a revolution in production capacities for the various cultures that have developed this technology. Today, cast iron typically refers to alloys that contain 2–4% C. This carbon alloying lowers the melting temperature from 1538 °C for pure iron to below 1200 °C. As discussed earlier, this technology was highly developed in China since the fifth century BC, and huge monuments remain from the seventh to eleventh centuries AD (Chen 2014; Wagner 2008). Blast furnaces in Europe became more commonplace following the

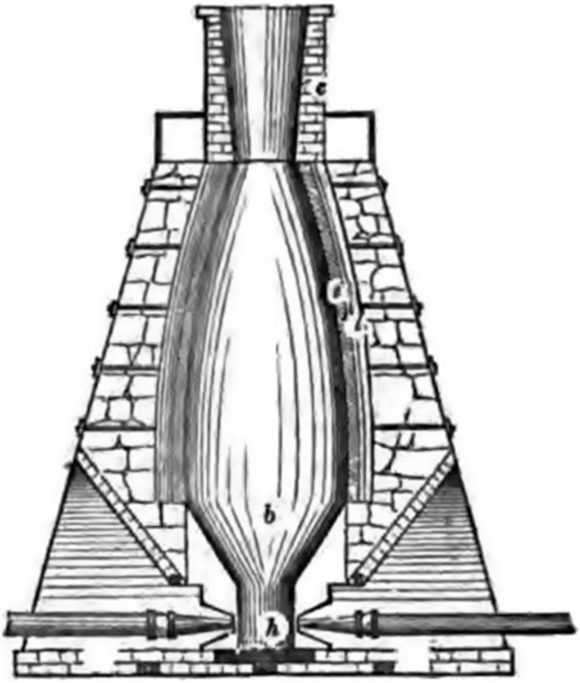


Fig. 4.9 Blast furnace of nineteenth-century America. h, hearth (typ. Square of 0.5–2 m wide, 1.5–2.5 m high); b, boshes (increasingly round with increasing height, 2.5–5 m round). (Illustration from Overman (1865, 509))

Middle Ages and come in numerous designs and forms. A cross-sectional drawing of a nineteenth-century American blast furnace is shown in Fig. 4.9 (Overman 1865). Ore and coke are fed from the top, smelting starts at boshes (b), and iron melting occurs in the hearth (h), while air blasts are injected into the side(s) of the hearth. Periodically, pig iron is drawn out from the bottom of the hearth. The total height could reach 10–15 m.

In Europe, cast iron usage started in the Middle Ages. Although high C iron pieces have been found since Roman times, these were not cast objects. As the demand for iron increased, more efficient blast furnaces appeared in Sweden by the twelfth century AD and in France and Germany by the thirteenth century (Buchwald 2005; Molinari 1912; Overman 1865; Williams 2012). These blast furnaces were for the production of a variety of cast iron products, cannons among them. Metallurgical process changes were identified through the study of nonmetallic inclusions in wrought iron products. Many balls and irregular pieces of pig iron were also found at the Lapphyttan site in Sweden (Buchwald 2005). Similar finds also exist from the eleventh- to thirteenth-centuries AD sites in Germany in the Swabian Alps (Williams 2012, 191). Von Baeckmann et al. (1977) set the earliest date of cast iron in Germany as AD 1380 and showed a photograph of a water pipe cast by ironmaster C. Slanterer in AD 1457. This was for the Dillenburg Castle of Count Johann IV.

The presence of phosphorus also affected the properties of these cast iron objects. Phosphorus additions lower the melting temperature of Fe-C alloys, since iron phosphide, Fe_3P, melts at 1100 °C and the Fe-10.5%P binary mixture melts at 1050 °C. A recent study of Italian castings gives the Fe-C-P melting temperature as 953 °C (the ternary eutectic temperature; Veronesi et al. 2009). This work also showed that greater than 1% P additions were commonly used throughout the nineteenth-century Italian castings, since P additions increase the fluidity of molten metal and allow for intricate castings. Although presence of Fe_3P increased the brittleness, it also imparted wear resistance, which the authors contend can still be exploited today. Early fifteenth-century guns from the Halberger Ironworks, Germany, were of gray cast iron, containing 2.2–3.5% C, 0.5–0.7% Si, 0.15–0.4% P, and 0.24–1.5% Mn. The presence of P seems to produce graphite flakes even at relatively low Si levels (Williams 2012). High P levels were also common in the late nineteenth-century pig iron in Germany, coming from the ores used. A 1912 German book on chemical analysis (Bauer and Deiss 1912) gave 2.5–3.5% P for white cast iron and 0.4–0.9% P for gray cast iron. Micrographs of such high-P cast iron from a 1796 Prussian bridge are given in Konat et al. (2005) and Pękalski and Rabiega (2011), showing phosphoric eutectic among ferrite-graphite-pearlite structures (see Fig. 4.10). Here, pearlite consists of ferrite and iron carbide with carbide being the gray phase due to chemical etching. Usually, a pearlite mixture takes a more regular lamellar arrangement (see Fig. 4.11b), and each grouping of near parallel plates is a colony. Today,

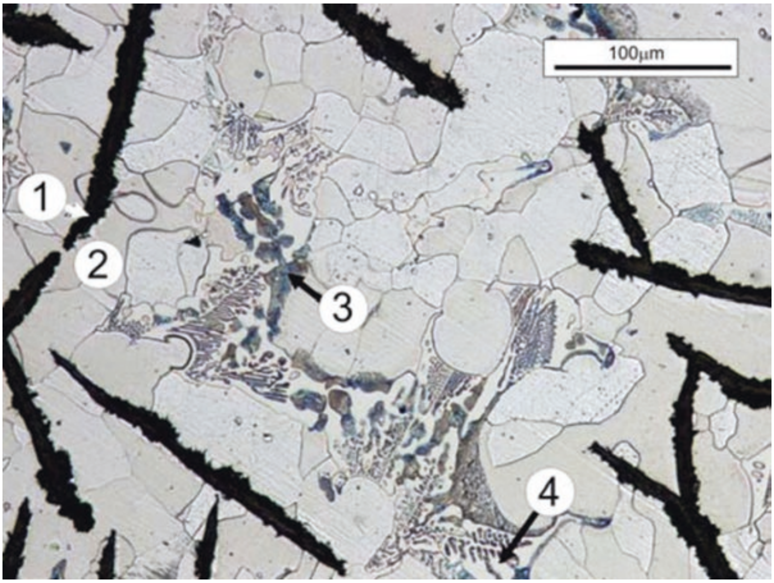


Fig. 4.10 Micrograph of gray cast iron from a 1796 Prussian bridge (Pękalski and Rabiega 2011). 1, graphite flake; 2, ferrite matrix; 3, pearlite colony; 4, phosphoric eutectics. (©2011 Archives of Foundry Engineering, used with permission)

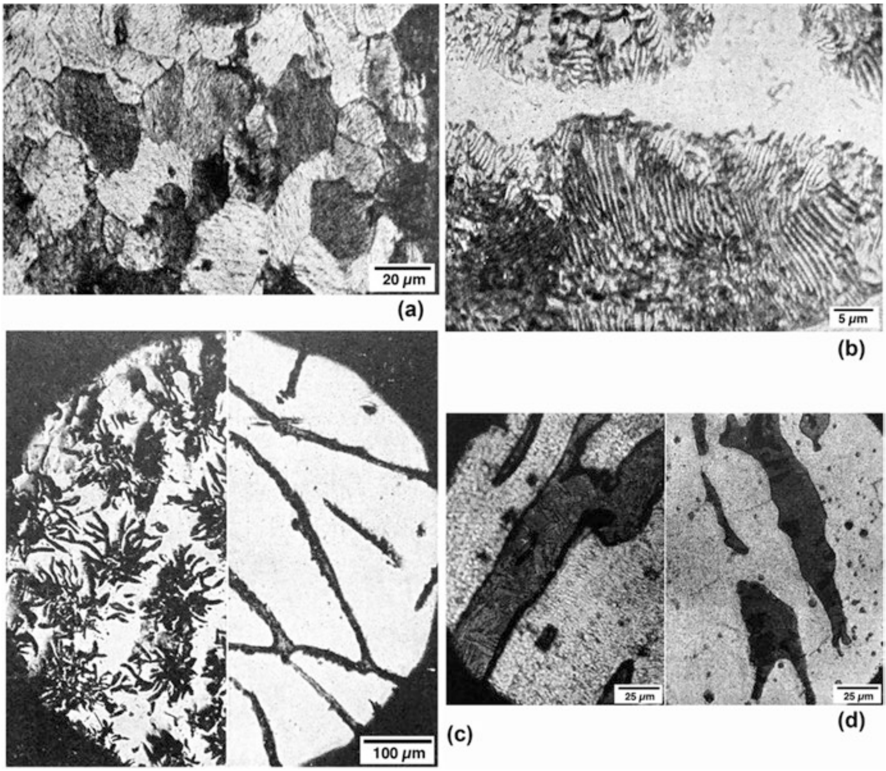


Fig. 4.11 Early micrographs of iron and steel. (**a**) ferrite, (**b**) pearlite (lamellar region) and carbide (light region), (**c**) gray cast iron with mottled graphite (left) and flaky graphite (right), (**d**) slag inclusions (dark regions). (Illustrations (**a–d**) from Bauer and Deiss (1912). Scale markers were added by the present author)

iron casting alloys are known as foundry pig iron and typically contain 3.4% C, 0.8–3.8% Si, <0.3% Mn, <0.1% P, and < 0.04% S (Davis 1996; Nippon Steel and Sumitomo Metals 2015).

As a result of differences in the alloy composition and cooling speeds, four different types of cast iron products can be obtained and the possibility of obtaining these has changed over time with the introduction of new technologies. We already noted the occurrence of white and gray cast irons. White cast iron consists of pearlite (a fine mixture of ferrite and carbide) and iron carbide. This is typically produced when the level of Si is lower than about 1%. Since ancient ironmaking did not achieve high enough temperatures to reduce silica (SiO_2), Si was always less than 0.5%, insufficient for preventing iron carbide formation during normal casting practice. Thus, most of the ancient Chinese cast iron products were of white cast iron (Wagner 2008). When casting thin cross sections, white cast iron results even in pig iron of higher Si levels. When the Si level is higher than 1%, we can obtain gray cast iron. Gray cast iron is a mixture of graphite in the iron alloy matrix. Cooling speed dictates the matrix type: with slow cooling, the matrix is ferrite (nearly pure iron with <0.01% C), while with faster cooling, the matrix is pearlite. Han era Chinese casting did include gray cast iron, identified by metallography. Wagner (2008) attributes this to very slow cooling from the melting temperatures using a heated mold. Gray cast iron was found to be stable, retaining its shape upon reheating and was utilized as material for casting molds. Many such gray cast iron molds have been excavated. However, chemical analysis showed low Si levels (<0.26%) for various molds from the He-3 (河三) iron office at Tieshenggou, Henan (Wagner 2008, 200). Seki (2008) collected analytical results from Chinese reports on seven cast iron products from Tieshenggou, also indicating low Si levels between 0.09% and 0.42% with the highest appearing in a malleable iron block. In fact, until the last quarter of the nineteenth century when European technology arrived, gray cast iron was unknown in places like Japan, where only direct reduction was utilized for ironmaking (Nakae 2009).

By the fifteenth century, European casting technology advanced greatly due to the need to cast large cannons and to avoid brittle white cast iron. A legend attributed the death of James II of Scotland to the explosion of his own cannon. Two early fifteenth-century cannons were found to be of gray cast iron, with their chemical analysis showing Si, Mn, and P (Williams 2012). In modern metallurgy, P in iron is considered only in negative terms because it can cause brittleness, but the Fe-P phase diagram has the same features as the Fe-Si system. This means P preferentially dissolves into ferrite and inhibits iron carbide formation. In these two cannons, Si levels were only 0.5–0.7%, so P and possibly Mn had helped produce graphite flakes, turning them into gray iron.

Darby's introduction of coke into blast furnace operations in AD 1709 appears to be the turning point for modern blast furnaces and bridge construction applications as mentioned at the beginning of this chapter. The use of coke instead of charcoal is expected to raise blast furnace temperatures and to increase the Si level. The chemical analysis of a cast iron strut for the Iron Bridge of 1779 contained 3.25% C, 1.48% Si, 1.05% Mn, 0.54% P, and 0.037% S (Tylecote 1991). Tylecote (1991, 1992) provided similar analyses of other eighteenth-century British cast irons. Surprisingly, increases in S were moderate despite the use of coke. A cast iron piece from the 1796 Prussian bridge at Łażany (Poland) was studied (Konat et al. 2005; Pękalski and Rabiega 2011). This piece was recovered from a river bottom with only minor corrosion in 1995. As shown in Table 4.1, the compositions are comparable to Darby iron, implying that coke was also used in Prussia, likely due to cost advantage. According to Swank (1892), uses of coke became widespread in England by the mid-eighteenth century. This is consistent with the tripling of pig iron production in the UK between 1720 and 1780, as shown in Fig. 4.2. Coke-fueled blast furnaces were used in continental Europe from 1767 (Molinari 1912).

One example of microstructures from this bridge is found in the micrograph of the Prussian gray cast iron shown in Fig. 4.10 (Pękalski and Rabiega 2011). Because of the high P level, phosphoric eutectics (4) are observed in addition to usual graphite flakes (1), ferrite matrix (2), and pearlite colonies (3). Pękalski and Rabiega (2011) also examined a few more nineteenth-century cast iron bridges and one from the 1876 Mieszczanski Bridge (also from Prussia), also included in Table 4.1. Here,

Table 4.1 Chemical composition of cast iron in European iron bridges

Element	Iron Bridge	Łażany Bridge	Coke pig	Mieszczanski	Charcoal pig	Coke pig
Year	1779	1796	1809	1876	1925	1925
Location	England	Prussia (Poland)	England	Prussia (Poland)	USA	USA
C	3.25	2.62 2.10	2.1	2.4	4.1	3.9
Si	1.48	1.78 1.48	3.5	2.5	1.98	2.54
Mn	1.05	0.72 0.61	–	0.8	0.6	0.9
P	0.54	0.41 0.57	0.75	0.8	0.13	0.4
S	0.037	0.035 0.04	0.3	0.09	0.012	0.025
Reference	Tylecote (1991)	Konat (2005), Pękalski (2011)	Guenyveau (1809)	Pękalski (2011)	Jominy (1925)	Jominy (1925)

the levels of Si, P, and S were higher. In comparison, a 1925 US study used two fuel types, charcoal and coke, in American blast furnace operation. Forty samples each were analyzed, showing 1.98% Si for charcoal and 2.54% Si for coke. Jominy (of the hardenability test) did discard data for Si lower than 1.25% from all the charcoal group (Jominy 1925). Thus, the difference must be greater than the 0.56% reported. Therefore, it appears that Darby's pig iron produced gray cast iron from the early eighteenth century. In fact, his pig iron found resistance from foundrymen as it required an extra step for Si reduction, later called refining, before it could be processed to wrought iron, unlike charcoal pig iron. Another problem of coke-based pig iron was the increased S content, which produced cracking at high temperatures (called hot-shortness) as iron sulfide melts at 860 °C. This does depend on the coal used as raw material since Jominy showed low S in his coke pig (see Table 4.1). In the above-cited analysis for the Iron Bridge, Mn content exceeded 1%. This should have been enough for Darby iron to avoid hot shortness. Darby achieved marketing success in producing thinner cast iron pots, pans, and many other products. This was due to the products being gray cast iron, which is more resistant to warping or cracking during its use. It can also be machined or filed unlike white cast iron.

At this point, it is instructive to view some old micrographs in Fig. 4.11a–d from a 1912 book published by Bauer and Deiss (1912). These microstructures include (a) ferrite of puddled iron, (b) pearlite-carbide mixture, (c) gray cast iron, and (d) slag inclusions in wrought iron. Samples are representative of late nineteenth–early twentieth-century materials. In ferrite, grain shapes are similar to today's low C steels, but numerous fine inclusions are present. The carbide region in b) is much thicker than in recent high C steels. Graphite flakes (Fig. 4.11c – right side) form continuous networks compared to individual shorter flakes in current gray cast iron. The shapes of graphite flakes are similar to those of Fig. 4.10. Mottled graphite flakes (Fig. 4.11c – left side) are also coarse. Slag inclusions were common at the time and quite large. These large inclusions no longer appear today, but more rounded oxide inclusions up to 10 μm and longer elongated MnS inclusions are still found in common structural steels. In welded zones, slag inclusions along with other weld flaws have to be carefully suppressed with good practice.

By the time Abraham Darby III supplied cast iron for the Iron Bridge, gray cast iron appeared to be commonplace since pig iron production shifted to coke-fueled blast furnaces. The use of cheaper coke also raised the furnace temperatures, allowing the reduction of silica (SiO_2) into Si dissolved in molten iron. Of 161 blast furnaces that operated in England in 1805, only two were still using charcoal (Molinari 1912). Contemporary chemical analysis of the pig iron (Guenyveau 1809) showed 2.1% C and 3.5% Si as listed in Table 4.1, though the Si level seems unusually high. Figure 4.12 shows the cross section of a reverberatory furnace that can be used for remelting pig iron lumps for casting (Overman 1865). Coal is burned at B with air supplied from its bottom through fire gratings. Hot exhaust gas travels in the chamber where hearth A is located and exits through a flue C to chimney D. Pig iron at hearth A is melted on the bed of sand and slag. On one side of the chamber, an access door (F) was made. This type of furnace greatly increased thermal efficiency and productivity. By separating fuel from metal, coal can be used without contaminating the metal. Radiative heating from the chamber roof is the important part of heat transfer. Figure 4.13 shows the only remaining reverberatory furnace (Nirayama, Izunokuni, Japan), which was built in 1857 relying on a Dutch book on cannon casting by Huguenin (Kanno 2011). Eight cannons were cast using this furnace, which had four hearths. The Nirayama furnace, however, lacked adequate air flow and the temperature achieved was insufficient for

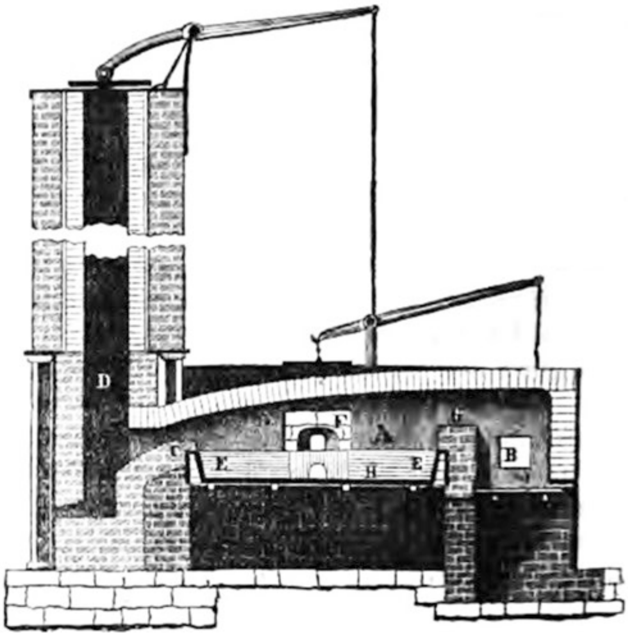


Fig. 4.12 Reverberatory or puddling furnace, which separates metal from the fuel, thereby reducing impurities in the final product. (Illustration from Overman 1865, 562)

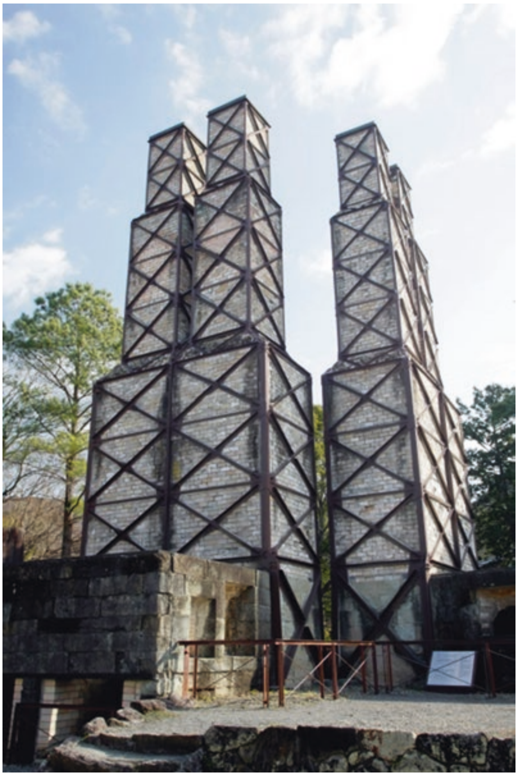


Fig. 4.13 Nirayama reverberatory furnace, Izunokuni, Japan, the only remaining reverberatory furnace of the nineteenth century. An iron frame was added for seismic reinforcement. Four hearths were built in the complex. (©2017 Tourism Shizuoka Japan, used with permission)

cast iron production (Kanno 2011). In early twentieth-century America, the Si level of pig iron reached 1.4 to ~3% (with P of 0.7–1%) reflecting higher blast furnace temperatures according to a 1911 book on foundry practice (Kirk 1911). Larger sizes of such furnaces and improved refractory bricks were also responsible for the higher temperatures achieved. In China, cast iron technology continued to advance and by the Tang era, large Buddha statues were cast at various locations. Perhaps the largest such monument is the Iron Lion of Cangzhou from AD 953, estimated to weigh 50 t. By then, the use of coke in blast furnaces had started in China. This is verified by increased S levels as well as by the absence of ^{14}C that can be utilized for dating; that is, ^{14}C in coal is too old for AMS dating (Chen 2014).

The lack of Si in the direct reduction of iron can be explained with thermodynamics. At 1200 °C, Si oxidation releases more than 20% free energy as compared to that released in the oxidation of C according to the Ellingham diagram (Kanno 2011; Stempo 2011). For smelting, a reduction reaction (opposite of oxidation) occurs, so Si reduction requires higher energy and temperature than that of iron. This diagram also indicates that the free energies of the oxidation reactions of C and Si become equal at 1520 °C assuming identical concentrations. That is, below this temperature, Si enrichment in iron is difficult. In light of this thermodynamic analysis, some earlier analyses of Roman cast iron objects can be reinterpreted. For example, Scott (1991) gave the chemical analyses of two iron lumps from the first century AD, one having 0.38% and the other 1.05% Si. Tylecote (1992) also cited 1.05% and 1.92% Si in high C iron pieces. These Si levels cannot be attained in the metal itself in Roman ironmaking, so it is likely that Si in slag inclusions was counted as well. More results of Celtic and Roman irons are given in Tylecote (1992), Pleiner (2005), and Lang (2017).

The third type of cast iron is known as malleable iron. This type starts from white cast iron, which is heated for days at 800–950 °C (which is above the critical eutectoid temperature of 727 °C) (Davis 1996). This heating decomposes iron carbides into temper carbon (or temper graphite), which are small irregular rounded (or nodular) graphite particles. The matrix is either ferrite upon slow cooling or pearlite upon faster cooling. During this long heating, the loss of carbon can occur in an oxidizing furnace environment, gradually reducing C content from the surface. This decarburized layer gradually thickens and the surface becomes softer and more ductile. This is called decarburized malleable iron.

The fourth type is known as ductile iron, in which nucleation of graphite nodules are induced using special additives, such as Mg and Ce. This special treatment, invented in the 1940s, produces a fine distribution of small graphite particles and imparts high ductility, for example, one gets fracture strain of 12–18% in grades with the tensile strength of 450–420 MPa. These are widely used in automotive applications today. Metallography of cast iron was reviewed in Radzikowska (2004).

Cast Iron Bridges

The Iron Bridge near Coalbrookdale in the UK is the first arch bridge of cast iron with a 31 m main span, finished in 1779 (opened for traffic in 1781). The bridge was designed by Pritchard and used cast iron components produced at Darby's ironwork in Coalbrookdale. The cast iron components, weighing as much as 5 t, were assembled using traditional construction techniques of mortise and tenon joints. These were tightened with wedges. Sizes of the components and joining methods can be seen in close-up photographs (Cossons and Trinder 1979). The total weight of the cast iron parts was 378 t. While some parts are now cracked, the bridge has withstood over 200 years of use, more recently as a pedestrians' bridge. Metallographic details could not be located, but the chemical analysis in the previous section indicates that these cast iron components are of gray cast iron. Bussell (2007) also considers historic cast iron of the period between 1780 and 1880 to be gray cast iron, dismissing white cast iron as irrelevant for construction uses.

The success of the Iron Bridge was followed by another arch bridge, the Buildwas Bridge designed by Telford, finished in 1796 with a main span of 40 m (Grover 2017). This had a more efficient design and needed only 181 t of cast iron. In continental Europe, also in 1796, a cast iron arch bridge was built at Łażany, Poland (Konat 2005). This bridge had a 12.5 m span and 5.8 m width and was built with 48 t of cast iron. In the period to 1879, many more bridges were built using cast iron in whole or in part. In 1811, Pope listed six cast iron bridges and a listing of more British bridges was given in Nicholson (1829). However, some engineers, including Brunel, remained suspicious of the suitability of brittle cast iron for bridge applications.

The first well-known disaster occurred in 1847 at the River Dee Railroad Bridge, designed by R. Stephenson (Anon 2017c; Lewis and Gagg 2004). He used cast iron parts for the girders, and some of them failed under tension from a passing train. The most serious disaster was at the Tay Bridge in Scotland in 1879, in which the failures of cast iron piers led to the loss of a train and 75 lives. There are many articles and books relating to this disaster, but Martin's paper and corollary web pages (Martin 2017; Martin and MacLeod 1995) give perhaps the most succinct account, including the official view of its cause being wind force. A recent reevaluation of the cause of this failure attributed it to fatigue failure of lugs on cast iron columns that formed the 27 m high pier (Lewis and Reynolds 2002). These lugs were integrally cast with the tubular columns and held bracing bars. Photos of the fracture surfaces in the paper (fig. 13 in particular) indicate progressive grayness variation. Such changes are expected of fatigue crack advances, which progress in an intermittent manner because wind-induced loading follows irregular patterns. As the crack length increases, the crack tends to grow faster, giving different light reflectivity. The loss of cross bracings most certainly reduced the stiffness of the pier and amplified the effects of gale force winds, which were blamed as the primary cause. Jones (1993) analyzed the wind force on the high girder part. He calculated that a 59 t force was applied on a 75 m segment of the high girder when the train was on the section and concluded that the collapse was caused by low tensile strength of cast iron lugs.

Another cause, persistently raised by many, is the compressive failure of cast iron columns themselves. That is, these could not withstand the bending force from the westerly wind. But this seems incorrect as tensile failure is the logical outcome of bending fracture of brittle structural members, which was not attested in any of the evaluations. From the observation of photographs of remaining pier structures, one finds that the pier failures were more likely from joint failures in the cast iron columns. Post-accident photographs show the first few piers of the high girder section either from the south or north had intact first tiers (the first from the south, No. 29 pier, had two intact tiers). Clean failures are indicated at the top joints. Detailed photographs also show unbroken flanges of the remaining columns and broken bolts (Lewis and Reynolds 2002). This implies the weakest link of these columns was the bolts holding the flanges together. Besides, if lugs suffered fatigue, these bolts were also cyclically loaded and weakened or fractured. In addition, the photograph (Lewis and Reynolds 2002, fig. 13) shows no obvious corrosion protection measures on these columns or bolts, which were constantly exposed to seawater splash. Combined with cyclic loading, rapid corrosion fatigue damages were expected. If this scenario holds, the cast iron columns themselves held but were blamed for the failure instead of the improper design of the column joints. In any event, by this time, advances in steelmaking made steel much more attractive due to strength and cost considerations, and cast iron apparently disappeared from the bridge engineers' minds.

Wrought Iron Bridges

Wrought iron was initially produced from spongy iron (or bloom) obtained by the bloomery process with a charcoal fire. The bloom was repeatedly heated and worked by hammering to squeeze out liquefied slags (mainly iron silicates), typically reducing the slag content to below 10%. It could contain a low C content typically less than 0.1%, but could also have up to 0.25% C due to the lack of control (Elban and Goodway 2002; Gordon 1996). High C iron lumps have occasionally resulted from the bloomery process, even since Roman times (Scott 1991; Tylecote 1992). The Tianma-Qucun pig iron ball (Chen 2014; Mei et al. 2015) appears to have been such a product. These lumps have mostly white cast iron structures (Navasaitis and Selskienė 2007). Since the sixteenth century AD, the Japanese tatara process has produced high C steel (called tamahagane) with 1–1.5% C along with pig iron (Suzuki and Nagata 1999). Such direct steelmaking (Barraclough 1990) was an exception, and indirect ironmaking followed the bloomery process as the mainstream technology.

In Europe, pig iron from blast furnaces was being converted to wrought iron and steel toward the end of the Middle Ages (Tylecote 1992; Williams 2012). This "finery" process oxidized C in pig iron by remelting it on a finery hearth over a charcoal fire with air blast from a tuyère. Molten iron drips down to the hearth bottom passing through an oxidizing atmosphere, resulting in a still porous bloom. When the oxidation process was terminated prior to complete C removal, steel was obtained. The bloom was heated and hammered to remove slag, making it into bar iron (or steel). This was prevalent in continental Europe until new steelmaking processes took over (Barraclough 1990). Finery forges were used until the end of the nineteenth century in the USA (Gordon 1996). By then, some of them had six tuyères on a single hearth.

At about the time of the Iron Bridge construction, an innovation occurred in European wrought iron manufacturing. This was Cort's puddling furnace (Mott 1977; Schubert 1975), based on the concept of the reverberatory furnace (Fig. 4.12), which had been used since the seventeenth century for melting various metals, including pig iron. The fining process was previously conducted in an open furnace (since before the Common Era in China), but heat loss was large and undesirable direct contact between iron and fuel occurred (when coal was used as fuel). The puddling method quickly spread in England and reached America in 1817 (Gordon 1996, 134).

Cort also introduced grooved rolling mills to produce shaped bars, angles, and channels directly from the wrought iron collected from the puddling furnace. Actually, the grooved rolling mill was invented in 1728 by Fleuer, who was French, and wires were made by the rolling process in eighteenth-century Europe (Worcester 1946). A drawing of a wire rolling mill is shown in Fig. 4.14 (Daniels 1893).

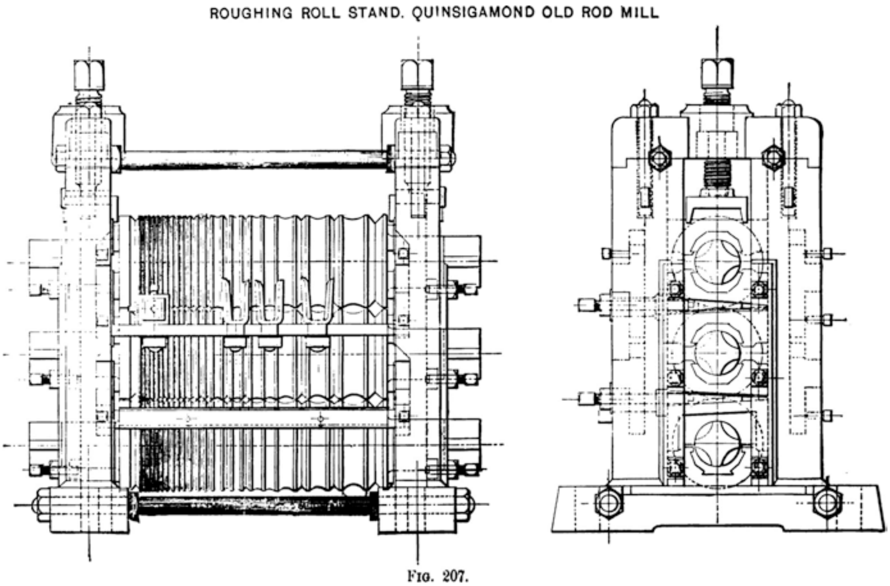


Fig. 4.14 Rolling mill with grooved rolls for rolling iron into wire rod. (Illustration from Daniels 1893, 888)

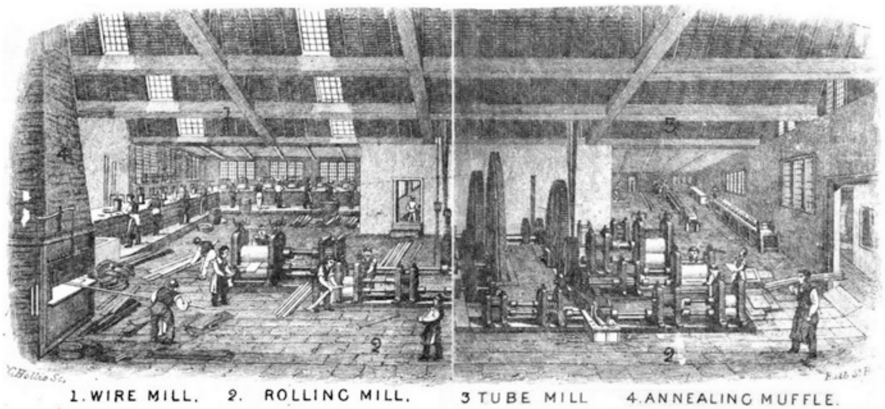


Fig. 4.15 Walker's rolling, wire, and tubing mills, Fazeley Street, Birmingham, England (Anon 1852). Wire mills (1) are in the back of the left side, several rolling mills (2) are in the middle, tubing mills (3) are in the back right, and the muffle furnace (4) is on the left

Figure 4.15 illustrates the inside of a mid-nineteenth-century factory in Birmingham, England (Anon 1852). It is naturally expected that such wires can further be drawn using drawing plates and water power. Apparently, grooved rolling mills had been used even earlier; such a rolling machine was used in England along with a slitting mill in 1697 (Swank 1892). (Here, slitting refers to slicing of bars into narrower strips, or wire rods, which are fed to grooved rolling mills, for making nails and wires.) By 1750, such mills existed in colonial America and were subjected to the British prohibition of the manufacturing of iron goods in the colonies (Swank 1892). One report described the prohibition to be of loosely enforced regulation and even colonial governors flouted the wishes of the British iron merchants. This prohibition was certainly unpopular and contributed to the independence movement (Schenck 1982). Thus, despite difficulties during the Revolutionary War of 1776, American engineers had the knowledge of wire-making once supplies of iron resumed and demand for wires returned. We will return to a discussion of iron and steel wires later in this chapter.

The puddling method, as mentioned above, melted pig iron on a hearth (A in Fig. 4.12). The hearth had a sand or coke dust bottom (later, iron oxides like slags and mill scales replaced sand). Molten iron reacted with silica in sand and formed an oxide slag, which covered the iron and reacted with its C while preventing iron from oxidation. As C in iron was reduced, its melting temperature was increased. Molten iron floating in the liquefied slag as small pea-sized particles started to join into large pasty masses. It was the puddler's task to manipulate these into round balls weighing 35–55 kg. When finished, fined iron balls were transported to a hammer or squeezer to drive out slag in the iron balls (Overman 1865). The most significant benefit of puddling over fining was the ability to use coal as fuel (Gordon 1996). The use of radiative heating separated burning coal from molten iron, preventing its contamination with S. However, in practice substantial amounts of slags were mixed with puddled wrought iron. The puddling method produced no improvement in this regard over bloomery or fined wrought iron.

These new wrought iron products widened design choices for bridge engineers and their use subsequently increased. These and other innovations reduced the iron price (measured in units of wheat) by a factor of two over the period 1782–1847 (Arai 2005). Even before Cort's inventions, wrought iron was available in Europe from improved blast furnace and finery operations. Besides local ironmaking centers, Sweden and Russia were major exporters of iron bars to the rest of Europe. For example, Sweden exported 40 kt of iron in 1740 (Jernkontoret 2015). Some of the export passed through Prussia (present-day northwest Poland), where many forging shops existed. This probably led to the construction of an iron chain suspension bridge at Glorywitz, Prussia, across the Oder River in 1734, maybe the first in Europe; no known technical information is available concerning this bridge (Plowden 1974). This was followed by the Winch Bridge in England in 1741. This was also an iron suspension type over the River Tees with a span of 21 m and 0.6 m wide rigid deck (Peters 1987; Plowden 1974). These iron chain bridges represent one of several ways of using wrought iron. Others used cable or eyebar chain for suspension and truss-type bridges, in addition to the cast iron arch bridge discussed previously.

Iron chain bridges were also built in the USA. In 1801, Finley built the first of more than 40 bridges of this design that incorporated a level deck with two wrought iron chains (Peters 1987; Plowden 1974). This was a significant advance in suspension bridge development and became the model of all such bridges built ever since. This first bridge was over Jacob's Creek at Uniontown, PA, and had a span of 21 m and deck width of 3.8 m. Each of the chain links was elongated to 0.9 m with 0.15 m width (estimated from a drawing in his portfolio, 1810) (Peters 1987). A famous Finley bridge was the 1807 Chain Bridge across the Potomac, above Georgetown. This had a span of 92 m and a 5.5 m wide deck. Each chain link was made of 38 mm square bar (Peters 1987). Finley conducted experiments determining the geometry of the loaded suspension chain and to find the force distribution on the catenary chain. He discovered that the force reached a minimum at the center. Most of these bridges had two chains (except one with four in Wilmington), which were perhaps too weak for the ever-increasing traffic loads that were not anticipated at the beginning of the nineteenth century. Fatigue failures were unknown until 1830. Whatever the exact cause, Finley's bridges were relatively short-lived and the last one was reconstructed in 1910.

Finley's work was improved in England and France. Pope (1811, 190) recognized, already in 1811, five weak points of the chain bridge design. In modern terms, three of them relate to the lack of fail-safe (or redundant) design; a failure of one linkage leads to the destruction of the entire structure. The fourth is the lack of rigidity against vibration and the fifth is the ductile-brittle transition of iron (Wright 2015b). This last weak point was most intriguing from a mechanical metallurgy aspect. That is, Pope raised this concern many years before it became a recognized problem. Pope stated as follows, "…the natural and certain tendency that frost produces upon all iron, to make it brittle, and consequently lessen its strength…".

This last point deserves special attention because of its recognized importance today in many engineering applications. It actually took more than a century to recognize the embrittling effects of low temperatures on usually ductile ferrous alloys and to incorporate them in engineering design (Siewert et al. 2000; Wright 2015b, 28; also see Briant Chap. 6, this volume). This realization was in response to a large number of the Liberty ships that suffered brittle cracking during World War II: 1500 significant cracks on 2710 ships built. Many Liberty ships were used in the North Atlantic, where winter water temperature decreased to 2 °C, which made the steel hulls brittle. Impact toughness was considered in steel design from the 1830s using drop-weight testing that provided a quantitative measure of brittleness. Charpy, a French engineer, recognized brittle failure problems in the late nineteenth century and invented a pendulum-based machine to determine the energy of fracture due to impact loading in 1901. But all these tests were done at room temperature. Epstein (1932) reported a sudden drop of impact fracture energy of low C steel at 0 °C or below, and temperature effects have been investigated since that time. This change in fracture mode became known as the ductile-brittle transition (DBT). The beneficial effect of Ni addition was found by Armstrong and Gagnevin (1940), and microstructural effects were reported by Hollomon et al. (1946). While few reports appeared during the early 1940s, Hollomon and Jaffe (1947) published a monograph, *Ferrous Metallurgical Design*, and provided substantial discussion on this topic, including strain-rate and stress concentration effects. Intensive fracture research followed in the 1950s and finally made engineers aware of the ductile-brittle transition phenomenon. George Irwin was the central figure in this fracture study, which then evolved into a new field of fracture mechanics. All current bridge designs benefit from analyses using fracture mechanics (Gdoutos 2005). Brittle failures of bridges have been recorded, but only two (out of about 160) bridge failures globally were attributed to low temperatures since 1950 (Anon 2017e). Thus, the serious consequences of the ductile-brittle transition were mostly avoided in steel bridges.

Let us now return to a chronology of more bridge failures and successes. Some chain bridges of the early nineteenth century were even more short-lived. For example, the Dryburgh Abbey Bridge over the River Tweed between Scotland and England with a span of 80 m was opened in August 1817 and was destroyed in January 1818 under a violent storm (Fernández 2003). Witnesses observed oscillatory motions of the bridge both vertically and horizontally. This demonstrated the fourth weakness Pope pointed out. This bridge was a simple one, built at minimal cost, and the deck was hardly stiff. Other bridge failures were reviewed in 1968 (Tweed 1969).

The next notable achievement appeared in 1820. The Union Bridge was completed over the River Tweed. The designer was S. Brown, who was an ex-Royal Navy captain (Kemp 1977). It was an iron chain bridge with a span of 137 m, 5.5 m width, and has remained open to road traffic even until today. Currently, this is the oldest suspension bridge in Europe. Instead of link chains, wrought iron eyebar chains were used, three each on either side (now with an additional wire rope for reinforcement). Eyebar chains were invented in 1805 in England, and Brown originated the idea of using his own patented eyebar chains for a suspension bridge incorporating it into a Runcorn bridge project proposal in 1814. By this time, he had already built a suspension bridge prototype of 32 m in length from his experience in the navy. He devised a new method for making eyebars and a unique method of linking. This can be viewed on some close-up images of this bridge (Fernández 2003 fig. 8.8) and on a contemporary sketch by R. Stephenson (Kemp 1977, fig. 2).

Another famous suspension bridge of iron chains opened in 1826 (Fernández 2003; Plowden 1974). Telford designed it to cross the Menai Strait in Wales with a span of 177 m but using a different chain design with punched hole eyebars. The length of each chain was 522 m, made up of 935 iron bars. These chains were replaced with more massive steel eyebars in 1938 to increase the loading capacity, which initially was only 4.5 t. Current chains have six eyebars for each segment and two chains are used on either side (Fernández 2003, fig. 8.10). The original eyebars were much smaller and were grouped into 16 chains with 5 eyebars for each segment (Fernández 2003, fig. 8.10). The parallel eyebar design increased the lateral stiffness against wind loading and satisfied the fail-safe requirement since the load is carried by other links even after a single link failure.

From a viewpoint of fracture design, the longer chain link or eyebar makes sense in the event that any chain or eyebar links potentially fail. With a reduced number of links and with longer eyebars instead, the probability of failure is lowered. Any given link is forge-welded and the chance of defective welding is hardly negligible. This is one of the reasons that the eyebar design approach persisted for over a century. As discussed in Appendix B, the Silver Bridge, at the Ohio-West Virginia border, which was finished in 1928, utilized an eyebar linkage design, albeit using steel components and without adequate fail-safe design elements.

In the mid-nineteenth century, wrought iron shapes of larger sizes became plentiful, and many truss bridges were constructed for normal traffic and for the railroad. In some, the design originated from wooden predecessors, while truss bridges with new designs were also introduced (Fig. 4.3b, c). The truss structures can be made with higher stiffness and avoid the vibrational instability that hampered suspension bridges. Many varieties of truss bridges were built. Even an introductory article of truss bridges lists 40 types (Brinckerhoff 2005). In terms of materials for building truss bridges, wrought iron still was the only choice until the 1870s, after which steels gradually replaced it.

Two other truss bridges are worth mentioning here (Plowden 1974). One is the Britannia Bridge at the Menai Strait designed by Stephenson. Completed in 1850, this was a tubular bridge for rail traffic and which used rectangular box-sections with two main spans of 140 m each. Tube sections were assembled using rivets. Another is Brunel's unique Royal Albert Bridge over the Tamar in England. This was finished in 1858 as a railroad bridge with two lenticular iron trusses of 139 m each. The total length was 667 m with 17 shorter spans.

Wrought iron was also used for building arch bridges, with two notable examples discussed here. The first is the 1864 Pfaffendorf Bridge in Koblenz, Germany. It had three spans of 97 m, each supported by three linked double arches. Its design was hailed at the 1867 Paris Universal Exhibition as the best railway bridge and appeared to have influenced Eads according to Kouwenhoven (1982). The last bridge of the iron era was the 1884 Garabit Viaduct in France by Eiffel with a main span of 165 m. This was for a single-track railroad, with trains passing 100 m above the river. This must have offered spectacular views on top of the bridge, albeit precariously high. See Griggs Jr. (2011) on other significant arch bridges of the nineteenth century. There was one infamous truss bridge disaster in 1876: the Ashtabula Railroad Bridge in Ohio (Weiser 2016). This was due to improper design and construction. The builder copied a wooden truss bridge and did not even join some of the steel components together as there was no inspection requirement.

It is important to examine the properties of the materials used for these bridges. Kirkaldy (1863) and Holley (1877) measured the strength of wrought iron. While their strength values are not so different from modern mild steel, the scatter was much larger. More recent studies added data on old wrought iron plates with chemical, mechanical, and microscopic evaluations. Many of the materials were from the last quarter of the nineteenth century (Buonopane and Kelton 2007; Elban et al. 1998; Elban and Goodway 2002; Gordon and Knopf 2005; Kelton et al. 2011; Sparks 2008; Wouters et al. 2009). All the reports showed the tensile strength of wrought iron plates to be between 180 and 460 MPa. Variability was high, as the wrought iron itself was not well defined in the 1850s according to Overman (1865). Some started from white iron with lower Si, while gray iron was higher in Si. By the late 1800s, quality improved, but slag content was still 5–10% (Elban and Goodway 2002; Gordon and Knopf 2005; Sparks 2008). The reduction in area also varied from 10% to over 50%. Thus, we have no good way to estimate quality without actual testing in tension since the usual correlation between hardness and tensile strength for steels is not obeyed (Gordon and Knopf 2005) and hardness-based strength estimates are often too optimistic and unreliable (Elban and Goodway 2002). This arises as hardness and tensile tests measure different properties. Hardness is the resistance against indentation under compressive force while tensile strength is the maximum applied force per unit area. Also the hardness is taken over a small volume under an indenter in contrast to the tensile testing with a bulk sample of tens of cubic centimeters. The largest of slag and other flaws within this larger volume dictates the strength as will be discussed below. A large scatter of wrought iron strength in fact reflects the presence of strength-limiting slag inclusions.

High inclusion contents in wrought iron reported in these studies (and also seen in a micrograph, Fig. 4.11d from Bauer and Deiss 1912) are in sharp contrast to low inclusion contents of ancient Chinese iron as discussed earlier (Chen 2014; Kitada 2009). This difference in inclusion contents appears to come from different fining methods used in Ancient China and in Europe and the USA during the Industrial Revolution. Chinese fining methods used pasty liquid-solid mixture in a ceramic furnace with limited contact with loose particles. On the other hand, the Western puddling method started by melting pig iron on a sand-lined hearth and generated a large amount of slag, which had to be squeezed out as was done in bloomery iron (Gordon 1996). While improvement was expected from the switch to the Bessemer method, it is uncertain how much actual reduction of inclusion contents in Bessemer steels was achieved. Inclusion reduction was achieved later by shifting to basic open-hearth steelmaking, which reduced S and P to below 0.04%. Slag inclusions were essentially gone, and remaining inclusions were MnS of less than 0.2% (Camp and Francis 1919). The topic of non-metallic inclusions became dormant until the 1950s (Wilson 1988). Only half a page was devoted to this topic in connection to fatigue strength in a 1300-page *Metals Handbook* (Lyman 1961, 224). This topic has been actively researched since then, and we now understand the deleterious roles of inclusions and have developed countermeasures (Wilson 1988).

Wire Ropes and Cables

Another essential form of iron for bridge application is wire. A foot bridge using iron wires was built in 1749 over the Tees near Durham, England, but with no technical information given (Nicholson 1829). When long, thin wires were available, these could be twisted to form wire ropes. In 1816, twisted wire cables were used for a suspension bridge at Fairmount Park, now part of Philadelphia, across the Schuylkill River (Peters 1987; Plowden 1974). It was built by Hazard and White and its span was 124 m. (From woodwork weight of 745 kg (1640 lbs), its length was about 137 m.) They owned a rolling mill and a wire factory in the vicinity. Peters (1987) suggested they probably rolled the iron wire themselves. There are two descriptions of the cables. Plowden (1974) quoted the cables as “six wires each 3/8 inch in diameter – three on each side.” Peters (1987 214) quoted the cables from

Cordier, a French tourist, as having a total diameter of 3/8 inch (9.5 mm). From the known weight of the bridge and required strength to support 1800 planks, it is necessary to have three strands of 9.5 mm diameter wires bundled together or twisted into a cable as Plowden wrote. This Schuylkill foot bridge was soon lost due to winter snow, and this form of bridge was no longer utilized seriously. While this bridge had a short life, the twisted cable may be the first modern use of wire ropes, one of the topics of this section. We begin with a discussion of the mechanical properties of wires used in these ropes and later cables.

Cold-drawn iron wires of the nineteenth century and modern steel wires are viable structural elements. When wires are drawn cold (without heating to red hot temperatures), work-hardening effects are accumulated and increase the strength of iron and steel but reduce ductility. Dufour in Geneva and the Seguin brothers in France obtained and tested wrought iron wires of different diameters in the 1820s (Peters 1987). Their data shows a general trend of increasing strength with reduced diameter. Tensile strength increased from 500 to 850 MPa when the diameter was reduced from 2 mm to 0.6–0.7 mm. These wires must have been drawn through a series of dies, receiving intermediate annealing. Diameters ranged up to 6 mm. Even at large sizes, drawing should be possible when the diametral reduction is kept small for each drawing step and water power was utilized. Most of the Dufour wires were made around Geneva, while the Seguins' wires were made in France.

Dufour's and Seguins' data given in Peters (1987) are plotted (in green curve) against the inverse diameter in Fig. 4.16. Dufour noted that tensile strength shows a relationship with inverse diameter given by

$$\text{Tensile strength}\left(\text{in MPa}\right) = 290.1 / d + 399.8,$$

where d is diameter in mm and 399.8 is a constant. Griffith (1921) found this relationship for the strength of glass fibers, and it also fitted with the strength data for metals by Karmarsch (1858). This equation still describes today's results for jute fibers and bamboo fibers (Bevitori et al. 2010; Wang and Shao 2014) and is now given a theoretical basis with Weibull statistics and weakest link theory (Weibull 1951, see below). Five more data sets at higher strength levels are also plotted in Fig. 4.16. The strength levels will be discussed later, but these data can be fitted to the Griffith equation above with different constants. Dufour recognized microscopic surface flaws normal to the applied force to be the key factor of wire strength (Peters 1987). Griffith (1921) independently arrived at this concept, that is, the strength is governed by the probability of finding the largest flaw, and developed it into a fracture theory, generally considered as a major foundation of fracture mechanics (Gdoutos 2005). Engineering historians need to note that Dufour's pioneering work, though little recognized, was a century before the seminal paper of Griffith (1921).

Changes in wire strength over the years can be seen in Fig. 4.16. Strength plotted as a function of wire diameter from five more studies is given in this figure to compare with the Dufour-Seguins data from the 1820s (the green curve). These are not directly comparable data, but general trends can be deduced. Data in purple points are for a high C steel (0.83% C, 0.59% Mn, 0.14% Si, 0.009% S, nil P) from the UK

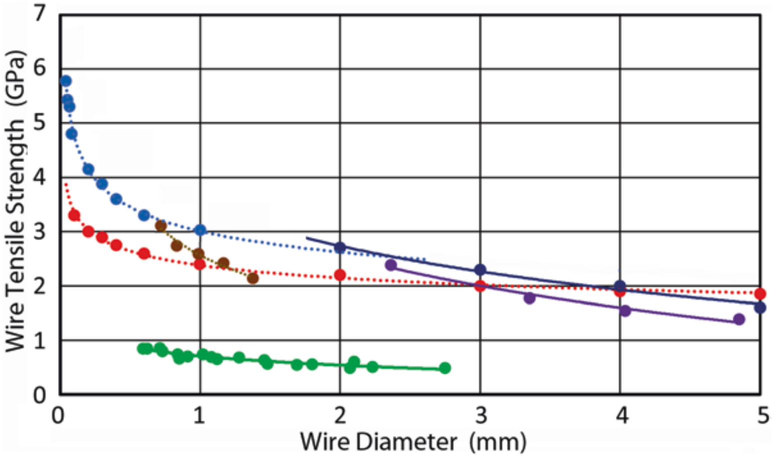


Fig. 4.16 The tensile strength of wires. 1820 data of Dufour and Seguins (Peters 1987), green; late nineteenth-century UK data (Smith 1891), purple; Watertown Arsenal 1894 data (Anon 1895), brown; spring steel wire specifications (Anon 2016), red; high C wire data (Kanetsuki et al. 1991), dark blue; high C wire data (Ochiai et al. 1993), blue

(Smith 1891), brown points are for US and German piano wires tested in 1894 at Watertown Arsenal (Anon 1895), red points are for a recent piano wire specification (Anon 2016), and two high C steel wires from Japan in dark blue and blue (Kanetsuki et al. 1991; Ochiai et al. 1993). From the 1820s to 1890s, threefold improvements can be seen for comparable wire diameters. This jump is due to the changes from iron to steel, improvements in steel quality, and from the patenting process of the 1850s. Recent data show slight improvements, but the changes are around 20% for thicker wires over a century. Note that the ASTM specifications A228 for strength (using their highest values) are lower than the data from the 1890s or at most comparable for some diameter ranges (except at 5 mm). It may suggest a lack of progress, but today's quality control procedures demand tighter property spread and other parameters such as fatigue strength and stress relaxation behavior. Continuous length of wires is another factor affecting the strength. Steel cleanliness is another aspect that needs to satisfy rigorous standards (see Briant Chap. 6, this volume).

We now return to bridge design. Following careful testing and design work, the Seguins built a model bridge of 18 m span at Annonay, France, over the Cance River in 1822 with a wire cable design of parallel wires (Peters 1987). Dufour built St. Antoine Bridge in 1823. This was a permanent installation over the Geneva ramparts with two 40 m spans that used three prefabricated cables of parallel wires on each side. The wire diameter was 2.1 mm and each cable consisted of 90 wires, capable of supporting a 113 t force. These wires had coating for corrosion protection and were spirally overwrapped with annealed iron wire (Peters 1987). Each of the builders published a book apiece in 1824, and their suspension bridge work became known, especially in French-speaking areas. The Seguins built over 180 bridges in all, while Colonel Dufour continued his military career, attaining the rank of general. A notable innovation of Dufour was a splicing method of parallel straight wires with only 50 mm overlap. This spliced wire was then overwound using thinner gage annealed wire. Surprisingly, this produced a better joint through friction than a looped and overwrapped joint. This method allowed endless wire supply based on finite length wires and minimized the bulging of cables. Smith (1891) credited Dufour's cable as the beginning of modern wire ropes in his book *Wire*, presumably being unaware of the Seguins' work.

We must be careful, here, with the use of words in order to distinguish between wire cables comprised of parallel wires, as used by the Seguins and Dufour, and wire ropes of twisted wires. In common English usage, wire cables are interchangeable with wire ropes, but twisted wire ropes disappeared from the context of bridge engineering since the mid-1840s. This is because wire cables have higher strength than wire ropes of the same size, and bridge suspension cables are used against static loads.

Wire ropes have a long history that goes back many years (Worcester 1946). The first known metal rope dated to 800 BC was found at Nineveh (today's Mosul, Iraq). The object is bound parallel wires and today is found in the British Museum. Twisted bronze wire rope of multiple helical strands from 500 BC was unearthed at Pompeii. This 4.5 m long rope is now in the Naples Museum. Wiredrawing dies have been excavated from Viking sites of ninth-century Denmark (Buchwald 2005) and also from other European sites dated to the Middle Ages. Drawing of hard steel wires was practiced in Germany by AD 1600 (Goodway and Odell 1987). In 1564, the Assay Master of the Royal Mint under Queen Elizabeth I invited a group of German wiredrawers to England. They started a wire factory at Tintern Abbey using water power and supplied other wiredrawers throughout England (Dove 1969; Lewis 1952). They hammered iron to 6 mm square rods and pulled them through wire dies with intermediate annealing in a kiln. They made 1.3 t of wires weekly as strong wires for carding were in demand for the textile trade, according to a noted wire-maker of nineteenth-century England (Bedson 1894).

By 1666, the wiredrawing technology was brought to America, according to Daniels (1893), and a commercial wire factory was opened at Norwich, Connecticut, in 1775 (Pops 2008). However, Lewis (1952) doubted American wire-makers could compete with imported wires (when available) before the Revolutionary War. In 1728, as mentioned above, a grooved rolling mill was invented by Fleuer, and wires were made by a rolling process in addition to drawing. High-strength bronze and steel wires were in demand for musical instruments, and these were highly refined by the early 1800s (Goodway and Odell 1987). It appears that medium-strength wires for bridge and engineering uses also progressed in the eighteenth century after Fleuer's invention, as this was easily adopted at various rolling mills. According to Daniels (1893), many wire rolling mills were built in post-American Revolutionary War. Such wires can then be drawn for finishing steps. In 1821, 250 t of wire was produced in the USA annually (Pops 2008).

In Geneva, Switzerland, 3–4 mm-diameter iron wires were readily available locally and from France in 1820–1822 (Peters 1987). These activities suggested supplies of iron wires were plentiful in Western Europe by the early nineteenth century, and the USA was not that far behind in wire production capabilities. In fact, wire-making was quite advanced by that time according to Nicholson (1829), who wrote a two-volume compendium of the early nineteenth-century technology. In the section on wire manufacture, he described the operation of a French factory, Mouchel at L'Aigle in Normandy in the 1820s. This factory produced 5000 t of iron wires annually, used an annealing furnace of 3.5 t capacity, and made thin iron wire down to 40 μm diameter. Fabrication techniques of wiredrawing plates were also detailed.

The original invention of wire ropes in the modern era is still unsettled. Despite the three cases noted above, this invention has been credited to Wilhelm (Julius) Albert of Clausthal, Germany, in 1829 (patent received in 1834) (Sayenga 2017). His rope was 18 mm in diameter using 3.5 mm iron wires in three strands of four-wire sub-strands and was used in 484 m-deep mine shafts in 1834 according to Verreet (2004). Verreet also noted that an Englishman named Lang received a British patent for changing the direction of individual wires in wire ropes, now known as Lang's lay (distinct from the regular lay). This was 1829, five years before Albert's German patent. This implies that wire ropes had been in wide use in England in the 1820s. In fact, Worcester (1946) described a steam plow that connects two plows by a wire rope for repeated travel on the opposite sides of a field in the 1830s. Mining engineers would surely have used such ropes together with steam engines before farmers. Another note from 1843 England pointed to Hungary and Austrian mines of the mid-1820s as the starting point of wire rope usage (Anon 1843). The Austro-Hungarian ropes used 4.6 mm-diameter wires. Three strands of five-wire sub-strands are made into a wire rope. This allowed for a 1/3 reduction in power needed; instead of six horses, the wire rope required only four horses. By this time in England, wire ropes were being used to draw railroad cars, and in 1842, England exported 12 t of wire ropes for this purpose to Belgium (Anon. 1843). Some evidence exists for Roebling, who started the first wire rope factory in the USA in 1841, concocting the initial concept of wire ropes back in Prussia in 1825–1829 (Sayenga 2009).

By 1830, wire cables, as opposed to wire ropes, had become very important for bridge construction, and many more wire cable suspension bridges were built in France. Inevitably, some of them were built poorly as new builders entered the field and failures and damages were common. France's Ponts et Chaussées Ministry directed Vicat to review bridge construction methods, and a report was issued in 1831 (Peters 1987). He was a theoretician and had only brief experience of bridge building but produced an outstanding report. He criticized various aspects and advocated improvements, including changes in iron quality control, wire manufacture, cable spinning (proposing aerial on-site spinning), and imposing waiting periods for concrete curing (up to 2 years), among others. Vicat's report introduced uniform practice in France and in neighboring countries, especially Switzerland. But the wire cable approach was rejected in the UK.

In 1834, the wire cable bridge reached another plateau with the completion of the Grand Prix Suspendu across the Sarine in Fribourg, located in western Switzerland (Peters 1987; Plowden 1974). It was built by Chaley and had a span of 274 m, the longest in the world till 1849. Chaley incorporated many improvements suggested by Vicat. Four main cables had 1056 strands of 3.1 mm-diameter wire. The cable was built up using a 20-strand segment at a time. The total weight of the cables was 2946 t. An interesting side story was that except for the French foreman, all the workers were inexperienced locals (Jameson 1835). They quickly learned the trade, built the bridge, and all survived the aerial work. An excellent construction system at work!

While many successes had been recorded with suspension bridges made with wire cables, occasional wind-related disasters continued. The Dryburgh disaster was noted earlier, but the bridge was of simple design (Anon 2017b). Also destroyed or damaged were Brown's Broughton Bridge and Brighton Chain piers (Kemp 1977). The most catastrophic failure occurred in 1850. This was the Basse-Chaîne Bridge in Angers, France (Peters 1987), noted earlier. While crossing it during a storm, 478 marching soldiers were thrown into the Maine River, and 226 of them drowned as the bridge went into violent oscillations. The vulnerability of suspension bridges to such oscillations was well known, but it was thought that avoidance of lockstep marching by the troops could prevent the problem. In this case, corrosion-induced weakening of cable anchorages also contributed to the failure (see below). Concrete-encased iron cables were thought to be protected against corrosion (as fresh concrete is highly alkaline), but cables debonded from concrete casing, and rust accumulated to 1 cm thickness at the anchorages. This bridge was of an 1832 design and the deck stiffness was inadequate. After this disaster, no suspension bridges were built in France for 20 years. Due to an inability to address these problems, after 1870, the cable anchorage system was forbidden by law.

French cable bridge technology was imported to the USA by Ellet (Lewis 1968), who studied at École Nationale des Ponts et Chaussées in Paris (1830–1831) (Plowden 1974; Peters 1987). In 1842, he built the first substantial wire cable suspension bridge in the USA, with a span of 117 m at Fairmount, near the Hazard-White Bridge of 1816, which by this time was long gone. (This bridge lasted till 1879.) Ellet next built the Wheeling Bridge over the Ohio River in 1849 (Peters 1987). This had a span of 308 m, the first to exceed 1000 feet. Twelve cables were used, each 420 m long and 19 cm in diameter, with the total weight of 1000 t. Each wire was 3.5 mm in diameter and Dufour's splicing method was used. The cables were created with parallel wires stretched along the main street of Wheeling and bundled and selvaged, that is, wrapped with thin wires, similar to Dufour's technique. However, it was built like many contemporary French bridges and lacked stiffness against wind-induced oscillations. During a storm in 1854, it was destroyed with witnesses seeing the deck raised to the level of the 20 m-high bridge towers (Reyes 2003). It was rebuilt in the 1860s and is still in active vehicular service. The National Park Service has bestowed the distinction of being the oldest suspension bridge in the USA to the Roebling Bridge of 1848 over the Delaware (Anon 1968a, 2015; Plowden 1974). It was originally built as an aqueduct but was converted to a road bridge in 1898. It was restored to the original design in 1980 and today is serving as a one-lane bridge.

The strength of wrought iron wires used in cables for various bridges has been studied. The wrought iron from an 1824 eyebar suspension foot bridge (at Wissekerke, Belgium) was recently examined (de Bouw and Wouters 2005; Wouters et al. 2009). It is of high-purity, low C (0.01%) charcoal-refined iron but with 0.14% P. Its tensile strength was 350 MPa and it had a 15–20% elongation. A part of its strength came from P in the ferrite matrix. According to Buchwald (2005), this P content raises the Vickers hardness by 20 (or 65 MPa in equivalent tensile strength). The Smithsonian Institution obtained some of the old Wheeling wires during a recent rehabilitation and examined them with modern instrumentation (Elban and Goodway 2002). Cross-sectional micrographs showed as-drawn cold-worked structures of wrought iron of low S and Mn with slag inclusions of varying distributions. The longitudinal section showed elongated ferrite grains and stringers of inclusions. These elongated ferrite grains are comparable to those in a modern low C steel, rolled 50–60% reduction (Anon 1972, 9). Larger (ca. 25 μm) inclusions were of iron oxide and smaller ones (5 μm) were mainly alumina. The researchers determined Vickers and Rockwell hardness values for these materials. These hardness values can be correlated to its tensile strength in ductile structural materials. The Vickers test uses a diamond indenter and the Rockwell-B test uses a 1.59 mm diameter steel ball as an indenter. Their Vickers results were reported to be about 230 and their Rockwell-B hardness values were approximately 85. The latter corresponds to a tensile strength of 250–400 MPa using the data of Gordon for the late nineteenth-century wrought iron plates (Gordon and Knopf 2005). Elban and Goodway (2002) noted that the bridge builder, Ellet, specified the strength of the suspension wire exceeding 50 tons/in^2 or 690 MPa. Clearly, he was overly optimistic for wrought iron of the 1840s, but the same hardness of 230 Vickers corresponds to a 735 MPa tensile strength for today's iron (Lyman 1961). Vickers hardness of high-purity iron (99.99%) was reported at 49, along with the tensile strength of 198 MPa (Cleaves and Heigel 1942). Kusakawa and Ohtani (1964) reported a Rockwell-B hardness of 10 for an annealed high-purity iron (presumably zone-refined). A recent test conducted by the author at UCLA gives a Vickers hardness of 104 for a heavily cold-rolled zone-refined iron (99.99%) sheet, probably from the same source of the late 1960s. Thus, a Vickers hardness above 104 should be treated as coming from additional hardening mechanisms to the ferrite matrix. The hardness value for the Wheeling wire is more than double the cold-worked pure iron, and this difference arose because of typical C contents of wrought iron of 0.02–0.05% (Holley 1877) and the presence of non-metallic inclusions. In modern commercially pure iron (e.g., 99.9%-Ferrovac E iron), the nominal C content is at 0.01%. UCLA samples of Ferrovac E have an annealed hardness of 105 and cold-worked hardness of 305 Vickers. In the case of a mild steel with 0.2% C, Ripling (1974) obtained Rockwell-B hardness of 98 and a tensile strength of 433 MPa, and the tensile strength further increased to 725 MPa after 50% rolling. As is well known, a small addition of C has a strong effect on the strength of wrought iron.

Moving beyond the French base of cable bridges, Roebling developed American cable bridge technology starting in the 1840s (Plowden 1974). He was an engineer of extraordinary talent. After coming from Prussia in 1831 with technical training and work experience as a civil engineer, he started wire rope making in rural Pennsylvania, at Saxonburg, the colony of 1600 acres he started with other German immigrants (Buonopane 2007; Güntherroth 2006; Gibbons 2006). In 1841, he developed a wire rope-making method, obtaining a patent for the process (US patent 2720, 1842). Roebling's initial 19-strand wire ropes (Gibbon 2006) were soon combined into more substantial rope, twisting together seven of the 19-strand ropes with over 50 mm diameter size. This was supplied to Allegheny Portage Railroad (APR) operating ropeways (aka inclined planes at that time) along the national road, replacing hemp ropes (Gibbon 2006; Sayenga 2009). For the commemoration of Roebling's 200th birthday, this rope was reproduced in stainless steel wires. A section is displayed in the APR Museum, Cresson, PA. According to his son's memoir (Sayenga 2009), he tried parallel wire rope first for the APR project with utter failure. He was next challenged with building the Allegheny Aqueduct in Pittsburgh (1844–45). He used suspension bridge technology for supporting the water-carrying channel. Each cable of 18 cm in diameter used 1900 parallel iron wires of 360 m in length and 3.2 mm in diameter, which were bundled and selvaged (continuously wrapped with annealed iron wire for corrosion protection) using a machine. This cable design originated in France and Ellet used it at Fairmount according to Plowden (1974). Ellet and Roebling met in the winter of 1840–1841. Plowden (1974) quoted Roebling's letter objecting to the French method. His son stated that Roebling learned the French method previously in Prussia (Sayenga 2009). Anyway, Roebling used parallel wires in cables at Pittsburgh and this appeared in his 1847 patent (US patent 4745) (Gibbon 2006). Apparently, he changed his cable design approach, although his criticism of Ellet could be only for pre-assembly of cables, which he avoided to prevent misalignment. All of the wires were made in Pittsburgh, which had a thriving iron industry (Gibbons 2006).

After building more aqueducts, in 1851 Roebling directed his energy to the Niagara Falls Railroad Bridge with a suspension design (Plowden 1974; Wood 2012). This was started by Ellet, who built a temporary cable bridge but who was ousted from the project. Roebling built a two-level wire cable suspension bridge of 251 m span. It was supported by four main cables of 25 cm diameter. The upper level was for a railroad crossing. The lower level was surrounded by a wooden truss, also supported with stays, gaining the stiffness needed against resonant oscillations. An old lithograph (Parsons 1857) also shows many guy wires from rocky shores below, presumably to suppress unwanted vibration. For this bridge, Roebling introduced aerial spinning of the cables. This appears to be his original invention, although Vicat proposed this method in 1832, as noted earlier. In those days, it must have been hard for Roebling to obtain Vicat's report, though he was fluent in French (Sayenga 2009). Roebling devised a mechanism to lay wires back and forth, and his invention has been used to this day. A figure in Okukawa et al. (2014, fig. 18.28) best illustrates how this method works and more details can be found in Takeno et al. (1997). After two more major bridges to his credit (a total of ten in his lifetime), Roebling designed the Brooklyn Bridge. He started surveying for the location in 1867 when he suffered an injury that claimed his life within 24 days. His son, Washington, succeeded him in the project and completed it in 1883 (Sayenga 2009).

The Brooklyn Bridge was indeed the next monumental bridge to be constructed. It was a suspension bridge using steel cables, crossing the East River with main span of 486 m. The four cables were 40 cm in diameter and 1150 m long. As was done at Niagara Falls, aerial spinning was used to install parallel wires. Wires for the cables were of galvanized steel of 4.2 mm in diameter with 1.1 GPa tensile strength. The initial plan was to use 5434 wires in 19 strands to provide a safer cable strength 3.6 times that of the expected load, but 150 more wires were added after discovering a fraud by the wire supplier, which submitted wire from elsewhere for initial supplier evaluation and also sent in wires rejected by the inspector. The wires were to be of crucible steel, a process discussed below, but a large fraction was of inferior Bessemer steel. The total amount of wire was 3100 t, so it was costly to produce this tonnage by the crucible method (Talbot 2011). Broken wires from the Brooklyn Bridge were later tested (Sluszka 1990) and the carbon content was 0.55–0.91%. The tensile strength was 1.1 GPa as specified, but the reduction in area was 0–26%, indicating that some wires were completely brittle. This study included no microstructural examination, but the strength level was probably achieved through air cooling from a high temperature (~800 °C or normalizing) and wiredrawing with tempering while passing the wire through a molten zinc bath. After 100 years, most of the galvanized zinc layer was gone and serious corrosion was found at many locations, especially at anchorages. Rehabilitation was completed for the cables in 1990 and for corroded deck steels in 2016.

The strength of structural wires improved starting from cold-drawn iron wires of the 1820s, used by Dufour and the Seguins and early steel wires used by Roebling in the 1880s. Around the 1820s, steel music wires started to be made using crucible steels, and there was some overlap in the individuals and technologies between the music wire and structural wire industries. A wire manufacturer, Webster's Penns Mill of Birmingham, England, used a Mn-containing steel from 1823 and dominated the European music-wire market for a while, followed by Müller (Vienna) and later by Pöhlmann in Germany (Hipkins 1883; Horsfall 1971). This use of Mn is a curious one as only a handful of people produced alloy steels then: Huntsman, Faraday, and Sheffield and affiliated craftsmen. On April 5, 1823, Webster's foreman, John Bird, overheard two Sheffield men discussing the merit of Mn addition to crucible steel while traveling on a coach. Bird immediately returned to Penns Mill and discovered an excellent steel formula (Horsfall 1971, 71), which they exploited in the music wire business.

Next came James Horsfall, also of Birmingham (Krauss 2015; Lewis 1952, 1969). He was listed as a wiredrawer in an 1847 directory but succeeded in greatly improving wire strength by inventing the Horsfall process, later known as the patenting process. He exhibited his music wires in the 1851 Crystal Palace Exhibition in London (Mactaggart and Mactaggart 1986, 31). Besides steel wires for piano, needles, and fish-hooks, he showed "new patent brass strings." Between 1854 and 1858, he obtained three British patents for improving wires for wire ropes and musical instruments. Apparently, he was successful in the music wire business in the early 1850s since securing a single patent was estimated to cost £110 (equivalent to £110 k today) (Bottomley 2014). In 1855, Webster and Horsfall formed a partnership and expanded Hay Mill factory with a sign that read *Webster & Horsfall's Patent Steel Wire Works*. "Patented" wires seemed to originate from this commercial naming. By 1905, "patented wire" was recognized in the *Encyclopedia Britannica* as "wire that was tempered by the Horsfall process."

Details of the Horsfall process or patenting were not evident in the only available patent document, British patents (BP) 1594 (Horsfall 1856). Three key steps in BP1594 were the following: (1) heating steel wire to redness and suddenly cooling it, (2) tempering in a molten lead bath, and (3) reducing wire diameter with cold-drawing. Only the titles of BP1104 (Horsfall 1854) and BP2486 (Webster and Horsfall 1858) are available. BP1104 was for music wires, while BP2486 referred to steel wire improvement. A later source (Harmonious Blacksmith 1869) implied that BP1104 described a process of hardening and tempering, followed by drawing wire through dies. Thus, the step of lead-bath tempering was added in BP1594. It seems natural that BP2486 progressed to quenching directly into a lead bath for tempering, avoiding the cooling-reheating steps. This is the patenting process we know today, which includes two important elements of direct quenching into a lead bath kept at a tempering temperature and of cold-drawing of hardened steel wires. The first element is now called the isothermal phase transformation where a high-temperature phase (called austenite) is converted to a very fine mixture of ferrite and carbide (pearlite) at a constant temperature. This mixture was originally called sorbate. The other element is Horsfall's recognition that a hardened steel wire can be cold-drawn to impart the strength beyond that of a simply hardened wire. This is indeed a revolutionary concept. However, this second part of Horsfall's invention is usually separated, and "patenting" indicates only the first step (Krauss 2015). Hopefully, Horsfall's contribution for combining the two processes will be rightly recognized.

Because wiredrawing processes occur mostly under compressive stresses, a large strain of 100–400% can be imposed in comparison to tensile deformation where hardened wires break after 5–20%. Heavy drawing can more than double the tensile strength of wires above that obtained by heat treatment (Kanetsuki et al. 1991; Tarui et al. 1996). These two elements combined led to a big jump in wire strength. The strengths of patented Webster-Horsfall wires were reported to be 1.3–1.9 GPa in 1862 as opposed to 1.2–1.4 GPa for heat-treated wires of other wire-makers (Shelley 1862). Wire diameters were not listed in this latter publication, but the report was on wire ropes, and the strength values may have been obtained on wires of 2–4 mm range. For such wires, the strength levels were within 15 to 30% of today's spring wires (red curve in Fig. 4.16). Thus, the Horsfall process already achieved the essential goal of patenting. Moreover, Webster-Horsfall apparently succeeded in keeping the secret of patenting for some time. Smith (1891) and Lewis (1919) described patenting methods in their books, but incorrect processes were mixed in. Eventually, other wire manufacturers had developed their own secret processes. In 1883, Pöhlmann (Nurunberg, Germany) had achieved wires with the strength of 1.71 GPa, Müller (Vienna, Austria) had achieved 1.54 GPa, and Webster-Horsfall

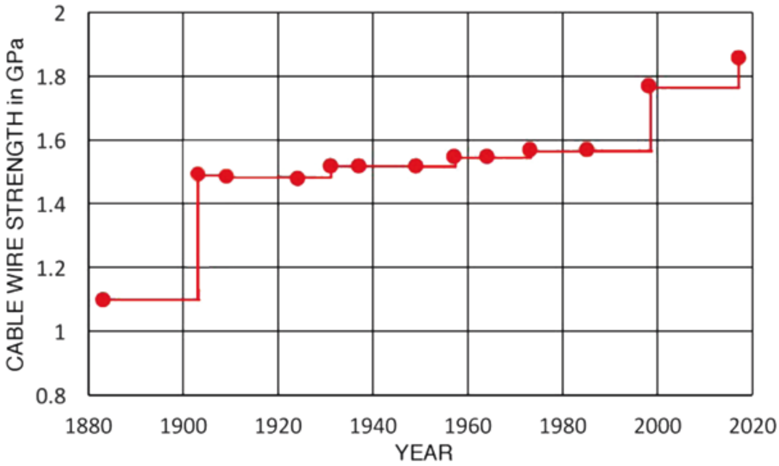


Fig. 4.17 The tensile strength of cable wire steel used in suspension bridges vs. year of their completion. (Sluszka 1990; Tajima 1987)

had achieved 1.44 GPa for piano wires of 1 mm diameter. The European competitors had 16% and 7% higher values (Hipkins 1883). Although no metallographic study can be found for Horsfall wires, the microstructures of modern patented wires can be found in Roffey (2013) and in Morgado and Brito (2015). These wires were from the Forth Road Bridge and a collapsed Portuguese bridge. All their micrographs show stretched fine pearlite structures of several microns widths.

In 1865, Webster-Horsfall supplied 1600 t of patented wires for the fabrication of the transatlantic cable and then delivered another 1600 t due to the loss of the first cable during installation. The wires were of modest strength at 1 GPa at 2.4 mm in diameter (Anon 1945). By the 1870s, continuous wiredrawing processes were developed, increasing the productivity (Lewis 1952). Piano wires were also applied to other uses when Lord Kelvin noted their potential in deep-water sounding applications in 1890 (Goodway and Odell 1987). The strength of bridge cable wires also improved. In addition to patenting, the use of open-hearth steelmaking was a major factor in the improvements. Here, the use of lime as flux or as furnace liner contributed to the reduction of P and S contents (Anon 1964; Camp and Francis 1951). Figure 4.17 plots the wire strength of suspension bridge cables starting from 1.1 GPa for the Brooklyn Bridge. The strength jumped to 1.5 GPa in 1903 for the Williamsburg Bridge (Sluszka 1990). After 85 years, actual measurements and statistical study revealed the Williamsburg Bridge wires had retained the initial strength of 1.5 GPa (Perry 1998). This was surprising, especially because the Williamsburg Bridge wires were not galvanized. The Manhattan Bridge (finished in 1909) had wires tested at 1.45 GPa, a 32% increase over 1883 Brooklyn Bridge wires (Tajima 1987). However, the design stress was still kept nearly unchanged. For the Golden Gate Bridge (1937 completion), the actual tensile strength reached 1.6 GPa (nominally 1.52 GPa) and the design stress was 67% higher than in the Brooklyn Bridge (Anon 2006a). The wire steel contained

0.81% C, 0.66% Mn, 0.24% Si, 0.026% P, and 0.03% S. This level of S was the best possible at that time as further reduction only occurred in the 1970s (Wilson 1988). This wire took advantage of the strengthening effects of Mn and Si and the patenting process was updated (Camp and Francis 1951), since quench-and-temper steel of a similar composition only gives 1.3 GPa tensile strength (Tweedale 1987). From 1903 to 1998, the wire strength slowly increased by 5%. Then, in 1998, it jumped 12% for the Akashi Kaikyo Bridge. This jump resulted from a new nanostructural innovation, to be discussed below.

The strength level of steel wire remained about the same for most of the twentieth century. Then, it jumped to 1.78 GPa and allowed for the Akashi Kaikyo Bridge in Japan to reach a 1991 m span (Kitagawa 2004). (It was built at 1990 m, but the 1995 Hanshin earthquake made it 1 m wider.) Two cables were used with 50 kt of wire. The higher strength wire usage saved 9 kt in comparison to 1.6 GPa wire. Regarding chemical composition, the main difference for this grade was a higher Si content. Si content was 0.24% for the Golden Gate wire (Anon 2006a) and this was raised to 0.9% (Tarui et al. 1996, 2003, 2005). The roles of Si are twofold. One is to add strength to ferrite. The other is to suppress coarsening of thin carbide layers during the galvanizing process, which exposes the drawn wire to a 450 °C zinc bath. This effect comes from the segregation of Si to 10 nm-thick zones at ferrite-carbide interfaces. These Si layers also reduced carbide fracture during drawing, making ferrite layers of less than 50 nm thickness possible and contributing to the development of wires with tensile strengths above 2 GPa. Such details can now be obtained using three-dimensional field ion microscopy (Sakon 2007). See a review by Lesuer et al. (1996) on other alloying effects.

The next step of using 1.9 GPa wire was for the Hong Kong-Zhuhai-Macau bridge in China, finished in 2018. This is for a cable-stayed section, nearer to the mainland. A cable-stayed bridge is like a suspension bridge, but cables are used to directly support a deck. This principle was used by Roebling to give more stability to the Niagara Falls Railroad Bridge. It allows designers new ways to seek efficiency and aesthetics. In terms of material usage in tension, this is identical to suspension bridges. See Fernández (2003) for more details on recent cable-stayed bridges and on increased reliance on concrete structures that are reinforced by advanced steel bars and cables. These steels for high-strength wires can be further strengthened by adding 0.2% Cr, reaching 2.0 GPa (Tarui et al. 2005). This was already developed in 2005, so its use is expected soon.

We close this section by considering two related problems that often are observed in the wires used to make ropes or cables. As indicated above, engineers must be aware of surface defects when predicting the strength of these wires. The most common way to analyze this effect of defect is through the Weibull (1951) probability distribution function, which is discussed in Appendix C. It was applied to several cases of yield, tensile, and fatigue strength values as well as British adults' height data and sizes of beans. This function has found many applications since, incidentally including archaeological analyses, such as use-life distribution of ethnographic artifacts and survivorship distribution of stone tools (Shott 2016; Shott and Sillitoe 2004). In bridge engineering, it is used in the prediction of bridge cable strength (Mayrbaurl and Camo 2004) and that of bridge deck remaining lifetime (Riveros

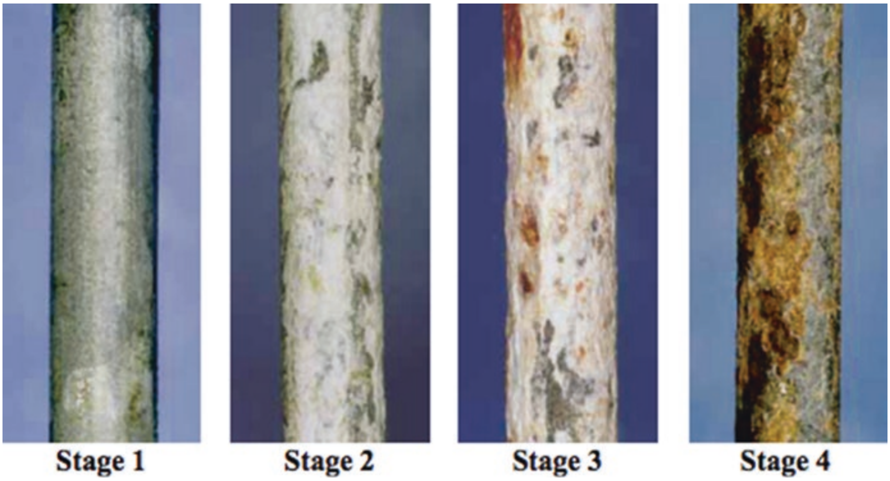


Fig. 4.18 Cable wires subjected to corrosion at different stages, as defined in NCHRP report 534. (Chavel and Leshko 2012)

and Arredondo 2010). However, it appears difficult to predict the lifetime of cable wires, since it is critically dependent on corrosive effects of the environment which can cause many surface defects.

The second critical problem is corrosion. Corrosion problems have existed ever since large-scale uses of iron and steel began. Paint, zinc, and other coatings, grease, oil, tar, and red lead (Pb_3O_4) paste, were some of the remedies that were applied as well as overwrapping cables with wires or metal sheets (Chavel and Leshko 2012; Hopwood and Havens 1984a, b). As the median age of US bridges approaches 40 years (Anon 2012), more effective evaluation of corrosion effects has become urgent. One approach is the use of Weibull statistics as mentioned above, adapted by the National Cooperative Highway Research Program (NCHRP) report 534 (Mayrbaurl and Camo 2004). Here, corrosion effects are categorized visually, classifying the condition into four stages, as shown in Fig. 4.18. Stages 1 to 4 are defined as follows:

Stage 1 – No corrosion (spots of zinc oxidation).
Stage 2 – White zinc corrosion product present (on entire surface).
Stage 3 – Occasional spots of ferrous corrosion (up to 30% of surface).
Stage 4 – Larger areas of ferrous corrosion (more than 30% of surface).

When the strength levels are determined for corroded samples at Stage 3, the average strength value was only reduced by 2–5%. Even at Stage 4, the reduction in strength was 6–11% compared to new or Stage 1 or 2. Distinguishing these levels of changes is quite difficult. Mayrbaurl and Camo (2004) introduced a constant in the Weibull function, called a shape parameter, for this task, since this has proven useful in predicting the quality of any structural element. Low values of the shape parameter (below 10) typically indicate brittle behavior, as in ceramics and in high-strength glass and carbon fibers, while ductile alloys have shape parameters of 90–100 (Meyers and Chawla 2009). In a specific case of evaluated cable wires from a bridge, the shape parameter was 70.6 for wires at Stage 1 or 2, 52.4 at Stage 3, and 33.4 at Stage 4. These had the tensile strengths of 1.65, 1.63, and 1.59 GPa, respectively. When wires deteriorated to show cracks, the shape parameter was down to 9.1 even though their strength was 1.38 GPa (Mayrbaurl and Camo 2004). When the data of the Williamsburg Bridge (Perry 1998) is subjected to Weibull analysis, the shape parameter of 36.8 is obtained, indicating the wires suffered corrosion effects. Steps of this analysis are given in Appendix C to show that procedures require only basic mathematical operations. These statistical analyses of cable wires are then applied to the prediction of the load capacity of bridge cables (Perry 1998; Mayrbaurl and Camo 2004), which is critical information for the safety and maintenance of bridges.

Experiences and lessons of the inspection and rehabilitation of parallel wire cables of suspension bridges have been assembled into NCHRP report 534 (Mayrbaurl and Camo 2004), which has a section detailing the splicing of new wire segments into a broken one. Photographs of such procedures can be found in Colford (2013). These show the repair of the cables for the active Forth Road Bridge, which was 40 years old at the time of repair. Colford also showed how a cable can be split open using wedges in order to reach inner wires. Severe corrosion evident in the wires indicates the need for rigorous corrosion protection measures. Most of these wrought iron cable suspension bridges suffered from corrosion and had to be rebuilt or rehabilitated. In the nineteenth century, the concept of corrosion protection was relatively primitive using oil or tar applications, if protection was applied at all. For example, the continuous zinc-coating method was only invented in 1860 (Hopwood and Havens 1984a).

Galvanizing, or coating steel with a thin coat of zinc, is currently the most common method of corrosion protection of steel. For bridge cables, it was first suggested in 1843, and a continuous hot dipping process was patented in 1860 (Sayenga 1999). In this method, steel wire is passed through a molten zinc bath. Hopwood and Havens (1984b) discussed galvanizing for bridge cables. Note that tinning was invented in 1620, but tin is much more expensive and impractical (Swank 1892).

Corrosion of cable wires remains a challenge as alloying options are limited. A new technology was introduced at Akashi (Saeki and Kawafuji 1998; Kitagawa 2004). This was to seal the cables using neoprene tape and dehumidify the inside by dry air injection, keeping the relative humidity under 40%. Kitagawa et al. (2001) estimated that in dry air it takes 184 years to consume zinc coating applied on the cable wires galvanized at 350 g/m^2. This method has proven effective and has been used inside and outside Japan, especially on older bridges as retrofit. These included the Chesapeake Bay Bridge and Humber Bridge (Beabes et al. 2016).

Steel Bridges

While many of the wires discussed above were steel, we now turn our attention to bridges where steel was employed in many different types of designs. The Eads Bridge crossing the Mississippi at St. Louis was opened in 1874, heralding the era of steel bridges (Kouwenhoven 1982; Plowden 1974). It was not all steel construction as the iron tonnage was higher than the steel (3158 t vs. 2390 t), but the steel used was revolutionary (Miller 1979). It was a high carbon steel (0.64–0.8% C) containing 0.45–0.61% chromium (Cr), the first large-scale application of an alloy steel. These compositions were average values of two separate analyses in 1928 and 1978. However, the designated steel supplier, Butcher Steel Works of Philadelphia, could not supply the steel used for staves, and no definitive record seems to exist as to who produced the steel. Four sources (Kouwenhoven 1982; Miller 1979; Murphy 1984; Tweedale 1987) gave different accounts. The Cr steel was used for 6216 staves inside a riveted iron sheet shell (6.4 mm thick) for 46 cm-diameter tubular sections of arches. The tubular sections were made like a wooden barrel, except with six long, curved staves and the continuous iron shell acting as hoops. Eads' document gave the arch section length of 3.65 m. In the shorter spans, 42 and 43 sections formed the upper and lower arches, while the longer mid-span had 44 and 45 sections as seen from an old drawing (Collins 2014; Gerhard 1880), and the span lengths were 153 and 159 m, respectively. The total number of arch sections was listed as 1026 (Miller 1979), but actually it was 1036. The thickness of the staves varied from 2.5 to 5 cm depending on the position, the thickest one at the base, and the weight was from 200 to 400 kg (Miller 1979). A total of 12 double arches were used, 4 to each span. The steel needed for the staves amounted to 1900 t (about 80% of the total steel tonnage). Two arches forming a double arch were vertically separated by 3.65 m and linked by iron bracing bars, reminiscent of the Pfaffendorf design (Kouwenhoven 1982). This design is also called a latticed arch. Note that Murphy (1984) provided many photographs showing construction details.

We need to consider the origin of chrome steel. Baur patented a method of making Cr steel in 1865 (Tweedale 1987; McCosh 1984), but actually it was Faraday who first made Cr steel in the 1820s (Hadfield 1932). Some cite his early papers (Keeney 1914; Rollinson 1973; Skrabec 2006), but Cr steels were not studied in depth by Stodart and Faraday (1822). The main alloying element in Faraday's material was Ni. Faraday's samples and records were examined by Hadfield (1932) over a century later. Faraday produced 0.5% and 2.4% Cr steels with high C contents, producing 725–970 MPa yield strength, as estimated by Hadfield. Indeed, it would seem that Faraday was the original Cr steel developer! From these early works, crucible steelmakers at Sheffield refined alloy steels and enlarged their operations, becoming the primary source of high-strength steel products for America (Barraclough 1990; Tweedale 2012, 1987). Krupp in Germany was another such source (Manchester 1968). Baur's method was presumably to add ferrochrome to a crucible with iron, but he apparently thought that the role of Cr was to be a replacement of C. Eads accepted this erroneous reasoning and paid $15,000 to Baur's

Chrome Steel Works in New York and secured a license to produce Cr steel at Butcher Steel Works in Philadelphia. However, Butcher, who apparently came from Sheffield in 1865 with experience of making crucible steels, was unable to produce chrome steel. As a subcontractor, he was to supply 2400 t of this new alloy to Eads through the Keystone Bridge Co. This steel was intended initially for bolt applications. This inability to fulfill the terms led to the cancelation of the Butcher contract, and Keystone turned to its home base, Pittsburgh, according to Tweedale (1987). Keystone's vice president was Carnegie, who already had his own steel mill in Pittsburgh. Although it did not have the recognition of the huge iron and steel industry, Pittsburgh had been the center of the specialty steel industry in the USA, just like Sheffield in England and Essen in Germany.

The reason why Butcher was involved in the first place is explained due to the financial arrangements for the bridge, which were conducted through Philadelphia. The use of Butcher steel was a condition set by Philadelphia financiers for emergency funding for Eads and for helping to sell mortgage bonds in London (Kouwenhoven 1982). Further details, especially where the steel components were produced and who was involved, became unclear. The most likely location was in Pittsburgh, where an English steelmaker was brought in to successfully produce the steel staves with crucible steel by casting (Miller 1979). Presumably, the license from Baur was transferred to the Pittsburgh operation. Murphy (1984) assigned this to Butcher, while Tweedale (1987) thought it went to Midvale Steel Works under W.R. Durfee. However, Midvale Steel Company records at the University of Pennsylvania Library indicated that Butcher was their president till his death in 1871, and Brinley was brought in as the steelmaker (Anon 2006b), after which the company thrived for a century as a special steel manufacturer till 1978. Their factory was always in Philadelphia. It appears that all these sources incorrectly identified William Butcher in Philadelphia as the same founder of W. & S. Butcher in Sheffield, when actually it was his son, William, Jr., working in Philadelphia. By the late 1860s, William Butcher, Sr., was in ill health, and his biography in W. & S. Butcher mentions no direct involvement in Philadelphia as the founder of Butcher Steel Works (Tweedale 2012). In fact, the biography noted that W. & S. Butcher had a subsidiary, Philadelphia Steel Works, which was sold when William, Sr., died in 1870. The Philadelphia William Butcher was the son, William, Jr., born in 1836. He had a business failure in 1863 with a debt of £23,000 before coming to the USA (Tweedale 2012), and it is unlikely that he had been trained as a steelmaker in Sheffield.

Despite the lack of details of manufacture, 6216 staves in Cr steel were delivered to Eads starting in May 1872 since six staves were needed for each of the 1036 sections (Griggs 2011; Murphy 1984). These were ordered to have the strength of 415 MPa, and all passed the testing. Eads required 100% testing (Miller 1979), but it is unclear what kind of testing was conducted since even hardness testing machines were unavailable at that time. Eads' initial requirements for iron and steel components are given in Miller (1979). For wrought iron, he required 345–622 MPa (50–90 ksi) and for steel 622–690 MPa. As discussed in the previous section, these strength levels for wrought iron or steel were unrealistic in the 1860s. For steel components, it was challenging enough to melt, cast, and fabricate these large parts. Eventually, many specifications were changed as the project moved forward. Besides, requiring a high tensile strength for compressively loaded arch components is not essential, except for forcing good quality control practice. The Eads Bridge remains in service with some restoration work, so the construction approach used is fully validated, and Eads' demands and adherence of high quality raised the US industrial standards ever since.

As for the use of chrome steel, later chemical analyses in 1928 and 1978 (Miller 1979) showed low levels of S, 0.009–0.022%, indicating charcoal-smelted iron as the starting stock. The amounts of Mn and Si were also low, 0.11–0.18% and 0.10%, respectively, again indicative of charcoal iron. The uniformity of C and Cr was remarkable for the early days of alloy steel manufacturing. Ready availability of ferrochrome for Eads' project in the 1870s is surprising, but apparently blast furnace smelting was applicable for its manufacture (Anon 2017a). Since chromite is a co-oxide of Fe and Cr, $FeCr_2O_4$, this should also be reducible by adding it to molten pig iron. While this ore was discovered in the USA in 1811, Turkey was the major supplier of chromite by 1860 as various chrome compounds were found to have many industrial uses (Anon 2011). Chief among them were yellow and orange pigments for paints from the 1820s. Chrome yellow paint has been seen everywhere in the USA covering school buses since 1939. Chrome yellow and orange were also used as cloth dye, especially popular in 1840–1850, as their commercial production started in the 1840s (Brackman 1989; Ono 1994).

A further note on crucible steel is needed here. Crucible steelmaking in the USA started in the mid-eighteenth century in New England. In Pennsylvania, 13 steel works were producing 1600 t in 1831 and 6078 t in 1850 (Swank 1892), and by 1867, there were six companies each with an annual production capacity of over 5 kt. For the USA, total output exceeded 30 kt in 1870, reaching 105 kt in 1900 (Tweedale 1987). Basically, this process uses a refractory pot, in which iron and carbonaceous raw materials are sealed. The pot is next heated in a high-temperature furnace, and the content is melted to form a steel. The product is solidified in the pot or by pouring into a mold for further working. When temperatures were below the required 1400 °C to melt the steel, steel was formed via solid-state diffusion of C into Fe in the method known as cementation, a process practiced in antiquity. In order to make cast steel components, however, steel must be molten, requiring these high temperatures. This method was utilized in South Asia by the third century BC (wootz steel), and the process was also known in Roman and Viking Europe (Balasubramaniam et al. 2015; Marshall 1951; Williams 2012). Modern European crucible steel started with Huntsman in Sheffield in 1741 (Tweedale 1987). By 1850, Sheffield annually produced 40 kt of specialty steels of various kinds. The skills and scale grew, for example, a 250 t ingot was poured from multiple crucibles, after which it was divided into smaller billets of high uniformity. The methods were kept in secrecy aided by division of labor to specialized trades. Still, steelmakers of various levels immigrated to Pittsburgh, partly lured by higher pay, and contributed to the city's development of these processes.

The first all-steel bridge was built in 1879. It was the Glasgow Steel Bridge in Missouri for Chicago & Alton Railroad (Plowden 1974). There were five spans with a truss structure. The material was mild steel, supplied by Carnegie's Thompson works that used the Bessemer process. The builder, General Smith, commented that it had 50% higher strength than wrought iron and more consistent properties, especially at low temperatures. Steel (and iron) strength of this period was highly variable (Sparks 2008), so it is difficult to estimate what level was achieved for this bridge. The comment on low-temperature behavior reflects high non-metallic inclusion contents in wrought iron, as noted previously. When non-metallic inclusions are reduced, mild steel has a higher ductile-brittle transition temperature by 30–40 °C compared to low carbon iron (see Briant Chap. 6, this volume).

The period of 1850 to 1880 witnessed the introduction of new methods of steelmaking in the Western world (Barraclough 1990). The Bessemer process uses the injection of air into molten pig iron. Oxygen reacts with carbon in iron and causes the metal to boil, reducing the C content in a short time (15–25 min). While steelmaking time and costs were reduced, impurities like P and S were not removed and nitrogen was added, causing cold brittleness problems. That is, Bessemer steels cracked upon cold working (Misa 1995). Another process, Siemens-Martin steelmaking, utilized a regenerative open-hearth furnace allowing high gas temperatures to 2000 °C with high thermal efficiency, which slowly oxidizes C in molten iron, thereby controlling the C content of steel well. Using a suitable flux such as lime, it can reduce P and S impurities (Misa 1995). Bessemer and Siemens-Martin (open-hearth) steelmaking started in the USA in the mid-1860s (Swank 1888). In 1876, 526 kt of Bessemer steel was poured and 21.5 kt of open-hearth steel was produced. For that year, crucible steel production (at 35 kt) was higher than that of open-hearth steel (Tweedale 1987). By 1880, the price of steel dropped sufficiently, making it competitive with wrought iron. With higher strength and consistent ductility (except at low temperatures), steel became the primary structural material for bridges. Bessemer steel production rapidly increased, reaching 1.07 Mt by 1880 and 6.69 Mt in 1900. Open-hearth steel growth lagged, with 101 kt in 1880 (but more than

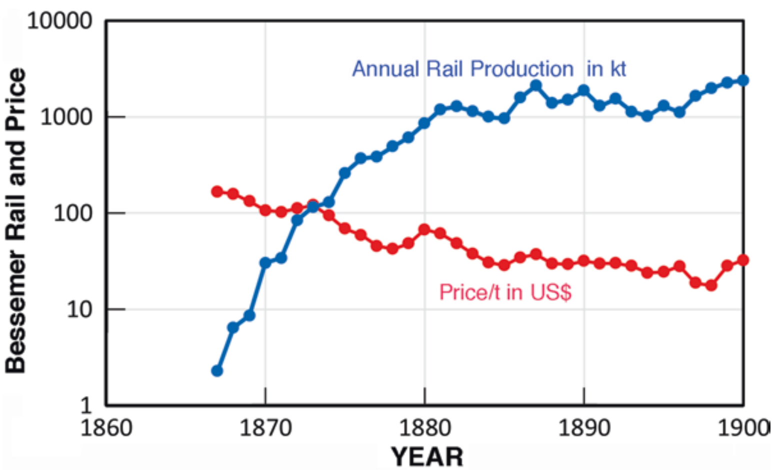


Fig. 4.19 Annual production of Bessemer steel railroad rail and its price in US$ per t. (Data from Swank (1901))

crucible steel's 65 kt) and 3.4 Mt in 1900. Still, the total steel output reached 10 Mt. Concurrently, the price of steel, represented here by rail, decreased steadily, as Fig. 4.19 shows. Steel bar price ($25/t) was still higher than iron bar price ($16/t) according to the data for 1900 (Swank 1901).

In Europe, the Forth Rail Bridge in Scotland initiated the steel era in 1890. It was a cantilevered design with two 520 m spans and three massive trussed superstructures (Fernández 2003; Plowden 1974). The bridge required over 50 kt of steel, joined together by 6.5 million rivets. (Arc welding was invented in 1881, but not practical yet.) The steels used here were made by open-hearth furnace or the Siemens-Martin method. Tubular components for the four towers in the middle were riveted together from curved plates. Riveting for towers and other truss elements had to be done as high as 90 m above the water (Magee 2007). According to Plowden (1974), several small bridges used steel, at least partly since 1828. However, steel uses were limited because of its high cost, having to be made by decarburizing pig iron or carburizing wrought iron at that time.

In the USA, some wrought iron bridges were still built for short spans, but steel increased its share with longer spans, which benefited more by reduced weight from higher strength. This change over was in part dependent on the availability of high-quality steel. Often, builders had to use steel only for critical components. As more and more steel was produced by the open-hearth method, after 1900, the quality and quantity problems started to diminish. One reason for better quality with the open-hearth method is easier composition control. As this is a slow process taking hours, real-time chemical analysis was possible. With the Bessemer process, steelmaking is done in 15–25 min, so there was no time to adjust chemistry or properties while the metal was molten. By 1907, the open-hearth steel reached 50% of all purchased steel market share, going to 80% and 90% in 1920 and 1950, respectively (Anon 2017d).

In the first half of the twentieth century, steel properties and qualities continued to improve. In part, this was due to consolidation of the steel industry, the steel monopoly orchestrated by Carnegie and Morgan. The scale of facilities, mostly the open-hearth type, became larger to accommodate increasing demands (albeit with periodic slumps), with steel production hitting the 80 Mt mark in 1950. This also allowed more organized research on steelmaking and alloy development. Most prominent was the US Steel Research Laboratory (opened in 1928), where Bain worked on phase transformation of steel, discovering the eponymous bainite (Krauss 2015). Effects of alloying were explored exhaustively and culminated in the high-strength low-alloy (or HSLA) steels of today. The first well-known example was T-1 steel from US Steel in the 1950s. For current bridge applications, HSLA specifications are designated as A709 under ASTM International (previously known as the American Society for Testing and Materials; Wright 2015b). The A709 specifications have three grades with high-performance steel (HPS) designation. HPS is followed by the yield strength in ksi (or in MPa), that is, HPS50W (345 W), HPS70W (485 W), and HPS100W (690 W). These have yield strengths of 345, 485, and 690 MPa, respectively. For the HPS grades, reduced C contents ensure good weldability, while fracture toughness is improved over older comparable grades without HPS. The maximum C levels are at 0.11, 0.11, and 0.08% for the three grades. Other alloying additions include a total alloying of less than 5% (6.7% + Nb for 100 W grade) of Mn, Cu, Ni, and Cr, plus about 0.05% of Mo and V. The additions of alloying elements of less than 0.05% are called microalloying elements. All these elements are added on an as-needed basis to get the required strength in combination with various processing methods of rolling and accelerated cooling.

Research on structural analysis of bridges also advanced (e.g., Okukawa et al. 2000; Tang 2000b). Analysis based on statics was extended to consider dynamics, vibration, and wind loading. Various new bridge designs were implemented and aesthetics consideration also received more weight. These are countered by ever-present economic demands of cost-cutting. New designers also failed to learn from history and repeated serious mistakes. We have noted that the Tacoma Narrows Bridge failed from the lack of consideration against wind-induced oscillations and resonant behavior, in particular. Stephenson was concerned about this vulnerability in 1821 (Peters 1987) and did not use suspension design. Roebling stiffened decks and added stays, not just relying on suspension cables. In the Tacoma case, these precautions were ignored. Another concept introduced by Telford in 1826 was fail-safe design. He used multiple chain elements for each section, which also improved the lateral and torsional stiffness (Grover 2017). The I-35W Mississippi River Bridge failure in 2007 and the Silver Bridge disaster of 1967 were traced to the absence of the fail-safe design concept, already forewarned by Pope (1811).

Bridges with a large variety of truss structures were dominant in the first quarter of the twentieth century. Reflecting the improvements in steel properties, and the reliability and relative stability of steel price (partly due to monopoly), both highway and railroad bridges were built in increasing number and size. The use of the cantilever design also increased. Massive structures were preferred over style and beauty as illustrated by Plowden (1974). In the second quarter, arch and suspension bridges came back. By this time, heat treatment of steel was well understood. Standardization efforts also commenced (Wright 2015b) starting with ASTM A36 grade (yield strength of 36,000 psi or 250 MPa) representing mild steel. This grading was based on mechanical properties. Higher-strength steels also were introduced, although their fracture behavior was not fully known.

The new era for arch bridges began with the Hell Gate Bridge (1919, 310 m span, New York City) (Plowden 1974; Fernández 2003). This is a trussed double-arched structure, from which a concrete railroad deck is suspended. This design inspired the Sydney Harbour Bridge, finished in 1932, which is, however, more famous among the general public (Fernández 2003; Plowden 1974). Lindenthal, the builder, selected a 0.3% C steel for the arch as he was able to get 260 MPa yield and 475 MPa tensile strength. The chemistry was controlled well, limiting impurities to 0.05% S and 0.04–0.06% P. These strength values can be obtained with air cooling from 900 °C (so-called normalizing). The next structure worthy of note here is Bayonne Bridge (1931, 500 m span, New York City). It was the longest arch bridge when built.

The steel used here was C-Mn steel, in lieu of Ni-containing steel. Ni steel was used by Lindenthal in 1909 but found to give no advantage for Hell Gate. We know now that Ni gives no benefit for bridge steels that have no need for a quenching heat treatment. (Ni does give better low-temperature toughness, but this is not crucial for a bridge in New York City.) In contrast, Mn is always used in low-alloy steels as it offers strengthening at low cost. Because of increased Mn additions, 0.3% C steel with normalizing heat treatment today has a 10% higher tensile strength over that of the 1930 steel.

For the second half of the twentieth century, three developments are noteworthy in steel technology. The first is the basic oxygen steelmaking or BOS. In the BOS process, the air blast in the Bessemer-Thomas method is replaced by pure oxygen. This was developed in Austria in 1952 as the Linz and Donawitz (or LD) process (Stubbles 2017). This was quickly adopted in post-World War II Europe and Japan, with the first LD operation starting at Yawata Steel, Japan, in 1957. The LD process lagged in the USA since large-scale open-hearth facilities were running near capacity, but eventually the BOS process (the preferred name in the USA) became dominant. The second one is thermomechanical control processing (Wright 2015b). This involves continuous manufacturing of steel from the molten state to the final products. Steel is cast continuously, mechanically formed by a series of rolling mills, and, in between, accelerated cooling is applied. These process steps are combined with fine adjustments of small alloying additions in increments of 0.01% (called microalloying), producing high-strength steels efficiently and at minimum cost. The third are the advances in welding technology (Wright 2015b). This allows for the construction of complex steel structures economically. Welding limited the use of high C steels because of cracking in the weld metals or in the heat-affected zones. No such cracking occurs in the microalloyed steels, as these have reduced C levels to below 0.1%, imparting them with good weldability. HPS steels discussed earlier are good examples of microalloyed steels. The last two developments in tandem have contributed to continual developments in steel bridge building. This is in part necessitated by increased competition from reinforced concrete structures for bridges. The concrete reinforcements are provided by steel cables in the forms of prestressing and post-stressing. The steel used for such structures are invisible from the outside. When the reinforcing steels fail, concrete has no tensile strength, so the concrete structures are in immediate danger. Thus, the role of steel here is just as important as in all other steel construction. The other steel use in concrete is in the form of embedded reinforcing bars. As concrete inevitably cracks, the reinforcing bars corrode and increasingly severe damage develops. This problem has limited the life of many concrete bridges and better approaches of corrosion prevention must be applied. Various methods are indeed being used toward this goal.

This chapter has focused on materials and design, but one more essential element needs to be added for successful long-term use of bridges. This is the maintenance of the bridges. It has long been an afterthought, but technology for condition monitoring and for repair must advance in parallel to the rest of bridge technology (Vardanega et al. 2016; Washer 2014). Today, structural health monitoring is making significant strides, but retrofitting many extant bridges is a huge challenge.

Concluding Remarks

From ancient times to the present, iron and steel have offered various solutions for bridge construction. This role will continue with improved properties of modern steel materials, allowing wider choices for bridge designers as safe and sustainable bridges are conceived. However, proper usage of available technology still dictates the limits of materials, joining methods, and corrosion protection. Lessons of history must not be forgotten, as it contains many examples of catastrophic bridge failure. Indeed, failures of modern bridges still concern us today, as we witnessed most recently in 2007 with the I-35 W Mississippi River Bridge in Minnesota, which collapsed due to the fracture of a single gusset plate. This was for the lack of fail-safe design. The weakness against vibration led to major disasters, including the 1850 Angers Bridge failure (Peters 1987) and the Tacoma Narrows disaster of 1940 (Plowden 1974). The weaknesses Pope raised over two centuries ago appear to be finally overcome in modern design, but bridge failures still occur.

In this review of ferrous metallurgy as applied to bridge construction, the evolution and breakthroughs have been tracked from the start of the Iron Age to the Space Age. There is a great deal more information not expressly covered in this chapter, but a materials science design approach of recent decades provides a consistent understanding of continuous historical metallurgical developments. Hopefully, a gap between the perspectives of the historian and the metallurgist has been narrowed.

Acknowledgments I wish to thank Dr. Brett Kaufman, Dr. Siran Liu, and Dr. Hongjiao Ma for their assistance in finding many articles and books originating from China. Many of these are not accessible with usual channels from California. I am also grateful to Dr. Hideo Akanuma for digital files used in Fig. 4.7 and to Mag. Hans Reschreiter, Prof. M. Kohler-Schneider, and Prof. Sabine Rosner for identifying the Hallstatt sword.

Appendix A: List of Bridges Discussed in This Chapter

Name	Material	Structure	Year built	Location	Country
The Iron Bridge	Cast iron	Arch	1779	Coalbrookdale	UK
Brooklyn Bridge	Steel	Suspension	1883	New York	USA
Akashi Kaikyo Bridge	Steel	Suspension	1998	Hyogo	Japan
Ikitsuki Ohashi Bridge	Steel	Truss	1991	Nagasaki	Japan
New River Gorge Bridge	Steel	Arch	1977	Fayetteville	USA
Golden Gate Bridge	Steel	Suspension	1937	San Francisco	USA
Normandy Bridge	Steel	Cable-stayed	1995	Le Havre	France
Pan Ho Bridge	Iron	Suspension	unknown	Shaanxi	China
Jihong Bridge	Iron	Suspension	1475	Yunnan	China
Shenchuan Iron Bridge	Iron	Suspension	581 or 680	Yunnan	China
Luding Bridge	Iron	Suspension	1706	Sichuan	China

Name	Material	Structure	Year built	Location	Country
Chung Riwoche Chakzam	Iron	Suspension	Fifteenth century	Tibet	China
Chuka-cha-zum	Iron	Suspension	Fifteenth century	Chuhka	Bhutan
Tachog Lakhang Chakzam	Iron	Suspension	Fifteenth century	Paro	Bhutan
Łażany Bridge	Cast iron	Arch	1796	Łażany	Poland
Mieszczanski Bridge	Cast iron	Arch	1876	Mieszczanski	Poland
Buildwas Bridge	Cast iron	Arch	1796	Buildwas	UK
River Dee Railroad Bridge	Cast iron	Beam	1846	Chester	UK
Tay Bridge	Cast iron	Truss	1879	Dundee	UK
Glorywitz Bridge	Iron	Suspension	1734	Glorywitz	Poland
Winch Bridge	Iron	Suspension	1741	Durham	UK
Jacob's Creek Bridge	Iron	Suspension	1801	Union Town	USA
Chain Bridge	Iron	Suspension	1801	Georgetown	USA
Dryburgh Abbey Bridge	Iron	Suspension	1817	River Tweed	UK
Union Bridge	Iron	Suspension	1820	River Tweed	UK
Menai Suspension Bridge	Iron	Suspension	1826	Anglesey	UK
Silver Bridge	Steel	Suspension	1928	Pt. Pleasant	USA
Britannia Bridge	Steel	Truss	1850	Anglesey	UK
Royal Albert Bridge	Steel	Truss	1858	Plymouth	UK
Pfaffendorf Bridge	Steel	Truss	1864	Koblenz	Germany
Garabit Viaduct	Steel	Truss	1884	Garabit	France
Ashtabula Railroad Bridge	Steel	Truss	1876	Ashtabula	USA
I-35W Mississippi River Bridge	Steel	Truss arch	1964	Minneapolis	USA
Tacoma Narrows Bridge	Steel	Suspension	1940	Tacoma	USA
Tees Bridge	Iron	Suspension	1749	Durham	UK
Fairmount Hazard-White Bridge	Iron	Suspension	1816	Philadelphia	USA
St. Antoine Bridge	Iron	Suspension	1823	Geneva	Switzerland
Grand Prix Suspendu	Iron	Suspension	1834	Fribourg	Switzerland
Broughton Bridge	Iron	Suspension	1826	Broughton	UK
Brighton Chain Piers	Iron	Suspension	1823	Brighton	UK
Basse-Chaîne Bridge	Iron	Suspension	1832	Angers	France
Fairmount	Iron	Suspension	1842	Philadelphia	USA
Wheeling Bridge	Iron	Suspension	1849	Wheeling	USA
Delaware Bridge	Iron	Suspension	1848	Delaware	USA
Suspension foot bridge	Iron	Suspension	1824	Wissekerke	Belgium
Allegheny Aqueduct	Iron	Suspension	1845	Pittsburgh	USA
Niagara Falls Railroad Bridge	Iron	Suspension	1855	Niagara Falls	USA

Name	Material	Structure	Year built	Location	Country
Eads Bridge	Steel/ iron	Arch	1874	St. Louis	USA
Glasgow Steel Bridge	Steel	Truss	1879	Missouri	USA
Williamsburg Bridge	Steel	Suspension	1903	Williamsburg	USA
Forth Road Bridge	Steel	Suspension	1964	Edinburgh	UK
Forth Rail Bridge	Steel	Truss	1890	Edinburgh	UK
Hell Gate Bridge	Steel	Arch	1919	New York	USA
Sydney Harbour Bridge	Steel	Arch	1932	Sydney	Australia
Bayonne Bridge	Steel	Arch	1931	New York	USA
Hong Kong-Zhuhai-Macau Bridge	Steel	Cable-stayed	2018	Hong Kong	China
San Francisco-Oakland Bay Bridge	Steel	Suspension	1936	San Francisco	USA
Chesapeake Bay Bridge	Steel	Suspension	1952	Maryland	USA
Humber Bridge	Steel	suspension	1981	Kingston	UK

Appendix B: Revisiting Silver Bridge Failure

It has been half a century since the failure of the Silver Bridge, and many publications and discussions have been dedicated to analyzing this incident. The following is an interpretation of the author based on his observations of the body of published research, as opposed to new primary experimental analysis.

The Silver Bridge was built in 1928 at Point Pleasant, West Virginia, across the Ohio River. The bridge was an eyebar-chain suspension bridge with a 214 m span. For each section, two eyebars were used, such that a single joint failure would lead to a bridge collapse. The eyebars were made of a high carbon steel, AISI-1060. The average chemical analysis of the broken eyebar was 0.59% C, 0.66% Mn, 0.145% Si, 0.03% S, and 0.041% P. These were water-quenched from 900 °C and tempered at 650 °C, giving the yield strength of 550 MPa, tensile strength of 830 MPa, elongation of 20%, and reduction in area of 50%. The design stress was 345 MPa. These are within the expected ranges for quenched-and-tempered 1060 steel. In addition, it had the ductile-brittle transition temperature of 104 °C and Charpy V-notch energy of 2.7–5.4 J at −1 °C (temperature at the time of failure). That is, the steel was used in a nominally brittle condition (Anon 1970, 1968b; Bennett 1969; Bennett and Mindlin 1973). However, the final fracture was fully ductile. As noted earlier, low-temperature brittleness of steels was still unknown in 1928, and stress concentration effects (Inglis 1913) were mainly of academic interest. Lichtenstein (1993) reexamined this failure. No change was suggested regarding the earlier conclusions, but he noted that the builder reduced the safety factor to 1.75 and kept the details of heat treatment secret from the outside designer. He also estimated that each of the two eyebars that initiated the failure was under a force of 4.5 MN (83% of the design load).

The Silver Bridge crossed the Ohio River in the east-west direction. The failed eyebar was at the first joint on the west side of the Ohio Tower (west tower), C13. It was the north-side eyebar on the south side chain, designated as #330 (see Fig. 4.20). The initial flat fracture and its direction are marked by a broken line and a small arrow. The National Bureau of Standards (NBS) and Battelle Columbus Lab. investigated the failure. The National Transportation Safety Board (NTSB) concluded that stress-corrosion cracking was responsible for the critical cleavage fracture event from a 3 mm-deep by 4.85 mm-wide crack on eyebar #330. This fracture initiation part is shown in Fig. 4.21a and is from the eyebar head that separated from the shank side and fell into the river. The initiator cracks were on the hole side near the south face, that is, the inner side of C13 joint. This NTSB conclusion fails to explain why the lower side of the eyebar #330 failed in flat mode while the upper part failed in a ductile manner (Bennett and Mindlin 1973). This ductile fracture occurred only after a large plastic deformation occurred in the eyebar head. This is inconsistent with NTSB view of brittle fracture. That is, if a small crack initiated a cleavage fracture of one side of the head, the other side of eyebar #330 should also fail in the same brittle manner. But it appears the material was ductile at the time of fracture, at the ambient temperature of −1 °C. Several more contradictions emerge when one examines NTSB and NBS reports and Bennett and Mindlin article (Anon 1970, 1968b; Bennett 1969; Bennett and Mindlin 1973).

1. The initial crack formed a corner clam-shell marking, indicative of fatigue crack initiation (Fig. 4.21a). This was on eyebar #330 and on the inner edge at the hole facing the connection pin of 203 mm diameter. A smaller crack found next to the larger crack, 11 mm total length, also exhibited clam-shell marks. Two arrows

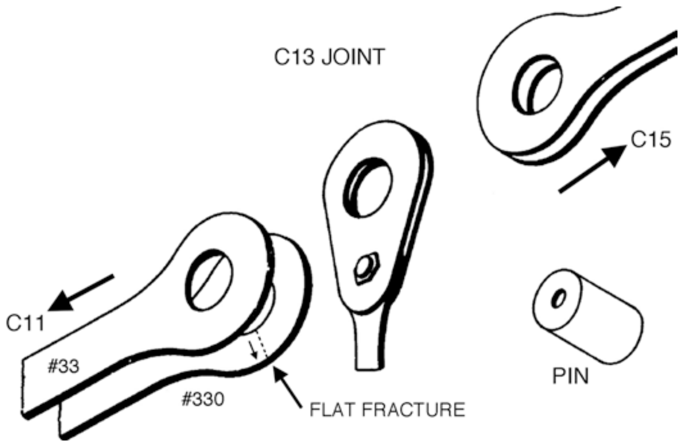


Fig. 4.20 Joint C13 of the south cable of the Silver Bridge. Joint C11 on the left (Ohio side) and C15 on the Ohio tower. View from the South to the North. Based on fig. 5b of NTSB Report HAR-71-01. (Anon 1970)

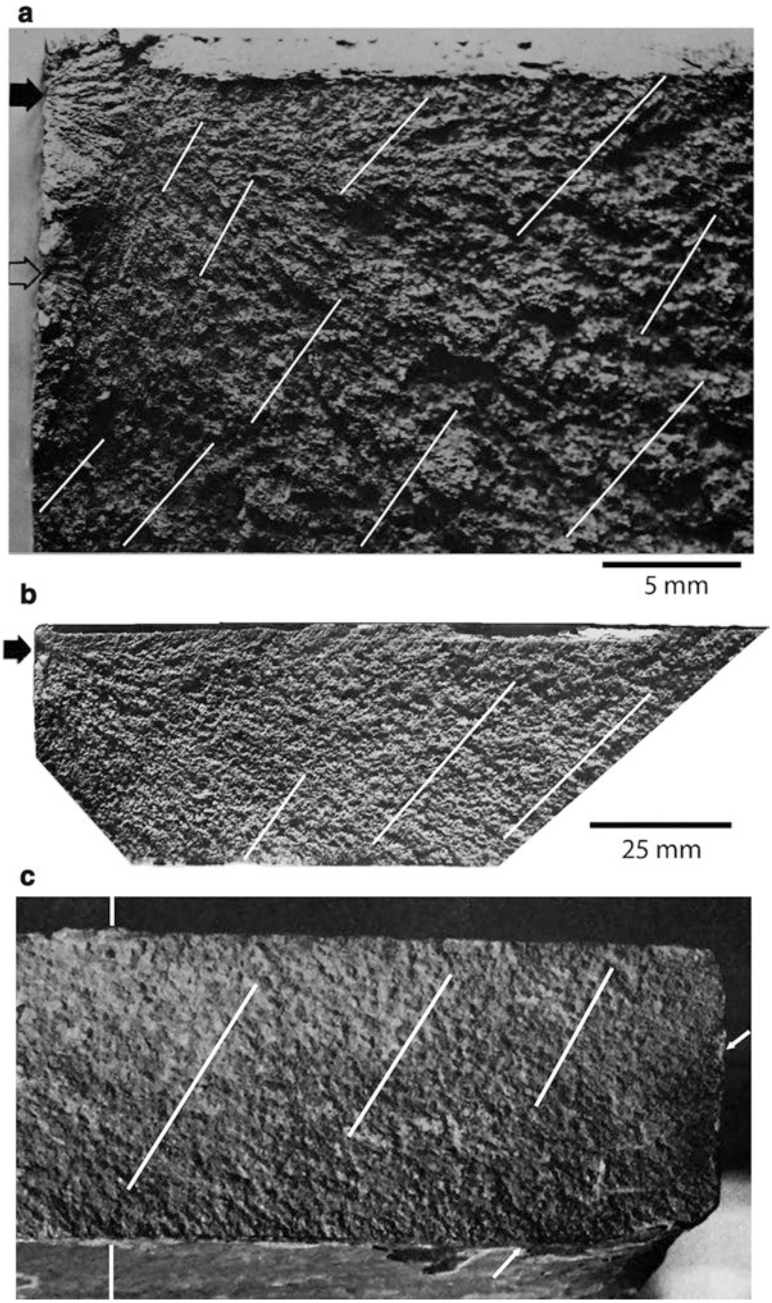


Fig. 4.21 (**a**) Enlarged fracture initiator cracks. Two arrows point to the center of the two thumb nail cracks. After cleaning. White lines indicate the directions of fatigue beach marks that are visible. (**b**) The hole-side half of the flat fracture surface of the outside piece. After cleaning. The same orientation as (**a**) with the two cracks at top left corner. (**c**) The outside half of the flat fracture surface before cleaning. Two vertical white lines indicate the center position. (Bennett 1969, figs. 5, 6, and 3).

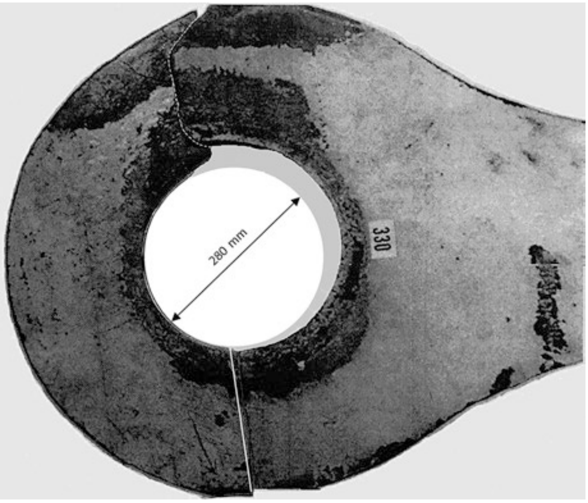


Fig. 4.22 Reconstructed head of eyebar #330. (**a**) Following fatigue cracking that produced flat fracture of the lower side of this eyebar. The white circle corresponds to the size of the pin, 280 mm in diameter. The white line on the lower side is the joined position of the flat fracture surfaces. The thin white broken curve on the upper side shows the outline of the shank side of the fractured eyebar (Anon 1970)

point to the center of the two thumbnail cracks. The fracture surface beyond these initiator cracks gave no indication of cleavage cracking and no chevron marks are visible. This crack propagated downward to the outside edge (Fig. 4.20).

2. When the flat fracture surface is carefully examined, one observes numerous nearly parallel, locally straight beach marks covering the entire fracture surface, indicative of fatigue. Fatigue striations are expected between these beach marks, but the magnification is inadequate to judge. Since this eyebar was exposed to weather, it is expected that fatigue was assisted by aqueous corrosion. The beach marks are indicated by thin white lines in Fig. 4.21a–c. In cleaned samples (Fig. 4.21a, b), features of the fracture surfaces are reasonably clear. Beach mark spacings were 0.2–0.3 mm at the start, but increased to ~0.8 mm at the mid-section. An overall trend of the beach marks is from the starting cracks at the top left (hole side) to the bottom right (outer edge). The dark band (marked with white arrows shown in Fig. 4.21c) appears to be a group of beach marks near the bottom right. This photograph was taken before cleaning and indications are generally fuzzy. Still, the beach marks can be traced.
3. When the broken-off outboard piece is joined to the shank side at the fatigue fracture position using photographic images, the combined image given in Fig. 4.22 represents the deformed eyebar geometry before the separation occurred. At this stage, the size of the hole was found to be enlarged by 28 mm (or 10%). This implies that the hole size was increased while the flat fracture was in progress before the separation occurred. This must have led to the reduction in the stress acting on eyebar #330 from the design value of 345 MPa. Taking the eyebar hole distance of 16.1 m (Bennett and Mindlin 1973), the eyebar strain was reduced by 0.174%, when #330 was elongated by 28 mm. This strain is larger than the applied strain of 0.164% (assuming the design stress of 345 MPa and the Young's modulus of 210 GPa). A large stress reduction occurred on #330, while loading the parallel eyebar #33 (the south side eyebar) to bear the load

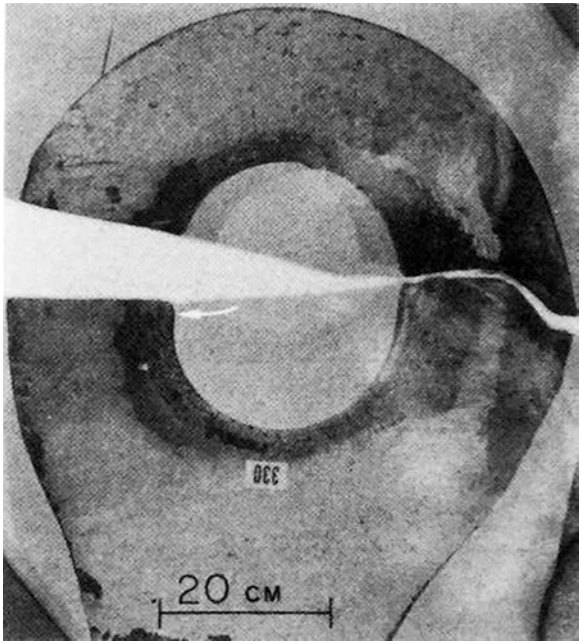


Fig. 4.23 Photograph of eyebar #330 (Ballard and Yakowitz 1970) with the upper side fractured pieces placed together at the ductile fracture location. The left-side opening represents the deformed shape of eyebar #330 prior to the final fracture

beyond its yield load. It was likely that eyebar #330 was deformed gradually as the fatigue crack extended, sharing the load between #33 and #330. Thus, eyebar #33 was also deformed, but data on this regard were absent in the NTSB/NBS reports. The tensile strength of the eyebar steel was 830 MPa (Bennett and Mindlin 1973), so #33 eyebar was able to carry double the design load by itself, though in unbalanced conditions. When the lower side of eyebar #330 severed, the geometry changed into a hook and its load capacity was decreased substantially. Using a mechanics of material formula from Boresi and Sidebottom (1985), the load capacity was calculated as 0.77 MN for the maximum stress reaching the tensile strength of #330 (830 MPa).

4. When the fractured pieces were matched at the ductile fracture side (Fig. 4.23 from Exhibit 16 (Anon 1968b)), representing the time of final fracture, the hole is enlarged by 35% in the length direction, leaving a 140 mm gap between the flat fracture at the hole side of eyebar #330, as was reported in Anon (1970). The width of the hole at the middle was also enlarged by 26.5%. This hook shape represented the condition before the final ductile fracture, which occurred when the load on eyebar #330 exceeded 0.77 MN. This condition was reached when the loading of eyebar #33 increased by also 0.77 MN (or deformed an additional 3.8 mm). By the time of the eyebar #330 separation, eyebar #33 was loaded higher than this level and the final fracture event was expected immediately.
5. Attribution to stress-corrosion cracking due to hydrogen sulfide gas was highly implausible in the wind-swept rural area where the bridge was located. Bennett and Mindlin (1973) immersed fracture test samples to 0.5% H_2S-5% NaCl aque-

ous solution and found threshold stress-corrosion fracture toughness of 17 MPa$\sqrt{m}$ (or 36 MPa$\sqrt{m}$ for 100+ *h*). They relied on the H_2S-SCC mechanism to justify their conclusion of brittle fracture of eyebar #330 starting from the small corner crack. If the same 0.5% levels of H_2S gas were present in air, this is two to five times over the lethal levels of H_2S gas, and yet the H_2S concentration is 1000 times less than in the liquid state. No such sources of pollution are known. H_2S is also 20% heavier than air and cannot possibly rise to the C13 joint, which was more than 30 m above the river. Since humans can easily detect 1 ppm level presence of H_2S gas in air, it is unlikely to have high enough levels of H_2S at the eyebar joint while no one noticed what would have been a rotten egg smell around the bridge in non-industrial Eastern Ohio. Ballard and Yakowitz (1970) also found Cl along with S, suggesting another source of S contamination to be from lubricant in the eyebar joint. This presence of Cl is incompatible with the H_2S hypothesis. The H_2S-based mechanism should be discarded.

From these observations, a likely fracture scenario is given in the following:

6. Fatigue cracks initiated at multiple locations, but two small corner cracks started to propagate, causing a flat fatigue fracture and separating the lower part of the eyebar #330. During the crack propagation and upon fatigue fracture, the hole was enlarged, reducing the applied load.
7. Upon the separation of the lower part of #330, the hole enlargement reached 2.8 cm, which was adequate to relieve the load on this eyebar #330, and the parallel eyebar #33 on the south side carried almost the entire load. This was possible as the maximum load (9 MN) of twice the design load was still below the tensile strength, but the deformation imposed on eyebar #33 simultaneously increased the load on eyebar #330 to its reduced capacity of 0.77 MN.
8. When eyebar #330 reached its loading capacity, the final ductile fracture of the upper part of eyebar #330 was ensured, followed immediately by the collapse of the bridge.

An alternate fracture mechanism may be considered based on elasticity analysis. At the initiator crack position on eyebar #330, an elastic stress concentration factor was calculated as 3.1 ± 0.4 (Trznadel 1978), which is enough to cause brittle fracture given the crack size and existing load. However, local plastic deformation substantially reduces this stress concentration factor. Applying the Neuber rule (Hertzberg 1996), the maximum stress is found to be less than 570 MPa (3% more than the yield strength) for the applied stress of up to 345 MPa, or the design stress. The calculated maximum stress is 7–8% less than the stress needed to fracture per Bennett and Mindlin (1973), and brittle eyebar fracture cannot be expected. In any event, it is doubtful whether this approach can resolve the issues arising from ductile final fracture and observations of fatigue markings. Bennett and Mindlin (1973) listed corrosion fatigue as a possible mechanism, though they discarded it. If one considers the Silver Bridge location in the Ohio River valley, where acid rain of lower than 4.5 pH had persisted from the 1950s to 2010 (Anon 1978, 2010), corrosion fatigue had to play a significant role in the progressive cracking of the fractured eyebar. Since acid rain continues over wide areas globally, this issue deserves careful consideration. In fact, severe corrosion found on the suspension cables of the Forth Road Bridge in Scotland (Colford 2013) may have also involved acid rain. Incidentally, the pH levels in Scotland were comparable to those of the Ohio River valley (Seinfeld and Pandis 1998).

The above re-examination of the Silver Bridge failure implies that the fail-safe feature was absent in the original design, which used an inadequate safety factor of 1.5. At this level, the working stress was comparable to the fatigue limit and was bound to cause the disaster. Unfortunately, the concept of fatigue crack growth was still not generally understood in 1928, and inspection methods were inadequate in the 1960s. It was also discovered that the post-failure investigation had serious deficiencies. The initial field examination prematurely concluded the flat fracture was due to cleavage. More failure analysis was done, but obvious features in fractography were overlooked as pointed out above. An illogical hydrogen-sulfide hypothesis was introduced and it continues as the prevailing view today. This hypothesis cannot explain the observed cracking as there were no possible industrial or natural sources of hydrogen sulfide gas at high concentrations at the bridge. Although the lack of primary evidence was a serious obstacle, available records led to a more coherent understanding of the sequence of failure events as presented here.

As most bridge maintenance is still primarily reliant on visual inspection, nondestructive evaluation is imperative for executing a systematic approach. Newer methods are starting to be used; for example, the San Francisco-Oakland Bay Bridge, Forth Road Bridge, and Humber Bridge have been continuously monitored using acoustic emission technology (Beabes et al. 2015; Johnson et al. 2012). Acoustic emission and other structural health monitoring methods can be found in recent publications (Kosnik et al. 2011; Ono 2014; Vardanega et al. 2016; Washer 2014; Wevers and Lambrighs 2009).

Appendix C: Weibull Analysis of the Tensile Strength of Williamsburg Bridge Wires

The data set given in Perry (1998) was evaluated for the Weibull shape parameter. Perry provided fracture load values of 160 samples. These values were sorted in increasing order and the number of breaks, B_n, for each increment of 50 lb_f, was determined. Here, n varies from 1 to 50 for the load range of 4800–7200 lb_f. Figure 4.24 shows a point plot of B_n vs. load (in blue), indicating a peak at ~6500 lb_f. By dividing B_n by the total sample number of 160, the probability distribution function (PDF) for wire fracture is obtained. When these are summed, cumulative PDF that varies from 0 to 1 is found, and it is plotted in Fig. 4.24 in red. Note that the distribution is skewed to the lower load unlike the normal (or Gaussian) distribution.

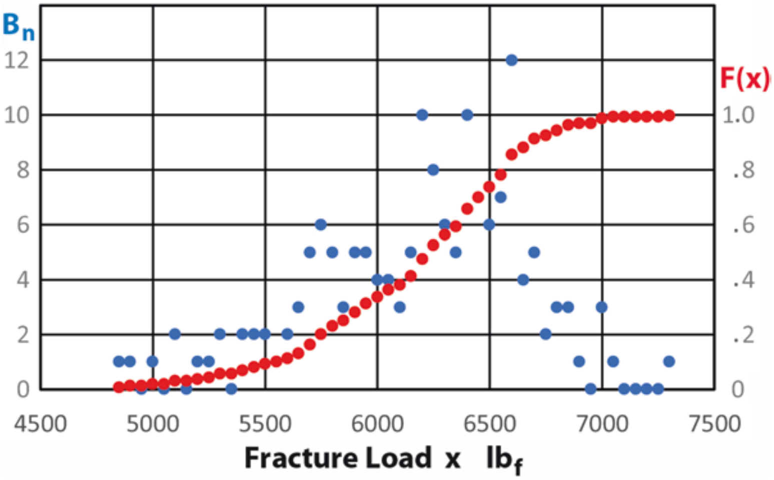


Fig. 4.24 The number of breaks per 50 lb_f load step, B_n (blue points, left scale), and cumulative PDF, $F(x)$ (red points, right scale), against fracture load, x, in lb_f

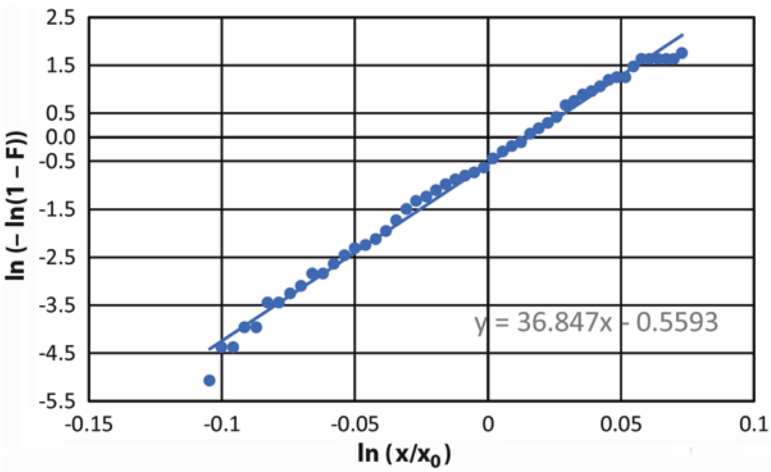


Fig. 4.25 Weibull plot of ln(−ln(1 – F)) against ln(x/x_0). The slope of 36.8 is the shape parameter, m

A Weibull distribution function is defined in terms of cumulative PDF, $F(x)$, as

$$F(x) = 1 - \exp\left(-(x/x_0)^m\right),$$

where m is the shape parameter and x_0 the scale parameter. In the present case, x is the variable and is taken as the load. It can also be considered as time when one needs to analyze the lifetime of components or structures. This is the simplest distribution and is known as a two-parameter Weibull distribution. By shifting terms and taking the logarithm twice, the above expression can be written as

$$\ln\left(-\ln\left(1-F\left(x\right)\right)\right)=m\ln\left(x/x_0\right).$$

By plotting the left-hand side against $\ln(x/x_0)$, m can be determined as the slope. The Weibull plot for the Williamsburg wires is shown in Fig. 4.25. Here, x_0 was taken as the average fracture load of 6170.56 lb_f (or the strength of 1.5 GPa). The point plot was fitted to a linear equation with $m = 36.8$. That is, these wires have the tensile strength level comparable to some modern wires, but with Stage 4 corrosion per NCHRP-534 (Mayrbaurl and Camo 2004).

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Chapter 5
Materials in the Aircraft Industry

Sharvan Kumar and Nitin P. Padture

History of Aviation

The Early Years

The dream to "soar like a bird" is as old as mankind, but the concept of an airplane has only been around for two centuries or so. Over this period, flight can be classified into the early period of lighter-than-air (balloons) and the subsequent development of heavier-than-air flying machines. Prior to this period, men and women tried to strap on wings or built machines with flapping wings to imitate birds, but with little success. Around 1490, Leonardo da Vinci sketched plans for a man-carrying machine with flapping wings (an ornithopter), a full-size model of which can be found in the Smithsonian Air and Space Museum in Washington DC, and a picture of it is seen in Fig. 5.1.

In 1783, the first clearly recorded manned balloon flight took place after the Montgolfier brothers developed the hot-air balloon and flew it across Paris. Two weeks later, hot air gave way to the first hydrogen-filled balloon flown by Professor Jacques Charles and the Robert brothers in Paris as well (Wiki: Montgolfier_brothers, January 19, 2018a). However, early balloon flight suffered from the inability to guide the direction of flight and was pretty much left to the mercy of the wind direction. The next 100 years saw the design and building of the fixed-wing aircraft. Sir George Cayley in 1799 described and defined the forces of lift and drag and generated the design for the first fixed-wing aircraft. He subsequently built and flew several fixed-wing crafts between 1799 and 1853. These aircrafts embodied the fixed wing to provide lift, flappers to provide thrust, and a movable tail (rudder) to provide control, and thus the science of modern-day aircraft was born (Wiki: George Cayley; April 09, 2018c).

S. Kumar (✉) · N. P. Padture
School of Engineering, Brown University, Providence, RI, USA
e-mail: Sharvan_Kumar@brown.edu; Nitin_Padture@brown.edu

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Fig. 5.1 The ornithopter model at the Smithsonian Institution based on the drawings of Leonardo da Vinci. (Figure used with permission of the Smithsonian National Air and Space Museum (NASM2013-02909. Photo by Mark Avino))

In roughly the following three decades, from about 1850 to 1880, designers began testing various types of engines that would propel their air vehicles. In 1857, Felix du Temple flew a model monoplane whose propellers were driven by a clockwork spring and later, a small steam engine. It took off under its own power, flew a short distance, and landed safely, recording the first successful flight of a powered aircraft (Wiki: Félix_du_Temple_de_la_Croix; March 10, 2018d). In 1864, Siegfried Marcus built an internal combustion engine with a carburetor (that he called a *vaporisater*) and an electrical ignition system that used a primitive magneto to generate a spark, although this engine was targeted for use in automobiles (www.asme.org; siegfried-marcus; MacRae 2012). In 1866, the Royal Aeronautic Society was formed in England, and in 1868, it sponsored the "First Great Aeronautical Exhibition." In 1876, Nikolaus Otto in Germany developed the four-stroke gasoline engine which is the basis for the modern internal combustion engine (Encyclopedia Britannica; Nikolaus Otto; October 03, 2016).

Between 1880 and 1900, several attempts to fly using powered vehicles were made with various levels of success and failure in Europe, the United States, and Australia and included pioneers like Otto Lilienthal, Lawrence Hargrave, Samuel Langley, Hiram Maxim, Wilbur Wright, and Orville Wright. In December 1903, Orville and Wilbur Wright made the first powered flight (Fig. 5.2) in a fully controllable aircraft capable of sustaining itself in the air at Kitty Hawk, North Carolina (heavier-than-air, gasoline-powered, propeller-driven biplane; Flyer I). The flight only lasted 12 s and extended 120 ft (Wiki; Wright brothers; April 03, 2018e). They made a few additional flights that day before a strong gust of wind rolled the aircraft over and smashed it.

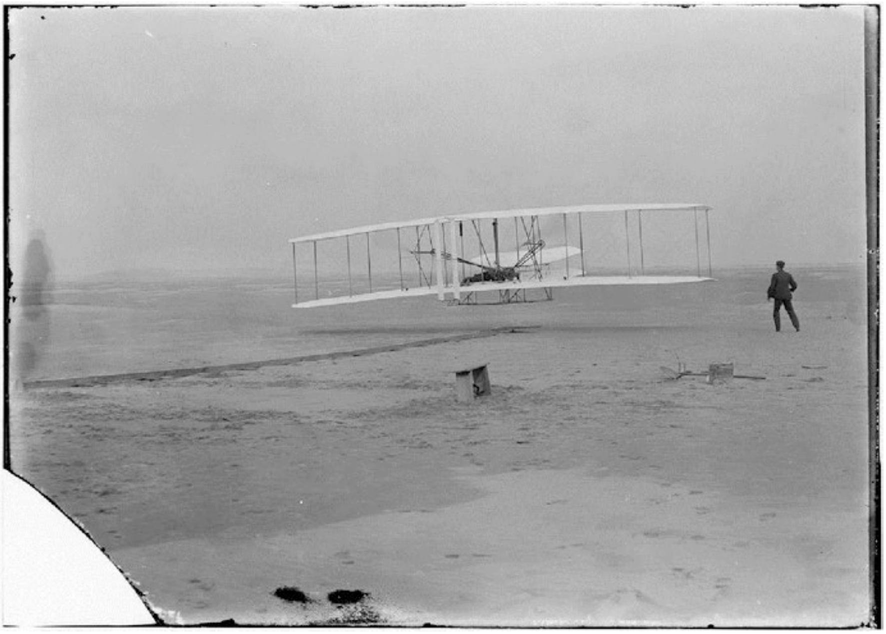

Fig. 5.2 The first powered, controlled flight by a heavier-than-air machine; Wright brothers, Kitty Hawk, NC, December 17, 1903 (https://www.airspacemag.com/history-of-flight/wright-brothers-first-flight-photo-annotated-180949489/). (Figure used with permission of the Smithsonian National Air and Space Museum, NASM 2003-3463)

The Flyer had a wooden frame made of spruce and ash. The frame was covered with a finely woven cotton cloth and sealed with canvas paint. The metal fittings were made from mild steel, and the aircraft was rigged with15-gauge bicycle spoke wire. The engine block was cast from an aluminum alloy consisting of 92% aluminum and 8% copper. Ninety years later, Gayle and Goodway (1994) demonstrated that this engine crankcase was composed of a bimodal distribution of *GP zones* (discussed below), indicative of *precipitation hardening*, even though the concept of precipitation hardening was unknown in 1903. The other parts of the engine were made from steel or cast iron, with the exception of the spark points which contained tiny bits of platinum (Crouch 2018).

From 1903 to 1940

The 30 years that followed the historic Wright brothers flight in Kitty Hawk were filled with inventions, development of new technologies, and implementation, in part spurred by the need for higher speeds, higher altitudes, improved reliability and increased maneuverability during World War I. Notable events included the following:

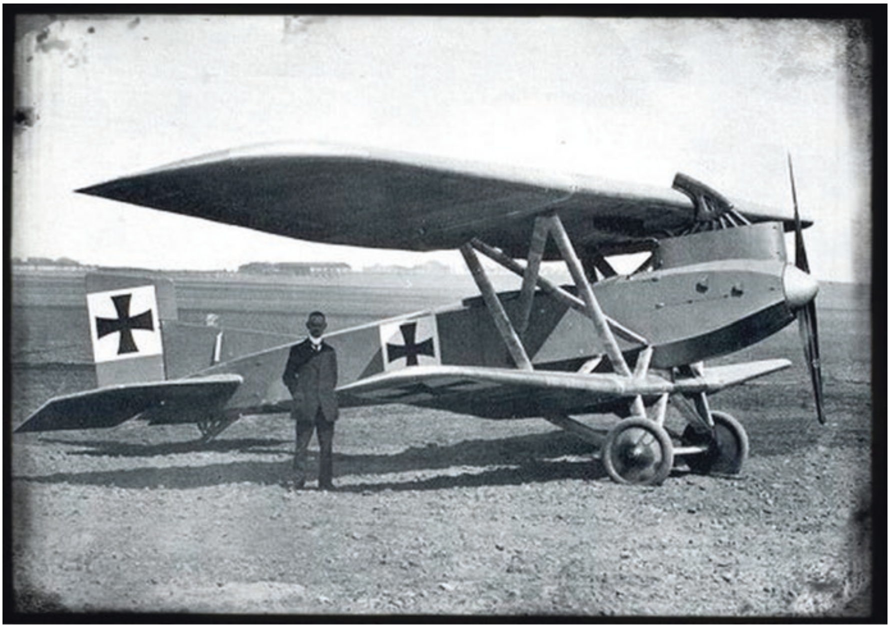

Fig. 5.3 Junker J4. (From: http://hugojunkers.bplaced.net/junkers-j4-j-i.html)

i. The development in 1914 of the automatic gyrostabilizer that became the basis for "automatic pilot"
ii. Several improvements in structure, control, and propulsion system design between 1914 and 1918
iii. The introduction of the first all-metal airplane (Junkers J4, Fig. 5.3), built largely using a lightweight precipitation-hardenable aluminum alloy that was trade-named Duralumin, by Hugo Junkers in Germany in 1917
iv. The inauguration of airmail service in the United States in Washington, DC, and in 1920, the first transcontinental airmail service from San Francisco to New York

In 1919, Britain and France introduced airborne passenger service across the English Channel. Charles Lindbergh completed the first nonstop solo flight from New York to Paris on the Spirit of St. Louis in 1927 in a single-seater Ryan monoplane. The year 1933 was special when the Douglas Company introduced the 12-passenger twin-engine DC-1 (Fig. 5.4a; wiki: Douglas DC-1; October 2017), and Boeing introduced the 247 (Wiki: Boeing 247; April 2018f) which was a twin-engine 10-passenger monoplane that was propeller-driven and had retractable landing gear that reduced drag during flight (Fig. 5.4b). In 1935, the first practical radar system for meteorological application was patented in England and was later extensively used during World War II to detect incoming aircrafts. By 1936, the Douglas Company produced the DC-3 (Wiki: Douglas DC-3; March 2018g) which incorporated many aviation-related engineering advances including almost completely

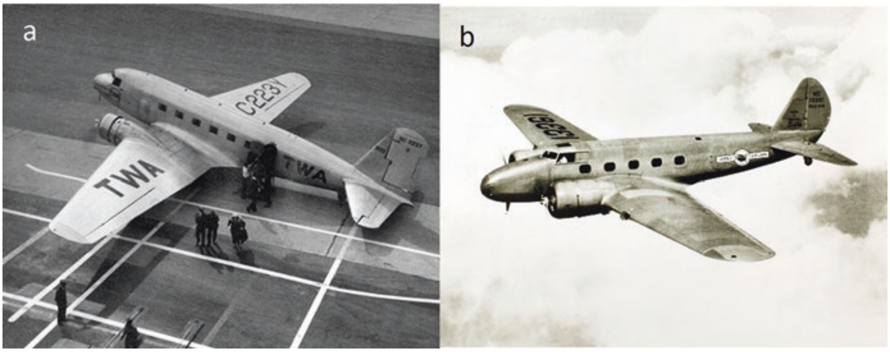

Fig. 5.4 (**a**) Douglas DC-1. (https://en.wikipedia.org/wiki/Douglas_DC-1; image from https://en.wikipedia.org/wiki/File:Douglas_DC-1.jpg) and (**b**) Boeing 247. (https://en.wikipedia.org/wiki/Boeing_247; image from https://commons.wikimedia.org/wiki/File:Boeing,_247.jpg)

enclosed engines to reduce drag, new types of wing flaps for better control, and variable-pitch propellers, whose angle could be altered in flight to improve efficiency and thrust. The DC-3 could accommodate 20 passengers and could be configured with sleeping berths for long-distance flights. By 1938, 80% of US passengers were flying in DC-3s, and a dozen foreign airlines had adopted the planes.

From 1940 to 2000

The period spanning World War II (1938–1945) witnessed significant scientific and technical developments in radar technology, radiowave navigation, and instrumented landing systems in the United Kingdom, Germany, and the United States. In 1942, Adolf Galland, the director general of fighters for the Luftwaffe and one of Germany's top pilots, flew a prototype of one of the world's first jets, the Messerschmitt ME 262 at 540 miles per hour. The first jet-powered commercial aircraft was the de Havilland Comet introduced in 1949 and making its first flight from London to South Africa in May 1952 (Wiki: De Havilland Comet; March 2018h).

The jet engine had a profound impact on commercial aviation. As late as the 1950s, transatlantic flights in propeller-driven planes lasted more than 15 h. But in the 1960s, aircrafts such as Boeing's classic 707 cut that time in half. Boeing introduced the 707 as its first four-engine jetliner (Fig. 5.5a), was in commercial service between 1958 and 1979, and is credited with ushering in the jet age (Wiki: Boeing 707; April 2018i). Increases in speed certainly pushed commercial aviation along, but the business of flying was also demanding bigger and bigger airplanes. In response, the Boeing 747 (Wiki: Boeing 747; April 2018j), a wide-bodied jet that was fitted with turbofan engines and came into service in 1969, is perhaps the biggest success story in modern commercial aviation (Fig. 5.5b). Other aircraft companies introduced their own commercial versions, the most notable being the DC-10

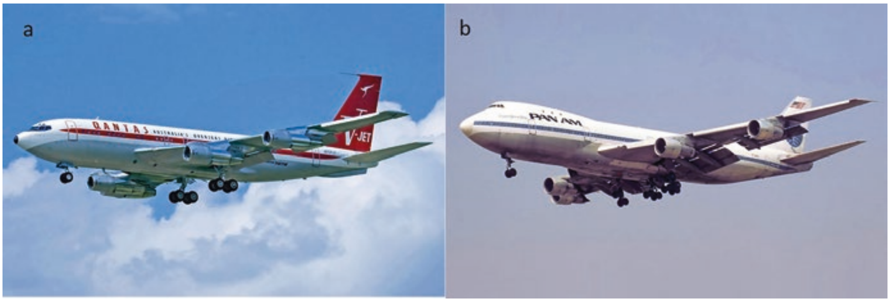

Fig. 5.5 (**a**) The Boeing 707 (https://en.wikipedia.org/wiki/Boeing_707; figure from https://commons.wikimedia.org/wiki/File:Boeing_707-138B_Qantas_Jett_Clipper_Ella_N707JT.jpg) and (**b**) the Boeing 747 (jumbo jet) (https://en.wikipedia.org/wiki/Boeing_747; figure from https://commons.wikimedia.org/wiki/File:Pan_Am_Boeing_747-121_N732PA_Bidini.jpg)

from McDonnell Douglas in the early 1970s (Wiki: McDonnell Douglas DC-10; April 2018k) and the L-1011 from Lockheed Corporation (Wiki: Lockheed L-1011 TriStar; April 2018l), both fitted with three-engines, two below the wings and one at the base of the vertical stabilizer/tail. Whereas the L-1011 used Rolls-Royce engines, the DC-10 original variants used GE engines (CF6) but subsequent longer-range variants used Pratt & Whitney turbofan engines.

Perhaps the two most popular commercial jet aircraft models today are the Boeing 737 and the Airbus 320. The Boeing 737 (Wiki: Boeing 737; April 2018m) was initially envisioned as a short- to medium-range twinjet aircraft and eventually developed into several variants. It entered airline service in 1968 as the original 100 version, and soon thereafter as the 200 version. Subsequently, in the 1980s, the longer 300, 400, and 500 models were launched, and were collectively called the 737 Classic series and had wing improvements and CF56 turbofan engines. The 737 Next Generation was introduced in the 1990s (600, 700, 800, and 900 models) and included increased wingspan, upgraded cockpit, and redesigned interior. Their lengths ranged from 102 to 138 ft.

On the other side of the Atlantic, a European consortium arose in the early 1970s under the name of G.I.E. Airbus Industrie, headquartered in France. Since then, Airbus has made significant progress in the aircraft market. Perhaps the most popular of the Airbus fleet is the family of the A320 aircrafts (Wiki: Airbus A320 Family; April 2018n), the biggest competitor for the Boeing 737 series. The first member of the A320 was launched in 1984 and was introduced into service by Air France in 1988. Like the 737, it used CFM56 GE engines till the V2500 engines became available toward the end of the 1980s. More recently, a new class of Airbus 320 called Airbus A320neo (new engine options) with the CFM International LEAP-1A engine and the Pratt & Whitney PW1100G engine was introduced by Lufthansa in January 2016.

In 1995, Boeing introduced the twin-engine 777 (Fig. 5.6a), the biggest two-engine jet ever to fly and the first aircraft to be produced through computer-aided design and engineering (Wiki: Boeing 777; April 2018o). The 777 is equipped with

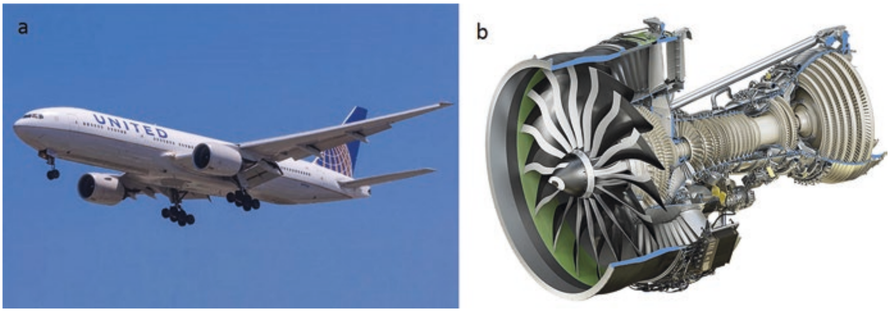

Fig. 5.6 (**a**) The twin-engine Boeing 777; image from (https://commons.wikimedia.org/wiki/File:United_Airlines_777_N797UA_LAX.jpg) and (**b**) the GE9X engine that powers it (https://en.wikipedia.org/wiki/General_Electric_GE9X). (Image used with permission from GE Aviation)

the GE90 engine (Fig. 5.6b) which is one of the world's most powerful turbofan engines (Wiki: General Electric GE90; March 2018p), although larger variants are now available like the GE90-115B which in 2002 set a world record of 127,900 lbf thrust. The GE90 engine was the world's first engine to be fitted with carbon fiber composite fan blades.

From 2000 to Present

Two of the state-of-the-art aircrafts introduced in the 2000s were the Airbus A380 and Boeing's 787 Dreamliner . The A380 (Fig. 5.7a) is currently the world's largest passenger aircraft (Wiki: Airbus A380; April 2018q) and is a four-engine, twin-isle, full-fuselage double-deck aircraft with 525 passengers seating capacity in a typical three-class configuration. The airports in which it operates had to be upgraded to handle it. It entered commercial service in 2007 with Singapore Airlines and is intended to fly long-range, nonstop flight segments (designed for 9780 miles) and at a cruising speed of Mach 0.85 (560 mph). The four engines that power the aircraft are either the Rolls-Royce Trent 900 engine or the General Electric/Pratt & Whitney Alliance Engine GP7200, each delivering roughly 70,000 lbf thrust. Different sections of the aircraft are made in Spain, Germany, France, and England and assembled in France. Carbon fiber-reinforced plastic composites are used for the central box of the wings, the horizontal stabilizers, the fin, the rear fuselage section, and the ceiling beams. The panels for the upper fuselage use a metal-plastic laminate composite called GLARE (see below), all in an effort to keep the vehicle weight to a minimum. Currently however, there are some questions and concerns about the sustainability of the A380 because it is too big, too expensive (purchase and operation costs), and does not fit the operation model (point-to-point versus hub-and-spoke) of many airlines. There has been no buy-in from US airlines thus far and only ten airports in North America currently handle A380s. This also has led to an unbalanced distribution of these aircrafts, primarily in the middle-eastern Gulf countries

Fig. 5.7 (**a**) The Airbus A380 (superjumbo); (http://www.aviationfigure.com/15-interesting-facts-about-airbus-a380/); picture taken from https://commons.wikimedia.org/wiki/File:1er_vol_bed_l'_A380.jpg and (**b**) the Boeing 787 Dreamliner (http://compositesmanufacturingmagazine.com/2018/01/boeing-787-10-dreamliner-cleared-commercial-service-federal-aviation-administration/). (Image taken from https://commons.wikimedia.org/wiki/File:All_Nippon_Airways_Boeing_787_Dreamliner_two.jpg)

where the total population is less than a tenth of that in North America. Furthermore, major freight carriers have not bought into the A380 and resale market for these behemoths when they come off lease appears gloomy (Goldstein 2018).

Airbus has recently also introduced the A350 XWB (extra wide body) long-haul, twin-engine family of aircrafts (Wiki: Airbus A350 XWB; April 2018s) with wing and fuselage constructed primarily of carbon fiber-reinforced plastics, seating from 280 to 360 passengers in a three-class layout, all to compete with the Boeing 787 and 777 fleet. Two versions in the family, the A350-900 and the A350-1000, entered service in January 2015 and February 2018, respectively.

The Boeing 787 Dreamliner (Fig. 5.7b) is a long-haul, mid-size wide-bodied, twin-engine jet airliner intended to replace the 767 but designed to be 20% more fuel efficient (Wiki: Boeing 787 Dreamliner; April 2018r and http://compositesmanufacturingmagazine.com, 2018). Its variants (three of them, 787-8, 787-9, and 787-10) seat 240–330 passengers in typical three-class seating configurations. The 787 is the first major commercial airplane to have a composite fuselage and composite wings and uses composites in most other airframe components. Boeing lists its materials by weight as 50% composite, 20% aluminum, 15% titanium, 10% steel, and 5% others (Hale 2006). Aluminum has been used throughout the wing and tail leading edges, and titanium is predominantly present within the elements of the engines and fasteners, while various individual components are composed of steel. The 787 Dreamliner's distinguishing features include mostly electrical flight systems, raked wingtips, and noise-reducing chevrons on its engine nacelles. The two different engine models are the Rolls-Royce Trent 1000 or the General Electric GEnx engines. The 787's cabin windows are larger than any other civil air transport in service and have a higher eye level so passengers can maintain a view of the horizon. The composite fuselage permits larger windows without the need for structural reinforcement. Instead of plastic window shades, the windows use smart glass (allowing flight attendants and passengers to adjust five levels of sunlight and visibility to their liking, reducing cabin glare while maintaining a view to the outside world. The internal cabin pressure and humidity control (programmable) are superior to previous aircrafts. The 787-8 entered commercial service in October 2011, while the 787-9 (a stretched variant), which is 20 ft longer and can fly about 500 miles (830 km) farther than the 787-8, entered commercial service in August 2014.

In the 2010 timeframe, the Boeing 737 Max series (Wiki: Boeing 737 Max; April 2018t) evolved with improved winglets and enhanced efficiency and fitted with the new CFM International LEAP engines (CFM International is a joint venture between GE Aviation in the United States and Safran Aircraft Engines (previously Snecma) in France). The 737 Max entered service in 2017, and Boeing had more than 3800 firm orders for the 737 Max as of July 2017.

Lastly, Boeing is now in the development and testing stage of its new wide-bodied, twin-engine long-haul series, the 777X (Wiki: Boeing 777X; March 2018u), which is expected to feature the new GE9X engines, new composite wings with folding wingtips, and other technologies incorporated in the 787. Two variants at least are scheduled, one being the 777-8 (seating 365) and the 777-9 (seating 414), the latter being a stretched version. Current plans are to have the 777-9 available in the 2019–2020 timeframe for commercial flight. Interestingly, the 777X is planned to retain its aluminum fuselage as compared to the composite fuselage of the 787 Dreamliner and its competitor, the A350XWB. The rationale is that the 787 was a replacement for the 767 and it needed fuselage redesign. Since all new tooling was required anyway, a composite fuselage was the result. In contrast, the 777's fuselage cross section remained unchanged, and so the decision was made to harvest much of the novel 787 technology but retain a metal fuselage.

The Jet Engine (From 1937 to Present)

A major milestone in aircraft development was the design of jet engines in 1937. The jet engine concept and design evolved independently in Britain (credited to Frank Whittle) and in Germany (credited to Hans Von Ohain). In 1939, the first jet aircraft, the Heinkel 178, took off, powered by von Ohain's HE S-3 engine (Wiki: Heinkel He 178; April 2018v). Almost 2 years later, in 1941, the Gloster E.28/39 was the first British jet to be flown using a Whittle engine (Wiki: Gloster E.28/39; April 2018w). This section details the general specifications of major jet engine types in a roughly chronological manner, synthesized mostly from publicly available information, largely drawn from Wikipedia. Undoubtedly it is the technology that was developed around this engine that has advanced air travel to the point it is at today.

In the early days, the turbojet engine dominated the scene. In the turbojet design, the air is sucked in through the compressor in its entirety and combusted in the combustion chamber with the fuel, and then the hot gases exit the engine through the nozzle via the turbine (that provided for the compressor rotation). The design was not fuel efficient at all as all the air had to be combusted; furthermore, the

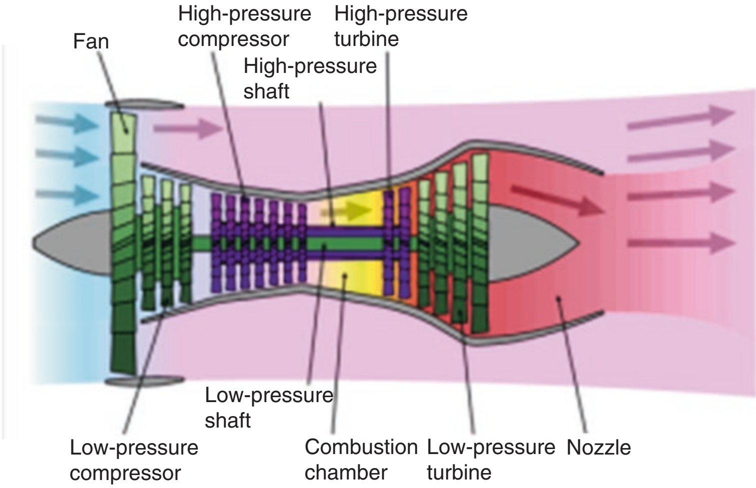

Fig. 5.8 A schematic illustration of a bypass engine (File:Turbofan operation.png. (2014, December 23). *Wikimedia Commons, the free media repository*. (Retrieved, April 14, 2018 from https://commons.wikimedia.org/w/index.php?title=File:Turbofan_operation.png&oldid=143753231)

engine was extremely noisy. This led to the design of bypass jet engines (Fig. 5.8) and their implementation in the civilian air transportation sector. In this design, some of the air bypasses the core, thereby improving fuel efficiency because only part of the air inducted by the fan needed to be mixed with the fuel and combusted; furthermore, the noise was significantly reduced because a layer of cool bypass air surrounded the hot air coming out of the turbines. The ratio of the mass flow of air bypassing the engine core compared to the mass flow of air passing through the core is referred to as the *bypass ratio*. Engines can be *low-bypass* or *high-bypass*. Most commercial airliners today employ the high-bypass type engine and have a huge fan at the front of the engine that generates the air intake, with most of the air bypassing the core. The common bypass ratio used to differentiate this type of engine from the type above is a bypass ratio of 3:1, which means three times the volume of air bypasses the core compared to the volume of air that travels through the core.

The family of CF6 high-bypass turbofan engines (produced by General Electric Aviation) was based on the TF39 (the very first high-bypass aircraft engine) and has been extensively used in many civilian aircrafts including the Airbus A310, Boeing 747-400, and the Boeing767 (Wiki: General Electric CF6; April 2018x). Since its introduction in 1971 in the DC-10, several variants of the CF6 have evolved with different thrusts, compressor and turbine stages, and fan size (the CF6-50, CF6-80, CF6-80A, CF6-80C2, and CF6-80E1).

In parallel, Pratt & Whitney's JTD9 engine (Wiki: Pratt & Whitney JT9D; January 2018y) was the first high-bypass engine to power a wide-bodied airliner (twin-aisle aircraft), the Boeing 747-100 (the original "jumbo jet"). Several models of the JTD9 were developed with thrusts ranging from 45,800 lbf to 56,000 lbf.

Production ceased around 1990, and the PW4000 engine family with thrusts ranging from 52,000 lbf to ~99,000 lbf became the successor to the JTD9 engines (Wiki: Pratt & Whitney PW4000; March 2018z). Three distinct families of the PW4000 are produced and are categorized based on fan diameter. The first family is the 94″-diameter fan with thrust ranging from 52,000 to 62,000 lbf, powering aircrafts such as the Airbus A310-300, the Boeing 747-400, and the Boeing 767-200/300. The second family is the 100″-diameter fan engine developed specifically for the Airbus A330 twinjet. It has thrust ranging from 64,500 to 68,600 lbf. The third family is the 112″-diameter fan engine developed specifically for Boeing's 777 and is currently available on the 777-200ER; it has thrust ranging from 86,700 to ~99,000 lbf, and it entered service in June 1995.

Pratt & Whitney's PW2000, which went into service in the 1980s (Wiki: Pratt & Whitney PW2000; January 2018aa), covered the mid-thrust range (~37,000 to ~43,000 lbf) and powered all models of the Boeing 757. An improved version of it was introduced in the mid-1990s called the reduced temperature configuration which increased reliability and durability and provided enhanced environmental performance while providing reduced total maintenance costs.

The CFM56 series is by a significant margin the most successful commercial aircraft engine of all time, with over 22,000 installed engines delivered as of 2015 (Morrison 2015). It is a family of high-bypass turbofan aircraft engines made by CFM International (CFMI), with a thrust range of 18,500–34,000 lbf (82–150 kN). The first engines entered service in 1982. In the early 1980s, Boeing selected the CFM56 engine for the Boeing 737-300 variant. As the 737 wings were closer to the ground than previous applications for the CFM56, it required several modifications to the engine. The fan diameter was reduced, which reduced the bypass ratio. The overall thrust was also reduced, from 24,000 to 20,000 lbf (107–89 kN), mostly due to the reduction in bypass ratio (Wiki: CFM International CFM56; March 2018ab). Subsequently, derivatives within this family of engines (CFM56-5A) have been fitted specifically to the Airbus A320 to power short- to medium-range flights.

The LEAP is a new engine design based on and designed to replace the CFM56 series, with 16% savings in fuel consumption by using more composite materials (polymer matrix and ceramic matrix composites) and achieving higher-bypass ratios of over 10:1. The engine also has some of the first FAA-approved 3-D-printed components. LEAP entered service in 2016 with major applications in the Airbus A320neo and the Boeing 737 Max families (Wiki: CFM International LEAP; April 2018ac).

The GE90 engines are a family of high-bypass turbofan engines built for the Boeing 777, entering service in 1995, and are physically some of the largest engines in aviation history. The fan diameter of the original series is 123″ (310 cm). The fan blade is made from carbon fiber composite, the first ever in commercial aviation, and uniquely curved to make it larger, lighter, and more aerodynamic than the more traditional titanium blade (discussed below). General Electric Aviation has continued to improve upon the original GE90 design and the GE90-115B, a high-thrust variant of the original GE90 generating up to 115,300 lbf thrust at sea level, making it the world's most powerful commercial jet engine, built exclusively for Boeing's largest 777 models—777-200LR and 777-300ER. Designed using three-dimensional aerospace computer modeling technology, the carbon fiber composite blade draws a massive amount of air into the engine while operating at a low noise level. Each blade is about 4 ft long and weighs less than 50 lbs.

Next came the GEnx engine which powers the four-engine Boeing 747-8 and the Boeing 787 Dreamliner (Wiki: General Electric GEnx; January 2018ad). The GEnx uses advanced materials and design processes to reduce weight, improve performance, and provide a fuel-efficient commercial aircraft engine. The GEnx engine is the world's first commercial jet engine with both a front fan case and fan blades made of carbon fiber composites. In addition, it has a reduced blade count in the fan (weight savings) and incorporates an innovative combustor technology called TAPS (twin-annular pre-swirl) that reduce NO*x* gases. Further, the low-pressure turbine (LPT) is lighter and more efficient than its predecessor and incorporates titanium aluminide blades in the sixth and seventh stages, further reducing engine weight by approximately 400 lbs. and contributing to increased fuel efficiency.

The GE9X is the latest high-bypass turbofan engine under development (Wiki: General Electric GE9X; March 2018ae) and is the engine targeted to power Boeing's new 777X long-haul airliner that is anticipated to enter service around 2020. The engine incorporates several advanced materials and revolutionary design that will make it 10% more fuel efficient than the GE90-115B while having reduced noise and NO*x* emissions. The bypass ratio is planned for 10:1 and the fan diameter is (134″) 340 cm. It has fewer blades (16 blades) than the GEnx (18 blades), and the bulk of the fan blades is made out of carbon fiber composite making the engine lighter and allowing the fan to spin faster. The fan blades have steel leading edges and glass fiber trailing edges to better absorb bird impacts. The TAPS technology is utilized in the combustor as in the GEnx, while ceramic matrix composite (CMC) liners are used in two combustor liners, two nozzles, and the shroud that enable withstanding higher temperatures. The first five stages in the compressor use "blisk" technology (integrated bladed disks), and the low-pressure turbine airfoils are made of titanium aluminides that are lighter than the more conventional nickel-based parts. Novel manufacturing technologies such as 3-D printing are used to produce various parts in the engine.

Meanwhile, Pratt & Whitney has been developing the PW1000G family of engines, including the PW1100G with a 81″ diameter fan composed of 20 blades, a high-bypass ratio of 12.5:1 and a thrust range of 24,000–35,000 lbf that entered service in January, 2016, and is currently powering the Airbus A320neo family of aircrafts (Wiki: Pratt & Whitney PW1000G; April 2018af). Others in the family are smaller engines and include PW1200G, PW1400G, and PW1700G with anticipated service entry dates in the 2019–2021 timeframe. These engines distinguish themselves with a new technology called geared turbofan technology (GTF) whereby a gearbox is introduced between the fan and the low-pressure compressor that enables them to spin at different speeds that are optimal for each (e.g., 4000–5000 rpm for the fan and 12,000–15,000 rpm for the low-pressure spool); this permits lower fan speeds which in turn enable higher-bypass ratios which results in reduced fuel consumption and reduced noise.

Engine Alliance is a joint venture between General Electric and Pratt & Whitney that manufactured the GP7000 turbofan engine and is an option for the Airbus A380 (Wiki: Engine Alliance GP7000; March 2018ag). With a fan diameter of 116″ (hollow titanium fan blades), a maximum thrust of 74,000–80,000 lbf, and a bypass ratio of 8.8:1, two versions, the GP7270 (the passenger version) and the GP7277 (the freighter version) were created for the A380, although Airbus subsequently canceled its freighter version of the A380.

On the other side of the Atlantic, another major aircraft engine producer, Rolls-Royce, has been developing several engines that have shared the market in powering modern passenger flights. Examples include the Trent 500, 700, 800, and 900, the Trent 1000, the Trent 7000, and the Trent XWB (Wiki: Rolls-Royce Trent; March 2018ah). All are developments of the RB211 high-bypass engine (37,400–60,600 lbf thrust) that first entered service in 1972 and has powered aircrafts such as the Lockheed L-1011 and the Boeing 747, 757, and 767. The Trent series evolved in the 1990s with thrust ratings ranging from 53,000 to 97,000 pounds-force (240–430 kN). Versions of the Trent are in service on the Airbus A330, A340, A350, and A380 and Boeing 777 and 787. Table 5.1 summarizes details on

Table 5.1 Trent family of bypass engines produced by Rolls-Royce

Engine model	Takeoff thrust (lb-force)	Aircraft type	Service entry	Notable features
Trent 500	56,000	Airbus A340	July 2002	Specifically designed for the A340; first Trent to feature high technology tiled combustor design
Trent 700	72,000 (max)	Airbus A330	March 1995	Only A330 engine with a wide-chord fan, reduced noise, emission, and fuel burn
Trent 800	75,000–95,000	Boeing 777	April 1996	Lightest engine on the 777; a Trent 800 EP package is available that delivers fuel burn savings
Trent 900	70,000–84,000	Airbus A380	October 2007	116″-diameter advanced swept fan; fan containment system is the first to be manufactured from titanium rather than Kevlar; the high-pressure shaft rotates in the opposite direction to the other two shafts for greater fuel efficiency
Trent 1000	62,000–81,000	Boeing 787	October 2011	10:1 bypass ratio; 2.8-m-diameter fan; a heated engine section stator system delivers advanced ice protection; New HP turbine with advanced cooling system to enable more thrust and efficiency
Trent 7000	68,000–72,000	Airbus A330neo	Not as yet	Highest-bypass ratio of any Trent engine; fully swept, wide-chord fan; 6 dB quieter than the 700 model; and 10% specific fuel consumption improvement over it
Trent XWB	74,000–97,000	Airbus A350	January 2015	Unique lightweight three-shaft design; the use of compressor blisk technology; optimized internal air system which reduces core air demand and reduces fuel consumption; highest efficiency turbine system of any Trent engine

some of these engines, their thrust capabilities, the aircrafts these engines power, and when they first went into service.

As innovations, developments, and implementation in aircraft structure and engine design have evolved, so has the range of materials implemented in making them. Thus, wood and cloth from the early days have progressively given way to metals and alloys, and more recently, to the incorporation of composites (both polymer matrix and ceramic matrix) and coatings. Such innovations in materials in the aircraft industry have been enabled by significant advances in materials processing and manufacturing technology, and have progressively enhanced performance through weight savings, increased speeds, improved fuel efficiency, reduced emissions, and quieter aircrafts. In the rest of this chapter, the focus is on the materials science and engineering developments that have made their impact on the evolution of modern commercial aircrafts; emphasis is placed on the fuselage, wings, and empennages on the one hand, and the propulsion system (aircraft engines) on the other. In so doing, and to maintain a manageable perimeter, the coverage is centered on subsonic passenger aircrafts powered by air-breathing turbofan bypass engines.

The Fuselage, Wing, and Empennage

In the early days of powered flight, roughly from 1903 to 1930, achieving the absolute minimum in weight was a practical requirement, in significant part due to the limitation of propulsion systems. Consequently, the strength-to-weight ratio was the primary selection criterion for materials for aircraft structure and propulsion. Nowadays, while lightweight is still very important, it is not sufficient and current design criteria are much more complicated. The transition from internal combustion piston engines to turbine engines was a quantum leap in aircraft technology although early turbine engines were limited by materials limitations, especially high operating temperatures. The desire to fly faster and longer distances placed additional new constraints such as higher temperatures due to frictional heating, and thus skin materials have progressed from wood and fabric to high-strength aluminum alloys, titanium alloys, and carbon fiber-reinforced polymer matrix composites. Multiple aircraft accidents that used high-strength aluminum alloys in the 1950s led to the recognition of the importance of damage tolerance under varying loading conditions, and today properties like fracture toughness and fatigue crack growth resistance are incorporated as primary design criteria in many aircraft structural products (Williams and Starke 2003). Developments of new alloys with improvement in such properties in fact have enabled revisions in design and further weight savings. Thus, there is a complex interplay between material properties-material chemistry-material processing and component design that has continually evolved from societal needs, desires, and constraints as well as from field experience that together have enabled substantial enhancements in aircraft performance, particularly over the recent decades.

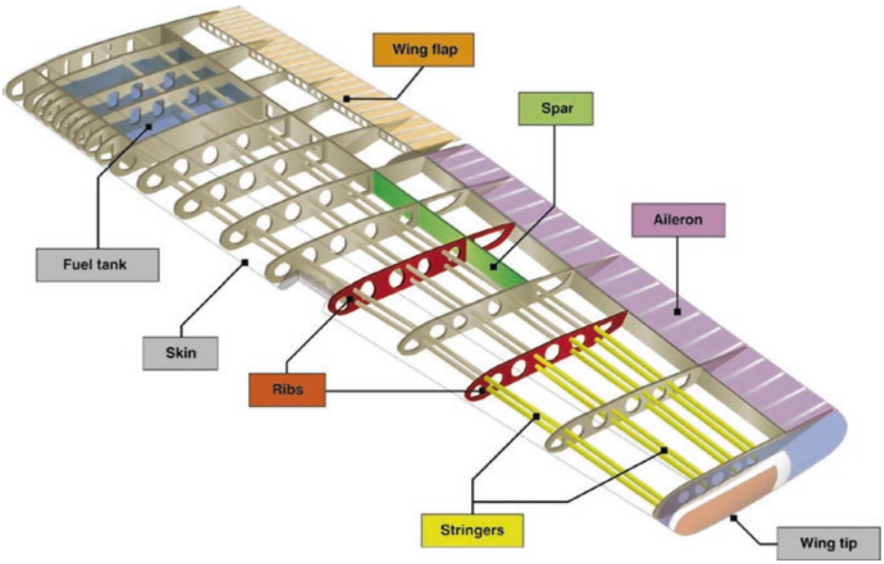

Fig. 5.9 The basic nomenclature associated with the aircraft wing structure. (Source: http://aerospaceengineeringblog.com/wp-content/uploads/2012/08/Airplane-Wing-Part-Diagram-Terminology.png; http://www.cfinotebook.net/notebook/aerodynamics-and-performance/aircraft-components-and-structure)

The basic airframe structure of an airplane can be broadly dived into four major components. The fuselage or the main body is where passengers and baggage are located and to which the wings and the empennage are attached. The wings provide the lift to the aircraft, with the front being called the leading edge and the rear being called the trailing edge. Ailerons and flaps are located on the trailing edge of the wings and can influence the wing surface area and airflow over the wing, thereby affecting lift in various phases of the flight (Fig. 5.9). Many modern aircraft also include winglets at the outer ends of the wings that help in reducing drag. The empennage or the ‘tail” of the aircraft includes the horizontal and vertical stabilizers (these control pitch and yaw, respectively), elevator, and rudder. The rudder is a part of the vertical stabilizer that allows the airplane to turn left or right when it is activated, while the elevator is located on the rear part of the horizontal stabilizer and moves up or down to enable moving the nose of the plane up or down. The undercarriage refers to the landing gear assembly and wheels and tires.

As these different components serve various complimentary functions, they also experience very different loading profiles (tension, compression, shear, constant load, fluctuating loads) during takeoff, in flight, and during landing, and therefore have received very different design and materials selection considerations. The interested reader is directed to the paper by Starke and Staley (1996) for a deeper discussion of loading modes experienced by the various components of the airframe. Although polymer matrix composites (PMCs) are being used in modern commercial aircrafts (e.g., PMCs in the horizontal stabilizer of the Airbus A340 and the Boeing 777), aluminum alloys continue to be the primary choice at present for airframes (Starke and Staley 1996). Titanium alloys have seen an increased role in commercial airliners such as the landing gear beam of the Boeing 747 as well as the landing gear assembly of the Boeing 777 (Williams and Starke 2003) but more so in military aircrafts as in the case of the SR-71 which had an all-titanium skin.

Aluminum Alloys

Aluminum alloys are typically used in wrought form (which means the starting material is an ingot/billet that is then either rolled into sheet or plate, extruded into bars or rods, or forged into net-shape that are then final-machined to dimensions) or as cast products. Primary structures (those whose failure endangers the aircraft (Starke and Staley 1996)) are wrought products, whereas secondary structures can be wrought or cast products. Sheet and plate in the 1–10-mm-thickness range are used for fuselage skin, while thicker plates in the range of 25–50 mm are used for wing covers, and the thickest plates up to 150 mm are used for bulkheads and wing spars. Extrusions are used for longerons and stringers in the fuselage as well as in the wings (these are the bars/rods that reinforce the fuselage axially or along the length of the wing structure; see Figs. 5.9 and 5.10). Forgings (open-die and closed-die) compete with thick plates for bulkheads and other internal structures.

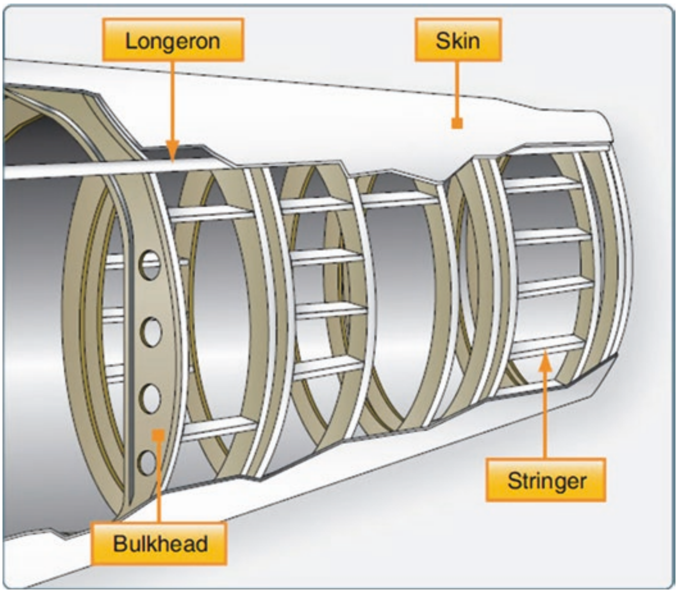

Fig. 5.10 Structural components of the airframe fuselage. (Source: http://www.flight-mechanic.com/fixed-wing-aircraft/)

Castings for airframe structures are produced using techniques such as sand casting, investment casting, and permanent mold casting (Kalpakjian and Schmid 2008), and the selection depends on size, weight, required dimensional accuracy, part criticality, cost, and property requirements. The mechanical properties of castings, particularly properties such as fatigue crack growth resistance and life, are often not as consistent or as good as the more costly wrought counterpart, but cost reduction can be an important aspect of the selection. Net-shape castings can also reduce complex machining operations and the number of joints in a complex-shaped component thereby making it more resistant to corrosion. Although castings have been used for both primary and secondary structural components in military aircrafts, their use in commercial aircraft is less common and has been restricted more to secondary structures like pulley brackets, ducts, and complex valve bodies of hydraulic control systems. Nevertheless, there is a gradual increase in the number of components using cast aluminum such as for flap tracks in the wing structure, and for passenger and baggage compartment doors, specifically by Airbus.

Superplastic forming of certain aluminum alloys is a third route used to make an array of secondary components for the commercial airframe (examples include baggage compartment doors, inner frame for the blowout door assembly for the Boeing 737, the Boeing 737 auxiliary power unit (APU) air inlet duct, and the Boeing 777 wingtip light housing (Hefti 2007)). Superplastic forming refers to a secondary metal forming operation where the metal experiences large deformations (200–1000% strains) without failing by necking/local thinning. The process is typically carried out at elevated temperatures that are typically excess of half the melting temperature, at strain rates of the order of 10^{-4} s^{-1}, and at very low stress levels (4–6 MPa for aluminum alloys). A special fine-grained equiaxed microstructure (<10 μm grain size) and resistance to cavitation/voiding are prerequisites; conventionally processed aluminum alloys do not exhibit this microstructure, and therefore special additional processing that adds cost is necessary to obtain such microstructures. By the way of dominant deformation mechanisms that occur during superplastic forming, grain boundary sliding and diffusion-controlled deformation mechanisms are high on the list. The process is slow, material costs are high, and specialized aluminum alloys (SUPRAL 100 and 220 and FORMALL 545 and 700) have been developed that exhibit superplastic characteristics. Nevertheless, superplastic forming offers economic advantages when a limited number of complex parts need to be made with expensive materials that have low formability as, for example, in the case of some titanium alloys.

Heat-treatable aluminum alloys, that is, those that are capable of being *age-hardened*, are primarily used as wrought products in airframes because of their ability to develop high specific strengths. Age-hardening or precipitation hardening is a two-step heat treatment (Porter and Easterling 1992), composed of a first "solution-treatment" step followed by a second "aging" step, that certain aluminum alloys can be subjected to and that enables them to develop a desirable microstructure composed of a homogeneous distribution of fine-scale precipitates in a matrix that substantially increases the alloy strength. By controlling the time and temperatures of this two-step heat treatment, a balance in properties can be obtained. Precipitation hardening has been even suggested as perhaps being the most significant metallurgical development of the twentieth century, and there are now many detailed reviews and overviews of the subject of precipitation hardening of aluminum alloys (Ardell 1985; Fine 1975; Kelly and Nicholson 1963; Polmear 2004; Ringer and Hono 2000). Alloys belonging to the 2XXX, 6XXX, 7XXX, and 8XXX series are candidates for precipitation hardening and are primarily used in airframe structures, with historically the 2XXX alloys being used when damage tolerance is the primary requirement and the 7XXX alloys being preferred where strength is the primary requirement.

A four-digit numerical system originally developed by the Aluminum Association and then accepted by most countries and known as the International Alloy Designation System (IADS) is currently used to describe wrought aluminum alloys (Table 5.2). The first digit indicates the alloy group/major alloying element (major alloying elements typically added to aluminum include Cu, Mg, Zn, Si, Mn, and Li), the second digit indicates the impurity limits/modification of the original registered alloy, and the last two digits identify the specific aluminum alloy. Experimental alloys are indicated by a prefix X. Table 5.3 shows specific compositions for a few aerospace aluminum alloys.

Casting alloys use a different notation. Two common casting alloys are A201.0 and A357.0. The first digit refers to the major alloying element and the second two digits identify a particular alloy composition. The zero after the decimal point identifies the product as a casting, while other numerals identify ingots. The letter prefix identifies impurity level starting with A; for example, A357.0 denotes a higher purity than the original 357.0.

Many, if not all the wrought alloys, are age-hardenable alloys, and as mentioned above, their properties can be tuned by controlling the precipitation hardening heat treatment. This has led to a series of heat treatment schedules that are coded by various letters and digits called "temper designations" as summarized in Table 5.4. These codes are usually added as suffixes to the alloy number (e.g., 7075-T6 or 2024-T3). Subsets of the temper that modify the properties further are denoted by one or more digits following the letter as shown in the examples above.

Table 5.2 Wrought aluminum alloy designation as per IADS

Four-digit series	Major alloying element
1XXX	99% minimum aluminum content
2XXX	Copper (Cu)
3XXX	Manganese (Mn)
4XXX	Silicon (Si)
5XXX	Magnesium (Mg)
6XXX	Magnesium and silicon
7XXX	Zinc (Zn), most contain magnesium as well
8XXX	Others, e.g., lithium (Li)

Adapted from Starke and Staley (1996)

Table 5.3 Nominal compositions (wt %) of some aerospace aluminum alloys

Alloy	Zn	Mg	Cu	Mn	Cr	Zr	Fe	Si	Li	Others
2014	–	0.5	4.4	0.8	–	–	0.7	0.8	–	–
2017	–	0.6	4.0	0.7	–	–	0.7	0.5	–	–
2024	–	1.5	4.4	0.6	–	–	0.5	0.5	–	–
2090	–	–	2.7	–	–	0.1	0.12	0.1	2.2	–
2219	–	–	6.3	0.3	–	0.2	0.3	0.2	–	0.1V
6013	–	1.0	0.8	0.35	–	–	0.3	0.8	–	–
7050	6.2	2.25	2.3	–	–	0.1	0.15	0.12	–	–
7075	5.6	2.5	1.6	–	0.23	–	0.4	0.4	–	–
7475	5.7	2.25	1.6	–	0.21	–	0.12	0.1	–	–
8090	–	0.9	1.3	–	–	0.1	0.3	0.2	2.4	–

Adapted from Starke and Staley (1996)

Table 5.4 Temper nomenclature for wrought aluminum alloys

Suffix letter F,O, H, T, or W indicates basic treatment	First suffix digit indicates secondary treatment used to influence properties	Second suffix digit for condition H only indicates residual hardening
F – As fabricated O – Annealed-wrought products only		
H – Cold-worked strain hardened	1 – Cold worked only 2 – Cold worked and partially annealed 3 – Cold worked and stabilize	2 – ¼ hard 4 – ½ hard 6 – ¾ hard 8 – hard 9 – extra hard
W – Solution heat-treated		
T – Heat-treated stable	1 – Partial solution plus natural aging 2 – Annealed cast products only 3 – Solution + cold work 4 – Solution + natural aging 5 – Artificially aged only 6 – Solution + artificial aging 7 – Solution + stabilizing 8 – Solution + cold work + artificial aging 9 – Solution + artificial aging+ cold work	

Adapted from Starke and Staley (1996)

Alloys in the as-fabricated state or in the annealed state are identified with the suffixes F and O, respectively; those supplied in the solution-treated condition are designated with a W, while those supplied in the solution-treated + aged condition are assigned the suffix T. Digits following T identify the type of aging treatment.

Four often-encountered heat treatments in the 2XXX series alloys like 2024 or 2090 and in the 8XXX series Li-containing alloys like 8090 are the T3, T4, T6, and

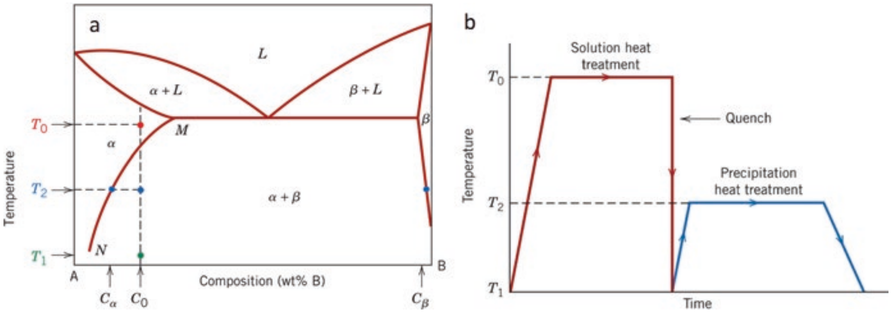

Fig. 5.11 (**a**) Schematic illustration of a binary phase diagram and a candidate alloy of composition C_o that is precipitation-hardenable, and (**b**) the two-step precipitation hardening treatment. (Figure taken from Materials Science and Engineering, Callister and Rethwisch (2013); image used with permission from John Wiley & Sons, Inc.)

T8 treatments. The T3 and T8 treatments include a deformation step after solution treatment like a 2–6% stretch that encourages precipitation and reduces subsequent aging time. Thus, T3 and T4 correspond to natural aging (aging at room temperature) with and without an intermediate stretch, while T8 and T6 correspond to artificial aging to peak or near-peak hardness with and without an intermediate stretch (also see Table 5.4). If aging is carried beyond the T6 condition, either to stabilize the microstructure or as often done to improve corrosion resistance, then the temper is designated T7.

Before discussing desired microstructures for various properties of interest in aluminum alloys, we should at least briefly develop an understanding of precipitation hardening in the 2XXX, the 7XXX, and the Li-containing alloys of relevance to the airframe industry.

In relatively simple terms, alloys amenable to precipitation hardening must exhibit a large maximum solubility for solutes and a rapidly decreasing solubility with decreasing temperature. Normally, such alloys under equilibrium conditions exhibit a multiphase microstructure (in the simplest cases, two phases at least: a matrix phase and a solute-rich second phase). When such an alloy is reheated into the single-phase region (temperature T_o in Fig. 5.11a) and quenched to low temperature (temperature T_1 in Fig. 5.11a), the second phase is unable to precipitate out, and so the single phase is retained in a supersaturated state. Importantly, a supersaturation of vacancies is also present in the microstructure. This is called the *solution-treated and solution-quenched microstructure*. When this supersaturated matrix is reheated and held at an intermediate temperature (T_2 in Fig. 5.11a) for a length of time, supersaturation is gradually relieved by a uniform distribution of fine precipitates, and the heat treatment step is called *aging*. A schematic illustration of this two-step heat treatment together with a schematic binary phase diagram at the A-rich end of an A-B system is shown in Fig. 5.11a, b (Callister and Rethwisch 2013).

The kinetics of precipitation are aided by the quenched-in excess vacancies as otherwise the equilibrium concentration of vacancies alone at the aging temperature would not be adequate to provide reasonable precipitation kinetics. During the solid-state precipitation process to relieve the supersaturation described above, for energetic reasons, the first phase to precipitate is often not the equilibrium phase but a metastable phase or series of metastable phases called *transition phases*. Eventually, the transition phases give way to the equilibrium phase. These transition phases are important in bestowing a good combination of mechanical properties to these solution-treated and aged alloys. Frequently, by the time the equilibrium phases precipitate out at the expense of the transition phases in an alloy, the material is excessively overaged and its properties are degraded. Thus, from a mechanical properties perspective, during aging, one goes from the solution-treated and solution-quenched condition where the material strength/hardness is not very high through an underaged condition where strength and hardness are increasing and reach a maximum at the so-called "peak-aged" condition; beyond peak aging, the strength and hardness begin to decrease and we are now in an overaged state.

In some instances, for example, in some 2XXX series of alloys, aging progresses as a function of time even at room temperature, and then the process is referred to as "natural aging" as opposed to "artificial aging" where a part is aged at an elevated temperature. Natural aging does not normally produce an overaged microstructure, and thus the strength/hardness shows a gradual continuous increase over long periods of time. This idea is utilized in hardening aluminum alloy rivets (e.g., alloy 2017 and 2024) used in airframes where the solution-treated and solution-quenched rivets are stored in a refrigerator to suppress natural aging and keep them soft until they are popped in place; thereafter the rivet hardens over time at room temperature and acquires the needed strength to function effectively. The Mg present in these Al-Cu alloys (Table 5.3) is believed to encourage natural aging. In this context, of historic relevance is the discovery of the phenomenon of age-hardening in 1906 and the patenting of an age-hardenable aluminum alloy with a bulk composition of Al (3.5–5.5 wt%)-Cu (<1 wt%)-Mn alloy containing <1.0 wt% Mg by Alfred Wilm which was commercialized by the company Durener Metallwerke in Duren in northwestern Germany and copyrighted in 1909 under the name Duralumin (Polmear 2004). The Junkers F13 which flew in 1919 was the first all-metal *passenger* aircraft and was built out of Duralumin. Alcoa in the Unites States released its own version of Duralumin in 1911, and this alloy is still available under the designation Alloy 2017 (see Table 5.3).

The full sequence of microstructure evolution upon artificial aging of a binary Al-Cu alloy can be represented as α supersaturated solid solution on aging decomposes to first form disk-shaped Cu-rich zones called GP (Guinier-Preston) zones that are homogeneously dispersed in the matrix; these disks are typically one to two atoms thick, about 10 nm in diameter, and spaced about 10 nm apart. GP zones do not have their own crystal structure. Further aging leads to the precipitation of a transition phase called θ" which has a tetragonal unit cell, is also plate-like in morphology, is ~10 nm thick, and about 100 nm in diameter. Longer aging times lead to the next transition phase θ', also with a tetragonal unit cell, a plate morphology, and size approaching 1 μm. By the time the microstructure is composed of a mixture of θ" and θ', the alloy is likely in the peak-aged condition. Overaging results in the formation of the equilibrium phase, θ, with the $CuAl_2$ stoichiometry, and this

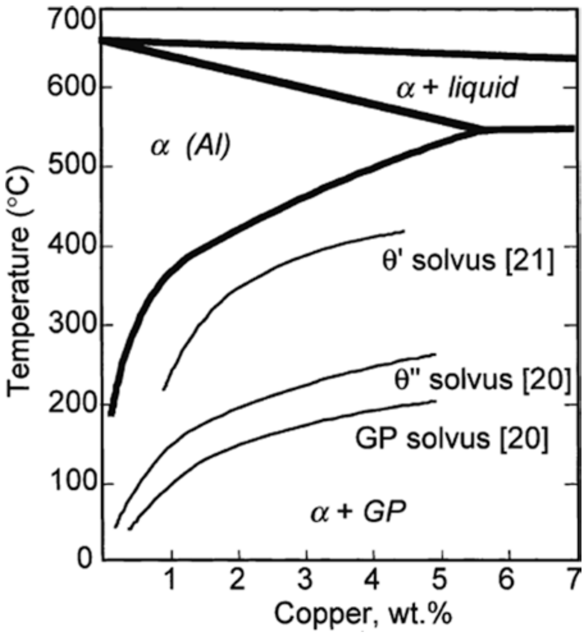

Fig. 5.12 Transition phases in the binary Al-Cu system and their temperature/composition range of existence. (From Ringer and Hono 2000) (Figure used with permission from *Elsevier*)

precipitate is relatively coarse and not particularly beneficial for mechanical properties. So overall, the aging sequence can be represented as α_{ssss} → GP zones → θ" → θ' → θ, where α_{ssss} represents the solution-treated and solution-quenched supersaturated aluminum-rich solid solution phase. Alloy composition, aging temperature, and prior deformation of the solution-treated and solution-quenched alloy all play a role in determining whether all or only some of these microstructural manifestations occur during aging. Thus, for example, moderately increasing the aging temperature of a particular alloy may discourage GP zones formation; rather the θ" phase comes out directly from the supersaturated matrix solid solution, and further increase in aging temperature may even preclude θ", while instead θ' comes out directly from the supersaturated matrix (Fig. 5.12). In alloys like 2024 or 2224 that contain about 1.5 wt% Mg in addition to Cu, the major strengthening phase is the S′ phase which is a precursor to the ternary S phase (Al_2CuMg) rather than the θ' phase.

Precipitation during artificial aging in the 6XXX alloys is complex and is strongly dependent on alloy composition. The properties of 6XXX Al-Mg-Si alloys are influenced by the precursor phases (monoclinic β" and hexagonal β') to the equilibrium cubic Mg_2Si phase (β). Even in the ternary system, the situation becomes more complicated as the overall alloy composition shifts to excess Si levels (i.e., when the Si level exceeds the Mg_2Si stoichiometry). Substantial additional complications arise from the fact that many commercial Al-Mg-Si alloys frequently include varying amounts of Cu in them, and this leads to the formation of many other equilibrium phases that coexist with β. The interested reader is directed to an excellent review of these aspects in Al-Mg-Si-Cu alloys by Chakrabarti and Laughlin (2004).

By comparison, in the 7XXX alloys which are used extensively for airframes, there is significantly more consensus on the microstructure evolution during artificial aging. These alloys usually show a strong age-hardening response, but one drawback is that they are susceptible to stress corrosion cracking (SCC), and this restricts their use in the peak hardness condition. Stress corrosion cracking is a phenomenon whereby an aluminum alloy which normally would not fail under a certain loading condition in an inert environment can experience failure in an aggressive environment including humid air. The phenomenon is more common in specific combinations of alloys and tempers like 7075-T6, 2024-T3, and 7079-T6, and these have contributed to more than 90% of SCC service failures of aluminum alloy products (Starke and Staley 1996). The T73 temper (essentially an overaged state) was developed for 7075 products to solve this problem, but the strength in this condition is lower than that in the 7075-T6 products. There is general agreement that the aging sequence can be represented as $\alpha_{ssss} \rightarrow$ GP zones $\rightarrow \eta' \rightarrow \eta$, where η is the equilibrium $MgZn_2$ Laves phase with the C14 hexagonal structure. The GP zones in Al-Zn-Mg alloys are rich in both Mg and Zn and are spherical in shape (unlike the disk-shaped zones observed in the Al-Cu alloy series). The structure of the η' transition phase has been extensively studied and debated, and a more detailed discussion of this aspect is available in the work of Ringer and Hono (2000). In the peak-aged T6 condition, strength is mainly derived from a fine distribution of the η' and some fine η, whereas in the overaged T73 condition, coarser particles of η dominate the microstructure, being distributed in the grain interior as well as at grain boundaries.

In the past thirty years or so, considerable research and development to incorporate lithium in aluminum alloys (Li decreases density and increases elastic modulus of aluminum, both of which are desirable attributes) has led to several new alloys being developed in the Al-Cu-Li family (e.g., alloy 2090 in Table 5.3), in the Al-Cu-Mg-Li system (e.g., alloy 8090 in Table 5.3), along with newer versions such as alloy 2195 (which includes Li, Cu, and minor levels of Mg, Ag, and Zr) that was used for the external tank of the Space Shuttle, as well as alloys like 2050, 2055, 2060, 2096, 2097, 2098, and 2099. The composition of some of these alloys is provided in Table 5.5 (Dursun and Soutis 2014). More metallurgical details on several of these so-called third-generation aluminum-lithium alloys for aircraft airframes can be found in the detailed review of the history of Al-Li alloys provided by Rioja and Liu (2012) and the overview of advanced aircraft aluminum alloys by Dursun and Soutis (2014). Some of these alloys find applications in the Airbus A380-800 and A380-800F in the lower wing structures and are intended to be used for the Boeing 777X cargo floor. Complex aging treatments combined with newer welding techniques (like friction stir welding) and advances in machining methods have enabled the use of these newer alloys while realizing significant weight savings and obtaining improved balance in properties.

Table 5.5 Composition of some "third-generation Al-Li alloys" compared to 8090 and 2090

Al-Li alloys	Li	Cu	Zn	Mg	Mn	Fe	Si	Cr	Zr	Ti	Others
2050	0.7–1.3	3.2–3.9	0.25	0.2–0.6	0.2–0.5	0.1	0.08	0.05	0.06–0.14	0.1	0.2–0.7 Ag
2090	1.9–2.6	2.4–3.0	0.1	0.25	0.05	0.12	0.10	0.05	0.08–0.15	0.15	–
2098	0.8–1.3	3.2–3.8	0.35	0.25–0.8	0.35	0.15	0.12	–	0.04–0.18	0.1	0.25–0.6 Ag
2099	1.6–2.0	2.4–3.0	0.4–1.0	0.1–0.5	0.1–0.5	0.07	0.05	0.1–0.5	0.05–0.12	0.1	0.0001 Be
2199	1.4–1.8	2.0–2.9	0.2–0.9	0.05–0.4	0.1–0.5	0.07	0.05	–	0.05–0.12	0.1	0.0001 Be
8090	2.2–2.7	1.0–1.6	0.25	0.6–1.3	0.10	0.30	0.20	0.10	0.04–0.16	0.1	–

Adapted from Dursun and Soutis (2014)

The "third-generation Al-Li alloys" evolved out of several years of lessons learnt from the first- and second-generation Al-Li alloys and is an outstanding example of alloy design through fine, thoughtful application of fundamental metallurgical principles. Quoting Rioja and Liu (2012), "understanding the influence of chemical composition and microstructure on mechanical and corrosion performance led to the simultaneous optimization of alloying additions and thermal-mechanical processing." Thus, Li and Mg provide density reduction and solid solution hardening and precipitation hardening, Cu and Ag enhance solid solution hardening and precipitation hardening, Zn is added for solid solution hardening and corrosion improvement, Zr and Mn control the degree of recrystallization and texture in the product, and Ti is a grain refiner during solidification of ingots, while Fe, Si, Na, and K are impurities that adversely affect fatigue response and fracture toughness and should be minimized.

The age-hardening precipitates found in Al-Cu-Li alloys like 2099 and 2199 are the ternary T_1 phase (Al_2CuLi), δ' (Al_3Li), and θ' (~Al_2Cu). In addition to these strengthening precipitates, additional phases called dispersoids (fine particulate phases) such as Al_3Zr and $Al_{20}Cu_2Mn_3$ also occur and influence toughness and enable recrystallization control as well as grain size and texture control. A schematic illustration of the microstructure that might be observed in an aged Al-Cu-Li 2099 alloy (Fig. 5.13) taken from Rioja and Liu (2012) emphasizes the complexity (but the versatility to manipulate as well) that is present in these alloys. Dispersoids are not unique to Al-Cu-Li alloys but in fact occur in many airframe aluminum alloys, and Table 5.6 (Starke and Staley 1996) summarizes findings in a few of these alloys.

In a well-annealed alloy, grains are typically equiaxed and randomly oriented; that is, with respect to a global coordinate system, each grain is differently aligned, crystallographically speaking, so that there is a distribution of crystallographic orientations along any selected global coordinate when summed over all the grains.

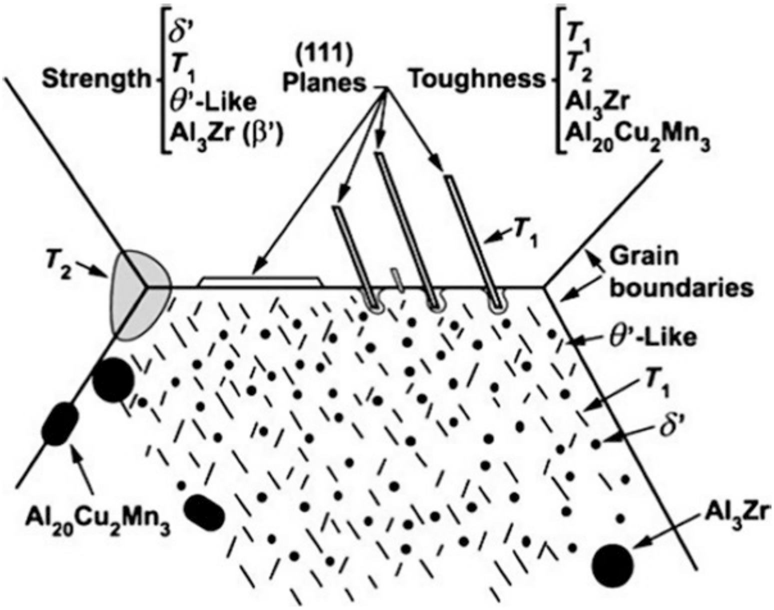

Fig. 5.13 Schematic illustration of the microstructural complexity that is present in Al-Cu-Li alloys like alloy 2099 (Rioja and Liu 2012). (Figure used with permission from *Springer*)

Table 5.6 Dispersoids in aircraft aluminum alloys

Alloy	Dispersoid
2X24	$Al_{20}Cu_2Mn_3$
6013	$Al_{12}Mn_3Si$
7X75	$Al_{12}Mg_2Cr$
7X50	Al_3Zr
7055	Al_3Zr
2090	Al_3Zr
2091	Al_3Zr
2095	Al_3Zr
8090	Al_3Zr

Adapted from Starke and Staley (1996)

However, when an alloy experiences considerable deformation such as extrusion or rolling, grains can develop a preferred orientation with respect to the deformation axis and then we say the material is no longer randomly textured but has developed a crystallographic texture which can be moderate or severe. Texture invariably leads to anisotropic properties in the material. Aluminum-lithium alloys, for example, can develop strong texture and texture gradients during fabrication, and this raises

Table 5.7 Property-microstructure relationships in aluminum alloys

Property	Microstructural feature	Function of feature(s)
Strength	Uniform dispersion of small, hard particles, fine grain size	Inhibit dislocation motion
Ductility and toughness	No large particles, clean grain boundaries, fine structure, no shearable particles	Encourage plasticity, inhibit void formation and growth, work harden
Fatigue crack initiation resistance	No shearable particles, fine grain size, no surface defects	Prevent strain localization and slip steps on surface, prevent stress concentration
Fatigue crack propagation resistance	Shearable particles, no anodic phases or hydrogen traps, large grain size	Encourage crack closure, branching, deflection, and slip reversibility
Pitting	No anodic phases	Prevent preferential dissolution of second-phase particles
Stress corrosion cracking/hydrogen embrittlement	No anodic phases or interconnected hydrogen traps, hard particles	Prevent crack propagation due to anodic dissolution or hydrogen embrittlement, homogenize slip
Creep	Thermally stable particles on grain boundaries, large grain size	Inhibit grain boundary sliding

Adapted from Starke and Staley (1996)

concern for design and manufacturing as well as in end use. Innovative heat treatment cycles have been successfully developed to combat these issues. In these Al-Cu-Li alloys, the extrusion and plate products are typically controlled to be unrecrystallized (Rioja and Liu 2012).

Mechanical properties of interest in airframe aluminum alloys, like any other application, are intimately connected to the underlying microstructure. Table 5.7 qualitatively describes desirable microstructural features for specific properties.

Improvement in key properties of aluminum alloys over the decades for the upper wing, the lower wing, and the fuselage of various aircrafts is shown in Figs. 5.14, 5.15, and 5.16, respectively, and taken from the review by Rioja and Liu (2012). For the upper wing structure, properties of importance include specific compressive strength (compressive strength/density), specific modulus, and fracture toughness. In Fig. 5.14 specific tensile yield strength is approximated for specific compressive strength. In the early years, the approach was to increase the specific strength of the upper wing to reduce weight until corrosion problems in the Boeing 707 aircraft forced a compromise in strength to enhance corrosion performance (by replacing the T6 tempers with the T7 tempers), but with time, newer 7XXX alloys with improved strength and corrosion resistance have been developed; however, the modulus (wing stiffness) has remained constant for the 7XXX alloys. This limits weight savings due to buckling-related issues, but the third-generation Al-Li alloys show significant improvement in modulus, comparable strength or better, and good corrosion and SCC resistance. In the case of the lower wing, key considerations are given to ultimate tensile strength and fracture toughness, and the continuous improvement in these properties with newer aluminum alloy development is evident in Fig. 5.15. Of relevance is the response observed for the third-generation Al-Cu-Li alloys 2060 and 2199 which are some of the best to date. For fuselage applications, the important properties are strength and fracture toughness in the LT direction (long transverse direction, i.e., perpendicular to the rolling direction) as this direction has the largest hoop stress. Once again, the improvements in these properties over the decades for several aircraft programs are evident in Fig. 5.16. Worth noting is the superior response of the three Al-Cu-Li alloys 2199, 2198, and 2060 all in the T8 temper.

Thus, as competition develops from other lightweight materials for airframe structures (like organic fiber-reinforced composites discussed later), the aluminum industry has continuously risen to the challenge; newer alloys with improved combination of properties are being developed, and improved manufacturing technologies building on existing infrastructure are being coupled with new joining and machining technologies. Together, these advances are being brought to the forefront to offer airframe manufacturers the possibility to design and develop new aircrafts with improved fuel efficiency, increased comfort, reduced emissions, and larger range.

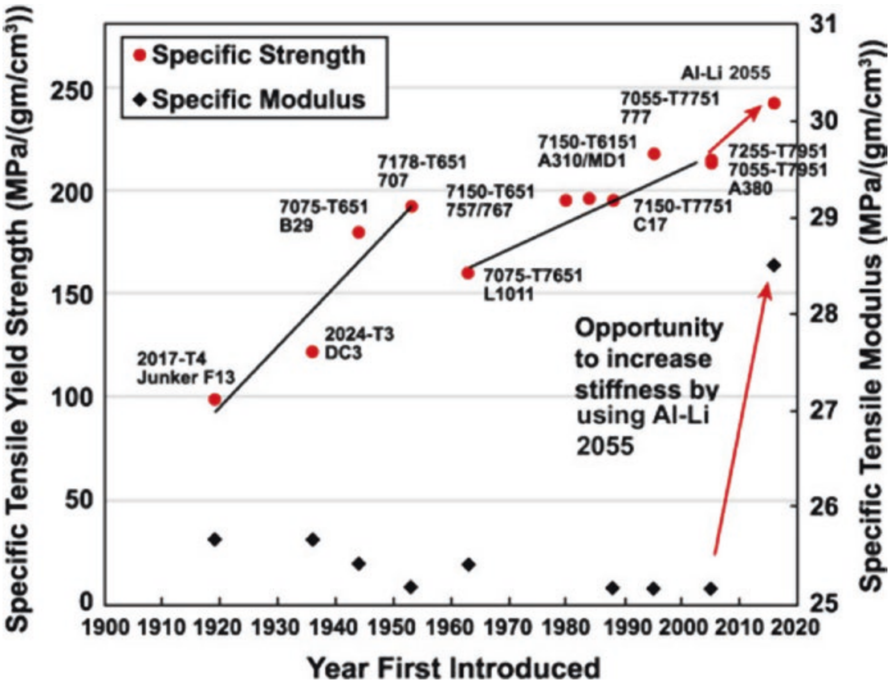

Fig. 5.14 Evolution of mechanical properties relevant to aircraft upper wing structure (Rioja and Liu 2012). (Figure used with permission from *Springer*)

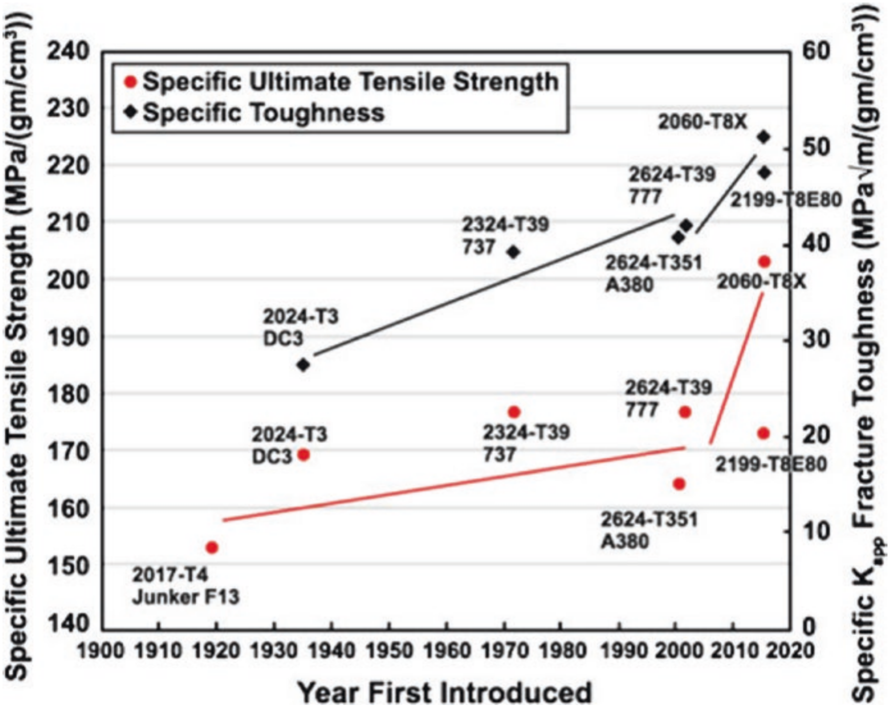

Fig. 5.15 Evolution of mechanical properties relevant to aircraft lower wing structure (Rioja and Liu 2012). (Figure used with permission from *Springer*)

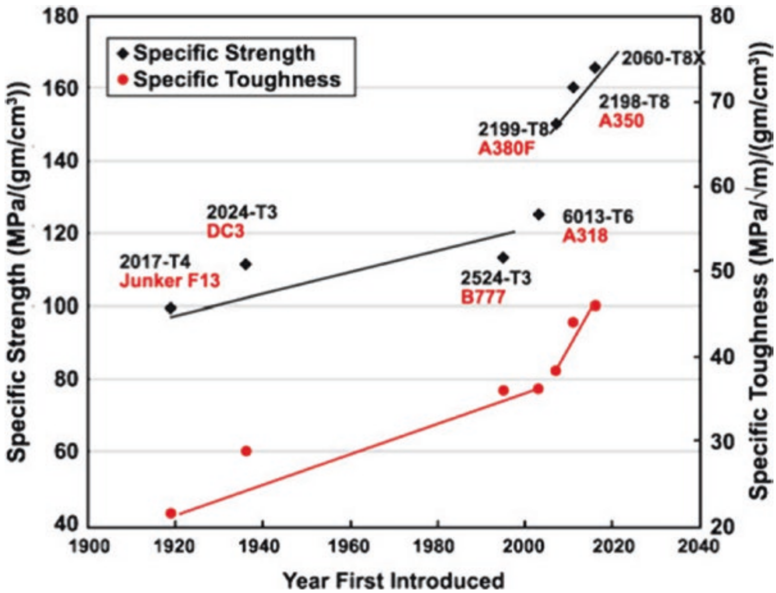

Fig. 5.16 Evolution of mechanical properties relevant to aircraft fuselage (Rioja and Liu 2012). (Figure used with permission from *Springer*)

Table 5.8 Examples of application of titanium alloys for airframe (Inagaki et al. 2014)

Material	Example of application
Ti-6Al-4V	Cockpit window frame, wing box, fastener
Ti-3Al-2.5V	Hydraulic pipe
Ti-10V-2Fe-3Al	Landing gear, track beam
Ti-6Al-2Sn-4Zr-2Mo	Exhaust, tail cone
Ti-15V-3Cr-3Sn-3Al	Duct

Titanium and Titanium Alloys

Titanium is an attractive candidate for aerospace applications with a density of 4.5 g/cm^3 and a melting temperature greater than 1600 °C. It also exhibits an allotropic transformation from α-Ti (hcp) at low temperature to β-Ti (bcc) at high temperature. Suitable alloying enables this transformation temperature to be shifted up or down as well as the creation of a two-phase $\alpha + \beta$ region in composition-temperature space. Accordingly, several commercial alloys have been developed that are all α (e.g., the four grades of commercial purity titanium), predominantly α (e.g., Ti-5Al-2Sn or Ti-6Al-2Sn-4Zr-2Mo), predominantly β (e.g., Ti-10V-2Fe-3Al), or two-phase $\alpha + \beta$ (e.g., Ti-6Al-4V). The density of Ti, though higher than Al, is significantly lower than steels, its melting temperature is almost 1000 °C higher than Al, and therefore its alloys are capable of much better warm temperature strength compared to Al. It is extremely corrosion resistant compared to Al and is not hydrogen embrittled like high-strength steels. Although compared to aluminum and steels, Ti metallurgy is younger (the first alloys were developed in the late 1940s in the United States), it has seen application in military aircrafts more so than in commercial aircrafts until recent times. In commercial aircraft, titanium alloys see usage in both the airframe sector and in the propulsion sector, but in this section, we continue to maintain our focus on the airframe (we will discuss the role of titanium and its alloys in aircraft engines in the propulsion section later). In the 1950s and 1960s, Ti alloys accounted for less than 2% of the structural weight of commercial aircrafts, whereas it accounts for nearly 9% of the structural weight of the Boeing 777 (Peters et al. 2003). Examples of alloys and airframe components where titanium alloys find applications are provided in Table 5.8 (Inagaki et al. 2014).

Commercially pure (CP) titanium is available in four grades and is categorized by strength, ductility, and formability (workability). CP1 grade has the lowest oxygen level, the highest corrosion resistance and formability, and the lowest strength, while CP4 has the highest oxygen level, highest strength within this family, and moderate formability. These are used for aircraft floors and ducts and pipings for water supply systems in the onboard kitchens and toilets where reduced weight and good corrosion resistance are of importance. Likewise, in the piping systems for deicing equipment, where corrosion resistance and thermal stability are important, commercial purity titanium is the material of choice. The alloy Ti-3Al-2.5V is a near-α alloy which is stronger than CP titanium and more cold-workable than

Ti-6Al-4V alloy; it is used in high-pressure hydraulic pipes in commercial aircrafts including in the Airbus A380. There is approximately 1 km of hydraulic tubing in each Airbus A380, and the use of titanium tubing provides a weight savings of 42% compared to stainless steel of equivalent quantity (Fine Tubes 2018). Because Ti-3Al-2.5V can be produced in strip and foil form, it is also used in the core of aircraft honeycomb panels (Boyer 1996, 2010).

The workhorse of the titanium industry is the $\alpha + \beta$ alloy, Ti-6Al-4V. One of its main attributes is that it is a forgiving alloy to work with; it is normally used at a minimum tensile strength of around 896 MPa, has good fatigue and fracture properties, and is used in all product forms including forgings, bars, castings, foil, sheet, plate, extrusions, tubings, and fasteners. There are four common heat treatments used for Ti-6Al-4V. These are (Boyer 1996, 2010):

i. Mill anneal (MA or A): most common heat treatment with strength of 896 MPa, fracture toughness of ~66 MPa$\sqrt{\text{m}}$, and reasonable fatigue crack growth rates.
ii. Recrystallization anneal (RA): this heat treatment is usually combined with the ELI grade of Ti-6Al-4V (extra low interstitial) and is a more damage-tolerant heat treatment—although the alloy has slightly lower strength than MA, improved fracture toughness (minimum of 77 MPa$\sqrt{\text{m}}$), and fatigue crack growth resistance and used for fracture critical applications in the B-1 and B-2 bombers.
iii. Beta anneal (BA): used in standard and ELI grades—strength is somewhat reduced, whereas fracture toughness and fatigue crack growth resistance are maximized (fracture toughness minimum is 88 MPa$\sqrt{\text{m}}$), while fatigue strength is degraded. This heat treatment is used for the damage-tolerant components in the F22 fighter and in the critical fittings attaching the composite empennage to the fuselage of the Boeing 777.
iv. Solution treated and aged (STA): provides the maximum strength but full hardenability is limited to about 25 mm. Titanium fasteners (hundreds and thousands of them on each commercial aircraft) are used in the STA condition with a minimum strength of 1100 MPa, with those with a diameter >19 mm used at a slightly lower strength. This heat treatment is not used for shaped components because of thermal stresses induced during water quenching (that are not relieved during aging) which lead to part warpage during machining.

The Boeing 757 utilizes titanium (Ti-6Al-4V) for the landing gear beam which is about 4.5 m long and 375 mm wide at its widest point and has a forging weight of over 815 kg (Boyer 1996, 2010) due to volume constraint problems; from a cost perspective, a high-strength aluminum alloy like 7075 would have been the preferred material, but to carry the required loads, the aluminum component would not fit within the envelope of the wing. Steel could have been used but it would have been heavier due to the higher density.

The cockpit window frames in the Boeing 757, 767, and 777 are machined from Ti-6Al-4V forgings in the BA condition, and the crown panel above them is fabricated from Ti-6Al-4V sheet (Boyer 1996). These items need to be made of high-strength Ti alloys as they need to withstand impact damage that can be incurred from bird strikes, but aluminum frames are adequate for other window frames. In the 777, Ti-6Al-4V superplastically formed sheet is used in the tail cone, while a casting approach is used for the exhaust duct of the auxiliary power unit (APU) because of the high temperature associated with these areas, being too high for aluminum alloys, whereas the weight penalty would be high if nickel-based superalloys or steels were used. Furthermore, Ti-6Al-4V plate about 5 mm thick, 762 mm wide, and 3.3 m long is used in the fin deck of the 777 where the composite vertical fin attaches to the fuselage; other critical fittings that attach the horizontal and vertical composite fins to the fuselage are all made out of BA Ti-6Al-4V forgings. This is due to the small thermal expansion mismatch between titanium and carbon fibers in the composite as well as the compatibility between titanium and graphite fibers in the empennage that prevent galvanic corrosion problems. Hence, there is not a need for reliance on a corrosion protection system (Boyer 1996; Peters et al. 2003). Other α/β alloys like Ti-6Al-6V-2Sn offer higher strength advantages than Ti-6Al-4V while also conferring increased weight savings, although the fracture toughness is reduced; this alloy has substituted for Ti-6Al-4V in some applications.

Beta (β) titanium alloys can be subjected to heat treatments that can result in high-strength levels (>1380 MPa) and therefore provide substantial latitude in tailoring strength-fracture toughness combinations while also possessing good stress corrosion resistance (ratio of stress corrosion threshold to fracture toughness is in the range of 0.8–1.0). They also offer fabrication advantages for sheet production due to their ability to be cold-rolled. The interested reader is referred to a recent overview of commercial alloy developments, underlying metallurgical principles and common microstructures, and successful applications of beta titanium alloys in the aircraft industry, as well as potential future applications for this family of alloys (Cotton et al. 2015).

Ti-13V-11Cr-3Al, a β alloy, was extensively used in the SR-71 “Blackbird” for wings and body skin, for longerons, ribs, bulkheads, and almost the complete main and nose landing gears, being primarily selected because of its thermal stability. However, designers no longer consider the balance in properties adequate for aircraft structure, and newer and better alloys are available.

Another β alloy that has seen usage in modern aircraft is Ti-15V-3Cr-3Al-3Sn because of the ability to produce this material in strip form. It has been used to make various springs for aircraft applications because titanium in general is an excellent spring material. With a density that is ~60% and a modulus that is 50% of steel, it provides for significant weight and volume savings; furthermore there are no corrosion problems with titanium springs. This alloy is also used in the environmental control system (ECS) ducting in the Boeing 777; the ECS provides air supply, thermal control, cabin pressurization, and avionics cooling, enables smoke detection, and provides fire suppression. About 49 m of 178-mm-diameter ducts with a wall thickness ranging from 0.5 mm to 1.0 mm is used per aircraft (Boyer 1996). Replacing the previously used lower strength CP titanium with thinner duct walls of this alloy resulted in weight savings. Castings of this alloy were also used (at a strength level of 1140 MPa) in the cargo handling area of the Boeing 777 and in the APU vibration isolator mounts. It replaced high-strength stainless steel, resulting in significant weight savings.

Ti-10V-2Fe-3Al is a β alloy used as a forging in three different strength levels (965 MPa, 1105 MPa, and 1190 MPa) (Boyer 1996). It also has excellent fatigue properties, and almost the entire main landing gear of the Boeing 777 is built of this alloy. It resulted in a weight savings of 270 kg per airplane when it replaced a high-strength steel and simultaneously eliminated the possibility for stress corrosion cracking which would have been an issue with the steel.

Titanium is in general very resistant to corrosion. One of the few corrosive media in the aerospace environment is hot hydraulic fluid. The hydraulic fluid used in commercial aircraft breaks down and forms an organo-phosphoric acid at temperatures in excess of ~130 °C (Boyer 1996, 2010). This can etch titanium, reduce its gauge section, and generate hydrogen than can produce embrittlement. Beta 21S, a Ti-15Mo-2.7Nb-3Al-0.2Si alloy developed by TIMET (Titanium Metals Corporation), is the only titanium alloy which is immune to this attack. Previously, steel- and nickel-based alloys were used, but the development of this alloy enabled titanium usage in the APU and nacelle areas of the 777, enabling significant weight savings.

These examples serve well to illustrate the continuous evolution in improved metals and alloys to respond to the needs of the airframe industry to be competitive as regulatory and market demands change with time. Considering that the predominant timeframe of materials and design evolution of aluminum and titanium alloys only extends over the past 60–70 years, it is impressive how commercial airframe technology has advanced; this indeed sets the stage for the evolution of another alternative to lightweight, high-performance metal and alloy technology, namely, *composite materials*.

Composite Materials

Polymer Matrix Composites (PMCs)

The primary motivation for replacing metallic materials with PMCs in aircraft structures has been weight reduction, while also increasing structural robustness (mechanical stiffness, strength, damage tolerance, etc.) and performance. Thus, these composites, which consist of a polymer matrix with short fibers of other materials embedded, have been playing a transformative role in increasing fuel efficiency and reducing greenhouse gas emission, and their use in aircraft structures has accelerated in recent years. Figure 5.17 shows the trend in the use of polymer matrix composites (PMCs) in commercial aircraft over the years. Initially, the amount of PMCs used in aircraft was small, primarily in light-structural and cabin components. Airbus was the first to introduce an all-PMC tail section in 1988 in its A320 fleet. About 11% of the Boeing 777 aircraft, which came into service in 1995, was made of PMCs by weight (excluding engines) (Irving and Soutis 2015; Rana and Fanguerio 2016). Fast forward to 2011 when the Boeing 787 Dreamliner aircraft was first introduced commercially—an impressive 50% of its weight was PMCs

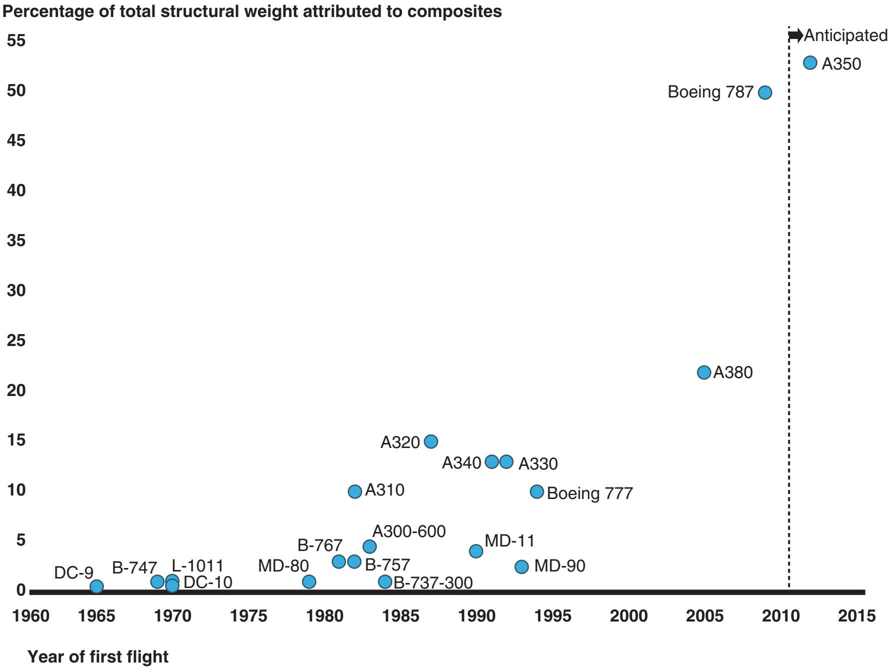

Fig. 5.17 Percentage of total structural weight attributed to composites in commercial airplane models over time (Rana and Fanguerio 2016). (Image used with permission from Elsevier Books)

(Fig. 5.17; Irving and Soutis 2015; Rana and Fanguerio 2016). This "true" mostly composite aircraft has a range of 7650–8500 miles and seats 210–290 passengers. The latest Airbus A350XWB aircraft boasts 53% PMCs by weight, with a range of up to 8500 miles and seats 250–400 passengers. This progress is largely due to the penetration of PMCs into true structural applications including wings, fuselage skins, landing gear, and even engines, together with the cost-effectiveness of composites (Irving and Soutis 2015; Rana and Fanguerio 2016). Figure 5.18 compares the materials' makeup of Boeing aircrafts over the years, showing that PMC parts have replaced many of the parts that were previously made of aluminum alloys, resulting in a total weight savings of about 30% (Drew and Mouawad 2013). Also shown in Fig. 5.18 is the makeup of the skin structure of the Boeing 787 Dreamliner aircraft.

In addition to weight reduction, there are several other important advantages PMCs can offer (Irving and Soutis 2015; Rana and Fanguerio 2016). Modern PMCs have higher static strength, fatigue resistance, toughness, damage tolerance, and corrosion resistance over metallic alloys. Also, PMCs are better at shielding electromagnetic waves, and they can be designed to have better thermal stability over a wide temperature range. Furthermore, PMCs are more amenable to embedding/integrating structural health monitoring (SHM) systems and actuators—"smart" materials. In terms of manufacturing, assembly, and maintenance, PMC compo-

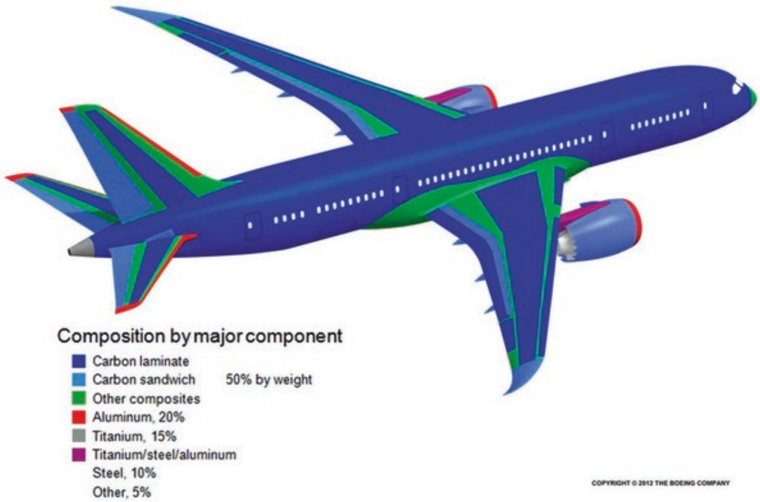

Fig. 5.18 Dreamliner composition by major components. (Image used with permission from Boeing Images)

nents can be formed into complex shapes, requiring reduced assembly, and they can be repaired. Thus, net-shape PMC components require significantly fewer joints and heavy fasteners (rivets, screws, bolts, nuts, etc.) which can be sources of failure in metallic components. This is driving an industry-wide trend of fewer components in overall assemblies, using one-piece designs wherever possible (Rana and Fanguerio 2016). There are however, still some manufacturing issues and safety concerns as composites technology is not as mature as its metals and alloys counterpart. Progress is being made to address these concerns, and composites are here to stay as the performance, efficiency, and cost benefits they offer have proven too great to pass up.

The bulk of the PMCs used in aircraft have continuous fibers (also called continuous fiber-reinforced polymers or CFRPs) with a high Young's modulus (E) (see Table 5.9) (Chawla 1998). As the name implies, the matrix in PMCs is a polymer which typically has a low E (generally <1 GPa). The introduction of unidirectional continuous fibers into the polymer matrix, with excellent bonding between the two, imparts the PMC with synergistic, significant improvements in a combination of mechanical properties—stiffness, strength, and toughness—not witnessed in the individual materials. Typically, PMCs contain 10%–60% fibers by volume. This uniqueness of composites is captured in Ashby's materials selection maps (density-stiffness and strength-toughness) displayed in Fig. 5.19 (Ashby et al. 2007).

The basic element of a PMC is a lamina, in which unidirectionally aligned fibers are embedded in the resin matrix, rendering the mechanical properties of the lamina anisotropic in-plane (Fig. 5.20a). Individual laminae are stacked and bonded

Table 5.9 Properties of some commercial fibers

Fiber		Diameter (d) (μm)	Density (ρ) (g/cm^2)	Young's modulus (E) (GPa)	Strength (σ_F) (GPa)
Glass	E-Glass	10	2.54	72	3.5
	S-Glass	10	2.49	87	4.3
Carbon	AS-1	8	1.80	228	3.1
	T-40	5	1.81	290	5.7
	GY-70	8	1.96	483	1.5
	P-100	10	2.15	758	2.4
Aramid	Kevlar-29	12	1.44	65	2.8
	Kevlar-49	12	1.45	131	3.6
	Kevlar-149	12	1.47	179	3.5

Adapted from Chawla (1998)

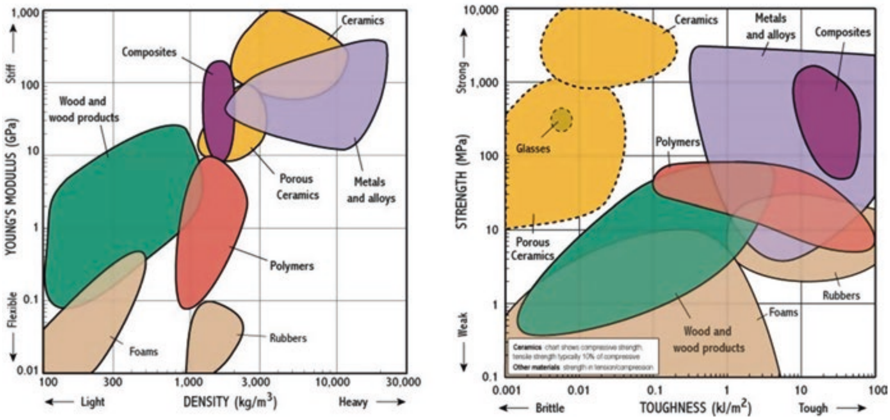

Fig. 5.19 Density-stiffness (left) and strength-toughness (right) "Ashby" design maps (Lovatt et al. 2000). (Data courtesy of Granta Design, Ltd., Cambridge, UK)

together to form a multi-ply laminate wherein the stacking can be controlled with respect to fiber orientation to a global reference coordinate system, and this can be done to obtain biaxial in-plane isotropy (Fig. 5.20b). Alternatively, the continuous fibers can be in the form of a woven fabric to form biaxially isotropic individual laminae (Fig. 5.20c; FAA 2012).

PMCs reinforced by glass fibers (also called fiber glass or glass fiber-reinforced polymers (GFRPs)) were first produced commercially in 1942, which was the culmination of simultaneous development of high-strength glass fibers and low-cure polyester resins. While PMCs first found use in marine applications (boats), in 1943 an exploratory program was launched at the Wright-Patterson Air Force Base in the United States to incorporate PMCs in aircraft structures. The introduction of better tooling, fiber architectures, and pre-pregs represented significant advances in PMC manufacturing. The pre-pregs are partially cured, pliable thermosetting polymers incorporating unidirectional fiber tows or fabrics. These can be stacked into

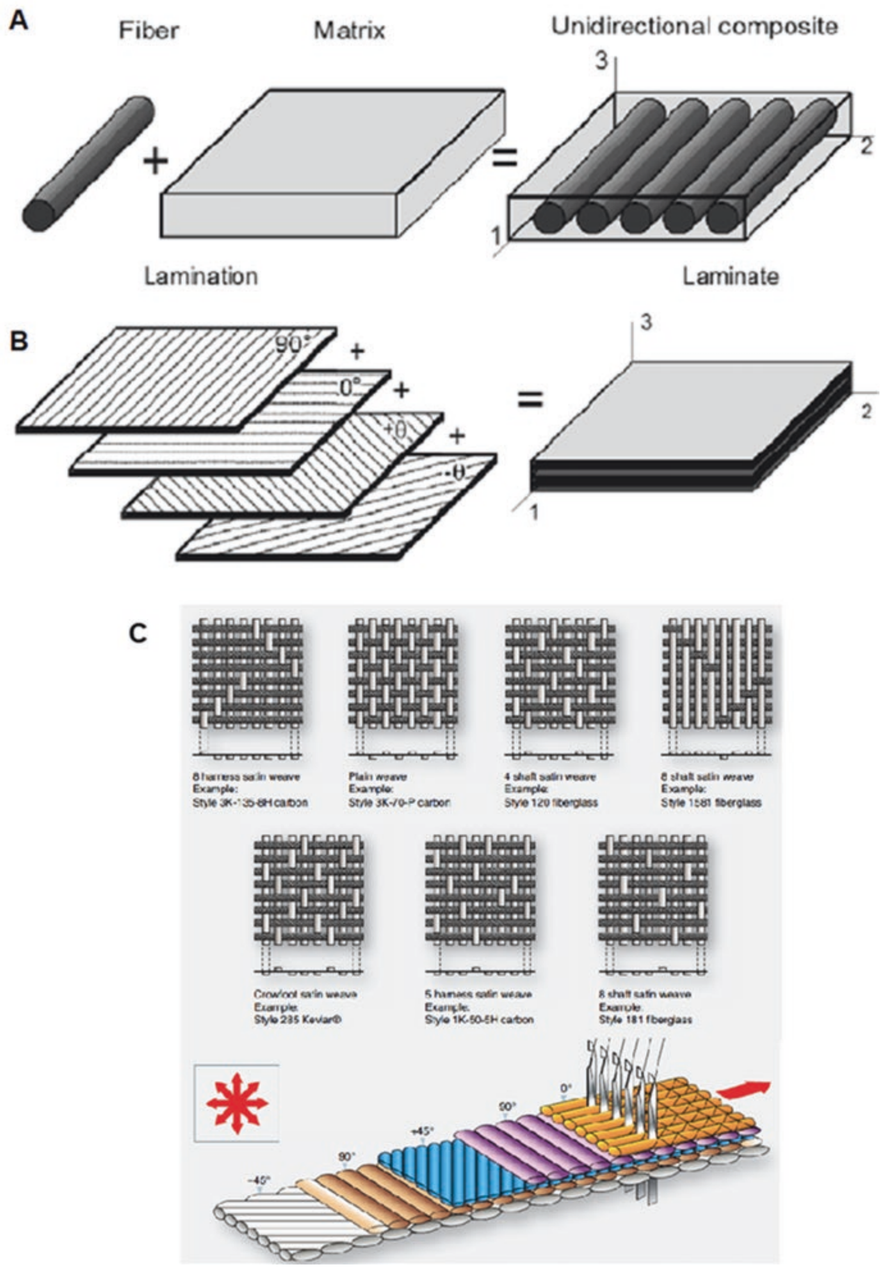

Fig. 5.20 Schematic illustrations of (**a**) unidirectional continuous fiber-reinforced composites and (**b**) laminates. (**c**) Different fiber weave patterns (FAA 2012)

Table 5.10 Properties of some commercial polymer matrices

Polymer matrix		Density (ρ) (g/cm^2)	Young's modulus (E) (GPa)	Strength (σ_F) (GPa)
Thermosetting	Epoxies	1.2–1.3	2.75–4.10	55–130
	Polyesters	1.1–1.4	2.10–3.45	35–104
	Vinyl esters	1.12–1.32	3.00–3.50	73–81
	Polyimides	1.32–1.34	3.90–4.10	39–83
Thermoplastic	Polyetheretherketone	1.32	3.24	15
	Polyphenylene sulfide	1.36	3.30	83
	Polyetherimide	1.27	3.00	105

Adapted from Mallick (1993)

laminates in molds or mandrels and autoclaved at desired pressures and temperatures to "fuse" the polymer matrix and cure it fully. While PMCs with glass fibers constitute about 90% of the total composites production (Rana and Fanguerio 2016), they have found limited use in aircraft. Typically, some cabin components and wing/fin parts are made of GFRPs in today's aircraft (Fig. 5.18).

The invention of carbon fibers in the early 1960s represented a "quantum" jump in PMC properties and performance. This is because, while E of glass fibers is limited to ~80 GPa, carbon fiber E can be as high as 900 GPa. The key to obtaining such extreme properties is the alignment of the graphene planes, which make up the graphite in the carbon fibers, along the fiber axis during processing (Chawla 1998). Several classes of carbon fibers are now available (Table 5.10), with the most popular for aircraft applications belonging to the high modulus (HM, E ~ 380 GPa), intermediate modulus (IM, E ~ 290 GPa), and high-strength (HS, E ~ 230 GPa, σ_F ~ 4.5 GPa) categories. Carbon fiber-based PMCs (so-called carbon fiber-reinforced polymers (CFRPs)) constitute the bulk of modern aircraft structures, such as the entire fuselage, wings, etc. (Fig. 5.18), whereas floorboards, tail-fin parts, engine nacelles, etc. are typically made of sandwich PMCs.

The commercial introduction of the aramid (Kevlar®) fiber in 1972 was another milestone in the progress of PMCs (Chawla 1998). Although aramid fibers are not as stiff as carbon fibers, they are impact-resistant, and are used in PMCs where that property is important. Aramid fiber-based PMCs have found limited application in aircraft, such as nose cones, but are widely used in armor applications and sporting goods (Chawla 1998).

There has been simultaneous development in polymer matrices (see Table 5.10; Mallick 1993). The bulk of the PMCs used in aircraft are made with thermosetting polymers. These start out as resins which are liquids that can then be easily impregnated into fiber preforms or as partially cured "tacky" semisolids that incorporate fibers in pre-pregs. The subsequent curing process, induced by heat and/or pressure in an autoclave, results in the cross-linking of the backbone carbon chains to form the solid polymer matrix. While the initial PMCs were made from polyesters, the stiffer and stronger epoxies are the most popular polymer matrices in aircraft PMCs today. Other raw materials used for thermosetting polymer matrices in PMCs used

Fig. 5.21 Fabrication of composite aft body of airliner. (Image used with permission from Boeing Images)

in interior parts of aircraft include vinyl ester and phenolic resins (Mallick 1993). High-temperature-resistant thermosets such as polyimides are also used in PMC matrices exposed to higher temperatures. The high-toughness thermoplastic polymers (not cross-linked), which melt upon heating, are also being used in PMCs to some extent, with polyetheretherketone being the prime example.

Significant advances in PMC manufacturing over the years have made it possible, for example, to fabricate large sections of the fuselage and the wings in single piece CFRPs (Fig. 5.21; Drew and Mouawad 2013). Great strides in testing, non-destructive evaluation, structural health monitoring systems, etc. have also helped make mostly composite aircraft structures possible.

Fiber Metal Laminates (FMLs)

Fiber metal laminates (FMLs) are hybrid composite structures based on thin sheets of metal alloys and plies of PMCs that are often adhesively bonded (Sinmazçelik et al. 2011). The technology draws on the advantages of the alloy system as well as the PMCs.

In the late 1970s, research at Delft University of Technology in the Netherlands showed that fatigue crack growth rates could be substantially reduced by laminating and adhesively bonding thin sheets of a material as compared to a thick monolithic sheet (Asundi and Choi 1997; Vogelesang and Vlot 2000). ARALL, aramid fiber-reinforced PMC laminated with aluminum, was introduced in 1978 and consisted of alternating thin sheets of aluminum with uniaxial or biaxial pre-preg layers. Four

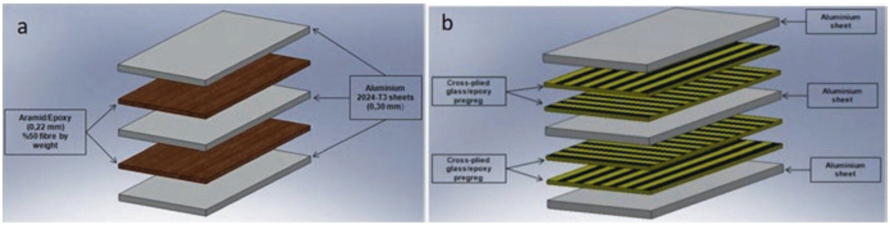

Fig. 5.22 A schematic of (**a**) the lay-up of the ARALL-2 laminate, and (**b**) a cross-ply GLARE laminate (Sinmazçelik et al. 2011). (Figure used with permission from *Elsevier*)

grades of ARALL are commercially available called ARALL-1, ARALL-2, ARALL-3, and ARALL-4 with 7075-T6, 2024-T3, 7475-T76, and 2024-T8 as the sheet aluminum components, respectively. In all cases, the metal sheet thickness is nominally 0.3 mm, and the PMC sheets are 0.22 mm thick. The aramid fibers to resin (thermosetting polymer matrix) ratio by weight is 50:50, and the fibers are unidirectional and oriented parallel to the aluminum sheet rolling direction (Fig. 5.22a, from Sinmazçelik et al. (2011), shows a schematic of the ARALL 2 laminate). ARALL laminates are attractive for fatigue-dominated structural parts like the lower wing skin and the pressurized fuselage cabin of the aircraft. ARALL was used in the former Fokker 27 aircraft lower wing panels and for the cargo door of the Boeing C-17 military aircraft.

In 1990, aramid fibers were replaced with high-strength glass fibers, and an improved version of ARALL called GLARE (glass fiber-reinforced PMCs laminated with aluminum) evolved and was commercialized. The better adhesion between the polymer matrix and the glass fibers in GLARE, together with the higher compression resistance of glass fibers over aramid fibers, and the overall superior properties made GLARE a more widespread and attractive choice over ARALL, and also made two-direction orientation of fibers possible (e.g., see Fig. 5.22b which is a schematic of a cross-ply GLARE laminate) making it more suitable to cope with biaxial stress states. Details for the six commercially available grades of GLARE FMLs are provided in Table 5.11. In all six grades, uniaxial glass fibers are embedded in an epoxy additive to create pre-pregs with fiber volume fraction of 0.60. During fabrication of the laminate, the pre-pregs are laid up in different fiber orientations between aluminum sheets as shown in Table 5.11 to produce the different grades, and the whole laminate is then cured. GLARE offers high impact resistance which makes it particularly suitable for airframe locations that are susceptible to bird strikes. GLARE is currently used in the main fuselage skin of the Airbus A380 and in the leading edges of the tail. (The interested reader is referred to the overviews by Sinmazçelik et al. (2011), Asundi and Choi (1997), and the recent book *Fatigue and Fracture of Fiber Metal Laminates* by Alderliesten (2017) for more details relating to fabrication and properties of ARALL and GLARE.)

Table 5.11 Commercially available grades of GLARE FMLs

Grade	Sub	Metal type	Metal thickness (mm)	Fiber layer (mm)	Pre-preg orientation in each fiber layer (°)	Characteristics
GLARE 1	–	7475-T761	0.3–0.4	0.266	0/0	Fatigue, strength, yield stress
GLARE 2	GLARE 2A	2024-T3	0.2–0.5	0.266	0/0	Fatigue, strength
	GLARE 2B	2024-T3	0.2–0.5	0.266	90/90	Fatigue, strength
GLARE 3	–	2024-T3	0.2–0.5	0.266	0/90	Fatigue, impact
GLARE 4	GLARE 4A	2024-T3	0.2–0.5	0.266	0/90/0	Fatigue, strength in 0° direction
	GLARE 4B	2024-T3	0.2–0.5	0.266	90/0/90	Fatigue, strength in 90° direction
GLARE 5	–	2024-T3	0.2–0.5	0.266	0/90/90/0	Impact, shear, off-axis properties
GLARE 6	GLARE 6A	2024-T3	0.2–0.5	0.266	+45/−45	Shear, off-axis properties
	GLARE 6B	2024-T3	0.2–0.5	0.266	−45/+45	Shear, off-axis properties

Adapted from Sinmazçelik et al. (2011)

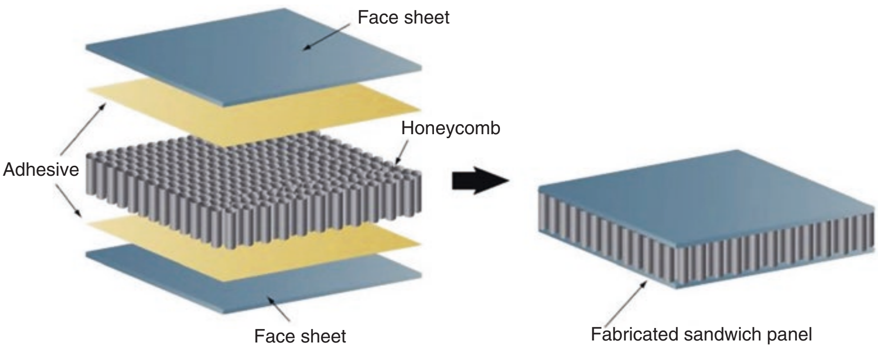

Fig. 5.23 Composite laminate sandwich structure. (Image used with permission from http://admatis.com/eng/competencies_material_science_sandwich.html)

Sandwich structures are also used in aircraft, where a lightweight "honeycomb'" core is incorporated between metal face sheets (Fig. 5.23), where the core is typically made of aramid "paper," PMC, or an aluminum alloy (Rana and Fanguerio 2016). A variation of aramid in the form of "paper" called Nomex® and Korex® has found use in honeycombs for sandwich structures in aircraft.

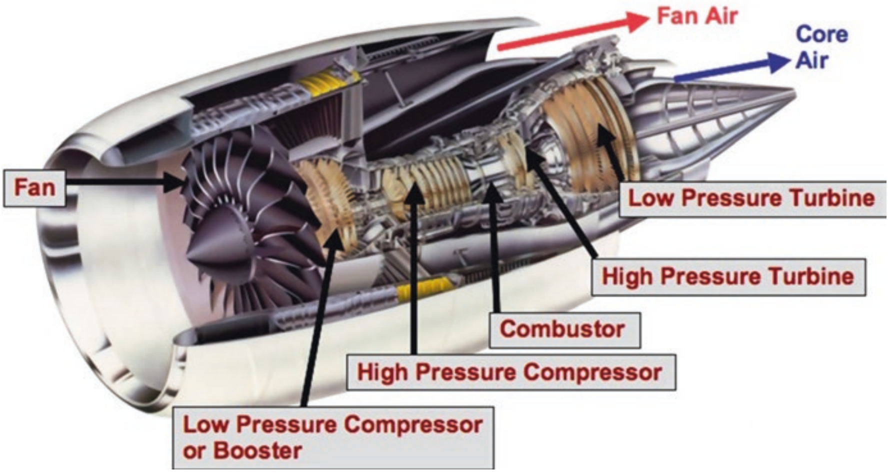

Fig. 5.24 A cutaway showing the various parts of a high-bypass aircraft engine (Williams and Starke 2003). (Figure used with permission from *Elsevier*)

The Propulsion System

The Anatomy of the High-Bypass Engine

In this section of the chapter, we will restrict ourselves in the interest of space to high-bypass air-breathing turbofan engines. The engine from the front to the rear can be broadly divided into the (i) air intake fan, (ii) the multi-stage (low-pressure and high-pressure stages) air compressor, (iii) the combustor, (iv) the high-pressure turbine, (v) the low-pressure turbine, and (vi) the exhaust nozzle (see Fig. 5.8, the schematic cross-sectional illustration in the section "The Jet Engine (From 1937 to Present)"; Fig. 5.24 shows a cutaway of a high-bypass engine with the various sections labeled).

In such engines, a large fraction (>80%) of the air intake bypasses the core of the engine (referred to as bypass air as opposed to core air) and provides the majority of the thrust. The core air is used to run the large fan in front of the engine by compressing it in the multi-stage compressor, mixing the compressed air with the fuel, and combusting the mixture in the combustion chamber; the hot gases that result then spin the multi-stage turbines in the aft of the engine that then spins the shaft and powers the intake fan; the hot gases exit at a high velocity through the nozzle in the tail of the engine. Thus, from a temperature profile point of view, the front end of the engine is cool but progressively warms as one approaches the combustion chamber, and the aft of the engine is hot. Thus, materials requirements in the modern-day jet engine is varied—from room temperature to excess of 1000 °C; furthermore, some parts are stationary, while others rotate, and therefore requirements are different. The hot gas environment in the engine is hostile to materials, and impact damages from foreign objects including bird strikes are issues that are routinely given due consideration, particularly so during takeoff and landing phases. Engine noise suppression is a significant issue and must be handled (imposed airport regulations and aircraft noise certification requirements). Noise arises due to a variety of reasons which include (i) turbulent mixing of high-velocity exit gases and cold air at the rear of the engine, (ii) compressor and turbine noises resulting from the interaction of pressure fields and turbulence from rotating blades and stationary vanes, (iii) fan noise, and (iv) the combustion chamber noise; but being located well inside the engine, combustor noise was not considered a dominant source previously. However, reduction in noise in the other parts of the engine by improving design has in part brought the combustion noise to the forefront (Dowling and Mahmoudi 2015).

Engines can be very large—for example, the fan diameter of the engine on the Boeing 777-300LR, a modern-day aircraft, is greater than 3 meters, and the engine weighs more than 7300 kg (Williams and Starke 2003). Due to the operating demands placed on engine components, weight reduction in engines is not easy, and here a parameter called specific thrust (thrust to weight ratio) is the figure of merit often used. Consequently, a specific thrust obtained by increasing operating temperatures and operating stresses is as important as weight reduction. In commercial engines, particularly twin-engine aircrafts used for long-range overwater flights like the Boeing 767 and 777, and the Airbus 310 and 330, reliability and durability are key product characteristics, and these engines are certified and rated using ETOPS (Extended-range Twin-engine Operational Performance Standards). A higher ETOPS rating means a longer flight overwater is possible, which means more direct routes with positive impacts on fuel consumption and flight times. In-flight shutdown of the engine reduces ETOPS ratings (materials-related shutdown is therefore not acceptable) and that translates into a very high degree of reliability demand on introduction of new materials. Engine durability (e.g., time between successive maintenance operations) has improved dramatically over the past decades, for example, from 500 h for the Boeing 707 in the 1950s to more than 20,000 h on the Boeing 747 (Williams and Starke 2003). This improvement has been attributed in part to more robust designs and in part to better materials, particularly considering that engine operating temperatures have increased significantly to improve fuel economy. A significant contribution to better materials has come from better melt practices, fabrication methods like forging, improved non-destructive evaluation methods, and enhanced fundamental understanding of microstructure-processing-property relationships in titanium and nickel alloys.

In considering materials evolution/development for the various parts of the engine, we will start with the front end (the cooler end) and progress to the rear (the hot end) and focus on how advancements in alloy design, improvements in materials processing, and development of new materials have all come together to produce larger, more fuel efficient, and greater range engines that power the aircraft that fly our skies today. There are other equally important developments in engine technology that relate to engine (and component) design that are not being considered in this chapter but have played, and will continue to play, a pivotal role in enhancing engine capabilities, but this chapter is focused only on the materials science aspect of the overall technology.

Titanium Alloys and Polymer Matrix Composites

Many modern subsonic aircraft engines for passenger or cargo transport use titanium and its alloys for the air-intake fan, the low-pressure compressor, and roughly two-thirds of the high-pressure compressor. The balance of the high-pressure compressor, the combustor, and the high- and low-pressure turbines are all made from Ni-based alloys, the choice primarily determined by temperature profiles in the engine. Titanium alloys were introduced in aircraft engines in the early 1950s by Pratt & Whitney and Rolls-Royce with compressor blades being the first to be made from this material class, followed by compressor disks. This was then followed by the front fan blades being made of titanium alloys like Ti-6Al-4V. The life of these fan blades is limited by high cycle fatigue and of course from foreign object damage like bird strike or hail. Since high cycle fatigue life scales with yield strength, in principle alloys stronger than Ti-6Al-4V are desirable, but manufacturing difficulties associated with the complex shapes and related economics have deterred their use barring exceptional situations.

The fan disk (to which the fan blades attach) has typically been a single titanium forging, and the two most common alloys in addition to Ti-6Al-4V have been Ti-5Al-2Zr-2Sn-4Cr-4Mo (called Ti-17) and Ti-6Al-2Sn-4Zr-6Mo (Ti-6-2-4-6). The limiting property for the fan disk at a given strength level are low cycle fatigue resistance and fatigue crack growth; advances in forging technology and the ability to develop desirable microstructures (a Widmansttäten or "basket-weave" microstructure) in a reproducible manner have enabled optimization of these properties. In this context, it is worth recalling the catastrophic uncontained tail engine failure in mid-flight in 1989 (the tail engine of a DC-10; United Airlines Flight 232) that destroyed all the hydraulic systems and forced an emergency landing in Sioux City, Iowa, where more than 100 fatalities resulted; more surprisingly, there were 185 survivors thanks to the heroic efforts and skills of the crew of that flight, and the DC-10 instructor who was on that flight. The engine failure was eventually attributed to the titanium stage I fan disk which had an inclusion (called a "hard alpha" inclusion resulting from a manufacturing step) that had produced a fatigue crack that had gone undetected in a previous inspection and resulted in fatigue failure during flight. The accident investigation also showed that the catastrophic disintegration of the disk produced debris with energy levels and a pattern of distribution that exceeded the protection levels provided for the hydraulic systems (National Transportation Safety Board 1990). Several enhanced and more stringent safety initiatives were put in place by the Federal Aviation Administration (FAA) following this tragedy and the lessons learned from it.

More recently, engine sizes have increased substantially as mentioned earlier, and this is driven by the desire to increase the bypass ratio to increase thrust. The consequence is that the fan blades have become very large and so fan blade flutter has become a problem. Fan blade tips can reach the velocity of sound and produce flow fields that result in shock waves. This led to advances in fan design that resulted in increased chord widths and reduced number of blades. However, this has resulted in weight penalty from these large blades, and so designers have resorted to alternatives to the old solid titanium-forged blades.

Fig. 5.25 PMC fan blade and casing for engines. (https://www.geaviation.com/commercial/engines/ge90-engine; Images used with permission from GE Aviation)

Multiple approaches have been taken to respond to the weight reduction: General Electric replaced the titanium blades in its GE90 engine with fiber-reinforced polymer matrix composite blades, but to counter erosion issues, these blades include a leading edge made of titanium (Fig. 5.25). Rolls-Royce and Pratt & Whitney have used the hollow titanium fan blade technology in their engines (e.g., in the GP7200 and the Trent 900 engines that power the Airbus A380). In the early iterations, these fan blades were comprised of titanium face sheets that were liquid-phase diffusion bonded to titanium honeycomb core, but advances in manufacturing methods enabled the blades to be produced from superplastically formed titanium sheets and solid-state diffusion bonding.

The fan blade containment casing is the near-cylindrical casing that surrounds the fan blades in the front of the engine (Fig. 5.25). The casing's primary function is to catch and contain a part or a whole blade that might detach in service (called fan blade off event—FBO event) so that the high kinetic energy fragments do not damage other engines or the fuselage. Traditionally, a thick solid metal skin casing (e.g., "hard wall" containment, a strong ductile steel casing) has been used, but this contributes to the engine weight particularly as the fan diameter has increased substantially in recent years in the very large engines. More recently, Kevlar fiber wraps have been used around a thinner metallic wall so that the metallic wall provides some containment and the stretching of the Kevlar fibers provides the remaining containment (soft wall containment), but the disadvantage of this system is that a large empty volume must be provided in the nacelle into which the expansion can occur (McMillan 2008). Thus, in the Trent 900 engines, a hollow titanium containment system that includes numerous crushing elements to maximize material involved in the arrest, but minimizing weight, is employed. The GEnx engine that powers the Boeing 787 Dreamliner that first went into commercial service in 2011 is the first engine to use all-PMC fan blades and all-composite fan containment casing, resulting in significant weight savings in the engine (Marsh 2006, 2012). The next-generation GE9X engine, which is in the process of being certified as of 2017, features a carbon fiber-reinforced PMC fan with thinner, lighter, and fewer blades.

Moving a little further back to the multi-stage compressor section of the high-bypass engine, we examine the low-pressure (LP) and high-pressure (HP) compressor rotors and air foils. The compressor rotor, also called a spool, is a multi-stage product made from several forgings that are ring-rolled and joined together before machining. The spool can incorporate as many as seven stages into a single component and can be joined by a technique such as friction welding. The first five stages are low cycle fatigue (LCF) limited, and typically Ti-6Al-4V would be a material of choice. The last two stages are creep-limited due to the higher temperatures experienced, and a material like Ti-6Al-2Sn-4Zr-6Mo + Si (the minor Si addition enhances creep resistance) would be a better choice as the maximum temperature limit of Ti-6Al-4V would be around 315 °C (Peters et al. 2003; Williams and Starke 2003). The benefit of the spool configuration is that bolted joints between stages where the bolt holes can act as a source of a fatigue cracks are eliminated. The final stages of the HP compressor experience temperature profiles above the capabilities of even the higher-temperature Ti alloys, and these are typically made of Ni alloys. Like the fan blades, most of the compressor air foils in the first six stages are made from Ti-6Al-4V, and here, life is limited by high cycle fatigue.

Another concern in the use of Ti alloys for rotating components is their propensity to burn. Thus, if a rotating blade rubs on the inside surface of the engine casing, localized heating of the blade tip can result in an exothermic, self-propagating oxidation reaction that results in a titanium fire. To combat this problem, Pratt & Whitney developed a Ti alloy called Alloy C (Ti-35V-15Cr) that is resistant to burning and finds application in some military aircraft engine components (Peters et al. 2003).

More recently, to reduce the weight of compressor rotor and air foils, and to extend life and inspection intervals, integrally bladed disks called "blisks" are used where the finished blisk (machined from an oversized forged disk) is a single assembly where the disk and blades are metallurgically bonded. This is now a standard feature in modern small- and medium-size compressors in military and commercial engines. Larger blades are generally attached to the disk by friction welding. In either case, the lack of a mechanical joint between the blades and disks eliminates common sites for fatigue crack initiation.

Lastly, titanium alloys are also used in static parts in the jet engine such as frames, manifolds, ducts, and tubes. The largest use is in cast frames where a single net-shape casting can replace a fabricated component comprised of many individual parts.

Ni-Based Superalloys

Basic Metallurgy

The very last stages of the compressor, the combustor, the high- and low-pressure turbines, and the nozzle all experience service temperatures that are too high for conventional titanium alloys (except for titanium aluminides discussed in a later section) and fall in the domain of superalloys, primarily nickel-based superalloys;

cobalt-based superalloys see some use in the combustor liner as well. The term "superalloy" was first coined shortly after World War II to describe a group of alloys developed for use in turbosuperchargers and aircraft turbine engines that required superior performance at elevated temperatures. Broadly, there are three families of superalloys, nickel-based, iron-based, and cobalt-based, which means that the identifying constituent is the majority species in the usually multicomponent alloy. Superalloys see a wide range of applications well beyond aircraft engines including chemical and petrochemical industries, nuclear power systems, medical devices, space vehicles, and steam turbines. Nickel-based superalloys can see use as high as 0.8–0.9T_m where T_m is the absolute melting temperature.

A variety of strengthening mechanisms are invoked in Ni-based superalloys and include solid solution strengthening of the Ni matrix with elements such as Cr, Co, and Fe, to name a few. Some commercial Ni-based superalloys that are primarily solid solution strengthened and used in aeroengine components include Hastelloy X (Ni-22Cr-18Fe-1.5Co-9Mo-0.6W-0.1C), Inconel 601 (60.5Ni-23Cr-14.1Fe-1.35Al-0.05C), and Inconel 617 (55Ni-22Cr-12.5Co-9Mo-1Al-0.07C). In contrast, other alloys are additionally precipitation strengthened with phases like γ' (Ni_3Al with the cubic $L1_2$ structure that exhibits an increase in strength with increase in temperature) and γ'' (Ni_3Nb with a body-centered tetragonal structure and found in Ni-Fe superalloys like Inconel 718 which also contain about 5% Nb). The γ' phase can also be solid solution strengthened by elements like Ti or Ta to yield precipitates like Ni_3(Al,Ti). The individual γ' precipitates are often cuboidal in shape, closely spaced in a face-on-face arrangement within individual grains of the Ni matrix (Fig. 5.26a). The volume fraction of the γ' phase in many of the superalloys can be 0.6 or higher, and it has been shown that stress-rupture strength increases with γ' volume fraction (Decker 2006).

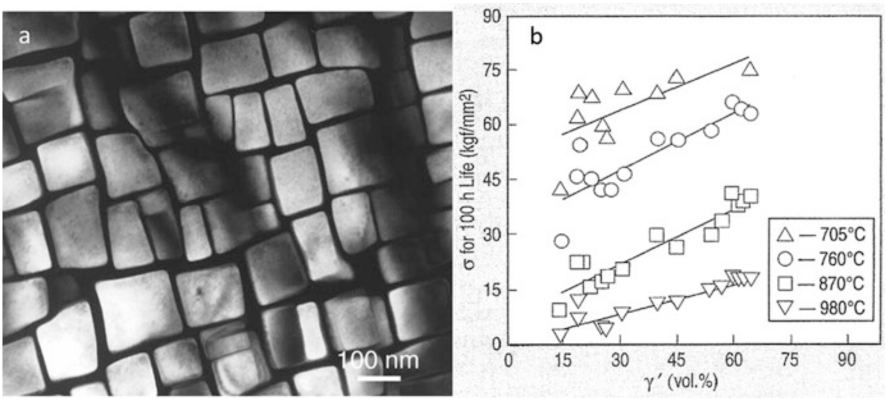

Fig. 5.26 (**a**) Cuboidal γ' precipitates in a γ grain (Image courtesy of Professor William Gale) and (**b**) stress-rupture strength as a function of γ' precipitates volume fraction at different temperatures (Decker 2006). (Image used with permission from *Springer*)

Beyond these precipitates, carbides such as the MC carbides (TiC, NbC, or TaC), chromium-rich $M_{23}C_6$, and the ternary M_6C can pin grain boundaries and discourage grain boundary sliding, but control of carbide size, morphology, and distribution is critical to prevent premature fracture.

Any discussion of superalloys would be incomplete without at least a brief discussion of the processing of these alloys, because developments in processing technology over the past five decades have played a key role in enhancing the utility of these alloys in the ever-increasing demands of aircraft engines. The specific engine component under consideration will dictate the optimal alloy composition based on service environment needs as well as the processing route that is best suited for the selected alloy composition. Thus, a casting process (investment casting, also known sometimes as the "lost-wax" process) is deemed best for making a turbine blade, whereas conventional casting plus forging and powder metallurgy processing followed by forging are the preferred pathways for producing turbine disks. Casting, extruding, and forging of superalloy turbine blades have given way to using net-shape casting of such blades due to the inherent complexities that were introduced in the shapes and internal cooling passages that were incorporated in these blades as engine design and demands continually increased. In addition, the net-shape casting approach permitted the transition from a fine equiaxed grain structure typical of forged microstructures (which is deleterious to creep resistance) to controlled longitudinally aligned grain structure (so-called directionally solidified structure) and to single-crystal turbine blades (devoid of grain boundaries) and therefore enhanced creep resistance.

Briefly, in the investment casting process, multiple wax patterns are produced of the final shape and attached to a main wax stem (the wax patterns themselves may be made by creating a metal mold and pouring molten wax into it). The entire assembly is dipped multiple times in a ceramic slurry and dried to form a shell around the wax pattern; the wax is then melted out leaving a ceramic mold (an expendable mold) which can then be fired to increase its structural integrity. This then becomes the mold into which molten alloy can be poured and allowed to fill the mold. Finally, the mold is broken off and the parts are retrieved. This approach allows casting of hollow compartments and pinholes even in thin sections and the ability to maintain excellent surface finish and high dimensional accuracy (for more details specifically on the application of investment casting to turbine blades, see Reed 2006; for historical development of lost-wax casting, see also Kaufman, Chap. 1, this volume).

Casting ingots of superalloys such as Waspaloy (58Ni-19Cr-13Co-4Mo-3Ti-1.4Al) and Inconel 718 (50–55%Ni-17-21%Cr-5%Nb-3%Mo-1%Ti-0.6%Al-balance Fe) is accomplished by using vacuum induction melting (VIM) followed by electroslag refining (ESR) and vacuum arc remelting (VAR)(called triple melting for applications where melt cleanliness is critical; alternatively, ingots may only be double-melted with VIM followed by VAR). The first commercial application of superalloys came in the 1950s with the production of 5 kg heats of Waspaloy by VIM, and each was forged into a single turbine blade. In the year 2000, the worldwide production of superalloys is ~30,000 tons (Reed 2006). In the VIM process, metallic charge is melted in ceramic crucibles using an induction power source where the charge itself participates in the heating process by coupling with the induction field, and this also produces electromagnetic stirring of the melt. Melting is carried out in a diffusion pump vacuum (better than 10^{-4} atm). The molten metal is then poured into individual molds, often through ceramic filters to prevent slag from entering the ingot; the process is a batch process and not continuous. The resulting VIM ingots typically contain casting defects resulting from inhomogeneous spatial distribution in chemistry during freezing (called microsegregation), shrinkage defects, and residual ceramic particles that need to be removed/reduced to exclude potential fatigue crack initiation sites in service. For these reasons, the ingot goes through a second (and possibly a third) remelting step such as VAR and/or ESR.

The VAR process involves melting of a consumable electrode of the superalloy into a water-cooled copper crucible in vacuum. The feedstock (electrode) is produced either by VIM or ESR. The electrode serves as the cathode, the molten pool on the top surface of the solidifying ingot serves as the anode, and an arc is struck between the two and provides the energy for melting the electrode. A molten film on the end surface of the electrode drips under gravity as droplets onto the solidifying ingot. VAR ingots can be several meters in length and therefore can weigh several tons. The resulting VAR ingot has chemistry and structure superior to the electrode from which it is obtained as tramp elements volatilize, and impurities like oxygen and nitrogen get degassed in vacuum during the process. The ESR process is similar to the VAR process in that an electrode is consumed by remelting, but here a molten slag pool is present between the electrode and the solidifying ingot so the process can be conducted in air. The big advantage is that the molten droplets pass through the molten slag to reach the solidifying ingot, and this enables these droplets to react with the slag, thereby removing oxides and sulfur. In triple-melted ingots, VIM is followed by ESR and then VAR to keep casting defects down in large ingots.

Such ingots then undergo thermal-mechanical processing to break down the cast microstructure (which is deemed undesirable for turbine disk service requirements), and to develop a uniform reduced grain size. The first step in the process is called "cogging" where the ingot diameter is reduced to half its original diameter by a series of hot deformation steps. This series of operations produces a fine uniform grain size. This product is then hot-forged in multiple steps (that include open- and closed-die forging) into the shape of a turbine disk. The final step is to optimally heat treat the disk to obtain the desirable quantity, type, size, and distribution of the strengthening phases. Beyond this, non-destructive evaluation and final shape machining take place.

Nowadays, many of the alloys that are used in disk applications in modern engines are extremely complex and not readily amenable to the cast-and-forge route. Examples of such superalloys include IN100 (Ni-10Cr-15Co-3Mo-4.7Ti-5.5Al-0.9V-0.06Zr-0.014B-0.18C) and Rene 95 (Ni-14Cr-8Co-3.5Mo-3.5W-3.5Nb-2.5Ti-3.5Al-0.9V-0.05Zr-0.01B-0.16C). In such cases, powder metallurgy processing is a viable alternative. The starting material is usually a VIM ingot. The ingot is remelted in a tundish in a protective environment/vacuum and then exits as a molten stream through a bottom nozzle in the crucible at which point it is impinged upon by several high-pressure gas jets (gas is usually argon or helium). This process atomizes the molten metal stream into particles that freeze in free flight to the bottom of the atomization chamber and are collected. Typically, a log-normal distribution of powder particle size results. The desired size range can be salvaged by screening the powders. The rapid cooling and particle size limit the scale of composition segregation (a major problem in bulk castings of complex alloys). The resulting powder is canned (e.g., steel cans), evacuated, sealed, and hot-consolidated under the combined influence of temperature and pressure in a chamber, the process being called hot-isostatic pressing (HIPing). The resulting "HIPed billet" is often then hot-extruded to destroy adverse microstructural features such as prior particle boundaries and to produce a fine grain size. The resulting product is then forged much the same way described previously for the casting route. The fine uniform microstructure obtained by the powder processing route often yields better properties than the casting route, but the powder route is usually more expensive.

An updated comprehensive description of the physical metallurgy, microstructure-processing-property relationships, and the applications of Ni-based superalloys in aeroengines is available in Reed (2006), and the interested reader is referred to it for deeper insights.

Combustor Case and Liners

The combustor, shown schematically in Fig. 5.27, is the part of the engine where the compressed intake air enters the chamber, mixes with the fuel, gets ignited, and produces high-pressure hot gases (Wiki: Combustor; Feb 2018ai). The process is complicated and needs to satisfy many constraints: the sustained fuel burn under varying conditions of takeoff, landing, and during cruise, the ability to reignite if a

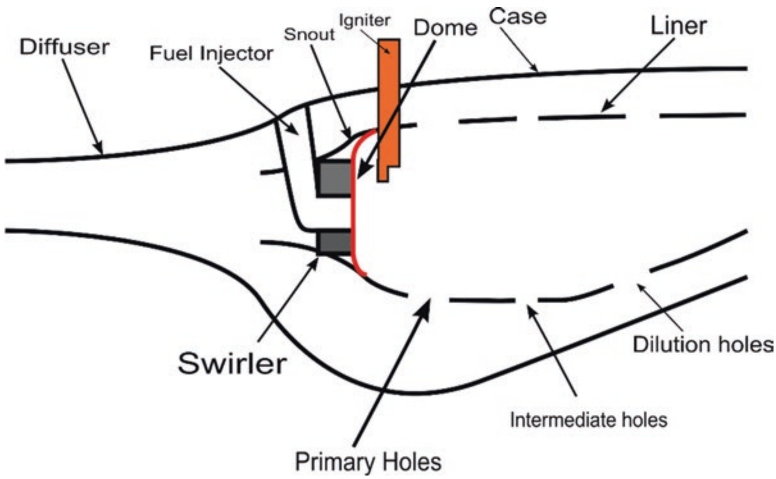

Fig. 5.27 A schematic illustration of a combustor in an aircraft engine. (Image taken from https://commons.wikimedia.org/wiki/File:Combustor_diagram_componentsPNG.png)

"flame-off" occurs in flight, the ability to maintain low-pressure loss across the combustor and uniform temperature at the outlet where the combustion product enters the turbine section to prevent hot spots in the turbine, the control of acoustics, and the reduced emissions.

The air from the compressor comes in at too high a velocity to be combusted efficiently, and it is the task of the diffuser to slow it down. The fuel injector enables the fuel to be dispersed in a fine spray. The dome and the swirler introduce turbulence in the air so the fuel and air mix well, and the igniter produces the spark to combust the mixture. The combustor liner contains the flame, and the perforations in the liner bring in cooler air at various points in the chamber (primary holes, intermediate holes, and dilution holes). The entire combustor chamber is contained within the combustor case which is thermally protected by the air flow between it and the combustion liner. On the other hand, the liner must withstand high-temperature cycles even though air film cooling is still present on the outside that reduces the severity of the situation. Unburned hydrocarbons, smoke, carbon dioxide, carbon monoxide, and nitrogen oxides (NO_x) are the primary emissions and need to be tamed to meet regulations.

High-temperature materials demands have continuously evolved with time as the air inlet temperature (called $T3$) from the compressor to the combustor and the hot gas exit temperature from the combustor to the turbine (called $T4$) have both steadily increased. Ni- and Co-based superalloys have been and continue to be used for combustor liners in sheet form. Typical Ni-based superalloys used include Hastelloy X and Nimonic 263 (nickel-chromium-cobalt-molybdenum superalloy), while a regularly used Co-based alloy is Haynes 188 (Co-22Ni-22Cr-14W-0.35Si-0.1C-0.03La) (Muktinutalapati 2011). Ni-based superalloys like Hastelloy X and Alloy 617 are used for combustor cans, injector nozzles, and flame holders.

Turbine Disk Alloys

Typically, operating temperatures for turbine disks tend to be significantly lower than those for turbine blades, but stresses are greater; disk design aims to keep operating stresses to a level where creep is not a life-limiting consideration (Williams and Starke 2003). Thus, low cycle fatigue life and fatigue crack growth are the limiting properties. Therefore, yield and tensile strength, ductility, and fracture toughness are also important considerations.

Common disk alloys include Inconel 718 (composition above), Astroloy (15Cr-17Co-5.3Mo-4Al-3.5Ti-0.06C-0.03B-Bal. Ni), MERL-76 (12.4Cr-18.6Co-3.3Mo-1.4Nb-0.2Al-4.3Ti-0.35Hf-0.05C-0.03B-0.06Zr-Bal. Ni), Rene 95 (composition above), and UDIMET 720 (17.9Cr-14.7Co-3Mo-1.25W-2.5Al-5Ti-0.035C-.033B-0.03Zr-Bal. Ni), to name a few. These Ni-based disk alloys, produced either by the casting route or by the powder metallurgy route as the case may be, have evolved in their capabilities in the past three decades and a comparison of the creep strength (time to attain 0.2% strain at a constant stress of 800 MPa) for a

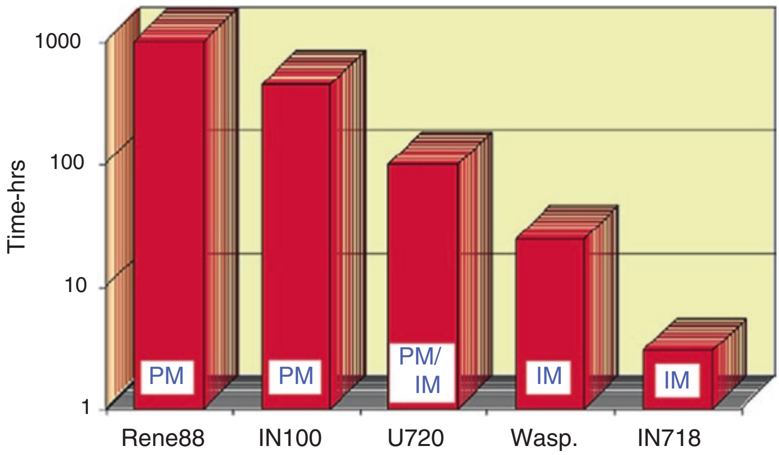

Fig. 5.28 Comparison of the creep strength of five Ni-based disk alloys. Time is for 0.2% strain at 650 °C at a stress of 800 MPa (Williams and Starke 2003). (Figure used with permission from *Elsevier*)

representative group of disk alloys at 650 °C from the work of Williams and Starke (2003), is shown in Fig. 5.28.

In considering alloy selection for turbine disks, microstructural consideration is critical, and since disks are wrought products that include grain boundaries, engineering grain boundaries is important to optimize properties of relevance. This in turn means an in-depth understanding of alloy chemistry-processing parameters and resulting microstructure. In this context, Reed (2006) clearly outlines three important guidelines for alloy selection.

1. To impart strength and fatigue resistance, the fraction of the γ' phase (and γ'' when present) should be controlled by the proper choice of the γ'-forming alloying elements (Al, Ti, and Ta) and having this phase between 40% and 55%, and heat treatment must be provided to ensure a uniform distribution of the precipitates. The variation in yield strength at 650 °C as a function of the volume fraction of the strengthening phases (γ' + γ'') is shown in Fig. 5.29 (taken from Reed (2006)).
2. The grain size should be chosen (typically in the 30–50 μm range) for the desired combination of yield strength and resistance to fatigue crack initiation (both scale inversely with grain size), and creep strength and fatigue crack growth resistance (which scale directly with it). These relationships are schematically illustrated for Udimet 720 in Fig. 5.30 (taken from Williams and Starke (2003)).
3. When added in small quantities, elements such as carbon and boron that segregate to the γ/γ' interfaces increase the work of cohesion and thereby improve the creep strength, creep ductility, and low cycle fatigue resistance; the optimal concentration is reported to be around 0.03 wt% B and about the same for C. Higher

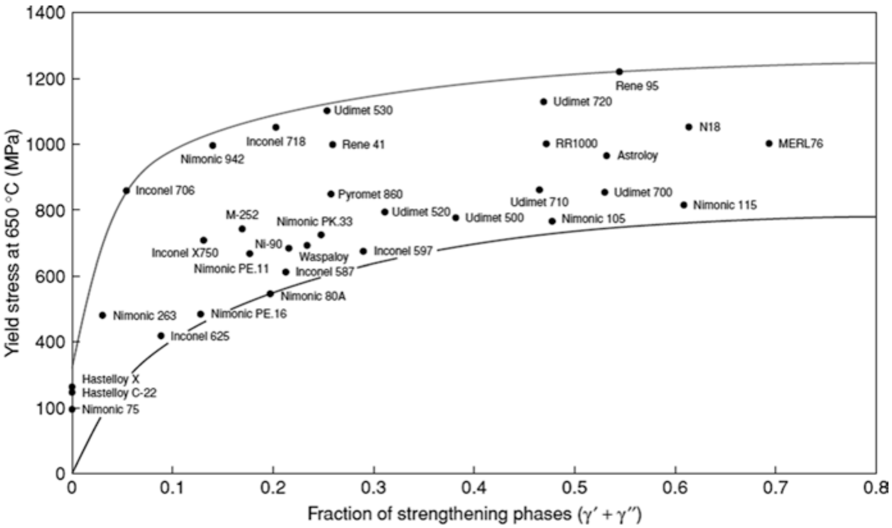

Fig. 5.29 Variation of the yield stress at 650 °C with the total fraction of the γ' and γ'' strengthening phases for a number of common turbine disk alloys (Reed 2006). (Image used with permission from Cambridge University Press)

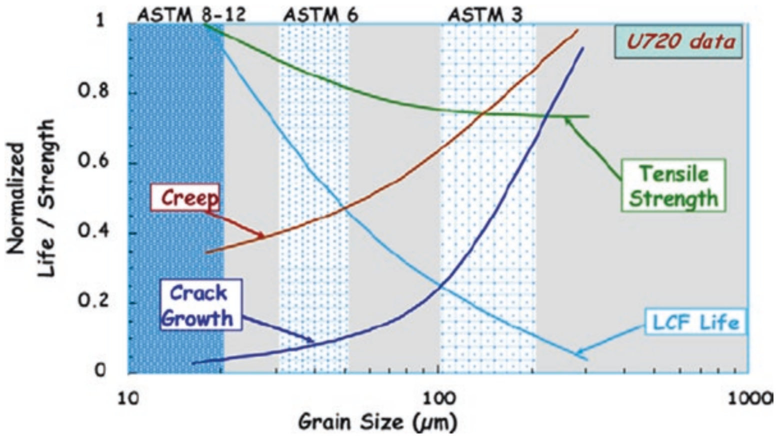

Fig. 5.30 Schematic drawing based on real data showing effect of grain size on creep, low cycle fatigue life, fatigue crack growth rate, and tensile strength (Williams and Starke 2003). (Figure used with permission from *Elsevier*)

amounts, resulting in the precipitation of carbides and borides, are not particularly effective in this respect.

Beyond alloy selection, processing for optimal microstructure, property evaluation, and fabrication of the disk, two other important considerations are service life estimation (called "lifing") and non-destructive evaluation methodologies. Different approaches are used to estimate the life of a turbine disk: life-to-first-crack approach, damage-tolerant lifing, and a probabilistic approach to lifing. More details on each of these approaches can be found in Reed (2006). Non-destructive evaluation is a very important aspect of disk technology. It is used to characterize the size and distribution of flaws resulting from manufacturing before the disk enters service, when the disk is removed from the engine, and before a decision is made to place it back in service. The various techniques used include (i) liquid dye penetrant method, (ii) eddy current method, (iii) x-ray radiography, and (iv) ultrasonic methods, the last of these being particularly important.

Turbine Blade Alloys

The high-pressure (HP) turbine blades (also called airfoils) are absolutely critical for performance of the engine; strength and oxidation resistance are usually the life-limiting properties (Williams and Starke 2003). Many engine properties like fuel economy and thrust depend critically on their ability to withstand operating conditions. Their task is to extract work from the hot gas stream emanating from the combustor and provide it to rotate the shaft that drives the high-pressure compressor. Reed (2006) provides a simple calculation that vividly impresses the role and rigor of these turbine blades in the engine, and the main points from his book are reproduced below. Consider an engine like the modern GE90 or the Trent 800. The temperature of the gas stream is ~1475 °C which is above the melting point of the superalloy from which the blades are made (internal air-cooling passages in the individual blades and/or insulating thermal barrier coatings on the blades prevent the blades from reaching their melting temperature). The high-pressure shaft develops a power of about 50 MW and assuming 100 blades, each blade extracts about 500 kW!! Assuming a 9 h/day, each row of blades is expected to last at least 3 years which translates into 5 million miles or ~500 circumferences of the world. The angular velocity of the blade is ~10,000 revolutions per minute which translates to a tip velocity greater than 1200 km/h. The centrifugal stress at the blade root is shown to be roughly 180 MPa, which in non-engineering terms can be likened to "hanging a heavy truck on each blade"! A cutaway of the GEnX-1B engine and the turbine section including the disk and blades on the shaft are shown in Fig. 5.31 from Bewlay et al. (2016).

In the early days, turbine blades were produced by extrusion and forging, but the resulting fine-grained equiaxed structure as well as the inability to make hollow blades with internal air-cooling passages without further machining made the processing route less attractive as the temperature demands in the engine increased. Additionally, more complex alloys developed to meet higher temperature demands made high-temperature deformation processing difficult as cracking and incipient melting accompanying increased processing temperatures became an issue. For these reasons, blade production by investment casting (described earlier) became the method of choice and is the practice all over the world today. Hollow blades could be produced in this manner, and by controlling the solidification parameters

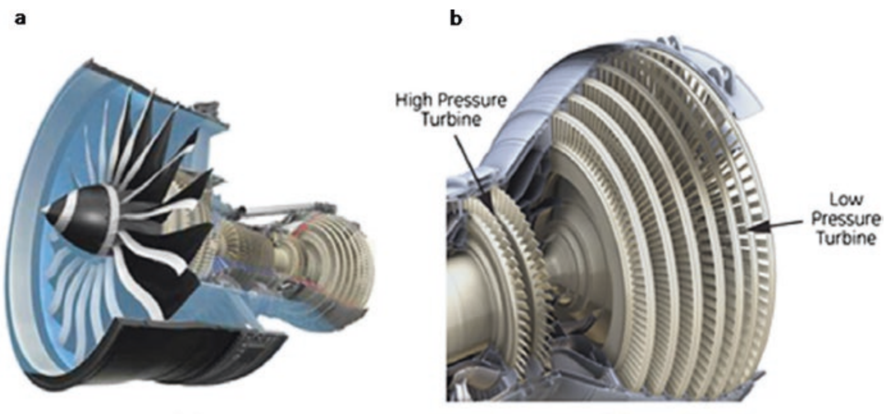

Fig. 5.31 Photographs of the GEnx-1B engine as used in the Boeing 787: (**a**) the complete engine and (**b**) the turbine section (Bewlay et al. 2016). (Image used with permission from Taylor & Francis Co.)

(heat flow/thermal gradient, solid-liquid interface velocity, etc.) in the process, equiaxed grains could be replaced with columnar grains aligned along the length of the blade (called directional solidification) enhancing creep resistance and eventually producing single-crystal blades with no grain boundaries at all in the blade. (This is accomplished usually by adding a small wax spiral/helix to the end of the wax pattern that then becomes a fine hollow in the ceramic mold; this acts as a single-grain selector during solidification of the metal, causing the rest of the blade to solidify with the selected grain orientation; (see example of the starter block and the "pigtail" grain selector used to produce a Trent 800 high-pressure turbine blade in Fig. 5.32a). Furthermore, by providing suitable cores in the pattern, hollow internal passages with good dimensional tolerances could be obtained in the castings. Examples of equiaxed, columnar-grained, and single-crystal Ni-based superalloy turbine blades and blades with complex contours and internal air-cooling passages produced by investment casting are shown in Fig. 5.32b, c, respectively. Developments in investment casting technology have been real enablers of progress in the turbine blade industry.

Alloy chemistry for producing single-crystal turbine blades has evolved since the 1980s, driven by increasing performance demands coupled with significant progress in processing capabilities. Concurrently, a significant data bank of knowledge and experience has evolved that has led to developing chemistry-microstructure-properties-performance relationships. The evolution of alloy composition over time has been categorized in four generations and is a commonly accepted nomenclature in the superalloy community (Table 5.12). The first-generation single-crystal superalloys included alloys that went by the tradenames of PWA1480 (a Pratt & Whitney alloy), RENE N4 (a General Electric alloy), RR2000 (a Rolls-Royce alloy), and CMSX-2 (a Cannon-Muskegon alloy), to name a few. Subsequently, second-generation superalloys like PWA1484, RENE N5, and CMSX-4 were developed

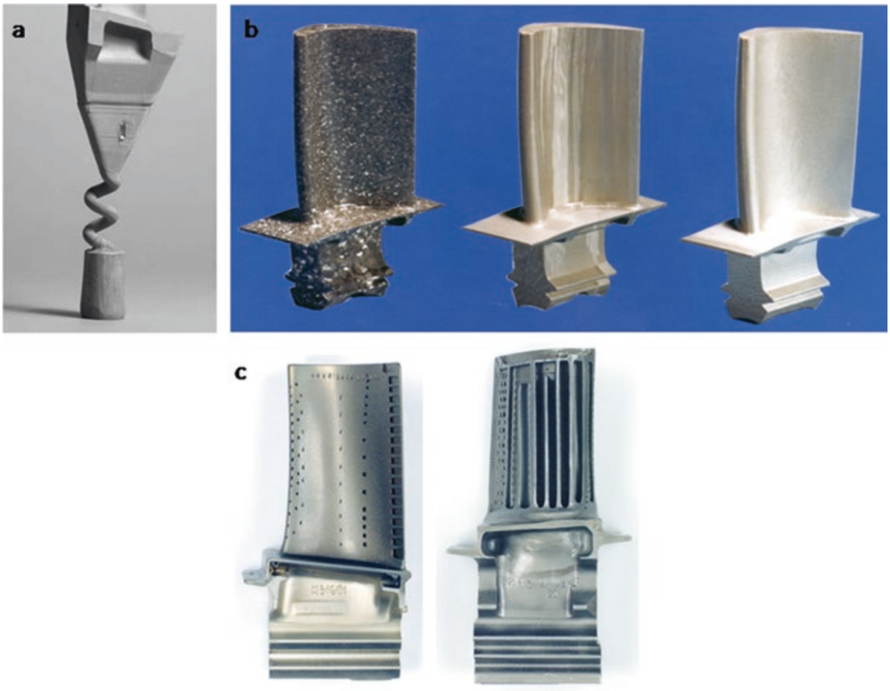

Fig. 5.32 (**a**) Starter block and the "pigtail" grain selector for growing single-crystal superalloy turbine blade (Reed 2006). (Image with permission from Cambridge University Press); (**b**) equiaxed, columnar-grained, and single-crystal Ni-based superalloy turbine blades by investment casting (Williams and Starke 2003; image used with permission of Elsevier); and (**c**) Ni-based superalloy blades by investment casting that include complex contours and internal air-cooling passages

where Re was introduced in the alloys, (emphasized in bold lettering in Table 5.12 below) and Ti was removed. The nominal compositions of these two generations of alloys are provided in Table 5.12 and may be compared.

Mechanical properties assessment at elevated temperatures for extended times showed that Re was beneficial to the creep resistance of these alloys. This and other factors led to the development of the third generation of single-crystal superalloys with even higher Re content (compare Re content in bold in second generation versus third generation); some examples include RENE N6 and CMSX-10. The creep resistance of the third-generation alloys was even more improved over the second-generation alloys, confirming the beneficial effects of Re additions. Reed (2006) states that while Cr and Co have only marginal effects in improving creep resistance, W and Ta are more potent but not as effective as Re. The best strengtheners appear to be those that diffuse slowest in Ni. However, these elements like Cr, W, Mo, and Re cannot be added in excessive amounts as they have deleterious effects on the properties. This is because in excessive amounts they precipitate intermetallic phases called TCP phases (topologically close-packed phases) that signal

Table 5.12 Composition (in wt%) of single-crystal Ni-based superalloys

First generation	
PWA1480:	10Cr-5Co-4W-5Al-1.5Ti-12Ta-balance Ni (density, 8.7 g/cc)
RENE N4:	9Cr-8Co-2Mo-6W-3.7Al-4.2Ti-4Ta-0.5Nb-balance Ni (density, 8.56 g/cc)
RR2000:	10Cr-15Co-3Mo-5.5Al-4Ti-1V-balance Ni (density, 7.87 g/cc)
CMSX-2:	8Cr-4.6Co-0.6Mo-8W-5.6Al-1Ti-6Ta-balance Ni (density, 8.6 g/cc)
Second generation	
PWA1484:	5Cr-10Co-2 Mo-6W-**3Re**-5.6Al-8.7Ta-0.1Hf-balance Ni (density, 8.95 g/cc)
RENE N5:	7Cr-8Co-2Mo-5W-**3Re**-6.2Al-7Ta-0.2Hf-balance Ni (density, 8.70 g/cc)
CMSX-4:	6.5Cr-9Co-0.6Mo-6W-**3Re**-5.6Al-1Ti-6.5Ta-0.1Hf-balance Ni (density, 8.7 g/cc)
Third generation	
RENE N6:	4.2Cr-12.5Co-1.4Mo-6W-**5.4Re**-5.75Al-7.2Ta-0.15Hf-0.05C-0.004B-0.01Y-balance Ni (density, 8.97 g/cc)
CMSX-10:	2Cr-3Co-0.4Mo-5W-**6Re**-5.7Al-0.2Ti-8Ta-0.1Nb-0.03Hf-balance Ni (density, 9.05 g/cc)
TMS-75:	3Cr-12Co-2Mo-6W-**5Re**-6Al-6Ta-0.1Hf-balance Ni (density, 8.89 g/cc)
Fourth generation	
MC-NG:	4Cr-<0.2Co-1Mo-5W-**4Re**-**4Ru**-6Al-0.5Ti-5Ta-0.1Hf-balance Ni (density, 8.75 g/cc)
MX4/ PWA1497:	2Cr-16.5Co-2Mo-**5.95Re-3Ru**-6W-5.55Al-8.25Ta-0.15Hf-0.03C-0.004B-balance Ni (density, 9.2 g/cc)
TMS 162:	2.9Cr-5.8Co-3.9Mo-**4.9Re-6Ru**-5.8W-5.8Al-5.6Ta-0.09Hf-balance Ni (density, 9.04 g/cc)

instability and reduce creep resistance of the alloy because these elements are not then available to participate in the γ/γ' microstructure. More recently, experiments have confirmed that the addition of ruthenium (Ru) improves the stability of Ni-based superalloys with respect to TCP phase precipitation, thereby enhancing creep resistance as illustrated in Fig. 5.33 (Yeh et al. 2004). Note that in Fig. 5.32, alloy RR 2100 has no Ru and alloy RR 2101 has 2% Ru.

Thus, the fourth-generation single-crystal superalloys were developed, and examples of such alloys include MC-NG (a French alloy developed and patented by ONERA), MX4/PWA1497 (a GE, P&W, NASA development), and TMS 162 (developed at NIMS in Japan). The compositions for these alloys are included in Table 5.12. Again, the Re and Ru content in these alloys are presented in bold lettering to emphasize their benefits to creep resistance. From these developments and associated experiences, Reed (2006) has listed a set of microstructure-based guidelines for single-crystal turbine blade alloy selection with enhanced creep resistance (similar to those previously listed for turbine disk alloys selection) that is reproduced below.

1. Proportions of γ' forming elements like Al, Ti, and Ta should be high such that the volume fraction of γ' is ~70%.
2. The composition of the alloy must be chosen such that the γ/γ' lattice misfit is small; this minimizes the γ/γ' interfacial energy so that γ' coarsening is restricted.

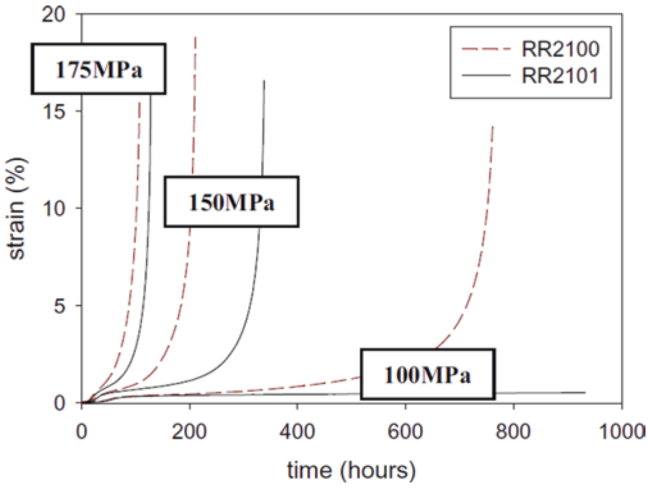

Fig. 5.33 Comparison of creep behavior at 1100 °C. At 100 MPa, RR2100 ruptured, while RR2101 still remained in steady state creep; the creep test for RR2101 was then interrupted. As the applied stress was increased (150 MPa and 175 MPa), the effect of Ru addition becomes less pronounced (Yeh et al. 2004). (Figure copyright 2004 by The Minerals, Metals and Materials Society. Used with permission)

3. Concentrations of creep-strengthening elements, particularly W, Mo, Ta, Re, and Ru, must be significant but not so great that precipitation of the topologically close-packed (TCP) phases is promoted.
4. The composition must be chosen such that surface degradation through exposure to the hot, working gases is avoided.

Each of these guidelines is founded on experimental results, experience, and fundamental principles of physical metallurgy. Although some aspects of alloy chemistry were cursorily discussed in this section, the interested reader is directed to Reed's detailed description of each of these guidelines (2006). The fourth guideline deserves some consideration as we have not discussed environmental degradation until now.

Oxidation is a problem and can result in loss in wall thickness of the blades and load-carrying capacity, and can set the stage for fatigue failure. The important oxides that need consideration are NiO (nickel oxide), Cr_2O_3 (chromia), and Al_2O_3 (alumina). Alumina is the most thermodynamically stable of the three and would be expected on this basis, but kinetics of oxidation are important as well. Nickel oxide forms rapidly, is friable, and thus spalls causing sustained attack; chromia at high temperature can convert to CrO_3 which is gaseous, and thus, oxidation rate can be high in a rapidly moving gas stream which is the case in the blade environment in service. When alumina scale growth occurs, oxidation is the slowest, and for this reason, in the first and second generation of superalloys, Al was added (~ 6 wt%) with the intent to form an alumina scale. Also trace additions of rare-earth elements like La and Y have been shown to be beneficial in enhancing oxidation resistance

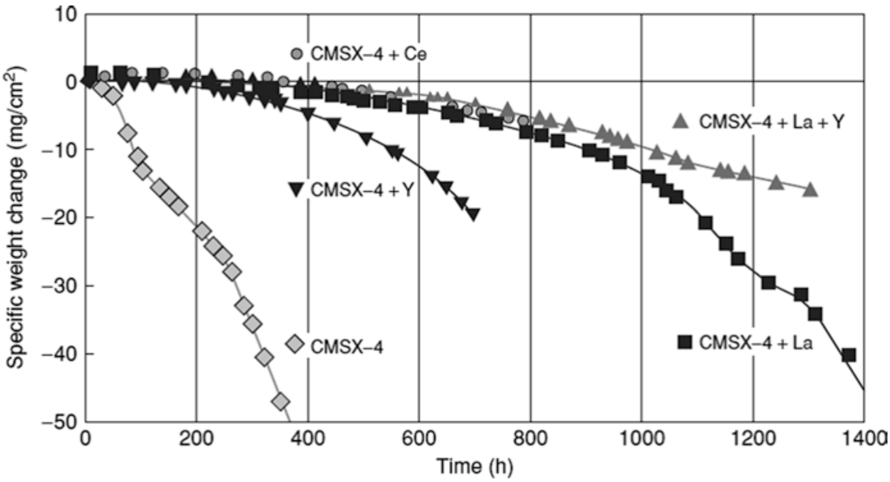

Fig. 5.34 Dynamic cyclic oxidation test results at 1093 °C for bare CMSX-4 alloy with and without reactive element additions (Harris and Wahl 2004). (Figure copyright 2004 by The Minerals, Metals and Materials Society. Used with permission)

(Fig. 5.34; Harris and Wahl 2004). In the more recent generations of superalloys, the intrinsic cyclic oxidation resistance was found to be not as good as it was in the first two generations (Reed 2006), suggesting that in alloy design, less emphasis has recently been placed on tailoring alloy chemistry for oxidation resistance as opposed to other mechanical properties and instead more reliance on coating technology (thermal barrier coatings, TBCs) to provide turbine blade oxidation resistance has become the trend.

The hotter the engine runs, the better is its performance and efficiency (Perepezko 2009; Padture 2016). The specific core power increase with increase in turbine rotor gas inlet temperature is illustrated in Figure 5.35a. The introduction of ceramic TBCs has boosted the maximum temperature in the hottest part of the gas turbine engine (gas inlet) to unprecedented levels (>1500 °C), resulting in extraordinary efficiency and performance gains, and a cleaner exhaust. TBCs are thin oxide-ceramic coatings (100 μm to 1 mm thickness) applied to metallic (typically Ni-based superalloys) components in the hot section of the engine (Clarke et al. 2012; Darolia 2013; Padture et al. 2002; Padture 2016). The metallic components are internally air-cooled, and the TBCs facing the high-velocity hot gas stream have low thermal conductivities, which allow the engine to operate at temperatures above the melting point of the superalloy. Figure 5.35b shows the progression of temperature capabilities of TBCs and the dramatic rise in the allowable gas inlet temperatures (Padture 2016). TBCs, typically made of ZrO_2 partially stabilized by ~7 wt% Y_2O_3 (7YSZ), have worked remarkably well. They have sufficient porosity and microstructural defects to reduce their thermal conductivity and make them compliant (strain-tolerant) in accommodating thermal strain. Most importantly, 7YSZ falls in a narrow composition range where the ferroelastic toughening mechanism is active, making

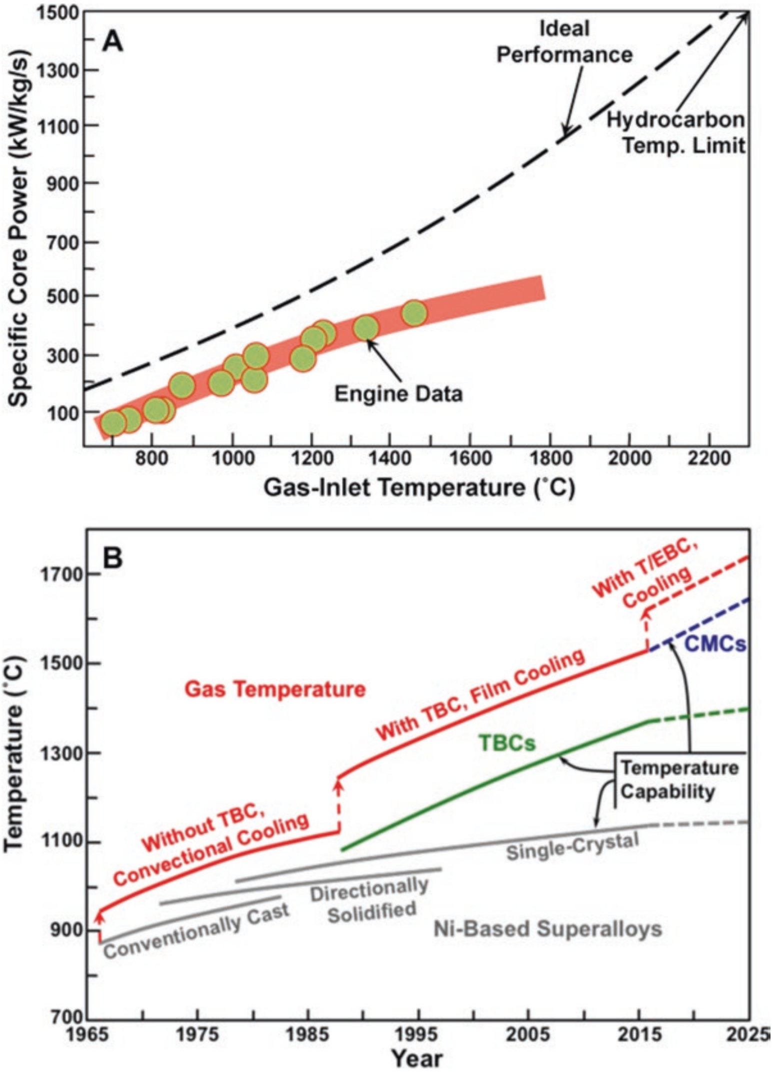

Fig. 5.35 (**a**) Specific core power of gas turbine engines as a function of gas inlet temperature (Padture 2016). (**b**) Progression and projection of temperature capabilities of Ni-based superalloy, TBC, and CMC gas turbine engine materials and maximum allowable gas temperatures with cooling (rough estimates)

7YSZ TBCs mechanically robust. However, 7YSZ TBCs face severe limitations as the demands on TBC temperature capability continue to rise. First, 7YSZ TBCs begin to lose their phase stability above ~1300 °C. Second, although 7YSZ TBCs have low thermal conductivity (~1 $W.m^{-1}.K^{-1}$), there is a need for TBCs with even lower thermal conductivities and approaches to scatter photons at high temperatures (Padture 2016). Third, for TBC surface temperature above ~1200 °C, silicates ingested by the engine from the atmosphere (runway debris, dust, sand, volcanic ash) melt and deposit on the TBC surface. The molten silicate, collectively referred to as CMAS (calcia-magnesia-aluminosilicate), penetrates deep into 7YSZ TBCs causing them to fail prematurely (Clarke et al. 2012; Padture 2016).

Thus, there is a need for TBCs that combine all the desirable attributes of 7YSZ, and at the same time address the above critical issues. Several TBC compositions (e.g., $Gd_2Zr_2O_7$, $2ZrO_2{\cdot}Y_2O_3$) are being pursued that not only have higher-temperature capabilities and lower thermal conductivities but are also resistant to CMAS attack (Clarke et al. 2012; Padture 2016). However, those compositions lack the ferroelastic toughening unique to 7YSZ. To overcome this issue, a multilayer approach is being pursued, where the different material layers that perform specific functions are positioned within the TBC stack. For example, in an otherwise low-conductivity, CMAS-resistant TBC, a thin layer of tough 7YSZ is buried at the relatively cooler TBC/metal interface that is prone to failure. However, when CMAS is present, the failure location can shift (Padture 2016). Also, the ubiquitous multiple hetero-interfaces in multi-layers can themselves fail during the thermal excursions experienced by the engine. An alternative approach that is being pursued is that of a single-layer TBC but with distributed multiple phases, where each phase performs the desired function. Some of the phases could also serve in-service diagnostic functions such as TBC “health” monitoring.

Nozzle

Nozzles are located at the tail of the engine and serve two major functions. They are designed to control the engine backpressure to provide optimum engine performance, and to efficiently convert potential energy of the exhaust gases to kinetic energy by increasing the exhaust velocity. Additional aspects include thrust reversing capabilities and thrust vectoring (more for combat aircraft). There are various types of nozzle design including convergent nozzles (used in turbojets and turboprops), co-annular nozzles (in turbofan engines), and convergent-divergent nozzles (in rockets, ramjets, supersonic aircraft). In turbofan engines, where a co-annular nozzle is used, the core air flows out of the central nozzle, the fan air flows out of the annular nozzle, and when the two flows mix, there is some enhancement in thrust, and such nozzles tend to be quieter than convergent nozzles. Thrust reversers are employed to decelerate the aircraft. and as the name suggests, the idea is to reverse the thrust against the forward travel of the aircraft and is employed after landing to reduce brake wear and shorten landing runway distances. Thrust reversers can consist of cups that swing across the end of the exhaust nozzle and deflect the thrust in the forward direction, or they are panels that slide backward and reverse only the fan thrust (the majority of the thrust).

Another aspect that deserves consideration is exhaust noise. Jet engine noise suppression has become one of the most important fields of research due to airport regulations and aircraft noise certification requirements. Although airframe generated noise is a factor to consider, the main source of the noise is from the engine. Jet

Fig. 5.36 A photograph of a chevron nozzle in an engine on the Boeing 787 Dreamliner. (source: https://commons.wikimedia.org/wiki/File:B787-2139.jpg)

exhaust noise results from the turbulent mixing of the exhaust gases with the atmosphere. Turbulence created near the exhaust exit causes a high-frequency noise, while further downstream from the exhaust, turbulence causes low-frequency noise. Noise-absorbing porous skins backed by a honeycomb core are sometimes used as liner materials for noise suppression. More recently, the Boeing 787 engines use what is called a chevron nozzle (serrated edges at the end of the nozzle; see Fig. 5.36) to effectively suppress noise with negligible performance penalty. Materials typically used in the nozzle area include nickel-based superalloys, titanium alloys, and more recently, ceramic matrix composites.

Titanium Aluminides

Implementation of TiAl Alloys

A class of materials that has been extensively researched over the decades that exhibits characteristics between metals and alloys on the one hand, and ceramics on the other, is called intermetallic compounds. Such compounds exhibit certain characteristics of metals and alloys in that they can be melted and cast into molds, can be shaped at high temperature by fabrication steps like extrusion and forging, but have mechanical properties that more often resemble ceramics in that they are brittle at low temperatures, and can retain strength and creep resistance at high temperatures. Some of these compounds that contain aluminum as one of the primary alloying elements, called aluminides, have been particularly studied as they also have excellent oxidation resistance. Thus, nickel aluminides (NiAl and Ni_3Al), iron aluminides (FeAl and Fe_3Al), and titanium aluminides (TiAl and Ti_3Al) have been the focus of considerable research over the past few decades

(Appel and Wagner 1998; Gamma Titanium Aluminide Alloys 2014; George et al. 1994; Liu and Kumar 1993; Ordered Intermetallics-Physical Metallurgy and Mechanical Behavior 1992). In the 1980s and 1990s, there was recognition that the titanium aluminides (TiAl), if successfully developed and implemented, would provide significant weight reductions in the aircraft engine (replacing Ni-based alloys in some hot parts of the engine) as well as in components like turbochargers and similar parts in automobiles; this provided the basis for a concerted worldwide effort to advance the science and technology of these alloys and initiate development strategies to implement them. It meant that what was a laboratory-scale curiosity in the 1960s and 1970s had to be transformed into a real product, provided there was adequate justification to do so. Intense alloy design and characterization efforts were initiated at universities and research laboratories around the world, and programs went into place worldwide to develop processing and manufacturing capabilities in the 1990s and the early 2000s. The metallurgical aspects of these TiAl-based alloys are briefly outlined in the next section.

In the 1980s, research at the General Electric Global Research Center led to the development of a TiAl alloy consisting of 48 at% Al-2 at% Cr-2 at% Nb and balance Ti (called 48-2-2); in the first half of the 1990s, the baseline GE90 engine weight requirements inspired a detailed assessment of the potential for TiAl applications. General Electric (GE) generated the first draft of the low-pressure turbine (LPT) blade design practice for a TiAl blade, including attachment considerations and key materials property requirements. To facilitate progress toward implementation of LPT blades, GE committed to designing, producing, and engine testing CF6-80C stage 5 LPT blades from GE 48-2-2. This exercise was successfully completed in 1994. This engine testing demonstrated that it was possible to manufacture, assemble, disassemble, inspect, reassemble, and run TiAl LPT blades and established the foundations for the commercial introduction of TiAl in aircraft engines. In 2006, GE announced the usage of 48-2-2 for making stage 6 and stage 7 LPT blades for the GEnx engine. As of now, over 1.5 million pounds of this alloy has been produced, and nearly 200,000 LPT blades fly around the world every day in the hundreds of engines that power several Boeing 787s and 747-8s. These engines deliver a 20% reduction in fuel consumption, 50% reduction in noise, and an 80% reduction in NO*x* emissions compared to previous engines in this class (Bewlay et al. 2016). Alloy 48-2-2 LPT blades are also a part of the new LEAP engines that are currently replacing CFM56 engines in single aisle aircrafts like the Boeing 737. Recently, Pratt & Whitney together with MTU Aero Engines in Germany has also started using another TiAl-based alloy (called a beta-stabilized alloy) in wrought form for LPT blades in its PW1100G engines.

Metallurgy of TiAl Alloys

The relevant portion of the binary TiAl phase diagram is shown in Fig. 5.37a (McCullough et al. 1989); the alloys of typical commercial interest contain 42–48 at% Al, but in addition may contain other alloying elements like V, Nb, Mo,

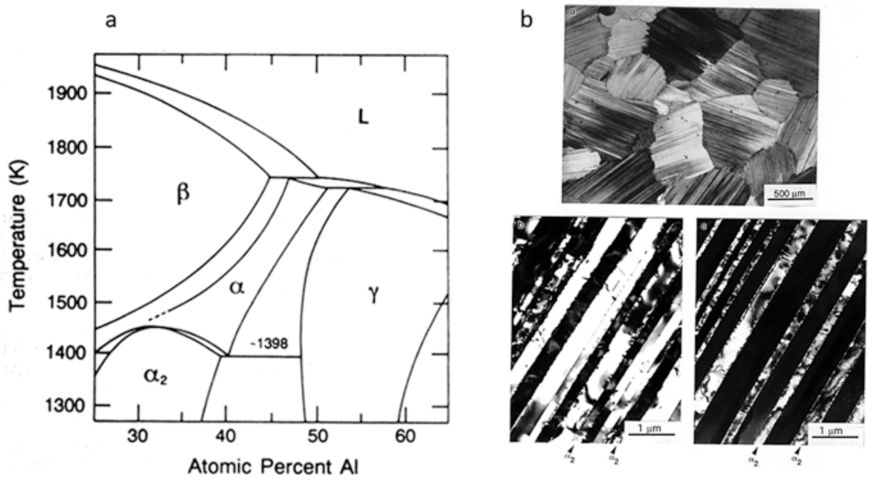

Fig. 5.37 (**a**) A portion of the binary TiAl phase diagram applicable to titanium aluminides (McCullough et al. 1989; figure used with permission from *Elsevier*) and (**b**) the as-cast microstructure in a binary Ti-46 at% Al alloy composed of TiAl (γ) and Ti_3Al (α_2) lamellae

or Cr (see, e.g., the composition of the GE 48-2-2 alloy described above). In such alloys, the microstructure is usually composed of two phases: the majority phase is TiAl (often called γ) which is an ordered compound with the $L1_0$ crystal structure (tetragonal structure composed of alternate layers of Ti and Al on the (100) planes), and the minor phase is Ti_3Al (often called α_2) which is also an ordered compound with the hexagonal crystal structure and belonging to a class designated $D0_3$. Depending on the processing condition adopted, the two phases can coexist in individual grains (called colonies) in a lamellar arrangement (Fig. 5.37b), as separate equiaxed grains, or as a duplex structure that is composed of some equiaxed grains and some lamellar grains. Being composed predominantly of Ti and Al, these materials have low density (~3.9 g/cc), excellent high-temperature properties (600 °C-800 °C range) due to their ordered crystal structures, excellent oxidation due to the high Al content, and minimal risk of engine fire sometimes associated with conventional titanium alloys.

For most structural applications, the duplex microstructure is preferred because it provides an acceptable combination of ductility and low cycle fatigue properties. In contrast, a fully or nearly fully lamellar microstructure can provide enhanced creep resistance and fracture toughness (note: in these materials, fracture toughness and ductility do not necessarily scale similarly as enhancements in these properties rely on different microstructural features). Thus, microstructural features like α_2/γ colony size, lamellae width, $\alpha_2$volume fraction and frequency of spacing, equiaxed γ volume fraction, etc., which are all influenced by both alloy chemistry and thermomechanical processing, affect the resulting properties. In the early stages, research was primarily focused on the binary alloys with varying Al content (42–48 at% Al), but *a second-generation of alloys* subsequently came into existence including the

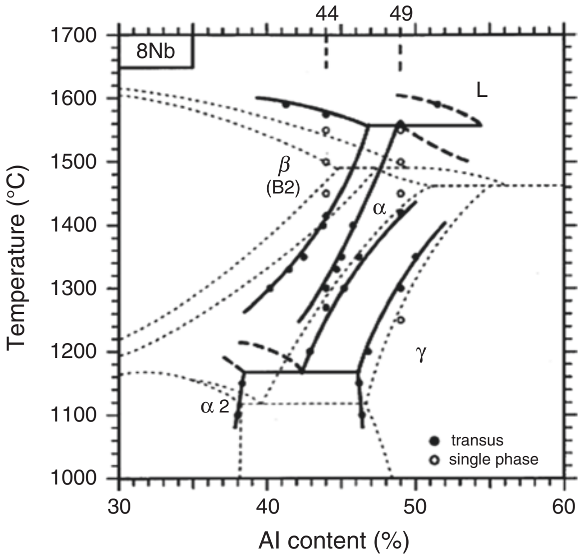

Fig. 5.38 The shift in the β phase field due to the addition of 8 at% Nb to the TiAl system. The dashed lines show the binary TiAl system, while the solid lines reflect the relative shift in the phase fields (Chen et al. 2007). (Figure used with permission from *Elsevier*)

48-2-2 alloy described above. These alloys included ternary and quaternary additions such as Cr, Mo, Nb, Ta, W, and V that influenced the relative stability of the high-temperature phase fields α versus β, etc. in the binary phase diagram shown in Fig. 5.37a and thereby significantly opened the processing window to develop and manipulate microstructure. These additions were referred to as β-stabilizers. An example of the shift in the phase fields due to the addition of 8 at % Nb is shown in Fig. 5.38 and taken from the work of Chen et al. (2007). In addition, boron, carbon, and silicon were considered in <1 at % levels to refine the cast grain size (boron) and enhance creep resistance (carbon and silicon). In these second-generation alloys, the Cr, Mn, and V levels were typically held between 1 and 3 at %, while the Nb, Ta, W, and Mo additions were maintained between 2 and 5 at % level.

Third-generation titanium aluminides are currently under development and include compositions of the type Ti-(45–48) at % Al-(0–10) at % (Cr, Mn, Nb, Ta)-(0–3) at % (W, Mo, Hf, Zr)-(0–1) at % (B, C, Si) and (0–0.5) at% rare-earth additions (Bewlay et al. 2016). By virtue of the higher levels of alloying additions, particularly Nb and Mo, the β phase is stabilized at higher temperatures, and therefore hot workability (extrusion and forging) is enhanced, but subsequent heat treatment can be used to reduce the β phase to obtain a balance in mechanical properties. Two examples of such alloys are the so-called TNB and TNM alloys, Ti-45Al-(5-10) Nb-0-0.5B, C (TNB and all in at %), and Ti-43.5Al-4Nb-1Mo-0.1B (TNM and all in at%). This TNM alloy is implemented in the Pratt & Whitney PW1100G engine for LPT blade applications.

The variation in specific yield strength (density corrected yield strength) for some TiAl alloys is compared to Ni-based superalloys such as IN 625 and Rene 95 in Fig. 5.39 (Clemens and Meyers 2016), and it is immediately evident why the TiAl alloys, despite the difficulties in processing them, are so attractive to the

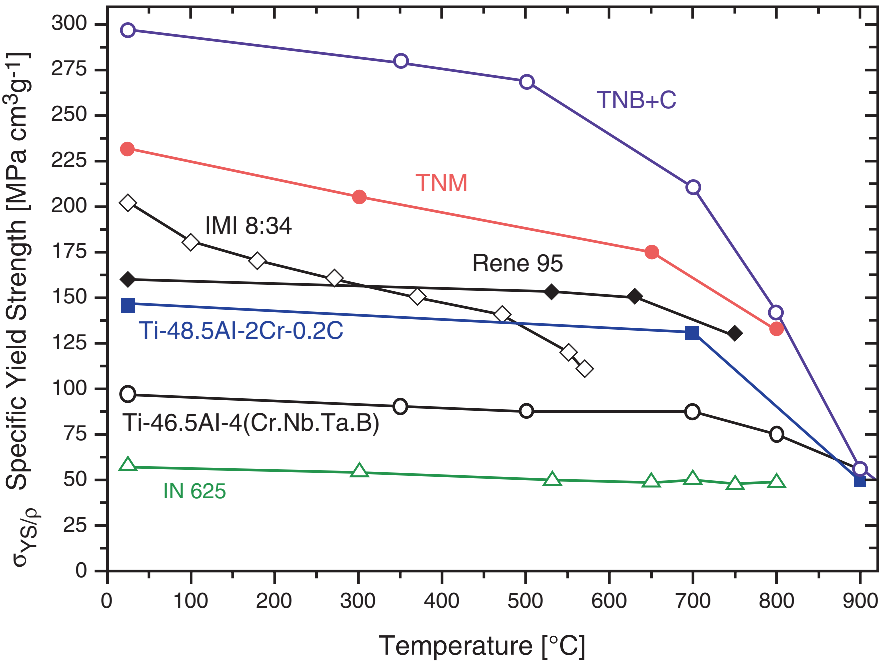

Fig. 5.39 Variation in specific yield strength with temperature for some γ-TiAl alloys relative to Ni-based superalloys (Clemens and Meyers 2016). (Figure used with permission from Taylor and Francis, Co.)

aircraft industry. Also noteworthy is the superiority in properties of the TNM and TNB alloys that are currently being designed and developed over the earlier TiAl alloys.

Ceramic Matrix Composites

While TBCs capable of handling higher temperatures are being developed, improvement in the temperature capability of Ni-based superalloys has remained relatively flat (Fig. 5.35A) (Padture 2016). As a consequence, the temperature-capability gap between TBCs and superalloys is widening. This necessitates more aggressive cooling to allow higher gas temperatures, but without commensurate increase in the specific engine power, resulting in rising inefficiency losses (Fig. 5.35B; Padture 2016; Perepezko 2009). The only way to address this issue is to use materials with inherently higher-temperature capabilities. Research into finding a replacement for Ni-based superalloys has been going on for decades, primarily along two lines (Padture 2016; Perepezko 2009): (i) Mo-based and Nb-based alloys and (ii) ceramic matrix composites (CMCs). It appears that CMCs are winning that race, as evinced

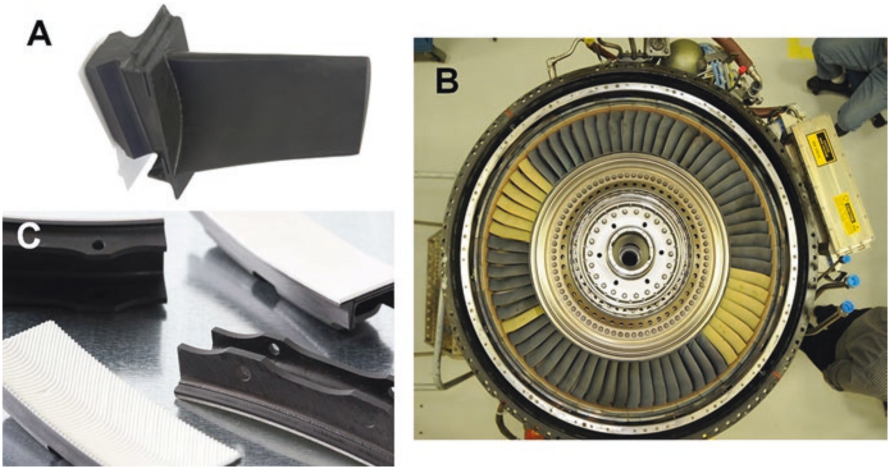

Fig. 5.40 Photographs of (**a**) CMC blade and vane, (**b**) engine with CMC blades (some with EBCs), and (**c**) CMC shroud with EBC. (Figure used with permission from GE Aviation)

by the significant investments made in CMCs by the major engine manufacturers and the recent demonstration of engines that use both stationary and rotating CMCs components in the hot section (Padture 2016; Zok 2016). Exhaust-section flaps/seals and afterburners made of CMCs have been used in military engines for years. CMCs research was very active in the late-1980s and the 1990s (Padture 2016; Zok 2016), but it waned due to processing problems, subpar performance, and prohibitive cost. But perseverance in addressing those issues has paid off, and engines with hot-section CMC components are already flying commercially (Fig. 5.40a–c).

CMCs are inherently lightweight, with about a third of the weight of superalloys, and hence have high specific strength (Fig. 5.41a; Padture 2016). CMCs are also more resistant to high-temperature oxidation and creep compared to superalloys (Fig. 5.41b). Unlike bulk ceramics, CMCs are damage-tolerant and notch-insensitive. Typical CMCs are comprised of a SiC-based matrix reinforced by SiC fibers, with a moderately weak fiber/matrix interface (e.g., BN, C) that enables extensive crack bridging by the fibers and frictional pullout, imparting damage tolerance. Carbon fibers are also used to reinforce SiC matrix to result in higher-strength C/SiC CMCs (Fig. 5.41a), but their life is significantly lower, making them more suitable for hypersonic and rocket engines applications (Padture 2016). Oxide CMCs on the other hand are oxidation-resistant but have lower strength (Fig. 5.41a) and creep resistance (Fig. 5.41b), and are limited to relatively less demanding applications, such as exhaust mixers (Fig. 5.42; Epstein 2013).

CMC parts are created additively, where fiber preforms in the shape of the part are first created, typically using 2-D angle-ply lay-up of flat or woven fiber tows (Padture 2016). The interface phase is deposited onto the fibers either before or just after the creation of the preform. This is followed by the incorporation of the matrix

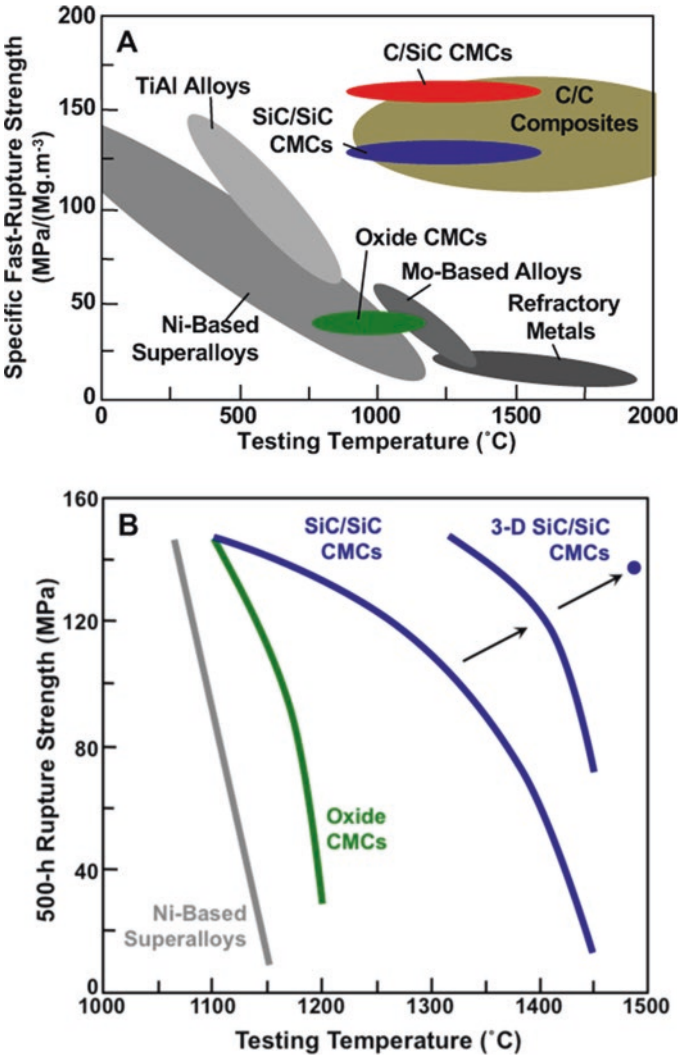

Fig. 5.41 (**a**) Specific fast-rupture strength as a function of temperature of various metals and composites. (**b**) 500-hour rupture strength as a function of temperature of Ni-based superalloys, oxide CMCs, and progressively improved SiC/SiC CMCs. The point on the right is 300-h rupture strength (Padture 2016)

phase within the empty spaces of the preform using a variety of infiltration-based methods. Typically, 2-D CMCs components are not hollow, which makes full matrix infiltration into the thick cross sections difficult, resulting in more porous interior regions. Furthermore, 2-D CMCs are invariably weaker (by an order of magnitude) along the transverse direction and are prone to "splitting" failure, which can be partially addressed by introducing fiber tows in the longitudinal direction

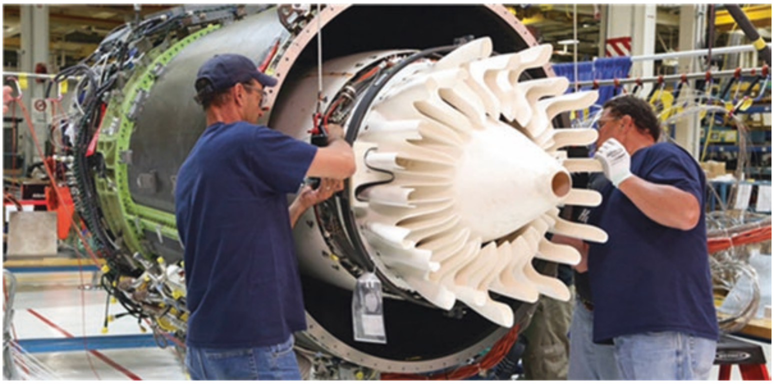

Fig. 5.42 Photograph of an oxide-oxide CMC exhaust mixer (Epstein 2013). (Figure used with permission from GE Aviation)

(Fig. 5.43a). Unlike in the case of metallic components, attachment and joining of CMC components to other engine parts are a challenge. In this context, integral ceramic textile structures (ICTSs)—the result of collaboration between disparate fields of textiles, mathematics, ceramics, and mechanics—is a new paradigm in CMCs that holds great promise in addressing all these issues, not only in gas turbine engines but also in hypersonic and rocket engines (Fig. 5.43b–d; Padture 2016).

Thermal/Environmental Barrier Coatings

The popular SiC-based CMCs are subject to active oxidation and recession in the water vapor-containing high-velocity hot gas stream, which have been attributed to the formation and volatilization of Si-O-H species. Thus, SiC-based CMCs need to be protected by thermal/environmental barrier coatings (T/EBCs). Initially, EBCs were developed for solid CMCs (uncooled) operated at relatively lower temperatures, and unlike TBCs, they were designed to be impervious (dense, crack-free) and have a good coefficient of thermal expansion (CTE) match with the CMC (Padture 2016). However, with the advent of hollow CMCs (possibly internally cooled) for use at much higher temperatures (>1600 °C surface and >1700 °C gas inlet temperatures), new T/EBC concepts and materials are being explored and tested (Fig. 5.42e, f). T/EBCs are invariably multilayer, with the first layer being the bond coat. Silicon is found to be a good bond coat material, but it melts at 1414 °C. Thus, higher-melting Si-based bond coat materials are being considered; prime among them are RE-Si alloys with Hf and/or Zr additions (RE is rare earth). Typically, the second layer is the dense, low CTE EBC, where RE silicates with various additions (HfO_2, Al_2O_3) are being considered. The fourth layer (overcoat) performs the function of a TBC, which has (i) low thermal conductivity and scatters photons, (ii) high strain tolerance, and (iii) resistance to CMAS attack. A compositionally graded intermediate third layer is typically included to mitigate CTE mismatch strain (Padture 2016).

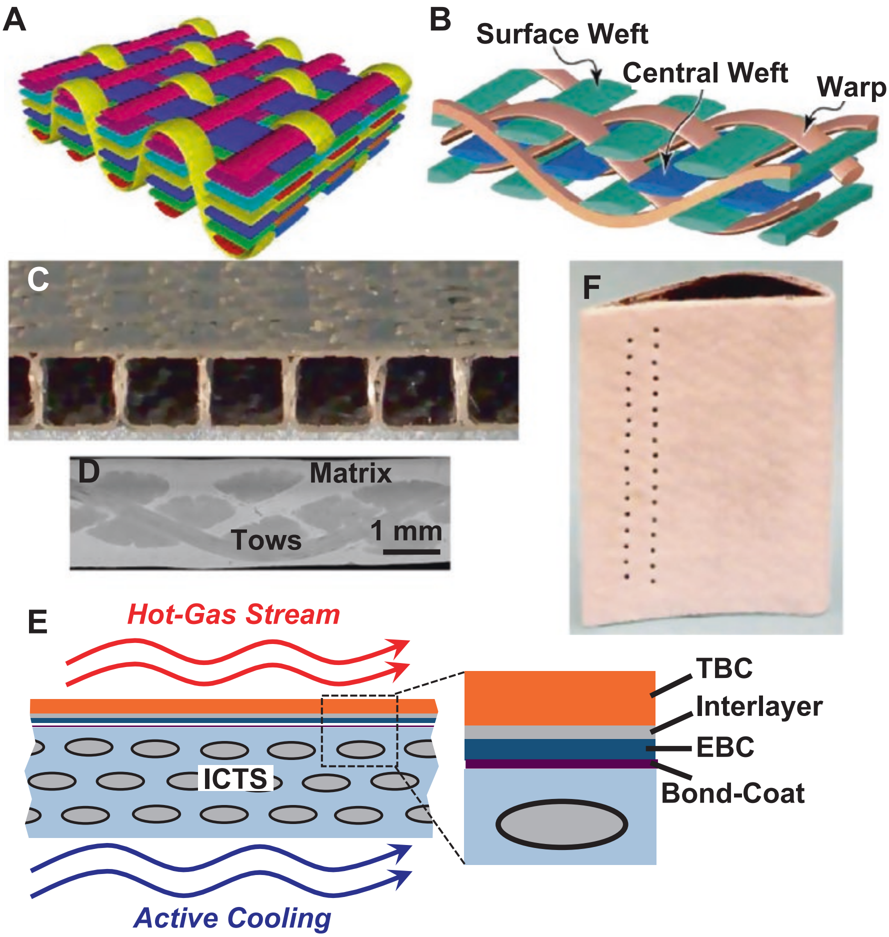

Fig. 5.43 Schematic examples of a 3-D fiber tow textile preforms: (**a**) 2-D cross-ply plate with occasional "warp" tow (yellow) and (**b**) full 3-D plate or shell. (C) Demonstration of fully dense, hollow ICTS (SiC/SiC) for actively cooled combustor wall for gas turbine or scramjet engine. (**d**) Scanning electron micrograph of the full cross section of the ICTS shell in (**c**) showing dense matrix, wefts, and a warp. (**e**) Schematic illustration of T/EBC on ICTS (not to scale). (**f**) Photograph of an EBC-coated hollow CMC vane (Padture 2016)

Closure

In this chapter, we have traced the remarkable evolution of civilian aviation over the past century from that first powered flight in a fully controllable aircraft capable of sustaining itself in the air at Kitty Hawk, North Carolina, in December 1903 to the present time when modern airplanes such as the Airbus 380 and the Boeing 787 Dreamliner transport tens of thousands of people every day across the oceans to the far corners of this earth. What involved weeks and months of travel in ships across the oceans 80 years ago has become a few hours of nonstop flights across continents and has transformed the very way in which travel is perceived globally. In the year 2016–2017, on average, there were roughly 9700 airplanes in the sky at any given time carrying about 1.25 million people; the number varies depending on the time of the year. In 1973, the number of air travel passengers worldwide was around 0.4 billion, whereas in 2005, according to the International Air Transportation Association (IATA), over two billion air journeys were undertaken. In 2017, this number just doubled to about over four billion (about ten times that in 1970). By 2036, it is projected that the number will approach eight billion annual aircraft passengers.

This remarkable transformation has been enabled by the development of new technologies (the high-bypass turbofan jet engine, the radar, etc.) which have gone hand in hand with the design and development of new materials. Specifically, looking back at the last 50–60 years, the scientific understanding and technological development and implementation of tonnage-scale manufacturing capabilities associated with aerospace aluminum alloys and nickel-based superalloys have been extremely impressive and nothing short of marvelous. Over the years, valuable lessons have been learnt that have constantly led to improvements in design and reliability. Many of the advances have been driven by consumer demands, government regulations, the global economy, and the allure of profits achievable through increased efficiency in the massive air travel industry. Basic demands of lightweight materials for fuel-efficient aircrafts have progressively been complemented with noise suppression, reduced emission, increased reliability of propulsion systems, enhanced safety, and increased passenger comfort. Long-range, nonstop flights with extended flight times overwater using twin-engine aircrafts have been enabled through innovative engine design coupled with advanced materials (combination of PMCs, lightweight high-temperature alloys, TBCs, and CMCs) and have added customer value.

Materials processing technology has evolved considerably in the past 40 years and has played a key role in the aircraft industry. The list includes the following:

i. Advances in clean melt technology
ii. Single-crystal growth of turbine blades of complex configurations with internal air-cooling passages
iii. Production of metal-polymer laminates like GLARE and ARALL
iv. Thermal barrier coatings development
v. Innovative processing of PMCs and CMCs in a precisely tailored manner including honeycomb structures that are effective in weight reduction and noise suppression
vi. Developments in advanced joining technologies including adhesive bonding and friction stir welding
vii. Advanced non-destructive evaluation and flaw detection methodologies

Newer approaches, such as additive manufacturing, are now being intensely pursued for future implementation.

Advances in computing capabilities will continue to positively impact not only the design, engineering, integration, and manufacturing aspects of the airframe and engine, but also will play a significant role upstream in materials design and process selection, and downstream in maintenance and performance prediction in aging aircrafts. For example, high-speed robots are currently being used to produce unique composites with complex curves to create what are called tow-steered composite wings that can reduce weight and reduce fuel burn. Likewise, morphing wings are on the design table—wings that can change shape to maximize performance regardless of aircraft weight, altitude, or speed. High aspect ratio wings much larger than those being used today are being examined to increase flight efficiency. These aspects will be integrated into a single cradle-to-grave process so that design and development of new materials and processes to produce components, integration into aircraft design and manufacturing and performance assessment, vehicle health (airframe and engine) monitoring, and life prediction will all become a single seamless protocol. Such multidisciplinary optimization is already coming into place, while others are being actively developed.

This chapter has primarily focused on subsonic civilian aviation powered by air-breathing high-bypass turbofan engines. However, throughout civilian aviation history, propeller-, turboprop-, and turbojet-powered aircrafts have had their fair share of participation, but these have all been replaced for the most part by turbofans. Likewise, we have not explicitly focused on cargo and military transport, although the former tracks civilian aircraft technology closely. Supersonic flights (speeds greater than the speed of sound, also called Mach 1.0) are and have been available since the second half of the twentieth century but are used primarily for military aircrafts or research, and only two, the Concorde and the Tupolev Tu-144, ever entered service for civil use as airliners. Description and discussion of airframe requirements and engine configurations in supersonic aircrafts (modification or using alternate engine types, such as low-bypass engines, afterburners, variable geometry nozzle, or ramjets or rocket engines) are different and outside the scope of this chapter. Lastly, hypersonic flights refer to speeds greater than five times the speed of sound, or Mach 5, where problems of heating and drag are acute, and there is ongoing research to examine the future potential and feasibility of civilian hypersonic flights.

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Chapter 6
The Development of Clean Steels for Steam Turbine Applications: Their Demand and Use

Clyde L. Briant

Introduction

The processing of metals has been performed for millennia. It began with the first uses of native copper and proceeded to smelting of copper ores and intentional alloying of the copper with elements such as tin and arsenic. The fundamentals of metal processing, from mining to use, were in place by approximately 4000 BC. By 1000 BC iron and steel had replaced copper for many applications. These processing technologies spread east and west from their original points of development in the Near East and southeastern Europe. Independent and similar metallurgical discoveries were also made in Mesoamerica (see Kaufman, Chap. 1, this volume; Killick and Fenn 2012).

As summarized in Table 6.1, the metallurgy of copper, iron, lead, silver, and gold were more or less established by 1000 BC (Killick and Fenn 2012). Other metals in great use today, such as aluminum and titanium, were not developed until the nineteenth century because winning them from their ores required either advanced chemical methods or electricity or both. More generally, the availability of electrical power allowed the development of large-scale processing equipment such as forges, rolling mills, and swagers that led, in turn, to processing much larger quantities of metal. In addition to these mechanical processing steps, the twentieth century saw rapid advances in new processes based on techniques such as powder metallurgy, spray deposition, and thin-film coatings.

Each of these processing topics and each type of metal have led to the production of many books, conferences, and patents. Since the motivation for these publications was often to report advancements toward the solution of an ongoing and major technical problem or need, they primarily, and often necessarily, considered only a particular technical aspect of the problem. As a result, they sometimes did not

C. L. Briant (✉)
School of Engineering, Brown University, Providence, RI, USA
e-mail: clyde_briant@brown.edu

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Table 6.1 Dates of earliest appearance of metals

Metal	Earliest appearance
Copper (native)	Late ninth millennium BC
Lead	Late sixth millennium BC
Copper (smelted)	Late sixth millennium BC
Silver (native/smelted)	Mid-sixth millennium BC/ early fourth millennium BC
Gold (native)	Fifth millennium BC
Iron	Early second millennium BC
Aluminum	Late nineteenth century AD
Titanium	Late nineteenth century AD
Manganese	Late nineteenth century AD
Vanadium	Late nineteenth century AD
Chromium	Late nineteenth century AD

From Killick and Fenn (2012)

portray the way in which various technologies interacted to solve a major problem facing an industry and how the solution was implemented. Furthermore, they often did not consider the importance of such human factors as maintenance and training in solving such problems or preventing them in the first place.

The relationship between a problem and an industrial advance that occurs through the interaction of different technologies and different groups of people who solve the problem demands more attention for several reasons. Identification of a well-defined need or technology-stopping problem focuses questions and can free up the funds to move the technology forward. Economics almost always plays a role in reaching a solution. The need can also prompt broad discussion and communication among workers in different technologies, each of which have their own cultures. These conversations, which might not ordinarily occur, lead to what I term a technology interaction sphere; that is a sphere of activity in which ideas are generated that integrate multiple technologies in order to address the problem.[1] These ideas would not evolve if the technologies stayed isolated. It is important to note that these interaction spheres are formed not just between technologists, but across the entire production and implementation chain. In particular, the interaction between managers who oversee the project and make final critical decisions and the workers carrying out the technology manufacturing can be extremely important, an idea developed in its general sense by Bijker (1995).

In this chapter I will take one problem and outline its history. I will do so in terms of how it arose and then how different technologies contributed to the solution. In doing so, I hope to provide at least a rudimentary account of how the problem was addressed and the efforts that were required on many different fronts to achieve a

[1] I borrow the term "interaction sphere" from the anthropology/archaeology literature. It was first coined by Caldwell (1964) to describe practices that were adopted by many different cultures, even though these cultures retained other practices that were specific to themselves. Thus, interactions between cultures led to wide and common adoption of some practices but not others.

solution. The problem I discuss is the disc fractures in the steam turbines used to provide electricity for the grid (Bodnar and Cappellini 1988; Curran 1986). We will enter the problem with a discussion of a particular fracture event and move on to the resulting effort to manufacture steel with low impurity content, as part of the effort to solve the problem. These impurities, such as phosphorus, tin, and sulfur, can cause the steel to be very brittle, and at least for a time, it was thought that the presence of these elements might greatly enhance stress corrosion cracking, which was seen as one of the primary mechanisms that led to the failures (Gray 1972). This effort to produce steels with low impurity concentrations attracted significant funding and research activity throughout the world in the 1970s and 1980s. Professional organizations and industry consortia played a major role in organizing these efforts. For those of us involved in this particular work, and thus part of the technology culture that formed around the investigation of embrittlement and clean steels,[2] it was often almost taken for granted that the production and use of these clean steels (i.e., steels with concentrations of these impurity elements below the level of approximately 25 parts per million in concentration) was a solution, perhaps the only solution, to this problem. But the solution to the turbine disc fracture problem, in the end, involved a number of different advances of which steel purity was only a part of the answer. Turbine redesigns to remove the locations of high stress and eliminate crevices that could exacerbate the corrosion were extremely important, as were manufacturing practices, control of the steam cycle, and control of start-up and operational procedures.

One final point should be mentioned before proceeding. As with any technological development or design advance, it is an ongoing process without a clear start and end date. For this chapter, I have begun with a specific failure in 1969 and, except for a brief look back at the history of these failures, proceed to the situation as it stood in approximately 2000, a time when significant technology development had been completed and the advancements had been recorded in the open literature. While these dates are somewhat arbitrary, they do allow us to examine the problem during a particularly active time when many people were engaged with it.

The Problem

We begin this section with a description of the failure of the low-pressure steam turbine at the Hinkley Point power station in Great Britain (Gray 1972; Kalderon 1972). This failure was not the first of this type that had occurred; indeed, the possibility that steels used for rotors and discs could fracture in a brittle manner had

[2] There have been many terms for steels with low impurities. These include clean steels, ultra-clean steels, high-purity steels, ultrahigh-purity steels, etc. Some of these have had specific distinctions at a given time. For clarity, I will just use the term clean steel to denote any steel in which there has been a concerted effort to lower the impurity level. Specific compositions will be given at various points in the paper to indicate how low a concentration of these impurities was obtained.

been an ongoing concern through the 1950s and 1960s (Emmert 1956; Mochel et al. 1956; Rankin and Seguin 1956; Schabtach et al. 1956; Schaefer 1956; Thum 1956). However, the careful and complete documentation of this particular failure published in the open literature (Gray 1972; Kalderon 1972) makes it an appropriate starting point for our discussion.

On September 19, 1969, a low-pressure steam turbine underwent a catastrophic failure at the Hinkley Point nuclear power station. The turbine had been taken off the grid for standard testing. During this test, the rotor, which had a normal rotational speed of 3000 revolutions per minute (rpm), was to be taken up to a rotational speed of approximately 3600 rpm and then brought back down to the normal operational speed. This testing was referred to as an overspeed test. The explosion occurred as the rotational speed reached 3200 rpm. Although there were operators present, no fatalities or serious injuries were reported. However, the potential for much more serious consequences was obvious and demanded that the problem be addressed in an expeditious manner.

When the explosion occurred, operators reported "a loud bang, flames from the area of the l.p. [low pressure] turbine cylinders with blown lagging and cleading from the l.p. crossover pipes, followed within a few seconds by an explosion and sheets of flames from the generator" (Kalderon 1972). The rotor shaft fractured completely in five separate locations and the attached discs were blown across the machine hall. Some pieces were ejected through the roof. Figure 6.1 shows a picture of the damage, and from this picture, if one notes the individuals in it, one can begin to appreciate the physical dimensions of the turbines and the high stakes of failure.

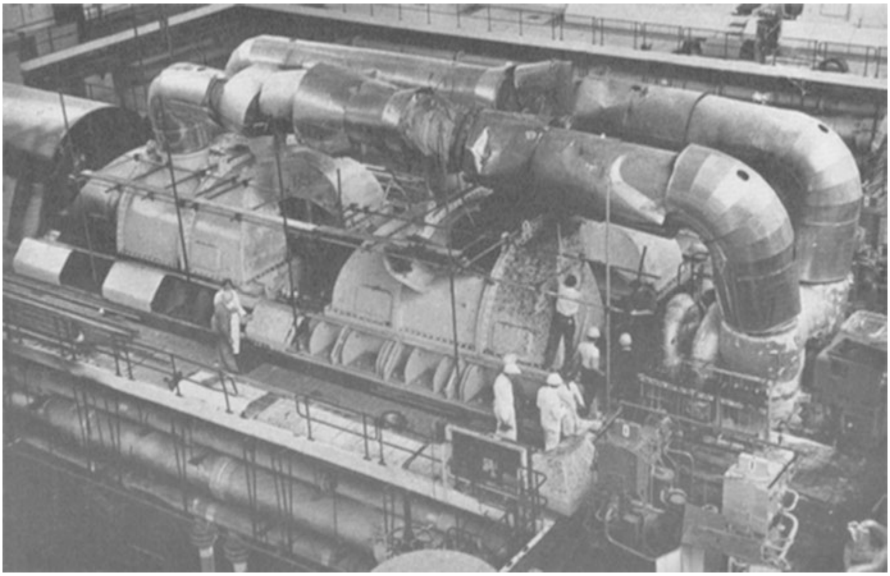

Fig. 6.1 A picture of the damage caused by the explosion at the Hinkley Point power plant. (From Kalderon (1972). Figure used with permission of SAGE Publications, Ltd.)

As a result of the explosion, a thorough forensic examination was performed. Pieces of the fractured discs were fitted back together (one disc required piecing together of 47 fragments) to try to determine the origin of the fracture. A mechanics analysis was performed on specific parts of the turbine. The temperature, pressure, and composition of the steam in the low-pressure section of the turbine were analyzed, and the steel used to make the turbine was characterized. We now consider the possible role that each of these played in the failure.

Turbine Design and the Mechanics of the Failure

Large steam turbines, of the size shown in Fig. 6.2, were developed to meet the demands for ever-increasing amounts of electrical power in the USA and Europe during the 1950s and were constructed and operated in the following way. A central shaft runs down the center of the turbine. There may be one or several of these in a series in a given turbine design. The discs are placed on this central shaft. Attached to these discs are the blades. High-pressure, high-temperature steam enters the turbine and interacts with the blades, causing the rotor to turn. The specific design of the turbine and the way in which the steam expands in the turbine, transferring its kinetic energy into rotational energy, vary with its size and power rating and the source of the steam. Attached to the end of the rotor is a generator that in its most basic form is a coil of copper wire spinning in a magnetic field. This rotation creates an electric current in the wire which flows to a transformer to provide electricity to the grid.

Steam turbines have been used to generate electricity since the early 1900s, but their size began to increase significantly after about 1940. As the demand for electricity increased, the utility systems had to grow, and this growth, in turn, demanded larger and larger steam turbines. Between 1940 and 1980, the power generation produced by power plants increased from approximately 100 MW to 1000 MW (Curran 1986). This increase in both the demand and the size of the turbine was accompanied by the use of higher-temperature and higher-pressure steam. Between 1950 and 2000, the peak temperatures rose from approximately 400 to above 600 °C, and the highest steam pressure from about 580 pounds per square inch (psi) (4 MPa) to above 4000 psi (27.5 MPa) (Masuyama 2001; Zhou and Turnbull 2003). With each of these increases in pressure and temperature, the efficiency increased by approximately a percent, a significant gain in this technology (see Masuyama 2001 for details of these increases). The steel that was used to construct these turbines had to withstand increased stresses from the larger size of the turbine and be able to maintain that strength at higher temperatures.

Steam turbines are often divided into sections that utilize different steam pressures and temperatures. The turbine that failed at Hinkley Point had both high-pressure and low-pressure steam inlets. The high-pressure steam reached a maximum temperature of 662 °F (350 °C) and a pressure of 615 psi (4.2 MPa), and the low-pressure steam had a maximum temperature of 639 °F (336 °C) and a pressure of

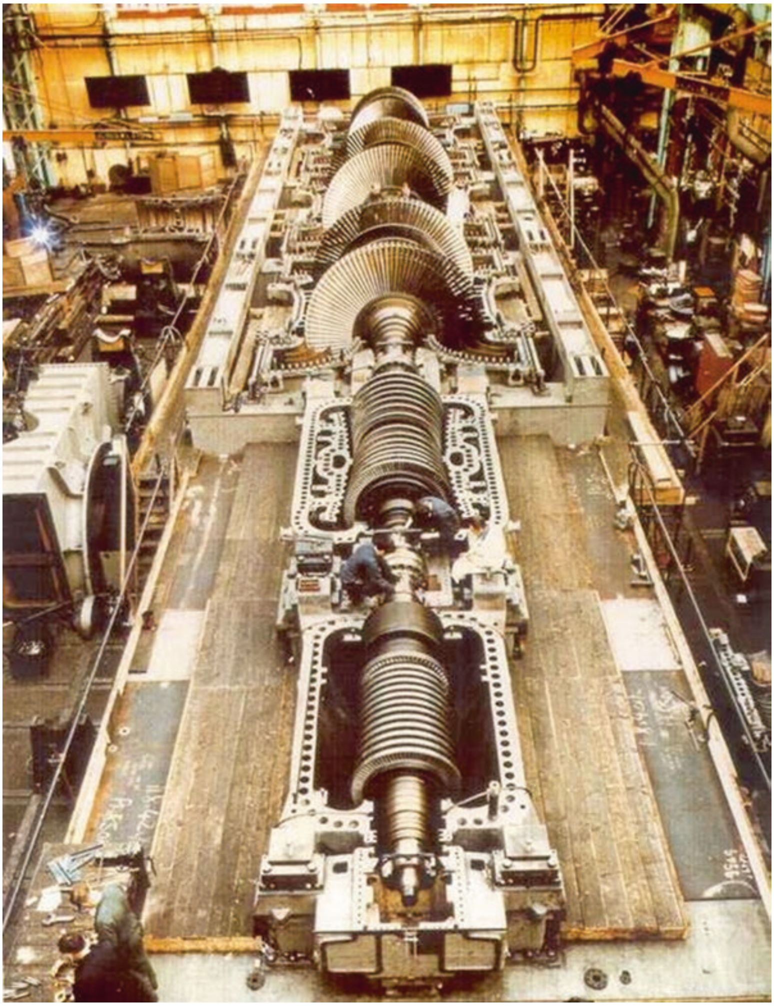

Fig. 6.2 A picture of a large steam turbine. (Picture used courtesy of and with permission of RWEnpower)

155 psi (1.1 MPa) (Kalderon 1972). The part of the turbine where the failure occurred was in the low-pressure section, where the conditions of the steam were such that it could condense to form water in certain sections of the turbine.

One of the critical manufacturing steps in assembling the turbine is the placement of the discs onto the central rotor. In the early use of steam turbines (before approximately 1940) single forgings, referred to as monoblock forgings, were often used to make the central shaft and discs (Curran 1986). However, following a demand for larger turbines, the discs and shaft were made separately, and the discs were assembled onto the central rotor shaft. The assembly design used for the

Hinkley Point turbine, as well as for many other power plants, was referred to as shrunk-on discs. The placement of the disc was achieved by heating the disc to expand the bore, sliding the disc onto the shaft, and allowing it to cool and contract to a snug fit. On the disc and the bore, there were mating slots, called keyways, into which a metal pin or key was placed to help hold the disc in place. Lyle and Burghard (1982) show schematics of different keyway designs.

As the forensic analysis of the Hinkley Point failure proceeded and ruptured discs were pieced back together, it became clear that the fracture had initiated at the keyway crown, as shown in Fig. 6.3. (A second failure also occurred in a turbine that was being tested to replace the original, damaged turbine, and this failure, too, originated in the keyway.) A mechanics analysis of the keyway showed that the tangential stresses at the crown of the keyway in the disc, resulting from the rotation of the turbine, would act to apply a force to separate the material in a line emanating from the crown into the disc. Because of the design of the keyway, the actual stress at a crack in the crown of the keyway would be approximately three times the applied stress that would be present if no crack were present at that point. Kalderon (1972), in his report on the investigation, notes "A small crack at the apex of the keyway could be catastrophic while in the absence of such a crack the presence of a keyway would be of no consequence even in a material of low fracture toughness. Conversely, the presence of a keyway in circumstances where cracking is also encountered could be catastrophic, while in [the keyway's] absence much deeper cracking of disc bores could be tolerated." As will be discussed below, changing the rotor design to eliminate the keyways was one of the most important steps in solving this problem.

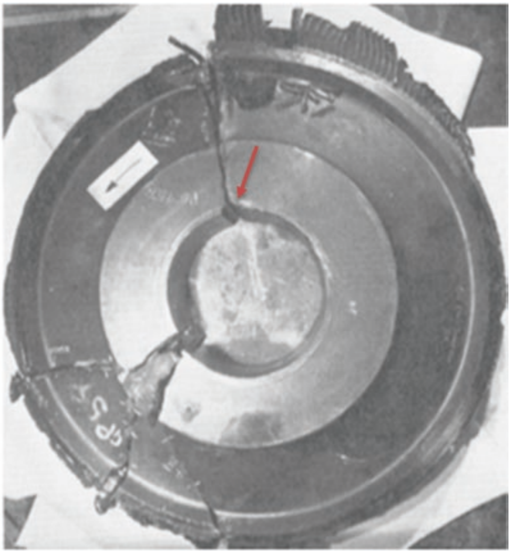

Fig. 6.3 A fractured disc that has been pieced back together after the Hinkley Point failure. Note the keyway in the upper portion of the inner annulus at approximately 11:30 denoted by the red arrow. (From Kalderon (1972). Figure used with permission of SAGE Publications, Ltd.)

The Steam Cycle and Stress Corrosion

Steam turbines operate by steam at elevated temperatures and pressures interacting with the rotor blades to cause the rotation of the turbine. The steam decreases in temperature and pressure as it expands in the turbine, and it can reach the point where water condenses on the cooler surfaces of the turbine. This point is referred to as the saturation point for the steam. The exact temperature and pressure will depend on the design and operation of the turbine, but condensation would probably occur most easily in occluded regions such as the keyway interface. The importance of understanding this condensation resulted from examination of the fracture surfaces of the discs and the location in the turbine of the specific discs that cracked. Cracking occurred on discs in regions where the low-pressure steam and the metal discs were at a temperature where condensation could occur. The investigation also showed that the part of the fracture surface nearest the keyway was discolored, which indicated that corrosion had occurred. This corrosion must have resulted from the presence of an aqueous solution (Gray 1972, Kalderon 1972). In some areas there were deposits left by the corrosive environment which also led to a concern about possible contaminants in the steam.

Figure 6.4 shows the estimated steam temperature and the disc temperature for the low-pressure turbine where the fracture occurred (Gray 1972). The steam at this point in the cycle was very near its saturation temperature. Contact with any surface below this temperature could cause condensation. The graphic shows that the metal temperature was bordering on this condensation temperature, and may have in some cases gone below it, which would then allow the steam to condense on this cooler surface. It is also important to note that at disc number 4, the metal temperature increased significantly as a result of heating from the high-temperature gland steam and no cracks were ever observed in this disc. Along with mechanical stress, corrosion resulting from the steam condensation appeared to be a central factor in causing the disc fractures.

The Steel

The third part of the analysis was an investigation of the steels used for the discs. For the low-pressure turbine discs, the steel had a composition of 3 wt% (from now on %) chromium, 0.5% molybdenum, 0.3–0.4% carbon, 0.2–0.3% silicon, and approximately 0.7–0.8% manganese.[3] This composition would be typical for a steel required to have a moderately high strength and high toughness, the latter a parameter that would describe its resistance to cracking. It was also a composition that was used for discs in power plants throughout the world (Bodnar and Cappellini 1988; Curran 1986). The steels employed in this particular application had been

[3] All compositions in this paper are in weight percent.

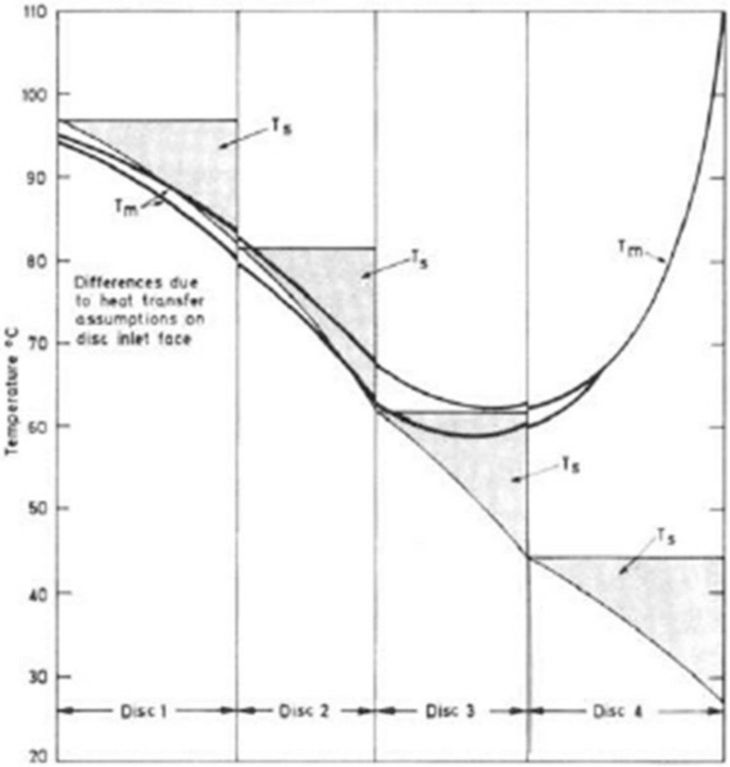

Fig. 6.4 The temperature of the metal, T_m (drawn lines), and the range of steam saturation temperature T_s (the gray triangles) at different discs in the low-pressure turbine. Note that at disc 4, the temperature of metal increases significantly. (From Hodge and Mogford (1979). Figure used with permission of SAGE Publications, Ltd.)

made by two different casting processes. One of these was acid open-hearth casting, and the other was basic electric arc casting. A primary difference between the steels produced by these two manufacturing processes was the impurity content. The acid open-hearth steels contained 0.025–0.034% sulfur and 0.025–0.032% phosphorus. In contrast, the basic electric arc heats contained 0.003–0.015% sulfur and 0.012–0.024% phosphorus (Kalderon 1972). The higher impurity content of the acid open-hearth method resulted from the fact that the slag in this melting process had a lower tendency to float and thus could be entrained in the solidified steel. It was also difficult to perform the refining processes that would be needed to remove elements such as sulfur and phosphorus with this type of process. Better refining could take place in the basic electric arc furnace, and during the 1940s and 1950s, there was a general switch to electric furnaces over the open hearths because of the significantly decreasing costs of electricity (Curran 1986).

It is also important to pay special attention to the heat treatments that had been applied to these forged discs. They had been held at a temperature of 900–930 °C for several hours after forming and then oil quenched to 300 °C. After that heat treatment, they were tempered at 600–650 °C and then slowly cooled at an initial rate where the temperature decreased at 60° per hour, and then at a still slower rate at temperatures below 500 °C (Kalderon 1972). The cooling rate was kept low to avoid the buildup of residual stresses (Bodnar and Cappellini 1988; Curran 1986).

Before continuing to analyze the role of the steel in this failure, two features common to many steels, including those used for discs in steam turbines, need to be described. The first is the ductile-to-brittle transition, and the second is the problem of temper embrittlement.

One of the properties of steels such as those used in these applications is that they undergo a transition from very brittle, low-energy fracture to very ductile, high-energy fracture as the temperature of their environment increases. At extremely low temperatures, a piece of steel that is notched can fracture in a brittle mode more like what one would expect for a ceramic. The temperature at which this type of failure will occur is usually well below even extremely cold outdoor temperatures. As the temperature is raised, the energy absorbed on fracture increases significantly, usually over a range of approximately 50 centigrade degrees. Over this temperature range, the fracture mode changes from a completely brittle to a completely ductile failure mode; a mixture of brittle and ductile fracture is observed within this range. Since this transition in fracture mode from brittle to ductile usually occurs at very low temperatures, an engineer can expect that at room temperature most steels will fail in a ductile manner with high absorption of energy.

The ductile-to-brittle transition temperature of a steel can be increased to well above room temperature if the steel contains sufficient concentrations of impurity elements such as phosphorus and sulfur and undergoes a heat treatment that allows these elements to segregate to the grain boundaries. It was known for many years that this increase in the ductile-to-brittle transition temperature, known as temper embrittlement, occurred if a steel was slowly cooled from a tempering treatment between 600 and 700 °C, but that this embrittlement could be avoided if the steel was rapidly quenched from the temper. For embrittled steels the transition temperature from brittle to ductile fracture can occur well above room temperature, with some transition temperatures measured above 200 °C. The fracture path in the embrittled steel becomes intergranular, as opposed to the transgranular brittle fracture normally observed (Briant and Banerji 1978).

The ductile-to-brittle transition temperatures for the steel samples taken from the fractured discs at Hinkley Point were measured as part of the investigation. The results showed that the transition temperatures for the acid open-hearth materials ranged between 104 and 200 °C and those for the basic electric arc steels were between 14 and 81 °C (Kalderon 1972). The brittle fracture mode in these tests was intergranular, as were the fractures that occurred in the actual disc failures (Fig. 6.5). Three important points should be noted. The first is that the transition temperatures were at or above room temperature in steels manufactured by both processes, and in

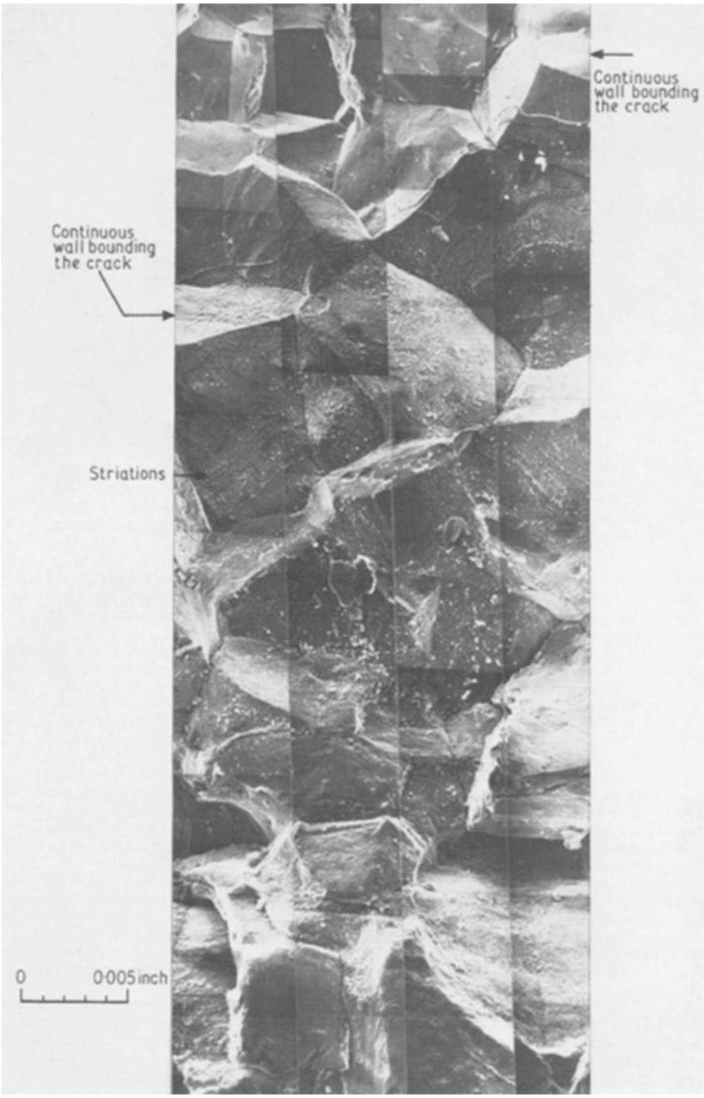

Fig. 6.5 The intergranular cracking that occurred in the Hinkley Point failure. (From Kalderon (1972). Figure used with permission of SAGE Publications, Ltd.)

some steels, they were above the operating temperature of the turbine, estimated to be between 57 and 90 °C in the turbine stages where the fractures occurred (Kalderon 1972). Thus, a brittle material was being used in service. The second point to note is that the higher transition temperatures in the acid open-hearth steels correlated with the higher impurity content in these steels. Third, the slow cool from 600 °C would allow the impurities present in the steel to segregate to the grain boundaries and cause temper embrittlement.

Other Reports of Failures and Consequences

Before proceeding with the discussion of changes in steelmaking and further analysis of the steam environment and the design of the turbine, it is important to realize that there were a number of other publications both before and around the time of the Hinkley Point event that catalogued and described similar failures (Emmert 1956; Mochel et al. 1956; Rankin and Seguin 1956; Schabtach et al. 1956; Schaefer 1956; Thum 1956). Summaries have also been given in later years of the cracking observed in discs and other parts of the steam turbine (Hodge and Mogford 1979; Lyle and Burghard 1982).

In the February, 1956, issue of *Metal Progress*, E. E. Thum (1956) summarized a daylong meeting of the American Society of Mechanical Engineers. His opening line states, "A half-century of almost perfect performance of large electrical machinery has been broken by four failures of massive rotor forgings since early 1953." His article goes on to describe these failures and how they had been interpreted. A brief summary of each of them is as follows:

- In January 1953, a 125,000-kW steam turbine with a speed of 1800 rpm failed at the Tanners Creek Station of the Indiana and Michigan Electric Co. It began vibrating, and half of the rim of one of the turbine wheels (discs) was broken away. This 1.02 Cr-1.13 Mo-0.27 V-0.36 C steel was tested and found to have only 1–2% elongation at 1000 °F (538 °C), whereas 2–10% elongation was expected. An analysis by GE, the company that built the turbine, suggested that steel quality could have played a role but also suggested that residual stresses from the heat treatment, added to the expected centrifugal and thermal stresses due to a sudden change in steam temperature, contributed to the failure (Rankin and Seguin 1956).
- On March 4, 1954, a completely finished generator intended for Arizona Public Service Co. burst into a large number of fragments while being tested at the manufacturers. This 2.5 Ni-0.55 Mo-0.32 C-1 Mn-0.06 V steel had a room temperature elongation between 5 and 7% and a reduction in area of 4–6%; these values contrast with the specified minima of 13 and 22%, respectively. It was suggested that the failure resulted from preexisting cracks caused by transformation stresses and trapped hydrogen (Schabtach et al. 1956).
- On September 17, 1954, a turbine burst at the Cromby Station of Philadelphia Electric Company after a weekend shutdown. This rotor was usually run at 3600 rpm but had been tested to 3780 rpm when the failure occurred. This particular rotor, which had a composition similar to the one that had fractured at the Arizona Public Service Co., had undergone a repair during its manufacture that required threaded holes be drilled into the rotor and threaded studs inserted. The crack started at the bottom of one of these holes where the stress intensity was 7.6 times greater than the normal or designed loading. It was also noted that the material below the hole contained hard brittle material resulting from alloy segregation (Schabtach et al. 1956).

- On December 19, 1954, a failure occurred at the Ridgeland Station in Chicago at a plant operated by Commonwealth Edison. The low-pressure turbine exploded during a routine overspeed test. When analyzed, the material, which was a Ni-Cr-Mo-V steel, showed insufficient ductility and the presence of numerous small cracks that were apparently already present in the material. The investigation concluded that these preexisting cracks could not be arrested once they started to propagate. It is also interesting that engineers from Allis-Chalmers suggested that materials should be qualified with Charpy testing in addition to smooth bar tensile testing. When measured on this steel, the transition temperature was found to be above the operating temperature (Emmert 1956), as was also the case for the Arizona and Cromby rotors (Thum 1956).

While the full analysis of these failures is interesting, the commentary that Thum (1956) provides after the failure descriptions is also important. He notes, "These recent failures, together with some other incidents where cracked forgings were discovered during periodic inspection, are responsible for the very cautious way in which the electrical industry has approached the problem of bigger and faster generating equipment. Three American manufacturers of such equipment – General Electric, Westinghouse, and Allis-Chalmers, joined whole-heartedly by five steel companies – are intently studying the problem, using not only scale models but also some full-sized forgings made by various steelmaking methods including one rotor from abroad." After praising the cooperation of the various industries, he concludes, "It would have been easy, in these four instances, for the electric utilities and manufacturing industries to have voted lack of confidence in the steelmakers, and vice versa – thus getting exactly nowhere. It is to the credit of all that this situation has been avoided."

While Thum's commentary mentions design and testing, it gives most attention to possible concerns with steelmaking, the best processes for this industry to consider, and the problem of making uniform, high-quality steel for such large ingots. The issue of better steelmaking was also discussed in various ASTM symposia. In 1967, ASTM published a series of papers in a volume titled *Temper Embrittlement of Steel* (Newhouse 1967). The introduction notes that the larger scale of new steam turbines required more massive sections, produced higher stresses in the steel, and in some cases increased operating temperatures. It further stated that "temper embrittlement is assuming increasing importance as an obstacle inhibiting progress in the design of heavy components." A second volume issued in 1971 (Newhouse 1971) presented a number of additional studies and pointed to the importance of Auger electron spectroscopy, a then new technique (described below) for detecting the segregants that caused this problem. The metallurgical community was clearly focused on the problem of producing a clean steel to solve the problem of disc fractures in steam turbines.

This emphasis on steel quality arose quite naturally from the realization that the heat treatments that were applied to disc steels that contained what were then typical levels of impurities would cause temper embrittlement. For example, the slow cool from the tempering treatment reported above for the steel used at Hinkley Point would cause segregation of impurities to grain boundaries. Since the slow cool was needed to avoid buildup of residual stresses, it seemed that the most appropriate fix would be to develop steels with extremely low impurity contents, in which the harmful elements would be present in such low concentrations that their segregation would be negligible. Also, there was concern that the hundreds or thousands of hours at the operating temperatures in the range of 400 °C could cause additional segregation of these impurities, and thus, embrittlement might develop during service. Furthermore, some preliminary research by the Central Electric Research Labs in the UK suggested that the condensate in the keyway could have been caustic and that steels that were temper embrittled were more prone to undergo stress corrosion cracking in such an environment (Adams et al. 1975; Atkinson et al. 1979; Gray 1972).

Altogether there seemed to be strong evidence to suggest that prevention of disc cracking lay primarily in preventing impurity segregation which, because of the required heat treatments, meant that the impurities could not be present in the steel in the first place. We therefore begin our discussion of the follow-on research with a discussion of steelmaking practices that allowed the production of clean steels and the laboratory work that was performed to understand in more detail the segregation and consequent embrittlement.

Research on Disc Steels

We divide this section into two parts. The first part concerns advances in steelmaking, and the second the improved understanding of the causes of temper embrittlement.

Steelmaking

At the time that disc cracking was occurring in low-pressure turbines, the steel that had been used for the discs had been made by several different methods. As described above, steels made by the acid open-hearth method tended to have a higher impurity content. However, with the decreasing cost of electricity, electric arc furnaces came into greater use. This practice allowed for better control of the impurity content in the steel because the steelmaker could make use of new refining processes (Bodnar and Cappellini 1988; Curran 1986).

The impetus to make cleaner steels for a number of applications was greatly enhanced by the development and scale-up of two important new processes: vacuum treatment of the melts and ladle metallurgy. By using vacuum pouring of the ingot, levels of hydrogen, oxygen, and nitrogen could be reduced, and with the advent of carbon deoxidation, the levels of oxygen could be reduced further through the evolution of CO (Bodnar and Cappellini 1988; Cramb 1999; Curran 1986; Szekely et al. 1988). Ladle metallurgy, in which the metal is poured into a separate vessel for further treatment, allowed for the use of multiple slags that would react with specific impurities and remove them as well as the use of various stirring and injection methods that would speed up the kinetics of the reactions between the slag and the impurities (Szekely et al. 1988; Fruhan 1985). In addition, as these processes were developed, great progress was made on modeling the solidification process, so an engineer could determine regions of the ingot where compositional inhomogeneities would most likely occur (Kawaguchi et al. 1986; Szekely et al. 1988).

Viswanathan (1997) has provided an excellent summary of the improved methods of steelmaking, and with the general application of these processes, along with careful selection of scrap input material, there was a general decrease in the average concentration of impurities over time and a resultant improvement in the reported ductile-to-brittle transition temperatures. Bodnar and Cappellini (1988) reported that the average phosphorus and sulfur concentration for rotor steels decreased from between 150 and 200 ppm in 1955 to below 50 ppm in 1990, and Viswanathan (1996) reported that over roughly the same time period, the typical ductile-to-brittle transition temperatures decreased from approximately 150 °F (66 °C) to below 0 °F (−18 °C). When all of these processes are optimized, compositions such as those shown in Table 6.2 can be obtained in very large ingots. (This table will be discussed in more detail later in the chapter.)

In addition to control of slag chemistry and vacuum treatment, a number of other practical changes were made in the steel production for turbines. These included better scrap selection which meant that lower impurities were present in the initial melt before refining, removal of up to 25% of the top of the ingot and 12% of the bottom (locations where impurities might concentrate because of solidification patterns), and the use of multiple synthetic slags (Bodnar and Cappellini 1988).

Table 6.2 Compositions of three large-scale steels of extremely high purity

Element	34-ton ingot manufactured by Vereinigte Edelstahlwerke AG (Viswanathan 1996)	120-ton ingot installed at the Kawagoe plant of the Chubu Electric Company (Viswanathan 1996)	135-ton ladle from a 570-ton ingot used for a monoblock forging. Manufactured by Japan Steel Works (Ikeda et al. 1996)
C	0.27	0.25	0.2
Mn	0.02	0.02	0.022
Si	0.01	0.03	0.018
S	0.001	0.001	0.0012
Ni	3.73	3.64	3.58
Cr	1.71	1.75	1.71
Mo	0.43	0.43	0.40
V	0.1	0.13	0.10
P	0.004	0.002	0.0029
Al	0.006	<0.005	
Sn	0.005	0.003	0.003
As	0.006	0.003	0.003
Sb	0.0015	0.0012	0.001

Temper Embrittlement

While research proceeded on how to make steels with low impurity contents, work was begun at a number of turbine manufacturers, steelmakers, and universities to understand all aspects of temper embrittlement. By simply comparing the ductile-to-brittle transition temperatures between tempered steels that were either rapidly quenched after tempering or slowly cooled from the tempering treatment, one could demonstrate that high-purity steels were not embrittled when slowly cooled after tempering, whereas those that contained impurities were embrittled by this slow cool. Neither high-purity nor commercial-purity steels were embrittled when rapidly quenched from the tempering treatment. While one could rightly say that the essential information that was needed had been obtained very early in this research, that the high-purity steels were not susceptible to temper embrittlement, another development allowed one to push this type of examination much further. In 1968, Harris (1968a, b) of the General Electric Company published two papers in which he demonstrated that by detecting low-energy electrons, known as Auger electrons, that are emitted from a material that is bombarded with an electron beam, one could determine the composition of the topmost atomic layers of a solid. That is because these Auger electrons, which occur by a secondary emission process, have very low energies; if they are emitted from atoms even a few layers below the surface, they do not have enough energy to escape. If one could fracture the sample and then examine the grain boundary fracture surface of the embrittled steel, one could demonstrate that the embrittlement was caused by the concentration of these impurity elements on the grain boundaries.

The development of Auger electron spectroscopy, the term by which Harris' technique became known, required another development that also occurred during the 1960s – the development of high-vacuum technologies. If a surface is exposed to air, it rapidly becomes coated in carbon and oxygen, and a technique such as Auger electron spectroscopy will only reveal those elements, since it only probes the very top atomic layers of the surface. Thus, a clean surface must be prepared in an ultrahigh vacuum and examined without exposure to air. Given that these temper embrittled steels were extremely easy to fracture along the grain boundaries, they could easily be broken in a vacuum chamber and their uncontaminated fracture surfaces analyzed.

These types of experiments were pioneered by Professor C.J. McMahon, Jr., at the University of Pennsylvania, and many years of research in his laboratory clearly determined the basic principles of impurity segregation to grain boundaries and the resultant embrittlement along with other important metallurgical variables such as hardness, grain size, and overall composition (McMahon 1976; Mulford et al. 1976a, b; Ohtani et al. 1976a, b; Ohtani and McMahon 1975).

Of all of the elements that have been found to cause embrittlement, two stand out and require special discussion. These are sulfur and phosphorus. Sulfur has been found to be an extremely potent grain boundary embrittler in iron, but in most practical steels, this element has not played an important role. The reason is that the sulfur is almost always precipitated as a manganese sulfide in the steel matrix and is simply not available to segregate to the grain boundaries. However, removal of sulfur is still extremely important because otherwise there will be such a high density of these sulfides that they will lead to internal cracking and tearing during the processing of the steel and result in lower fracture energies. In addition, these sulfides are preferred sites for corrosive pitting, a process which appeared often to be the initiation of the corrosion crack that gave rise to fracture.

Phosphorus is a different matter. It readily segregates to grain boundaries in steels, and because of its small atomic size, it diffuses more rapidly and at lower temperatures than many of the other embrittling elements such as tin and antimony. For example, even after 100 h at 400 °C, phosphorus segregation will occur and cause significant embrittlement. Furthermore, while most of the other embrittling elements show little tendency to segregate at the high temperatures that would be encountered as the steel solidifies from the melt, phosphorus readily segregates to grain boundaries at temperatures as high as 1200 °C. Finally, there are no elements that can be added to the steel that would precipitate phosphorus in the way that manganese precipitates sulfur. While some elements such as titanium and niobium will form stable phosphides, they have a greater tendency to form carbides in the steels. The only element that appears to counteract phosphorus embrittlement in some way is molybdenum; its positive effect may come from an inherent strengthening of the boundaries rather than inhibiting phosphorus segregation.

Bringing Research and Practice Together

With the result of these studies of segregation and the clear demonstration that impurity elements increase the ductile-to-brittle transition temperature when they have segregated to the grain boundaries, the next question was whether or not steel companies could make castings of the required size that had extremely low impurity concentrations and whether or not these castings would have sufficient strength. The answer to this question came through a series of projects, many sponsored by the Electric Power Research Institute (EPRI) and performed primarily at Japanese and European steel companies. Initially small laboratory heats were made that would have the desired composition. These were then scaled up to larger heats of material.

Viswanathan (1996) summarized a number of these studies. The overall conclusion is that high-purity steels can be made as large castings and that these steels can have the required strength. Table 6.2 shows the chemistries of a series of ingots, two of which weighed over 100 tons. It is clear that phosphorus and sulfur had been kept to a very low level even in these very large castings. The high-temperature strength of these materials was also satisfactory. As an example, a 34-ton heat was prepared by Vereinigte Edelstahlwerke AG, Austria, and tested in a variety of labs as a part of the EPRI-sponsored study (Jaffee et al. 1986). After the first heat was tested, the nickel content was increased to 3.5–3.75% to increase hardenability, and the subsequent heats met all desired mechanical properties. As a result, a 3.5Ni-Cr-Mo-V rotor with extremely low impurity concentrations was installed at the Chubu Electric Company's Kawagoe Plant in Japan (Viswanathan 1996). The high purity of this steel allowed the low-pressure turbine to operate 30 centigrade degrees higher than the normal operating temperature because there was no concern for embrittlement occurring during operation. This increased temperature improved the efficiency by approximately 0.1% (Viswanathan 1997).

However, an important question was whether or not the turbine manufacturers and utilities would use this high-purity steel. EPRI carried out a survey to examine this question. The survey results reported by Nutting (1996) suggested that among the major producers of steels for electric power generation, only 5% of their capacity was devoted to steels for this application. Of this capacity, only 3.5–5% were produced to an "EPRI superclean specification." One reason for this lack of orders appeared to be cost. The steelmakers polled in the EPRI survey indicated that a premium of 15–20% would be charged in relation to conventional grades for ingot weights up to 100–150 tons, and a higher premium would be charged for ingot weights in the range of 300–600 tons. While it was clear that most of these steelmakers could make superclean steel if requested, it was also clear, as noted above, that the impurity concentration of conventional steels was decreasing to the point that it might not be necessary to demand the extreme purities proposed by EPRI, especially if input scrap was carefully chosen. Nutting (1996) concludes:

> In spite of the clear advantages of using superclean 3.5Ni-Cr-Mo-V steel for LP rotors, only a small proportion of the recently installed rotors are in the new material. It is difficult to understand why. It could be that wider usage will develop from their application to discs and it may be that as more LP rotors are used in nuclear plant[s] where stress corrosion cracking is more prevalent, the advantages of superclean steels will become more apparent. Whatever should develop, there would appear to be no great difficulty in obtaining suitable forgings, the initial cost premium is not high in relation to the finished cost and there appears to be no difficulty in fabrication. Is it the fault of the plant makers for not stressing the advantages? Or should the plant users take a more active role in specifying their needs?

Research on Design, Steam, and Repair

The fact that the turbine manufacturers did not readily choose to use the extremely high-purity steels might at first seem surprising, since it would appear that these steels would provide a major part of the protection from cracking that they needed. However, the story was more complex. While the use of high-purity steel would clearly eliminate temper embrittlement, it was not clear that the use of these steels would eliminate the stress corrosion cracking that had initiated the cracks in the first place. Conventional steels were becoming increasingly cleaner, and it was also becoming apparent that plant practice played an important role in controlling these fractures.

To discuss these other factors, we begin with the immediate steps taken by the Central Electricity Generating Board (CEGB) in the UK immediately after the Hinkley Point failure. The CEGB operated the Hinkley Point power plant, and the CEGB director of operations was charged with coordinating the examination and rehabilitation of existing turbines. These steps are described in detail by Hodge and Mogford (1979) and are summarized here.

Groups were formed to examine the design, manufacturing resources, metallurgical factors, and chemical factors that could lead to cracking. The analysis of the failures at Hinkley Point as well as examination of other rotors of similar design pointed to the keyways as the most susceptible site for cracking. This observation seemed logical based on the increased mechanical stress at the keyway and the fact that the keyway could provide a natural crevice to enhance stress corrosion cracking. Thus, engineers at CEGB could conclude that the most susceptible turbines would be low-pressure turbines with keyed and shrunk-on discs. Those would have the keyway present and have discs that operate in a portion of the steam cycle where condensation might occur. To plan for the rehabilitation program, the turbines were divided into three groups based on the likelihood that they could contain cracks. The three groups were those of the type where cracks had been observed when the rotor was dismantled, those of the type where conditions strongly inferred that cracking should be present, and those of a type where there was a strong inference that cracking should be present but there were also possible alleviating conditions such as lower stresses. As Hodge and Mogford conclude, "it was possible, therefore, even before many factors were understood, to infer that early stage discs on LP rotors of non-reheat turbines ran the greatest risk of cracking." They also very importantly noted that all of this work had to occur while electricity continued to be generated at a time when there was "little surplus capacity."

The most immediate recommendation, so that electricity could continue to be generated as the turbines were repaired, was to reduce the amount of overspeed testing (recall that the failure at Hinkley Point had occurred during an overspeed test) and also to have the trip setting for overspeed set as low as possible without giving false indications. This practice would limit the high stress excursions experienced by the discs. It was also recommended to run the turbines at the most constant conditions possible and that during a cold start, the rotors should be pre-warmed before being brought to the operating speed to be sure that the steel was above its ductile-to-brittle transition temperature and to be sure the steam did not condense in the keyway.

The next step was to discontinue the use of any discs that were found to be cracked and to replace them with pressure-reducing plates fitted to the rotor shafts. While this approach decreased the power output of the plant by 7–10 MW, it provided for safe operations. The longer-term solution was to bore the keyway out of the cracked discs and to replace the shaft with one of a larger dimeter that could accept these repaired discs. A cylindrical button-type arrangement was used to keep the discs in place and aligned on the rotor shaft. These cylindrical buttons were placed on less highly stressed areas of the discs. In addition to repairing the rotors with new oversized shafts that could accept the bored out and keyway-free discs, new rotors without keyways were ordered for complete replacement.

While this large-scale repair effort was being performed to provide an immediate solution to this problem, research also continued to understand the fundamental causes of the fractures. This research involved both careful cataloging of observations made in the dismantled turbines along with laboratory experiments to characterize the material behavior in similar conditions of stress and environment. The results of this work led to interesting and not completely expected conclusions that undoubtedly had an impact on the decisions made by turbine manufacturers and users.

The conclusions, primarily summarized by Hodge and Mogford (1979), were the following:

1. Disc cracking was related to rotor design and not steel composition. Cracking always occurred in regions of the turbine where condensation could occur.
2. Ni-Cr-Mo-V and Cr-Mo steels were of similar susceptibility to cracking based on observed cracks in dismantled rotors. Kalderon and Gray, in a discussion of Gray (1972), note that in a wet environment a 3Ni-Cr-Mo steel which had superior fracture toughness to a 3Cr-Mo steel cracked significantly, whereas the 3Cr-Mo steel with a composition similar to those that failed at Hinkley Point did not crack in a dry environment. This example and many others clearly showed that material composition and toughness were not the single root cause of the failures.
3. For one particular design of rotors, there was no difference in susceptibility between acid open-hearth and basic electric 3Cr-Mo discs, again based on observed cracks in dismantled rotors. Thus one could not say that the acid open-hearth steels, which were less pure and had a higher ductile-to-brittle transition temperature, were always more susceptible to cracking in practice. In the same type of rotor, 3Ni steels were not observed to crack.
4. Although many turbine deposits were chemically analyzed, no compositional correlations were found with disc cracking. This result was borne out in the extensive review by Zhou and Turnbull (2003).
5. While crack initiation in the lab was found to be more rapid for steels that were temper embrittled, the crack growth rate was not obviously affected by this embrittlement. However, crack initiation was not eliminated in the high-purity materials tested in the laboratory (Turnbull and Zhou 2003).
6. The dimensions of the crevice played an important role in enhancing crack growth, with larger gaps less susceptible to cracking. Lab specimens exposed to steam for 10,000 h that had a crevice with a gap of 0.05 mm or less had cracks initiated in them. Specimens that had crevices with gaps of 0.25 or 1 mm did not crack (Lyle et al. 1985).

A significant amount of this additional laboratory research was directed at determining whether or not segregated impurities that caused temper embrittlement would also raise the susceptibility to stress corrosion. As mentioned above, this work showed that while high-purity steels were much more resistant to temper embrittlement, one could not make a strong case that they were more resistant to stress corrosion cracking (Lyle et al. 1985; McMinn et al. 1985; Rosario et al. 1998), although they did appear to be more resistant to crack initiation by pitting (Holdworth et al. 1996; Turnbull and Zhou 2003). Overall, the laboratory variables that did appear to enhance stress corrosion cracking were an increase in the yield strength, aeration of water in the test environment (effectively increasing the oxygen concentration), and the presence of a crevice such as would occur in a keyway (Hodge and Mogford 1979).

These results also corresponded well with examination of cracked discs taken out of service. Cracking occurred when a liquid phase could exist, that is at a point when the steam could condense, and the occurrence of cracking could not be correlated with other impurities found in and around the crack. Stress also was found to be a critical factor. Lyle et al. (1985) reported that 31 of 44 rotors with 112-cm last-stage blades developed disc cracks, while 3 of 15 rotors with 102-cm last-stage blades developed cracks. The latter had stress levels at the bore that were 70–80% of those in the large rotor. Lyle and Burghard (1982) also found in their survey of US nuclear plants that the design of the keyway was important. Hemispherical keyways which had a very tight tolerance were prone to initiate cracking. Rectangular keyways which had a larger gap between the raised portion on the shaft and the mating surface on the disc did not crack.

But equally important was the effect of plant practice. Evidence collected on US plants indicates that crack depth increased with the number of plant start-ups and with the occurrence of condenser leakages leading to air in the system (Lyle and Burghard 1982). Hodge and Mogford (1979) also noted that plant operation could be important, since cracks were observed in some discs and not in others that were of the same design. Also, it is interesting to note that in their recommendations, Lyle et al. (1985) emphasized plant operations as critical. Thus, we have a situation where the material, regardless of temper embrittlement and impurity segregation, can be susceptible to cracking in condensed steam, independent of whether the steam is pure or contaminated in some way. The exact crack growth rates can vary, but cracking does appear to occur (McMinn et al. 1985; Turnbull and Zhou 2003).

All of these results point to the importance of lowering stresses and removing tight crevices. With high stress and the presence of crevices, any of these steels, independent of purity level, could crack. Thus, it is not surprising that the elimination of the keyways which removed tight crevices and also removed an area of stress intensification apparently solved this problem for the CEGB (Lyle and Burghard 1982), and that other methods that eliminated the keyways, such as the use of monoblock forgings in which the discs and rotor were forged from a common piece of material, were adopted by other companies (Ikeda et al. 1996; see discussion by Mitchell (1972) to Kalderon and Gray 1972). It is then not surprising that companies were not as interested in the extremely high-purity steels and opted to put less restrictive values on impurity content in the alloy through scrap selection and other methods rather than pay a premium for the clean steels. The importance of temper embrittlement would be to affect the crack length that would lead to unstable rapid fracture. If the stress was lowered and the possibility of crevice corrosion removed through the elimination of keyways and impurities controlled to a reasonable level through scrap selection, the risk of cracking should be greatly reduced. Hodge and Mogford (1979) conclude:

> The materials engineer must recognize that the steel in current world-wide use (3½NiCrMoV) is susceptible to stress corrosion in pure steam and if cracks form they may grow at a significant rate. It would be possible to tolerate such a situation if the critical crack size for fast fracture were much larger than the maximum amount of crack growth. The completely safe situation demands a guarantee that cracks could never initiate but in reality it may be necessary to accept the possibility of cracking at a known rate and assume the steel is sufficiently tough or the stress sufficiently low to tolerate the crack.

Technology Interaction Spheres

We now wish to consider this problem in terms of the bigger picture of technology cultures and interaction spheres. Our idea is that around each of the technologies that contributed to the solution of this problem, there are distinct cultures based on training, ideas, and experience but that the larger integrated solution occurs when these cultures interact. These interactions give rise to a new set of ideas that would not have occurred without bringing the technologies together.

Most of what is written on this topic has been about major technology breakthroughs. One can site Bijker's study (1995) of the bicycle, bakelite, and incandescent bulb. Each of these had a variety of inventors, and each is built on a number of scientific breakthroughs. And each could be identified with a specific material or object that defined the interaction point between technology and society. But the discussion of this problem is different. Since the primary purpose of large steam turbines was to generate electricity, one could argue that society was essentially blind to these underlying developmental advances, since electricity was generally available and the only real impact to society might come through the cost of electricity. The availability of electricity had an enormous positive impact, but when the work reported on here was being performed, electricity was available to almost everyone. Yet, these great advances were being made in various technologies related to steam turbines, and for many individuals working on these advances provided fulfilling careers and salaries for their livelihood. The difference here is that in considering the interaction spheres that gave rise to these advances, one must focus not just on an object (the steam turbine) but on the practice and organization, or development, of technology to solve a problem so that the industry can continue to grow and satisfy the needs of the society that consumes, and in this case relies on, the product. The general concern of these types of industry-limiting problems has been discussed by Hughes (1983) for the power generation industry. He termed these types of problems as reverse salients, a term he borrowed from military history.

In thinking about the problem, it is useful to draw on studies of innovation diffusion and in particular on the studies of innovation in organizations, since these advances in turbine technology were occurring in the context of very large organizations. Schroeder et al. (2000) have outlined a number of observations that they note are common points in terms of innovations made by organizations. While several of these are not directly applicable to our discussion, there are some that are clearly relevant. We briefly discuss these here.

The first observation listed by Schroeder is that the innovation is stimulated by a shock, either internal or external to the organization. Clearly the failure of these large steam turbines provided this shock. While we have described one particular failure here, namely, the one at Hinkley Point, the entire power generation industry was concerned with these failures (Lyle and Burghard 1982). From the fiscal standpoint, the possibility of severe electrical outages and the cost of the turbine were two main reasons for concern. In 1982 it was estimated that replacement of an entire turbine would cost \$2–6 million and that the cost to buy replacement electricity for a 1000 MW nuclear plant would run \$0.5–1 million per day (Lyle and Burghard 1982). Furthermore, the potential for worker injury in explosions caused by their failure could expose the companies to liability.

Another of Schroder's observation was that as innovation develops, the old and the new exist concurrently, and over time they are linked together. Unlike a recall of a particular product, large steam turbines could not be completely shut down and replaced but had to be slowly replaced over time. New plants could be configured with new technologies, but the older plants still had to be used. As shown in the report by Hodge and Mogford (1979), it was possible to stage these repairs, beginning with the most suspect rotors, and gradually replace all that were of concern. Over time, engineers recognized what actually needed to be changed and what could remain unchanged.

A third observation is that an initial idea tends to proliferate into several ideas during the innovation process. One can draw a parallel here to the various types of investigations that took place in response to these failures. These included mechanical analysis, steam cycle analysis, corrosion tests, development of clean steel, and new designs of rotors that eliminated the keyway. Around each of these, there is a technology culture of interacting people, but as these groups begin to interact with each other, to provide new ideas to each other, the final solutions were reached that were accepted by multiple organizations.

It is clear that for these interactions to occur there have to be mechanisms to facilitate them. Some of these would come strictly through market forces, the lines of purchasing and the requirements placed by the buyer of the technology or object on the seller. But those types of interactions do not necessarily lead to the idea exchange and debate that are so crucial to solutions of problems of this magnitude. In this particular case, it is clear that the ASME, ASTM, and EPRI helped organize cooperative programs where these ideas could be shared and discussed. The importance of these organizations in using their convening power, and in some cases their funding power, to encourage this integration must be emphasized. An industry approved forum in which ideas can be exchanged is critical for advancement. Viswanathan (1997), who led many of these efforts for EPRI, notes, "It was generally agreed [from the EPRI survey described above] that the need for clean/superclean steels *must be placed in the context of design and operational requirements*. It is not our objective to make steels as clean as they can get but as clean as we need them" (italics added). Knowing how clean a steel is needed must come through interactions of people who bring all possible contributing solutions to the table, along with operational experience, and then decide how to integrate them in practice.

Let us pursue these ideas further. As one pathway to the solution of the problem discussed here, there was an effort to manufacture high-purity steels. The technology was developed to meet this goal. The development required interaction between steel producers and their suppliers, and the turbine manufacturers who might incorporate this material into their design. But after testing and proof-of-concept trials had been completed, a decision had to be made as to whether or not this new product would be used. In this case, the result of investigations of the mechanics of the turbine design and the stress corrosion of steels in high-purity steam indicated that steels of *extremely* high purity, which had been the aim of these technology developments, were not required. By placing reasonable, not stringent, requirements on the impurity levels in the steel, one could avoid a brittle material at the turbine operating temperatures, and by elimination of the keyways, high stresses that would lead to fracture would be reduced along with the sites where crevice corrosion began.

It is important to emphasize the point that as a result of this synthesis of ideas, which results from what I term a technology interaction sphere, decisions are made based on the information that is part of this sphere. These decisions determine the direction that a particular technology will take. This outcome points to the fact that those making the decision must have full knowledge of all of the technologies that are coming together. Furthermore, this knowledge must include contributions from all levels in the various contributing organizations. The inputs from the workers tasked with making the product or its parts are as critical as the sophisticated engineering evaluation or the detailed financial considerations. All are important. Establishing an interaction sphere where all of these factors come together is a critical challenge for the decision-makers.

This situation leads to another question and that is one of retention of the knowledge that is developed, particularly the valuable knowledge that has been generated but may not be incorporated into the solution. As part of the practices developed to solve this problem, significant research was performed that elucidated many aspects of the properties of clean steel. The utilities and the turbine manufacturers chose, on the whole, not to use the steels of the very highest purity. Rather they took advantage of the general improvements made in steelmaking that led to production of conventional steels of adequate purity. The question, then, is whether or not all of this knowledge will be retained in some form. There is a vast amount of knowledge developed around making extremely high-purity steels, steel embrittlement, and impurity segregation that appears to be no longer under active discussion. It is important that it be maintained and archived in a readily accessible way.

Finally, it should be noted that when we look back on a problem such as the turbine failures discussed here, it is all too easy to make it sound like everything happened in sequence and that it occurred in a very thoughtful progression. That is undoubtedly not the case. In any problem there are ups and downs, economic and technical competition, pet solutions of different groups, proprietary solutions and applications, and dead ends. However, there is value to looking at the summary of it all and understanding the great importance of shared ideas and the importance of different technologies coming together in interaction spheres to create new solutions and consensus. When Caldwell (1964) first introduced the idea of interaction spheres, his comment was that it was the way civilizations move forward. While turbine cracking is not as grand as a civilization, it is important to note that these interactions are the way technologies move forward.

Conclusions

This paper has traced a central part of the history of catastrophic failures in large steam turbines and the resulting industry solutions to this problem. Particular focus is given to the role that the material of construction, low-alloy steel, played in this problem and the efforts of the steelmaking industry to develop materials that would prevent the problem. Enormous improvements were made in the making of these steels so that they were immune to temper embrittlement, and clear demonstrations were given that these special steels could be made on a scale that was needed for these large turbines. However, the brittle steels were not the entire cause of the problem. Condensed steam, crevices, and mechanical design were also crucial components. The final solution involved dealing with all aspects of the problem. As it turned out, improvements to conventional steels which resulted from this overall effort were sufficient for this application. It is proposed that we can think of these integrated solutions as resulting from technology interaction spheres. The ideas from certain groups come together and lead to new ideas that would not have been possible without the stimulation of thinking from other groups. It is these combining technologies that lead to the big next steps in engineering and design.

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