

# Metal and Materials Engineering: Historical Prospect



**Raunak Pandey, Nannan Wang, Bibhuti B. Sahu, Srikanta Moharana,  
and Santosh K. Tiwari**

**Abstract** Materials are the backbone of our society and have become a functional part of the engineering process for the formation and modifications of technologies that have intrigued humankind. It is impossible to think about the next generation of technologies without discovering new materials. However, for the investigation of new materials, knowledge of the historical prospects of materials is very crucial. This chapter is dealing with the historical prospects of different kinds of materials, including ceramics, glasses, metals, non-metals, alloys, plastics, composites, and nanomaterials. The chapter deals with the different ages of material development, including stone, metal, copper, bronze, iron, and modern ages. Furthermore, the material engineering task at hand required the selection or development of a unique material, which in turn allowed for novel approaches to designing the final product. The materials way of thinking requires a system perspective or the abandonment of the linear concept of innovation.

**Keywords** Historical prospective · Materials · Engineering nanomaterials · Composites · Polymers

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R. Pandey

Department of Chemical Science and Engineering, Kathmandu University, Dhulikhel, Kavre, Nepal

N. Wang

Key Laboratory of New Processing Technology for Nonferrous Metals and Materials, Guangxi Institute Fullerene Technology (GIFT), Ministry of Education, School of Resources, Environment and Materials, Guangxi University, Nanning 530004, China

B. B. Sahu (✉)

Department of Physics, Veer Surendra Sai University of Technology, Burla, Odisha, India  
e-mail: [bibhubhusan78@gmail.com](mailto:bibhubhusan78@gmail.com)

S. Moharana

School of Applied Sciences, Department of Chemistry, Centurion University of Technology and Management, Burla, Odisha, India

S. K. Tiwari

Department of Chemistry, NMAM Institute of Technology, Nitte (Deemed to Be University), Karnataka 574 110, India

# 1 Introduction

Our universe is made up of different kinds of materials, and the entire phenomenon that is happening in this universe has somewhat of a connection with the type and properties of materials. Since the prehistoric era, our ancestors have made progress and developed their lives through the utilization of various kinds of materials. They were using different kinds of materials as survival tools in terms of foods, habitats, protection, and migration from one place to another [1, 2]. The real progress in the use of materials by our ancestors from 2.6 million years ago to the present has been accounted for in Table 1, along with the important milestones achieved in the particular time period [1–4]. Indeed, with time, the use of materials by mankind has changed as per their requirements, especially, for the improvement of life quality and sustainability. Similarly, with time, the scalability of the use of different kinds of materials has also changed. For example, over the last 50 years, silicon (liquid silicone, fluorinated silicone, high-consistency silicon rubber, silicon foam, and silicon emulsions) and carbon (such as carbon black, graphite, carbon felt, carbon sheets, carbon foam, carbon paper, carbon tapes, carbon cloth, carbon brushes, carbon resins, fullerenes, carbon nanotubes, carbon nanoplates, carbon nanopowder, and carbon nanopowder) have been widely used in different industries dealing with computers, automobiles, electronics, clothing, waterproof devices and textiles, construction, health care, etc.

Similarly, during the last two centuries, different kinds of metallic and non-metallic materials like aluminum, iron, copper, zinc, gold, ceramics, polymers, and their derivatives (metal alloys, hybrid material composites, and blend composites) have been innovated as per the requirements of engineering and industries [1, 2, 4]. These materials have drastically changed in terms of properties and applications due to the advanced cerebral features of human civilization and the highly advanced lifestyle of human beings. For example, just a hundred years ago, it was impossible to replace the bones in our body with any artificial material owing to adoptability, toxicity, and durability issues. However, at present, due to the rapid progress in materials processing, we have different kinds of excellent artificial materials that can be easily used as an alternative for the bones. Thus, materials have endured drastic measures to develop and modify them for exceptional uses in human civilization, and we have tried to provide an overview of how these materials were developed to this stage from the earliest known age of the Stone Age [1, 2]. The study of the link between the processing of materials, their structure, their qualities, and their performance is what material science is all about, which is given a concise idea by the schematic as shown in Fig. 1.

In Western Europe, the Iron Age started around 3000 B.C. and is still going strong now. Iron and steel, being both stronger and more cost effective, had a profound impact on people's day-to-day lives [1, 2]. In the modern materials age and throughout the Iron Age, several novel materials (ceramic, semiconductors, polymers, composites, etc.) have been developed and offered to the market. In order to become familiar with the interconnections between the structure of the material and its processing and performance, a synthesis of advanced materials with intelligence has been done.

**Table 1** Important developments and achievements that human civilization has achieved in terms of material processing from the Stone Age to the Advanced Ages [1–3]

S. no	Ages	Key development and notable achievements
1	Stone age (2.6 M years ago)	(a) Wood, bone, fibers, feathers, and animal skins were used as materials for building weapons, ornaments, shelters, utensils, etc (b) Earlier, they were handheld, but in later years, the stone flakes were attached to wooden handles (c) The Egyptians used to make pottery, and glazed minerals were also used to decorate it
2	Copper–Stone age (3000 BCE–1000)	(a) Carving or hammering copper led to the start of the copper age (b) After the discovery of its manufacturing, copper and stones became inseparable parts of the copper age (c) Copper smelting was considered to be borrowed from pottery manufacturing (d) Copper utensils, weapons, and ornaments were found in the Egyptian graves. The use of copper in various activities in China through the epics of Shu Chiang was also found (e) Weapons such as a copper axe with wooden handles were utilized (f) Egyptians also manufactured glasses and glazes for utensils and decorations (g) The glassblowers did not figure out how to pick a specific color until they had worked with a lot of different ones. Oxides of manganese, copper, cobalt, iron, tin, antimony, and lead were used as pigments. The opacifiers, which were admixtures used to make glass opaque, were composed of $Cu_2O$ and $Sb_2O_3$ , along with $CaO$ , $PbO$ , and $SnO_2$
3	Bronze age (3300 to 1200 B.C)	(a) When human beings discovered the ways to craft bronze by adding tin and arsenic to copper, this led to the start of the Bronze Age (b) At first, the alloy of copper and arsenic was fabricated, but arsenic was later substituted by tin to form bronze (c) Thought to have originated in the Middle East or the Mediterranean region, bronze was also found in Thailand, India, and China during these times (d) Bronze was utilized in crafting weapons, utensils, bracelets, ornaments, two-tone bells, human and animal figurines, etc (e) The Chinese were masters of producing bronze tools and equipment, as no traces of hammering for the fabrication of the appliances were found. Also, beautiful figures were carved in the appliances (f) The Uneticians were skilled bronzesmiths who crafted safety pins, tools, weapons, and jewelry that they traded with the Middle East and Western Europe (g) The Indus Valley Civilization mastered the use of bronze in the creation of human-like objects such as figurines, vases, arrowheads, spearpoints, knives, and axes (h) The use of gold, fur, amber, glass beads, bracelets, and necklaces in application as well as currency was also found

(continued)

**Table 1** (continued)

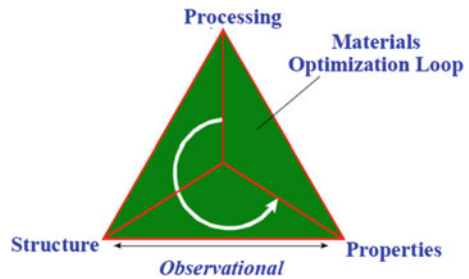
S. no	Ages	Key development and notable achievements
4	Iron age (600–1200 B.C)	<p>(a) The discovery of meteoritic iron and its use in tools shaped the formation of the Iron Age</p> <p>(b) Pure iron was achieved by hammering the slag when copper was smelted from malachite in the presence of iron oxide. Today, this type of iron is known as wrought iron</p> <p>(c) The discovery of steel was also made when iron was heated with charcoal, which led to the combination of iron and carbon, forming steel. Romans, Hittites, and some ancient Greek texts from the first millennium B.C. suggest different procedures for the formation and improvement of carbonized iron or steel</p> <p>(d) Chinese people improved the steel by removing excess carbon from iron, allowing the fabrication of a metal jacket</p> <p>(e) The mass production of steel and iron materials by the Chinese people was done through casting; however, the Western people relied on shaping and carbonizing their goods individually by hammering</p> <p>(f) Structures, monuments, utensils, wootz steel, weapons, ships, helmets, glass cups, glass windows, glass flowers, fruits, etc., were built using iron materials</p> <p>(g) Iron production, copper-based alloy manufacturing, lead, and silver manufacturing were enhanced during these times</p> <p>(h) Steel manufacturing through the casting process and puddling process yielded appliances such as plowshares, hoes, cart bearings, and harness buckles used in agriculture in China, while the Western people formed weaponry, utensils, and other utilities from steel using the hammering process of wrought iron in the presence of carbon to form steel</p>
5	Medieval age (500 to 1400 CE)	<p>(a) The beginning of steel manufacturing was done in the Iron Age, but this got more attention in the medieval age</p> <p>(b) Manufacturing of swords and weaponry, utensils, megastructures, ships, other transport vehicles, etc., through brass, steel, iron, copper-based alloys, etc., was conducted</p> <p>(c) Production of transparent glasses in most of Europe and smalt glass, mosaics, and art glass production in Roman civilizations and other parts of Europe were observed</p> <p>(d) The post-medieval age was the foundation stone of the industrial revolution in Europe, with improvements in the metallurgy and manufacture of steel, iron, copper, lead, silver, gold, etc</p>

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**Table 1** (continued)

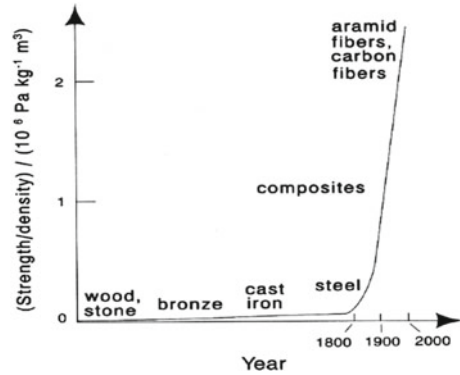
S. no	Ages	Key development and notable achievements
6	Industrial revolution (1760–1840)	(a) The industrial revolution shaped modern metallurgy and material sciences (b) With advancements in the production and manufacturing of iron, steel, lead, copper, silver, alloys, and so on, charcoal to coke was the primary fuel for factories (c) Different techniques for the fabrication of these materials were also discovered, and the ones that were already discovered were enhanced for more efficient production
7	After the revolution (1840–1945)	(a) Large-scale production of metals started with metals such as wrought iron, mild steel, gold, silver, brass, bronze, and other metals that are useful in buildings, weaponry, vehicles, utensils, etc. The addition of various reagents to the metals, like oxides, acids, and bases, and the removal of phosphorous were done for better performances, efficiency in production, the achievement of high-quality materials, etc (b) The development of enhanced furnaces and manufacturing units for the production of these metals was also done
8	Advanced ages (1950–present)	(a) The study of composites, plastics, metals, metalloids, non-metals, etc., for the production of electronics, energy, materials, automobiles, industries, and other applications that have leaped mankind into a more advanced age was done

**Fig. 1** Schematic illustration of the processing, structure, quality, and performance of materials science



The characteristics of materials have come a long way, increasing our knowledge of the correlation between their structure and composition [1, 3, 5]. The tremendous improvement in the strength to density ratio of the materials has allowed for the creation of many novel items, from dental materials to tennis racquets, among many others, as has been well demonstrated in the graph given in Fig. 2. From the literature, the most current chapter provides an overview of the historical development of metal working and metal engineering at a high level. Furthermore, this chapter will offer a broad view of the history of materials, starting from the Stone Age to the contemporary age of diverse materials and engineering [1, 5].

**Fig. 2** Presentation of strength/density ratio with respect to the years



## 2 Historical Panorama in Metals and Materials

### 2.1 Stone Age

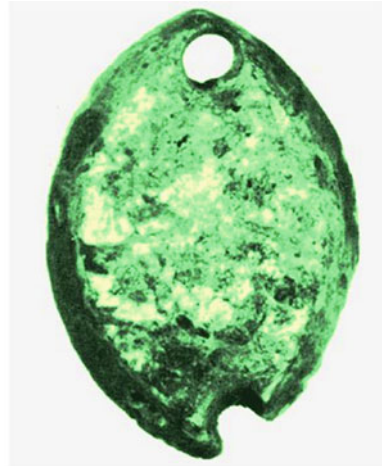
Materials have constrained mankind essentially from the very beginning of its existence. Stone and wood were predominantly used by mankind as the tools for survival, but other materials such as fibers, bone, clay, animal skin, and shells also had very specific purposes for the people of the Stone Age [1, 2, 6]. Materials in the Stone Age served specific purposes in weapons for hunting, utensils, tools, and for creating jewelry or decorations, which was the means of self-expression. A rise in human consciousness coincided with greater usage and the production of ever-more complex materials. In other words, it appears that more developed civilizations invented and utilized more complex materials, whose origins can also be found in the Stone Ages. This remark still holds true today, most likely. Historical periods have been labeled by researchers according to the materials that were most often employed during that time period. The Copper–Stone Age (also known as the Chalcolithic period), the Bronze Age, and the Iron Age are all periods that fall under this category. It is estimated that the Stone Age began around 2.5 million years ago. There are three periods that make up this era: the Paleolithic, the Mesolithic, and the Neolithic (New Stone Age). The development or vast use of materials started mostly during the Neolithic and Chalcolithic periods. So, we have focused on the discussion of these periods in the case of the Stone Age. Surprisingly, despite pottery’s significant importance over long stretches of time, these classifications do not contain a “ceramics age.” Certain linguistic usages have adopted the names of specific metals. For instance, the Greeks distinguished between the Golden Age and the Silver Age, the former of which was said to be characterized by peace and happiness. These disparities have more figurative connotations than literal descriptions of the materials that were employed. In particular, the human race has always placed a high value on gold. Medals are awarded in gold, silver, or bronze for exceptional performances (in sporting events, etc.). Gold, silver, and iron are used to classify specific wedding anniversaries. Up

until very recently, the mastery of materials has been primarily attained by empirical methods or, at its best, through a type of alchemy. Systematic investigation only produced the interdisciplinary field of study known as materials science in the nineteenth and twentieth centuries. Later chapters will go into more detail on this and provide examples. Before materials take on their ultimate shape and designation, they frequently need to be cut, shaped, or smoothed. To accomplish this, a tool that is more powerful than the work item must be used. For example, wood can be shaped into different pieces by using flint stones that have a sharp edge. In order to obtain stool tools from big and bulky rocks, percussion flaking has been done. Striking a lump stone with another helps achieve the rocks' specific shapes as desired. It is a common practice to employ flaky edges as blades for the purpose of hunting and survival. To provide a more secure grasp and a more robust application of force while using stone tools, people throughout the world from 5,000 to 10,000 years ago began engineering these flakes of stone with wooden handles derived from vegetable resins or fibers [1, 4–8].

## 2.2 *Metal Ages*

It is not immediately apparent why stone-based societies finally gave way to metal-based ones. As a side note, this change did not occur in all regions of the world at the same time. If it did happen at all, the introduction of metals took place over a period of about 5,000 years and seems to have started separately in a number of different places. For instance, metals were utilized quite early on in Anatolia, which is now a part of Turkey and serves as a bridge between Asia and Europe. Once upon a time, this area was home to a sophisticated culture that cultivated grain-bearing grasses (such as wheat and barley) and raised cattle, sheep, and goats as livestock. The transition from a nomadic to a settled civilization allowed individuals to devote more time to activities other than the necessity of finding and preparing food for the next meal. So, it is not strange that people would be curious about things like copper, gold, silver, mercury, and lead concentrations in their immediate area. Metals in their pure state (not combined with other elements as they are in ores) can be worked into different shapes and hardnesses by hammering and heating, respectively. Pieces of native metals likely commanded a high price due to their limited availability and rarity. Stone was still the material of choice for most tools and weapons, since pure metals were often too pliable to be a suitable substitute. As a result, pure metals, notably copper, silver, and gold, were primarily put to use in the creation of ornaments and decorations as well as for the performance of rituals. Figure 3 displays an example of one of the very oldest copper artifacts, which is an oval-shaped pendant that is 2.3 cm in length and 0.3 cm in thickness. It was discovered in a cave in the northeastern region of Iraq. As a result, the beginning of the metal ages coincided with the beginning of the Copper Age, and the conclusion of the metal ages coincided with the end of the Iron Age [1, 9, 10].

**Fig. 3** Copper pendant that was discovered in the Shanidar Cave of North-Eastern Iraq. It was thought be completely mineralized and have been built at about 9500 B.C. by carving the malachite ore and finished with abrasive [11]



### 2.3 Copper Ages

Sometime around 9500 B.C., people probably started working with local copper by pounding it or maybe even cutting out copper ore, marking the beginning of the Copper Age. Copper was used in each of these procedures. Having metal cooking implements must have given their owner a sense of pride. In particular, copper's availability and striking appearance made a tremendous impact (especially after men learned how to smelt it). In conclusion, there was a long period of overlap between the Stone Age and the Copper Age. This is why this time period is called the Chalcolithic or the Copper–Stone Age. The earliest known usage of copper by human's dates back to the Neolithic era, around 8000 B.C., yet it will be difficult to pinpoint an exact date for this discovery. Copper tools and weaponry dating back to roughly 5000 B.C. were unearthed from ancient Egyptian tombs. The epics of Shu Ching claim that copper was in use in China much before 2500 B.C. Native copper, which was discovered in large quantities around Lake Superior in Michigan, USA, at the turn of the Common Era (100–200 AD), was likely used for decoration. Some scholars have suggested that indigenous people in the Americas were already making use of copper by 4000 B.C. Once upon a time, the native copper and other metals were likely mined to near exhaustion. This led Neolithic man to look elsewhere for metals, specifically at the minerals themselves. Malachite is a very popular copper resource. It is possible that Neolithic man encountered it in significant numbers in places like Anatolia and the Sinai Peninsula. Cyprus, which is abundant in chalcopyrite, is only one example of a potential copper ore deposit (a copper-iron sulfide). Now, after the discovery of various copper ores, the process of smelting copper ore in order to remove oxygen, sulfur, and carbon was not and is not an easy task. Extreme heat, more than the melting point of pure copper (1084 degrees Celsius), and a “reducing atmosphere” (an atmosphere devoid of oxygen and rich in carbon monoxide) are both required.



Charcoal is created by burning wood or other materials. When the moment is right and the conditions are ideal, oxygen is drawn out of the copper ore, where it interacts with carbon monoxide to generate gaseous carbon dioxide, which is then released from the ore. The last stage of the reduction process requires a fluxing agent, such as iron ore. Additionally, it aids in the last step of separating the molten copper from the slag once the melt has cooled. This takes place after the melt has cooled. Iron ore, in particular, combines with the unwanted sand particles already present in the ore. Massive amounts of heat were generated by burning charcoal, and then air was blown onto the burning charcoal either by physically pushing the air into the furnace through bellows and/or blow tubes (called *tuyères*) or by situating the furnace on the peak of a mountain and taking advantage of the updraft winds. To this day, nobody knows how Neolithic men could have figured out this sequence of actions without the help of initiates or at least some degree of intuition. Recent research by archeometallurgists has disproven the hypothesis that copper may have been accidentally generated in campfires whose surroundings would have consisted of rocks containing copper ore. This was done to disprove the theory that copper was created accidentally in campfires. It is impossible to melt copper in a campfire because the temperatures involved (600–700 °C) are not high enough and the reducing atmosphere does not stay long enough. However, lead may be recovered from its ores and smelted using this process due to its lower melting temperature [1, 9, 10].

The “technique” of copper smelting is now widely believed to have been adapted from the skill of pottery production, which originated around 9000 BCE (or earlier in some regions). The contention relies on the assumption that pottery production and copper smelting happened simultaneously. A fertility statue known as the “Venus of Vestonice” was unearthed in the Czech Republic. It was made of baked clay and dates back to around 23,000 B.C. It is believed that this figure was made from the first cooked clay object. However, it appears that the development of both pottery making and copper smelting occurred simultaneously. For instance, Neolithic man learned that clay bricks hardened when dried in the sun but softened when treated with rain, a second time, allowing for more flexibility. Intentionally exposing the mud bricks to the heat of a fire to hasten the drying process is probably what led to the discovery of an irreversible hardening process. At temperatures around 500 °C, clay undergoes a chemical transformation that gives it a permanent consistency and renders it impenetrable in terms of water storage. This discovery likely prompted the methodical growth of pottery making and the construction of kilns to replace traditional methods of drying clay in the open air. These two changes occurred gradually over time. Surely Neolithic man knew that a mound of wood fuel on top of shattered pottery and dirt would cause a temperature increase [1, 9, 10, 12, 13].

The oldest known account of glass fabrication was known to have occurred in Egypt and Mesopotamia during the sixteenth–fifteenth centuries B.C., but the oldest known glass was discovered in Egypt around the thirty-fifth century B.C. Royal

families exhibited the ornaments and beads that were manufactured using the glass, along with a beautiful vessel made of hollow glasses. Three methods were known to produce glasses in the presence of heat: consistent hammering, polishing, drying, cleaning, etc. Most ancient Egyptian spectacles, even those of similar design, were opaque and came in a rainbow of colors. The low temperatures of the first glass-making pit kilns and the use of a wide range of admixtures—typically classified as either dyes, decolorizers, or opacifiers—were to blame. As far as can be told, the initial translucence and color palette of ancient glass were determined by random admixtures. The glassmakers did not figure out how to select a certain color until they had already amassed a great deal of experience. Dyes were made from the oxides of several metals, including manganese (Mn), copper (Cu), cobalt (Co), iron (Fe), and antimony (Sb). Moreover, lead (Pb) oxide was used. Opacifiers included copper oxide ( $\text{Cu}_2\text{O}$ ), antimonous oxide ( $\text{Sb}_2\text{O}_3$ ), calcium oxide (CaO), lead oxide ( $\text{Pb}_2\text{O}_5$ ), and tin oxide, which made the glass behave as see-through. Tin oxide and lead oxide ( $\text{PbO}$ ) were also used as opacifiers ( $\text{SnO}_2$ ). As a result, the metal ages began with the Copper Age. That was back in the day when people first started working with copper to make tools, artifacts, utensils, weapons, and so on [2, 14, 15].

## 2.4 *Bronze Age*

Without a doubt, one of the most important discoveries ever made was that adding tin to copper while casting could provide a large amount of extra strength in the cast form without the need for additional cold working. However, it is possible that the idea developed slowly through time and that there was a time when arsenic and very small amounts of tin were used together in the Near East. Sometimes, the Bronze Age is broken up into early, middle, and late segments based on the typology of the metals used during the era, but this is far from the rule. Arsenical coppers and straight tin-bronzes, neither of which contain arsenic or lead, were the metals of choice in prehistoric Britain and Ireland. Straight tin-bronze, with tin concentrations commonly exceeding 10%, was a common alloy throughout the Middle Bronze Age (Sn). Despite the fact that the alloy often contained 10% tin, lead was first used in castings at the end of the Bronze Age. Lead's usage did not explode the moment it was introduced; in fact, it appears to have been confined to the southeast of the country in Britain. However, in other regions, lead is frequently found in bronzes without any attempt being made to date when lead was used in the creation of the bronzes. Because of this, the period is best divided into three parts: the early, exploratory age; the middle, complete Bronze Age; and the late, full Copper Age [3, 16, 17]. Clearly, the people of the Chalcolithic era knew that copper had a number of advantages over other materials like stone and organic matter that made it the material of choice for a variety of tasks. Copper's malleability and ductility made it possible to shape the metal into useful shapes, while the metal's slicability made

it possible to shape it into sheets and other shapes without sacrificing its ductility. Copper was employed by Chalcolithic people because of its durability, which may be enhanced by plastic deformation during hammering. Now that molten copper can be poured into molds and allowed to cool slowly, more complex forms of copper may be made. However, Chalcolithic man probably worried at least a little bit about porosity due to surface oxidation and gases trapped during the melting and casting processes. On the other hand, cast copper tends to be somewhat pliable, making it unsuitable for use in the creation of long-lasting tools or weapons. Ultimately, it was obvious that a different strategy was needed, one that placed a premium on imagination. A different material was required. It was determined that this material was bronze. It is unclear if Chalcolithic man discovered the toughness of cast alloys could be greatly improved by adding different metals to copper through experimentation or by sheer luck. No matter the method of discovery, it is known that the hardness of the cast alloy was significantly increased (an alloy is a combination of several metals). Cast bronze is harder than pure copper without any further hammering, thus it may be used right out of the mold. As an added bonus, it is possible that Chalcolithic man knew that some copper alloys had a substantially lower melting temperature compared to pure copper (by roughly 100 °C) and that molten alloys flowed more smoothly throughout the casting process. As expected, some of the impurities in the copper ore made their way into the molten metal. Sulfur, phosphorus, and iron were among the contaminants found. Rarely detected elements included arsenic, antimony, silver, lead, iron, bismuth, and even tin. To a lesser extent than in an alloy, these impurities were not present in the final product. Except for bismuth, which may make copper brittle even at extremely low concentrations, these impurities often do not have much of an influence on copper's features. It appears that the first important and intentional addition to copper was arsenic (at least in the Middle East). However, alloying may be achieved there by melting together arsenic-containing ores and copper ores. Easily accessible copper-arsenic ores might be found there. Metal objects from the Middle East that date back to 3000 B.C. often included copper, but they also contained arsenic at levels of up to 7%. There is a compelling case to be made for highlighting a piece of archeological evidence that was discovered in the year 1961 A.D. A total of 429 artifacts, the great majority (428) of which were fashioned of a copper-arsenic alloy, were discovered in the almost inaccessible "Cave of the Treasure," which is located near the cave in which the Dead Sea Scrolls were unearthed. They probably belonged to a temple or shrine and were brought there by refugees around 3000 B.C. There were 240 intricately decorated mace heads discovered, as well as other treasures such as chisels and axes of various sizes and shapes. On the other hand, copper-arsenic alloys saw little application. There was probably an investigation into the deaths of metalworkers at some point when it was discovered that they had been caused by arsenic fumes emitted during the melting process. Finally, the ideal alloy mass percentage of 10% was reached after determining that tin was the best component to mix with copper. The copper-tin alloy in question is better known by its common name, bronze. Copper with 10% tin has a melting temperature of roughly 950 °C, while pure copper's melting point is 1084 °C. The melt can be poured into the molds without any problem, and there are no difficulties with porosity (air pockets). Most

importantly, the alloy is already rather tough after casting and the subsequent cooling process, but it may be worked even further to increase its hardness by hammering. Overall, the copper-tin alloy outlasts the copper-arsenic alloy and is far less brittle. The reader is invited to weigh in on a few intriguing issues. One is the debate over whether bronze was “made” in a single location (the Middle East, as many experts once believed) or separately at a variety of places across the world. There has not been a final word on this matter yet. However, recent archeological evidence suggests that in addition to the Mediterranean region, considered by many Westerners to be the “cradle of civilization,” independent bronze-producing centers existed in Northern Thailand (Ban Chiang) in the third or fourth millennium B.C. and also in the isolation of China during the Shang dynasty beginning around 1400 B.C. These geographically isolated areas seem to have experienced a transition into the Bronze Age in ways that were inconsistent with one another [1–3, 10–18]. For instance, Indo-China produced a great deal of bronze, and it is thought that many staple crops, such as rice, bananas, coconuts, yams, taro, and sugarcane, were first brought to humankind from that region. The locals built their dwellings from bamboo, made a living as potters, and raised pigs, chickens, and cows, among other domesticated animals. Bronze axes, spearheads, socket tools, bronze bracelets, clay crucibles, and sandstone molds have all been uncovered in this region, dating back to between 3000 and 2300 B.C. The most intriguing find was made when archeologists realized the people of Ban Chiang appeared to have skipped the stages of copper manufacturing and arsenical bronze, going straight to the tin-bronze period. There was no doubt that everything needed to cast bronze could be found in one place (in contrast to the Near East, as we shall elucidate below). Rich alluvial concentrations of tin and copper ores have been discovered in locations ranging from Southern China to Thailand and Indonesia. One of the most intriguing findings by archeologists is that the Thai people appeared to have existed in a “calm bronze period.” This conclusion is based on the lack of discoveries of bladed weapons such as swords, battle axes, daggers, and mace heads. Rather, bronze was mostly used for decorative purposes. The fact that so many infants were buried with bronze bracelets suggests that they were not a sign of social status [18–20].

In contrast, during the Shang dynasty (1600–1122 B.C.), early Chinese bronze was mostly employed for ceremonial containers to offer food and drink to ancestral spirits. The Shang dynasty saw the construction of these ships [1–3]. Somewhere between 3 and 30% tin and 3% and 5% lead can be found in bronze (which makes the melt flow easier). Numerous animals, like elephants, water buffaloes, tigers, and even fabled dragons, are depicted in the relief patterns on bronze artifacts from the Shang era. The Chinese have a lot of experience with casting. This was accomplished by first cutting the desired patterns into already-burnt clay molds. No more forging or pounding of metal was performed. A massive cauldron that weighs 875 kg in its entirety and was cast in one piece stands as proof of their skill. (Local villagers used it in 1939 A.D. to store food for their pigs; it was discovered in Anyang.) Another recent astounding find was a set of bronze bells from 433 B.C. that were

buried in a tomb belonging to the Marqui Yi. The design of these instruments allows for a lower pitch to be produced when hit in the middle as opposed to the edges. According to modern academics, the two tones represent the Chinese concept of a universe ruled by two opposing forces, Yin and Yang, who coexist in harmony (such as day and night, heaven and earth, sun and moon). Supposedly, the two-tone bells represented the harmonious coexistence of opposing forces. Music was highly valued by the Chinese of that time since it was a means by which they could express their appreciation to the generations gone before them for blessing them with health and wealth. This was not a party with music provided by bells and drums, but rather a ritual meal shared with and celebrated by their forefathers [20, 21].

The sum of the reputed archeological evidence seems to indicate that during the Chalcolithic period, there were no major known tin sources located in the Near East, with the possible exception of some native tin in the Zagros Mountains, which are situated on the eastern edge of the Mesopotamian plain. However, if they were real, they vanished almost immediately after being uncovered. Instead, documents detailing massive caravans used to transport tin have been uncovered. It is also possible that tin was transported all the way from the Middle East to the Far East by coastal ships. Recently, a shipwreck carrying tin was discovered during excavations off the coast of Israel. There was no readily available tin for experimentation or the accidental discovery of bronze; therefore, it is still unclear how the Bronze Age may have begun in the Mediterranean region about 2000 B.C. Due to the lack of evidence to the contrary, it is important to explore the possibility that bronze technology was exported from the Far East or another place to the West. Malachite and cassiterite, tin and copper ores, are found on the southern slopes of the Caucasus in what is now Armenia. One theory puts this out as a possible tin source. It is likely that tin-bronze was made when these minerals were accidentally heated together [22, 23].

Some scholars believe that trade connections linking the Middle East and Eastern Europe (where tin may be found in Bohemia, Saxony, and other locations) date back to 2500 B.C. Because of this, we may now focus on the Europeans, and more specifically, the Uneticians, who became the dominant population in Europe around 1500 B.C. [1–3]. The Uneticians were named after a small town near Prague that influenced a large area, specifically the Rhine Valley and Ukraine. The Uneticians were highly proficient bronzesmiths who mass-produced a wide range of goods. Jewelry, implements (such as axes and plowshares), weapons, and clothing pins were among the items produced. One product, a neck ring, was produced in such quantity that it was used as a kind of money, meaning that it could be traded for more valuable commodities like gold, furs, amber, and glass beads. The high volume of manufacturing made this a realistic option. However, these neck rings appeared to be very similar to those discovered in Syria [2, 3, 19, 22]. Results of unethical labor have been found in many tombs across the British Isles, Scandinavia, and Ireland, indicating that they traded with more than just the southern areas. They were original minds that developed innovative uses for existing ideas or made copies of popular items. Actually, it was the Uneticians who thought of using a safety pin.

Archeologists excavating sites linked to the Unetic civilization have found knitting needles, the remnants of a complicated loom, and a strainer used in the production of cheese [3, 4]. A Bronze Age settlement wonderfully preserved in a peat swamp near the Federsee (a lake in southern Germany) yielded a large number of bronze-metal artifacts. These included axes, chisels, spears, knives, bracelets, pins, and a chain. Aside from the region around the Indus River in northwest ancient India, this was another crucial area for the advancement of bronze technology in this part of the country. The Harappan culture, which flourished there between 7000 B.C. and 1500 B.C., was an extremely sophisticated civilization (until the Aryans invaded the land). Excavations at Mehrgarh, which took place in what is now Pakistan, indicate that the Harappans were skilled bronze artists as early as 2300 B.C. In the case of bronze, the Harappans employed lost-wax casting, annealing, and riveting. During this time period, they also developed the ability to manufacture human figures, containers, arrowheads, spearheads, knives, and axes. Evidence from bronze sickles found at the site suggests that the area was used for agricultural purposes. Huge mountains of copper slag indicate that the copper ores used in these processes came from the plains around the southern end of the Indus River (Mohenjodaro) and from areas to the northwest of the Indus valley, in what is now called Afghanistan [3, 18–22]. The copper ingots discovered in this area have a shape like a half circle. Similar to the Near East, though, tin's history is clouded by mystery. Researchers believe the middle and Western Indian Deccan Plateau was the point of origin [24, 25]. Copper smelting occurred across the Harappan civilization, not just in urban centers. However, various Indian communities spread out over the continent have the technology to work with copper and bronze, but not always at the same degree of sophistication. Greek mythology contains a written record devoted to the metal bronze. The Greek deity of fire, Hephaestus, crafts a superior shield for Achilles out of copper, tin, silver, and gold in Homer's *Iliad*, which was likely written between 800 B.C. and 700 B.C. [18, 19, 22–24].

Finally, it is theorized that the indigenous inhabitants of the central highlands of Peru used bronze technology both before and during the Inca Empire. Around 1450 A.D., or maybe even earlier, this technology is said to have first appeared. In contrast to European and Asian standards, the maximum allowable arsenic content in the products (including pins, chisels, and axes) was only 1.5%, while the allowable tin content was 3% or less. Most of the objects unearthed here lacked even trace levels of alloy components, much less enough to noticeably change their mechanical qualities. Therefore, the deliberateness of the alloying process is up for debate. Regardless, potential tin resources would have been nearby in Northern Bolivia. As opposed to popular belief, bronze technology was developed not just in the Middle East but also in other parts of Europe and Asia [1, 3]. In conclusion, several parts of the ancient globe had intricate bronze technology.

## 2.5 *Iron Age*

Historians have suggested a time range of 1500–1000 B.C. for the start of the Iron Age (at least in some parts of the world). This does not mean that people did not know about iron before that time; on the contrary, this was the case. Meteoritic iron, which includes a substantial quantity of nickel, was likely used by ancient people as early as 4000 B.C. They hammered and shaped it into various tools and weapons. It is easy to see why iron was called “metal from the skies” in so many languages as it is believed that meteoric iron was used, hence his name. Until this reason, stone, copper, and bronze were widely used in construction for at least the first two millennia BCE [3, 9, 10]. However, iron ores served a few essential functions far into the Chalcolithic period and beyond the Bronze Age. In the analysis of the manufacture of copper, fluxing agents are necessary during the smelting process for copper when malachite is present. When melting the metal, iron oxide was added to get rid of the unwanted sand particles that are found in malachite. Over time, slag formed, and as the melt cooled to the right temperature, the copper was easily separated from the slag [2, 3, 10]. Iron, however, has a high melting point of 1538 °C; hence, there has been much debate in the academic community over whether or not prehistoric humans could have obtained this metal from on-Earth resources. For the Western (or eastern) half of the planet, such a high temperature was unthinkable at that age. But the answer to how humans obtained iron is taken from the previously mentioned slag as an example, where large quantities of it have been uncovered in areas that were once home to extensive copper smelting activity [1, 3, 9, 25].

It was discovered that this slag included some reduced iron, but in a porous form now known as “sponge iron” or “bloom.” Once the slag was studied, the findings became clear. Slag can be broken up and removed, and the iron can become more compacted when bloom is hammered at high temperatures for an extended period of time [3, 16, 17]. With this technique, you may get iron that is nearly pure. Modern metallurgists use the term “worked iron” to describe the final product (also written as wrought iron). It takes a temperature around a thousand degrees Celsius lower than what is needed to melt pure iron in order to reduce iron ore into spongy bloom. The use of this technique to produce iron seems like a logical beginning point for the manufacture of iron in that period. This technique reveals that the heat was never turned up high enough to melt anything. But iron in its purest form is extremely malleable, much more so than bronze. Furthermore, pure iron corrodes extremely rapidly when exposed to air with a high humidity content. This suggests that, prior to the knowledge of how to produce “good iron,” as it was characterized in ancient writings, prehistoric humans probably were not too interested in the metal itself. There is widespread agreement among archeometallurgists that the Hittites, or more likely Hittite subjects (known as the Chalybes), who resided in what is now Turkey but was then known as Anatolia-Mesopotamia, were responsible for the finding of high-quality iron. The Hittites were effective colonizers; they eventually came to rule over large swaths of the Mediterranean, including Assyria, Babylon, and parts of Northern Palestine. It is generally agreed that the Hittite administrative system was

more advanced than that of its neighbors and that the Hittite legal system prioritized reparation above punishment. The Indo-Germanic Hittite language was recorded using hieroglyphics or cuneiform, a syllabic writing method borrowed from the Mesopotamians. As a global people, the Hittites communicated with one another using Akkadian. Iron swords, spears, and arrows were their most effective weapons [3, 26, 27], with the mythology claiming that they could easily pierce their enemies' bronze shields.

Although the speed and agility of their nimble chariots certainly helped them win, their superior design was also likely a factor. For two centuries, from around 1400 B.C. [1, 3] to around 1200 B.C., the Hittites allegedly kept their method of making high-quality iron a secret. Hammering the bloom to remove the slag and compress it after many heating cycles in a charcoal furnace at temperatures close to 1200 °C with the goal of softening the bloom produced good iron. During the heat treatment, the bloom and, eventually, the iron were often exposed to carbon monoxide gas, which was created by the burning charcoal. According to previous statements, this technique aids in facilitating carbon diffusion into the iron's surface. This process results in an iron-carbon alloy known as steel, which, while having a carbon content of just about 0.5% (as in the preceding example with bronze, Cu-10% Sn), is far more resistant to abrasion and corrosion (steel is defined as iron that contains up to 2.11 mass percent carbon). The carbon content of steel ranged between 0.3% and 0.6% of the original steel. Cold work helps to increase strength. The inhabitants of the Iron Age must have also realized that limiting carbonization to an object's surface (like the edge of a blade or the tip of a tool) produced a balance between great surface hardness and outstanding interior ductility. Iron with a surface carbon concentration of 1.5%, the result of a process called "selective steeling," has been found as early as 1200 B.C. The manufacturing of modern case-hardened iron is quite similar to this technology. But for a long time, no one realized the role carbon played in establishing the tenacity of iron and steel. Actually, Aristotle (384–322 B.C.), an ancient Greek scholar and philosopher, was one of many who believed (incorrectly) that steel was a purer form of iron due to the "purifying impact of charcoal fire." When cast iron was dissolved in acid, a "graphite-like residue" was left behind that was not spotted until 1774 A.D. by a Swedish metallurgist named S. Rinman. A further seven years passed before Bergman and Gadolin released their results on the varied carbon levels in the various irons and steels. Two more discoveries, probably made in the first millennium BCE, improved the quality of the carbonized iron even further. One such method is called "quenching," and it involves plunging a piece of red-hot carbonized iron into a tub of ice water to cool it down quickly. To our surprise, Homer describes this procedure in great detail in *The Odyssey*. By increasing its strength, the material being worked on might become so tough that it cracks easily when handled. Blades of quenched swords, tools, and other equipment may have developed fractures or even shattered as a direct result of this. The second discovery was made at the end of the first millennium B.C. and entailed briefly heating the previously quenched steel to temperatures of around 600 °C. This treatment, now known as tempering, restores some of the material's ductility and reduces some of its brittleness, but at the expense of some of its hardness [25, 26].



A high-carbon percentage makes the iron in a structure very brittle. The substance easily breaks or shatters when struck, leaving it nearly unusable for tools and weapons. This means that cast iron needs further processing. The Chinese probably invented this novel treatment around 500 B.C. Surface carbon from high-carbon iron was removed as part of the process. This procedure led to the creation of a steel coat with properties on par with those of steel made in the west by carbonizing wrought iron [1–6]. To accomplish the intended outcome of decreasing the carbon content of the cast iron, the iron was heated in the presence of air at temperatures ranging from 800 to 900 °C. Carbon monoxide gas is released into the environment when oxygen from the air combines with some of the carbon already there. The Chinese and Mediterranean peoples both arrived at quite similar solutions, albeit independently. Nonetheless, they ended up at the same place in the end. While the Western world had to form and carbonize its items one at a time by hammering, the Chinese could form their products via casting, allowing for simple mass manufacturing. The ability to mass-produce their goods was, however, the greatest benefit of Chinese technology. Another major technological innovation originated in China during the first century of the Common Era (A.D.). Carbon-rich iron has to be agitated in order to stimulate a reaction between carbon in the melt and the air. In this way, the carbon content of the melt was already low enough to allow steelmaking. This technique, often known now as puddling, was found in England in 1784 A.D. Massive industrial complexes were active around Zheng-Zhou and other locations throughout the latter half of the Han period (202 B.C.–A.D. 220). Several gigantic furnaces, each measuring about 4 by 3 m in size and towering about 3 m tall, were housed in these structures. The iron from these furnaces might have weighed several tons per day. Stack casting, in which many molds are piled on top of one another, was also pioneered in China. Up to 120 distinct spells might be cast at once. Production of plowshares, hoes, cart bearings, and harness buckles was so extensive that each item could be made at a cheap per-unit cost. As a result, it is possible that agriculture improved, leading to larger production and a larger population [9, 26–28]. This was because it facilitated the widespread availability of tools essential for agricultural labor, such as plows, cultivators, and diggers. Thus, the Iron Age paved the way for the discovery of iron and steel and the mass manufacture of these materials, laying the framework for the progressive development of structure in the contemporary world, whether consciously or not. Since this era marked the beginning of the efforts to create the modern world, its time range is considered to be the basis for the modern age as a whole.

### 3 History of Glass Materials

Glass has been used as a separate material since around 2500 BC, mostly as beads. It may have originated in India or Mesopotamia and was then introduced to Egypt and other nations in Europe. Glassware first emerged in 1450 B.C., under the rule of Thutmose III, an Egyptian pharaoh from the eighteenth dynasty. The Crystal Palace, erected by Joseph Paxton in 1851 A.D. to hold the Great Exhibition, served as a

precursor to the use of glass as a construction material. The public began using glass as a construction material for residential and horticultural architecture as a result of Paxton's groundbreaking new structure. With the assistance of renowned French glassmaker Georges Bontemps, the British Crown Glass Company (later Chance Brothers) was the first business to use the cylinder process to create sheet glass in 1832 [1, 2].

## 4 Brief History of Polymeric Materials

The original meaning of the term “plastic” was “pliable and readily moldable.” It was only recently given a name for the class of materials known as polymers. Polymers are composed of lengthy chains of molecules, and the term “polymer” implies “of many pieces.” In nature, polymers are abundant. The component of plant cell walls known as cellulose is a widely used natural polymer. John Wesley Hyatt created the first synthetic polymer in 1869 A.D. after being motivated by a New York company's \$10,000 reward for anybody who could come up with an alternative to ivory. By combining cellulose, which is made from cotton fiber, and camphor, Hyatt discovered a plastic that could be molded into a variety of shapes and made to resemble natural materials such as tortoise shell, horn, linen, and ivory [29, 30].

## 5 Brief History of Carbon Materials

Carbon has been used since at least 3750 B.C., when the Egyptians and Sumerians reduced copper (Cu), zinc (Zn), and tin (Sn) ores to produce bronze. As early as 157 A.D. [38, 39], animal and plant-based carbons were used to treat a variety of illnesses. The absorptive capacity of carbon-derived compounds from various sources was first observed in 1773 A.D. by Car Wilhelm, a chemist from Pomerania, a region of Europe on the Baltic coast that was governed by Sweden. However, Eponit (trade name), the first activated carbon manufactured industrially, was initially marketed by the Austrian Fanto Works in 1911. The municipal water treatment sector is now the greatest market for activated carbon [31, 38, 39].

## 6 Brief History of Nanomaterials

One of the most intriguing instances of nanotechnology in the ancient world was presented by the Romans in the fourth century AD, who employed nanoparticles and structures. One of the most remarkable works of ancient glass art is the Lycurgus cup, which is part of the British Museum collection [32–35]. It is the first well-known instance of dichroic glass. Dichroic glass refers to two distinct glass kinds that,

depending on the illumination, may change color. The Advanced Research Project Agency (ARPA) of the USA initiated the fabrication of material science during the advanced modern ages [32–35]. ARPA funded a project in material science with five esteemed universities in the USA in 1960 A.D., which led to the initiation of the formation of a new branch of science and technology called “Material Science and Engineering.” As for the modern world, extensive use of nanomaterials began in that year [36, 37, 40].

## 7 Conclusions

The historical perspective provides an overview of how the modifications have been made to achieve the goal with improved inherent properties. However, the historical prospect of material and material engineering will provide a brief and detailed idea about the modifications that have taken place since the primitive age. This alteration of improvement is still in the process of evolving, although with the industrial revolution, there has been a significant acceleration in the development process. The “materials method of thinking,” which led to the unlikely development of a generic concept of materials, emerged just recently. However, in the twentieth century, they were reimagined as a generic entity to be examined in a multidisciplinary techno-scientific paradigm rather than as separate entities that posed challenges to scientific reason in the context of the contemporary scientific paradigm. The significant position of materials has been profoundly reshaped in this historical process, where science, technology, and society are interconnected; they are no longer seen as preconditions placing restrictions and limitations on engineering, but rather as objects of design. This chapter will provide the connecting link between the past, present, and future of materials and material engineering with the knowledge of historical perspectives and statistics regarding the development of materials over the course of history.

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## References

1. Hummel RE (1998) Understanding materials science: history, properties, applications. Springer, New York, p 407
2. Gnesin GG (2016) Revisiting the history of materials science glass, glaze, and enamel over the millennia. I. Glass. Powder Metallurgy Metal Ceramics 54(9):624–630
3. Tylecote RF (1977) A history of metallurgy. Br Corros J 12(3):137–140
4. Cahn RW (2001) The coming of materials science. New York

5. Hill JD (1994) Barry Cunliffe (ed.). *The Oxford illustrated prehistory of Europe*. xii+ 532 pages, 46 colour plates, 19 maps. 1994. Oxford: Oxford University Press; ISBN 0–19–814385–0 hardback£ 30. *Antiquity* 68(260):668–670
6. Mehl RF (1984) Brief history of the science of metals. AIME
7. Wilson A (1994) *The living rock: the story of metals since earliest times and their impact on developing civilization*. Woodhead Publishing
8. Lessem D (1994) *The iceman*. Crown, New York
9. Raymond R (1984) *Out of the fiery furnace: the impact of metals on the history of mankind*. Penn State Press
10. Smith CS (1977) *Metallurgy as a human experience*. ASM International (formerly American Society of Metals), Materials Park, OH
11. Smith CS (1977) *Metallurgy as a human experience: an essay on man's relationship to his materials in science and practice throughout history*. American Society for Metals
12. Harrison RJ (1980) *The beaker folk: copper age archaeology in western Europe*, vol 97. Thames and Hudson
13. Parr JG (1958) *Man, metals, and modern magic*. Published jointly by American Society for Metals [and] Iowa State College Press, Cleveland, Ohio; Ames, Iowa
14. Scheel B (1989) *Egyptian metalworking and tools*. Shire Publications, Aylesbury, UK
15. Spindler K (1994) *The man in the ice*. Harmony, New York
16. Craddock PT, Gale D (1987) Evidence for early mining and extractive metallurgy in the British Isles: problems and potentials. In: *Science and archaeology Glasgow 1987*. Proceedings of a conference on the application of scientific techniques to archaeology, Glasgow, pp 167–191
17. Stickland P (1975) *The recovery of tin into copper by surface additions of tin-bearing minerals*. Under graduate dissertation, Department of Metallurgy, Cambridge
18. Dickinson O, Dickinson OTPK (1994) *The Aegean bronze age*. Cambridge University Press
19. Cunliffe B (ed) (2001) *The Oxford illustrated history of prehistoric Europe*. Oxford Illustrated History
20. Fong W (1980) *The great bronze age of China*. Knopf, New York
21. Chase WT (1991) *Ancient Chinese Bronze Art*, China House Gallery, China Institute in America, New York
22. Higham C (1996) *The bronze age of Southeast Asia*. Cambridge University Press
23. Mellaart J (1966) *The chalcolithic and early bronze ages in the Near East and Anatolia*
24. Langmaid NG (1976) *Bronze age metalwork in England and Wales*, shire archaeology series. Shire Publications, Aylesbury, UK
25. Pigott VC (1992) Iron versus bronze. *J Metals* 42ff
26. Macqueen JG (1986) *The Hittites and their contemporaries in Asia Minor*, vol 83. Thames and Hudson
27. Pleiner R, Wertime TA, Muhly JD (1980) *The coming of the age of iron*. Yale University Press, Newhaven and London, p 40
28. Schmidt PR, Childs ST (1995) Ancient African iron production. *Am Sci* 83(6):524–534
29. Nicholson JL, Leighton GR (1942) *Plastics come of age*. Harper's Magazine, p 306
30. Freinkel S (2011) *Plastics: a toxic love story*. New York, Henry Holt, p 4
31. Gupta T (2018) Historical production and use of carbon materials: the activated carbon. In: *Carbon*. Springer, Cham, pp 47–70
32. Bayda S, Adeel M, Tuccinardi T, Cordani M, Rizzolio F (2019) The history of nanoscience and nanotechnology: from chemical–physical applications to nanomedicine. *Molecules* 25(1):112
33. Geiger RL (1992) Science, universities, and national defense, 1945–1970. *Osiris* 7:26–48
34. Choi H, Mody C (2013) From materials science to nanotechnology: Institutions, communities, and disciplines at Cornell University, 1960–2000. *Hist Stud Nat Sci* 43(2):121–161
35. Bensaude-Vincent B (2001) The construction of a discipline: Materials science in the United States. *Hist Stud Phys Biol Sci* 31.2:223–248
36. Tiwari SK, Kumar V, Huczko A, Oraon R, Adhikari AD, Nayak GC (2016) Magical allotropes of carbon: prospects and applications. *Crit Rev Solid State Mater Sci* 41(4):257–317

37. Tiwari SK, Mishra RK, Ha SK, Huczko A (2018) Evolution of graphene oxide and graphene: from imagination to industrialization. *Chem Nano Mat* 4(7):598–620
38. Inagaki M (2006) *Carbon materials science and engineering: from fundamentals to applications*. 清华大学出版社有限公司
39. Inagaki M, Kang F (2014) *Materials science and engineering of carbon: fundamentals*. Butterworth-Heinemann
40. Sudha PN, Sangeetha K, Vijayalakshmi K, Barhoum A (2018) Nanomaterials history, classification, unique properties, production and market. In: *Emerging applications of nanoparticles and architecture nanostructures*. Elsevier, pp 341–384