Patricia Silvana Carrizo *Editor*

Reverse Engineering of Ancient Metals

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Patricia Silvana Carrizo
Archaeometallurgy Area/Metallurgy Laboratory
National Technological University
Mendoza, Argentina

ISBN 978-3-030-72841-0 ISBN 978-3-030-72842-7 (eBook)
https://doi.org/10.1007/978-3-030-72842-7

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Preface

For some time, there has been a growing interest in the application of analytical techniques to metallic materials from archeological, historical, and heritage sites, whether these pieces belong to rescues from archeological sites or are present in museum collections or are part of private collections. However, it is necessary to be able to disseminate the analysis techniques used, and thus the application of the scientific research method that is the product of the crossing of relevant information from technical data related to the research object and from historical bibliographic information and historical archives. All this guides the way to develop through the Reverse Engineering of Ancient Metals, since when analyzing the piece or ancient object, a reverse path is made to analyze and to know the possible ways of manufacturing of certain historical, prehistoric or pre-industrial object, or even of recent times and while the piece or object in cuestion is analyzed, the answers sought are obtained about its specific manufacturing process, the raw materials used and/or if there was any heat treatment, even if by chance,incipient or well developed, and therefore it is also possible that more and new questions will appear on this journey.

The purpose of this book is to explain Reverse Engineering to advanced undergraduate and graduate engineering students, mainly engineering: chemistry, materials, metallurgy, electromechanics, and civil engineering, and it can even serve as a reference guide for academic researchers. Some chapters of this work can even be used to delve into theoretical topics in chairs such as Materials Sciences present in the curriculum in all engineering undergraduate careers.

In careers in the field of archeology, this book is also recommended, because not all archeologists and archeology students have knowledge of materials sciences, metallurgy, metallographic techniques, resistance of materials, and even how all of the above is related with chemistry.

This work turns out to be enjoyable to read with a large number of images for greater understanding and not being tedious to read as would happen with the typical bibliography related to materials science and engineering, that is, it is not a typical technical book. For this reason, the book is easy to read, agile, and arises from a different concept when presenting technical knowledge; here a deconstruction procedure is handled ("allusive *to dismantling*, through an intellectual analysis, a certain conceptual structure") relative to the used raw material, form of preparation, control of the fire, ovens, primitive techniques of production and manufacture of the old metallic elements. A separation is made between non-ferrous metals and their alloys, as well as ferrous metals and their alloys, all from a Mesoamerican perspective of our continent through the participation of Latin American contributors; this will be reflected in the various case studies that will help readers to better understand the theoretical chapters.

This book is recommended, due to its nature of general interest, for students and professionals in the tourism area, professionals in conservation and restoration areas, as well as for cultural management personnel and museums, both public and private, as they could expand their knowledge and transfer it to society through guided tours, since it is my particular interest at all times to achieve the socialization of science, dismantling pre-existing myths, and it is a goal as a researcher-teacher to widely bring this knowledge to even larger audiences.

The information presented should allow the reader to understand and critically evaluate:

- Metallographic technique as a fundamental tool to address archeological, historical, prehistorical, pre-capitalist, and historical industrial metal studies;
- The importance of the data obtained from the application of these techniques and those generated by the application of other additional techniques;
- The possibility of using nondestructive and noninvasive techniques applied to the study of metallic heritage as a great tool;
- Relative studies on corrosion and corrosive processes in old metals and consequently their protection by coatings;
- The validity of these interpretations made in conjunction with the responsible consultation of the historical bibliography, government archives, and data base;
- Various techniques for the preservation, cleaning, and restoration of metals and additionally, depending on the case, repair by means of welding.

My personal experience in ancient metals research prepared me to take on the task of writing this book. I am a chemical engineer by profession; my path began by linking me with an amateur archeology group in the museum of my hometown. To later dedicate myself entirely to metallurgy, that is how I aplied to the metallurgy laboratory of my university when I was still a third-year student of chemical engineering and it was precisely there that I acquired much of my knowledge regarding the analysis of causes of failure of industrial metals and with this knowledge acquired in relation to the metallographic techniques, measurement of hardness, microhardness, and analysis of chemical composition with portable spectrometer, I could then began to apply this basic knowledge to the study of old metal objects, and with the passage of time I also progressed and improved as specialist in the area, surely I stumbled and also fell, but I always got up again and thanks God that there was always someone close to me with a lot of empathy, like the last Director of the Americanist and Regional Museum: Omar Daniel Giunta† (a kiss to heaven dear friend) who always encouraged me not to lower my arms and to continue being doing what I am most passionate about and it is an incredible blessing really to be a chemical-metallurgical engineer because in this way the vission and scope are more broader.

After the road traveled, I see with satisfaction that this field of research is being recognized as an area of great importance in terms of engineering, therefore it is possible to transfer the knowledge acquired to the chairs related to material sciences. I am even aware that there is still a lot of work to be done on the subject and I also have more dreams to conquer. The personal need to carry out a posgraduate study, a doctorate in engineering also came into my life, and thus I returned to my chemical roots, but relating everything to ancient metals, so it was that my thesis was a corrosion inhibitor coating type for historical and patrimonial metals friendly with the enviroment.

I am so grateful to the authors who contributed to the theoretical chapters of this project: Rafael Colás, Luis Reyes, Oscar Zapata (all from Mexico), Cecilia Deyá (Argentina), and Luisa Vetter (Peru). I thank those who added their case studies so that this book is more generous in content and especially to my three students in the area of Reverse Engineering—Rocío Algañaraz, Noelia Ibañez, and Marcos Giupponi—for their interest demonstrated and for being companions of dreams and adventures since our relationship transcended the walls of the laboratory.

I am especially indebted to my parents Petrona and Rubén, as I was completely absent myself from daily family life in order to carry out and finish this work in a timely manner, for which I thank them for their generosity and support. Also special thanks to Anita Lekhwani for approaching me with this book proposal for Springer Nature as well as to the team of reviewers and editors assigned to this project.

I consider that there is no doubt that the COVID-19 pandemic changed our routines and realities, but as a way to rescue the positive aspect of the aforementioned world mundial crisis, in my particular case: working on the writting of this book with commitment prevented me from sucumbing to loneliness, isolation and the uncertainty of the future. Thus, working from home, I focused all the energies on finishing this job in the best possible way with dedication and affection.

Mendoza, Argentina Patricia Silvana Carrizo

Introduction to Reverse Engineering of Ancient Metals

There are several problems of authentication and validation of metal artifacts of need all the evidence provided by metallographic evaluations, as well as their mechanical properties or whether there were incipient or non-involved thermal treatments. For this reason, a particular case study on pigments in pictorial works of art is included through the portable X-Ray fluorescence technique (XRF) and the respective statistical analyses for proper validation.

Reverse engineering processes involve the investigation of historical and heritage metals through metallographic techniques with which information about life can be obtained in times past, that is, how people produced and used metals and alloys. It involves the study of a wide range of metal-related objects that have survived the passage of time and have reached us in the present. These metallic objects, the results of the original processes of metal and metallurgy production, reached their current states after being subjected to one or more of many processes, including trade, use, modification, disposal, and possibly some degradation in the soil and/or alteration in museums or private collections.

These artifacts have been recovered from a variety of archeological contexts, such as housing sites, industrial facilities, metal infrastructures, public transport, funeral contexts (burials), hordes, and ceremonial sites (including offers, river deposits, or other sacred places). It is useful to think that each of the objects that come to us from the past must have a story to tell, a story that, if you read and interpret, can contribute to our general understanding of the past and respond to questions about the technologies used by certain group of people and this information found can be helpful and applicable to the development of new materials or improvements to existing techniques, this being one of the greatest challenges facing reverse engineering.

Reverse engineering requires multidisciplinary information and experience when studying heritage objects. A variety of analytical techniques included in these reverse engineering processes are metallographic microscopy, scanning electron microscopy, chemical analysis, X-ray diffraction spectrometry, dimensional measurements, Charpy impact test, stress, vibrational and hardness tests.

This volume begins with an introduction to these types of research and the origin of the field of *Archaeometallurgy* (Chap. 1) and a series of chapters about basic characteristics of historical non-ferrous metals and their alloys, including Chaps. 2–4.

Likewise, Chap. 5 discusses *Ancient Ferrous Metallurgy: Historical and Social Perspective.*

After all this theoretical part of ancient non-ferrous and ferrous and its alloys, a series of chapters are dedicated to the methodology and preparation of specimens for study (Chap. 6).

Subsequently, Chaps. 7–9 discuss the topic of corrosion in a very developed way (Chap. 7), how to preserve metals from corrosion (Chap. 8), and an interesting topic that is the conservation of old metals (Chap. 9).

Chapter 10 is on repair by welding *(Antique Metals Welding and Reparation),* and a final theoretical chapter (Chap. 11) is about the great advance of technology in the investigation of ancient and patrimonial metals.

Chapter 12 consists of 11 study cases in ancient and historical metals (Chap. 12) where, through the studied pieces, the manufacturing methods used by different cultures are observed, with an above all Latin American vision of culture of the native peoples and also of historical heritage pieces studied that correspond and belong to museums and sites in Latin America. All this information is closely related to the contents developed in the theoretical chapters, with a wealth of images, which makes this book on *Reverse Engineering of Ancient Metals* as didactic as possible.

Finally, Chap. 13 contains two works that, due to their interest and avant-garde, and although they are not strictly research in ancient metal metallurgy, deserve to be added to this work. They are:

> *Analysis of inorganic pigments in unknown works of the painter Fernando Fader by means of X-ray Fluorescence (XRF),* (Carrizo, P.; Ortigala, J.; Aguilera, C.)
>
> *Antimony as a luxury good in the Sicán culture, north coast of Peru,* (Vetter, L.; Carneiro, J.; Tuesta, Y.; Saavedra, J.)

This book offers an exhaustive presentation of the reverse engineering processes and metallographic techniques of great use for professors of the Department of Materials Science and engineering students, for archeologists, historians, history students and tourism students, for museum units and its staff, conservators-restorers, and for all those interested in learning about the ancestral manufacturing culture of this part of the world.

The great contribution that Reverse Engineering can make to society from an educational, cultural, and patrimonial point of view is unquestionable because if we know where we come from, we can know where we are going.

Patricia Silvana Carrizo
Archaeometallurgy Area/Metallurgy Laboratory
National Technological University
Mendoza, Argentina

Contents

Chapter 1
Archaeometallurgy

Patricia Silvana Carrizo

It is useful to think each of the objects that comes to us from the past must have a story to tell; a story that, if read and interpreted correctly, can contribute to our general understanding and even some of this information can be recovered and applied to the development of new metal alloys, studies related to corrosion, and development of material conservation processes.

In this way, archaeometallurgy is an interdisciplinary and international field of study that examines all aspects of the production, use, and consumption of metals from approximately 8000 BC until now, although, in general, this review is limited to mining and metallurgy in pre-industrial societies.

Most of this literature was not written with an anthropological reading in mind, but many of its central themes are relevant to some current debates in anthropology.

Since the 1970s, studies in archaeometallurgy have been explicitly concerned with the materiality of metals and with the highly variable value of precious metals in time and space. Exact criteria have been developed to distinguish transfers of transmitted technologies from generation to generation from independent inventions. Archaeometallurgists have also done important work in the social construction of technology in precapitalist economies.

Among the new approaches that encompass archaeological and metallurgical research is the study of technological change, conceived from a double orientation: internal and external. The internal one explains the change from the technological system itself, that is, considering what changes and how it changes, based on preexisting knowledge and innovation. This part of the research has been strongly linked to the Technology History approach. The second orientation, that is, the external one, tries to answer the question: why does technology change?

From the scientific point of view, we can highlight a trend that is gaining greater weight: interdisciplinarity, an unavoidable challenge for any successful scientific

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P. S. Carrizo (✉)
Archaeometallurgy Area/Metallurgy Laboratory, National Technological University,
Mendoza, Argentina

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_1

approach. The archaeometallurgist scientist no longer works alone and in isolation but has to be understood and coordinated with all kinds of specialists and specialties; this fact produces a positive effect, not only from the methodological point of view but also the theoretical, as the prospects for teamwork are expanded.

In summary, archaeometallurgy offers a lot of interest for the anthropological and social sciences that study growth, the dissemination of knowledge, and value systems, before the capitalist era.

Archaeometallurgy: Studies of Invention, Innovation, and Dissemination

Archeometallurgy, in its advancement, has benefited in some way due to technological development, either in laboratory equipment or in portable equipment that greatly facilitate the task of the archaeometallurgical researcher and in this way archeometallurgy has taken giant steps in recent decades in the advancement of knowledge and this accompanied by the application of the scientific method to approach each investigation, which often resembles a forensic expertise, with the difference that the pieces of the historical heritage are prohibitive to be cut unless expressly authorized by the authorities competent. Despite these limitations mentioned, the archeometallurgy that uses metallographic techniques for research as a means, has made it possible to carry out the reverse path, that is, through applied techniques it is possible to do the reverse path in the manufacture of the pieces in question and obtain information on the raw material used, on how was its manufacturing process, whether or not there was presence of an incipient heat treatment, or study the characteristics of its state of conservation to this day, since the findings in this type of research are really exciting and incredibly surprising and at the same time that they relate to all the historical information of the object or piece and it is so in these instances, due to the interaction shown, is that the researcher always needs to transmit his new and useful discoveries as contributions to the knowledge to the field.

In fact, archaeometallurgy offers us, among its applications, studies of invention, innovation, and dissemination in modern times, as if there were no fundamental differences in the processes of creation between industrial and pre-industrial societies.

General Information About the Applied Techniques

Archaeometallurgy studies all the processes derived from obtaining old metal parts. These can come from mining, reduction and smelting furnaces, mold processes, cold or hot forging processes, and finishing processes (decoration, patina, cementation, etc.). This research field is also interested in the current state of these metal parts, studying:

- The geochemical environment of the soil in which they have been found.
- The characterization of the corrosion layer.
- The observation of the structural aging of the metal or alloy.
- The variation of mechanical properties over time.

Studies Involved in Each Archaeometallurgy Research

- Metallographic study (optical microscopy, scanning electron microscopy, high resolution scanning electron microscopy, transmission electron microscopy, electron microscopy).
- Chemical composition with portable X-ray diffraction spectrometer for non-ferrous materials.
- X-ray diffraction in laboratory equipment.
- Mechanical tests (mechanical traction, bending, compression, hardness, micro hardness, impact Charpy); obviously, these tests are performed only when they are previously authorized by the competent authority.
- Non-destructive tests (radiography, ultrasound, penetrating inks).

Applications

- The metallographic and mechanical studies of the archaeological pieces examined provide valuable information on mining forms, old extractive metallurgy, casting and casting processes, hot or cold forging, thermo mechanical treatments applied, surface finishing treatments, provenance, and the age of the piece itself is achieved indirectly through the timeline of the metallurgy evolution and its techniques processes.

Metallurgy, Ways to See and Value

The claim that technologies are socially constructed has become axiomatic among historians and sociologists of technology since the early 1990s [1]. Heather Lechtman (archaeologist and materials engineer) was one of the first advocates of this view [2]. She argued that in different regions of the world distinctly different technological trajectories could be recognized, so she coined the term “technological styles.” The essentially identical concept of “technological choices” was developed independently in France [3–5].

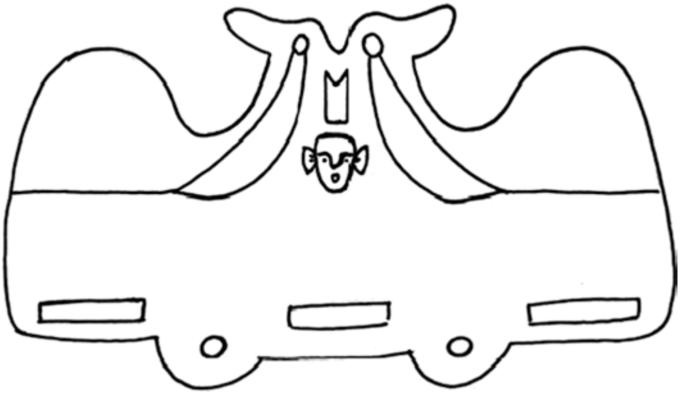
Archaeometallurgy provides some of the best examples of precapitalist technological styles. For example, historical documents and ethno-archaeological field research show that in many African societies iron smelting was understood exactly as equivalent to gestation and birth, illustrating the symbolic appropriation by men of the generative powers of women. The oven was a woman, the iron flower that grew in the oven was the fetus, and her male assistants were simultaneously husbands and midwives. In some cases, this equivalence was explicit, with furnaces modeled as women's bodies or bellows as male genitals. More commonly, it was implicit in the behavior of ironworkers, who were often forbidden to have sex during the process and were often isolated in the foundry fields to ensure compliance [6, 7].

Another example of this is given by the *Mapuche* people in South America who, through the jewels of their well-known *Mapuche* Silverware, sought a link with the Universe, how human life and other philosophical ideas are generated, and embodied them in the making of their jewels. The *Mapuche* people, similar to any other people since time immemorial, tried to understand where life came from, how it was generated, who made life possible here, who generated the *Mapuche* human life, the relationship between the *Mapuche* being and the other elements of nature, who administers and controls the human race in all their spiritual movements.

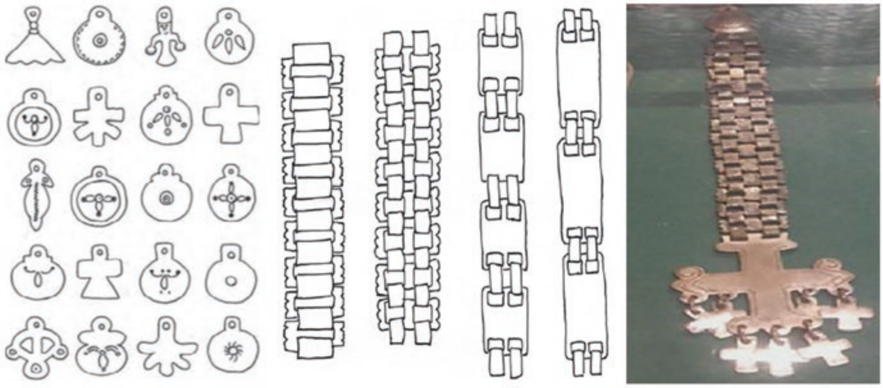
For the First idea of how life was generated, the ancients say that there was a moment in time when the universe was in complete disorder and chaos. Large explosions followed each other, the stars collided, until a great *newen* (spiritual force) appeared, imposed itself on other *newenes* in the cosmos and ordered it, also resulting in the generation of life in the *Wajontu mapu* (earth globe). This great *newen* that can generate life has a dual duality: it has the two energies—the positive and the negative—these are not opposed, but on the contrary they are complementary; they are in reciprocity and in balance. It also has both sexes, the masculine and the feminine, which is the only way to generate life; this aspect is of real importance because it supports the *Mapuche* religious structure in terms of its authorities.

This great *newen* is called *El Mapun* and is a great cosmic energy. The generation of life in the *Wajmapu* is carried out considering three elements: the energies of the cosmos in particular that of the *ahtü* (sun), the energies of *ko* (seas, lakes, and rivers), and the energies of the plain earth or *Naüq Mapu*. Also, these three energies must be in balance, complement, and reciprocity, so that these conditions are maintained over time; it is essential to develop religious spiritual activities that the *Mapuche* human being carries out such as prayers and thanks. Thus, the life of nature appears in the *Wajontu mapu*: time and years, day and night, moon, thunder, lightning, rivers, lakes, mountains, snow, wind, rains, heat, trees, plants, animals, fish, insects, and birds also appear. Each and every one of them with energies and sexes for their multiplication, all distributed in the plain of the *Wajontu mapu* (globe) with defined spaces and with owners, the g*eh* [8] (Graphic 1.1).

- **The *Mapuche* philosophy and spirituality are condensed in the *Keltatuwe*.**



Graphic 1.1 How life was generated



Graphic 1.2 Diagrams of various known pins in the *keltatuwe*, chains of different types used in *keltatuwe. Photo 1* *Keltatuwe* belonging to the Aboriginal collection of La Pampa and Patagonia from La Plata National Museum of Natural History, Buenos Aires Province, Argentina

When we see the different jewels of the *Mapuche* Silverware, we must stop to analyze the *Keltatuwe* (pin) because the contents of the idea of how life in general appears in nature are expressed in its upper plate (Graphic 1.2).

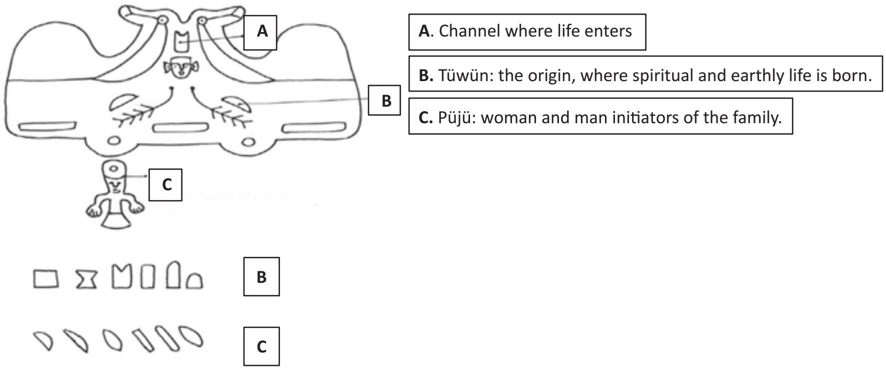
The *Mapuche* authorities: *Fücha Chaw, Kushe Ñuke, Mür* (parity), and *xürgen* (symmetry) are principles of life, not just opposite or complementary, intrinsically necessary and the origin in themselves. *Meli Newen, Weche,* and *Üjcha* express experience, wisdom, youth, strength, vigor, fertility, and fertile creation, all of which give the *Mapuche* religious basis for the construction of future jewels. The *rüxafe* managed to define a design that considered these elements as duality and determined that it was a bird's body with two heads, which are sometimes facing each other and other times they are looking in opposite directions. The reason why sometimes it is represented as a bird and other times as a large fly is determined to be because they are the only ones that can fly so high into the cosmos and that can disappear from our view demonstrating the infinity of the universe.

The *Mapuche* ancestors created the design of the top plate of the *Keltatuwe* based on harmony, on balance (it is a symmetrical piece); sometimes it has the figure of a face with human forms, which represents *Elmapun* (sometimes he has big ears). It is noteworthy that although the *Mapuche* jewelry is best known for their work in silver, this was not the only material that they worked with. Various studies indicate that they started working with copper and that although they went through various stages of development and improvements in their silver works, they never abandoned copper [9]. (See Chap. 12: Case Studies on Reverse Engineering of Ancient Metals, “Border Archaeometallurgy: Pieces Found in the *Mapuche* Cemetery of Cerro Mesa, Malargüe, Mendoza.”)

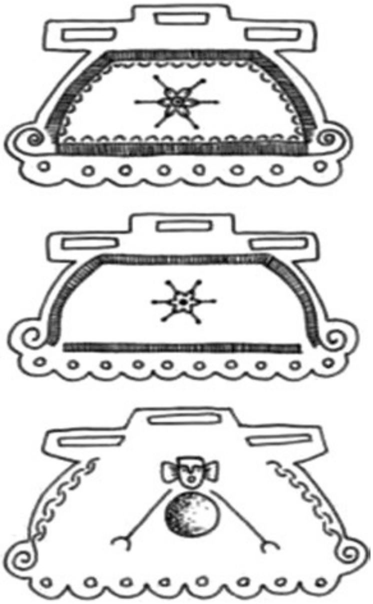
For the Second idea of how the *Mapuche* human life was generated, the ancients said that a long time passed and in the sky there was a very sad star who cried because she was alone, *Elchen* (who is a cosmic spiritual force) takes the sad star in his hands, and transforms her into a woman and deposits her on the *naüq* (surface), then takes another star, transforms it into a man and places him next to the woman to accompany her, so *Elchen* deposited several couples in different places where the sun rises.

These spiritual places are called *tuwün* (the origin); there the spirits recreate, reproduce, and define the roles and functions. The channel of human life comes through women, and when all *Mapuches* are born they have a duality: an organic-biological part and a spiritual part; the spirit in life is called *püjü*. In the top plate of the *Keltatuwe* (pin) all these contents of the *Mapuche* philosophy are expressed. The various incisions have shown this, the channel of life in general has different forms (see Graphic 1.3).

The incision that represents the *tuwün* has several lines that join them to another line that has a beginning and ends in two holes in which hang figures called *püjü*



Graphic 1.3 Family founders’ distribution and their spirits



Graphic 1.4 Diverse designs of the bottom plate of a *keltatuwe*

that represent the initiators or founders of the families in the *Naüq Mapu* (the plain of the *Wajmapu*); these family founders remain in the collective memory and their spirits are represented on this top plate of the *Keltatuwe* (Graphic 1.4).

Archaeometallurgists have long been aware of spatial and chronological differences in the value of metals and have often tried to link this with their colors [10–12]. The Eurasian obsession with gold and silver began in the Balkans around 5000 BC and was gradually adopted throughout the continent, except in the central plain of China, where these metals were ignored in favor of tin bronze [13]. Gold and silver were also highly valued in Egypt, Nubia, and Carthage, but neither gold (Au) nor silver (Ag) was used south of the Sahara (except in Nubia and Eritrea pre-axumite/axumite, which had commercial ties with the Mediterranean) until the Islamic era, when sub-Saharan Africa became the main source of gold for Eurasia. At this point, African elites that emerged to control the gold trade adopted the use of gold as a marker of distinction [14–17]. The absence of gold from previous archaeological sites cannot be attributed to ignorance because trajectories or currents could be analyzed with little effort, and Iron Age Africans certainly had the technology to melt it. However, as [7] has so convincingly demonstrated, they largely preferred the red color of unalloyed copper, which they largely reserved for ornaments, using iron for weapons and tools.

Gold was the first metal used in South America, and subsequently elaborate chemical treatments were invented to develop a variety of surface colors in the *tumbaga* bodies (copper, gold, and silver alloy) [18–20]. The symbolic meaning of these colors in prehistoric contexts is unknown, but there is an ethnographic link between metallurgy and cosmology in Colombia, where the symbolism of the *Tukanoan* color has approximately 30 shades between yellow-white (the sun, male power) and copper red (the waning moon, female generativity defined as the ability of the adult to commit to the establishment and guidance of the next generation). Ideally, "the sun fertilizes a bright new moon, which then passes through a sequence of yellowish, reddish and coppery phases that are compared to the embryonic development process" [21]. The triad of silver, copper, and gold metallurgy was extended by sea from Ecuador to Mexico [12] where metals were used almost exclusively for ornaments.

One of the most suggestive features of pre-Hispanic Andean metallurgy is that the technical procedures that were developed and the gradual increase in production over the centuries were not driven by practical considerations. It was not the intention of the ancient artisans to obtain more efficient and lasting tools or more powerful weapons but rather to put forth effort, inventiveness, and focused creativity for the achievement of pieces with certain aesthetic qualities, while paying close attention to certain cultural norms—not only physical and chemical—for the transformation of materials. The processing of the raw materials involved cultural principles that the original peoples used to order and structure their reality in a similar way to what they did with language, achieving a connection between heaven and earth.

The Symbolic Power of Metals

In the last part of this chapter—Archaeometallurgy—special reference is made to the Andean metallurgy because this work focuses on the metallurgy developed by native Latin American peoples and also refers to the precapitalist infrastructure.

The appreciation for metal goods not only resided in the energy of work and the technical knowledge applied to production but also in the connections that metallurgical activities and their products maintained with the rich Andean mythical universe, many of whose elements remain current to the present day. In Los Andes, nature was conceived as an integrating totality in which men connected with these entities following the principles of reciprocity that prevailed in everyday relationships.

Respectful activities with them and offerings were the way to win their will and collaboration in personal or community ventures. Thus, the products of nature can only be used by applying the appropriate techniques and rituals. Nature, rather than exploiting itself, was cultivated in all its aspects and man acted as a midwife of its fruits.

For example, in Inca times, the mountains that housed metal deposits were especially revered and received sacrifices and offerings. The mines were considered *huacas*, (see Chap. 12: Case Studies on Reverse Engineering of Ancient Metals: "Gold Artifact Production During the Central Andean Formative Period: New Evidence from Chavín de Huántar and Caballete, Perú"), that is to say sacred places, and with the arrival of the Spaniards, this term became synonymous with hidden treasure. The miner was linked intimately with the land "*Pachamama,*" the mineral was treated as another lively element of nature, which was reproduced, raised, and harvested just like crops. Even today, ceremonial procedures continue to be practiced, considering the miners responsible for the life of the mine and its products.

The ethnographic and archaeological information available from Los Andes related to ceremonial activities around metallurgical production is unfortunately very scarce; however, the creative process required the consent of supernatural powers and that played a very important role in several areas [22]. According to elements of the Andean worldview and the information of societies from other continents, they give rise to the idea that in pre-Hispanic times, smelting events were surrounded by significance and mysticism that brought them closer to the supernatural spheres. Today's traditional goldsmiths retain behaviors that have nothing to do with technical procedures but are fundamentally linked to deep conceptions rooted in the past. In San Pablo, department of Cuzco-Peru, the goldsmiths refuse to recast old pieces because they contain the souls of their previous owners and could punish them, and because Tuesdays and Fridays are considered evil days for metals, they should not face foundry tasks on these days [23].

With the arrival of the industrial society, the idea triumphed that the metalworking industry should be motivated by the desire for progress and that it was governed by the criteria of efficiency and utility. Then, the metallurgical work of yesteryear was reduced to a long process of experimentation and mastery of techniques and materials, from the simple to the complex determined by the laws of physics and chemistry and totally separated from the social context. However, Andean events are far from responding to a natural evolution of metallurgy, but they respond precisely to deeper imperatives, intimately linked to culture and in a particular way to the future of the cosmos. Although in their jewels the original Andean peoples unknowingly complied with the laws of physics and chemistry known to everyone today, in their creations this important fact was implicit. Adding to our delight and utmost admiration for the abilities of the ancient metal craftsmen, in the *Mapuche* language: the *rüxafe*.

It was the structural elements of societies that established the requirements to which the qualities of metal objects should be adjusted and the ways in which they should be processed. Andean metallurgy could be said to place both the technical and the symbolic on an equal footing, giving rise to goods full of meaning that transcends its apparent functionality.

At this stage, copper represents the material that enabled not only developing a technology with its own characteristics in the ancient world but also allowed expressing the most intimate foundations of the Andean universe [24, 25].

Conclusion

In the past 50 years, archaeometallurgy has become a well-integrated and highly productive interdisciplinary field of study, but archaeometallurgists have not yet managed to convince most archaeologists of the relevance of their work, perhaps due to the existing separation between what are social sciences and exact or hard sciences where precisely it is framed: engineering. Many of the leading figures in the field of archaeometallurgy today were trained in disciplines such as geology, chemistry, and materials science and have tended to focus on the technical problems of reconstruction and provenance. Another reason, of no less importance, is that archaeometallurgy is now large enough to support a series of specialized conferences, with the consequence that much of these works tend to be presented there or at specialized meetings of archaeological scientists. A third important reason is that some of the most interesting work has been done in East Asia, Africa, and Latin America and is rarely summarized for academics who are not specialists in those areas.

Thus, stemming from engineering and materials science, the great development in increasingly sophisticated laboratory equipment, including portable ones, obviously put in the forefront those who have been trained in the branches of engineering, generating an extraordinary development niche and future knowledge to unveil.

References

1. MacKenzie, D., Wajcman, J.: The Social Shaping of Technology, 2nd edn. Open University Press, Buckingham (1999)
2. Lechtman, H.: Style in technology—some early thoughts. In: Lechtman, H., Merrill, R. (eds.) Material Culture: Styles, Organization and Dynamics of Technology, pp. 3–20. West, New York (1977)
3. Cresswell, R.: Transferts de techniques et chaînes opératoires. Tech. Cult. **2**, 143–163 (1983)
4. Lemonnier, P.: Elements for Anthropology of Technology. Museum of Anthropology, University of Michigan, Ann Arbor (1992)
5. Lemonnier, P.: Technological Choices: Transformation in Material Cultures Since the Neolithic. Routledge, New York (1993)
6. Childs, S.T.: Style, technology and iron smelting furnaces in Bantu-speaking Africa. J. Anthropol. Archaeol. **10**, 332–359 (1991)
7. Herbert, E.: Iron, Gender and Power: Rituals of Transformation in African Societies. Indiana University Press, Bloomington (1994)
8. Antinao, J.P.: Sociedad y Cosmovisión en la Platería Mapuche. Universidad Católica de Temuco, Temuco (2010)
9. Campbell, R.: Entre el Vergel y la Platería Mapuche: El trabajo de los metales en la araucanía poscontacto (1550-1850 D.C.) (2004)
10. Herbert, E.: Red Gold of Africa: Copper in Precolonial History and Culture. University of Wisconsin Press, Madison (1984)
11. Hosler, D.: The Sounds and Colors of Power. MIT Press, Cambridge (1994)
12. Hosler, D.: West Mexican metallurgy: revisited and revised. J. World Prehist. **22**, 185–212 (2009)

13. Linduff, K., Mei, J.: Metallurgy in ancient Eastern Asia: retrospect and prospect. J. World Prehist. **22**, 265–281 (2009)
14. Austen, R.: Trans-Saharan Africa in World History. Oxford University Press, New York (2010)
15. Huffman, T.: Mapungubwe and Great Zimbabwe: the origin and spread of social complexity in southern Africa. J. Anthropol. Archaeol. **28**, 37–54 (2009)
16. Killick, D.: Cairo to Cape: the spread of metallurgy through Eastern and Southern Africa. J. World Prehist. **22**, 399–414 (2009)
17. Killick, D., Fenn, T.: Archaeometallurgy: The Study of Preindustrial Mining and Metallurgy. Annu. Rev. Anthropol. **2012**, 559–575 (2009)
18. Lechtman, H.: A pre-Columbian technique for electrochemical replacement plating of gold and silver on objects of copper. JOM. **31**, 154–160 (1979)
19. Lechtman, H.: Andean value systems and the development of prehistoric metallurgy. Technol. Cult. **25**, 1–36 (1984)
20. Lechtman, H.: Technologies of power: the Andean case. In: Henderson, J.S., Netherly, P. (eds.) Configurations of Power, pp. 244–280. Cornell University Press, Ithaca (1993)
21. Reichel-Dolmatoff, G.: Things of beauty replete with meaning metals and crystals in Colombian Indian cosmology. In: Furst, P.T. (ed.) Sweat of the Sun, Tears of the Moon: Gold and Emerald Treasures of Colombia, pp. 17–33. Natural History Museum of Los Angeles County, Los Angeles (1981)
22. Shimada, I.: Aspectos tecnológicos y productivos de la cultura Sicán, costa norte del Perú. Gaceta Arqueológica Andina **13**, 15–21 Lima (1987)
23. Valencia, A.: La platería tradicional en un pueblo del sur del Perú. In: Ravinés, R. (ed.) En Tecnología Andina, pp. 535–554. Instituto de Estudios Peruanos, Lima (1978)
24. González, L.: Recuerdos de bronce. La metalurgia prehispánica tardía en el noroeste argentino, in *Ponencia a 51° Congreso Internacional de Americanistas*, Santiago (2003)
25. González, L.: De texto catálogo “El arte del cobre en el mundo andino”, in *El arte del cobre en los Andes Prehispánicos: Historias de poder, brillos y colores* (2004)

Chapter 2
Non-ferrous Metals of Antiquity: Historical Copper and Copper Alloys

Patricia Silvana Carrizo

Metals represent, like all other materials, a tool, an opportunity that has historically been used by those who possessed or took possession of material resources and practical skills: they were of direct importance to the cultures that used them, but also in relation to use and knowledge they acquired of neighboring populations. In the different areas of the vast Andean territory, the trajectory that followed metallurgy acquired its own peculiarities, but everywhere the main impulse for production and for technical innovation in the Andes was connected to social status and the religious sphere, where metals served as a means to bridge this world with the supernatural [1], unlike in the Old World, so it is no accident that advances in technical sophistication and in the scale of production went hand in hand with the growth of organizations whose sociopolitics became increasingly extensive and complex and were legitimized through religious structures. As Heather Lechtman has pointed out, Andean metallurgy was, first and foremost, a communication technology [2].

There is no place or date of birth of metallurgy: the discovery of metals and their alloys traditionally dates back to random events in a region; the specific circumstances in which the "discovery" of metals in the Andes occurred are unknown. Ancient settlers may have been attracted to certain types of rocks with particular qualities, such as specific weights or bright colors [3].

Generally speaking, human discovery of the useful properties of metals, specifically gold, silver, and native copper and meteoric iron, for creating ornaments and tools is likely connected with the natural occurrence of metals in the metallic state (native metal). The raw metal available in nature had to be molded to its desired shape, by means of elementary mechanical machining, hammering, bending, drilling, polishing, or more sophisticated heating, melting, and casting techniques. A

P. S. Carrizo (✉)
Archaeometallurgy Area/Metallurgy Laboratory, National Technological University,
Mendoza, Argentina

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_2

metal hardened by repeated hammering could be molded into blades or tips that could be cut or drilled with great effectiveness [4].

In the sense of metal hardening, copper works were carried out, in the Lurín Valley (Lima), called the initial period (2000–900 BC), there are copper and gold sheets in contexts dated between the 13th and 10th centuries BC, these very thin sheets of copper were made by hammering native copper and adhering very thin sheets of gold also by hammering. These findings highlight the deveopment of metallurgy in the northern Andes and the process by which it evolved over subsequent centuries, that is, the manufacture of objects, even three-dimensional ones, from the elaboration of hammered sheets. The metal was treated as a solid, leaving aside its liquid condition under the effects of temperature [5]. Further, the association of metals with the ceremonial spheres of society was also established. The foundations of the Andean worldview and the principles that regulated the future of the world were expressed through these materials, the methods by which they were processed, and the prescriptions for their use; in addition, they represented a means for materializing the ideology that governed daily life. One of the most suggestive features of pre-Hispanic Andean metallurgy is that the development of technical processes and the increase in the scale of production over the centuries was not driven by practical issues but instead concentrated people's creativity and efforts on fabricating pieces with esthetic qualities, devoting considerable attention to cultural norms, in addition to physical and chemical norms for the transformation of materials, since cultural principles were very immersed in the methods used to process raw materials. The production of metal articles was the most complex technological undertaking that pre-Columbian societies faced, both for the effort invested in work and for the technical knowledge and training of artisans. It involved a long sequence of tasks beginning with the detection and acquistion of metal ores, their preparation by crushing, smelting, and, finally, the manufacture of objects [6] (Fig. 2.1).

Eventually exposure to fire, at high temperatures, eliminated a material's ability to harden by hammering and restored ductility: this may be considered the first step in the birth of metallurgy. The metallic material's prolonged exposure to fire could lead to its melting, which would resolve in the desired ways; this is the starting point

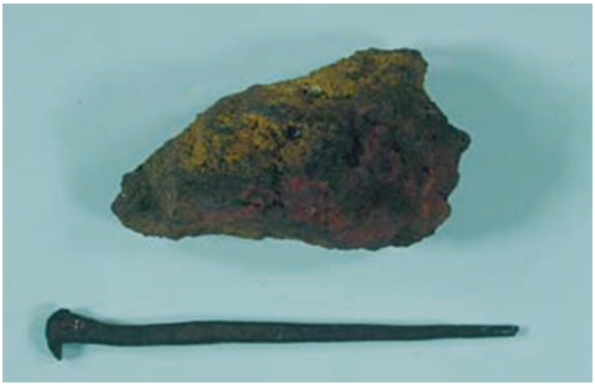


Fig. 2.1 From ore to finished product

of casting techniques applicable to both bulky objects and small jewels [7]. Copper, which was called *anta*, served, instead of iron, to make weapons of war, knives, carpenter's tools, pins to hold feminine mantles, hoes to dig the earth, and hammers for silversmiths. For these reasons, they considered copper very valuable since for them it was more useful than gold and silver and the demand for it was greater than that for any metal [8].

However, the most important source of metals is not a native one: with the exception of gold, the seven metals known since ancient times (gold, silver, copper, iron, tin, lead, and mercury) are present in oxidized form to produced minerals distributed in more or less accessible deposits to exploit. The extraction of metals from minerals, known as extractive metallurgy, represented an obstacle that was first identified and then overcome to make available large amounts of metal. The Andean region constitutes an area of the planet endowed with a great variety and richness of metal ore deposits. However, the spatial distribution of deposits is not regular, which means that not all pre-Hispanic communities that populated the extensive landscape of the Andes had access to the same minerals. This led to the fact that in certain areas, metallurgists developed specific types of alloys unlike those in other areas and that metal ores were transported long distances by caravans of llamas. Therefore, findings are known, especially in the highlands of Bolivia, northern Chile, and northwestern Argentina, where gold and its alloys do not seem to have been emphasized and bronze (copper-tin alloy) was privileged; it is possible that these differences not only accorded with certain cultural criteria mentioned earlier but also led to a dissimilar distribution of the minerals used.

From a chemical point of view, metal must be reduced in a stable oxidized form by the oxidation of carbon to carbon oxide or carbon dioxide, an operation that is carried out at high temperatures by burning wood or coal (pyrometallurgy): the carbon from these two sources, therefore, simultaneously serves as a chemical reagent and as a fuel. The operation is much easier to carry out under conditions in which the oxidized form is less stable, the reaction temperature is high, and the reagents and final products are more fluid.

In nature, some metals can be presented in more or less pure form, a state that is known as *native*. In this case, they can be worked directly to shape objects. Copper can be found in the native state, such as in veins or plates between rocks, sometimes in high volume. When hammered it can form sheets that are then trimmed or folded to obtain the desired instrument. In the case of copper, the hammering lead to hardening, and then the material becomes brittle. This requires heating events, an operation called annealing, to restore ductility. However, in most cases copper is present in various chemical combinations, each corresponding to a specific mineral. The oxidized forms present in real minerals are of a very varied nature (oxides, hydroxides, carbonates, silicates, sulfides) with different levels of oxidation, and the metal to be extracted is barely present only in a pure mineral: primitive mining activity likely provided a set of different polymetallic minerals to identify, separate, and eliminate with more or less effective techniques. To synthetically describe the operations of extractive metallurgy, it is necessary to simplify the table of the numerous alternatives, idealizing the mineral as if it were a pure oxide and with a single level of oxidation, since copper will preferably be referred to as the starting mineral. Copper oxide (CuO) is taken as a reference, and the final product is pure copper. It is possible to assess the difficulty of obtaining the metal using thermodynamics and the Gibbs function. The variation of the standard free energy (ΔG_0) of the oxide formation measures its stability: the more negative the value, the more stable the oxide will be, and the more expensive the metal extraction will be. Table 2.1 shows the value of ΔG_0 of the seven metals of antiquity (plus some unknown metals at those times), under conditions of ambient temperature; in the second column, the melting temperature (T_m) of the pure metal is reported. If the melting temperature of the oxides and the metal is not reached, the thermodynamic reference remains valid, but the reaction proceeds very slowly. Metals are classified by decreasing values of ΔG_0, that is, ordered from the high instability of the gold oxide (ΔG_0 positive, therefore, unstable oxide and metal available in nature in a metallic state) toward the stable ones such as iron and tin. The order of the table follows the ease with which metals deteriorate and wear out from corrosion. The third column of Table 2.1 shows a reduction in temperature by pyrometallurgy (T_p): it represents a conventional temperature necessary to reduce carbon oxide with the formation of carbon monoxide (CO). This temperature is linked to the stability of the oxide and loses its importance as it moves away from higher temperatures.

The sequence in which the four metals (Au, Ag, Cu, Fe) are identified follows the decrease in ΔG_0, as shown in Table 2.1. Mercury, lead, and tin are examined for their use in the manufacture of the most widespread objects in ancient times, such as ornamentation and utensils, and since there are objects made with lead in cultures prior to the Incas, tin was part of the tin-bronze alloy and mercury was used as pigment. The melting temperature (T_f) column is less selective because gold, silver, and copper fall in a homogeneous field, easily practicable with primitive ceramic kiln techniques, while iron would take a few millennia of practice before building appropriate furnaces that could supply cast iron. The “difficulty” in the extraction of metals from minerals was the discriminatory factor for the development of the

Table 2.1 Properties of metals and their oxides

Metal/oxide	**ΔG_0 (kJ/moles O_2) at room temperature**	**T_m melting metal temperature (°C)**	**T_p pyrometallurgy temperature (°C)**
Au / Au_2O_3	+100	1063	–
Ag / Ag_2O	−20	961	–
Hg / HgO	−110	-38	–
Cu / CuO	−280	1083	–
Pb / PbO	−380	327	–
Ni / NiO	−430	1455	–
Fe / FeO	−520	1538	700
Sn / SnO_2	−540	231	650
Zn / ZnO	−640	420	950
Ti / TiO_2	−850	1670	1650
Al / Al_2O_3	−1050	660	2000

metallurgy of single metals relates to the high melting temperature of iron with respect to that of copper, and this is confirmed for the diffusion of copper and its alloys instead of iron, despite the greater availability of iron minerals compared with copper, although iron was used as a flux for arsenical copper alloys on the north coast of Peru [9].

As for the mechanism that would have favored the invention of the different pyrometallurgical processes, we enter the field of scientific hypotheses and fantastic reconstruction. Perhaps at some point and accident, the first metallurgist noted that showy copper ores, when subjected to high temperatures, produced a different material, which was liquid first and then solid when cooled. Centuries of experience would have allowed the ancient Andean settlers to establish criteria for determining the locations where mineral deposits were concentrated. There is very little evidence of pre-Hispanic tillage in the Andes; among the reasons for this is the fact that European conquest led to reoccupation of the mines, with the consequent destruction of their ancient vestiges. Indigenous miners, equipped with stone hammers and wooden barrets, rather than open large galleries, concentrated their efforts on following the path of valuable veins. In the regions of the landscape where mineral deposits surfaced, trenches and tunnels were dug [10].

One of the hypotheses on the invention of pyrometallurgical processes could relate to the random presence of minerals, such as refractories, present in furnaces for ceramic cooking or in the pots of the food to be cooked. It is also conceivable that the discovery of the reducibility of metallic minerals and the subsequent development of extractive metallurgy processes were repeated and forgotten several times and in different places due to the presence or simultaneous disappearance of the essential elements.

Copper

Copper actively participated in the dissemination of the religious conceptions of pre-Hispanic societies because of its intrinsic physical qualities, such as brightness and color, the latter being modified through alloys. Owing to its plasticity, it also allowed for the creation of objects, both by plate embossing and casting in molds, with significant representations of sacred messages. Additionally, its production involved applying a particular level of technical knowledge and training, which were probably restricted to certain sectors of society. Pre-Hispanic metallurgists, rather than mere artisans, were intermediaries between humans and deities, possessors of both technical and esoteric knowledge, and this double status was exploited by the political-religious elites who ruled the destinies of the communities that populated the Andean space. The control of the production and social distribution of goods was a strategic tool for the emergence and expansion of the complex social organizations of the Andes. As a result, the former metallurgists were able to develop in copper some of the highest expressions of pre-Hispanic art (Table 2.2).

Table 2.2 Main copper minerals available for pre-Hispanic metallurgists

Mineral	Composition	Color
Cuprite	Oxide—CuO—(88%Cu)	Red
Azurite	Carbonate—$Cu_3(OH{\cdot}CO_3)_2$—(69% Cu)	Blue
Malachite	Carbonate—$Cu_2(OH_2.CO_3)$—(57% Cu)	Dark green
Brochantite	Hydroxysulfate—$Cu_4(OH)_6SO_4$—(56.2% Cu)	Green
Chrysanthemum	Phyllosilicate—$(Cu, Al)_4H_4(OH)_8Si_4O_{10}{\cdot}nH_2O$—(24%Cu)	Green
Chalky	Sulfur—Cu_2S—(79%Cu)	Gray
Bornite	Sulfur—Cu_5FeS_4—(34% Cu)	Red
Calcopyrite	Sulfur—$CuFeS_2$—(34% Cu)	Golden
Tennantite	Sulfur—Cu_3AsS_3—(38% Cu)	Greenish gray
Enargite	Sulfur—Cu AsS_4—(48% Cu)	Purplish gray
Atacamite	Halide—Cu_2Cl $(OH)_3$—(59% Cu)	Green
Tetraedrite	Sulfur—Cu_3SbS_3—(24/45% Cu)	Greenish gray

Working only with reference to copper, a series of events can be formulated, without defining where and when, that led to the birth and initial development of metallurgy according to a chronological order: (1) use of copper ores for ornaments (e.g., malachite, turquoise) or as pigments (e.g., azurite); (2) collection crushing and milling of native copper; (3) cooking of crushed native copper until it is molten; (4) collection, preparation, and reduction of "oxide" type minerals; (5) roasting of sulfide type minerals for production of oxides; (6) processing of complex sulfides of "chalcopyrite" type; (7) recovery of gold and silver from copper. The first two phases do not require the use of fire, which is indispensable for the others; the last stage should not necessarily be later than the previous ones [11].

Extractive metallurgy came into being only at the fourth event, and this will be our point of departure. For the processing of the mineral, prior to its smelting, the extracted minerals had to be reduced to small fragments, not only to facilitate the physical-chemical reactions that would take place at high temperatures but also to separate the sterile rock, called a bargain. In many cases, milling operations were carried out with heavy stone hammers similar to those used in mining. Archaeological investigations have identified spaces reserved for the processing and accumulation of minerals, called courts, and that usually present a kind of flat stone tiling [12]. The largest indigenous device for mineral milling was the *maray*. Although it had many variants, the basic model was formed by a large rock, with heights ranging between 0.85 and 1.50 m, sometimes in the shape of a pyramidal trunk. Its convex base allowed it to move by rocking using a wooden lever that was fixed at the top. The *maray*, also called *quimbalete* or *batán*, rested on a flat rock on which the ore to be crushed was placed [13].

Figure 2.2 shows a combustion reaction of carbon, contained in a piece of coal, to form carbon monoxide, CO (in fact, CO_2 is also formed, but this does not matter to us at the moment) under the action of oxygen flow. Combustion produces heat, and hot combustion gases rise. Copper minerals of the oxide type are true oxides,

Fig. 2.2 Combustion of C to CO

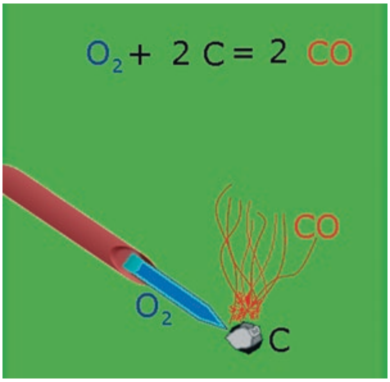
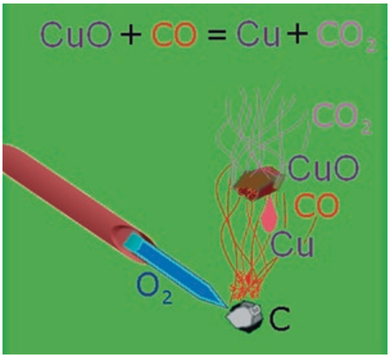


Fig. 2.3 Reaction between CO and Cu with molten metallic copper formation



such as Cu_2O cuprite (88% Cu) and CuO tenorite (79.9% Cu), but also hydrated carbonates that can easily be transformed into high-temperature oxides.

In Fig. 2.3 the simplified combustion reaction is proposed in order to be able to explain the process that occurs between copper oxide (schematized as everything and only CuO) and a flow of carbon monoxide (CO). The reaction that takes place, if the temperature is high enough, leads to the formation of metallic copper, represented by a drop of molten metal that pours down and the hot carbon dioxide (CO_2, gas) that evolves or rises towards above.

In the presence of another carbon (Fig. 2.4), CO_2 is transformed into CO. By superimposing another mineral and other coal and blowing from the bottom, a gas flow (cold oxygen that converts to carbon monoxide and hot carbon dioxide) is generated that rises from the bottom up and while in countercurrent a flow of mineral, coal, and metal that falls to the bottom of the vessel.

The vertical flow can be usefully maintained in a vessel or vessels capable of collecting reactants and reaction products and thus avoiding the dispersion of the heat produced by combustion since this heat is so necessary for the effective performance of the reactions: it is the diagram of a metallurgical furnace blown from below and fed from above, proposed in (Fig. 2.5). The furnace must be built or

Fig. 2.4 Formation of newly available CO for further reduction

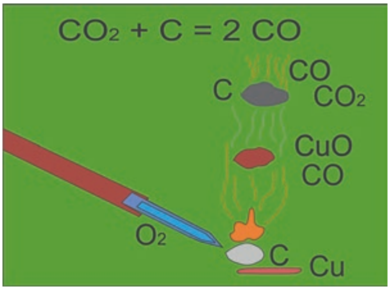
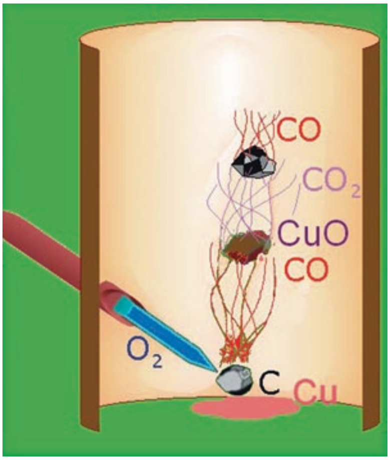


Fig. 2.5 Principle of operation of an oven by pyrometallurgy loaded from the top and insufflated from the bottom



internally lined with refractory stones capable of withstanding the high temperatures reached.

In the cases proposed in the figures, coal is completely converted into gas, and oxide produces metal and gas. The reality is much more complex and “dirty”: if air composed of four-fifths nitrogen and only one-fifth oxygen is insufflated, coal transports moisture and organic products and leaves an ash residue; the mineral is never pure but contains other components that can undergo extraction reactions and partly form slag, an omnipresent and indispensable component of each metallurgical process. The ancient metallurgist, who proceeded only empirically, was able to treat a very specific type of mineral, one available locally, on the basis of which experience and knowledge were accumulating and being transmitted from generation to generation [14].

Even when mine ore has been properly prepared and reduced to small fragments, it usually arrives in the smelter container or vessel accompanied by remains of the rock in which it was trapped. These remains can hinder reduction operations or be incorporated into molten metal, resulting in a poor-quality product. To eliminate them, fluxes are used, which are materials that at high temperatures combine with unwanted substances to form slags. Pure metals usually have a very high melting point, copper's being 1083 °C. However, additional elements in ores generally contribute to lowering the melting point, although values are always maintained that require the use of finishing techniques.

Therefore, smelters needed to design adequate structures and procedures to produce high temperatures and provide sufficient fuel, a problem that could play an important role or decisive role than the availability of minerals in metallurgical activities. To melt minerals, under the necessary reducing conditions and temperatures, a large structure is not essential. However, temperatures of 700 or 800 °C will hardly be reached in open stoves, even under optimal conditions, that is, well below the 1000 °C that is necessary for the processes to take place. To remedy the problem, a way had to be found to blow a stream of forced air into the fire, that is, a countercurrent, whereby the old metalworkers breathed combustion air by blowing into tubes or blowers [15], gathered in groups of 10 or 12 around the oven; using copper or ceramic tubes they blew in the air necessary for combustion. This method was used until bellows were introduced by the Spaniards. But the most publicized foundry artifact was the *huayra*, a stove whose name is due to the fact that it took advantage of the winds to function and apparently there were several models, but all responded to the same principle of operation. The simplest version consisted of a low turret of accommodated stones leaving holes where the wind penetrated. A second, more advanced, version incorporated clay to fix the stones of the walls. The third version, which was portable, consisted of ceramic vessels of circular section, wider at the top than at the base, about 1 m high and approximately 0.40 m in diameter. The body had numerous holes to allow air to enter and fuel to combust. Apparently, each hole had a flange where embers were placed so that the air entered preheated, thereby achieving great energy savings in the combustion process and better yields. Among the descriptions of this apparatus according to the chroniclers is that of Baltasar Ramírez from 1597 [16]. The proposed scheme, described previously, can justify the production of a limited amount of metal, articulated in the ignition and preheating phases of the furnace, loading with coal and ore, and subsequent shutdown of the furnace with the consequent extraction of molten metal. But continuous operation was also possible by loading the raw materials without interruption from the mouth of the oven, pouring the molten metal from the bottom, and blowing air through the blowers that resist the high temperatures inside the oven. In experimental archeometallurgy experiments, the reduction of malachite with charcoal is easily and quickly achieved in furnaces blown with hand bellows.

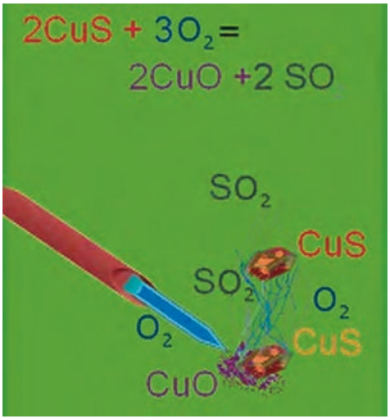
With regard to fuel, although charcoal was the ideal fuel for metallurgical work in ancient times, due to its high calorific value and declining capacity to dissociate ores, it seems that the Andean smelters took advantage of various products. Several chroniclers mentioned unprocessed firewood, *taquia* breads (*llama* manure), and even resinous shrubs such as *yareta*, *jarilla*, and *ichu*. Other chroniclers also indicate the use of carob, *chunque*, *chañar*, and *Chilean willow* as fuels available for work [17]. As for the crucibles and molds involved in metallurgical operations, they were usually manufactured in ceramics. The basic ingredients, as in pottery, were clay and antiplastic materials, but the functional requirements forced special preparation. While common ceramics begin to melt at around 1000 ° C, refractories must resist higher temperatures and also demonstrate some chemical immunity to the action of hot metal. Refractory finds are frequent in Andean metallurgical activity sites and usually, the pieces are very fractured, perhaps due to the conditions of use to which they were subjected, they tend to show thick walls, thermo-altered surfaces, and adhesions of slag or metal. Crucibles usually take the form of small bowls, and in many cases, they have notches around the mouth, which perhaps were intended to fix green wooden rods with which the operators manipulated the pieces. A type of refractory with special characteristics as disclosed by Niemeyer [18], was a container with thick walls, conical shape, 10 cm high, and with a hole in the bottom, which was complemented by an elongated piece of the same material and who served to plug that hole. According to Niemeyer, the vessel was not designed for the smelting of minerals but to collect or receive liquid metal from an oven and then distribute it to molds, uncovering the bottom hole.

The complex system of this piece, like the "spoons" of modern foundries, highlights the technical capabilities of the Andean metallurgists. There is even a report on the presence of a layer of a whitish substance on the surfaces of refractories, which would have acted to prevent adhesions with molten metal. The cavities of molds and crucibles covered by a white film is a constant in northwestern Argentina, and the analysis performed suggests that the substance would have been prepared with a clay solution of calcined and ground bones.

Once the raw metal is obtained, it is necessary to move on to the manufactured article in finished form. The skills required to achieve the goal are different from those required in extractive pyrometallurgy, and over time, the two concepts have clearly differentiated, even if initially there was considerable overlap between them. As regards the manufacture of metal objects, once the Andean craftsmen obtained molten metal, they made sheets using hammers and anvils, alternating their forging actions with annealing processes, used to restore the ductility of copper. They achieved a high level of mastery in this technique, which was one of their favorite techniques [19]. Their instruments were mostly made of stone and wood, their hammers did not have wooden handles, the instruments were shaped like dice with rounded edges; they were large, medium, and small in size; some were elongated to enabling hammering out concave areas, and such hammers were held with both hands. They also used flat-end cylinders, embossers and polishers, made of highly polished volcanic stones of various colors. These were the tools of skilled craftsmen whose handling required a long period of study to master [20]. The objects were also obtained by casting liquid metal into molds, which could be opened, in one piece, or closed, formed by several removable elements. A special category was "lost wax" casting, used for the production of objects with complicated sculptural or decorative details [21].

It is worth mentioning that the most common copper minerals are not oxides but sulfides, such as calcosine, also chalcocite, Cu_2S (79% Cu), and covellina, also called covellite, CuS (66.4% Cu). The furnace described earlier only works with oxides; therefore, it is necessary to introduce a preliminary stage, already well known since ancient times, called *sulfur roasting*, which transforms sulfides into oxides, producing sulfur dioxide SO_2, so sulfurous ores first had to be transformed into oxides by means of the roasting operation, in which the ore is heated in the

Fig. 2.6 Copper sulfide roasting scheme



open air and the excess sulfur is eliminated as fumes. Figure 2.6 shows a diagram with roasting reactions, which require lower temperatures than those necessary for metal extraction. The sulfide is considered to be ideally composed only of CuS and that the oxide produced is only CuO, these considerations are made in order to simplify the processes that occur. The reaction is exothermic and, once started, provides much lower fuel consumption as the sulfur content is higher. The reaction requires a simpler furnace and must be carried out before the other processes or stages because, if it happened together with those of oxide reduction, it would create numerous problems in the management of the processes, which the old metallurgists would have had a hard time bring under control.

The complication for Andean metallurgists of having to invent a new stage or step of the process to apply to a morphologically diverse mineral seems obviously remarkable and was overcome. Perhaps then, as a possible hypothesis that would have come to their aid, was the discovery of a conformation of the underground copper ore deposit with a core composed of oxides that could be reduced locally on the surface to native copper and that would provide the ore to the ancient metallurgical man. Taking advantage of this type of deposit, the ancient metallurgist discovered over time a starting material with increasingly difficult characteristics from both mineralogical and metallurgical points of view but that was always able to supply the same metal and with the guarantee that it always consisted of copper ores. It should be further pointed out that the most widespread and exploited copper ore in ancient times was a mixed copper and iron sulfide known as chalcopyrite and attributable to the $FeCuS_2$ formula (34% Cu).

From the chalcopyrite, the image of the pyrometallurgical processes is further complicated because the useful part, of the copper present in the pure mineral, decreases to approximately 1/3 and is equal to the iron component, the presence of the iron coming from the chalcopyrite dirties the pyrometallurgical process and represents a garbage that is introduced into the processing cycle; that must be previously overcome before reaching the copper sulphide, to then be able to obtain the oxide that will be sent to the treatment already seen, therefore, it is necessary to separate the ferrous component from the cuprous by roasting. Figure 2.7 shows the

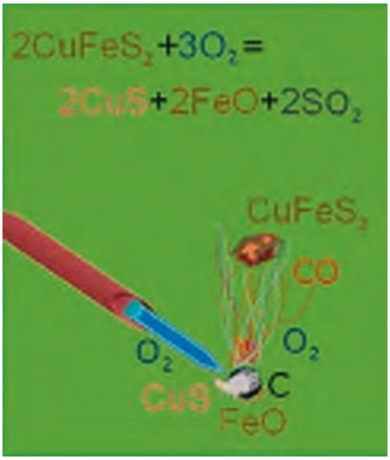


Fig. 2.7 Roasting of chalcopyrite with production of CuS and FeO

pattern of reactions that occur during roasting of chalcopyrite ($CuFeS_2$): a copper sulfide (CuS) and an iron oxide (FeO) are formed that can be easily separated if both are in liquid state. However, iron oxide is not liquid at temperatures of around 1200 °C, traditionally considered as the maximum temperature obtainable in primitive furnaces: it is therefore necessary to add a dividing or precipitating agent like silica (SiO_2) that binds to FeO to generate liquid Fe_2SiO_4 at the indicated temperatures.

This reaction can also occur spontaneously in the contact of the melt with the natural refractories based on silica (SiO_2) and coming from the walls of the old furnaces. The availability of an iron silicate (Fe_2SiO_4, fayalite) as a waste product of copper metallurgy has been seen by some as the occasion of the birth of the steel industry.

Copper Alloys

Having clarified the essential operations of extractive copper metallurgy, some fundamental discoveries of the metallurgy of products remain, first of all, the best performance of alloys compared to pure metals. A simplification, explicitly established, is to consider pure metals, while in reality we are dealing mainly with alloys consisting of a base metal and several components, some useful, some neutral, and others harmful.

Copper in the liquid state has the ability to mix with other metals, producing an alloy that is a material with different physical characteristics in the solid state. It seems likely that the first alloys were produced randomly using polymetallic ores, in particular for alloys composed of copper-arsenic (Cu-As), arsenic unknown as an element and isolated only in the 13th century, and it was widely used in primitive metallurgy and for the own arsenical bronzes, which are copper-tinarsenic (Cu-Sn-As) alloys. For millennia, the world of metallurgy was the domain of knowledge transmitted orally. The most widespread copper alloy in ancient times is bronze, which consists of variable tin additions depending on the use and processing technology of the piece. Although these mixtures can be formed randomly, from the entry into the molten metal of minor elements present in the ore of origin, pre-Hispanic metallurgists intentionally produced a variety of alloys, including bronzes.

In the Andean region, three types of bronzes were developed, each with a clear spatial distribution, probably related to the availability of mineral resources. On the north coast of Peru and in Chile are found predominantly copper and arsenic alloy artifacts associated with Vergel culture [22], while in the South Andean region bronze, a copper-tin alloy, was preferred. (See in Chap. 12, Case Studies in Reverse Engineering on Ancient Metals, "Border Archaeometallurgy: Pieces Found in the Mapuche Cemetery of Cerro Mesa, Malargüe, Mendoza-Argentina").

Prehistoric copper artifacts are easy to find in alloy with other elements such as arsenic (As), antimony (Sb), tin (Sn), lead (Pb), zinc (Zn), iron (Fe), sulfur (S), phosphorus (P), nickel (Ni), cobalt (Co), silver (Ag), and gold (Au), in percentages by weight ranging from fractions to units, depending on the region of origin of the mineral and the extraction technique used. (See in Chap. 13 Special Case Studies on Reverse Engineering: "Antimony as Sumptuary Good in the Sicán Culture, Northern Coast of Perú").

A rare ternary bronze, with copper, arsenic, and nickel, had a more or less prolonged moment of acceptance in the Tiwanaku sphere of influence, centered on the southern shore of Lake Titicaca. With the expansion of the Inca state, bronze became popular in most of the Andes. In this sense, as the Quechua language spread, bronze was imposed as part of the maneuvers aimed at homogenizing the cultural mosaic of the Inca Empire. Of course, this imposition was specifically aimed at the northern territories, where arsenic bronze (Cu-As) reigned, as opposed to the southern regions where tin alloy was manipulated long before. Several investigations determined that, while in pre-Inca times of conquest the main alloy of bronzes was arsenic, there would be a perceptible change towards tin as an alloy [23].

It should be remembered that metallurgy allows the recycling of artifacts that are no longer useful, with the simple fusion of scrap metal, and allows one to empirically test the effects of mixing metal pieces of different origins and different compositions.

A metallurgical revolution in antiquity happened, therefore, with the identification of the useful effects of additions and the conscious production of an alloy to obtain optimum material characteristics. The presence of alloy elements can be useful in increasing the mechanical characteristics of a material, such as hardness, or in changing the appearance and color of an ornament, although it can also be detrimental, for example, with respect to fragility.

Thus, the addition of copper or silver in gold plating is a conscious act of changing the color and brightness of the final product, which can be observed or explained based on the social values—prestige and power—that drove the development of Andean metallurgy. Such values manifested themselves, among other ways, through the underlying symbolism of the colors of gold and silver and bright surfaces. Thus, it has been proposed that alloys such as copper with silver and copper with gold (also called *tumbaga*) arose and were perfected in the central Andes (they extend from Peru to the snow-capped Tres Cruces hill on the border with Argentina and Chile) due to the range of colors with which they could give an object. Quoting [5], after exhaustive studies, established that some objects were entirely gold or silver in appearance, the ancient andean metallurgists used what Lechtman called a replacement electrochemical bath. The process was developed by the *Moche* and was applied only in their area of influence, and consisted of immersing the copper in an electrochemical bath in which, thanks to the action of mineral salts, the noble metal is dissolved, either gold or silver. The noble metal dissociates or in other words, it separates from the mineral salt solution and its adhesion to copper occurs, covering its surface, thus remaining as a bath or coating, which at first glance looked like all piece was made of either gold or silver. (See in Chap. 12 Case Studies of Reverse Engineering on Ancient Metals: "Gold Artifact Production During the Central Andean Formative Period. New Evidence from Chavín de Huántar and Caballete, Perú").

Another system for beautifying surfaces, known as gold or silver by reduction, was based on subjecting an alloy of copper and gold or silver to a sequence of hammering and annealing. After each heating, the copper on the surface was oxidized and could be removed, while the noble metal remained unchanged. The succession of hammering, heating and removal of copper oxides gradually led to the enrichment of gold or silver from the surface of the sheet. In this sense, objects are known that look like gold but only have 12% of that alloying element. This technological innovation had a much greater significance in the Andes.

The treatment of molten copper with a mineral, calamine ($ZnCO_3$), capable of producing an alloy, *orichalcum* (now known as brass) without knowing that the effects were due to a metal different from the others, zinc (Zn), unknown as an element and isolated in the 16th century. But, although most authors agree that this alloy was introduced in America by the Spanish conquerors, the alternative that the brass was produced by ancient metallurgists should not be ruled out, since it is common or normal to find records of this type of pieces. These brass pieces contain zinc in appreciable proportions, particularly in the early days of northwestern Argentina, and it is considered that this is due to the smelting of copper with zinc-containing minerals, such as: calamine ($ZnCO_3$) [24].

The evolution of the metallurgical capacity of the ancient artisans is easily followed by modern analytical means, which differentiate the oldest from the most recent bronzes because they contain percentage amounts of tin that vary from a few units for mechanically worked bronzes by plastic deformation, up to more than 10% for liquid bronzes, with the possible addition of lead to improve castability, and when a little more than 20% of lead was added, mirrors could be manufactured and, centuries later, the bells arrived.

The extractive metallurgy of copper still has a historical aspect of considerable interest, closely related to the metallurgy of gold, silver, and lead. To recover the gold and silver possibly present in the raw ore and transferred to the molten copper, large amounts of lead were added to obtain a single bath of molten metal. During subsequent slow cooling, lead and copper become insoluble and are separated by a phenomenon called *liquefaction*; the two precious metals, initially in alloy with copper, move when alloyed with lead by a phenomenon known as *segregation*. In this way, a kind of lead is obtained that sequesters the gold and silver initially contained in the ore of an almost pure copper. This technique is described in Renaissance texts, but perhaps it had already been practiced in ancient times. Anyway, it is advisable to remember that this is not the main source of the two precious metals.

The recovery of gold and silver from lead (the typical treatment of the *argentiferous galena*) is obtained with the cupellation technique used in colonial times and therefore applied in the Andean area. This technique consists of the reoxidation of the molten metal, which is to say, it goes through the exact opposite process to that of extractive metallurgy: lead, which has a more negative standard free energy (G_0) of oxide formation than that of silver and gold, is oxidized to litharge (PbO) by a flow or stream of air. The litharge, see Figure 2.8, is removed from the metal bath, while the two precious metals, always more concentrated, remain at the bottom of the cupel, which is the container in which the process takes place. Lead oxide, which can supply the raw material to produce metallic lead, differs from the initial one by the absolute lack of gold and silver: systematic analysis of archaeological finds has allowed to identify artifacts produced or manufactured with this lead from recovery. The process of cupellation was probably known as early as the fourth millennium BC and was surely practiced by Greek metallurgists.

It is known that metals of archaeological interest do not leave useful traces for dating artifacts. However, it has been treated, with varying degrees of success, to obtain information on the origin of the mineral used in the first extraction by analyzing the presence of secondary elements that follow the metallurgical fate of copper or primary alloy elements. Archaeometers take advantage of the properties of lead isotopes (204, 206, 207, and 208) because they are present in a relationship that is characteristic of the reservoir and remains substantially unchanged during extractive metallurgy, postprocessing, and corrosion or corrosion process degradation, The isotopic analysis of an artifact allows to identify with good reliability the reservoirs from which the metal can come, comparing or contrasting the lead isotopes with the values of the ratios: 208/206, 207/206, and 204/206, with those available in the literature and is advisable to avoid to combine with minerals or wastes of diverse origin. It is possible to "date" the melting lands, which have remained included, using the thermoluminescence methods.

In Roman times, metallurgy, manual labor, and service par excellence provided useful materials for war, work, or art, but they had no incentive to spur progress. Only at the end of the Middle Ages and with the Renaissance would the innovations of the time have occurred, such as the use of hydraulic energy or the production of cast iron, and with it, the subsequent conversion into iron and steel, before reaching modern knowledge of the processes and products that only the scientific revolution allowed to achieve (see in Chap. 12 Case Studies of Reverse Engineering in Ancient Metals: "Study of Archaeometallurgy, Heritage and Preservation of the Old Iron Bridge over the Mendoza River").

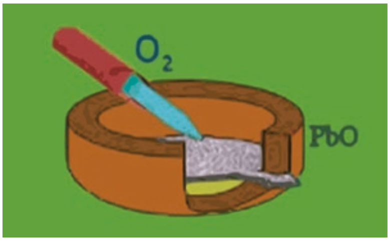


Fig. 2.8 Operational scheme of lead cupellation

References

1. Antinao, J.: Sociedad y Cosmovisión en la Platería Mapuche. Universidad Católica de Temuco, Temuco (2010)
2. Lechtman, H.: Reflexiones sobre la metalurgia de América. En Metalurgia de la América Precolombina. In: Memorias 45° Congreso Internacional de Americanistas, pp. 301–306. Banco Popular, Bogotá (1988)
3. Tylecote, R.: Una Historia de la metalurgia, 2nd edn. The Institute of Materials, Londres (1992)
4. Habashi, F.: Una historia de la metalurgia. Métallurgie extractive du Québec, Enr (1994)
5. Lechtman, H.: Reflexiones sobre la metalurgia de América. En Metalurgia de la América Precolombina, pp. 301–306. Memorias 45º Congreso Internacional de Americanistas. Banco Popular, Bogotá, Colombia, (1988)
6. Antinao, J.: Sociedad y Cosmovisión en la Platería Mapuche. Universidad Católica de Temuco, Temuco, Chile (2010)
7. Lechtman, H.: La metalurgia precolombina: tecnología y valores. In: Los Orfebres Olvidados de América, pp. 9–18. Museo Chileno de Arte Precolombino, Santiago (1991)
8. Cavallini, M.: Fortuitum & sordidum opus. Notas sobre la historia de la metalurgia. Perugia (2005)
9. Carcedo Muro, P.: Crónicas Inca Garcilaso, pp. 286. En: Metalurgia precolombina: manufactura y técnicas en la orfebrería Sicán. En: Oro Antiguo del Perú, pp. 265–305. Banco del Perú, Lima (1992)
10. Cavallini, M.: La Scoperta dei Metalli: Mitologia e termodinámica. En: Enco Journal, Roma, Italia (2007)
11. Garden, C.: Los metales en el mundo antiguo. Editorial Laterza, Bari (2002)
12. Nuñez Regueiro, V.: La metalurgia Condorhuasi-Alamito (siglos III al V DC.). Anales de Arquitectura y Etnología, pp. 46–47:107–164. Universida Nacional de Cuyo, Mendoza, Argentina (1992)
13. Lechtman, H.: A metallurgical site survey in Peruvian Andes. J. Field Archael. **3**, 1–42 (1976)
14. Forbes, R.: Studies in ancient technology. En: E. J. Brill, 3 vols., Leiden, Netherland (1955)
15. Ravines, R.: Metalurgia, pp. 478. En: Tecnología Andina, pp. 476–487. Comp. R. Ravines. Instituto de Estudios Peruanos, Lima, Perú (1978)
16. Pedersen, A.: Metalurgia andina prehispánica americana, III, pp. 39–50. En: Actas 1° Congreso de Historia de Catamarca, Argentina (1996)
17. Niemeyer, H.: La ocupación incaica en la cuenca alta del río Copiapó, pp. 4:165–294. En: Comechingonia, Córdoba, Argentina (1986)
18. Niemeyer, H.: Dos tipos de crisoles prehispánicos del Norte Chico, p. 94, En: Boletín del Museo Arqueológico de La Serena 17:92–109, Chile (1981)
19. Lothrop, S.: Tumba de un orfebre peruano, pp. III, 2:146–150. En: Revista del Museo Nacional de Antropología y Arqueología, Lima, Perú (1955)
20. Grossman, J.: Un antiguo orfebre de los Andes, pp.521–527. En: Tecnología Andina. Comp. R. Ravines, Instituto de Estudios Peruanos, Lima, Perú (1978)
21. González, L.: El caso de la cera perdida. Metalurgia prehispánica y recursos en el valle de Yocavil (1994)
22. Campbell, R.: Entre el Vergel y la Platería Mapuche: El trabajo de los metales en la araucanía poscontacto (1550–1850 D.C.) (2004)
23. Bezur, A., Owen, B.: Abandoning arsenic? In: Technological and Cultural Changes in the Mantaro Valley, vol. 41, pp. 119–129. Boletín Museo del Oro, Bogotá (1996)
24. González, L.: Bronce bajo el sol. Metalurgia prehispánica en el Noroeste argentino, pp. 97–131. En: Masked Histories. Editores. Stenberg, P. y Muñoz, A., Etnologiska Studier 43, Gotemburgo (1999)

Chapter 3
Ancient Lead, Mercury, and Tin

Rafael Colás

Introduction

Two books published towards the middle of the sixteenth century can be considered the foundation of the knowledge of mining and metallurgy. The first one, *Pirotechnia*, was written by the Italian Vannoccio Biringuccio and first published 1 year after the author's death in Venice in 1540 [1]. The second one, *De Re Metallica*, by Georgii Agricolae was printed in Basilea in 1556 [2]. A third, less-known book from Bernardo Pérez de Vargas, *De Re Metalica*, in short, was printed in Madrid in 1569 [3]; this work may be considered a plagiarised version of the works from Agricolae and Biringuccio.

The works by Biringuccio and Agricolae represents the experience and knowledge accumulated for generations is different methods and processes used in mining and metallurgy, rather than discoveries or inventions of their own.

Most of the work on minerals and metals can be derived from the work from the alchemists [1–4]. Early civilisations identified up to seven metals, and seven different celestial bodies that were thought to surround and rotate around the earth. Such coincidence in numbers suggested a relationship between metals, celestial bodies and deities (Table 3.1). Gold was identified by a circle and was associated with the Sun by virtue of its bright yellow colour. Silver was identified by a half circle resembling the crescent Moon and was associated with it due to its colour and brightness. Iron was the metal associated with war and was identified with the planet Mars and its symbol denoted a shield and a spear. Copper was denoted by a full circle due to its red colour that is closer to gold than the other metals and a cross at its bottom to resemble a narrow hand, and it was associated with the planet Venus. The metal mercury, known also as quicksilver or running silver, was associated with the planet of the same name; the symbol includes a circle topped by the crescent of silver to

R. Colás (✉)
Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León,
San Nicolás de los Garza, Mexico

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_3

Table 3.1 Alchemic symbols, planets and gods associated with the seven metals of antiquity

Symbol		Metal	Roman name	Celestial body	Roman god	Greek god
☽	Ag	Silver	*Argentum*	Moon	Diana	*Artemis Ἄρτεμις*
○	Au	Gold	*Aurum*	Sun	Sol	*Helius Ἥλιος*
♀	Cu	Copper	*Cuprum*	Venus	Venus	*Aphrodite Αφροδιτη*
♂	Fe	Iron	*Ferrum*	Mars	Mars	*Ares Ἄρης*
☿	Hg	Mercury	*Hydrargyrum*	Mercury	Mercury	*Hermes Ἑρμῆς*
♃	Pb	Lead	*Plumbum*	Saturn	Saturn	*Cronos Κρόνος*
♄	Sn	Tin	*Stannum*	Jupiter	Jupiter	*Zeus Ζεύς*

denote the similarity in colour and brightness. Mercury was not recognised as a true mineral by Biringuccio but it was classified as a semimineral [1]. The symbols for tin and lead have some similarity because they were once considered variants of the same metal or a debased form of silver. Their symbols have curved sections that recall the crescent of the Moon. Tin was associated with the planet Jupiter and lead, which is heavy and dull, was associated with Saturn, which was the farthest known planet [4]. The origin of lead and tin was uncertain in ancient times. Pliny the Elder, in Book XXXIV of his Natural History, mentions two types of lead, dark and white, this last being the more valuable and known by the Greeks as '*cassiteros*', which results to be tin [5].

The ancient Egyptians, Phoenicians and other cultures in the Middle East were well acquainted with simple metallurgy and are believed to have imparted their knowledge to the Hebrews, Greeks and Romans. There are several references to extraction metallurgy made in the Old Testament of the Bible, showing that this was known at the time. There is evidence that gold and copper were obtained from native ores prior to recorded civilisation in Asia Minor and Egypt; silver, iron, tin and lead were refined by smelting around 3500 to 2000 BC in Asia; mercury was reduced in the first millennium BC in Spain [4, 6, 7].

Lead

Lead is a metallic element. Its symbol is Pb (*plumbum*), which has the atomic number 82. It is a heavy metal with a density of 11.34 g/cm^3, and melting and boiling points of 327.46 and 2022 °C, respectively. Lead crystallises in to a body centred cubic structure; therefore, it is soft and malleable at room temperature. Its surface is silvery with a hint of blue when fresh, but tarnishes to a dull grey tonality when exposed to air due to the formation of $PbSO_4$ or $PbCO_3$ layers from atmospheric SO_2 and CO_2. Its density made the alchemists believe in the possibility of transmuting lead into gold that has a density of 19.30 g/cm^3 [8].

Lead does not occur in an elemental state; its principal mineral ore is called galena. The mineral had to be crushed, smelted and refined. Galena is mostly made of lead sulphide (PbS). The sulphide was roasted to oxidise it into lead oxide, called litharge, and sulphur dioxide (PbO and SO_2), the latter of which is lost to the environment.

$$2PbS + 3O_2 \rightarrow 2PbO + SO_2$$

Pliny the Elder mentions in Book XXXVI that lumps of the oxide were mixed with charcoal and fed into furnaces in which hot air was blasted by bellows to enhance the production of lead [5].

$$PbO + C \rightarrow Pb + CO$$

An alternative method was that that of heating the oxide together with galena to obtain metallic lead and sulphur dioxide [5].

$$2PbO + PbS \rightarrow 3Pb + SO_2$$

An overview on the use of lead from ancient to modern times can be consulted elsewhere [9]. The early mining and fabrication of lead must have resulted in environmental contamination and poisoning that caused many deaths among miners. Slag remains in former mines exploited by Carthage and Rome around Cartagena, southern Spain, attest such pollution [10]. The earliest records of miners who developed ailments that resulted in their early demise were documented by the Egyptians, Greeks and Romans [11, 12].

Silver is commonly found in galena ores; the process known as cupellation was developed to obtain silver by means of the selective oxidation taking place in a shallow bowl, called a cupel, in which the lead ore is roasted:

$$Ag + 2Pb + O_2 \rightarrow 2PbO + Ag$$

Lead was oxidised to litharge, so the silver within the ore was recuperated from the roasted remains [9, 13].

Metallic lead artifacts were an essential part of Greek and Roman civilisations, as lead became the most important metal in daily life [9]. Evidence of the extensive production of lead, which can be related to extensive economic growth in ancient times, is attested from the pollution records obtained from the analyses of peat bog and ice cores [14, 15]. It is widely accepted nowadays that lead in water distribution and domestic systems constitutes a major health hazard. The ancient Roman world was unaware of these risks, and it is not known how far the network of lead pipes in ancient Rome compromised health, particularly in the population of higher prominence that had access to water from domestic pipes, rather than from public fountains [16]. Cosmetics used from ancient times are usually made of lead compounds. Galena was widely used as black eye paint by many cultures; oxidised lead can range through white to shades of yellow and red. White lead, a mixture of hydrocerussite, $2PbCO_3{\cdot}Pb\ (OH)_2$, and cerussite, $PbCO_3$, was used for cosmetics and paints [12, 17].

Metallic lead is easily malleable and has a low melting point, which make it ideal for sheets used then for the fabrication of water pipes made by *plumbarii* (plumbers) from fitted rolled sheets in a variety of diameters [5, 18]. But lead was known to be dangerous and, for that reason, pipes made of clay were preferred, as Vitruvius explains, “Water conducted through earthen pipes is more wholesome than that through lead; indeed, that conveyed in lead must be injurious, because from it white lead ($PbCO_3$, lead carbonate) is obtained, and this is said to be injurious to the human system. Hence, if what is generated from it is pernicious, there can be no doubt that itself cannot be a wholesome body. This may be verified by observing the workers in lead, who are of a pallid colour; for in casting lead, the fumes from it fixing on the different members, and daily burning them, destroy the vigour of the blood; water should therefore on no account be conducted in leaden pipes if we are desirous that it should be wholesome. That the flavour of that conveyed in earthen pipes is better, is shewn at our daily meals, for all those whose tables are furnished with silver vessels, nevertheless use those made of earth, from the purity of the flavour being preserved in them” [18, 19].

The most probable cause of chronic lead poisoning, known as plumbism or saturnism, due to the character of the god Saturn, was the consumption of lead-contaminated wine. Hippocrates (460–377 BCE) described the symptoms of lead poisoning as appetite loss, colic, pallor, weight loss, fatigue, irritability, and nervous spasms, which are the same symptoms that are used today to make a diagnosis for lead poisoning [10]. Pliny the Elder describes in Book XIV how unfermented grape juice was boiled in lead vats to concentrate its natural sugars. The *mustum*, must, was reduced to one half (*defrutum*) or even one-third its volume (*sapa*) [5]. Reaction of the acetic acid, produced while the wine was being heated with lead, produces lead acetate, $Pb\ (CH_3COO)_2$, which is known as lead sugar. It has been suggested that the erratic behaviour and neurological ailments of some Roman emperors was due to lead intoxication. The extensive use of wine and food sweetened by lead acetate is well documented, as well as the extensive use of lead cups and vases and the addition of lead shavings to acidic wine by the aristocracy and patricians [10]. Studies of patrician and slave skeletons show a higher lead content in bones from patricians [19]. The question on the effect of lead poisoning on the decline of the Roman empire is open, with arguments for and against it [9–12, 16, 19–24].

Writings of medieval physicians indicated an awareness of both the sources and symptoms of lead poisoning. French and Spanish authorities prohibited the addition of *sapa* to sweeten wine. German authorities made wine adulteration a crime punishable by death in 1478. Addition of *sapa* not only sweetens the wine, but also inhibits spoilage by interfering with enzyme activity [10].

The high density and softness of lead precludes it for use in military objects, although projectiles such as sling bullets and shots were made of lead [9], and later on it was used in the manufacture of leaded darts (*plumbata*) [25]. Lead sheathing was used by the Roman navy to protect their ships from marine fouling and corrosion [26]. Lead was used to manufacture various devices due to the resistance to maritime corrosion. A further advantage of lead is its density, so it was used in the manufacture of soundings, ballast and anchors [9, 27].

Sand cast lead is the oldest method to produce of lead sheets. Lead was poured in an elongated mould made of pressed sand and was left to solidify to obtain a flat sheet that can then be cut and rolled up for easy transport and laid down. The thickness and quality of the sheet were determined by the skill of the caster and the rate of metal pouring; that process is used nowadays with little changes to produce lead sheets [28]. It was mentioned above that lead was used in aqueducts to and pipes [16, 18], but also to protect buildings and roofing such as the exterior of the Hadriatic concrete dome of the Pantheon (Rome), which was covered with lead roofing by Emperor Constans II in 663 A.D [9]. Lead provides corrosion protection in humid environments as a series of carbonates or hydrocarbonates, such as cerussite, $PbCO_3$, hydrocerussite $Pb_3(CO_3)_2(OH)_2$ or plumbonacrite $Pb_{10}(CO_3)_6O(OH)_6$, are formed [29]. It is difficult to obtain thin lead strips of consistent thickness by sand casting, which increases the weight of roofing and the mechanical demands on the building. Thin strip of consistent thickness was obtained by rolling the stock between concentric cylindrical tooling, and examples of lead roofing can be found in numerous buildings [30, 31]. The invention of metal rolling is attributed to Leonardo da Vinci, who described the machines and processes towards the end of the fifteenth century. No evidence of the construction of such equipment, nor any mention of rolling, is found in either *Pirotechnia* [1] or *De Re Metallica* [2], which were published over 50 years later. A model of the rolling mill designed by Leonardo is exhibited in the *Museo Leonardiano de Vinci* [32].

Mercury

Mercury is a metal, with symbol Hg (*hydrargyrum*), that remains in liquid state at room temperature as its melting point, −38.87 °C, is below the freezing temperature of water. Its corresponding boiling point is also low, 356.9 °C. Its volume expansion is uniform in the liquid state, and it does not wet surfaces due to its high surface tension. Its density changes from 13.69 to 14.18 g/cm^3 during solidification into a rhombohedral structure. Some of its properties, such as its shiny appearance and liquid state at room temperature, can be attributed to its atomic configuration that resists the removal of external electrons and behaves in a similar way to noble gases, which results in weak bonds and low melting temperature [8].

Pliny quotes in Book XXXIII that "there is a mineral also found in these veins of silver, which yields a humour that is always liquid, and is known as quicksilver" [5]. Its name derived from its liquid state and bright silver tonality at room temperature. Its main mineral ore, cinnabar (HgS), is of a vivid red colour pigment (vermillion) that has been used for decorating Egyptian tombs and Roman villas, and for making rouges and other beauty products. The earliest documented use of cinnabar comes from Italy and Spain, where it was used as a preservative for human bones during the Neolithic Age [6, 7, 33]. Pliny the Elder, in Book XXXIII of Natural History, writes on the different uses and characteristics of mercury; it is mentioned that all substances will float on it, with the exception of gold, due to the difference in densities, and it should be considered an excellent gold refiner.

He also mentioned the use of a red pigment to colour the Greek ships that participated in the Trojan war and called it *cinnabaris*, rather than *miltos* or minium. He also wrote that "The ancients used to paint with cinnabaris those pictures of one colour, which are still known among us as *monochromata*" [5].

Minium is called red lead; it is a tetroxide, $Pb^{2+}2Pb^{4+}O_4$, and is mistaken with cinnabar due to its bright red colour [34]. The ships were painted red due to the antifouling effect caused by either the presence of mercury in cinnabar or that of lead in minium. Cinnabar was a sought-after pigment as it stable, has a deep tint and hue, and good covering characteristics, and is compatible with media such as oils, watercolour, egg tempera and fresco. Vermilion was first made by heating, crushing and washing the mineral to obtain a relatively pure and usable pigment [35, 36].

Refining of mercury from cinnabar is described in the works by Biringuccio and Aggricolae by roasting and distillation [1, 2]. The ore was mixed with charcoal and charged in furnaces that were heated to temperatures above the boiling point of mercury; oxygen from the air reacted with sulphur from the ore to form sulphur dioxide and reduce the metal. Liquid mercury was recovered by condensing the gases:

$$2\mathrm{HgS} + 2\mathrm{O}_2 \rightarrow 2\mathrm{Hg} + 2\mathrm{SO}_2$$

Workers in mercury smelters were exposed to gases and were subjected to mercury poisoning, with scarce knowledge about its causes. Aggricolae wrote "If the fumes give out a very sweet odour it indicates that the quicksilver is being lost, and since this loosens the teeth, the smelters and others standing by, warned of the evil, turn their backs to the wind, which drives the fumes in the opposite direction; for this reason, the building should be open around the front and the sides, and exposed to the wind" [2]. Improvements in the recovery of mercury gases by enhancing condensers reduced the incidence of poisoning [33, 37, 38]. Mining and smelting from early ages have released large quantities of mercury to the atmosphere and caused widespread contamination of water and soil in the vicinity of mining districts [7, 39].

Mercury is often found in Mesoamerican tombs in the form of cinnabar, although its liquid form is rare. Research conducted in 2003 in the ancient city of Teotihuacan, about 40 km northeast of Mexico City, revealed traces of liquid mercury in chambers within a 300 m long tunnel under the Feathered Serpent Pyramid. It was postulated that mercury recreated lakes and rivers within the representation of the underworld, the mythological realm where the dead reside [40].

The first reliable mention of mercury in medicine comes from Hippocrates (460–377 BCE); in his *Materia Medica Hippocrates*, which is the attempt towards a systematic enumeration of medicines occurring in all the Hippocratic writings, *kinnabari* and *miltos* are listed as ingredients in ointments [41]. Pliny, Book XXXXIII, wrote in reference to cinnabar: "I look upon all the recipes given as highly dangerous which recommend its employment for medicinal purposes; with the exception, perhaps, of those cases in which it is applied to the head or abdomen, for the purpose of arresting *hæmorrhage*, due care being taken that it is not allowed to penetrate to the viscera, or to touch any sore. Beyond such cases as these, for my own part, I should never recommend it to be used in medicine" [5]. Mercury is used to make dental amalgams that are mentioned to be used for the first time in China [42].

It was mentioned above that mercury was used by Romans to separate gold by combining with gold and silver to form semiliquid amalgams. These were applied over metal surfaces for plating; the mercury is vaporised and the resulting gold or silver layer polished or burnished. Vitruvius wrote in his Book VII: "Quicksilver is used for many purposes; without it, neither silver nor brass can be properly gilt. When gold is embroidered on a garment which is worn out and no longer fit for use, the cloth is burnt over the fire in earthen pots. The ashes are thrown into water and quicksilver added to them; this collects all the particles of gold and unites with them. The water is then poured off and the residuum placed in a cloth which when squeezed with the hands, suffers the liquid quicksilver to pass through the pores of the cloth but retains the gold in a mass within it" [17].

The introduction of the *beneficio de patio* (backyard benefit) process in the silver mines of New Spain by Batolomé de Medina in 1555 promoted amalgamation to a high scale in which a mixture of ground and roasted silver ore and mercury was spread out on a paved area, to be crushed by different means. The mercury in excess was separated from the ore and the remaining amalgam was heated to recover the silver and some mercury. Such a relatively easy extraction process led to its extensive use in the Spanish Americas for more than 300 years [43–45].

Tin

The chemical symbol of tin is Sn (*stannum*); it can be found in two allotropic phases. β-tin, the metallic one, is called white tin and crystallises in a body centred tetragonal (BCT) structure. It is stable above 13.2 °C, is malleable and relatively soft, and has a silvery white tonality. In contrast, α-tin, which is called grey tin, is stable below the above-mentioned temperature, is brittle and has a diamond cubic crystal structure. The density of β-tin is 7.265 g/cm^3, changes to 5.769 g/cm^3 in α-tin producing a 27% volume increase during the $\beta \rightarrow \alpha$ transformation, which induces the formation of cracks which start at the surface and proceeds through the metal. Tin has a melting point of 231.88 °C and a boiling point of 2625 °C. The transformation from white- to grey-tin is difficult to initiate and can be retarded by the presence of alloying elements or trace impurities. The damage produced by the transformation has made it to be called as tin pest. One of the causes that is mentioned for the demise of Napoleon's army during their retreat from Moscow in the winter of 1812 was the disintegration of the tin buttons of the French soldiers' coats due to the freezing temperatures [46].

There is evidence from both archaeology and literature that tin was one of the earliest metals to be known and used. The origin of tin was confusing, as was mentioned above; Pliny refers to two types of lead, black and white, with the latter being tin. He quotes that this metal can be found in isles in the Atlantic, called *Cassiterides*, and was available in Roman times from mines in what is today Portugal, Spain, France and England [5]. Biringuccio mentions that he has never seen tin ores due to the scarcity of its deposits, although he says it is abundant in certain regions of England, Flanders and Bohemia [1]. It is thought that the tin required to produce bronze weapons in Egypt was obtained from ores in Turkey [6, 7].

The main ore of tin is cassiterite, also called tinstone, made of SnO_2. The ore can be processed to obtain tin by smelting, although recovery is poor due to losses to the atmosphere as volatile stannous oxide is formed as an intermediate product during the reduction of cassiterite [47, 48]:

$$\mathrm{SnO_2 + CO \leftrightarrow SnO + CO_2}$$

$$\mathrm{SnO + CO \leftrightarrow Sn + CO_2}$$

Pure tin would seem to be common considering that it could easily be obtained from cassiterite. However, the pure metal was rarely used in ancient times because it cost much and was not easily accessible. The major portion of tin was used in making bronze, pewter and soldering [49]. Pliny the Elder writes in Book XXXIV of The Natural History, "We must, in the next place, give an account of the ores of brass, a metal which, in respect of utility, is next in value; indeed, the Corinthian brass comes before silver, not to say almost before gold itself" [5], which can be considered a misnomer, for, in modern terms, brass is the alloy of copper and zinc, rather than with tin, which is bronze. Tin may be considered one of the first strategic commodities, as it is attested by the ingots found in sites and ship wrecks [50–52], and by the fact that tin was alloyed with copper for the manufacture of the utensils and weapons that gave the name Bronze Age.

Addition of tin to copper results in an increase in hardness and reduction in the wear of tools and weapons. The melting point of pure copper is reduced from 1085 °C to around 1000 °C when 10% of tin is added [53]. The fluidity of the melt is enhanced, which facilitates casting. Similar effects can be obtained with the addition of arsenic, but without the toxicity hazards [6, 54]. Bronze can be obtained by four different methods: melting a mixture of metallic tin and metallic copper, addition of tin ore to molten copper, smelting of ore containing both tin and copper, and by co-smelting of the mixture of copper and tin ores [47, 55–58].

The amount of tin used in bronze weapons was under 15% [54], as tin will be kept in solid condition at temperatures above 350 °C; precipitation of ordered orthorhombic Cu_3Sn will occur below this temperature [53]. Metallographic examination of bronze blades shows that the weapons were cast, as it was possible to cold-work them to increase their hardness when the alloying content was kept below 8% [54]. Alloys with higher contents may be cold-worked by controlling the deformation and by imparting short annealing cycles at temperatures close to 600 °C [59]. Bronze has been used to cast bells and other musical instruments due to its sonority, which is a result of the rigidity of the metal and its resonance, which reaches its best with approximately a 4:1 ratio of copper to tin [60, 61].

Pewter is a tin alloy that has a long history. It was originally cast with contents of up to 20% of lead and smaller amounts of copper and antimony. Probably the earliest pieces were made in Egypt more than 3000 years ago, although the development of pewter for the manufacture of household and ornamental uses can be attributed to the Greeks; pewter became widespread in Roman times after the conquest of Britain in the first century AC [49]. Pliny the Elder mentions in Book XXXIV, "Pieces of black lead cannot be soldered without the intervention of white lead, nor can this be done without employing oil; nor can white lead, on the other hand, be united without the aid of black lead" [5]. This is due to the occurrence of the eutectic reaction in the Pb-Sn system that takes place at 183 °C with a 61.9% of lead [62].

Concluding Remarks

Lead, mercury and tin are known since antiquity as their ores are easily reduced and can be obtained in furnaces that work at relatively low temperatures. Lead was the most used of the three as it is easy to melt and cast into shapes that were used for making household goods. It was extensively used in Roman times to conduct water in aqueducts or pipes. Lead ingestion causes saturnism, and as such can be considered one of the many causes for the demise of the Roman Empire; the higher classes were more exposed to poisoning either from water or from the consumption of wine sweetened with lead sugar. Its high density makes lead common with alchemists looking to transmute it into gold.

Mercury is a rarity among metals, as it is liquid at room temperature and was widely used to separate gold and silver by amalgamation. Mercury is toxic and, due to its low boiling point, its fumes can dissipate in regions close to the sites at which it was beneficed. The main ore, cassiterite, has a bright red colour and was used as a cosmetic and for paints, increasing with it the risk of poisoning. Ores from mercury and lead were used to paint ancient ships and act as antifouling agents.

Tin can be easily reduced and was used to alloy it with copper to produce bronze in weapons and other utensils. It can be considered that tin was the first worldwide strategic commodity, as its availability is limited to specific regions. Its main ore, cassiterite, was used also as a pigment for paints. Tin has an allotropic transformation at 13.2 °C that causes a volume transformation of 27%; the change in volume promotes failure and cracking, and the phenomenon is called tin pest.

References

1. Biringuccio, V.: Pirotechnia (1540). Translated by C.S. Smith and M.T. Gnudi, MIT Press, Cambridge (1966)
2. Agricola, G.: De Re Metallica (1556). Translated by H.C. Hoover and L.H. Hoover. Dover Publications, New York (1950), reprint of the 1912 edition. https://www.gutenberg.org/files/38015/38015-h/38015-h.htm
3. Pérez de Vargas, B.: De Re Metalica: En el qual se tratan muchos y diuersos secretos del conocimiento de toda suerte de minerales, de como se deuen buscar ensayar y beneficiar, con otros secretos e industrias notables: assi para los que tratan los officios de oro, plata, cobre, estaño, plomo, azero, hierro y otros metales, como para muchas personas curiosas, Madrid. https://babel.hathitrust.org/cgi/pt?id=ucm.532248626x&view=1up&seq=1 (1569)
4. Habashi, F.: The seven metals of antiquity. Min. Proc. Extract. Metall. **117**, 190–191 (2008)
5. Pliny the Elder, The Natural History. https://www.perseus.tufts.edu/hopper/text?doc=Perseus%3atext%3a1999.02.0137
6. Ogden, J.: Metals. In: Nicholson, P.T., Shaw, I. (eds.) Ancient Egyptian Materials and Technology, pp. 148–176. Cambridge University Press, Cambridge (2000)
7. Gnesin, G.G.: Revisiting the history of materials science: on the origin of metallurgical technologies in the bronze age. Powder Metall. Met. Ceram. **52**, 477–488 (2013)
8. Haynes, W.M., Lide, D.R., Bruno, T.J. (eds.): CRC Handbook of Chemistry and Physics, 97th edn. CRC Press, Boca Raton (2016)
9. de Keersmaecker, M., Dowsett, M., Adriaens, M.: A short historical overview on the use of lead. In: Adriaens, M., Bioletti, S., Rabin, I. (eds.) Chemical Interactions Between Cultural Artefacts and Indoor Environment, pp. 193–214. Uitgeverij Acco, Leuven (2018)
10. Lessler, M.A.: Lead and lead poisoning from antiquity to modern times. Ohio J. Sci. **88**, 78–84 (1988)
11. Nriagu, J.O.: Occupational exposure to lead in ancient times. Sc. Total Environ. **31**, 105–116 (1983)
12. Nriagu, J.O.: Lead and Lead Poisoning in Antiquity. Wiley, New York (1983)
13. Stos-Gale, Z., Gale, N.: The sources of Mycenaean silver and lead. J. Field Archaeol. **9**, 467–485 (1982)
14. Shotyk, W., Cheburkin, A.K., Appleby, P.G., Fankhauser, A., Kramers, J.D.: Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountains, Switzerland. Earth Plan. Sc. Lett. **145**, E1–E7 (1996)
15. McConnell, J.R., Wilson, A.I., Stohl, A., Arienzo, M.M., Chellman, N.J., Eckhardt, S., Thompson, E.M., Pollard, A.M., Steffensen, J.P.: Lead pollution recorded in Greenland ice indicates European emissions tracked plagues, wars, and imperial expansion during antiquity. Proc. Natl. Acad. Sci. **115**, 5726–5731 (2018)
16. Delile, H., Blichert-Toft, J., Goiran, J.-P., Keay, S., Albarède, F.: Lead in ancient Rome's city waters. Proc. Natl. Acad. Sci. **111**, 6594–6599 (2014)

17. Welcomme, E., Walter, P., van Elslande, E., Tsoucaris, G.: Investigation of white pigments used as make-up during the Greco-Roman period. Appl. Phys. A Mater. Sci. Process. **83**, 551–556 (2006)
18. Vitruvius, M.: On architecture. http://penelope.uchicago.edu/Thayer/E/Roman/Texts/Vitruvius/home.html
19. Hodge, T.A.: Vitruvius, lead pipes and lead poisoning. Am. J. Arch. **85**, 486–491 (1981)
20. Gilfillan, S.C.: Lead poisoning and the fall of Rome. J. Occup. Med. **7**, 53–60 (1965)
21. Mackie, A.C., Townsend, A., Waldron, H.A.: Lead concentrations in the bones of Roman York. J. Arch Soc. **2**, 235–237 (1975)
22. Nriagu, J.O.: Saturnine gout among Roman aristocrats: did lead poisoning contribute to the fall of the empire? New Engl. J. Med. **308**, 660–663 (1983)
23. Scarborough, J.: The myth of lead poisoning among the Romans: an essay review. J. Hist. Med. **39**, 469–475 (1984)
24. Hernberg, S.: Lead poisoning in a historical perspective. Am. J. Ind. Med. **38**, 244–254 (2000)
25. Conyard, J.: Recreating the late Roman army. Late Antiq. Archaeol. **8**, 523–567 (2013)
26. Rosen, B., Galili, E.: Lead use on roman ships and its environmental effects. Int. J. Naut. Archaeol. **36**, 300–307 (2007)
27. Oleson, J.P.: Ancient sounding-weights: a contribution to the history of Mediterranean navigation. J. Rom. Archaeol. **13**, 293–310 (2000)
28. Prabhakar, A., Salonitis, K., Jolly, M.: Characterisation of lead sheet manufactured using traditional sand-casting technique. In: Tiryakioğlu, M., Griffiths, W., Jolly, M. (eds.) Shape Casting, pp. 283–292. Springer, Cham (2019)
29. Rocca, E., Mirambet, F., Steinmetz, J.: Study of ancient lead materials: a Gallo-Roman sarcophagus-contribution of the electrolytic treatment to its restoration. J. Mater. Sci. **39**, 2767–2774 (2004)
30. Oldrieve, W.: The ancient roof of Glasgow cathedral: its condition and restoration. Proc. Soc. Antiq. Scot. **50**, 155–172 (1916)
31. Kitching, C.: Re-roofing old St Paul's Cathedral, 1561–66. London J. **12**, 123–133 (1986)
32. http://www.museoleonardiano.it/eng/museum/collection-of-models/detail?modelId=116
33. Parsons, M.B., Percival, J.B.: A brief history of mercury and its environmental impact. In: Parsons, M.B., Percival, J.B. (eds.) Mercury: Sources, Measurements, Cycles, and Effects, pp. 1–20. Geological Association of Canada, St. John's (2005)
34. Edwards, H.G., Farwell, D.W., Newton, E.M., Perez, F.R.: Minium; FT-Raman non-destructive analysis applied to an historical controversy. Analyst. **124**, 1323–1326 (1999)
35. Gettens, R.J., Feller, R.L., Chase, W.T.: Vermilion and cinnabar. Stud. Conserv. **17**, 45–69 (1972)
36. Nöller, R.: Cinnabar reviewed: characterization of the red pigment and its reactions. Stud. Conserv. **60**, 79–87 (2015)
37. Rocha, J.B.T., Aschner, M., Dórea, J.G., Ceccatelli, S., Farina, M., Silveira, L.C.L.: Mercury toxicity. Biomed. Res. Int. **2012**, 831890 (2012)
38. Bernhoft, R.A.: Mercury toxicity and treatment: a review of the literature. J. Environ. Public Health. **2012**, 460508 (2012)
39. Rytuba, J.J.: Geogenic and mining sources of mercury to the environment. In: Parsons, M.B., Percival, J.B. (eds.) Mercury: Sources, Measurements, Cycles, and Effects, pp. 21–41. Geological Association of Canada, St. John's (2005)
40. Shaer, M.: A Secret Tunnel Found in Mexico may Finally Solve the Mysteries of Teotihuacán. Smithsonian Magazine. https://www.smithsonianmag.com/history/discovery-secret-tunnel-mexico-solve-mysteries-teotihuacan-180959070/ (2016)
41. Materia Medica of Hippocrates. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5828757/
42. Bharti, R., Wadhwani, K.K., Tikku, A.P., Chandra, A.: Dental amalgam: an update. J. Conserv. Dent. **13**, 204–208 (2010)
43. Nriagu, J.O.: Mercury pollution from the past mining of gold and silver in the Americas. Sci. Total Environ. **149**, 167–181 (1994)

44. Guerrero-Quintero, S.J.: The environmental history of silver refining in New Spain and Mexico, 16C to 19C: a shift of paradigm. Ph.D. Thesis, McGill University, Montreal (2015)
45. Jauregui-Correa, J.C., Escamilla-Gonzalez, O.: Modeling an antique grinding mill of Guanajuato silver mines. In: Zhang, B., Ceccarelli, M. (eds.) Explorations in the History and Heritage of Machines and Mechanisms, pp. 101–112. Springer, Cham (2019)
46. Gialanella, S., Deflorian, F., Girardi, F., Lonardelli, I., Rossi, S.: Kinetics and microstructural aspects of the allotropic transition in tin. J. Alloys Comp. **474**, 134–139 (2009)
47. Berger, D., Figueiredo, E., Brügmann, G., Pernicka, E.: Tin isotope fractionation during experimental cassiterite smelting and its implication for tracing the tin sources of prehistoric metal artefacts. J. Archeol. Sc. **92**, 73–86 (2018)
48. Berger, D., Brügmann, G., Pernicka, E.: On smelting cassiterite in geological and archaeological samples: preparation and implications for provenance studies on metal artefacts with tin isotopes. Archaeol. Anthropol. Sci. **11**, 293–319 (2019)
49. Penhallurick, R.D.: Tin in Antiquity. Its Mining and Trade Throughout the Ancient World with Particular Reference to Cornwall. Routledge, London (2017)
50. Grant, M.R.: The sourcing of southern African tin artefacts. J. Archeol. Sci. **26**, 1111–1117 (1999)
51. Meharg, A.A., Edwars, K.J., Schofield, J.E., Raab, A., Feldmann, J., Moran, A., Bryant, C.L., Thornton, B., Dawson, J.J.C.: First comprehensive peat depositional records for tin, lead and copper associated with the antiquity of Europe's largest cassiterite deposits. J. Archeol. Sci. **39**, 717–727 (2012)
52. Wang, Q., Strekopytov, S., Roberts, B.W., Wilkin, N.: Tin ingots from a probable bronze age shipwreck off the coast of Salcombe, Devon: Composition and microstructure. J. Archeol. Sci. **67**, 80–92 (2016)
53. Li, M., Du, Z., Guo, C., Li, C.: Thermodynamic optimization of the Cu-Sn and Cu-Nb-Sn systems. J. Alloys Comp. **477**, 104–117 (2009)
54. El Morr, Z., Pernot, M.: Middle Bronze Age metallurgy in the Levant: evidence from the weapons of Byblos. J. Archeol. Sci. **38**, 2613–2624 (2011)
55. Timberlake, S.: The use of experimental archaeology/archaeometallurgy for the understanding and reconstruction of Early Bronze Age mining and smelting technologies. In: La Niece, S., Hook, D.R., Craddock, P.T. (eds.) Metals and Mines: Studies in Archaeometallurgy, pp. 27–36. Archetype Publications, British Museum, London (2007)
56. Rostocker, W., Dvorak, J.R.: Some experiments with co-smelting to copper alloys. Archeomaterials. **5**, 5–20 (1991)
57. Heeb, J., Ottaway, B.S.: Experimental archaeometallurgy. In: Roberts, B., Thornton, C. (eds.) Archaeometallurgy in Global Perspective, pp. 161–192. Springer, New York (2014)
58. Zou, G., Cui, J., Liu, X., Min, R.: Investigation of early Bronze Age civilizations in Yunnan: A scientific analysis of metallurgical relics found at the Guangfentou ruins in Jiangchuan. Archaeol. Anthropol. Sci. **11**, 15–31 (2019)
59. Nerantzis, N.: Shaping bronze by heat and hammer: an experimental reproduction of Minoan copper alloy forming techniques. Medit. Archaeol. Archaeom. **12**, 237–247 (2012)
60. Audy, J., Audy, K.: Analysis of bell materials: tin bronzes. China Found. **5**, 199–204 (2008)
61. Debut, V., Carbalho, M., Figueiredo, E., Antunex, J., Silva, R.: The sound of bronze: virtual resurrection of a broken medieval bell. J. Cult. Herit. **19**, 544–554 (2016)
62. Ohtani, H., Okuda, K., Ishida, K.: Thermodynamic study of phase equilibria in the Pb-Sn-Sb system. J. Phase Equilib. **16**, 416–429 (1995)

Chapter 4
The Use and Meaning of Gold in Ancient Peru

Luisa Vetter and Paloma Carcedo

Introduction

When Europeans arrived to the Americas, they found gold somewhat easily in the form of gold nuggets in riverbeds. A very shiny, bright yellow “stone” probably caught the attention of the ancient inhabitants of this territory, who decided to collect it and work it. It is quite possible that in the beginning, they thought that it was a stone or hard rock, and, therefore, they decided to work it like one. It would have been to their great surprise to discover that it could be deformed plastically to create a sheet without needing to be heated. This first process allowed ancient man to realize that the element before him could be transformed through percussion and thus given one form or another depending on his needs. In this simple way, metalworking began and the first goldsmiths emerged, along with artistic creation with this material.

In effect, the oldest known gold objects are not weapons, but rather small plates that were sewn onto clothes, and necklace beads, normally alternated with semiprecious stones such as chrysocolla$[(Cu,Al)_4H_4\ (OH)_8\ Si_4O_{10}\cdot nH_2O)]$, sometimes called “siliceous copper.”

L. Vetter (✉)
Pontifical Catholic University of Peru, National Science Academy of Peru, Lima, Peru

P. Carcedo
Universidad de Lima, Santiago del Surco, Peru

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_4

Fig. 4.1 Left: gold nugget; Right: gold associated with quartz. MOP (Museum of Gold of Peru and Weapons of the World, Lima) collection. (Photo: L. Vetter)

Gold: Extraction and Transformation

Gold can be found in three forms in nature: in tiny particles in pyrite (FeS_2) or arsenopyrite (FeAsS), in veins or seams of quartz (SiO_2), or in placer deposits or riverbeds. In Pre-Columbian times, gold was exploited by way of the latter two minerals mentioned above (Fig. 4.1).

The archaeological evidence and the chronicles reveal the work carried out by ancient miners to obtain precious metals, such as gold, silver, and copper, from inside the earth. These three native metals were those most exploited in Pre-Columbian times (Fig. 4.2), although platinum and minerals such as lead, tin, and arsenic, among others, were also worked.

Various minerals or native metals could be identified by their bright colors or their density. Like their European counterparts, pre-Hispanic Andean miners were well aware of the physical characteristics of the minerals and native metals, which could be identified through the senses, such as taste and smell,[1] as well as touch (hardness) and sight (color).

According to Craddock, the main “placer” deposits (term used by Spanish miners in the Americas to denominate deposits of metalliferous substances and precious metals mixed with sand and rocks) are found in the sand and gravel of rivers that flow under veins or primary seams (depressions). In this stage, the flowing water separates the dense minerals, such as gold, from the other materials and they are concentrated according to density. Many of the famous gold deposits in ancient times were of this type [1, p. 27].

It is probable that the majority of gold extraction in Pre-Columbian times was from placer deposits, as indicated by Fernández de Oviedo,[2] who also points out the amount that had been extracted, and continued to be extracted upon his arrival, from

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[1] Such is the case with arsenic, whose garlicky smell makes it easily identifiable.

[2] Sixteenth-century chronicler who was named first chronicler of the New Indies in 1533 by Emperor Charles V.

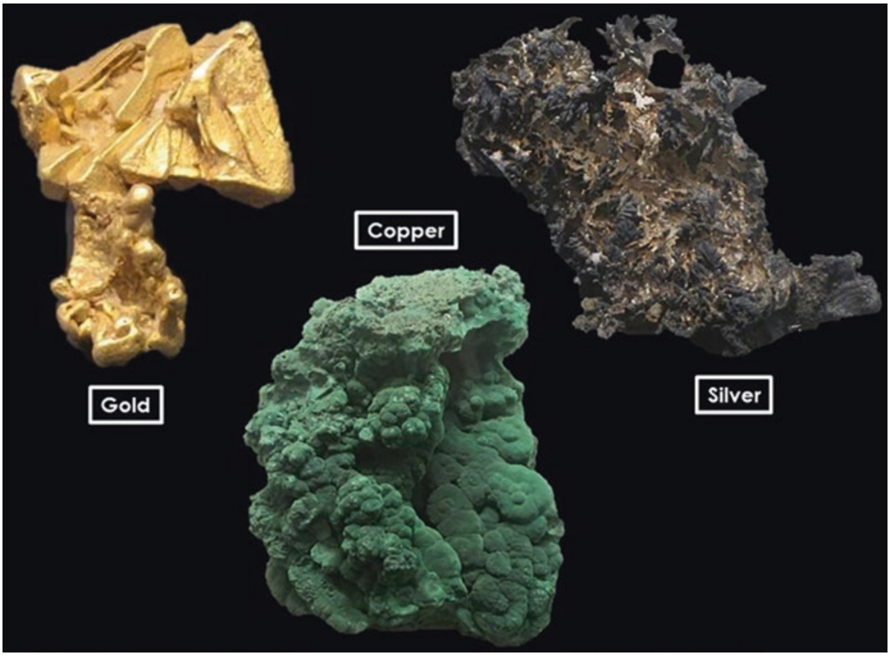

Fig. 4.2 Native metals: gold, copper, and silver. (Photo: L. Vetter)

Fig. 4.3 Indigenous people panning for gold in the river (Fernández de Oviedo, 1851/1535)

the rivers of the island of Española (present-day Dominican Republic and Haiti). This chronicler presents a drawing in which three indigenous people are performing the labors of gold extraction from a riverbed with the aid of pans (Fig. 4.3).

Nevertheless, ancient miners were no strangers to work in mines, where they obtained minerals such as copper, silver, lead, tin, and arsenic, among others. Cieza de León, another chronicler from the sixteenth century, points out this work in Antioquía, narrating the following:

Fig. 4.4 Mine at Cerro Mellizo, North Coast of Peru. (Photo: L. Vetter)

> Well coming back to the topic, I remember when the graduate Juan de Vadillo and I discovered that a cleric with the armada, named Francisco de Frías, had discovered, in a house or raised cabin in the town of Buritica, a 'Totuma', which is similar to a large *albornía* filled with dirt: and the thick and large grains of gold are separated out in it. We also say there the sources and mines where they collected it from, and the clubs or hoes that they used for the work. When Captain Jorge Robledo settled this city of Antiocha it was to see these deposits, and they washed a pan of dirt, and a very small quantity of something came out: a miner confirmed that it was gold: another said that it wasn't, but rather that it was what we call 'margajita': and since we were on our way, we didn't look any more at it [2, Ch. XIV, p. 60].

Some of the mines exploited in Pre-Hispanic times on the North Coast of Peru were Cerro Blanco, Cerro Barranco Colorado, Cerro Mellizo, and Cerro Morro Éten, in Lambayeque [3] (Fig. 4.4). Lechtman [4] carried out extensive research on the possible mines exploited in Pre-Hispanic times, both on the North Coast of Peru and in the Andean highlands. In the Titicaca Basic, metals such as gold, silver, and copper were exploited starting in the Tiahuanaco Period. These mines included Porco, Carabaya, Huancané, Chuquiabo, and Chincane, located close to the Desaguadero River [5]. Potosí was another important mine exploited since Pre-Columbian times [6], and its exploitation continues to this day (Fig. 4.5).

The archaeological evidence also allows us to know the type of toolkit used for the exploitation of mines, comprised of stone hammers with wood handles, animal horns or antlers, wood hoes, baskets or leather bags for extracting and transporting the mineral, as well as wood or metal pry bars to loosen the mineral from the wall (Fig. 4.6).

Several of the mines famous during Colonial times were already known by the Inca administration, although the scale of exploitation was lesser than at the peak of Colonial mining. Murúa attributes the discovery of silver deposits at Porco, Potosí, and Tarapacá, as well as that of gold deposits at Chuquiapo and Carabaya, to Túpac Inca Yupanqui, who took advantage of the mineral richness of the new province of Tawantinsuyo (in the Bolivian highlands), ordering the manufacture of dishes and drinking vessels, possibly for the purpose of making public offerings to the *huacas*

Fig. 4.5 Potosí. Atlas of Sea Charts, Peru (circa 1585)

Fig. 4.6 Stone hammer with wood handle [7]

that would endorse his government over the other peoples, as well as favor and protect him from adversity [8, Book I, Ch. 25].

In general, the ancient Americans were not only great miners, but also had great skills in transforming minerals into metal, as is the case of the Sicán (900–1375 C.E.) on the North Coast of Peru, who transformed minerals from copper and arsenic to obtain arsenic bronze, from which they manufactured agricultural tools that allowed them to expand their agricultural borders, among various other uses [3, 9, 10].

As a native metal, or one that requires no transformation processes in contrast with those minerals and metals that are not found in nature in a native state, gold passed immediately from extraction to the worktable of the goldsmith, who deformed it plastically by pounding with stone hammers of differing hardness. These did not have wood handles (Figs. 4.7 and 4.8), but rather were fitted to the size of the artisan's hand. Some chroniclers describe the manner in which ancient goldsmiths produced metal pieces. One of these was Garcilaso de la Vega, a *mestizo* chronicler from the sixteenth to seventeenth centuries, who commented:

Fig. 4.7 Stone anvils and hammers for plastic deformation. (Photo: P. Carcedo)

Fig. 4.8 Various stone instruments for gold working, with different shapes and sizes. (Photo: P. Carcedo)

> And beginning with the silversmiths, we will say that, with having such a great number of them and with working perpetually at their trade, they did not know how to make anvils from iron or other metals […] For anvils, they used other very hard stones, of a color between green and yellow; they flattened and smoothed ones with others; they worked with some instruments that they make from copper and brass, mixed together; they are in the shape of dice, with blunt corners; some are large, as large as can fit in the hand for the stronger blows; others are medium-sized and others small and others elongate, for concave hammering; they use these hammers in the hand to pound with them as if they were pebbles. They did not know how to make files or burins […] [11, Volume I, Book II, Ch. XXVIII, p. 156].

In their excavations, archaeologists have not only found hammers and anvils, but also report the occasional finds of clay objects such as molds and crucibles. Furthermore, chisels, awls, and burins were some of the tools that ancient goldsmiths produced to work the pieces that would then be used by the ruling elite (Figs. 4.9, 4.10, 4.11, 4.12, 4.13, and 4.14).

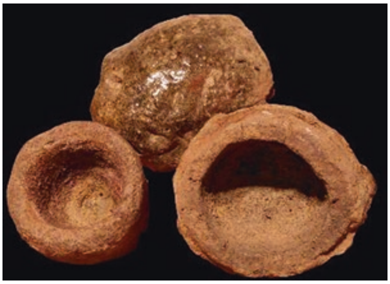

Fig. 4.9 Clay crucibles for gold working. Private collections. (Photo: L. Vetter)

Fig. 4.10 Stone ingot mold. MOP. (Photo: L. Vetter)

Fig. 4.11 Gold ingots. MOP. (Photo: L. Vetter)

Fig. 4.12 Clay bivalve mold for casting [12]. (Photo: L. Vetter)

Fig. 4.13 Gold chisels for manufacturing and decorating gold objects ([12], MUCEN (Museum of the Central Reserve Bank of Peru, Lima)). (Photo: L. Vetter)

Benzoni, who was an Italian merchant and traveler, makes the following comments regarding gold working and its associated tools:

> This Province of Quito is of temperate climate, which is why the Kings of Cuzco lived there most of the time, in many sites maintaining workshops for goldsmiths, who, without knowing the use of any instrument from iron, laboring roughly made marvelous things, proceeding in their work in this manner. In the first place, when they melt the gold and the silver, they place the metal in a long or round crucible, made from a piece of rag smeared with wet

Fig. 4.14 Gold and silver awls for gold working with precious metals. MOP. (Photo: L. Vetter)

Fig. 4.15 Goldsmiths working [13]

> dirt and crushed coal; once the crucible is dry, they put it in the fire with the amount of metal that can fit in it, and with five or six reed tubes, sometimes more, sometimes less, they blow so much that these end up melting and passing; then, sitting on the floor, the goldsmiths, with some black stones worked for this type of labor, helping one another, make or better said made in their time of prosperity, that which they had been ordered to produce, that is, hollow statues, drinking vessels, sheep, jewels, and, finally, all sorts of figures of the animals that could be seen. [13, pp. 118, 119].

This traveler also records his description in the only existing drawing of gold working in the Central Andes[3] in Pre-Hispanic times, which is shown in Fig. 4.15.

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[3] From a metallurgical point of view, the region of metalworking in the Central Andes consists of southern Ecuador, Peru, and the Peruvian-Bolivian highlands. It is in this area where metallurgy emerged in America and its technology was spread toward the north and south of the continent.

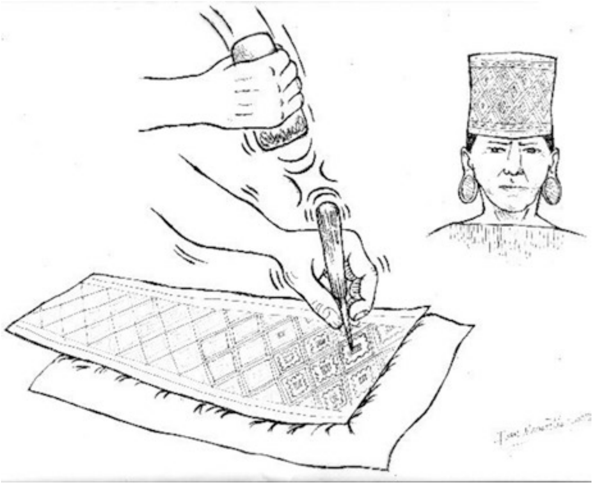

Fig. 4.16 Representation of the embossing technique used for the decoration of a crown [12]

Objects were manufactured with techniques such as chiseling, puncturing, and inlaying as we can observe in Fig. 4.16, but also, different alloys were developed that allowed for the creation of surfaces of different colors and tones.

As we will see later on, when we discuss the significance of metals for Andean man, both gold and silver, and metals in general, played an important role in the Andean worldview. For this reason, ancient goldsmiths manufactured pieces from gold with different alloys to achieve different color tones, sounds, and finishes. Therefore, pieces that at first glance could seem to be gold could actually contain between 50 and 10% of this metal, with the rest being copper and/or silver, in an alloy known as *tumbaga*.

Tumbaga refers to various ancient alloys that could be binary (gold-copper or silver-copper) or trinary (gold-copper-silver), although occasionally with the intervention of other chemical elements such as arsenic. Lechtman, a researcher who has dedicated her efforts to the study of *tumbaga*, mentions that: “When copper and gold are melted together, they combine easily. After cooling and solidifying they remain combined; they form a series of solid solutions with all the possible range of proportions. Pre-Columbian gold and copper alloys varied widely in their composition: some were so low in gold that they had just 12% of this metal. The color of the alloy depends on its composition. The *tumbagas* with a high concentration of copper have a red or pink color; those with a greater quantity of gold are yellowish. Silver is also found in many of these allows. This could be due to the gold being added to an alloy of silver and copper or to the gold already containing a certain amount of silver, since the gold nuggets from Andean placers normally contain it. Although *tumbaga* was first produced in the Central Andes, in later periods it was a common alloy in many other places in Central and South America in Pre-Columbian times; it was even known in México” [14, p. 26].

This technique of gilding a piece of metal was seen for the first time by the chronicler Fernández de Oviedo, who relates the following on his journey to Santo Domingo and the Antilles:

> […] as the Indians know very well how to gild the pieces and things that they work from copper and very little gold. And they have such delicacy and excellence in this, and they give such a high luster to that which they make golden, that it seems it as such good gold, as if it were of 23 carats or more, according to the color that it attains by their hands. They do this with certain boiling methods, and it is such a great secret that if any of the silversmiths in Europe, or anywhere else, where among Christians were to use or know it, he desired to be a very rich man, then in a short time he would be one with this manner of making golden. This remarkable way does not belong to this island or to other neighboring ones; because it is not made except on the Mainland, and there a large quantity of the low gold gilded in the manner that I have said is seen; but since it is done on purpose, I wanted to make mention of this peculiarity here (in *this book of records*). I have seen the boiling method, and Indians have shown me it; but I could never, by flattery or any other way, get the secret out of them, and they denied that they made it, but rather in other faraway lands, pointing to the South or the southern region [15, Book VI, Ch. VIII, first part, p. 189].

Fernández de Oviedo was one of the first naturalists who arrived to America and was interested in the natural history of its inhabitants. He mentions the second way of gilding metal, which today is known as *depletion gilding* (gilding by depletion or enrichment). This technique was developed for the first time in the Andean region; by this process, a *tumbaga* ingot was deformed plastically with successive reheating, and in this way the copper oxide would emerge to the surface and could be removed when this was cleaned. This process was carried out several times until the surface became enriched in gold. But if the *tumbaga* alloy was ternary, after the cleaning of the surface and the removal of the copper oxide, a combination of gold and silver would remain. In order to remove the silver, the surface was covered with a corrosive paste of ferric sulphate, sodium chloride, and water, which dissolved the silver, leaving only the gold on the surface [14, pp. 26–27]. Fernández de Oviedo is possibly the first Spaniard to make reference to this gilding technology. The evidence indicates that it was mastered with greater precision in the region of present-day Colombia and Peru. However, there is also archaeological evidence indicating that this gilding technique was also known in Mexico, Panama, and Costa Rica [14, 16].

Ancient goldsmiths also knew the technique of fusion gilding, which consists of plastically deforming a copper ingot with consecutive annealing until a sheet is formed. A coating of gold alloy is applied to one of the sheet's faces, on which a process of depletion gilding or gold enrichment is carried out as a finishing technique. The metallographic analyses carried out by Scott on a sheet from a pectoral ornament from Nariño, in Colombia, indicate that a "diffusion bond between the hammered and annealed copper sheet and the applied layer of gold alloy" was formed, by which it can be deduced that this process was finished with hammering and annealing posterior to the coating of the piece. The analyses by electron microprobe reveal very pure copper, and for the coating they reveal an alloy of 59% gold, 8% silver, and 33% copper, which constitutes an intentional *tumbaga* alloy [17, pp. 284–287].

Another technique, reproduced in the laboratory by Lechtman, is gilding by electrochemical replacement, in which aqueous solutions of corrosive salts are employed to dissolve the gold. To achieve this, the researcher prepared a corrosive bath consisting of potassium aluminum sulphate, potassium nitrate, and sodium chloride, a mixture which was dissolved in water in equal parts. These corrosive salts are found in the Peruvian coastal desert. The gold was heated between two to 5 days, and was thus easily dissolved. The solution turned out to be too acidic, so sodium bicarbonate was used to neutralize it. After submerging the copper sheet for 5 min in this neutralized solution, a uniform gold surface was obtained. In order for this gold coating to not detach, the piece was heated between 650 and 800 °C to achieve a strong metallurgical join between the interface of the gold and the copper [14, p. 23].

These weren't the only gold alloys that were produced in ancient times. The latest archaeological research of Izumi Shimada and his team reveals that, during the Middle *Sicán* Period (900–1100 C.E.), there were two large precious metal workshops in the Great Central Plaza of the site of *Sicán*. Their excavations exposed four superimposed floors, food residues, and abundant evidence of burning, including a series of large open ovens (over 1 m in width), coated in adobe. According to the researchers, these characteristics indicate that the workshops underwent an intensive and continuous use. The activities carried out by the goldsmiths seem to have been the consolidation of metal nodules to produce ingots, the purification of these ingots, molding and the forging of preforms, and the preparation of sheets of metal through numerous cycles of hammering and annealing to increase their hardness and at the same time elongate them in the desired direction; these last activities would have taken place very close to the oven. According to the analytic studies carried out by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS), as well as electron probe micro-analyzer (EPMA), *tumbaga* was produced in this workshop. This research discovered that the production of *tumbaga* in this workshop was not limited to the copper–gold–silver alloy, but rather that alloys of arsenic copper were made, to which silver was added, and after this intentional ternary alloy, variable concentrations of gold were added to achieve different properties of color and hardness, depending on the goldsmith's requirements [18].

Having reviewed how ancient Americans extracted gold and created objects from different alloys and with various tools, we will now analyze the marks that the manufacturing techniques left on these objects, which can be observed through various analytic techniques, allowing for a greater understanding of the technology developed in ancient times.

The Marks Behind the Tools

Archaeologists use various physiochemical techniques to gain a detailed understanding of the technology employed by ancient metalworkers to produce gold and silver objects.

We will present some analyses carried out on gold, gold–silver, and gold–silver–copper pieces using digital radiography and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS).

For the digital radiography, a device called Digital Radiography Equipment was used, by the maker VIDISCO, model RAYZOR X, with X-ray source General Engineering 270 kV constant. To determine the alloys used in the manufacture of the objects, the pieces were analyzed by means of energy dispersive X-ray spectroscopy (EDS) with scanning electron microscope (SEM) JEOL JSM-IT300, with an acceleration voltage of 20 kV with ZAF correction.

Head-Shaped Rattle

The head is composed of two sheets joined by silver solder. The headdress has been embossed, as have the eyes, nose, and mouth. The eyeball is represented with a sheet of silver which appears to have been joined by plating, while the ear ornament has been placed by way of a mechanical join (Figs. 4.17 and 4.18a, b).

Fig. 4.17 Head of a Moche figure with ear ornaments and silver eyeballs with irises of semiprecious stones. Poli Collection. (Photo: L. Vetter)

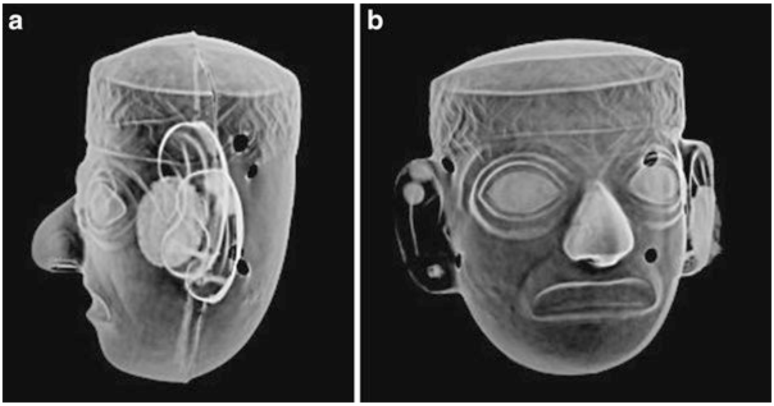

Fig. 4.18 (**a**, **b**) Digital radiograph of the head showing the join of the sheets by welding. (Photos: J. Ruiz)

Two-Headed Serpent Nose Ornament

This nose ornament was made from several sheets that were cut to give them the form observed in the different parts of the object, such as the heads of the two-headed serpents or the bands connected by twisted wires. The rings have been made from strands of metal of practically homogeneous diameters (Figs. 4.19, 4.20, 4.21, and 4.22).

Fig. 4.19 Nose ornament from the Early Intermediate Period depicting two-headed serpents. Poli Collection. (Photo: L. Vetter)

Fig. 4.20 Digital radiograph of the nose ornament highlighting the welding points. (Photo: J. Ruiz)

Fig. 4.21 Rings with very similar diameters (1.661 and 1.601 mm). (Photo: J. Ruiz)

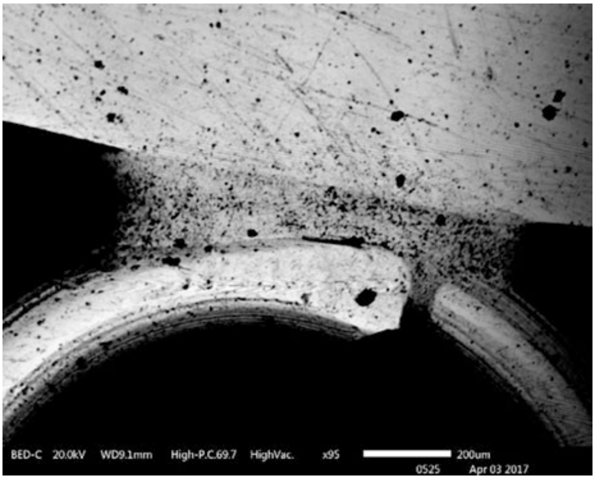

Fig. 4.22 Evidence of welding. (Photo: J. Ruiz)

Table 4.1 Chemical composition by EDS of the different parts of the nose ornament

Two-headed serpent nose ornament	Gold	Silver	Copper
Head	82.8	12.8	4.4
Band or strand	97		3
Weld	74.2	22.5	3.4

The radiograph shows the welding points, which can be observed at a greater magnification in the SEM images, along with the mounting of the parts and the rings. The distinct composition of the band with the serpent heads can be justified by the welding work (Table 4.1). This contains an increased percentage of silver, which allows for a lower fusion point, thus avoiding the melting of the rest of the piece.

Bicolor Nose Ornament

This piece has been made from various sheets, some silver and others gold, apparently joined mechanically. The gold sheet on the lower edge depicts a serpent or ichthyomorphic being made by embossing (Figs. 4.23 and 4.24).

In the radiograph, two different-colored alloys can be observed. The black/brown and the silver areas have the same density and thus are actually the same material; the black could simply be due to the corrosion of the silver. It seems that the silver sheet isn't welded, but rather is hammered. The chemical composition is shown in Table 4.2.

Fig. 4.23 Gold and silver nose ornament from the Early Intermediate Period depicting serpents or an ichthyomorphic being. Poli Collection. (Photo: L. Vetter)

Fig. 4.24 Digital radiograph of the nose ornament showing the gold and silver sheets. (Photo: J. Ruiz)

Table 4.2 Chemical composition by EDS of the different parts of the nose ornament, with the yellow area corresponding to gold and the white area corresponding to the silver sheet

Bicolor nose ornament	Gold	Silver	Copper	Iron
Yellow	86.1	13.6		0.3
White		97.7	1.4	0.9

Nose Ornament with Incrustations

This object was manufactured with sheets, bands, twisted strands of metal, and hollowed granules. The work is very uniform, as shown in the photomicrographs. The SEM of the granules shows high regularity of shape and size, as well as very fine welds, which shows the expertise of the goldsmith. The granules' dendrites are normal and correspond to a heating slightly greater than that of the welding. The strands seem to be made by hammering and are very uniform (Figs. 4.25, 4.26, 4.27, and 4.28).

Fig. 4.25 Gold nose ornament from the Early Intermediate Period, made with twisted strands, granules, and incrustations of semiprecious green stones. Poli Collection. (Photo: L. Vetter)

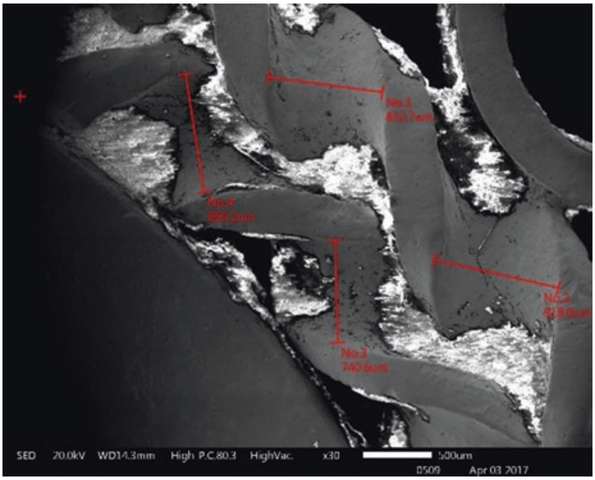

Fig. 4.26 The distances between the twists of the strands are very regular, between 740.6 and 918µm. (Photo: J. Ruiz)

The antimony present in the solder seems to belong to the modern cleaning products present in the concavities, not to the composition of the solder. The composition of the granules indicates a very high-quality alloy (Table 4.3).

Based on what we have presented here, we can say that ancient goldsmiths worked with diverse techniques of manufacture and decoration, with which they were able to create marvelous pieces that we can appreciate today due to the work of archaeologists. In the following section, we will present the first gold objects recorded in Peru, with information about the types of contexts in which they appeared.

Fig. 4.27 The granules have almost the same diameter. The measurements present in the photomicrograph are 1793 and 1749 mm. (Photo: J. Ruiz)

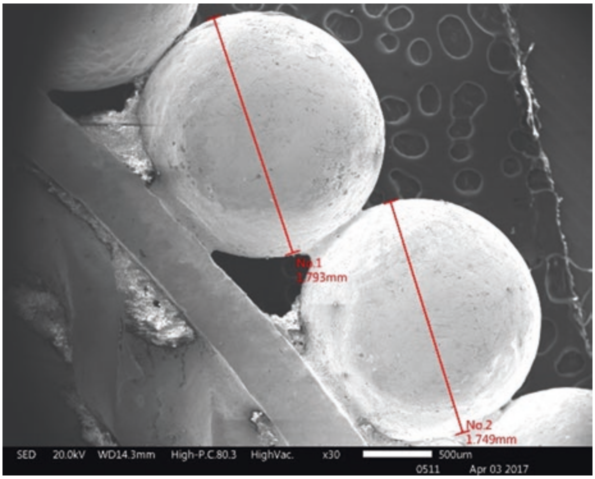

Fig. 4.28 The dendrites' granules near the welding points can be observed. (Photo: J. Ruiz)

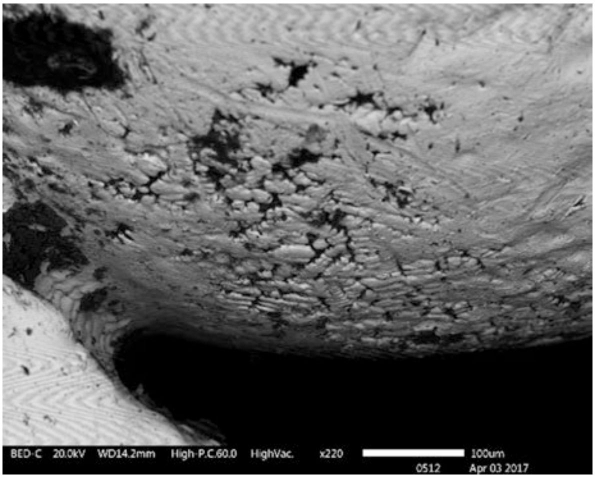

Table 4.3 Chemical composition of the granule and the solder

Nose ornament with incrustations	Gold	Silver	Copper	Antimony
Granule	95.2		4.8	
Solder	80.6	6.3	3.6	9.4

Archaeological Evidence of Gold in Pre-Columbian Cultures in Peru

We will present the evidence that exists up to this moment from archaeological discoveries revealing metalworking by Pre-Columbian cultures in the region of present-day Peru (Map 4.1).

Map 4.1 Map of Peru showing the Pre-Hispanic sites with evidence of metallurgical or goldsmith workshops, or contexts in which metal objects have been found. (Elaborate by L. Vetter)

Archaic Period (6000–1800 B.C.E.)

In the Andean region, there are two sites with the earliest dates for working with gold, which is currently understood to be the first metal worked by ancient metalworkers. Both sites are located in the Southern Andes in present-day Peru. The first is Waywaka, in Andahuaylas, where Grossman recovered some very thin sheets of gold accompanied by circular beads of semiprecious blue stones from a funerary context. The individual was also accompanied by a "goldsmith's toolbox," so named because three hammers and an anvil, all made from stone, were found inside of it. This context has been dated to ca. 1680 to 1410 B.C.E [19]. The other find also belongs to a funerary context excavated by Aldenderfer and colleagues in Ilave, Puno, at the site of Jiskairumoko, and it consists of a necklace of tubular beads made from gold sheets associated with circular beads of blue semiprecious stones. This archaeological context was dated to ca. 2155 to 1936 B.C.E [20].

Therefore, the find of Jiskairumoko represents the earliest object worked in gold in the Andean region. The necklace was made from gold sheets rolled to form nine tubular beads that were strung from a cord with semiprecious stone beads. Although the find from Waywaka is more recent, the pieces are less worked than the earliest ones from Puno, since in the former case they are small sheets of gold without a defined shape or function. Nevertheless, though the metalwork from Andahuaylas could be considered "inferior" to that from Puno, the first goldsmith's toolbox was found there, according to its discoverer [19].

Along these lines, the "inequalities" in the technology, size, and design, among other aspects, in the objects from different cultures would seem to be evident; this is due, in large part, to the absence of archaeological investigations, which impedes the establishment of a clearer picture of the development of metallurgy in the Central Andes. These gaps could be due to the fact that in early times, communities were very small and there wasn't communication among them, since in many cases they were isolated. The geography of our region is extremely complex, with deserts, mountains, and jungles, complicating the contact among communities that could be less than 1 km apart, but with the distance not being flat but rather requiring people to climb large mountains to arrive at their destination.[4] In summary, this panorama didn't allow for a fluid communication in early times, although centuries later, through the conquest of territories to obtain new resources, roads were created that allowed for greater communication among communities.

Initial Period (1800–800 B.C.E.)

In this period, small laminated objects continued to be manufactured, such as those recovered on the Central Coast, on the terrace of the main pyramid at Mina Perdida (1500–1100 B.C.E.) [22].

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[4] For more information on this subject see Salaverry [21].

Meanwhile, on the North Coast, a find that stands out is that of a laminated copper disc, possibly gilded, excavated as a funerary offering at the site of Puémape, in San Pedro de Lloc, and dated to between 1500 and 1300 B.C.E [23].

In the Northern Andes, the first evidence of goldwork was recovered by Burger at the archaeological site of Chavín de Huántar and consists of a conical piece made from a sheet of gold. It was dated to 1200 B.C.E [24].

Early Horizon (800–200 B.C.E.)

The pieces from this period are small, thin sheets, although there are also large pieces, thick sheets with diverse iconography, use of pigments, and incrustations of other materials.

On the South Coast, the Paracas culture developed (800–200 B.C.E.), characterized by its production of thin laminated pieces from gold, cut sheets in the form of pendants, ear ornaments, and diadems with embossed and incised decoration and of great size, as well as some tweezers [25].

The excavations at the site of Morro de Éten (600–400 B.C.E.), located in Lambayeque on the North Coast, revealed various very thin sheets, a laminated circular pendant, a sheet rolled into a tube, small tubular sheets, and a ring made from twisted wires, all of which were made from gold [26, 27].

Another site on the North Coast, also in the Lambayeque region, where evidence of goldwork was recovered from two funerary contexts, is Chongoyape (400–300 B.C.E.). One of them corresponds to a male individual buried with crowns, ear ornaments, and gold tweezers. The second was that of a male individual accompanied by two women who had, as part of their burial goods, *tupus* or pins, rings, embossed and fretted gold plates, as well as ceramic and stone pieces. All of the metal objects were of great size, laminated, and had embossed decoration [28, 29].

The Japanese Mission carried out excavations at Kuntur Wasi, Cajamarca, during the 1990s. There they discovered eight tombs with gold objects, including crowns, nose ornaments, ear ornaments, plates made from think, and embossed sheets with incrustations of shells and semiprecious stones, as well as cinnabar pigment. The first six tombs correspond to the Kuntur Wasi Phase (800–500 B.C.E.), while the last two are from the Copa Phase (500–250 B.C.E.) [30–33]. The work by Seki at Pacopampa, from 2009 to 2012, revealed the tomb belonging to the "Dama de Pacopampa" ("Lady of Pacopampa"), dated to ca. 900 B.C.E. As a part of her burial goods, two cylindrical ear ornaments and two triangular earrings with embossed designs of ribbons in the shape of an inverted "U" were found [34]. In addition, in the 2015 field season, a gold necklace was found in the funerary context of an elite individual, which Seki called "The Tomb of the Serpent-Jaguar Priests," whose iconography depicts a mythical being with the body of a serpent and the head of a feline, who must have been an important entity in the religion and worldview of that society [35].

Early Intermediate Period (200 B.C.E.–600 C.E.)

In this period, goldwork achieved great development, above all on the North Coast. In effect, the societies of the Peruvian North Coast, such as the Vicús (200 B.C.E.–200 C.E.), attained a very high level in metalworking, producing pieces of great size with thick sheets and in golden copper, including pectoral ornaments, crowns, and nose ornaments of embossed gold [36]. With respect to the Moche (100–700 C.E.), metalworking experienced extraordinary development using all known techniques, such as molding, laminating, embossing, fretting, incrusting, and many others. They worked with gold, silver, and copper, and alloys such as *tumbaga*, to produce golden or silvery pieces, or a combination of the two. Objects such as bicolor nose ornaments, ear ornaments, pectoral ornaments, headdresses, and many others were manufactured with great mastery [37–39].

Gabriel Prieto carried out excavations at a cemetery of sacrificed children at the site of Pampa La Cruz in Huanchaco, in the region of La Libertad on the Peruvian North Coast. In these tombs from the Virú occupation (100 B.C.E.–450 C.E.), a series of offerings was found, including a copper hook of approximately 10 cm wrapped in a gold sheet. For Prieto, the size of the hook indicates its use for catching large fish and sharks, an activity still practiced today in the area [40].

On the South Coast, the Nazca goldsmiths (50–650 C.E.) continued the Paracas tradition of producing gold pieces from thin sheets, but they also manufactured miniature pieces such as diadems and nose ornaments, and new forms such as bracelets and feathers [25].

In the cemetery of Tablada de Lurín (100 B.C.E.–300 C.E.), on the Central Coast, as part of the funerary goods, a series of metal objects such as crowns, diadems, necklaces, nose ornaments, and others were found. Some of the manufacturing techniques used were fusion gilding and depletion (or enrichment) gilding [41].

Middle Horizon (600–1000 C.E.)

This period was characterized by the predominance of the Wari empire, whose capital was established in the region of present-day Ayacucho, in the Southern Andes, but exerted a strong presence on the Peruvian coast in valleys such as Ica and Huarmey, with its strategic presence standing out at the coastal oracle of Pachacamac.

The Wari produced miniature laminated pieces as well as laminated objects of greater size, such as ear ornaments, drinking vessels, rings, *tupus*, spoons, necklace beads, and molded objects such as *piruros*, among others. They used the technique of incrustation of semiprecious stones and shell, in addition to producing gold and silver objects, such as ear ornaments, with mechanical and metallurgical joins [42, 43].

Late Intermediate Period (1000–1450 C.E.)

During this period, the same techniques continued to be used as in the previous period, especially in the case of the Sicán on the North Coast, who continued the metalworking tradition of the Moche, producing the same forms as well as others, such as drinking vessels, gloves, and masks from gold and *tumbaga*, employing decorative techniques such as setting, incrusting, miniature feathers, and cinnabar paint [44, 45].

The Chimú (1375–1450 C.E.) of the North Coast, like the Ychsma of the Central Coast, continued the metalworking tradition of the Sicán, although they manufactured more pieces from silver, with gold being less worked. The use of *tumbaga* wasn't very common, and neither were bimetallic pieces, but they continued using forms such as anthropomorphic effigy vessels, drinking vessel rattles, masks, figurines, tweezers, and others, as well as the same manufacturing techniques [46].

Late Horizon (1450–1532 C.E.)

In the Inca period, evidence was found for the use of gold to produce metal pieces, although the Inca are known to have had little expertise in these arts. Aware of their lack of expertise in metalworking, they decided to transfer expert goldsmiths from other parts of Tawantinsuyu, such as the goldsmiths of the North Coast and the center of present-day Peru, to different parts of the empire such as Cusco, Jauja, and Chicha, among other locations [47]. Pérez Trujillo has carried out excavations since 2013 at the site of Qotakalli, where various metal pieces such as *tupus* and sequins have been found; some of them seem to be made of gold or gold alloys. These pieces were found in funerary contexts, as well as in spaces apparently used as metallurgical workshops [48]. During this period, the goldsmiths brought from the diverse corners of Tawantinsuyu produced figurines or *capacochas* in gold and silver with the techniques of lamination and molding, as well as *tupus* and *porras*, among others [49].

Divine Gold

> […]Vichama, seeing the world without men, and the *huacas* and the Sun without being worshipped, he begged his father the Sun to raise new men, and he sent him three eggs, one of gold, another of silver, and a third of copper. From the gold egg came the *Curacas*, the *Caciques*, and the nobles that they call second persons and principle ones; from the silver one were engendered the women of these and from the copper one the common people, that they call *Mitayos*, and their women and families […] [50, Book II, Ch. XIX, p. 413–414].

We cannot understand the material culture left to us by the Pre-Columbian cultures if we don't understand the meaning of the objects in the context in which they were created. We would have to close our eyes and transport our minds and senses to an aboriginal world in which the sounds, colors, smells, sensations, virtues, defects, or qualities of the animal, plant, or mineral world are what dictate the guidelines of religious, mystical, earthly, and supernatural beliefs. These principles would be manifested in diverse ways, especially in gold, the reason for this article.

The qualities and characteristics of color, the form of the piece, the sound it emits, the shine or brightness that emanates from it in movement, and even the embossed or engraved scenes on it refer us to cosmic worlds inhabited by the ancestors and the supernatural deities who are connected to the earthly world through ritual.

The American indigenous cultures observed, respected, and venerated nature and the world surrounding them. Their beliefs, rituals, myths, and daily routines were organized by imperceptible forces that governed the order of the universe and of men. They did not understand an earthly or spiritual world without paying homage to these forces that gave them their daily sustenance, liberated them from illness, and protected them from their enemies. All that surrounded them was connected to nature, and to nature they directed their prayers, paid homage, and focused their attention to portray its characteristics on the objects they produced as works of art of exquisite beauty.

Transforming a raw material, such as the precious metal gold, into a sacred object, was an arduous task in all ancient cultures because it implied not only great technical experience but also a profound comprehension of the worldview, ideology, and religious beliefs of the people who manufacture it, which were exteriorized on every one of the objects created. For this reason, they should be admired not only for their artistic beauty, but also as carriers of an ancestral ideology, thus playing a conciliatory role between the divine and the human [51].

Perhaps due to the difficulties in obtaining and transforming it, it is metal itself, in the most varied compositions, that is the material most often employed in offering to the gods through rituals and offerings at all the stages of metallurgical production; for example, through payments to the earth for the extraction of mineral from mines, offerings in metallurgical centers and goldsmith workshops, and, finally, finished objects in tombs, together with the deceased and as part of the funerary goods that accompanied them to the world of the ancestors. Minerals and metals formed a part of the underworld or *Ukhu Pacha*. The indigenous people worshipped the fertile earth they called Pachamama, a divinity that was associated with the arrival of the Europeans to the American continent and associated by Christianity with the Virgin Mary for the catechistic goals of colonialization. They worshipped and revered the mines that they called *copa*, and the metals called *mama*, and the stones from the metals (minerals) that they called *corpa* because they were torn from Mother Earth [52, p. 177].

Today, it is common to find the remains of payments to Mother Earth in mines: coca leaves, chicha, and even animal fetuses [3]. The rituals celebrated in honor of the earth were highly related to those of the moon, since both, at least during Incan times, were identified as feminine beings and were associated with fertility and the lunar cycles that served to establish the agricultural cycles. It is important to note that in the Andean world, everything that involves extracting something from

Mother Nature to transform it encloses attributes tied to magical and shamanistic powers originating from the mine itself, which are also present during its transformation in a melting oven and even up to its earthly use or as goods destined for the other world.

The genius of the ancient goldsmiths allowed them to transform what Mother Nature or *Pachamama*, a force in the form of a woman concerned with providing and ensuring the continuity of the production of the earth and therefore of subsistence, offered them into objects of great beauty. Thus, precious artifacts of gold and silver were combined with other elements such as colored precious and semiprecious stones, brightly colored feathers, and textiles with thousands of designs and hues, in order to portray a universe of codes that reflected not only the worldview and ideology of a people, but also its sensitivity. Color, sound, movement, brightness, and shine, characteristics of the metal objects of the Central Andes, referred to the four elements that moved the Universe: air and its opposite, water (sound, movement, and libations), and fire and its opposite, earth (brightness, shine, and color) (Figs. 4.29 and 4.30).

These opposites ruled their worldview, and relationships were explained by duality represented by the opposition of complementary concepts. For example, in the animal kingdom there are two groups that are clear examples of the concept of opposites: the birds that fly through the air are in contact with the light, they are warm-blooded, they sing melodically, and they often have multicolored feathers (they represent air); and their contrast would be the frogs or toads, cold-blooded amphibians that seek shade, and whose voice is monotone (water) [53]. Both representations are recurrent, for example, in the metalwork of the Middle Sicán Phase or the Lambayeque Phase (950 C.E.–1100 C.E.), whose tombs have revealed a large quantity of metallic objects as part of their funerary goods.

The metal piece, therefore, had to be an object that would carry with it implicitly the rich and majestic universe of the worldview without ceasing to provide visual delight through its contemplation. In this manner, they created “multisensory” pieces that, with their movement, evoked the sound of the birds, the murmur of the

Fig. 4.29 Gold and golden copper crowns with feathers of various colors from the Amazon, as well as feathers made from gold sheets. Poli Collection. (Photo: L. Vetter)

Fig. 4.30 Nose ornaments with pendants of different shapes that produced diverse sounds and shines. Poli Collection. (Photo: L. Vetter)

sea, the pitter patter of the rain, or the roar of the jaguar. The brightness and shine that emanate from a gold piece remind the man contemplating it that there was a god the Sun who gave life, allowed the seeds to germinate and grow, and, together with the Moon, his wife and sister, ruled and regulated the cycles of the agricultural calendar. The color of silver evoked the powerful goddess the Moon as well as the sea or the goddess of the sea, *Mama Cocha*, mother of all the waters, including lakes, lagoons, rivers, or springs; the sea that provided them with food and life and who, like the Sun, could also destroy or devastate if they did not follow her commands.

In the Incan worldview, the *Inti* or Sun was the most important divinity in the pantheon, and was associated with gold, which was the “sweat of the sun.” *Mama Quilla*, or the Moon, was the sister and wife of the Sun, and was associated with silver, which was the “tears of the Moon.” The Inca wore objects of gold while the *Coya* wore those of gold. According to the chronicles, the Sun, and therefore gold, was related to the right side, to men, masculinity, and natural phenomena. The Moon, and therefore silver, was connected to the left side, to women, femininity, and fertility. Pre-Columbian Andean cultures were not the only ones to identify gold with the Sun and silver with the Moon (Figs. 4.31 and 4.32). The Mesoamerican peoples also considered gold and silver to be divine representations of the Sun and the Moon. In Nahuatl, gold was related to the solar deity (probably Curicaueri) and was considered to be his excrement, while silver corresponded to the excrement of the moon Xaratanga [55, p. 70].

In spite of the imposition of the cult of the Sun by the Inca when they conquered the coast of the Central Andes, the Moon continued to be highly revered in all of the coastal cultures, even more so than the Sun. Regarding this, the chronicler Antonio de la Calancha says: “The Indians of Pacasmayo, and the other valleys of the plains, worshiped the Moon as the principle and superior God, because she reigned over the elements, raised the food, and caused commotions of the sea, lightning, and thunder. Her shrine was in a *huaca*, that was called Sian, that in the Yunga language, means house of the Moon; they considered her more powerful than the Sun, because he did not appear at night, and she could be seen during the night and the day….” [50, Book III, Ch. II, p. 552] (Fig. 4.33).

From a Western point of view, copper is not considered to be a precious metal, but to ancient Peruvians, it was both an essential and symbolic metal, on an equal level to gold and silver. It gave objects a reddish color like the blood of the

Fig. 4.31 Bicolor nose ornaments of gold and silver that show opposites and complements: the son and the moon; day and night; feminine and masculine. Poli Collection and MOP [54]. (Photo: L. Vetter)

Fig. 4.32 Drinking vessels of gold and silver that combine both metals. The top ones depict figures related to nature, while the bottom ones represent the god of the Sicán culture. These latter ones are rattles and produce sounds when they are raised to drink. Private collection. (Photo: L. Vetter)

vanquished, and when used in alloys it gave hardness and strength to the metal pieces; it is for this last reason that we consider it to have symbolized the "soul" of many pieces. Metallurgists learned to gild and add silver to objects in copper, to play with colors, and to produce objects of great size such as the crowns and pectoral ornaments of the cultures of the North of Peru, such as the Vicús (200 B.C.E.–200 C.E.). They also utilized copper, with its reddish color, in pieces made exactly the same in gold and silver, such as the Moche *chalchalcas*, thereby giving all the pieces the same tone. According to Reichel-Dolmatoff [53], in some tribes of Colombia, copper colors implied a certain idea of danger or illness. But copper was also employed in the production of diverse tools for metalworking (molds, chisels, etc.), mining, or the famous points and bars in multiuse tools such as *allachus, kituchis*, and *chaquitacllas* for working in the fields [57]. We now know the importance held

Fig. 4.33 Drawing by the indigenous chronicler Guaman Poma de Ayala showing the Inca and his Coya paying tribute to the Sun god [56, p. 194]

by their tools for artisans, being so personal that they only passed to other hands upon death, or were buried with them.

Therefore, during Pre-Hispanic times, the use of metal, and especially precious metals, carried with it implicitly diverse codes and meanings, some perceptible and others indecipherable. Through finds in tombs excavated in different parts of Peru, especially those from the Moche and Sicán or Lambayeque cultures, it is evident that metal is a symbol of earthly power and defines social classes as well as the religious and political roles of the buried figures. The ruling classes used gold, silver, and copper in their funeral goods (Figs. 4.34, 4.35, and 4.36). The lower classes only used copper, but were accompanied by their tools.

Ethnographic studies in various indigenous communities in Colombia and other areas of the American continent have demonstrated that the light or shine that emanates from objects, whether metallic, stone, shell, feather, or cloth, is a primordial factor that connects them to the realm above the earthly one and to cosmic forces [58]. Therefore, the fascination they felt for gold makes sense, with its almost blinding brightness when the sun's rays reach it and its incorruptible character, as well as their use of gold for the creation of an endless number of cosmogonic myths. The worldview and mythology of these societies, and their different systems of social beliefs and rituals, relate the symbolic properties of gold, its alloys, and its transformations (melting, alloying, and molding) to schemes and models of the life of man

Figs. 4.34 Batons combining gold and silver, which produce sound upon movement. Poli Collection. (Photo: L. Vetter)

Fig. 4.35 Gold bracelets with diverse iconography, depicted by embossing or twisting strands. Poli Collection. (Photo: L. Vetter)

and the power of shamans [59, 60]. The indigenous Americans understood the world from a multisensory perspective, in which the processes of "germination" or formation, extraction, melting, and transformation of metals, as well as their qualities such as color, smell, sound, and brightness, were processes comparable to human, animal, or plant life. In other words, they absorbed concepts and qualities from the natural world and translated them into material culture. They conceived of metal as a living being with the same cycles of life, capable of engendering and reproducing itself in the interior of the earth through the mediation of *Pachamama*. In this sense, metal is, as defined by Falchetti [60], a sort of embryo or seed, so the lord of metals and metallurgy was a being associated with the origins of seeds, and in the Andean case, *Pachamama*. Just like human beings, metal becomes ill (oxidation) and dies (loses its shine), but it can also be transformed, like man, so that upon dying it passes to another world where the ancestors dwell.

According to this view, metal germinates or fertilizes the earth, is born and is extracted from the mine, develops and transforms into objects, becomes ill with

Figs. 4.36 Drawing by the chronicler Murúa showing the Inca being carried on a litter [8, Book I, Ch. 40]

oxidation, dies when it loses its color or shine, and is reborn when it returns to the earth with burials to convert itself once again into mineral. The indigenous worldview conceived of metal as a living being that is transformed during the different technological and metallurgical processes of its production. Life, death, sickness, natural phenomena, or supernatural forces are interpreted by each society through their myths and staged in the rituals directed by shaman-priests or high dignitaries, who are connected to the supernatural forces and other unearthly worlds that rule our own.

The power of using metal was, among the indigenous peoples from Mesoamerica to the Andean region, more symbolic than a manifestation of richness in the European manner; metal was not a good that served to buy or sell products as in the economic structures of the Old World. With respect to this, the *mestizo* chronicler Inca Garcilaso de la Vega says:

> […] they didn't sell or buy anything with silver or gold, nor did they pay the warriors with it […], and for this reason they considered it a superfluous thing, because it was neither for eating nor for buying things to eat. They only valued it for its beauty and splendor, for ornamentation and serving in the royal houses and temples of the Sun and house of the virgins […] [11, Volume II, Book V, Ch. VII, p. 71].

Metal was also not an indispensable good for the production of weapons as it was in the Old World, although some weapons were made from this material, such as

Fig. 4.37 Mace heads of golden copper. Poli Collection. (Photo: L. Vetter)

clubs, maces, and axes: "[…]pikes and halberds and maces and axes for weapons, of silver and copper and some of gold, and with slings and spears of palm, with burnished points" [61, Book I, Ch. XIV, p. 58] (Fig. 4.37).

Rather, metal was of little utility since the concept of war in the Andean world was applied between ritual and territorial conquest, and hand-to-hand combat was preferred. The ancient Andean cultures preferred to use other materials that better served their military tactics, such as fabric, wood, and stone. The majority of offensive weapons, such as slings, spear throwers, or arrows, were made from textiles, stones, and hardwood, and the majority of defensive arms, such as shields, helmets, and pectoral protectors, were made from padded cotton fabric. Metal rarely occupied a prominent position among the weapons, since they did not produce swords, daggers, knives, or European-style armor. Garcilaso de la Vega says: "[…]they must have known how to make all of the offensive weapons that are needed in war, at least the most common ones and those that do not have need for smithery, such as bow and arrows, a spear that could be called a *bohordo*, (because it is thrown with the help of a stick or cord); a lance (with a sharpened point instead of iron); a sling of hemp (or grass, as out of necessity they use and take advantage of everything…)" [11, Volume II, Book 6, Ch. XXV, p. 197].

Andean goldsmiths preferred to use objects made with many joined sheets and in this way create mobile pieces of extraordinary size that emitted the desired sound and movement [62]. Perhaps they were looking to relate the sonorous characteristics and movement of the pieces to the natural and animal world. In other words, they aimed to imitate the singing of the birds, the whisper of the wind, the murmur of the sea, or the call of an animal. In the ceramic vessels from the Moche culture, we can find figures with bells and rattles of gold, silver, and copper (*chalchalcas*) sewn onto ceremonial outfits, especially in the case of warriors (Fig. 4.38). There are also rattle drinking vessels of gold, silver, and copper that, although they seem to be of the same shape and size, produce very different sounds or musical tones from one another, which allows us to identify the different figures that took part in

Fig. 4.38 Gold rattles or *chalchalcas* with the figure of the Throat Cutting God. Poli Collection. (Photo: L. Vetter)

Fig. 4.39 Moche gold trumpets. Poli Collection. (Photo: L. Vetter)

ritual ceremonies. Drums and trumpets were used both in war and in celebrations, and flutes and reed pipes were mostly festive and were utilized in different rituals, as we will see in the descriptions of funerary rituals (Fig. 4.39).

> […] and in all of them (celebrations) there are fasts and confessions and, once these are finished, they drink, dance and sing and move rhythmically, and the women play their tambourines, which all of them have, and some sing and others respond […] [63, p. 60].

Metal, in combination with feather and textile art, visually characterized the elite figures, especially when participating in a ritual. As an element of support for social, political, and religious symbols, metal differentiated the ceremonial actors when they were representing mythic or divine beings, offerors, priests, warrior chiefs, or ancestors, thus playing a sacred and symbolic role.

Fig. 4.40 *Unku* or male shirt made with plates of gold that were sewn onto fabric. Poli Collection. (Photo: L. Vetter)

The complexity and paraphernalia of Pre-Hispanic ritual cannot be understood without the majesty of metal objects, as headdresses, clothing, and liturgical objects, such as cups, were as much involved in the ritual as the myth itself. The sound, color, splendor, and shine of the metals were essential elements that were integrated together into a mystic and indivisible whole during the liturgical act. Andean images and representations move in a world of myths and rituals whose iconographic essence transcends the barriers between the mythic and the real. Many of the metallic pieces were sewn onto cloths or *unkus* with brightly colored feathers, whether on the garments of elite soldiers or as adornments on characters[5] (Fig. 4.40).

In ancient Peru, feathers were widely used with not only a decorative value, but also a sacred one, as they represented the upperworld, the *Hanan Pacha*, and what this represented, such as birds. There are myths and rituals that connected humans to the power of the heavens. The link between metal, cloth, and feather adornments was so tight that it is very difficult to separate the symbolic relationship among these three elements.

Gold, silver, and copper objects formed an important part of the paraphernalia for rituals, according to the chroniclers' descriptions of the different rituals that were celebrated during the 12 months of the year. Therefore, these metal objects should be imagined within the context for which they were produced, where the ritual and the magic of the myth explain the use of the metal. It is possible that some metallic objects, such as headdresses, diadems, nose ornaments, ear ornaments, pectoral ornaments, scepters, and necklaces, were used only in certain ritual ceremonies or as a distinctive sign of certain elite characters.[6] While these elements bring us closer to the political and religious power of the figures that made up the

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[5] Jiménez [64] confirms that the garment that best expressed the power of the members of the Moche elite was the shirt with metal plates.

[6] The use of silver or copper sandals by figures of the Moche elite is mentioned in Jiménez [64], in reference to the textiles found by Donnan at Pacatnamú.

elite, such as warrior priests, *curacas*, and shamans, they must also be seen as objects that not only differentiated earthly power but also the different characters into which they transformed through the carrying out of a ritual. Taking this into account, the headdress would be the primordial element that distinguished the characters and the roles they played in and throughout the ceremony. In this way, metal was converted into an element not only of social status but also of religious and symbolic connotation that accompanied whoever used it both in life and after death.

The tombs of the Moche elite, such as those of Sipán or the Señora de Cao, or those of Sicán, in Batán Grande, where the figures were buried with abundant metal objects that formed part of the attire or costumes alluding to the identities and/or roles that they performed in life, indicate the importance of entering the afterlife while identified with the role that they played in this one or that they would play in the next. Many of the figures depicted in Moche iconography were real and fulfilled the function of ancestors in the world of the living.

The crowns found to this date belong to Pre-Inca cultures; they would have had an interior frame of fabric or reed that would have served as a cap to hold up the metal sheet. In the coastal cultures of the North, such as the Vicús, Moche, Sicán or Lambayeque, and Chimú, the use of metal was a fundamental part of their clothing. Diadems, crowns, caps, ear ornaments, nose ornaments, pectoral ornaments, necklaces, rings, calf coverings, bracelets, hanging adornments sewn onto textile such as rattles or bells, plates, coxal protectors, and headdresses formed a part of the paraphernalia that accompanied the elite figures until their burial and consequently the afterlife (Fig. 4.41).

> It is very common among the Indians to put silver in the mouths of the deceased when they bury them and in their hands and on their bosoms or on the other parts that they could, and to dress them in new things and folded clothes within their shrouds…everything that would serve them in the afterlife…they also tend to give and eat and drink at the time of burial of the deceased…with a sad song…the time of gifts…and they tend to come together for

Fig. 4.41 Crowns with headdresses combining different metals. MOP. (Photo: P. Carcedo)

> anniversaries or monthly…or year to year...they also believe that the spirits of the dead…go around visiting their relatives [8, Book 3, Ch. LXII].

With the start of the conquest, the value of gold became distorted as it was converted into a corrupting element that separated and put two cultures into confrontation: the Spanish and the Andean. Pizarro's proposal, in November of 1532, to have a room filled with gold objects as a ransom for the Inca Atahualpa was the beginning of the end for an ideology contained in its representation on gold objects. The sacred metal was converted into economic value and never again was a golden piece produced under Pre-Hispanic concepts and uses. In spite of this, the insides of the Andes continued to "reproduce" metal and for many centuries their *huacas* safeguarded treasures that did not fall into the hands of the conquistadors, but that suffered constant looting that still persists to this day.

The majority of gold and silver objects that are exhibited in museums and private collections come from looting and were part of important funerary goods placed with great care in the tomb, recreating and meticulously planning the cosmos of the deceased.

Final Comments

The Pre-Columbian cultures that developed in the territory that is currently occupied by Peru amazed the Europeans, since the first years of the conquest, with the sophistication of their objects worked in gold. Unfortunately, at that time these pieces were not understood or valued, until the 1960s when Peruvian archaeology began to develop as a profession. In the following decades, different archaeological and research projects began to utilize multidisciplinary focuses in which new technological and analytical advances applied to metals started to become very relevant. In the last three decades, studies on the metallurgical and goldsmithing technologies of the ancient Peruvians have shown us that the technological genius of these cultures is found in their wise use of nature's resources and a manifest ingenuity of the goldsmiths, who not only knew how to produce their own tools, but for centuries also sought incessantly for new techniques to help reflect in their works the feelings and spirit of the people who created them. For this reason, metal, never seen as an economic good, symbolized the base upon which their own creed and religiosity was reflected. Today, we call these creations "works of art" because of the beauty they enclose, but for the people who made them, they were the most intimate reflection of their spirituality.

Acknowledgments We wish to express our gratitude to the Poli Collection, the Museum of Gold of Peru and Weapons of the World, the National Sicán Museum, and the Museum of the Central Reserve Bank of Peru for allowing us to photograph part of their collections, which we presented in this chapter. Also, to Jesús Ruíz Saavedra for carrying out the digital radiography and SEM-EDS analyses.

References

1. Craddock, P.: Early Metal Mining and Production. Smithsonian Institution Press, Washington, DC (1995)
2. Cieza de León, P.: Crónica del Perú. Segunda Parte. Fondo Editorial de la Pontificia Universidad Católica del Perú, Lima (1553/1995)
3. Shimada, I., Craig, A.: The style, technology and organization of Sicán mining and metallurgy, northern Perú: Insights from holistic study. Chungara, Revista de Antropología Chilena. **45**(1), 3–31 (2013)
4. Lechtman, H.: A metallurgical site survey in the Peruvian Andes. J. Field Archaeol. **3**(1), 1–42 (1976)
5. Stanish, C.: Ancient Titicaca. The Evolution of Complex Society in Southern Peru and Northern Bolivia. University of California Press, California (2003)
6. Cruz, P., Absi, P.: Cerros ardientes y huayras calladas. Potosí antes y durante el contacto. In: Cruz, P., Vacher, J.-J. (eds.) Mina y metalurgia en los Andes del Sur: desde la época prehispánica hasta el siglo XVII, pp. 91–120. Institut de Recherche pour le Développement/Instituto Francés de Estudios Andinos, La Paz/Lima (2008)
7. Salazar, D., Jiménez, C., Corrales, P.: Mining and metallurgy: from the cosmos to earth, from the earth to the Inka. In: The Footsteps of the Inka in Chile, pp. 61–71. Museo Chileno de Arte Precolombino/Banco Santiago, Santiago de Chile (2001)
8. de Murúa, M.: Historia General del Piru. Edición facsimilar de J. Paul Getty Museum Ms. Ludwig XIII 16. Getty Research Institute, Los Ángeles (1613/2008)
9. Vetter, L.: El uso del cobre arsenical en las culturas prehispánicas del norte del Perú. In: 49Congreso Internacional de Americanistas, Quito. Boletín Museo del Oro, vol. 41, pp. 63–81 (1996)
10. Hocquenghem, A.M.: Una Edad del Bronce en los Andes Centrales. Contribución a la elaboración de una Historia Ambiental. Bulletin del'Institute Français d'Études Andines. **33**(2), 271–329 (2004)
11. de la Vega, I.G., Garcilaso de la Vega, I.: Los comentarios reales de los incas. Colección de Historiadores Clásicos del Perú, Tomos I y II. Lima, Perú. www.HistoriaDelNuevoMundo.com (1609/1918)
12. Vetter, L.: Plateros y saberes andinos: el arte orfebre en los siglos XVI y XVII. Centro Bartolomé de las Casas/Academia Nacional de Ciencias, Lima (2016)
13. Benzoni, G.: La Historia del Mondo Nuovo. (Relatos de su viaje por el Ecuador. 1547-1550). Traducida por primera vez en lengua castellana por Carlos Radicati Di Primeglio, autor de la introducción y de las notas. Guayaquil, Ecuador (1572/2000)
14. Lechtman, H.: Metalurgia superficial precolombina. Investigación y Ciencia. **95**, 20–28 (1984a)
15. de Oviedo, G.F., Fernández de Oviedo, G.: Historia general y natural de las Indias, Islas y tierra-Firme del Mar Océano. Primera parte. Imprenta de la Real Academia de la Historia, Madrid, España, www.HistoriaDelNuevoMundo.com (1535/1851)
16. Easby, D.T.: Pre-hispanic metallurgy and metalworking in the New World. Proc. Philos. Soc. **109**(2), 89–98 (1965)
17. Scott, D.: Dorado por fusión y dorado de lámina en Colombia y Ecuador prehispánicos. In: Metalurgia de América Precolombina. 45o Congreso Internacional de Americanistas, Universidad de los Andes, pp. 307–340. Banco de la República, Bogotá, Colombia (1986)
18. Shimada, I., Szumilewicz, A., Valdez, R., Merkel, J.: La producción artesanal a gran escala y el centro religioso andino: una reconsideración. In: Ponencia presentada en VI Congreso Nacional de Arqueología. Ministerio de Cultura, Lima (2019)
19. Grossman, J.: The Waywaka gold: New chronometric evidence. Andean Past. **11**, 123–138 (2013)
20. Aldenderfer, M., Craig, N., Speakman, R., Popelka-Filcoff, R.: Four-thousand-year-old gold artifacts from the Lake Titicaca basin, southern Peru. Proc. Natl. Acad. Sci. **105**(13), 5002–5005 (2008)

21. Salaverry Llosa, J.A.: Principales características macro ecológicas de los Andes peruanos. In: Macroecología de los Andes peruanos: Situación actual y dinámica de cambio en los últimos 2000 años. Institut Français d'Études Andines, Lima. http://books.openedition.org/ifea/5508 (2006). https://doi.org/10.4000/books.ifea.5508
22. Burger, R., Gordon, R.: Early Central Andean Metalworking from Mina Perdida, Peru. Science. **282**(5391), 1108–1111 (1998)
23. Elera, C., Pinilla, J.: Research summary of the Proyecto Arqueológico Puémape (1987-1989). Willay. **34**, 2–4 (1990)
24. Lechtman, H.: Technical examination of a gold-alloy object from Chavín de Huántar. In: Burger, R. (ed.) The Prehistoric Occupation of Chavín de Huántar, Peru, pp. 271–276. University of California Press, California (1984b)
25. Velarde, M.I., Castro de la Mata, P.: Transición Paracas-Nasca, continuidad e innovación en los metales. Boletín de Arqueología PUCP. **25**, 135–145 (2018)
26. Elera, C.: Investigaciones sobre patrones funerarios en el sitio formativo de Morro de Éten, valle de Lambayeque, costa norte del Perú. Memoria de Bachillerato en Arqueología. Pontificia Universidad Católica del Perú, Lima (1986)
27. Vetter, L., Petrick, S., Olivera, P.: Estudio arqueométrico de piezas de oro de Morro de Éten, Perú. In: Vetter, L., Vega-Centeno, R., Olivera, P., Petrick, S. (eds.) Actas del II Congreso Latinoamericano de Arqueometría. Lima, 19 al 21 de octubre de 2009, pp. 73–86. Fondo Universidad Nacional de Ingeniería/Organización de Estados Iberoamericanos/Instituto Peruano de Energía Nuclear, Lima (2011)
28. Lothrop, S.K.: Gold ornaments of Chavín style from Chongoyape. Peru. Am. Antiq. **3**, 250–262 (1941)
29. Lothrop, S.K.: Gold artifacts of Chavín style. Am. Antiq. **3**, 226–239 (1951)
30. Hirao, Y., Ohnishi, J., Onuki, Y., Kato, Y.: Chemical composition of samples excavated from Kuntur Wasi archaeological site, Peru. Archaeol. Nat. Sci. **25**, 13–30 (1992)
31. Kato, Y.: Resultados de las excavaciones en Kuntur Wasi, Cajamarca. Senri Ethnol. Stud. **37**, 203–228 (1993)
32. Burger, R.: Chavin. In: Boone, E.H. (ed.) Andean Art at Dumbarton Oaks, vol. 1, pp. 45–85 (1996)
33. Onuki, Y.: Ocho tumbas especiales de Kuntur Wasi. Boletín de Arqueología PUCP. **1**, 79–114 (1997)
34. Seki, Y., Villanueva, J., Sakai, M., Alemán, D., Ordóñez, M., Tosso, W., Espinoza, A., Inokuchi, K., Morales, D.: Nuevas evidencias del sitio arqueológico de Pacopampa, en la sierra norte del Perú. Boletín De Arqueología PUCP. **12**, 69–95 (2008)
35. Villanueva, J.P., Seki, Y., Morales, D.: La tumba de los sacerdotes de la serpiente-jaguar en Pacopampa. In: Actas del III Congreso Nacional de Arqueología, vol. I, pp. 271–282. Ministerio de Cultura, Lima (2018)
36. Diez Canseco, M.: Los metales Vicús en las tumbas del cementerio de Yécala. In: Vetter, L., Téllez, S., Vega-Centeno, R. (eds.) Arqueología peruana. Homenaje a Mercedes Cárdenas, (pp. 85–114). Instituto Riva-Agüero de la Pontificia Universidad Católica del Perú / Centro Cultural La Casona de la Universidad Nacional Mayor de San Marcos, Lima (2011)
37. Alva, W.: Sipán. Descubrimiento e investigación. QW Editores, Lima (2015)
38. Donnan, C.: Moche Tombs at Dos Cabezas. Cotsen Institute of Archaeology at UCLA. Monograph 59. California (2007)
39. Schorsch, D.: Silver and gold Moche artifacts from Loma Negra, Peru. Chicago J. Metropolit. Mus. J. **33**, 109–136 (1998)
40. National Geographic: Descubiertos los restos de pescadores de tiburones de hace 1900 años enterrados con extremidades de más. https://www.nationalgeographic.es/historia/2018/04/descubiertos-los-restos-de-pescadores-de-tiburones-de-hace-1900-anos-enterrados (2018). Accessed 8 Jan 2020
41. Castro de la Mata, P.: Tecnologías de cobre dorado y evidencias de reutilización de piezas de metal en el cementerio prehispánico de Tablada de Lurín, Lima-Perú. In: Roberto Lleras (ed.)

Metalurgia en la América Antigua. Teoría, arqueología y tecnología de los metales prehispánicos, pp. 481–500. Fundación de Investigaciones Arqueológicas Nacionales/Banco de la República de Colombia/Instituto Francés de Estudios Andinos (2007)

42. Anónimo: Cajamarca: Encuentran piezas de oro y plata en la ciudad de Cutervo [en línea]. La República [Lima], 27 de abril de 2017. http://larepublica.pe/sociedad/869859-cajamarca-encuentran-piezas-de-oro-y-plata-en-la-ciudad-de-cutervo (2017). Accessed 10 Dec 2017
43. Giersz, M.: Castillo de Huarmey. Un centro del imperio Wari en la costa norte del Perú. Ediciones del Hipocampo, Lima (2017)
44. Shimada, I.: Cultura Sicán: Dios, riqueza y poder en la Costa Norte del Perú. EDUBANCO, Lima (1995)
45. Carcedo, P.: Reflexiones sobre la producción sicán y chimú de vasos tipo kero y discos en plata: su iconografía y su relación con las miniaturas chimú. Bulletin de l'Institut Français d'Études Andines. **46**(1), 37–75 (2017)
46. Vetter, L.: La orfebrería inca en la costa peruana. Cuadernos del Qhapaq Ñan **6**(6), 66–93. Ministerio de Cultura, Lima, Perú (2018)
47. Vetter, L.: La platería andina colonial a través de la historia de la familia Sacayco. Historia y Sociedad. **35**, 113–138. http://orcid.org/0000-0002-4708-0488 (2018)
48. Pérez Trujillo, A.: Investigaciones arqueológicas en la zona arqueológica de Qotakalli. In: Resultados preliminares de los trabajos de investigación en la zona arqueológica de Qotakalli, años 2014-2016, pp. 9–40. Dirección Desconcentrada de Cultura, Cusco (2016)
49. Vetter, L., Guerra, M.F.: Los tupus y estatuillas de plata inka: una aproximación a sus aleaciones. Bulletin de l'Institut Français d'Études Andines. **46**(1), 171–192 (2017)
50. de la Calancha, A.: Crónica Moralizadora del Orden de San Agustin en Peru con sucesos egemplares en esta Monarquía. Fondo Antiguo de la Universidad de Sevilla. Biblioteca Virtual Miguel de Cervantes. http://www.cervantesvirtual.com/obra/coronica-moralizadora-del-orden-de-san-augustin-en-el-peru-con-sucesos-egenplares-en-esta-monarquia (1584/1654)
51. Carcedo, P.: Estudio de los metales en el arte y las artesanías en el antiguo Perú. Tesis para el optar el grado de doctora. Universidad Complutense de Madrid. Facultad de Geografía e Historia, Madrid (2017)
52. Carcedo, P., Vetter, L.: Uso de minerales y metales a través de las crónicas. In: Los incas, Arte y Símbolos, pp. 167–214. Colección Arte y Tesoros del Perú. Banco de Crédito del Perú, Lima (1999)
53. Reichel-Dolmatoff, G.: Orfebrería y chamanismo: Un estudio iconográfico del Museo del Oro. Colina, Medellín (1990)
54. Vetter, L., Guerra, M.F.: Simbolismo de las narigueras peruanas y aproximación a su manufactura durante el Periodo Intermedio Temprano. Bulletin de l'Institut Français d'Études Andines. **48**(2), 109–133 (2019)
55. Roskamp, H.: Los nahuas de Tzintzuntzan-Huitzitzilan, Michoacán: historia, mito y legitimación de un señorío prehispánico. Journal de la Société des Américanistes. **96**(1), 75–106 (2010)
56. Guaman Poma de Ayala, F.: Nueva Coronica y Buen Gobierno. In: Franklin Pease, G.Y. (ed.) Tomos I y II. Fondo de Cultura Económica, Lima (1615/1993)
57. Hocquenghem, A.M., Vetter, L.: Las puntas y rejas prehispánicas de metal en los Andes y su continuidad hasta el presente. Bulletin de l'Institut Français d'Études Andines. **34**(2), 141–159 (2005)
58. Saunders, N.J.: Catching the light: technologies of power and enchantment in Pre-Columbian goldworking. In: Quilter, J., Hoopes, J.W. (eds.) Gold and Power in Ancient Costa Rica, Panama and Colombia. A Symposium at Dumbarton Oaks, pp. 15–49. Dumbarton Oaks Research Library and Collection, Washington, DC (2003)
59. Reichel-Dolmatoff, G.: Orfebrería y chamanismo: un estudio iconográfico del Museo del Oro del Banco de la República, Colombia. Villegas Editores, Bogotá (1988)
60. Falchetti, A.M.: The seed of life: the symbolic power of gold-copper alloys and metallurgical transformations. In: Quilter J., Hoopes J.W. (eds.) Gold and Power in Ancient

Costa Rica, Panama and Colombia. A Symposium at Dumbarton Oaks, Washington, DC, pp. 345–382 (2003)
61. de Zarate, A.: Historia del descubrimiento y conquista del Perú. In: Franklin Pease, G.Y., Hampe, T. (eds.) Fondo Editorial de la Pontificia. Universidad Católica del Perú, Lima (1577/1995)
62. Carcedo, P.: Metalurgistas y orfebres precolombinos: entre lo humano y lo divino del metal. In: Incas, Y.l.l. (ed.) Catálogo de la exposición, pp. 91–103. Museo de América/Ministerio de Cultura, Madrid (2005)
63. de Arriaga, J.: La extirpación de la idolatría en el Perú. Estudio preliminar y notas de Henrique Urbano. Centro de Estudios Regionales Andinos Bartolomé de Las Casas, Cuzco (1621/1999)
64. Jiménez, M.J.: El vestido de los reyes y príncipes de Moche. In: Señores de los reinos de la Luna. Colección Arte y Tesoros del Perú. Banco de Crédito del Perú, Lima (2008)

Chapter 5
Ancient Ferrous Metallurgy: Historical and Social Perspective

Luis Arturo Reyes and Oscar Zapata-Hernández

Introduction

The term “archaeometallurgy” was coined in 1970s by Beno Rothenberg, since its emergence, it was pointed away from only describing the artifact formation. The study provided more information to archaeologists by exploring the archaeological record of the process left. The final objective was pointed to a more complete vision of the development technology for a particular culture in a defined period. Archaeometallurgy has provided helpful information to archaeologists and anthropologists in the pursuit of a more complete understanding of the role of metals in the structure, organization, and development of societies [1, 2]. The metal production and usage of items can be divided into two branches. The first deals with the metal technology and manufacturing. The second part covers the social features of metal usage of a particular society.

In this context, archaeometallurgical studies can provide information regarding trade networks, interchange interactions, sources, physical characteristics, and the uses and disposal of the objects. The mixture of these two aspects agglutinates the most significant information about implementation of metals in a particular culture [2].

The iron technology developed gradually. Iron substituted other metals in the development of tools or weapons only after various centuries of continuous progress. The evolution from the Bronze Age to the Iron Age took place in Near East around 1200 BCE, where iron smelting began to displace copper alloys and the practice spread out. In early iron production, one of the limiting factors was the availability of wood for charcoal. However, iron ores were in quantities enough for ancient production levels. The earliest produced iron is from Tell Asmar in Mesopotamia and Tall Chagar Bazaar in North Syria [1].

L. A. Reyes (✉) · O. Zapata-Hernández (✉)
Universidad Autónoma de Nuevo León, Facultad de Ingeniería Mecánica y Eléctrica,
San Nicolás de los Garza, Nuevo León, Mexico

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_5

The ancient Anatolian people known as Hittites developed skills of iron smelting creating efficient tools and weapons. After their empire fall about 1200 BC, the Hittites workers split into different cities allowing two centuries later their arrival to Europe [3]. Tribes in Africa used iron at least as early as 800 CE, showing well-advanced techniques [4].

The crucible steel in India, also known as Wootz, can be traced back to the third century BCE [5]. Cast iron in China extends even further, possibly to the sixth century BCE [6]. Iron casting in China has led archaeologists to visualize iron technology in that region as a source of inspiration for European iron casting development. In Han China, malleable cast iron generated most agricultural implements, while during that time Romans made artifacts from wrought iron [7]. The trading of Romans involved exchange of iron with India and China, as Pliny the Elder noted that the best iron was sent by the Chinese [8]. These events are a clear demonstration of how technologies have great influence on the course of history. The accessibility of iron silicate, a by-product of copper metallurgy, was perceived as the reason for the emergence of the iron industry and the steel. Although copper was more abundant than iron ores, the resources of early population were not enough to achieve the required temperatures.

In Asia, during the early medieval period, the Altay represented a major area of iron and ironworking production. Altay in the 600–1000 CE was closely linked to the history of inner Asian nomadic tribes such as Altayans, Tuvinians, Khakas, and Shori tribes. Turkic-speaking tribes played major roles in the process of early state formation among these ancient nomads. The first large Turkic state, the Turkic Khaganate, emerged in 552 CE comprising Altay tribes. The Turki dominated a vast part, from western Manchuria to Iraq and Byzantium. But many years of war with China and fratricidal conflicts led to the downfall of this state in 744 CE. During that time, the Turkic Khaganates were concerned with becoming a supplier of iron by gaining the vast ore resources of Altay region.

The progression from the production of bronze artifacts to those of iron began during the fifth to third centuries BCE. The analysis of iron ore, metallurgical furnaces, fuel, and slags shows that in the medieval epoch, iron was extracted exclusively by the blooming technique. This represented a direct chemical reduction of iron from iron ore. As a result of chemical reactions, one part of the oxides was reduced to metallic iron. This iron was formed in separate grains that fused together into a friable iron sponge (bloom) that contained a certain quantity of slag in its interstices. Another part of the iron oxide reduced to ferrous oxide (FeO), combined with oxides compounded in the iron ore, to form an easily melted iron-rich slag that flowed down in the blooming furnace.

The most important condition of the blooming process is the creation of a temperature exceeding 1000 °C throughout the entire working space of the furnace. However, the great demand for iron caused the Altay metallurgists to search for ways to increase metal production by increasing furnace volume. The investigation of bloom slags shows that iron smelting took place at a sufficiently high temperature (1300–1600 °C). Attaining such a temperature required a great expenditure of physical energy and enormous experience in managing the blooming process. The smelting of metal was conducted with a single technology in furnaces of a unique type. The blacksmiths of Altay had great influence in the standardization of products that facilitated the lifestyle of the people that in turn benefited the growth of the economy [9].

It has been reported that iron artifacts until fourteenth to fifteenth centuries CE were made of two-stage process [10], such as extraction of iron from ore by smelting process and smithing process [10]. The blacksmith was considered to be the principal contributor to the creation of earliest conceptions of materials and understanding their behavior [11]. Its origin is believed to be around 1500 BCE [2].

In the premodern times, wrought iron was believed to be probably made in open hearths in locations with strong winds. As a result, a mixed iron and liquid slag in a mushy condition was obtained since the maximum temperature at that time was about 1000–1200 °C. Then, the final product was obtained by hammering [11]. At that time blacksmithing involved heating iron until a certain color was seen. Then, strength of iron was characterized based on hardness (scratching) and bending at ambient temperature. Some magnetic qualities were measured using lodestone [11]. A large number of products made during medieval blacksmithing includes swords, lances, arrowheads, siege weapons, armor, shield, tools, nails, doors (for church and castles), ornaments, knives, etc. [12]. One of the limitations of forging iron blooms is that during forging, slag inclusions open up resulting in cracks in the materials. To solve this problem, forge welding was applied [13]. An example of forge welding is the fabrication of large iron cannons like the one found at Thanjavur, India (Fig. 5.1) [14].

Since the beginning, the metal practice was implemented for the creation of armaments. Different analyzes conducted on weapons from the second millennium BCE belonging to ancient civilizations (Vikings, Persians, Assyrians among others) revealed the implementation forging strategies to achieve the perfect point for the ideal weapon all from iron and alloys. They mainly sought to have hardness and a good persistent edge but without reaching the point that the weapon becomes fragile

Fig. 5.1 Seventeenth-century forge-welded iron cannon [14]

with fissures and failures. These failures were reduced thanks to the implementation of coal and iron mixtures and derivatives. Furthermore, new forging methods were implemented allowing the reduction of impurities generated. Earliest blades hardened by heat treatment were produced to be tough and shock resistant; the hardness property improves the cutting ability and wear capability. Tough cores and hard sharp edges provide a balance of desired properties.

However, the control of carburization and quenching process was a difficult task. The hardness growth in quenching process was due to martensite creation, a metastable structure that develops in steels on rapid cooling, and embrittlement was avoided by carburization on cutting edges [15].

Iron smelting in the Roman Empire consisted of extracting molten slag from the bloomery furnace. Within the furnace, an iron bloom was to be collected in the solid state. After meltdown, the bloom would be withdrawn, and the furnace, if necessary, could be repaired or relined and reutilized [16]. Germanic iron smelting with high phosphorous iron ores was smelted in furnaces where the collected slag was placed below the furnace shaft.

The solid matter of a pit is thought to characterize the slag deposit from a single smelting period. A new pit would be dug for each following smelting [16]. High-carbon steel used in toolmaking could be obtained from solid state process such as the Roman iron punch found in Heeten, which was manufactured from extensively forged iron thin strips of metal that were then carburized and welded together [16].

Iron smelting in India must have started sometime during the second millennium BCE. The thermo-mechanical process for forging Wootz steel and its heat treatment were known only to Indian blacksmiths [17]. They gained experience about the effect of carbon on the physical properties of iron and developed the process of carburization and hardening treatment. This process has been known as “steeling” and it has been widely used for making arrowheads, knives, swords, etc., having very sharp and strong cutting edge.

The surgical knives used by Susruta (500 BCE) were probably prepared from carburized iron. The famous Iron Pillar at Delhi is the earliest heavy iron forging existing on record dating back to 400 CE. The pillar, weighing approximately six tones, had been most probably made by forge welding large number of refined iron blooms to first make massive cylindrical blocks and then joining them using iron inserts [17].

Ancient Chinese skilled people developed iron casting techniques in the Spring and Autumn time (770–473 BCE). About 2000 years ago, during Warring States Period (476–221 BCE), craftsmen had already found out the way to make iron more strong and tough. The cast iron is a product of melting iron (pig iron) in a blast furnace, with quantities of iron, limestone, and coke, and taking several steps to remove undesirable contaminants. Carbon and silicon content are adjusted to the desired levels. Other elements can be added to the melt before the final form is produced by casting. The principal advantages of cast iron are its fluidity, lower amount of shrinkage when cooling from the molten state, and the very different properties that are conferred upon it. Its disadvantages are its weakness and lack of ductility and malleability. In cast iron, graphite is the largest portion and one of the most important constituents. The carbon that does not precipitate as graphite forms first as austenite, which later decomposes into ferrite and cementite. In short, all the carbon in cast iron will ultimately be found partly in the form of graphite and partly in the form of cementite. White cast iron presents a carbon content often of 3 or 4%, in the form of cementite; white cast iron will possess largely the properties of cementite. It is very hard and brittle, being machined only with the greatest difficulty, and it has great wear-resistance capacity. Gray cast iron castings usually contain 2%, or more, of graphite. The nature and constitution of gray cast iron is far more difficult to understand than that of steel, and even greater is the difficulty of predicting the effect of any change in composition or in constituents [18].

Cast iron tools were widely used in China around 1000 years of the beginning of the Warring States Period (476–221 BC). The introduction of cast iron artillery was a great contributor to cast iron application. By the middle of the fifteenth century cast iron guns are commonplace, as evidenced by both textual and artifactual evidence. Iron cores were used in iron mold casting; metal mold casting was mostly used to produce agriculture tools, hand tools, and chariot fittings [19].

In China, blast furnace iron production was practiced earlier than in Europe. The technology of cast iron was transferred from China to Europe. The earlies travelers observed a flourishing iron industry in the south of the Caspian Sea close to the silk route. Therefore, the use of technology derived from China is conceivable [19].

The largest blast furnaces were developed in Sichuan, China, a hilly region surrounded by high mountain ranges. Figure 5.2 presents a diagram of a blast furnace utilized in the early 1930s for iron smelting. Luo Mian recorded the process [7].

Sichuan smelted iron formed in the blast furnace was transformed to wrought iron in a puddling furnace. The diagram reproduced here as Fig. 5.3 depicts the

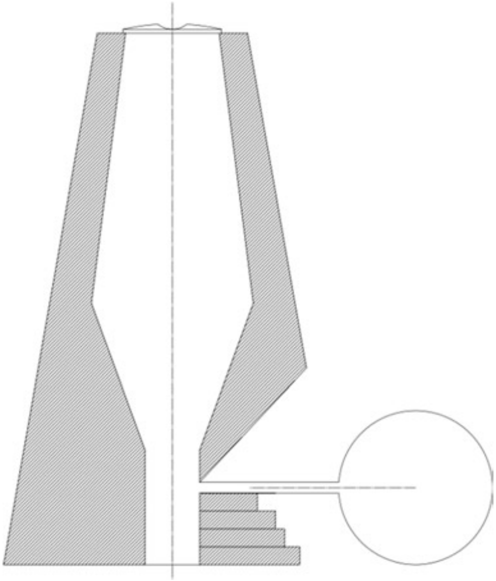

Fig. 5.2 Sichuan blast furnace iron smelting modified from Luo Mian (1936: pp. 19–21) [7]

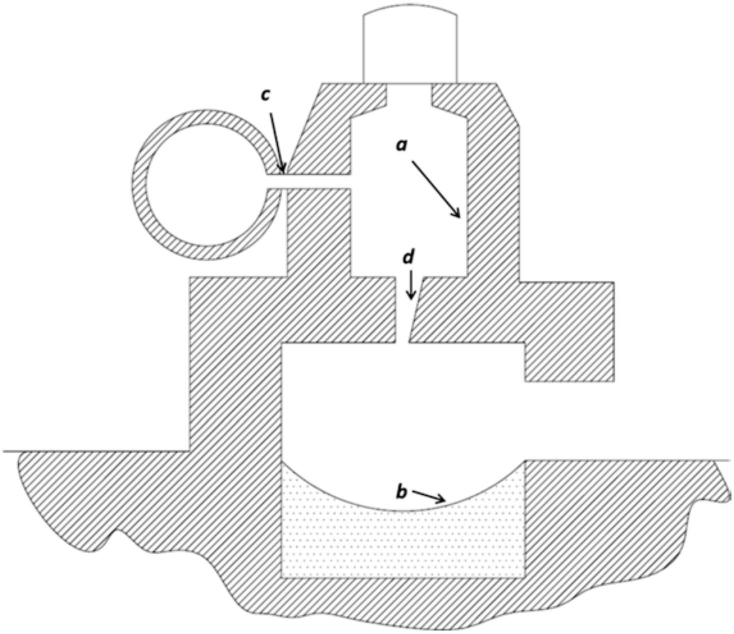

Fig. 5.3 Puddling furnace built entirely of a refractory sandstone. In the closed firebox, charcoal is burned. (**a**) Firebox. (**b**) Puddling bed. (**c**) Blast pipe. (**d**) Flame channel [7]

process. The furnace is constructed fully of refractory sandstone, and charcoal is burned in the firebox. Blast is blown into the firebox, while the flame moves downward into the puddling bed.

Henry Cort patented the puddling process in 1784. This process was in essence very similar to Sichuan process. Henry Cort's innovation has a great advantage compared with the previous process since it allows to single-out the fuel from the iron and consequently makes possible the use of coal in transforming cast iron to wrought iron. A key change in the industry was the usage of mineral coal rather than charcoal in iron smelting process. In 1937, with the start of full-scale hostilities with Japan, Sichuan took a new path where government and most of China's universities and scientific institutes moved there [7].

In the late eighteenth century, there was a great demand for pig iron to be refined with coal as fuel. This allowed the passage to puddling iron, which contained less slag, less sulfur, and very low carbon content. This puddled iron was also very variable in its properties. It was more consistent than the irons produced previously and with the method it lends itself to the production of much larger quantities. Figure 5.4 shows a microstructure of historical forged iron bridge (1898) from Mendoza, Argentina.

The Iron Bridge in Shropshire, England, was the first cast iron bridge built during 1770s by Abraham Darby III. The application of the steam engine to power blast bellows, starting in 1743 in Britain, was a key factor in increasing the production of

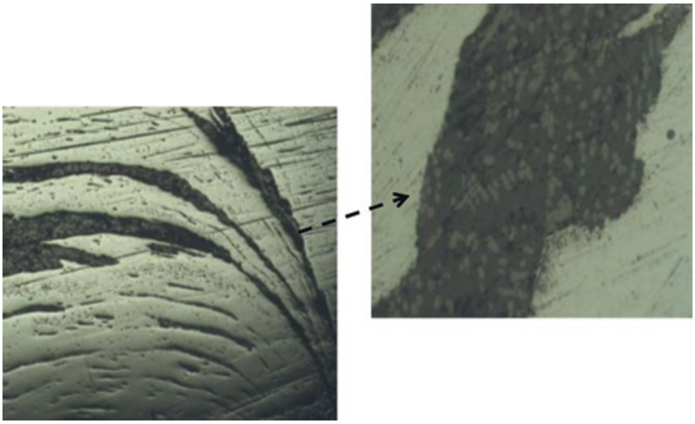

Fig. 5.4 Microstructure of historical forged iron bridge (1898). Equiaxed ferrite grains with a certain amount of inclusions of the silicates, sulfides, phosphates, and iron oxides present in dendritic form. (See Chap. 12: Case Studies of Reverse Engineering on Ancient Metals: Archaeometallurgical and Heritage Study on the Iron Bridge Over the Mendoza River)

cast iron. These took production to an increasing level in the 1750s. Cast iron bridges became commonplace as the Industrial Revolution surged. The best way of using cast iron for bridge construction was by using arches, so that all the material are in compression. Cast iron typically is very strong in compression and comparatively brittle in tension. It was cheaper than wrought iron and thus more common for building artifacts. Cast iron bridges were replaced in England by steel equivalents by 1900 owing to the widespread concern about cast iron under bridges on the rail network in Britain. The replacement bridge was built with wrought iron and steel [20].

Mesoamerican expertise in the creation of metal artifacts had evidently been incorporated by diverse ethnics in early Classic period (CE 300–900) and by diverse groups of Mesoamericans during the Postclassic time (CE 900–1521) [21]. Over the course of several centuries, the spread of metallurgical technology between South and Central America probably occurred. Since the beginning, metal objects engaged spiritual and sacred connotations for Mesoamerican people; however, ferrous technologies were not developed by the pre-Columbian people.

The technology behind metal items in particular manufacturing techniques is based on research and understand of metallurgical concepts. Archaeological metal research extended to consider the furnace design and efficiency in addition to raw materials from the smelt process. The railroads have been of great importance for the growth and prosperity of South American region. The vast quantity of iron needed for construction of railway networks across Argentina's territory was supplied by the British Empire. An enormous variety of products could be made of cast iron, not only for railway lines and stations but also for every product needed in urban constructions [20]. An important example of cast iron work is the threaded bolt of Buenos Aires to the Pacific Railroad, in which through metallographic

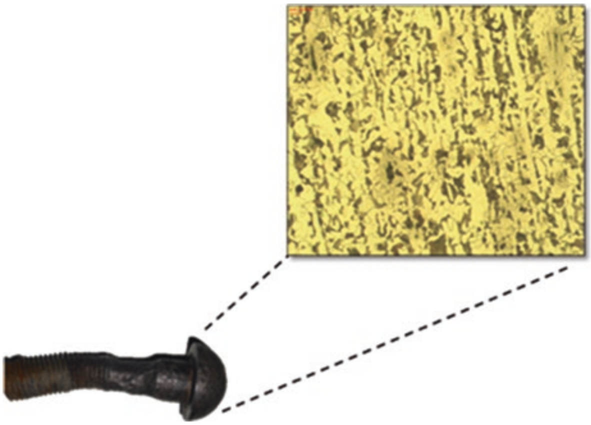

Fig. 5.5 Threaded bolt of Buenos Aires to the Pacific Railroad; a metallography was taken at ×100. (See Chap. 12: Cases Studies of Reverse Engineering on Ancient Metals: Archaeometallurgical Study of Pieces from Buenos Aires to Pacific Railway, BA&P, in Mendoza, Argentina)

analysis of two pieces it was evaluated the probable manufacturing techniques of the parts. In addition, this information allows to compare techniques and materials from that era with the current one and see how much it has varied. Figure 5.5 presents a metallography of the bolt's head, where a ferrite-perlite structure is observed. There seems to be a decrease in grain size due to machining work. During this investigation, it was determined that the pieces would be made of metals that would resemble some steels that are also used today to withstand large loads. Numerous metal installations in the twenty-first century with which our grandparents, great-grandparents, and parents grew up, and even we, are already part of archaeometallurgy. Cases such as Monterrey foundry is part of industrial evolution of México.

It is worth mentioning the influence of British in South America, developing, and raising Paraguay iron industry and technology around the years 1850–1870. Important events occurred during this period such as the triple alliance war (1864–1870), a war between Paraguay and triple alliance of Argentina, Brazil, and Uruguay. The war caused: a significant decline in the prosperity of the economic and metallurgical development of Paraguay, important demographic disaster, and considerable loss of their territories. In addition to the loss of their land, they were forced to pay financially after the acceptance of the free navigability of their rivers. Their lands, factories, and services were privatized. Furthermore, the destruction of blast furnaces by explosives, isolation of weapons, and the demolition of fortifications [22, 23]. Paraguayan political model was an independent system which consisted in a monopoly for wood trade and blast furnaces, this regime facilitated the foundation of the national steel industry. Paraguayan mining was noted for its iron resource, allowing the construction of ships in their own shipyards, railroads, and telegraphs.

The installation of the blast furnaces of Ibicuy for the purpose of weapons production and the hiring of the first English technician Henry Godwin in the year 1848 had a transcendental role in Paraguay industry and the expansion of plants through the Mbuyapey area. The blast furnace of Ibicuy was the first foundry, which was a breakthrough in the country of Paraguay. The foundry of Ibicuy was composed of vast buildings, workshops, and sheds, mainly highlighting its blast furnace that admits a load of 5000 pounds of ore and consumes an equal weight of charcoal.

The principle of operation of this furnace includes a series of processes, which are scorification, decarburization, and recarburization while the contents rotate [24].

Already at the end of the eighteenth century there was a demand for pig iron (an impure form of iron), to be refined with coal as fuel. This allowed the passage to puddling iron, which contained less slag, less sulfur, and very low carbon content. Henry Bessemer patented in 1855 the first cheap process for the manufacture of steel. Henry Bessemer was a British inventor who was inspired by the situations of war, in which his country needed abundant steel production. This event inspired him to develop a better process. In Thomas-Bessemer converter, the rotating furnace (Bessemer oven) lined with refractory bricks inside throws hot air over the iron–carbon mixture. The principal phases of the Bessemer process are: scorching, decarburization, and recarburization. Some of the modifications Bessemer made in the steel process took reference four elements that are essential to the modification. These are: shape of the converter, nature of lining, composition of metallic charge, and composition of blast [25].

In México, the arrival of blast furnace technology was during 1807 through the Guadalupe ironworks created by Andrés Manuel del Rio in Michoacán, with a reverberatory furnace and a blast furnace. At that time, New Spanish mining faced serious obstacles such as the insufficient supply and shortage of iron used in the elaboration of tools used in the mines, or metal that was brought from Biscay. The ironworks equipment and tools in Michoacán generated bases for the establishment of the blast furnace in Monterrey at the beginning of the 1900s for large-scale production. It should be mentioned that the invention of blast furnaces replaced the old technologies such as the Catalan furnaces.

Steel industrial progress in México gave a high priority to in-house steel production over imports from developed countries. The emphasis on industrial growth in Monterrey was due to several factors such as geographical position, large investment of government, and visionary people focusing on the potential of steel industry. During that time there was a huge demand of steel due to the industrialization of the country motivated by President Porfirio Díaz. The investment allowed the edification of large production foundry that included exploitation of iron ores and coal, smelting, processing, and product sales activities [26].

The blast steel furnace known as “Fundidora Monterrey” started operation in 1903; it was the most important steel industry in Latin America at that time. The foundry started with the blast steel furnace No. 1, which had a capacity to produce 350 tons of pig iron per day and had 32 m of height and a crucible diameter of 3.6 m; each of these had four stoves and 14 steam machines that had a force of 4600 HP that gave power to the air blowers [27]. The existence of mineral deposits of iron and coal in the region as well as abundant water at that time in Monterrey were decisive factors for the start of the steel industry. In the first years, *Fundidora Monterrey* faced serious economic difficulties: the global crisis of 1907, the flood in the city in 1909, and the start of the Mexican Revolution in 1910 [28]. Figure 5.6 shows the facilities of *Fundidora Monterrey*, México [29].

Fundidora Monterrey operated for 86 years. During that period, three blast furnaces were installed and departments were adapted for finished product, foundry and machinery, and structures and transportation. The blast furnace No. 1 ran from

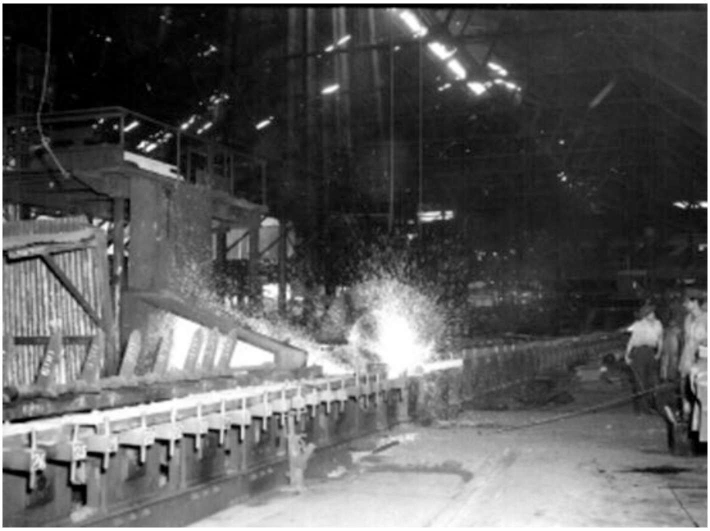

Fig. 5.6 Facilities at Fundidora Monterrey [29]

1903 until the start of 1940s. Operation of blast furnace No. 2 took place early 1940s to meet the demand of the U.S market where steel production began to grow considerably due to the World War II. To accomplish the objective, *Fundidora Monterrey* established various growth strategies to modernize the facilities and increase and adjust the existing ones [26].

The blast furnace No. 2 had a diameter of 4.75 m, height of 51.21 m, and a total volume of 500 m^3. It was designed to produce 500 tons of pig iron per day. The third blast furnace was constructed in the 1960s to meet the demand for steel making. It had a diameter of 8.5 m, automatic charge operation, and a blower of 15,000 HP. It was designed to produce 1500–20,000 tons of pig iron per day, starting operation in 1968 [26]. Monterrey foundry was closed in 1986 by the government; the foundry, for 86 years, had a key place in the steel production of México. Nowadays, after its closing, a steel museum was adapted in the old blast furnace No. 3 structure—a cultural space that commemorates its history and recreates the steel industrial process promoting scientific instruction and technology among the people [30].

References

1. Weeks, M.E., Leichester, H.M.: Elements known to the ancients. In: Discovery of the Elements, pp. 29–40. Journal of Chemical Education, Easton (1968) ISBN 0-7661-3872-0. LCCN 68-15217
2. Simmons, S.E., Shugar, A.N., editors.: "Archaeometallurgy in Ancient Mesoamerica." Archaeometallurgy in Mesoamerica: Current Approaches and New Perspectives, University Press of Colorado, 1–28 (2013)
3. Coghlan, H.H.: Prehistoric Iron Prior to the Dispersion of the Hittite Empire Man, vol 41, pp. 74–80 (1941)

4. Cline, W.: Mining and Metallurgy in Negro Africa, pp. 17–23. George Banta Publishing, Menasha (1937)
5. Forbes, R.J.: Metallurgy. In: Charles, S., Holmgard, E.J., Hall, A.R., Vol, I.I. (eds.) A History of Technology, pp. 41–48. Oxford, New York (1956)
6. Van Kkhoan, K.: Tekhnologiya isgotovleniye zheleznykh i stal'nykh orudiyi truda Yuzhnoy Sibiri (The technology of manufacturing tools in Southern Siberia). Sovetskaya arkheologiya. **4**, 110–124 (1974)
7. Needham, J.: Science and Civilisation in China, vol 5, Chemistry and Chemical Technology, Part 11: Ferrous Metallurgy. Cambridge University Press (2008)
8. Markov, G.E.: Kochevniki Aziyi (The Nomads of Asia). Izd. Moskovskoi gos univ., Moskva (1976)
9. Ziniakov, N.M.: Ferrous metallurgy and blacksmith production of the Altay Turks in the sixth to tenth centuries A.D – Synthesis. Arctic Anthropol. **25**(2), 84–100 (1988)
10. McDonnel, G.: Iron and its alloys in the fifth to eleventh centuries AD in England. World Archaeol. **20**(3), 373–382 (2010)
11. Sherby, O.D., Wadsworth, J.: Ancient blacksmiths, the Iron Age, Damascus steels and modern metallurgy. J. Mater. Process. Technol. **117**, 347–353 (2001)
12. http://www.medieval-life-and-times.info/medieval-life/medieval-blacksmith.htm
13. https://exarc.net/issue-2014-2/at/soil-iron-product-technology-medieval-iron-smelting
14. Balasubramaniam, R., Saxena, A., Anantharaman, T.R., Reguer, S., Dillmann, P.: A marvel of medieval Indian metallurgy: Thanjavur's forge-welded Iron Cannon. JOM. **56**(1), 17–23 (2004)
15. The hardening of iron swords. J. Archeol. Sci. **2**, 199–207 (1975)
16. Godfrey, E., van Nie, M.: A Germanic ultrahigh carbon steel punch of the Late Roman-Iron Age. J. Archaeol. Sci. **21**, 1117–1125 (2004)
17. Prakash, B.: Ancient Indian Iron and steel: an archaeometallurgical study. Indian J. Hist. Sci. **46**(3), 381–410 (2001)
18. Stoughton, B.: The Metallurgy of Iron and Steel. McGraw-Hill, New York (1908)
19. Derui, T., Haiping, L.: The Ancient Chinese Casting Techniques. The 69th WFC Paper (2010)
20. Juarez, L.: Documenting Scottish Architectural Cast Iron in Argentina, ABE J. **5**. Online since 01 December 2014, Connection on 04 February 2020. http://journals.openedition.org/abe/821. https://doi.org/10.4000/abe.821 (2014)
21. Hosler, D.: Copper tin bronzes in Mesoamérica. Anales de Antropología. **18**(1), 1–34 (1981)
22. Villanueva, R.A.: Historia de la siderurgia en argenti-na. Recuperado 3 diciembre, 2019 (2015)
23. Pla, J.: Los Británicos en el Paraguay. Revista de historia de América. **71**, 54 (1971)
24. Pan American Institute of Geography and History, Los Británicos en el Paraguay, pp. 343–344 (1970, diciembre)
25. Bessemer's volcano and the birth of steel: making this versatile metal plentiful gave rise to Christmas and an understanding of modern physics, Am. Scientist, **104**(1), 12+ (2016), Gale Academic Onefile. Accessed 4 Dec 2019
26. Cantu Delgado, J.: Rebuilding the spirit of place: The Fundidora Park of Monterrey. In: 16th ICOMOS General Assembly and International Symposium: 'Finding the spirit of place – between the tangible and the intangible', Quebec, 29 Sept–4 Oct 2008 (2008)
27. Pérez L.A., de Jesús Pérez y Peniche J. A Summary of the Principal Findings of the Case-Study on the Technological Behaviour of the Mexican Steel Firm Altos Hornos de Mexico. In: Katz J.M. (eds) Technology Generation in Latin American Manufacturing Industries. Palgrave Macmillan, London (1987)
28. Nierman, D.: Fundidora con raíces de acero, p. 29. Fi-deicomiso Parque Fundidora, Monterrey, Nuevo León (1991)
29. Instituto Nacional de Antropología e Historia, Instalaciones interiores de la fundidora Monterrey, Monterrey, Nuevo León, México Ca., http://mediateca.inah.gob.mx/repositorio/islandora/object/fotografia%3A202424 (1940)
30. Juárez, Á., Oscar, J.: Los altos hornos de la Fundidora de Fierro y Acero de Monterrey. Ingenierías. **10**(36), 40–46 (2007). ISSN 1405-0676

Chapter 6
Application of Metallographic Techniques to Studies in Ancient Metals

Patricia Silvana Carrizo

General Concepts

Metallography is thus an important tool that can provide clues to an object's manufacturing technology or help answer questions that arise during a conservator's treatment of an object. It is possible to provide information on the following range of topics: (1) The manufacturing processes used to produce an object, either cast in a mold or if the object was worked to shape it by hammering and annealing. (2) The thermal history of the object: quenching and tempering processes can produce definitive changes in the microstructure that can be seen in the section. (3) The nature of the metal or alloy used to make the object; an example of this is that many degraded silver objects are made of silver and copper alloys, and both components are clearly visible in polished and etched sections; they are shown as a copper-rich phase and as a silver-rich phase. Although it can sometimes be very difficult to get an idea of the chemical composition just by looking at the microstructure, additional evidence must be obtained here using appropriate analytical method, such as X-ray reflection (fixed and portable XFR), which is noninvasive and is one of the complementary techniques to a metallographic study. (4) The nature of the corrosion products and much useful and varied information can be obtained from corroded fragments or pieces of corrosion crusts because there may be residual metal structures within the corrosion layers and unusual morphology of the corrosion products themselves, even changes brought about by conservation methods. It should be noted that great advances have been made with the advent of the scanning electron microscope, which is a very powerful tool, in addition to light microscopy, for many of these types of investigations.

If it is necessary to cut the object to carry out the study, the first and most important thing is that it must have the authorization of the owner, whether the piece

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P. S. Carrizo (✉)
Archaeometallurgy Area/Metallurgy Laboratory, National Technological University,
Mendoza, Argentina

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_6

comes from the public sector (museums) or the private sector (collectors). But first of all, an attempt should be made to carry out the metallographic study without cutting the piece or doing as little damage as possible, since a 10 mm^3 sample taken from the appropriate area is sufficient to make the evaluations. It must be made very clear to the owner of the study piece, whether public or private, that once the investigation is completed the piece is returned to the museum or private collector, along with a technical report written as a result of the examination that includes multiple micrographs of the structure and each micrograph with the corresponding magnification, the technical report must even have the entry number assigned to the sample in the laboratory and finally both numbers (the entry number assigned to the sample and the technical report) must coincide, this favors quality control, internal and external audits of the laboratory, as well as contributing to the order in the management of records of metallographic files of the laboratory.

Sometimes it may be necessary to carefully examine objects to be studied, either in a museum or in a laboratory, to evaluate and determine the number of samples to be taken, depending on the objects from samples are being taken.

In the last 20 years, great advances and improvements have been made in metallographic techniques; it is no longer necessary to extract a large amount of sample from an object to study it, as was required previously. The extent of damage to objects has therefore been greatly reduced; in fact, with many corroded metallic or fragmentary objects, the loss can be insignificant and the information obtained can be very important. The only difficulty in taking small samples has to do with whether the sample is representative of the general structure of the object [1].

The fact that even metallographic studies can be carried out in situ is exceptional, especially when one cannot take the object out of the museum or private collection to a metallographic laboratory using portable laboratory equipment.

Although it is often difficult to achieve a good photomicrograph, because the surface under study must be flat, and both roughing and polishing of the area must be done without damaging the object, but the task, although complicated, is not impossible either and in these cases a very important criterion to apply is to choose a “study area” that is then not visible to visitors to the museum or private collection, these are precautions to take into account.

Macrography

A macroscopic or macrographic test consists of observing the appearance of a piece or a flat section of a metallic sample, duly polished and attacked with an appropriate reagent. Although at this stage it is not always necessary to carry out this polishing step properly and attack with special reagents. Observation is conducted by the naked eye, then with a stereoscopic magnifying glass or a microscope of no more than 10× magnification (in the latter case, it is necessary to attack with suitable reagents). But the most usual thing is to observe the piece carefully with the naked eye and continue the study with a stereoscopic magnifying glass and taking photos

Fig. 6.1 (**a, b**) Stereoscopic magnifying glass and threaded bolt of trans-Andean Railway

with a digital camera. This is the first record of how the piece is received in the laboratory, so obtaining images from various areas is considered to be of great importance. This preliminary study makes it possible to determine the zone or zones where the following metallographic study will be carried out: the micrograph. The document obtained either by photographing or in some way reproducing the macrostructure is called a macrography [2] (Fig. 6.1).

Micrography

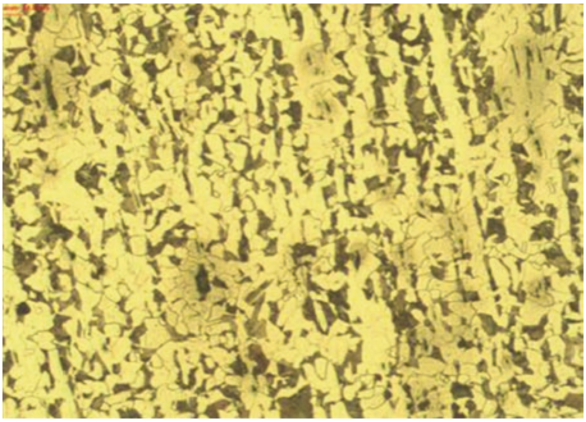
The mechanical properties of an alloy depend not only on its chemical composition, that is, on the weight percentage of each element, but also on the way in which they are presented. Thus, for example, the chemical elements that form an alloy can be in the form of a homogeneous solid solution, a eutectic mixture, or an intermetallic compound with a defined chemical composition, dispersed within a solid solution, and so forth.

Each of these components is called a metallographic constituent, and the properties of the alloys largely depend on their proportion, form of presentation, and extension, and their recognition constitutes the micrographic analysis of the alloy (Fig. 6.2).

Metallographic Sampling of Metals

There are often severe restrictions on the amount of metal that can be removed from a heritage artifact for a metallographic examination. In addition, the sample must be small, so if necessary it can be included in resin and polished for examination,

Fig. 6.2 Micrograph of microstructure of threaded bolt of trans-Andean Railway, in which a ferrite-pearlite structure is observed



although great care must be taken at all stages of preparation. Although obviously it is much easier to work with larger samples, this depends on the standards of the museum; however, if you have complete artifacts or substantial fragments available for sectioning, then it is advisable to extract two cuts, longitudinal and transverse. For example, when the test area shows us an undistorted dendritic structure (which would indicate that the part was cast), then it is not taken as definitive that the entire object will reveal the same structure. On the other hand, we can find case studies such as, for example, a fine and worked sheet, pieces of wire or small pieces of jewelry that, due to their small size, would not be uncommon to find a homogeneous and relevant structure.

But with larger artifacts, such as axes, knives, swords, and large castings, a very difficult problem can be elucidated, so it is safest to make two cuts: a longitudinal and a transverse one. Since a complete interpretation of the metallographic structure of an artifact, such as an ax, is required, then it is almost essential to take two samples. Another good example would correspond to a piece of wire or rod where longitudinal and cross sections are of potential interest. Here the cross and longitudinal sections can be obtained from a single sample by cutting wire into two pieces, longitudinal and transverse, and then mounting them in resin to form a bar and thus easily manipulate the sample.

Because of this there are a number of criteria that samples must meet: (1) The object must be photographed or drawn before taking the sample. This is especially important if the dimensions of the object are fundamentally altered by the material removed. (2) The microstructure of the samples must not be modified in the extraction process. (3) The sample must be representative of the object as a whole or of a selected characteristic or area of the object. (4) The orientation of the sample relative to the entire object should be carefully recorded and, if it is not obvious where the sample was taken from, the position of the object in question should be marked on a photograph or drawing of the object.

There are a number of possibilities for extracting a sample, inevitably depending on the nature of the object and the metal or alloy of which it is made.

Micrographic analysis of a metal is done on a polished specimen of the material that is attacked with a suitable reagent. Each metallographic constituent has a certain rate of reaction with the attack reagent. Less attachable constituents will be brighter and reflect more light in the microscope, making them clearer for observation. This difference allows the different constituents to be detected and their proportion, distribution, grain size, and so forth to be determined. Each metallographic constituent is made up of a large number of crystals, which together constitute the metallographic grain. The grain edges are attacked with greater intensity because they are more reactive and are called the "grain boundary."

In the metallographic microscope we detect the different metallographic constituents and the grains that form it, their metallographic structure. The crystalline lattice formed by the atoms within each grain is not visible under a metallographic microscope. Its study requires the application of other techniques, such as X-rays, for example. The correct preparation of a specimen for microscopic observation is of fundamental importance. For this, the results of the macroscopic observation are taken into account and then the following steps are taken to prepare metallographic specimens, which must be respected and developed with special care:

1. Selection of place and extraction of sample.
2. Assembly of the specimen.
3. Roughing.
4. Polished.
5. Attack with reagents.
6. Microscopic observation.
7. Registration of images and results.

Selection of Place and Extraction of Sample

Much of the success of the micrographic study to be carried out depends on the correct choice of the sample extraction site. There is no fixed rule that determines the place to choose; the criteria to follow varies in each particular case; as a guide some common examples are given here: if you study laminated bars or profiles, such as railway rails (see Chap. 12: Study Cases; "Archaeometallurgy Study of a Piece of Rail from the Guido Station Belonging to the Trans-Andean Railway"), specimens should be removed from their ends and middle part, making cross cuts. Cross sections and at the same time longitudinal sections will be studied in the extracted pieces. If the profiles are of large dimensions, the sections to be studied will produce specimens from the edges and the center, being able to take advantage of the pieces extracted in restoration-conservation works, as is the case of metallic infrastructure works (see Chap. 12: Study Cases; "Archaeometallurgy, Heritage and Preservation Study of the Iron Bridge over Mendoza River). In the case of molded parts (cast iron), sections normal to the casting plane will be chosen, which allow observing the variation in structure from the edge to the center.

In the case of broken pieces, samples must be obtained from the fracture area without deteriorating the fracture surface in subsequent polishing. When the broken parts are rolled or forged, the cutting planes must be matched with cross or longitudinal sections to the fibers of the material. It is also advisable to choose samples far from the break in order to investigate possible chemical or structural heterogeneities.

Once the site has been chosen, the sample must be extracted.

In the case of soft metals, such as annealed carbon steel, puddled iron, bronze, brass, and gray cast iron, the cut should be made with hand saws or refrigerated metallographic cutters. The softer the metal, the larger the tooth of the saw must be (that is, fewer teeth per inch) in order for the chip to be easily removed from the cut, preventing it from clumping to the surface to be studied, which would falsify subsequent observation.

Hard metals, such as alloy steels, quenched steels, and treatment-hardened nonferrous alloys, must be cut using very thin (1.5 mm) abrasive disks of carborundum or diamond powder, spinning at high speeds, and with strong liquid cooling to prevent heating of the material to be cut. It is very important, during the extraction of the sample, as well as during its subsequent manipulation, to avoid any heating above 80–100 °C, which could produce microstructural modifications, falsifying observations. Whenever possible, the dimensions of the extracted sample should be compatible with easy handling for polishing [3] (Figs. 6.3 and 6.4).

Fig. 6.3 Cut with handsaw of a rail piece for study

Fig. 6.4 Image of metallographic cutter

Mounting or Inclusion of Sample

Generally, cut and extract sections of approximately 10–20 mm and heights of 10 mm are chosen. In the case of very small parts, such as needles, clock shafts, nails, lamp filaments, or shavings, it is convenient to prepare special assemblies using Bakelite, that is, with thermosetting resins, which are molded with the piece inside using a small press such as a heater called a metallographic embedding machine. If the material or pieces of objects could suffer damage in the metallographic embedding machine, then they should be placed in small PVC tubes (which will serve as a mold) using acrylic resins made up of two parts (resin and hardener); the quantities of both components will be detailed in the product packaging and will need to be exposed to air for setting or curing, since they generally emit an astringent and powerful odor, which is why they are generally placed near windows until they completely harden and are ready for the next stage.

A number of proprietary synthetic resins on the market are designed as embedding materials for metallographic samples; epoxy, polyester, and acrylic resins are the most common. For routine use, a polyester-type inclusion resin and peroxide catalyst can be used; one drop per milliliter of catalyst is mixed into the resin, which will begin to gel after approximately 5 min and should therefore be used quickly.

In other types of resin brands, 15 mL of resin is enough to fill several molds 18–30 mm in diameter that are made of polyethylene or silicone rubber. Curing is best done at room temperature; samples can be removed from the mold after 2–4 h, but the specimens do not reach their maximum hardness until approximately 8 h. Manufacturers indicate that the slightly tacky surface on the set resin is due to oxidation reactions, which can be minimized by covering the mold while setting the resin. This, however, is seldom a serious problem, and the resin will provide satisfactory edge retention and low porosity during curing.

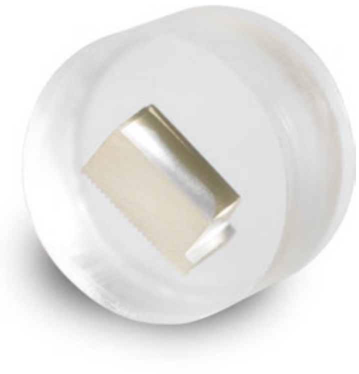


Fig. 6.5 Test tube of acrylic resin

Fig. 6.6 Typical mounting press

Another recommended method for achieving good edge retention involves carefully placing the sample in a silicon rubber mold half filled with acrylic resin and allowing it to set. Then the mold is completely filled with resin. In this way the sample is embedded without the need for a support bar. As in the previously mentioned cases, the tablets or test pieces can be removed from the mold after 3 or 4 h but do not reach their maximum hardness until approximately 8 h, that is, when the curing of the acrylic resin or polyester is completed (Fig. 6.5).

In the case of epoxy-type resins, the most commonly used is Bakelite (thermosetting resin, also called thermoplastic), which comes in powder form, and these inclusions are made in what is called a metallographic embedding machine that works at constant pressure and temperature; as previously established, each process to obtain specimens or tablets takes a constant time of 13 min, and they are ready to start with the next step, roughing and sanding, so this type of resin does not need extra time for curing or any extra treatment. Note that this type of resin is used with a metallographic embedding machine, taking care not to break the sample when placing it in the equipment to obtain metallographic specimens [4] (Figs. 6.6 and 6.7).

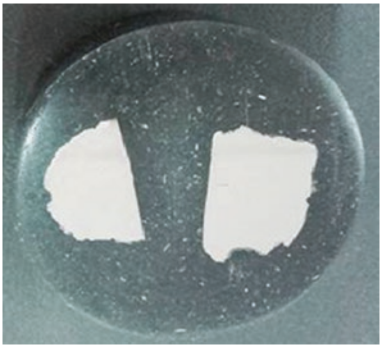


Fig. 6.7 Sample of specimen embedded in Bakelite resin

Roughing or Preliminary Sanding of Embedded Sample

The specimen, also called a tablet, will undergo fine roughing by the use of very good-quality sanding papers. Sanding papers used in metallography are classified according to particle size by the numbers 80–120–140–160–180–220–240–280–320–400–500–600–0–00–000–0000–00000 (the zeros are also called 0–2/0–3/0–4/0–etc.) arranged in the direction of increasing fineness, and they are water-based sandpapers.

Roughing can be done manually, passing the test piece on the sandpaper placed on a flat surface, or mechanically with the paper stuck on a metal disk that rotates at speeds of 400–600 rpm; in this case, portable equipment is used when the part cannot be transported to the laboratory, so there is a series of equipment suitably designed for use in such special cases.

The most desirable procedure, although not always usual, is to have the piece for study in the laboratory and in this particular case of fine roughing sandpaper is used, the researcher or laboratory technician must be careful to rotate the test tube 90º each time the technician or researcher changes from one given sandpaper to the next, this is done in order to obtain perpendicular lines and to have an indication of how much material the last used sandpaper has removed relative to the previously used sandpaper. Excellent results are achieved with water-based sandpaper, they are sandpaper of good quality and grains similar to emery. In this case, the roughing is done by hand, fixing the sandpaper on a straight and flat base, and during the whole operation, it must be in permanent contact with a jet of cold water from the tap that continuously rinses both the sandpaper and the sample of metal. This action has the advantage that due to the washing effect, the surface of the paper is not saturated with sandpaper particles, which speeds up the roughing operation, and there is also no possibility of heating the sample by mechanical effect.

It is very important to completely remove scratches from the previous sandpaper because otherwise it will be very difficult to remove them in the next operation, polishing.

With very large specimens a new strip of sandpaper should be used and successively longer sanding times are needed as the paper becomes thinner. This ensures complete removal of deformed material from the sample surface prior to polishing.

Special care must be taken with metallographic preparation of soft metals, such as gold alloys, zinc alloys, or certain copper alloys, beyond that taken with samples of iron, steel, or cast iron in archaeological contexts.

The specimen should be held in such a way that it does not rock or fall off the roughing or sanding plane, otherwise it will be very difficult to obtain an optically flat surface and too much pressure should not be applied to avoid rounded edges on the specimen, otherwise later observation with the metallographic microscope would be very complicated. The roughing is finished when a perfectly flat face is obtained, with very fine lines all over the surface and oriented in the same direction. The fineness of the last sandpaper used depends on the hardness of the metal to be polished; the thinner the paper, the softer the sample will be. After fine sanding, the specimen and the operator's hands should be thoroughly washed with plenty of running water to avoid scratching the sample on its way to the final polishing operation [5].

Polishing

Polishing is done to eliminate all fine scratches produced during roughing, with a specular surface generally obtained. Polishing can be done by mechanical or electrolytic means.

Mechanical Polishing

- Metallographic polisher
- Metallographic polishing is carried out on cloth fastened to metal polishing disks using abrasives in liquid suspension. The types of cloth used include billiard cloth, corduroy, cotton velvet, silk, or specially prepared cloth that is commercially available under different names, depending on its origin. The most commonly used abrasives are magnesium oxide, alumina (aluminum oxide), chromium oxide, iron oxide in the form of very fine powders (500–600 meshes) suspended in liquids, although distilled water is generally used to prepare these suspensions.

For its preparation, a small amount of abrasive is mixed in one liter of water, stirred with a glass rod until a homogeneous mixture is obtained and it is left to rest for a variable time, generally not less than 30 min. The liquid is then siphoned with the aluminum oxide in suspension, avoiding dragging the thickest decanted material, thus obtaining a suspension of alumina (Al_2O_3) in 30 min or less in ready-to-use conditions. This suspension is poured dropwise onto the well-stretched cloth and

Fig. 6.8 Polishing operation in rotary polisher

attached to the polishing disk that rotates at variable speeds of approximately 400 rpm. The rough sample is held firmly on the rotating disk, printing a counterclockwise rotational movement, or constantly moving it back and forth according to the radius of the disk, avoiding keeping the sample in a static position during the polishing operation (Fig. 6.8).

It is difficult to quantify how much pressure must be used to hold a specimen on the polishing cloth, as very low pressure slows down the polishing speed and can cause pitting on the surface, while too much pressure can distort the surface. The correct polishing pressure varies with different metals and the correct technique can only be learned through practical experience. The cloth should always be kept damp, intermittently adding the suspended abrasive or just a little water to take advantage of the remaining alumina concentrated in the central area of the cloth disk. In this operation all scratches produced by the final sanding papers and even the finest ones produced by the polishing should disappear.

It is important to note that polishing should not extend beyond what is necessary because surface distortion of the metal may occur. In very soft metals, a distorted layer usually forms, which is removed by attacking the polished specimen with a reagent that dissolves the layer and then polishes again. This operation can be repeated several times. Once the test piece is polished, it is washed thoroughly with water and rinsed with alcohol or acetone, and can be dried faster if palced before a stream of hot air (hair dryers are commonly used). Once this is done, the sample can be observed under a microscope. The polished specimen should be handled with care, avoiding contact of its surface with fingers or any other object that might stain or scratch it. A greasy impression left by fingers will produce spots, even streaks, which will result in uneven attacks.

When metallography needs to be carried out in a museum or when a piece is from a private collection, portable equipment should be used to obtain as much

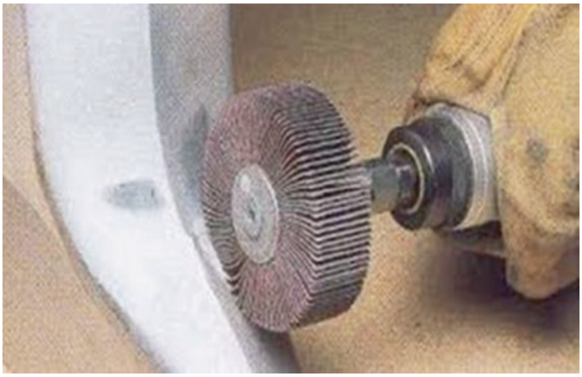


Fig. 6.9 Mechanical polishing “on site” with abrasives and terry cloth with diamond paste

Fig. 6.10 Elements used to prepare metal surfaces with mechanical polishing

information as possible. Thus, an object can be polished with a kind of rotary lathe that uses small polishing disks and diamond paste in tubes (Figs. 6.9 and 6.10).

This starts with thicker grinding disks and then continues with thinner grinding disks, although onsite work involves a more limited variety of thicknesses of roughing papers, but obviously those necessary for quality work and not primarily destructive. The principles and procedures to follow are identical to and as rigorous as those carried out in a laboratory.

For older metals, the best results are obtained by polishing on mineral oil lubricated diamond powder impregnated rotary polishing discs. Diamond powders are generally supplied as paste tubes or in aerosol cans in an oil-based suspension. The usual range of diamond powder sizes are: 6 μ (six microns), 1 μ (one micron), and 0.25 μ (a quarter micron). After initial polishing with 6 μ (six micron) diamond paste, the sample should be washed in water, rinsed with ethanol or acetone and dried. It can then be polished with 1 μm (one micron) diamond paste for at least five minutes. For many routine purposes, this is sufficient, and the sample must be carefully washed to remove all traces of the polishing compound and rinsed with ethyl alcohol or acetone, then dried with hot air, to make the specimen ready for examination under the metallographic microscope. For very high-quality work, it should be finished with a final polish using a 0.25 μ (a quarter micron) diamond paste.

Electrolytic Polishing

Mechanical polishing produces, among other defects, a distortion of surface layers, especially in soft metals and their alloys and in those that harden by deformation. The intrinsic relationship between the microstructure of both metals and alloys with respect to their mechanical properties, heat treatments, and corrosion resistance makes the study of the microstructure of these materials a useful tool for both technical-scientific research and the control and prediction of properties in components in operation. Metallographic analysis as such was originally devised considering the destruction of a specimen that had to be cut to a size suitable for handling; however, the need for a control in the analysis of failure in service made it necessary to devise a local polishing mechanism without destruction of the part.

Electrolytic polishing produces surface finishes of the same quality as those obtained with a good mechanical polish but in less time, since it does not require successive attacks and polishing to eliminate distortions. It has the following disadvantages. Possible destruction of nonmetallic inclusions, production of relief in certain cases due to the difference in the attack speed of the constituents, and mounting of stained surfaces in specimens in plastic since they can be attacked by various electrolytes and generate wavy surfaces. This mechanism was proposed in 1957 by French metallurgist Pierd A. Jacquet, who developed a method called *tampon*, which makes possible the in situ polishing of most metals and alloys for industrial, heritage, and industrial uses, especially when an object cannot be studied in a metallurgical laboratory. Jacquet also devised a method called nitrocellulose metallographic replicas that makes it possible to obtain an exact copy of a metallographic structure that can be observed by transparency or reflection, according to the ASTM E-1351 standard.

The method is fundamentally based on equalizing the surface of metals by the effect of selective electrolytic corrosion of the protruding parts of a specimen. The sample is roughened with fine emery paper and placed as an anode in an electrolytic cell, using a suitable metal as the cathode. For each metal or alloy, a suitable electrolyte is used and a relationship between current density and voltage, as an important factor that varies in each case, is established. The electrical part consists of an adjustable autotransformer that supplies a rectifier that supplies a maximum current of 2 amps (generally 0.2–0.4 amps) with 50 V. Instead of dipping the poles into a container with the electrolyte, Anode **A** in Fig. 6.11 connects to the probe, and Cathode **B** is a wire that ends in a stainless-steel pencil on whose tip is a cotton swab. This swab is dipped in the electrolyte and touched to the test tube repeatedly until polishing is complete. The method has the following advantages, among others: it can be used as a nondestructive test since the apparatus is transported to the desired site and allows for in situ polishing, polishing lasts just a few seconds, and

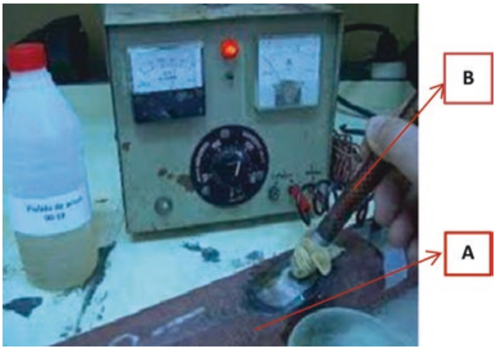


Fig. 6.11 Electrolytic polishing

it allows for the use of explosive reagents (such as perchloric or acetic acid) since in these small quantities no danger is posed.

Electrolytic polishing can be done from the roughing stage to provide a more perfect finish than that obtained by with manual polishing. Disadvantages occur with many archaeological samples due to the extensive corrosion they may have suffered. The presence of these corrosion products means that local anode/cathode reactions can occur with excessive dissolution of the sample as a result. If a phase of a biphasic alloy is slightly corroded, it can preferably be attacked at an accelerated speed.

Mechanical polishing methods are generally preferable unless there is a particular reason to use other techniques, for example, granulated gold spheres, which are difficult to attack, can be polished and attacked at the same time using the same cell where previously the electrolytic polishing was carried out.

A freshly polished section must be metallographically examined as soon as possible under a metallographic microscope to verify that there are no streaks, lines, or so-called kite tails that constitute the defects of a metallographic specimen, because when conducting the attack or engraving with specific reagents, these defects from poor preparation of the specimens or area to be examined are magnified, and the metallographic analyst tends to be confused with what he observes as the particular internal structure of the material. It can even happen that some surfaces fog up quickly and will have to be polished again. To begin with, old metal samples should always be examined in the polished state and record what was observed (taking a photomicrograph) because many features may be visible under the microscope prior to an actual chemical attack with special reagents [6].

A metallographic sample that is suitable for macroscopic or microscopic investigation must have a representative flat area. To clearly distinguish the structure, this area must be free of defects caused by surface deformation, stains, or scratches. On certain samples, the edges must be well preserved to investigate gilding or tinning, for example. Even for a routine examination, poor sample preparation can cause problems because improver observations or conclusions may lead to invalid interpretations of visual evidence.

Chemical Attack

A chemical attack can be carried out by immersing the sample with the polished surface face up in a suitable reagent or passing a cotton swab soaked in said reagent or dripping reagent on it for a time on the order of seconds or minutes. It is convenient during the attack by immersion and dripping to move the specimen continuously so that the reagent is renewed on the surface, producing a more homogeneous attack. Then the specimen or the area of the material where the attack was carried out is washed with water, cooled with alcohol or acetone and dried with a jet of hot air, taking care never to touch the freshly polished specimen or the area of the piece. where the attack was made because they are very susceptible and can be scratched again. Taking as a reference ASTM E-407 (Standard Practice for Micro-etching of Metals and Alloys) in which the steps to follow for the micro-etching of metals and alloys are detailed, different attack reagents are used according to the phases to be observed selective chemistry.

Background of chemical attack: The basis of the chemical attack consists of the different dissolution rates of the various metallographic constituents of the sample in the reagent used. The one with the highest reaction speed will attack the fastest and look darker under a microscope, while the least attackable will remain brighter, reflect lighter, and therefore appear lighter under a microscope. Likewise, in metals of a single metallographic constituent, the attack will reveal the grain limits. This is because these limits are the areas with the highest internal energy and the highest number of impurities, and therefore they react most quickly with the attack liquid. In monophasic metals, that is, of a single metallographic constituent, the different grains may also appear with a different brightness (the less bright ones appear darker), due to the different crystallographic orientations of the different grains, which cause different attack speeds. In all cases, it is advisable not to attack the test piece, since this will stain and cover the structure or cause corrosion, which, in technical metallographic language, means that the part or the area under attack will *burn*.

It is preferable to err on the side of a deficient attack than excess because another attack can always be conducted. On the other hand, the test pieces that have been attacked must be sanded and polished again. In general, to observe the sample at low magnification, a greater attack is needed and with high magnification, the attack is less even if it is to observe fine details. General-purpose reagents exist for detecting the structure of each family or group of alloys. For example, ferrous alloys (steels and castings) are generally attacked with Nital or Picral reagent: a solution of nitric or picric acid in 2–5% ethyl alcohol. Copper alloys are generally attacked with a mixture of ammonium hydroxide and hydrogen peroxide, for example. In addition to these general reagents, there are other more specific reagents that are used for special uses and for more complete metallographic studies than those proposed in a general attack. The list of the most used general and specific reagents is found in Tables 6.1 and 6.2 respectively, as well as their preparation method [7].

Table 6.1 Reagents for cast iron and steel

Iron, steel, and cast iron reagents	Description
Nital reagent 2, 3, 5 2 mL nitric acid, HNO_3 (depending on 2%, 3%, 5%) 100 mL ethanol, C_2H_5OH	Suitable for revealing the microstructure of carbon steels. Alcohol can be methanol or ethanol. Enhances the interface between carbides and the matrix. Blackens perlite
Picral reagent 100 mL ethanol, C_2H_5OH 2 g picric acid, $C_6H_2(OH)s(NO_2)_3$	The most common engraver for wrought iron and carbon iron steels. Often useful for steels treated with iron and heat, perlite, and martensite. Fe_3C is light yellow stained. Nital and Picral can be mixed in a 1:1 ratio
Oberhoffer reagent 500 mL distilled water, H_2O 500 mL ethanol, C_2H_5OH 42 mL hydrochloric acid, HCI 30 g ferric chloride, $FeCl_3$ 0.5 g stannous chloride, $SnCI_2$ (add HCl at end)	After etching, the section should be rinsed in a 4:1 mixture of ethanol and hydrochloric acid. Useful for steels and for plate segregation studies (e.g., arsenic segregation)
Heyn's reagent 20 mL distilled water, H_2O 20 g copper (II) ammonium chloride, $Cu_2Cl(NH_4)$	Copper precipitates should be cleaned from the surface with distilled water or washed with distilled water from a wash bottle. Useful for the segregation of phosphorous in steel
Klemm's reagent 50 mL saturated aqueous sodium thiosulfate solution, $Na_2S_2S_3$ 1 g potassium metabisulfite, $K_2S_2O_5$	Phosphorous segregation in cast steels and cast iron
Beraha's reagent 100 mL distilled water, H_2O 24 g sodium thiosulfate, $Na_2S_2S_3$ 3 g citric acid, $C_6H_8O_7$ 2 g cadmium chloride, $CdCl_2{\cdot}2H_2O$	Use it for 20–40 s. Chemicals must dissolve in given sequence. Each component must be dissolved before adding the next. Store in the dark below 20 ° C. Filter before use. The solution remains active for only 4 h. Used as an etching dye for iron and carbon steels. Ferrite is stained brown or violet. Carbides, phosphides, and nitrides can only be lightly stained
Alkaline sodium pyrate 2 g picric acid, $C_6H_2(OH){\cdot}(NO_2)_3$ 25 g sodium hydroxide, NaOH 100 mL distilled water, H_2O	This solution is useful to distinguish between iron carbide and ferrite in steels. It can be used as a boiling solution for 10 min or more if necessary. Iron carbide, Fe_3C Darkened by reagent, ferrite not affected. Etching in this solution can provide a good indication of spacing of perlite sheets
Dimethylglyoxime and nickel test Some older steels contain nickel as a major impurity	A simple test is to take a nickel footprint by pressing a blotting paper soaked in dimethylglyoxime against the polished section when the nickel rich areas are revealed by brown spots on blotting paper

Vilella's reagent 1 g picric acid, $C_6H_2(OH)\cdot(NO_2)_3$ 100 mL ethanol, C_2H_5OH 5 mL hydrochloric acid, HCI	A reagent that can be used for 5–40 s and clearly reveals the needles on the martensite plate It is useful for exposing the austenitic grain size of quenched steels if this feature is noticeable
Whiteley's method 5 g silver nitrate, $AgNO_3$ 100 mL distilled water, H_2O	Technique for revealing sulfur inclusions in steel and other alloys. Soak polishing cloth in freshly prepared solution Cloth is then washed to remove all excess solution Polished surface of sample is carefully rubbed onto prepared surface of fabric. Any sulfur inclusion present should be stained dark brown

Table 6.2 Reagents for alloys of gold, silver, copper, bronzes, etc.

Reagents for alloys of Gold, Silver	Description
Aqua Regia 40 mL nitric acid, HNO_3 60 mL hydrochloric acid, HCI	Used for a few seconds or up to a minute. Use cool Aqua Regia is a strong and highly corrosive oxidizing solution. Provides grain contrast on most alloys
Hydrogen peroxide/iron (III) chloride 100 mL distilled water, H_2O 100 mL hydrogen peroxide, H_2O_2 32 g ferric chloride, $FeCl_3$	Sometimes useful for variable carat gold jewelry alloys and Au-Cu-Ag alloys
Tin reagent Ammonium polysulfide, $(NH_4)_2S_x$	Saturated aqueous solution of ammonium polysulfide. Use for 20–30 min. Clean with cotton after engraving. Can be used for all kinds of tin alloys. Nital or Picral can also be used (see engravings for iron, steel, and cast iron)
Zinc reagent Palmerton's reagent 100 mL distilled water, H_2O 20 g chromic oxide, CrO_3 15 g sodium sulfate, Na_2SO_4 (anhydrous) ó 35 g sodium sulfate, $Na_2SO_4\cdot 10H_2O$ It can be used for seconds or minutes HCl concentrated to 50% in distilled water: 50 mL hydrochloric acid, HCI 50 mL distilled water, H_2O	Zinc alloys are difficult to prepare mechanically. False microstructures are common because deformation is difficult to prevent This solution is sometimes useful for both swab application and immersion
Reagents for Lead alloys Reactivo a base de glicerol 84 mL glycerol, $HOCH_2CHOHCH_2OH$ 8 mL glacial acetic acid, CH_3COOH 8 mL nitric acid, HNO_3	Use only fresh Gives grain limit contrast
Glacial acetic acid 15 mL glacial acetic acid, CH_3COOH 20 mL nitric acid, HNO_3	Useful for soldering of lead and Pb-Sn alloys. If you experience difficulty in preparing lead alloys, a good technique is to try to finish the polishing with fine alumina powder (0.25 μm) suspended in distilled water with a 1% solution of aqueous ammonium acetate
Reagents for copper alloys Aqueous ferric chloride 120 mL distilled water, H_2O 30 mL hydrochloric acid, HCl 10 mL ferric chloride, $FeCl_3$	Produces grain contrast. Very useful for all copper-containing alloys, such as arsenical coppers, bronzes, brass, etc. Engraving time is given in a few minutes in some books, but ancient metals engrave faster. Reduce time to 3–5 s at first
Alcoholic ferric chloride 120 mL ethanol, C_2H_5OH 30 mL hydrochloric acid, HCI 10 mL ferric chloride, $FeCl_3$	Same as aqueous ferric chloride, except that there may be some advantages to using an alcoholic solution (e.g., fewer stains)

(continued)

Table 6.2 (continued)

Reagents for alloys of Gold, Silver	Description
Reagents for grain limits Aqueous ammonium persulfate 100 mL distilled water, H_2O 10 g ammonium persulfate, $(NH4)_2S_2O_5$	It only takes a few seconds for all these recorders unless otherwise specified Produces grain contrasts. Records the grain boundaries. It must be used fresh. Do not save it. Saturated chromium (VI) oxide solutions must be handled with great care. Chromic oxide (CrO_3) and organic mixtures can be EXPLOSIVE
Ammonia / hydrogen peroxide 25 mL distilled water, H_2O 25 mL ammonium hydroxide, NH_4OH 5–25 mL hydrogen peroxide, H_2O_2	Use cool only Adding large amounts of H_2O_2 creates a better grain contrast; adding less H_2O_2 creates better grain boundary engraving
Reagents for Iron oxide layers Solution 1 10 mL distilled water, H_2O 5 mL nitric acid, HNO_3 to 1% 5 mL nitric acid to 5% 5 mL aqueous thioglycolic acid to 5%, HOCH • COSH Solution 2 15 mL distilled water, H_2O and 5 mL formic acid, solution of HCOOH (a) 15 mL de H_2O y 5 mL fluoroboric acid, F_2BO_3 (b)	– Dampen for 15–60 s. engravings Fe_2O_3; Fe_3O_4 is not attacked – Clean for 5 s with solution (a) followed by solution (b) for 2 s For Fe_3O_4 only
Reagents for silver alloys Acidified potassium dichromate 10 mL sulfuric acid, H_2SO_4 100 mL potassium dichromate, saturated $K_2Cr_2O_7$ with water 2 mL sodium chloride, saturated solution of NCI dilute 1: 9 with distilled water before to use It can also be used without the addition of sulfuric acid	Useful for silver and copper and silver alloys
Ammonium persulfate/potassium cyanide 100 mL distilled water, H_2O and 10 g ammonium persulfate, $(NH_4)\cdot S_2O_5$ (a) 100 mL H_2O and 10 g potassium cyanide, KCN (b)	Solutions (a) and (b) must be mixed before use in a 1:1 ratio After use, rinse sink with plenty of water Never mix with acids. Potassium cyanide solution is poisonous. Also useful for gold alloys, silver alloys, copper alloys

Other Methods of Chemical Attack

Another type of attack used to reveal the metallographic structure of a sample is the electrolytic attack.

- Electrolytic attack:
- Attack by an electrolytic method is of particular interest to reveal the structure in materials such as strongly cold-deformed alloys, alloys resistant to corrosion and heat, and alloys that present surface passivity during usual attacks. An electrolytic attack consists in passing a direct current, which varies from a fraction of an ampere to several amperes of intensity, through an electrolytic cell that contains an appropriate electrolyte and in which the test piece is the anode, with the cathode being the buffer. The choice of electrolyte depends on the metal or alloy to be attacked and the microstructural constituents that the attack is to reveal. Generally, it is done after electrolytic polishing in the same electrolytic cell but at a much lower voltage. An anodic solution is used as in electrolytic polishing, but in polishing the solution is undifferentiated, while here the solution is selective (Figs. 6.12 and 6.13).

Microscopic Observation

This involves examining polished sections of metallic materials using a special microscope that reflects light that passes through the objective lens onto the surface of the sample. The reflected light returns through the objective to the eyepiece, which makes it possible to study the structure of the section surface (Figs. 6.14 and 6.15).

Fig. 6.12 Electrolytic Cell

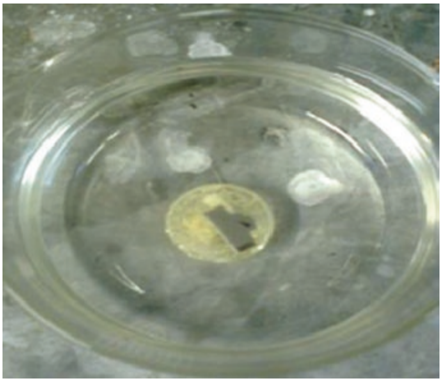


Fig. 6.13 Cross section test tube in an electrolytic bath of oxalic acid

Fig. 6.14 Observation on site of a historical canyon belonging to the San Carlos Fort Museum (Mendoza-Argentina) using a portable microscope

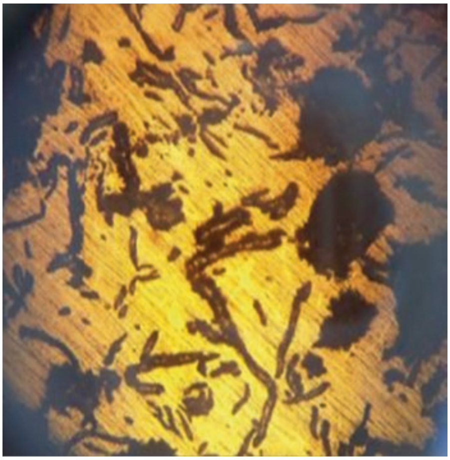


Fig. 6.15 Micrograph showing a structure of gray cast iron and corrosive pitting

Reflected light microscopy is used for metallographic examination because metals cannot transmit light in thin sections in the same way as ceramic or mineral materials. In general, a sample, which may be small, of the object under study should be taken, and a small area of a relatively flat surface should be polished on the object using a portable mini lathe fitted with fine polishing discs; although this method is somewhat uncomfortable to perform, it is ideal in case we do not have the piece for study in the laboratory.

Useful information can be obtained from samples as small as 1 mm^3, with a minimal amount of damage to the piece, or the other option is to use the portable microscope without cutting a sample from the piece and working directly in the museum as the above pictures show.

Optical Microscopy: Principles

Optical Microscopy (OM) uses visible light to create an enlarged image of the sample to be studied. All metals are opaque to visible light, this implies that light does not penetrate inside but is reflected, consequently the observation of reflected light by light microscopy allows observing the surface of the material. Different regions of the microstructure of a material produce different reflections of light, and therefore different contrasts in the image that is observed. Therefore, before analyzing a sample, it is polished and chemically treated with a suitable reagent.

Because of chemical attack, grooves are formed in the grain boundaries since the atoms in the grain boundaries are more chemically reactive and dissolve more easily than the atoms contained inside the grains. These grooves reflect light at a different angle from that of the crystalline grains, making them highly visible in the image provided by the light microscope.

Inverted Microscope or Inverted Stage Optical Microscope

As the name implies, an inverted microscope is upside down compared to a conventional microscope. The light source and condenser are under the platform pointing downwards. The targets and turret are under the platform pointing upwards. The binocular tube is the only element that is in the same position as in a conventional microscope and finally the sample or test tube is placed on a platform or mechanical stage that is called inverted because it is located on the top unlike conventional microscopes.

A variety of inverted microscopes are available depending on one's aim. Microscopes can have different types of lenses, eyepieces, maximum allowed magnification, focus, and other features. Such microscopes differ from biological ones in that the object being studied is illuminated with reflected light since metallic samples are opaque to light. The microscope's operation is based on the reflection of a horizontal light beam coming from the source. Its operation is based on the reflection of a horizontal light beam from the source, said reflection is produced, by means of a flat glass reflector (mirror), downwards, through the microscope objective on the surface of the sample. Some of this incident light is reflected off the surface of the sample and will be amplified as it passes through the lower lens system, hits the target, and continues up through the flat glass reflector (mirror), then is amplified again on the upper lens system (eyepiece).

Components

An inverted microscope has the following components:

Lamp holder**:** socket containing a lamp that is the halogen light source.

Filter holder**:** container into which specific filters are inserted for the type of lighting required for making observations. A cobalt filter, which is blue, turns light from yellow to white, and the image is seen in a bright field (a type of lighting that makes it possible to observe dark samples against a light background). A green filter is essential for phase contrast (such lighting differentiates images by degree of tone, brightness, or color).

Diaphragm opening**:** device with which the level of light emitted by the lamp is graduated. It can be kept low to easily focus on noncolored samples or open for phase contrast.

Condenser**:** lens system that collects light rays and converges them into a focus. It is located directly above the microscope platform and coupled with the aperture of the diaphragm to regulate resolution, perform contrast, and reduce glare.

Support: supports condenser and lamp to maintain the stability of the microscope.

Mechanical platform**:** metallic platform where samples to be observed are placed; it has a central hole that communicates the light from the condenser with objectives.

Mechanical trolley**:** hollow support with a strip that allows the trolley to move on the mechanical platform, from right to left or from top to bottom.

Objectives**:** complex lens system located under mechanical platform. Current high-power objectives have a very short working distance and therefore must be brought close to the sample for focus; objectives on inverted microscopes are adapted to work at long distances owing to sample thickness.

The magnification of the lenses can be as follows: 50×, 100×, 200×, 500×, 800×, 1500×. Although commercially available inverted microscopes have two objective displays, the first with 4×, 10×, 20×, 32×, and 50× magnifications and the second with 4×, 10×, 20×, 40×, 50×, 100×, 500×, 800×, and 1000× magnifications.

Object holder revolver**:** device where objectives are assembled.

Other important parts**:** micro and macrometric buttons, binocular and trinocular tubes (if there is a phototube to modify the camera), eyepieces, diopter ring (correct for diopter difference between both floors), button to adjust voltage bulb (regulates voltage input to microscope, prolonging its life), receptacle for cable connected to microscope fuse [8] (Figs. 6.16 and 6.17).

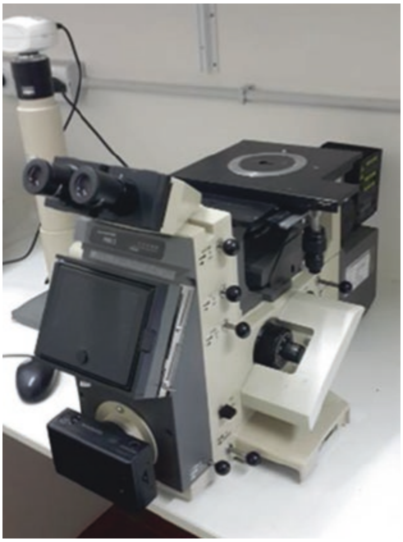


Fig. 6.16 Inverted stage microscope

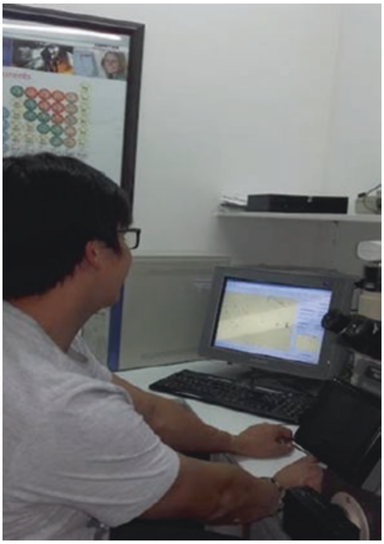


Fig. 6.17 Image acquisition software

Registration of Images

Visual evidence should be described, preferably with accompanying photographic records of the microstructure at appropriate magnification. The inclusions or corrosion products that are present when the section is examined in a polished state should be noted because these will dissolve or be partially removed by attack.

If necessary, a photograph should be taken in the preattack state to show the range and type of inclusions present. It is important to obtain an overview of the sample at low magnification (approximately 50×) before proceeding to observe particular features at higher magnifications.

Some samples will appear almost inert before attack if the metal or alloy is not corroded and is relatively free of slag particles, oxide inclusions, or other impurities. In these cases, it is permissible to proceed to an attacked surface fairly early in the examination. The details of the attack solution used should be recorded.

The increase, of course, should be recorded with any notes made about the structure once the details can be seen. The range of characteristics that can be made visible by chemical attack will vary depending on the type of sample examined. Details that are not evident using a reagent can only become visible after another reagent has been tested, so the assumption that all microstructural details are evident should be resisted when using a specific attack reagent.

The following characteristics must be observed: (1) The range and type of grains present. Their size can be compared to, for example, an eyepiece marked with grain sizes or with standard grain size numbers from ASTM E-112. (2) The presence of different phases. (3) Significant heterogeneity or differences between various areas of the sample. (4) Grain sizes, surface deformation characteristics, or heat-treated areas at cutting edges and worked surfaces. (5) Distribution of inclusions, weld lines, slag particles, or porosity. (6) The presence of surface or gold coating. Careful examination at high magnification is sometimes necessary to establish the presence of surface coatings, leaf gilding, or amalgam gilding, for example. (7) The distribution of any corrosion products present and the existence within corrosion layers of pseudomorphic remains of grain structure or other microstructural characteristics, the presence of remaining metallic grains, and unusual layers or characteristics. (8) Indications of thickening of grain limits or precipitation of another phase in grain limits. (9) Presence of twin lines within grains and whether such lines are straight or curved. (10) The presence of voltage lines within grains. (11) Whether dendrites in cast alloys show indications of core removal and approximate spacing (in microns) of dendritic arms, if these are clearly visible. (12) Remember that a polished section is a two-dimensional representation of a three-dimensional object. If the structure is complex, as in patterned welded steel blades, for example, supplemental information such as X-rays will be available to reveal the internal pattern. (13) Presence of intercrystalline or transcrystalline cracks in samples. (14) Indications of thickening of grain boundaries. (15) Presence of precipitation in second phase at grain boundaries (discontinuous precipitation) or precipitation within grains (as in the case of Widmanstatten precipitation). (16) Evidence of martensitic transformation or heat treatment used in manufacturing process.

There may, of course, be other important structural details, but this short list covers most of the features that can be seen with a metallographic microscope. Care should be taken not to confuse the notes made on specimens under different polishing or engraving conditions because afterwards it can be very difficult to reproduce the exact surface examined [9].

Also, if careful notes on the sample number are not kept, it can be very difficult to establish which sample was examined. The same care must be applied to filing photomicrographs in folders whose names will be the inventory number assigned to the part in question within the metallographic laboratory.

Other Complementary Techniques in Metallographic Studies

Microhardness: Principle

Hardness tests are classified into approximately three types: indentation hardness test, dynamic hardness test, and scratch hardness test.

The indentation hardness test is the most commonly used today. This test penetrates the surface of the tested part with permanent deformation using a diamond-tip indenter or other rigid body and determines the hardness of the tested part based on the load used to generate the deformation and the dimensions of the generated deformation. The commonly used methods are Vickers hardness, Rockwell, and Brinell.

The dynamic hardness test gives the tested part an impact from an indented made of hard material (hammer) and determines the hardness of the test part based on resistance to deformation or rebound of the hammer.

The scratch hardness test is the most traditional. This test determines the hardness of the test piece based on a zero value proposed by another piece or a rigid needle.

Vickers Hardness

A microdurometer uses the indentation hardness method. It has the following types of loads: 5 g, 10 g, 15 g, 25 g, 50 g, 100 g, 200 g, 300 g, 500 g, 1000 g, and 2000 g.

The microdurometer, which is a laboratory equipment, the indenter or penetrator for measuring Vickers microhardness (it is a diamond point in the shape of a straight pyramid with a square base that has an angle between opposite faces at the vertex of 136°); the Knoop hardness indenter (it is a straight pyramid-shaped diamond point with a rhombic base that has vertex angles between two opposite edges of the first 172° 30′ and the second 130°), the Brinell hardness indenter (it is a 10-mm diameter hard dial).

In a Vickers microhardness test, the hardness test is carried out with loads not exceeding 1 kg (1000 g). Most microdurometers are from 100 to 500 g. Hardness is endurance that opposes the plastic deformation of a material, the resistance that materials have to penetration by harder materials. The penetration is carried out with a square diamond pyramid. The opposite faces of the pyramid form an angle of 136°, as the depth of the indentation is obtuse (Fig. 6.18b).

Analysis of Microhardness Measurement

The Vickers hardness (HV) is defined by the load ratio P between the indentation surface S for which the diagonal L is used (Eq. 6.1).

$$\mathrm{HV} = 1854\left(\frac{P}{d^2}\right) \tag{6.1}$$

Description of Microdurometer

The microhardness tester consists of a Vickers diamond-tipped hardness indenter, that is, with a square pyramid. The loads that this machine has range from 10 g to 1000 g. When the Start key is pressed, the indenter lowers and marks the surface of the sample. Later, the diagonals (d_1, d_2) (Fig. 6.18a) are measured and in a table already tabulated with the weight used and the measurements we know the Vickers microhardness (HV), which can also be calculated and would give the same value. It is a simple equipment, if the steps are followed correctly (Figs. 6.18a, b and 6.19).

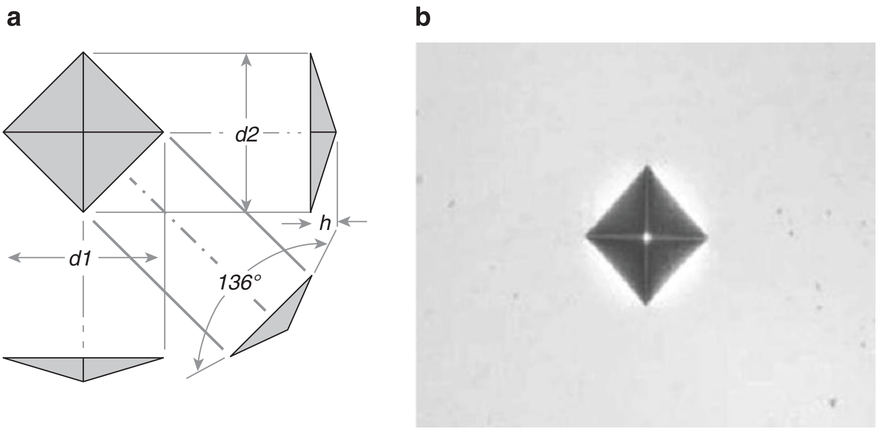


Fig. 6.18 (**a**) Vickers penetrator d_1 and d_2 = indentation diagonals. (**b**) Typical indentation

Fig. 6.19 Microdurometer

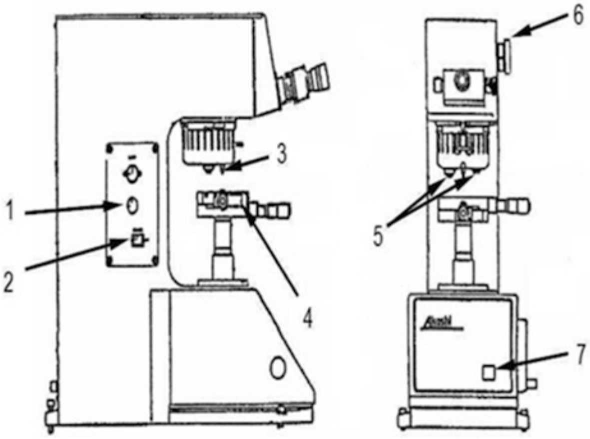


Fig. 6.20 Parts of a microdurometer. (1) Time regulator. (2) Switch. (3) Penetrator. (4) Jaw. (5) Objectives. (6) Load selector (7) Start Button and red light

Constituent Parts of Microdurometer (Fig. 6.20)

Experimental Process of Microhardness Measurement

1. Turn on microdurometer.
2. Set load at 200 g. A small load is chosen to occupy the minimum surface and thus enable measuring the hardness near the fracture.
3. Place sample in clamp.
4. Focus on sample.

5. Change magnification for measurement magnification. Focus on specimen at this magnification.
6. Change indenter magnification.
7. Start penetration with 200 g and about 15 s. The microdurometer stops warning only when the red light goes out. Do not handle equipment while charging.
8. Change to measurement magnification and measure diagonals.
9. Find diagonals in table; with each load, the average is calculated, yielding the material's Vickers hardness.
10. Repeat until 10 indentations are obtained. The first three indentations are considered. Approximately 1.5 times the diagonal of an indentation must be left between indentations so that the measured surface is not affected by the previous indentation.
11. Subject specimens to cavitation and, consequently, to fatigue, plot Vickers hardness values obtained as a function of the distance traveled in the measurements [10].

Figure 6.21 shows an image of the bench durometer that works with higher loads and is used in larger pieces. The Rockwell hardness or Rockwell hardness test is a method to determine hardness, that is, the resistance of a material to penetration.

The Rockwell hardness test is the most widely used method to measure hardness because it is very simple to conduct and does not require special knowledge. Different scales can be used that are based on the use of different combinations of penetrators and fillers, which allows practically any metal or alloy to be tested.

There are two types of penetrators: 1/16-, 1/8-, 1/4-, and 1/2-inch hardened (tempered and polished) steel spherical balls, and a 120° ± 30′ angle diamond taper penetrator and rounded vertex forming a spherical cap of radius 0.20 mm (Brale), which is used for the hardest materials. The test consists in arranging a material with

Fig. 6.21 Bench durometer for Rockwell hardness

a flat surface at the base of the machine. A preload of less than 10 kg is applied, basically to eliminate elastic deformation and obtain a much more precise result. Then a force ranging from 60 to 150 kgf is applied to it for compression for about 15 s. The load is removed, and, using a Rockwell durometer, the hardness value is obtained directly on screen, which varies proportionally with the type of material used. To avoid very large errors, the thickness of the specimen of the material in question must be at least ten times the depth of the tread. Values below 20 and above 100 are usually very imprecise and should be scaled. The change of scale is defined in guidelines since the analysis of copper will differs from an analysis of steel. These tables provide information about which scale to use so as not to damage the machine or indenter being used, which is usually expensive [11].

Rockwell hardness
HRA: Scale A, weight 60 kg, diamond cone.
HRB: Scale B, weight 100 kg, 1/16″ diameter steel ball.
HRC: Scale C, weight 150 kg, diamond cone.

Acknowledgements I wish to express my gratitude to engineer Miguel Ángel Franetovich (Metallurgy Laboratory Director at UTN FRM with completed mandate) for having confidence in me and letting me grow in the archaeometallurgy field and reverse engineering. In addition, I thank the research interns Franco Foti Valles (2018) and Matías “rabbit” Yañez (2017).

References

1. Metallography and Welding, vol 3, Student Notes, UTNFRM (1960)
2. Kehl, G.: F. D. T. Foundations of Metallographic Practice. Aguilar, Madrid (1954)
3. Bénard, J., Michael, A., Philibert, J., Talbot, J.: General Metallurgy. Editorial Hispano Europea, Spain (1973)
4. Scott, D.: Metallography and Microstructure of Ancient and Historic Metals. The Getty Conservation Institute, Los Angeles (1991)
5. Student Notes Volume 3, UTNFRM: op. cit. (1960)
6. Guliaev, A.: Metallography, vol. 1. Editorial MIR, Moscow (1978)
7. ASM Metals Handbook, vol. 9. ASM International, USA (2009)
8. Brooks, C.: Failure Analysis of Engineering Materials. University of Tennessee, Knoxville (1993)
9. Scott, D., Schwab, R.: Metallography in Archaeology and Art, Cultural Heritage Science. Springer, Switzerland (2019)
10. Instruction Manual of Akashi MKV-HO Brand Microdurometer. Laboratory Metallurgy, UTNFRM (2014)
11. Coca, P., Rosique, J.: Knowledge, Testing and Treatment of Materials. Cosmos Editions (1962)

Chapter 7
Corrosion on Ancient Metals

Cecilia Deyá and Patricia Silvana Carrizo

Corrosion: A Bit of History

The spontaneous destruction of metals in contact with the environment started as human concern when humanity began to use metals in everyday life. However, there is no clear record of where and by whom this phenomenon was described as corrosion for the first time. Robert Boyle in 'The works of the Honorable Epitomized' in 1675 described the process between a metal and the environment as corrosion:

$$\text{Metal} + \text{Environment} \rightarrow \text{Corrosion}$$

It was Michael Faraday who gave the relation between electric current and a chemical reaction and Ulick R. Evans, Hoar, Bannister, Thornhill, Agar, Mears and Brown showed that Faraday's law can be applied to the corrosion of metals [1].

In 1889, Walther H. Nernst suggested that the degradation of the metal involves the reaction

$$\text{M} \rightarrow \text{M}^{n+} + \text{ne}^{-}$$

and Pissarzevski, Brodsky and Izgarishev suggested that water molecules are involved in the dissolution of metals. Also, Nernst in 1900 gave the relation between the activity (concentration, $[M^{n+}]$) of the metal ions and the electromotive force (potential, E)

C. Deyá
CIDEPINT-CONICET, La Plata, Buenos Aires, Argentina
e-mail: c.deya@cidepint.ing.unlp.edu.ar

P. S. Carrizo (✉)
Archaeometallurgy Area/Metallurgy Laboratory, National Technological University, Mendoza, Argentina

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_7

$$E = E^0 - \frac{RT}{nF} \ln \left[M^{n+} \right]$$

being T the temperature (in Kelvin), R the gases constant ($R = 8.31$ J/kmol), n the number of electron moles involved, F the Faraday constant ($F = 96500$C) and E^0 the standard corrosion potential, which is the value of E at $T = 273$ K, $[M^{n+}] = 1$ M.

In 1905, Julius Tafel confirmed experimentally the relation between the potential and the velocity of the reaction given by John Butler and Max Volmer [1].

In 1938, Wagner and Traut developed the mixed-potential theory that interprets the corrosion process as a superposition of electrochemical partial reactions [1, 2]: one that generates electrons and the other that consumes these electrons. The key point of the theory postulates that cathodic (reduction, reaction that generates the electrons) and anodic (oxidation, reaction that consumes the electrons) partial reactions occur at the phase boundary metal/electrolyte in constant change with random distribution of location and time of the individual reactions [2].

The main anodic reaction is:

$$M \rightarrow M^{n+} + ne^-$$

that involves the dissolution of the metal while the most common cathodic reactions are

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$2H^+ + 2e^- \rightarrow H_2$$

oxygen and proton reductions, respectively.

Corrosion was defined by Revie and Uhlig as the destructive attack of a metal by chemical or electrochemical reaction with its environment [3] and Hoar defined corrosion as ‘the reaction of a solid or liquid metal with a non-metallic environment’, involving not only the degradation of the metal [4]. Fontana defined corrosion as the destruction or deterioration of a material because of reaction with its environment [5] and Shreir considers also that non-metallic materials can corrode, as they are deteriorated from chemical causes [6]. On the other hand, the degradation of metals when water is involved is considered as ‘wet corrosion’ but there is a ‘dry corrosion’ when metals degrade in contact with oxygen, halogens, hydrogen sulphide, sulphur vapour etc. A characteristic of ‘dry corrosion’ is that the initial oxidation of the metal, the reduction of the nonmetal and the formation of the compound occur at one and the same place at the metal–nonmetal interface [6].

So, taking these into account, two definitions of corrosion can be given: as the reaction of a material with its environment and as the reaction of an engineering constructional metal (material) with its environment with a consequent deterioration in properties of the metal [6].

In order to study corrosion of different metals, several classifications of the forms of corrosion were given by Fontana [5], Shreir [6] and Bardal [7] (Fig. 7.1).

Fig. 7.1 Uniform corrosion in steel structures of FFCC N°2 Railroad, Luján de Cuyo, Mendoza, Argentina

Types of Corrosion

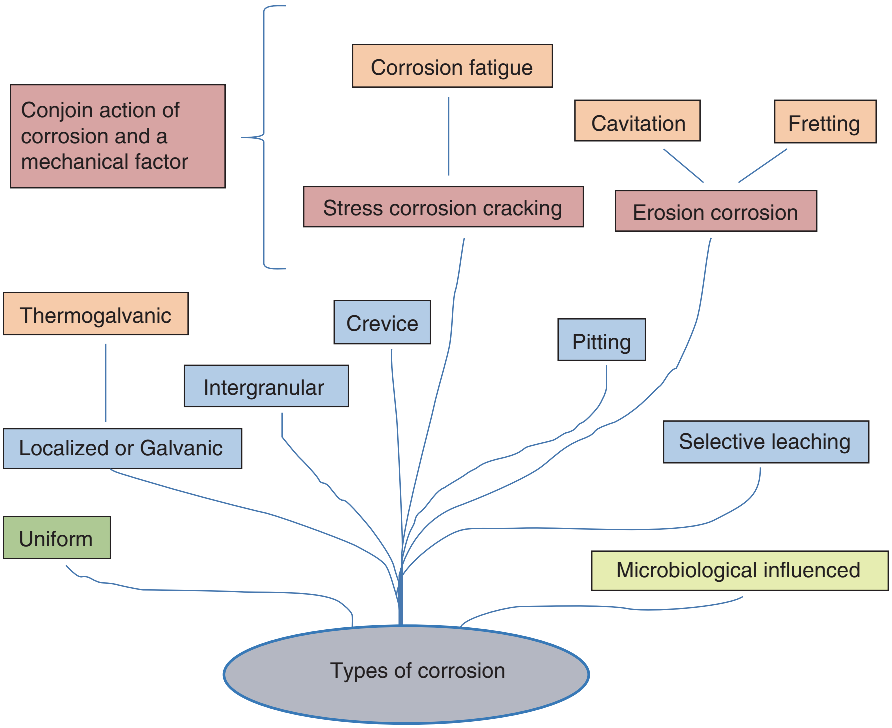
The most used classification of the corrosion process, done by Mars G. Fontana and Norbert. D. Greene, is due on the appearance of the corroded surface.

Uniform or General Corrosion

Takes place when the electrochemical corrosion is the only deterioration mechanism; anodic and cathodic reactions take place all over the electrode surface, but not simultaneously at the same place, and there are no significant macroscopic concentration differences in the electrolyte along the metal surface, and the metal is fairly homogeneous [7].

Steel and copper alloys are more vulnerable to general corrosion than other alloys. Uniform corrosion often results from atmospheric exposure (polluted industrial environments); exposure in fresh, brackish and salt waters; or exposure in soils and chemicals. The rusting of steel, the green patina on copper, tarnishing silver and white rust on zinc on atmospheric exposure are due to uniform corrosion [8]. Figure 7.1 shows general corrosion in a steel structure of a railroad bridge.

When corrosion occurs under different conditions than the mentioned above, the following forms can be defined:



Scheme 7.1 Types of corrosion

- Galvanic (two-metal) corrosion.
- Crevice corrosion (including deposit corrosion).
- Pitting corrosion.
- Selective attack, selective leaching (de-alloying).
- Intergranular corrosion (including exfoliation).
- Erosion corrosion.
- Stress corrosion cracking.

Bardal included four more types, particular cases of the abovementioned: thermogalvanic, cavitation, fretting and corrosion fatigue [7] (Scheme 7.1).

Galvanic Corrosion

When a metallic and electrolytic contact is made between a more noble metal and a less noble one, the corrosion rate will increase on the latter and decrease on the former. Galvanic corrosion, also known as dissimilar metallic corrosion or bimetallic corrosion, also appeared when a metal or alloy is electrically coupled to a conducting non-metal in the same electrolyte, as a galvanic cell is created [7]. The corrosion potential and current of the galvanic cell depend on the properties of the electrolyte and polarization characteristics of anodic and cathodic reactions [8].

The standard corrosion potential can give an idea of the possibility of galvanic corrosion but the environment in which the metal is immersed is not considered in these values. To solve this problem galvanic charts are used, in which the metal (pure or allied) and the environment are taken into account [7]. However, both charts are thermodynamic so no information about the corrosion rate is given and inversion of the potentials can occur due to the passivation of one of the metals in some environments.

Galvanic corrosion is one of the major corrosion problems of aluminium and aluminium alloys, particularly when aluminium or its alloys are exposed in waters containing chlorides or other aggressive species [7]. Cast iron corrodes because of exposure of its graphite phase to the surface (graphitic corrosion), which is cathodic to both low-alloy and mild steels [8].

Thermogalvanic (Bardal [7])

Thermogalvanic corrosion may occur when a galvanic difference arises in a metal under a temperature gradient in a corrosive environment. Usually, the hot area of the metal is the anode while its cold area is the cathode due the anodic properties of the material depend on the temperature. Besides, the properties of the environment along the metal surface will also vary [7].

Crevice Corrosion

This is a type of localized corrosion concentrated in crevices in which the gap is sufficiently wide for liquid to penetrate into the crevice and sufficiently narrow for the liquid in the crevice to be stagnant. This is most frequently observed in environments containing chlorides, but can also occur in other salt solutions [7]. An important factor is the formation of oxygen concentration cells due to a difference in O_2 concentration inside and outside the crevice. Inside the crevice, the amount of O_2 is much lower than outside (where O_2 can easily reach the metal), generating anodic inside and cathodic outside areas. As the area inside the crevice surface (anode) is often smaller than the outer surface (cathode), a large corrosion current is concentrated on the anode, so corrosion rate is very high inside the crevice [7].

Crevice corrosion is affected by several factors, metallurgical, environmental, electrochemical, surface physical, geometrical nature, but one of the most important factors is the crevice gap [7]. Various metals, for example, Al, Fe, Cr and Ni, may suffer from crevice corrosion [7].

Pitting

Pitting corrosion is one of the most serious types of corrosion. It starts at the defects in the passive (protective) film of a metal (thinning, rupture, scratch, pore etc.) when the defect cannot be healed. In these circumstances the pit is anodic in relation to the remainder surface and leads to the dissolution of metal. Once the process of dissolution starts, the dissolution is generally autocatalytic [8]. Although in appearance pitting corrosion may seem unimportant, the depth of the pit and pit propagation rate are extremely dangerous [8].

Pitting corrosion is often a concern in applications involving passivating metals and alloys in aggressive environments (containing chloride, bromide, iodide, perchlorate ions) [8]. Figure 7.2 shows a pit on steel protected with a passive film. Copper and copper alloys may pit in fresh water, particularly at temperatures above 60 °C and pH lower than 7.4, and where the ratio between sulphate and carbonate contents in the water is relatively high [7].

Selected Attack

This form of corrosion is observed in alloys in which one element is clearly less noble than the other(s). The corrosion mechanism implies that the less noble element is removed from the material leaving it porous. Regions that are selectively corroded are sometimes covered with corrosion products or other deposits, so the attack may be difficult to see [7].

In the dezincification of brass, zinc is selectively removed from the alloy and copper remains [7]. Other examples are the destannification of bronze (tin is selectively removed) [9] and the graphitization of grey cast iron, where the iron is corroded away and graphite is left on the surface [7].

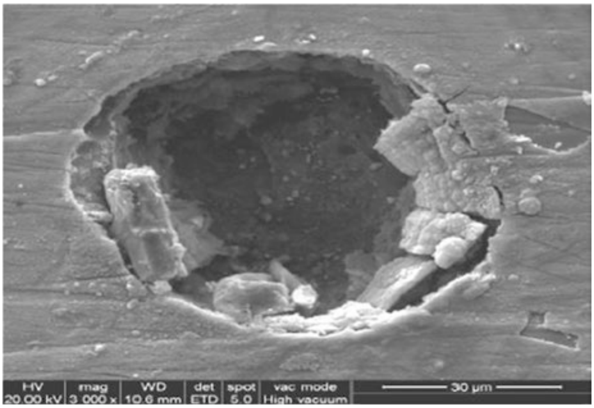


Fig. 7.2 SEM micrograph of a pit formed on steel panels protected by a passive film, immersed in NaCl

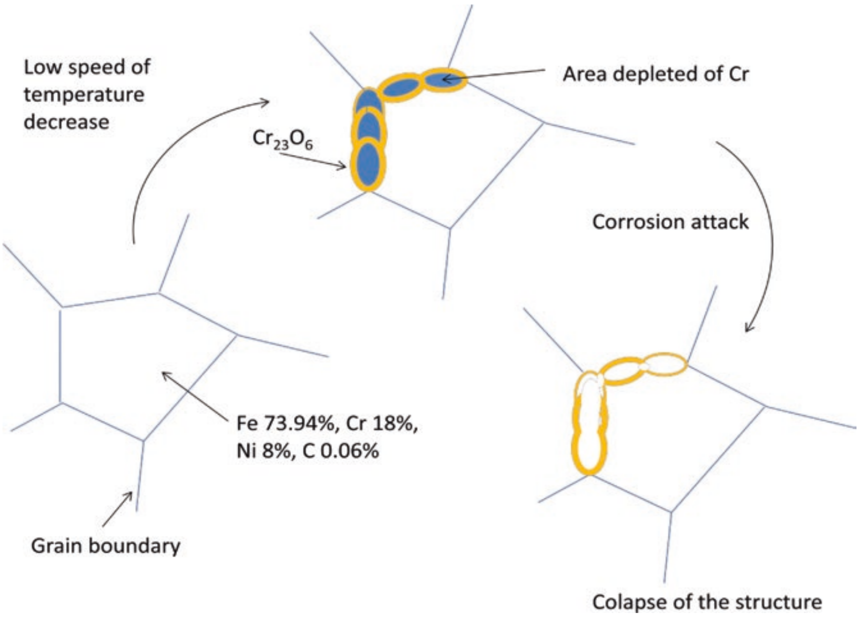
Intergranular Corrosion

Intergranular corrosion is localized attack on or at grain boundaries (anode) with insignificant corrosion on other parts of the surface (cathode). The ratio between the cathode and the anode areas is very large, and the corrosion intensity can therefore be high [7]. It is a dangerous form of corrosion because the cohesive forces between the grains may be too small to withstand tensile stresses; the toughness of the material is seriously reduced at a relatively early stage, and fracture can occur [7].

The different concentrations can be due to the precipitation, in the boundaries, of compounds rich in alloying elements that are essential for corrosion resistance. This precipitation can occur at high temperatures (during production, fabrication, welding) and the regions adjacent to the grain boundary will be depleted of the alloying resistant elements [7, 8].

Intergranular corrosion occurs in stainless steels (smaller amounts of Cr in the grain boundaries) and alloys based on nickel, aluminium, magnesium, copper and cast zinc [7] (Scheme 7.2).

Erosion-corrosion and stress corrosion cracking are caused by the joint action of corrosion and a mechanical factor. Bardal included in this section fretting corrosion and corrosion fatigue [7].



Scheme 7.2 Intergranular corrosion due to $Cr_{23}O_6$ formation in stainless steel grain limits

Erosion–Corrosion

Erosion–corrosion occurs when there is a relative movement between a corrosive fluid and a metallic material immersed in it and the material surface is exposed to mechanical wear effects leading to increased corrosion. The deposits of corrosion products are worn off, dissolved or prevented from being formed, so that the metal surface becomes active. Most sensitive materials are those normally protected by corrosion products with inferior strength and adhesion to the substrate, for example, lead, copper and its alloys, steel.

Examples of erosion–corrosion are cooper alloys exposed to a fluid in motion. Copper alloys are protected reasonably well by surface oxides and hydroxides at lower velocities of fluid but when the velocity exceeds a critical value, the protective layers are dissolved and the alloy will suffered corrosion [7].

Cavitation (Bardal [7])

This corrosion form is closely related to erosion corrosion, but the appearance of the attack differs as the attack in this case consists in deep pits perpendicularly to the surface, localized close to each other, making a rough, spongy surface [7]. When vapour bubbles (formed in low-pressures zones) collapse close to the metal surface cause a concentrated and intense impact against the metal. This impact induces high local stress and possibly local plastic deformation, removing parts of the protecting film, leaving the metal active [7].

Fretting Corrosion (Bardal [7])

Fretting wear occurs at the interface between two closely fitting components when they are subject to repeated slight relative motion (slip). The exact mechanism of combined fretting and oxidation is not fully understood but one of the mechanisms proposed is that the relative motion between the parts may promote oxidation of the surface, the oxide film is partly worn off, fresh metal surface, highly active is left and oxidizes again [7].

Stress Corrosion Cracking

Stress corrosion cracking can be defined as crack formation due to simultaneous effects of static tensile stresses and corrosion. The tensile stresses may be internal stresses induced by cold working, welding or heat treatment or may be originated from external load, centrifugal forces or temperature changes. The cracks are mainly formed in planes normal to the tensile stresses, and propagate more or less branched. If they are not detected in time, they will cause fracture of the piece [7].

Corrosion Fatigue (Bardal [7])

Corrosion fatigue is crack formation due to varying tensile stresses combined with corrosion. The difference between stress corrosion cracking and corrosion fatigue is that the last one develops under varying stresses while the first one is under static stresses. Alternatively, corrosion fatigue may be defined as fatigue stimulated and accelerated by corrosion.

Microbiological-Induced Corrosion

Biofilm consists of microorganisms held together with excreted slime. Its formation occurs in four stages: (1) bacterial attachment to the surface, (2) micro-colony formation, (3) early development and maturation of the biofilm and (4) dispersion of cells into the surrounding environment. The members that constitute the biofilm become integral to the survival of the biofilm since they secrete extracellular enzymes to digest external substrata as nutrient sources. These exopolysaccharides (EPS) facilitate the attachment of the cells to a surface and are an important component of the biofilm [10]. Amino acids and / or nucleotides present in EPS can bind, chelate, adsorb and complex multivalent cations as well as changing local pH, changing the local environment [11]. When these biofilms are attached to a metallic surface anodic and cathodic reactions can be enhance, enhancing corrosion rate of the metal [12]. Organic acid, secrete by bacteria and fungi can promote electrochemical oxidation by removing or preventing the formation of the passive layer [12, 13]. Elemental sulphur, metal sulphides, thiosulphates and tetrathionates can be oxidized to sulphuric acid by sulphuric bacteria affecting also the passive film. *Gallionella, Leptothrix and Thiobacillus* spp. can oxidize ferrous ions to ferric ions creating a dense deposit so that in an oxygenated environment the area immediately under the deposit became deprived of oxygen generating differential aeration cells and enhancing corrosion [11, 12, 14].

The main reactions are:

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{+2} + 2\mathrm{e}$$

$$\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} + \mathrm{e} \rightarrow \mathrm{OH}^-$$

$$4\,\mathrm{Fe}^{+2} + \mathrm{O}_2 + 5\mathrm{H}_2\mathrm{O} \rightarrow 4\,\mathrm{Fe}(\mathrm{OH})_3 + 8\,\mathrm{H}^+$$

being the last one carried out by bacteria to obtain energy [14].

Under anaerobic conditions, sulphate-reducing bacteria (SRB) use SO_4^{2-}as electron acceptors to obtain energy [14]. In this case, the reactions are:

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{+2} + 2\mathrm{e}$$

$$\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{H}^+ + \mathrm{OH}^-$$

$$H^{+} + e \rightarrow H$$

$$SO_4^{2-} + 8\ H \rightarrow S^{-2} + 4\ H_2O$$

$$Fe^{+2} + S^{-2} \rightarrow FeS$$

The SRB remove the adsorbed hydrogen from the cathode, by means of their hydrogenase system, depolarizing the reaction and force more iron to be dissolved at the anode [14]. Characteristic corrosion by SRB on metal surfaces results in pitting corrosion [14].

In the case of copper and brass, microorganism that produce ammonia can cause stress corrosion [13].

Corrosion of Selected Metals

Lead

Lead has good resistance to atmospheric corrosion due to the formation of a passive film of α-PbO [15]. Owing to the formation of this film, which composition depends on the atmosphere involved, lead exhibits excellent resistance to air (dry or humid). The presence of gases, such as SO_2, SO_3, H_2S, CO_2, has little effect [15, 16].

$$PbO + 6\ CO_2 + 3\ H_2O \rightarrow \underset{\text{Plumbonacrite}}{6\ PbCO_3 \cdot Pb(OH)_2 .PbO}$$

In distilled water free from gases, corrosion is slight but increased in the presence of oxygen [8, 16]. In natural waters, lead corrosion is slow, due to the presence of carbonates, while in waters containing carbonic acid corrosion occurs due to the conversion of carbonate in the protective film into soluble bicarbonate, $Pb(HCO_3)_2$ [8, 17]. In the case of rain and condensation water, the dissolved CO_2 can react with the lead oxides to form carbonates such as plumbonacrite [15, 16]. Lead usually has excellent resistance to sea-water as the carbonates present forms a protective film [16]. Variations in soil composition can result in important corrosion on lead surfaces. The soils may differ in degree of aeration, water content, presence of various chemicals and bacteria; the worst combination of soils is wet clay and cinders. The carbon in the cinder acts as cathode, and the portion of the lead in contact with clay becomes the anode and corrodes [16]. Soil containing rotting vegetables, containing organic acids and carbon dioxide, corrodes lead (phenol corrosion) [16]. Some corrosive compounds present in the soil are nitrate and chloride ions, alkalis and organic acids while some protective constituents are silicates, sulphates, carbonates, colloids and some organic compounds [17].

Acetic acid and acetates rapidly attack lead. The protective film of lead oxide is very soluble in both, yielding basic salts which become carbonated in the atmosphere to form basic lead carbonate far from the surface so, affords no protection against further attack [8, 16].

$$PbO + 2\ CH_3COOH \rightarrow \underset{\text{Lead acetate}}{Pb\ (CH_3COO)_2} + H_2O$$

Lead acetate acts also as a catalyst as its favours the transformation of environmental CO_2 to lead carbonates such as plumbonacrite, hydrocerussite and cerussite, being plumbonacrite the most stable one [15]:

$$10\ Pb(CH_3COO)_2 + 13\ H_2O + 6\ CO_2 \rightarrow \underset{\text{Plumbonacrite}}{6PbCO_3 \cdot 3Pb\ (OH)_2 \cdot PbO} + 20\ CH_3COOH$$

$$3\ Pb\ (CH_3COO)_2 + 4\ H_2O + 2\ CO_2 \rightarrow \underset{\text{Hydrocerussite}}{2PbCO_3 \cdot Pb\ (OH)_2} + 6\ CH_3COOH$$

$$3\left[6PbCO_3 \cdot 3Pb\ (OH)_2 \cdot PbO\right] + 2\ CO_2 + H_2O \rightarrow 10\left[2PbCO_3 \cdot Pb\ (OH)_2\right]$$

$$2PbCO_3 \cdot Pb(OH)_2 + CO_2 \rightarrow \underset{\text{Cerussite}}{3\ PbCO_3} + H_2O$$

Lead is resistant to oxalic, tartaric and fatty acids only in the absence of oxygen [15]. Formic acid in the presence of oxygen corrodes lead rapidly [16].

Cases of several corrosion due to the attack of organic acids to lead and lead alloys are presented in several organs in many European churches (Fig. 7.3) as the pipes are attack by the acids (acetic and/or formic acid) from the wood of the building [18, 19].

Fig. 7.3 Corroded lead made organ pipe after about 15 years on the wooden support in the organ of Madonna delleLaste Sanctuary (Trento, Italy)

Copper

Copper possesses good corrosion resistance primarily because it is relatively immune. The potential range where the material is active in aqueous solutions is so high that reduction of hydrogen ions is not a possible cathodic reaction. Therefore, copper is immune for example in oxygen-free acid solutions, except if some other oxidizer is present [7]. Copper also has a high degree of resistance to atmospheric corrosion because a protective layer of corrosion products is developed. This layer is called *patina* by Gilbert [20] and FitzGerald et al. [21], while Piccardo et al. [22] considered a difference between the natural corrosion products and the artificial artistic products which they named 'patina'.

The nature of the corrosion products formed on copper exposed to the atmosphere depends on the environmental conditions, on the age of the deposits and on sheltered conditions [20, 23, 24]. The compounds in the patina have been identified as cuprite (Cu_2O), in the inner layer; brochantite, $CuSO_4{\cdot}3Cu(OH)_6$, $Cu_4SO_4(OH)_6{\cdot}H_2O$ (posnjakite), and antlerite $Cu_3SO_4(OH)_4$. In some cases, small quantities of basic carbonate, $CuCO_3{\cdot}Cu(OH)_2$ (malachite) and, near the sea, basic chloride atacamite and some polymorphs such as paratacamite and botallackite, $CuCl_2{\cdot}3Cu(OH)_2$ and nantokite (CuCl) can be present [8, 20, 23–25]. In general, CO_2 concentration is too low for malachite to be stable (except in ground copper pieces); however, some carbonates can be found in patinas [26]. See also, in Chap. 12: Cases Study: 'Conservation of a Historical Coin from 1853 Rescued in the Fortin Villa 25 de Mayo-Mendoza'.

In rural areas, the main component is cuprite [27]. However, many other compounds can take part of the patina formation, as nitrates, organic acids, iron and manganese ions etc., [26, 28]. Reactions that explain the formation of the patina occur in humid atmospheres that converts carbonyl sulphide (COS) in hydrogen sulphide (H_2S), and sulphur dioxide (SO_2) in SO_4^{-2} ions. These compounds will react further on humid copper to form the patina. While the anodic reactions are the oxidation of Cu, the cathodic reaction is the reduction of O_2,

$$Cu \rightarrow Cu^{+} + e^{-}$$

$$Cu^{+} \rightarrow Cu^{2+} + e^{-}$$

$$O_2 + 2H^{+} + 2e^{-} \rightarrow 2OH^{-}$$

and OH^- will be present in many of the patina compounds.

Some of the possible reactions are [26, 28]:

$$H_2S + 2\,Cu^{+} \rightarrow \underset{\text{Chalcocite}}{Cu_2S} + 2\,H^{+}$$

$$SO_4^{-2} + 4\,Cu^{2+} + 8\,H_2O \rightarrow \underset{\text{Posnjakite}}{Cu_4\left(SO_4\right)\left(OH\right)_6 \cdot 2H_2O} + 6H^{+}$$

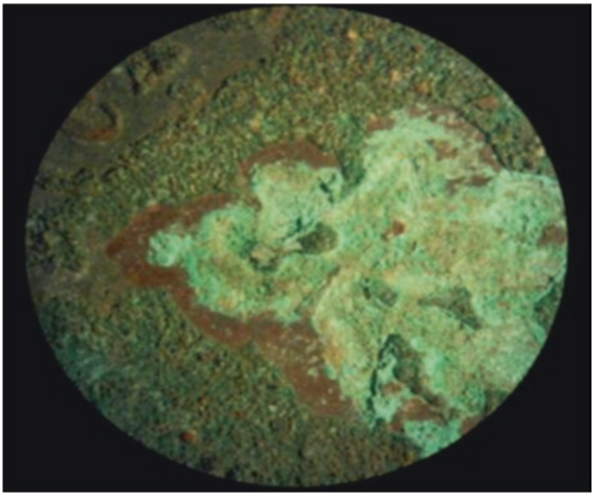


Fig. 7.4 Macroscopic view of the nonporous layer of malachite, $CuCO_3 \cdot Cu(OH)_2$, on the obverse of the historic copper coin belonging to Museum of May 25 Village Fort, San Rafael, Mendoza. Archaeometallurgy Area, Metallurgy Laboratory, (UTN FRM)

$$Cu_4(SO_4)(OH)_6 \cdot 2H_2O \rightarrow \underset{\text{Brochantite}}{Cu_4SO_4(OH)_6} + 2H_2O$$

Other compound that can be formed is antlerite, but in more acidic conditions than brochantite [29] (Fig. 7.4).

When the marine coasts are polluted, mixtures of sulphate and chloride compounds are present. The first species to form as corrosion products are basic chlorides rather than basic sulphates; with longer exposure time, basic chloride and basic sulphates, coexist [25, 27].

As the different copper compounds has different colours, depending on the patina compositions is its predominant colour and it varies from bluish-green to dark brown to black (Table 7.1) [27, 30, 31].

In sea water immersion conditions and in the splash region, the patina is entirely composed of paratacamite, formed on a Cu_2O layer adhered to the metal surface [25]. The composition may change to calcium carbonates compounds ($CaCO_3$, aragonite and calcite) as time elapsed due to a layer of fouling growth on the copper surface [25].

When water speeds are low and deposits settle on the surface (particularly at water speeds below about 1 m/s), pitting of copper and copper alloys is liable to occur by differential aeration effects [20]. This may occur under dead barnacles or shell-fish, while the decomposing organic matter assists the corrosion process [20].

When copper is buried, corrosion is important in rifle peat, cinders and tidal marsh. In the case of some of the alloys, corrosion is particularly severe in the cinders [20].

Table 7.1 Copper corrosion compounds and main environment where they can be found

Compound formula	Compound name	Colour	Main environment
$CuSO_4 \cdot Cu_3(OH)_6$	Brochantite	Bluish	Industrial
$Cu_4SO_4(OH)_6 \cdot H_2O$	Posnjakite	Bluish	Industrial
$Cu_3SO_4(OH)_4$	Antlerite	Greenish	Industrial
$CuCO_3 \cdot Cu(OH)_2$	Malachite	Greenish	In soil
$CuCl_2 \cdot 3Cu(OH)_2$	Atacamite Paratacamite Botallackite	Greenish	Marine
CuCl	Nantokite	Greenish	Marine
Cu_2O	Cuprite	Dark red	Rural
Cu_2S	Chalcocite	Black	Industrial

Table 7.2 Copper common alloys

Alloy	Main compounds
Brass	Cu + 10–45% Zn
Copper–nickel	Cu + 5–30% Ni
Tin-bronzes	Cu + 8–12.5%Sn + 0.020–4% P
Aluminium–bronze	Cu + 5–10% Al
Silicon–bronzes	Cu + 1.5–3% Si + 0.5–1%Mn
Nickel silvers	Cu + 10–30% Ni + 10–30% Zn

Copper alloys (Table 7.2) are sensitive to sulphur-containing species, such as H_2S, and stagnant water conditions as well as high flow velocities [7]. Nickel addition allows handling of increased flow rates in water systems while zinc confers greater resistance to sulphide attack [8]. Corrosion rates of brass and bronze are generally lower compared with copper in low chloride-containing environments. However, while brass has similar corrosion rate at chloride-rich marine conditions, bronze, on the other hand, shows higher corrosion rate in this environment [24].

Brass

Brass is an alloy between copper and zinc. It has 10–45% of Zn. Alloys with less than 35% of Zn are α-brasses, while those with more Zn are α,β-brasses (duplex), see Fig. 7.5a, b the metallography image of a historical brass tack with dezincification process. These alloys have higher tensile strength than pure copper, but they suffered from selective corrosion in some environments [20].

The mechanism of dezincification of brass is not clear yet. Corrosion may occur by a mechanism of selective dissolution of zinc or a mechanism of dissolution of Zn and Cu and the redeposition of Cu [20]. According to Zhou et al., in synthetic tap water, the second mechanism seemed to be occurring [32].

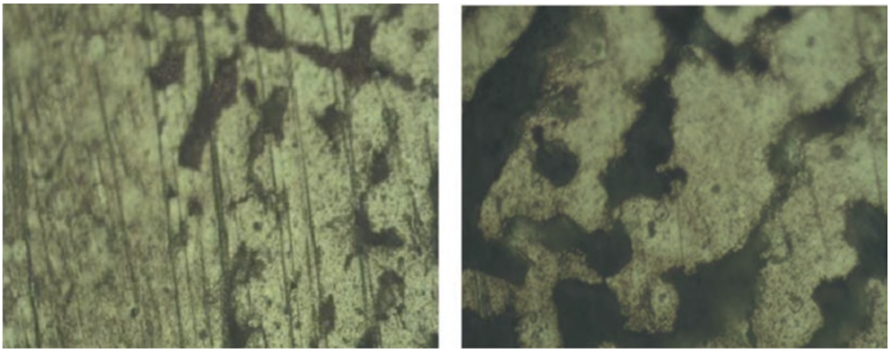


Fig. 7.5 (**a**) Dezincification images of a brass tack ×200. (**b**) ×500 observed by optical metallographic microscope. Archaeometallurgy Area, Metallurgy Laboratory (UTN FRM)

Table 7.3 Chemical composition of a Brass Historical Tack

% Cu	% Al	% Si	% Zn	% Pb	% Fe	% Sn	% Ni	% Zr	% Nb
20.9	2.23	1.67	3.87	0.7	0.29	0.25	0.037	0.025	0.017

Note: The chemical elements of the sample were determined with an XRF portable spectrometer. Archaeometallurgy Area, Metallurgy Lab, (UTNFRM)

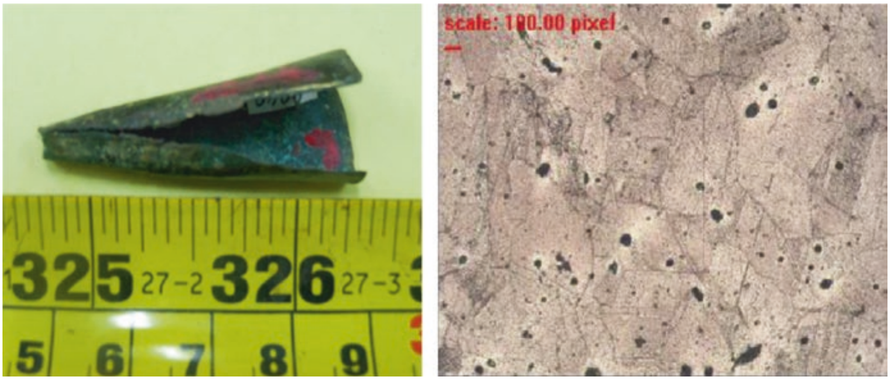


Fig. 7.6 (**a**) Macroscopic image of corrosion process brass cone, Magnification: ×200. (**b**) Microstructure of α-Brass, of the type Brass with Lead (Cu-Zn-Pb). The metallographic structure is very similar to the Copper-Zinc (Cu-Zn) alloy, Lead (Pb) appears as small dark particles at the grain boundaries. Archaeometallurgy Area, Metallurgy Laboratory, (UTN FRM)

However, it is clear that dezincification depends on the phases present in brass [32]; with a single-phase brass, the whole of the metal in the corroded areas is affected and dezincification may proceed fairly uniformly but when the zinc-rich β phase is present (See Table 7.3, Figs. 7.6 and 7.7), dezincification will occur preferentially in this phase [20] (Tables 7.4 and 7.5).

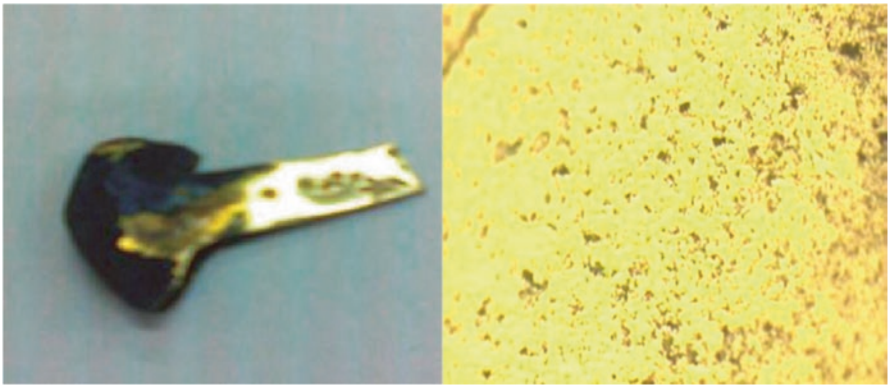


Fig. 7.7 (**a**) Macroscopic observation of bluish corrosive damage on historical brass clamp. Brochantite or Posnjakite patinas ($CuSO_3Cu\,(OH)_6$ or $Cu_4SO_4(OH)_6{\cdot}H_2O$). (**b**) Clean brass structure with 0.05% oxygen. Reagent: Copper Chloride 1 M (×100). Archaeometallurgy Area, Metallurgy Lab, (UTN FRM)

Table 7.4 Chemical composition of a Historical *Mapuche* Cone Brass

% Cu	% P	% Si	% Zn	% Pb	% Fe	% Sn	% Ni	% S
66.6	0.39	2.92	26.2	2.6	0.59	0.12	0.040	0.43

Note: The chemical elements of the sample were determined with an XRF portable spectrometer. Archaeometallurgy Area, Metallurgy Laboratory, (UTNFRM)

Table 7.5 Chemical composition of a Historical Clamp Brass

% Cu	% Al	% Si	%Zn	% Pb	%Mn	% Co	% Nb	% Zr	% Cr	% Ti	% Y
33.6	1.29	0.48	15	0.11	0.019	0.010	0.033	0.013	0.012	1.90	0.037

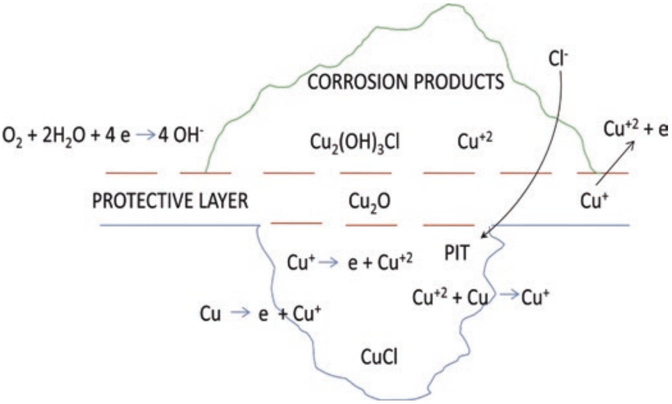
Note: The chemical elements of the sample were determined with an XRF portable spectrometer. Archaeometallurgy Area, Metallurgy Lab, (UTNFRM)

Bronze

In the case of bronze, it can also suffer destannification as well as decuprification. Destannification is the selective removal of tin from a tin bronze leaving residual copper, while decuprification is copper selective dissolution from the alloy [9, 33]. Robbiola et al. [34] joined the study of these removals in the study of bronze corrosion. The corrosion products were classified as:

Type I: A bilayer structure containing low copper and high amounts of tin together with soil elements within the outer layer and oxides or hydroxides within the internal layer. These layers have grown up without volume change and have corrosion resistance properties [34].

Type II: A three-layer structure containing an external altered zone of green Cu(II) compounds, a red layer of cuprous oxide, often disrupted or fragmented and an



Scheme 7.3 Bronze disease

internal layer with different possible colours (yellow, orange, brown), with lower copper amounts and relatively higher tin contents than in the alloy, associated also with soil elements, mainly O and Cl. The composition of this internal layer depends on the environment, as a function of the severeness of the attack [34].

Both types are due to an initial dissolution of the alloy which leads to the formation of passive blocking or non-passive surface layers, a propagation step controlled by mass transportation through the deposits leading to a steady state (the corrosion rate decreases with time down to values close to zero), and a possible corrosion resumptions in order to take into account the deviations to the basic structures [34].

A pitting corrosion present in bronze is the bronze disease, a process of interaction of chloride-containing species within the bronze patina with moisture and air, often accompanied by corrosion of the copper alloy itself [35, 36]. The products of the reaction are light green, powdery, voluminous basic chlorides of copper, which disrupt the surface and may disfigure the object [36].

Bronze disease occurs due to chloride presence between the cuprite protective layer and the metal (Scheme 7.3).

In the presence of O_2, Cu is oxidized to Cu_2O such as:

$$4\,Cu + O_2 \rightarrow 2\,Cu_2O$$

and a protective film is formed. However, in the presence of chloride:

$$Cu + Cl^{-} \rightarrow CuCl + e-$$

and

$$2\,CuCl + H_2O \rightarrow Cu_2O + 2H^{+} + 2Cl^{-}$$

occur, forming chloride ions readily to react with Cu. Besides,

Fig. 7.8 Protect film of Cu_2O on the Historical Bronze Bell from (1884) belonging to San Carlos Fort Museum, Mendoza, Border Archaeometallurgy Project

$$Cu^{+} \rightarrow Cu^{2+} + e-$$

which in turn attacks copper metal to form more cuprous ions [35].

$$Cu^{2+} + Cu \rightarrow 2Cu^{+}$$

This reaction is cyclic and occurs below the Cu_2O film, forming a pit on the metal that can destroy the piece (Fig. 7.8a, b). This destruction is mainly due to a small anodic area (inside the pit) with a high dissolution rate and a huge cathodic area (protective metal) with a much lower reaction rate.

Cast Iron

Casts Iron are Iron-Carbon (Fe-C) alloys with a Carbon (C) concentration greater than 1.7%. Besides constituent Carbon (C) they contain: Silicon (Si), Manganese (Mn), Sulphur (S) and Phosphorus (P), the latter are considered impurities. The relative amounts of Silicon (Si) and Manganese (Mn) influence the properties of the cast iron (See Figs. 7.9 and 7.10). A general classification of cast iron can be seen in Table 7.4.

There are two fundamental types of cast iron. The *white cast iron*, where all the carbon is combined in the form of cementite (Fe_3C intermetallic compound of high hardness) and the *grey cast iron* in which part of the carbon is in free form: as graphite. The first, that is, the white cast iron is obtained by rapid cooling and Manganese catalyst. The second, that is, the grey cast iron is obtained by slow speed. It is suggested to see in the Chap. 12: Cases Study: ‘Archeometallurgical and Historical Study of Metallic Defense Elements Belonging to the San Carlos Fort Musseum in the Uco Valley, Mendoza, Argentina’. Gray cast iron are the most used industrially,

Fig. 7.9 French cast-iron cannon belonging to San Carlos Fort Museum, Mendoza, Border Archaeometallurgy Project

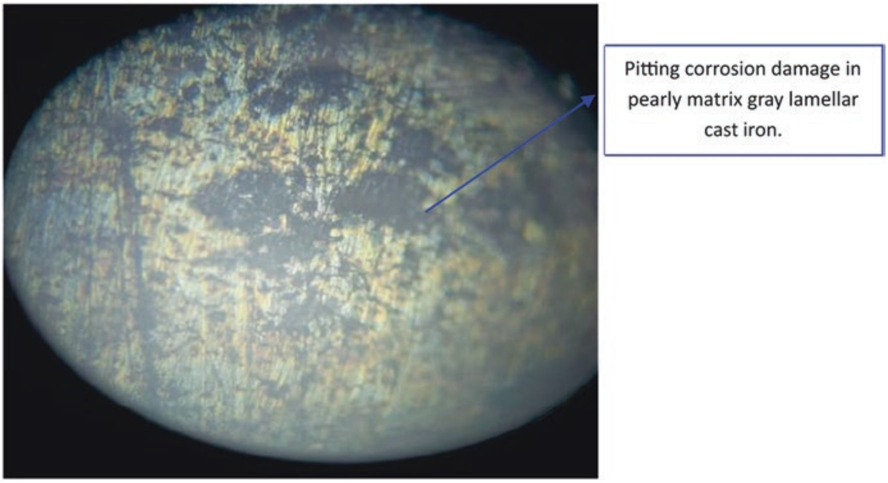


Fig. 7.10 Metallography of the grey lamellar cast iron corresponding to the historical canyon of the previous image. Archaeometallurgy Area, Metallurgy Laboratory, (UTN FRM)

its formation is catalysed with the presence of greater amounts of Silicon (±2%) and with slow cooling.

The typical composition for obtaining a graphite microstructure is 2.5–4% carbon and 1–3% silicon. Silicon (Si) plays an important role in differentiating grey cast iron from white cast iron; this is because Silicon (Si) is a graphite stabilizer. This means that it helps precipitate graphite from iron carbides (Fe_3C) [37] (Table 7.6).

Another important factor that helps the formation of graphite is the speed of solidification of the laundry:

Table 7.6 Characteristics of some cast iron alloys

Cast iron alloy	Carbon microstructure	Matrix	Main characteristic
White	Carbide	Perlite	Brittle, hard
White	Carbide Graphite flakes	Perlite, ferrite or a mixture of both	Brittle, machinability
Ductile or nodular	Graphite nodular or spheroids		
High silicon			Resistance to corrosion, hard, brittle
Malleable	Graphite spheres	Perlite or ferrite	Ductility
Ductile	Graphite nodular	Ferrite	Hot workability, strength

- Slow speed will tend to produce more graphite and a ferritic matrix.
- Moderate speed will tend to produce a greater pearlitic matrix.
- To achieve a 100% ferritic matrix, the cast iron must be subjected to an annealing heat treatment.
- Rapid cooling will partially or totally suppress the formation of graphite and will instead help the formation of cementite, which is known as white cast iron.

Many properties of cast iron are first influenced by the form in which the carbon is present (graphite or carbide) and secondly by whether the matrix material is ferritic or perlitic.

Cast iron without external protection resists concentrated sulphuric acid (>70%) fairly well at room temperature under stagnant conditions [7].

However, hot acid may attack grey cast iron along graphite flakes and cause cracking [7]. High silicon cast iron (Si > 14%) resists corrosion except in contact with hydrofluoric acid [7].

Graphitic corrosion has been observed on buried pipelines after many years of service in grey cast iron. Grey cast iron has a continuous graphite network microstructure that is cathodic to iron and remains as a weak, porous network when iron is selectively removed from the alloy [8]. These type of corrosion occurs when the soil are corrosive or very corrosive, with resistivity in the range of 820–4200 Ωcm [8].

Wrought Iron

Wrought Iron is a material whose microstructure consists of inclusions of silicate slag, sulphates and even phosphates embedded in a matrix that can vary from being totally ferritic to the inclusion of large amounts of perlite, often distributed in a very heterogeneous way. Slag inclusions are usually lengthened in the working direction by the hot forging processes that are used to process the molten material and shape the wrought iron objects [38].

Wrought Iron, also called laminate, has been produced in many countries of the world during a period of time that goes from the Iron Age (second millennium BC) until well into the twentieth century. It was initially produced by two clearly different technologies: direct fusion in Blommery furnace and alternative indirect fusion [39]. (See in Chap. 12: Cases Study: 'Archeometallurgical and Heritage Study on the Iron Bridge over Mendoza River'). Wrought iron is an iron alloy with very low carbon content in contrast to molten iron, and has fibrous inclusions, known as slag. It is resistant, malleable, ductile and easy to weld. Historically known as 'commercially pure iron'; however, it actually no longer qualifies because current commercially pure standards require a carbon content of less than 0.008% by weight.

Wrought iron has been used for many centuries, and is the 'iron' that is known in Western history. Throughout much of the Middle Ages was the iron produced by the direct reduction of minerals in Bloomery oven operated manually, the hydraulic energy to give movement to the mechanisms began to be used in 1104. The process consisted of charging coal and iron ore and then igniting, blowing air through a nozzle to heat to a temperature below the melting point of the iron. During the fusion, the slag melted and the carbon monoxide in charcoal served the purpose of reducing the iron ore, which was transformed into a spongy mass without passing through the liquid state. In addition, as a result of the process, the material used to include a large amount of slag, which could be further eliminated or expelled to a greater or lesser extent by the hammering. During the Middle Ages, the force of water was applied to the process, mainly for feeding the bellows and then for the movement of hammers for forging. And this was the culmination of the direct process for the manufacture of iron, which survived in Spain and southern France as Forges Catalan in the mid-nineteenth century, in Austria as Stuckofen in 1775 and near Garstang in England until around 1770. The process Bloomery produced the so-called coal iron and continued until the end of the eighteenth century. Also, with the successive inventions and improvements to the process, wrought iron was produced from pig iron with forged or since the industrial revolution in a home in Lancashire, the resulting metal was highly variable, both from the chemical and the slag content.

Already at the end of the eighteenth century there was a demand for pig iron (an impure form of iron), to be refined with coal as fuel. This allowed the passage to puddling iron, which contained less slag, less sulphur, and very low carbon content. Here the iron was kept separate from the fire in a reverberatory furnace to prevent harmful sulphur and phosphorus from entering the finished iron. This puddled iron was also very variable in its properties, it was more consistent than the irons produced previously and the method it lends itself to the production of much larger quantities. In 1876, the annual production of puddled iron in the United Kingdom alone was four million tons [40] (Figs. 7.11 and 7.12).

It is observed in the macroscopic examination what exemplifies the typical damages induced by external corrosion, observed in a great number of structural elements both on the downstream sides and on the upstream sides. It must be taken into account that the great separation of the rivets is not suitable for the thickness of the iron plates (10.05 mm). This easily allows the penetration of moisture between the contact planes so that the expansion of oxide, due to the subsequent volume, increases. It includes the deformation of the iron plates and sections in the connections of the composite struts [41].

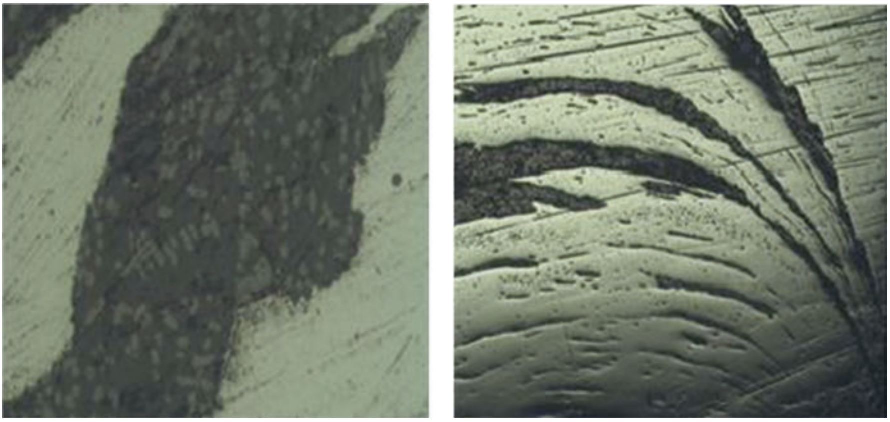


Fig. 7.11 (**a**) Microstructure of historical forged iron (1898), equiaxed ferrite grains with a certain number of inclusions of the silicates, sulphides, phosphates and iron oxides present in dendritic form. (**b**) Image detailing the forging lines, Archaeometallurgy Area Metallurgy Laboratory (UTN FRM)

Fig. 7.12 (**a**) Macroscopic observation of the bridge corroded structure. (**b**) Column detail image from third section and external corrosive damage

References

1. Groysman, A.: Humanitarian aspects of corrosion science and technology. In: Groysman, A. (ed.) Corrosion form Everybody, pp. 231–286. Springer, New York (2010)
2. Wagne, C., Traud, W.: Classic paper in corrosion science and engineering with a perspective by F. Mansfeld: on the interpretation of corrosion processes through the superposition of electrochemical partial processes and on the potential of mixed electrodes. Corrosion. **62**, 843–855 (2006)
3. Revie, R.W., Huhlig, H.H.: Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering, vol. 4. Wiley, Hoboken (2008)

4. Hoar, T.P.: Electrochemical principles of the corrosion and protection of metals. J. Appl. Chem. **11**, 121–130 (1961)
5. Fontana, M.G.: Corrosion Engineering, 3rd edn. McGraw-Hill, Singapore (1987)
6. Shreir, L.L.: Basic concepts of corrosion. In: Cottis, B., Graham, M., Lindsay, B., Lyon, S., Richardson, T.J.A., Scantlebury, D., Scott, H. (eds.) Shreir's Corrosion. Basic concept, high temperature corrosion, pp. 89–100. Elsevier, Amsterdam (2010)
7. Bardal, E.: Corrosion and Protection, 1st edn. Springer, London (2004)
8. Sastri, V.S., Ghali, E., Elboujdaini, M.: Corrosion Prevention and Protection: Practical Solutions, 1st edn. Wiley, West Sussex (2007)
9. Bosi, C., Garagnani, G.L., Imbeni, V., Martini, C., Mazzeo, R., Poli, G.: Unalloyed copper inclusions in ancient bronze artefacts. J. Mater. Sci. **37**, 4285–4298 (2002)
10. Negi, A., Sarethy, I.P.: Microbial biodeterioration of cultural heritage: events, colonization, and analyses. Microb Ecol. **78**, 1014–1029 (2019)
11. Usher, K.M., Kaksonen, A.H., Cole, I., Marney, D.: Critical review: microbially influenced corrosion of buried carbon steel pipes. Int. Biodeterior. Biodegrad. **93**, 84–106 (2014)
12. Bonfanti, A., Lecomte, C., Little, B.J., Lee, J.S.: Bioactive environments: corrosion, in: S. Hashmi (Ed.), Reference Module in Materials Science and Materials Engineering, 533–537 (2018)
13. Iverson, W.P.: Biological corrosion. In: Fontana, M.G., Staehle, R.W. (eds.) Advances-in-Corrosion-Science-and-Technology, pp. 1–42. Plenum Press, New York (1972)
14. Gu, J.-D., Mitchell, R.: Biodeterioration. In: Dworkin, M., Falkow, S., Rosenberg, E., Schleifer, K.-H., Stackebrandt, E. (eds.) The Prokaryotes, pp. 864–903. Springer, Singapore (2006)
15. Palomar, T., Cano, E.: Comparative assessment of mechanical, chemical and electrochemical procedures for conservation of historical lead. J. Cult. Herit. **30**, 34–44 (2018)
16. Wesson, H.C., Littauer, E.: Lead and lead alloys. In: Shreir, L.L. (ed.) Corrosion, pp. 4.68–4.85. Newnes-Butterworths, London (1976)
17. Hofmann, W.: Lead and Lead Alloys: Properties and Technology, 2nd edn. Springer, London (1970)
18. Chiavari, C., Martini, C., Prandstraller, D., Niklasson, A., Johansson, L.-G., Svensson, J.-E., Åslund, A., Bergsten, C.J.: Atmospheric corrosion of historical organ pipes: The influence of environment and materials. Corros. Sci. **50**, 2444–2455 (2008)
19. Deflorian, F. and Fedel, M.: Electrochemical analysis of the degradation of lead alloy organ-pipes due to acetic acid. J. Cult. Herit. 254–260 (2013)
20. FitzGerald, K.P., Nairn, J., Atrens, A.: Chemistry of copper patination. Corros. Sci. **40**, 2029–2050 (1998)
21. Piccardo, P., Bongiorno, V., Campodonico, S.: Artistic patinas on ancient bronze statues. In: Dillmann, P., Watkinson, D., Angelini, E., Adriaens, A. (eds.) Corrosion and Conservation of Cultural Heritage Metallic Artefacts, pp. 193–212. Woodhead Publishing, Sawston (2013)
22. FitzGerald, K.P., Nairn, J., Skennerton, G., Atrens, A.: Atmospheric corrosion of copper and the colour, structure and composition of natural patinas on copper. Corros. Sci. **48**, 2480–2509 (2006)
23. Leygraf, C., Odnevall Wallinder, I., Tidblad, J., Graedel, T.: Atmospheric Corrosion, 2nd edn. Wiley, Hoboken (2016)
24. Núñez, L., Reguera, E., Corvo, F., González, E., Vazquez, C.: Corrosion of copper in seawater and its aerosols in a tropical island. Corros. Sci. **47**, 461–484 (2005)
25. Graedel, T.E.: Copper patinas formed in the atmosphere II. A qualitative assessment of mechanisms. Corros. Sci. **27**, 721–740 (1987)
26. Morcillo, M., Almeida, E., Marrocos, M., Rosales, B.: Atmospheric corrosion of copper in Ibero-America. Corrosion (NACE). **57**, 967–980 (2001)
27. Graedel, T.E., Nassau, K., Franey, J.P.: Copper patinas formed in the atmosphere I. Introduction. Corros. Sci. **27**, 639–657 (1987)

28. Watanabe, M., Higashi, Y., Ichino, T.: Surface observation and depth profiling analysis studies of corrosion products on copper exposed outdoors. J. Electrochem. Soc. **150**, B37 (2003)
29. de la Fuente, D., Simancas, J., Morcillo, M.: Morphological study of 16-year patinas formed on copper in a wide range of atmospheric exposures. Corros. Sci. **50**, 268–285 (2008)
30. Di Carlo, G., Giuliani, C., Riccucci, C., Pascucci, M., Messina, E., Fierro, G., Lavorgna, M., Ingo, G.M.: Artificial patina formation onto copper-based alloys: chloride and sulphate induced corrosion processes. Appl. Surf. Sci. **421**, 120–127 (2017)
31. Zhou, P., Hutchison, M.J., Erning, J.W., Scully, J.R., Ogle, K.: An in situ kinetic study of brass dezincification and corrosion. Electrochim. Acta. **229**, 141–154 (2017)
32. Huang, W., Winfried, K., Evelyne, G., David, A.S.: The metallography and corrosion of an ancient Chinese bimetallic bronze sword. J. Cult. Herit. **37**, 259–265 (2019)
33. Robbiola, L., Blengino, J.M., Fiaud, C.: Morphology and mechanisms of formation of natural patinas on archeological Cu-Sn alloys. Corros. Sci. **40**, 2083–2111 (1998)
34. MacLeod, I.D.: Bronze disease: an electrochemical explanation. ICCM Bull. **7**, 16–26 (2015)
35. Scott, D.A.: Bronze disease: a review of some chemical problems and the role of relative humidity. J. Am. Inst. Conserv. **29**, 193–206 (1990)
36. Reynaud, A.: Corrosion of cast irons. In: Richardson, T.J.A. (ed.) Comprehensive Corrosion, pp. 1379–1788. Elsevier, The Hague (2010)
37. Metallography and Welding, vol 3, Student Notes, UTNFRM (1960)
38. Scott, D.: Metallography and Microstructure of Ancient and Historical Metals, Chap. 2, p. 12. The Getty Conservatory Institute. ISBN 0-899236-195-6 (1991)
39. ASM Handbook, Metallography and Microstructures, vol 9 (2004)
40. Mattolini, M.: Class Notes and Dissertation about the History of Metallurgy. Mendoza, Argentina (2013)
41. Gentili, C., Saisi, A.: One-Year Dynamic Monitoring of a Centenary Iron Arch Bridge Experimental Vibration Analysis for Civil Engineering Structures. Ouro Preto, Brazil (2013)

Chapter 8
Coatings for Metals Protection

Cecilia Deyá

Surface Coatings

Surface coating describes any material that may be applied as a thin continuous layer to a surface, while paint is traditionally used to describe pigmented surface coatings as distinct from clear films which are more properly called lacquers or varnishes [1]. Paints and surface coatings have two main purposes: to provide aesthetic characteristics to the surface or to solve protective problems (or both) [1].

The requirements for paint depend on the substrate and on the environment the painted substrate will be in contact with. Both factors, together with application method and curing conditions will be important during the formulation of the paint [1].

Coatings will protect the metal substrate by two main methods [2]:

Barrier: creating a physical barrier between the metal and the environment.

Active: protecting the substrate by an active action of one or more components in the composition. For example, anticorrosion paints would protect the metal substrate by the action of anticorrosive pigments while antifouling or antifungi paints would have antifouling or antifungi compounds in their composition.

If the paint would be in direct contact with the metal, its main characteristics should be corrosion protection. In this case, anticorrosive pigments must be added and adhesion to the metal is a highly important issue. Barrier properties and gloss degree are not very important in this case. On the other hand, if the paint would be in direct contact with the environment, top coat paint, then barrier, chemical resistance and aesthetic properties are very important. Moreover, if the painted substrate would be exposed to ultraviolet (UV) light, it should be UV resistant in order to delay photooxidation. So, in general, several layers of coating with different

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C. Deyá (✉)
CIDEPINT (CONICET-CICPBA-Ing. UNLP), La Plata, Buenos Aires, Argentina
e-mail: c.deya@cidepint.ing.unlp.edu.ar

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_8

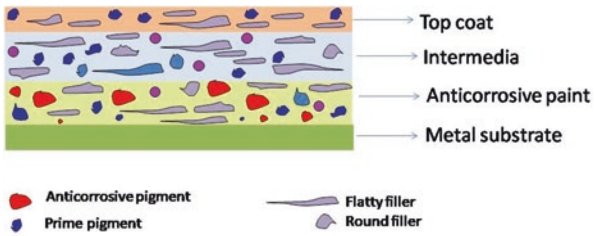

Fig. 8.1 Structures of the dried paint

formulations are applied on a substrate in order to completely protect it. The different formulations include different compounds (Fig. 8.1).

The main components of paints are resin, pigments, solvent and additives. The resin, or binder, is the film forming material of the paint and it provides the physical structure. It will bring the paint characteristics such as chemical and UV-resistance, adhesion to the substrate, cohesion between the pigments, flexibility, hardness and water and oxygen transport. The most important resins use for anticorrosive protection are polyurethanes, epoxy, alkyd, polysiloxanes, acrylics, polyvinyl butyral [2]. Polymers of different types and molecular weights are usually blended to provide the balance of properties needed for a particular type of coating [2].

Polyurethanes**:** Polyurethane resins have excellent water resistance, good resistance to acids, alkalis and solvents, good abrasion resistance and, in general, good mechanical properties [2]. There are two types or polyurethane resins: one component that cures with moisture of the environment, and those of two components that cure by a chemical reaction between the components, with a limited pot-life after mixture. In the first case they are tolerant to damp surfaces.

Epoxy**:** Epoxy resins can bring very strong mechanical properties, very good adhesion to metal substrates, excellent chemical and water resistance; however, they are susceptibility to UV degradation and can be sensitive to acids. Epoxy coatings are two-component system and cure by chemical reaction.

Alkyds**:** They are one-component air-curing paints and, therefore, are fairly easy to use. They are also relatively inexpensive and can be formulated into both solvent-borne and water-borne coatings. Alkyd paints cure by reaction with the oxygen in the atmosphere and can become brittle as the coating ages. Alkyds cannot tolerate alkali conditions; they are somewhat susceptible to UV radiation and they are not suitable for immersion service [2].

Polysiloxanes**:** Polysiloxane resins are very UV-resistant with excellent gloss retention, good adhesion and cohesion properties and good chemical resistance. They can be used to formulate barrier or high-solid and low-volatile organic compound-coating. However, they have a limited surface tolerance, so they are usually applied on top of a primer [2]. Polysiloxanes can be formulated as both single component (that is cure with humidity in the atmosphere) and two component (that is cures by chemical reaction between the components) [2].

Table 8.1 Main characteristics of the resins [2]

Resin	Resistance					
	Chemical	UV	Immersion	Humidity	Alkalinity	Heat
Polyurethanes	Good	Depends	Excellent	Excellent	Good	Good
Epoxy	Excellent	Bad	Excellent	Excellent	Excellent	Excellent
Alkyd	Good	Susceptible	Bad	Bad	Bad	
Polysiloxanes	Good	Good				Susceptible
Acrylics		Excellent				

Acrylics**:** Acrylic resins usually refer to water-borne or latex formulation. These resins have outstanding UV stability and good mechanical properties, particularly toughness. Due to their UV resistance, they are suitable for applications in cases in which retention of clarity and colour is important. They are, however, sensitive to alkali environments [2].

Polyvinyl Butyral**:** Polyvinyl butyral resin is used in temporary protective primers. These primers are useful to protect metal during transportation but also to enhance paint adhesion.

The main characteristics of the resins can be seen in Table 8.1.

The pigments are the insoluble solid particles of the paint. They are classified as prime pigments (titanium dioxide, carbon black, iron oxides, zinc oxide) and fillers such as talk, barite and mica, that will complete the pigment formula. In the first group, the refraction index is higher than the one of the resins, so the underneath substrate could not be seen; these pigments give colour to the paint. In the second case, the refractive index is similar or lower than the one of the resins and they are not involved in optical performance [3–6].

Fillers, or extenders, can be used to improve the barrier protection afforded by the paint by selecting platy ones that will enlarge oxygen and water paths through the paint dried film [7] (Fig. 8.1). Such pigments have a large aspect as talc, mica. Incorporating some surface modifications to these pigments, the corrosion protection afforded by the paint can be improved [8].

Other pigments, important in the anticorrosive paints, are the anticorrosive ones (Fig. 8.2).

Traditional anticorrosive pigments were based on chromate and lead compounds such as basic zinc potassium chromate, zinc tetraoxichromate, read lead, lead oxide, lead cyanamide, lead silicochromate, dibasic lead phosphate, calcium plumbate [2, 9]. However, nowadays they are banned due to toxicological issues and zinc phosphate and phosphate-based pigments, being non-hazardous, are more acceptable inhibitors [10–14].

Zinc Phosphate**:** Zinc phosphates provide corrosion protection to metals through multiple mechanisms that mainly involved the formation of protective layers. These layers can be formed by phosphates, insoluble basic salts, organic complexes formed due to the reaction of zinc with some of the resin compounds, $\gamma\text{-Fe}_2O_3$ [2].

Polyphosphate and Other P-Based Anions**:** When polyphosphates, pyrophosphates and hypophosphates are used results depend on the pigment (type of anion

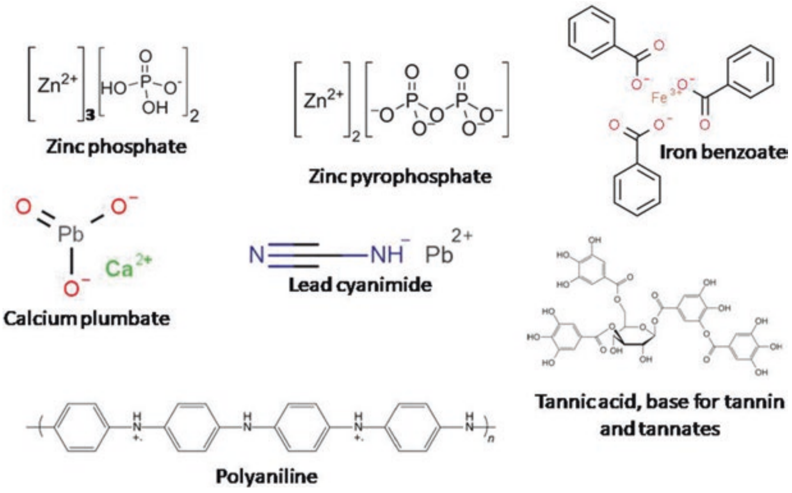

Fig. 8.2 Structure of some anticorrosive pigments

and cation), the type of fillers (presence of pH regulators such as ZnO and MgO) and the resins [11, 15–21] used.

As phosphorous causes eutrophication of fresh water reservoirs [22], other non-phosphate-based pigments were studied such as benzoates [23, 24], polyaniline and conductive polymers [25–28], exchanged silicates [29, 30], exchanged silica [12, 31–33], tannins and other organic compounds [34–36] and ferrites [12, 37].

Benzoates**:** The mechanism of the protective action of benzoates on steel substrates involves the anion adsorption onto the active sites of the metallic surface providing an effective protective layer [23, 24].

Polyanilines**:** Polyanilines protect the underlying steel either by barrier protection, generation of electric field, controlled inhibitor release mechanism, anodic protection or by combination of these mechanisms [25, 26].

Exchanged Silicates**:** Silicates such as zeolites or halloysites are modified with passivation compounds (lanthanum or cerium ions, 2-mercaptobenzothiazole) that are released during paint exposition protecting the metal substrate [29, 30].

Exchanged Silica: The protection afforded by exchanged silica in paints relies upon the high pH of the pigment and the composition of the protective layer rather than on its ability to exchange aggressive ions [31].

Tannins**:** Tannins and tannates can protect steel by forming iron tannates complexes [34–36]. As tannins can be obtained from natural sources, they are studied nowadays as natural anticorrosive pigments.

Organic Compounds**:** The use of organic compound in metal corrosion protection is an important field nowadays as most of them can be extracted from plants [38, 39]. However, being soluble it is difficult to incorporate them directly to a coating and some strategies like encapsulated or incorporating in zeolites or halloysites are being studied [30, 40]. Benzoates were successfully incorporated by precipitation with suitable cations in order to obtained slightly soluble salts [23, 24].

Ferrites**:** Ferrite pigments' protection is based on the cation solubility and their role to create an alkaline environment at the coating–metal interface. Their performance depends on the type of cation [12, 37].

Solvents are divided in dissolvents, which dissolve the resins; and dilutants, which do not dissolve the resin and are used to control the viscosity of the paint. The more important solvents are white spirit, toluene, xylene, cellosolves; they are selected depending on the resin. Water is being introduced as dilutant in order to diminish the number of organic solvents use in coatings. This incorporation was done mainly due to toxicological and environmental concerns but it introduced lots of improvement in resins, application methods, additives etc. [41–44].

Additives are compounds added in very small amounts that modified some of the paint characteristics. They can be useful during paint manufacture, application, drying. Most of them became important with water-borne paint technology. The more important additives are driers, coalescents, thickeners, antifoaming, flash rusting inhibitors, light stabilizers.

Driers**:** Driers are used in the case of alkyd resins to accelerate film formation. Radical chain reactions are involved in this case and salts of fatty acids (2-ethylhexanoate, neodecanoate, octoate) and metals like cobalt, iron, manganese, vanadium, calcium are used [45, 46].

Coalescents**:** Coalescent or temporary plasticizer has the function of enabling or optimizing film formation from polymer dispersions under given conditions of application [47].

Thickeners**:** Thickeners or rheological agents are added to paint in order to impart the required rheological characteristics to the system to flow, level and to have adequate sag resistance, brushability and thickness. The selection of the thickeners depends on the resin and the solvent: hydrogenated castor-oil, polyurethanes, organo-clays, cellulose derivatives are used [48].

Antifoaming**:** Antifoaming agents are added to paint for foam control during manufacture and application [49, 50]. Simple silicon oils are often used as foam inhibiting agents. Other compounds could be triglycerides, fluorocarbons, solid particles of silica of calcium soaps, various amphiphilic molecules (alcohols, fatty acids, fatty esters), or specific polymers with partial solubility in water (polymers, based on oxyethylene, oxypropylene and oxybutylene units) [49, 50].

Flash Rusting Inhibitors**:** Flash-rust is the corrosion of metals that can occur during drying of water-based paints. Flash-rusting inhibitors are either water-soluble or water-emulsifiable substances, which prevent corrosion of ferrous metals during the drying time of the paint [51, 52].

Light Stabilizers**:** Light stabilizers are added in order to prevent UV-light degradation of the resins. They can be classified as UV absorber or quencher that destroys the excited states of polymer when a functional group has already absorbed radiation, and radical scavengers that can destroy radicals formed due to light interaction with the polymer. While acrylate chains or aliphatic polyesters cannot absorb light, they can contain light-absorbing impurities. Polymers such as polystyrene or aromatic polyesters absorb UV light themselves and are susceptible against photo-oxidative degradation even without impurities [53].

Besides differences in paint composition, different paint has different pigment/resin ratio. This ratio is taking into account as Pigment Volume Concentration (PVC) and defines as [54–56]:

$$\mathrm{PVC} = \frac{\text{Volume of pigment}}{\text{Volume of pigment} + \text{Volume of resin}} \tag{8.1}$$

There is a critical value of PVC, the CPVC (Critical Pigment Volume Concentration), that considers the exact amount of binder to fill in the voids and wet the pigment particles [55]. If PVC < CPVC, the pigment particles are separated and the barrier properties of the paint are enhanced. This is used when the paint will protect by barrier, such in the case of top coat. If PVC > CPVC, there is not enough binder, relative to the pigment, and air becomes part of the film, the barrier properties of the paint are poor, the paint film is porous [54–56]. This is the case of anticorrosive paints, as water must enter in order to dissolve the active pigment to protect the substrate [23, 29].

In the case of protection of heritage cultural objects, depending on the metal, the coating should be transparent so the metal substrate can be seen and no prime pigments are used [57]. In these cases, for example, when copper or bronze is used, lacquers or varnishes, or silane coatings are applied (Fig. 8.3). Different organosilanes have been used as precursors to prepare sol-gel coatings to improve corrosion resistance of metals [58, 59]. The most important advantages of the sol-gel method are: lower processing temperature, no limitations about the size or shape of the substrate, the possibility of working in a continuous process in normal atmospheric conditions, homogeneous and constant thickness of the film, higher control of films composition and lower production costs [60].

Alkoxysilanes have the general formula R'-Si-$(RO)_3$, being R' a hydrocarbon chain, functionalized or not and RO an ethoxy or methoxy group, easily hydrolysable [61]. These silanes interact with the metal forming Si–O–Metal covalent bonds by the reaction between the hydrolysis products of RO-groups (RO-H, silanols) and the oxyhydroxides present on the metal [61]. These bonds, being covalent, are very strong. Moreover, the silanol groups present in one molecule can react with similar groups in other molecule forming Si–O–Si bonds, which stabilize the film by cross-linking (Fig. 8.4). In the case of copper and its alloy, silanol groups are not well connected to the surface and silanes containing a mercapto group in the functionalized chain has been used to improve the adhesion of the silane compounds on copper surface [62, 63].

The characteristics of the film formed on the metal and the protection afforded to the substrate depend on several variables such as: pH of hydrolysis, type of solvents, time of hydrolysis, presence of additives and/or dopants, way of application, time and curing temperature of the film [62–64]. Moreover, the thickness of the film could vary depending on the number of applications of the silane solution on the metal [65].

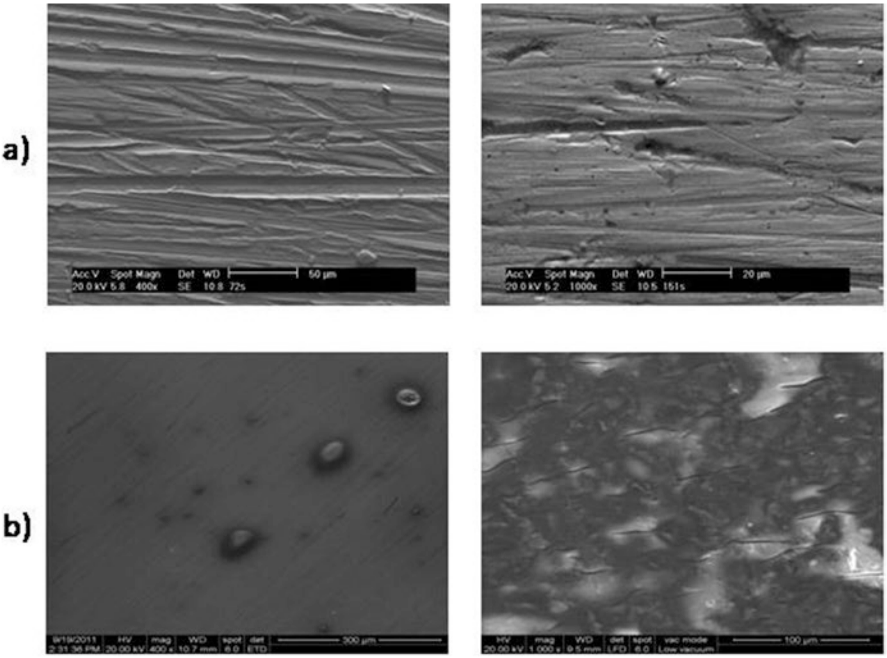

Fig. 8.3 SEM micrographs of silanes film on (**a**) copper, (**b**) steel

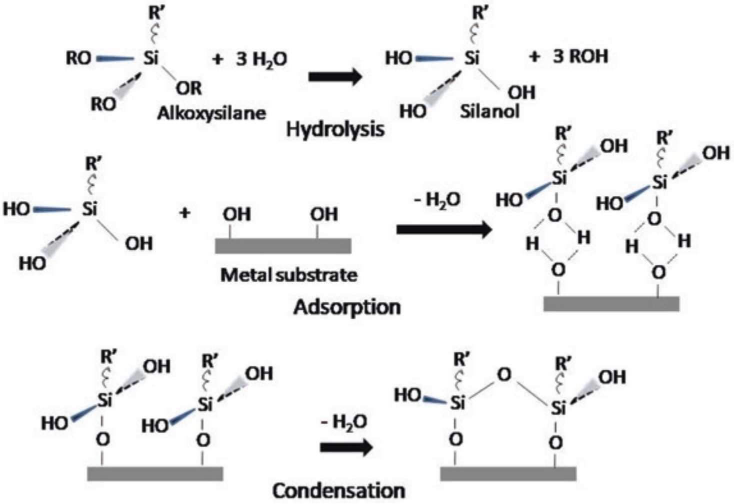

Fig. 8.4 Process of silane film formation

References

1. Lambourne, R.: Paint Composition and Applications - a General Introduction. In: Lambourne, R., Strivens, T.A. (eds.) Paint and Surface Coatings. Theory and Practice, pp. 1–18. Woodhead Publishing, Cambridge (1999)
2. Knudsen, O.Ø., Forsgren, A.: Corrosion Control Through Organic Coatings, 2nd edn. Taylor & Francis, Boca Raton (2017)
3. Goldschmidt, A., Streitbeger, H.-J.: BASF Handbook on Basics of Coating Technology. Vincentz, Hannover (2007)
4. Braun, J.H.: White pigments. In: Koleske, J.V. (ed.) Paint and Coating Testing Comment Manual, pp. 159–178. ASTM, Philadelphia (1995)
5. Spinelli, F.R.: Black pigments. In: Koleske, J.V. (ed.) Paint and Coating Testing Comment Manual, pp. 179–189. ASTM, Philadelphia (1995)
6. Lewis, P.: Inorganic colores pigments. In: Koleske, J.V. (ed.) Paint and Coating Testing Comment Manual, pp. 209–213. ASTM, Philadelphia (1995)
7. Ralston, H.P.: Extender pigments. In: Koleske, J.V. (ed.) Paint and Coating Testing Comment Manual, pp. 217–222. ASTM, Philadelphia (1995)
8. Kalenda, P., Kalendová, A., Štengl, V., Antoš, P., Šubrt, J., Kváča, Z., Bakardjieva, S.: Properties of surface-treated mica in anticorrosive coatings. Prog. Org. Coat. **49**, 137–145 (2004)
9. Funke, W.: Organic coatings in corrosion protection. In: Wilson, A.D., Nicholson, J.W., Prosser, H.J. (eds.) Surface Coatings, 2nd edn, pp. 107–135. Springer, Dordrecht (1988)
10. Gimeno, M.J., Puig, M., Chamorro, S., Molina, J., March, R., Oró, E., Pérez, P., Gracenea, J.J., Suay, J.J.: Improvement of the anticorrosive properties of an alkyd coating with zinc phosphate pigments assessed by NSS and ACET. Prog. Org. Coat. **95**, 46–53 (2016)
11. Heydarpour, M.R., Zarrabi, A., Attar, M.M., Ramezanzadeh, B.: Studying the corrosion protection properties of an epoxy coating containing different mixtures of strontium aluminum polyphosphate (SAPP) and zinc aluminum phosphate (ZPA) pigments. Prog. Org. Coat. **77**, 160–167 (2014)
12. Zubielewicz, M., Gnot, W.: Mechanisms of non-toxic anticorrosive pigments in organic waterborne coatings. Prog. Org. Coat. **49**, 358–371 (2004)
13. Romagnoli, R., Vetere, V.F.: Non-pollutant corrosive inhibitive pigments: zinc phosphate, a review. Corros. Rev. **13**, 45–64 (1995)
14. Taketani, Y., Kondo, H., Kropman, M.: Propertary aluminum triphosphate pigments for waterborne coatings. Polym. Paint Col. J. **183**, 270–271 (1993)
15. Blustein, G., Deya, C., Romagnoli, R.: Synergism in anticorrosive paints. Bull. Mater. Sci. **39**, 749–757 (2016)
16. Deyá, M., Vetere, V.F., Romagnoli, R., del Amo, B.: Aluminium tripolyphosphate pigments for anticorrosive paints. Pigm. Resin Technol. **30**, 13–24 (2001)
17. Deyá, M.C., Blustein, G., Romagnoli, R., del Amo, B.: The influence of the anion type on the anticorrosive behaviour of inorganic phosphates. Surf. Coat. Technol. **150**, 133–142 (2002)
18. Hernandez, M., Genescá, J., Uruchurtu, J., Galiano, F., Landolt, D.: Effect of an inhibitive pigment zinc-aluminum-phosphate (ZAP) on the corrosion mechanisms of steel in waterborne coatings. Progr. Org. Coat. **56**, 199–206 (2006)
19. Deyá, M., Blustein, G., Romagnoli, R., del Amo, B.: Zinc hipophosphite: a suitable additive for anticorrosive paints to promote pigments synergism. J. Coat. Technol. Res. **6**, 369–376 (2009)
20. Deyá, M., Vetere, V., Romagnoli, R., del Amo, B.: Aluminium tripolyphosphate pigments for anticorrosive paints. PigRes. Tech. **30**, 13–24 (2001)
21. Deyá, M., Romagnoli, R., del Amo, B.: Calcium tripolyphosphate: an anticorrosive pigment for paints. J. Coat. Technol. **73**, 57–63 (2001)
22. Nasir Khan, M., Mohammad, F.: Eutrophication: challenges and solutions. In: Ansari, A.A., Gill, S.S. (eds.) Eutroficación: Causes, Consequences and Control, pp. 1–16. Springer, New York (2014)

23. Blustein, G., Di Sarli, A.R., Jaén, J.A., Romagnoli, R., Del Amo, B.: Study of iron benzoate as a novel steel corrosion inhibitor pigment for protective paint films. Corros. Sci. **49**, 4202–4231 (2007)
24. Blustein, G., Romagnoli, R., Jaén, J.A., Di Sarli, A.R., del Amo, B.: Zinc basic benzoate as eco-friendly steel corrosion inhibitor pigment for anticorrosive epoxy-coatings. Colloids Surf. A Physicochem. Eng. Asp. **290**, 7–18 (2006)
25. Sazou, D., Deshpande, P.P.: Conducting polyaniline nanocomposite-based paints for corrosion protection of steel. Chem. Pap. **71**, 459–487 (2017)
26. Deshpande, P.P., Bhopale, A.A., Mooss, V.A., Athawale, A.A.: Conducting polyaniline/nano-zinc phosphate composite as a pigment for corrosion protection of low-carbon steel. Chem. Pap. **71**, 189–197 (2017)
27. Hájková, T., Kalendová, A., Kohl, M.: Anticorrosion and physical properties of organic coatings containing perovskites surface modified by polyaniline or polypyrrole phosphates. Chem. Pap. **71**, 439–448 (2017)
28. Deshpande, P.P., Jadhav, N.G., Gelling, V.J., Sazou, D.: Conducting polymers for corrosion protection: a review. J. Coat. Technol. Res. **11**, 473–494 (2014)
29. Roselli, S., Deyá, C., Revuelta, M., Di Sarli, A.R., Romagnoli, R.: Zeolites as reservoirs for Ce(III) as passivating ions in anticorrosion paints. Corros. Rev. **36**, 305–322 (2018)
30. Zahidah, K.A., Kakooei, S., Ismail, M.C., Bothi Raja, P.: Halloysite nanotubes as nanocontainer for smart coating application: a review. Prog. Org. Coat. **111**, 175–185 (2017)
31. Romagnoli, R., Deya, M.C., del Amo, B.: The mechanism of the anticorrosive action of calcium-exchanged silica. Surf. Coat. Int. J Part B Coat. Trans. **86**, 135–141 (2003)
32. Vasconcelos, L.W., Margarit, I.C.P., Mattos, O.R., Fragata, F.L., Sombra, A.S.B.: Inhibitory properties of calcium exchanged silica epoxy paintings. Corros. Sci. **43**, 2291–2303 (2001)
33. Goldie, B.P.F.: Calcium exchanged silica anticorrosion pigment: a review. JOCCA. **71**, 257–269 (1988)
34. D'Alessandro, O., Selmi, G.J., Deyá, C., Di Sarli, A., Romagnoli, R.: Formulation and assessment of a wash-primer containing lanthanum "Tannate" for steel temporary protection. J. Mater. Eng. Perform. **27**, 687–704 (2017)
35. D'Alessandro, O., Selmi, G.J., Deyá, C., Di Sarli, A., Romagnoli, R.: Lanthanum derivative from "Tara" tannin for steel temporary protection. Ind. Eng. Chem. Res. **57**, 3215–3226 (2018)
36. Hadzich, A., Flores, S., Caprari, J., Romagnoli, R.: Study of zinc tannates prepared with Tara powder (Caesalpinia spinosa) as anticorrosive pigments in alkyd paints and wash primer formulations. Prog. Org. Coat. **117**, 35–46 (2018)
37. Abd El-Ghaffar, M.A., Ahmed, N.M., Youssef, E.A.: A method for preparation and application of micronized ferrite pigments in anticorrosive solvent-based paints. J. Coat. Technol. Res. **7**, 703–713 (2009)
38. Amitha Rani, B.E., Basu, B.B.J.: Green inhibitors for corrosion protection of metals and alloys. An overview. Int. J. Corros. Papar nº 380217 (2012)
39. Tasić, Ž.Z., Petrović Mihajlović, M.B., Radovanović, M.B., Antonijević, M.M.: New trends in corrosion protection of copper. Chem. Pap. **73**, 2103–2132 (2019)
40. Abdullayev, E., Abbasov, V., Tursunbayeva, A., Portnov, V., Ibrahimov, H., Mukhtarova, G., Lvov, Y.: Self-healing coatings based on halloysite clay polymer composites for protection of copper alloys. ACS Appl. Mater. Interfaces. **5**, 4464–4471 (2013)
41. Beetsma, J.: Alkyd emulsion paints: properties, challenges and solutions. Pigm. Resin Technol. **27**, 12–19 (1998)
42. de, Y.P.L., da Conceicao, T.F., Spinelli, A., Scharnagl, N., Pires, A.T.N.: Chitosan coatings crosslinked with genipin for corrosion protection of AZ31 magnesium alloy sheets. Carbohydr. Polym. **181**, 71–77 (2018)
43. Mikkonen, K.S., Kirjoranta, S., Xu, C., Hemming, J., Pranovich, A., Bhattarai, M., Peltonen, L., Kilpeläinen, P., Maina, N., Tenkanen, M., Lehtonen, M., Willför, S.: Environmentally-compatible alkyd paints stabilized by wood hemicelluloses. Ind. Crop. Prod. **133**, 212–220 (2019)

44. Pathan, S., Ahmad, S.: Green and sustainable anticorrosive coating derived from waterborne linseed alkyd using organic-inorganic hybrid cross linker. Prog. Org. Coat. **122**, 189–198 (2018)
45. Dubrulle, L., Lebeuf, R., Thomas, L., Fressancourt-Collinet, M., Nardello-Rataj, V.: Catalytic activity of primary and secondary driers towards the oxidation and hydroperoxide decomposition steps for the chemical drying of alkyd resin. Prog. Org. Coat. **104**, 141–151 (2017)
46. Bieleman, J.: Driers. In: Bieleman, J. (ed.) Additives for Coatings, pp. 202–226. Wiley, Weinheim (2000)
47. Doren, K.: Coalescing agents. In: Additives for Coatings, pp. 180–199. Wiley, Weinheim (2000)
48. Bielernan, J., Kroon, G.: Thickeners. In: Bielernan, J. (ed.) Additives for Coatings, pp. 9–63. Wiley, Weinheim (2000)
49. Denkov, N.D., Marinova, K.G., Tcholakova, S.S.: Mechanistic understanding of the modes of action of foam control agents. Adv. Colloid Interf. Sci. **206**, 57–67 (2014)
50. Heilen, W., Silber, S.: Defoaming of aqueous paint materials. In: Bieleman, J. (ed.) Additives for Coatings, pp. 100–111. Wiley, Weinheim (2000)
51. Braig, A.: Corrosion inhibitors. In: Bieleman, J. (ed.) Additives for Coatings, pp. 291–305. Wiley, Weinheim (2000)
52. Graystone, J.A.: Coatings for buildings. In: Lambourne, R., Strivens, T.A. (eds.) Paint and Surface Coatings. Theory and Practice, pp. 330–410. Woodhead Publishing, Cambridge (1999)
53. Bolle, T.: Light stabilizers. In: Bieleman, J. (ed.) Additives for Coatings, pp. 269–290. Wiley, Weinheim (2000)
54. Stieg, F.B.: The influence of PVC on paint properties. Prog. Org. Coat. **1**, 351–373 (1973)
55. Lestarquit, B.: Geometry of a paint film: Basics revisited. Prog. Org. Coat. **90**, 200–221 (2016)
56. Asbeck, W.K., van Loo, M.: Critical pigment volume relationships. Ind. Engi. Chem. **41**, 1470–1475 (1949)
57. Lasseter Clare, T., Swartz, N.A.: Characterization of high performance protective coatings for use on culturally significant works. In: Atul, T., Rawlins, J., Hihara, L.H. (eds.) Intelligent Coatings for Corrosion Control, pp. 641–671. Elsevier, Amsterdam (2015)
58. Chico, B., Galván, J., de la Fuente, D., Morcillo, M.: Electrochemical impedance spectroscopy study of the effect of curing time on the early barrier properties of silane systems applied on steel substrates. Progr. Org. Coat. **60**, 45–53 (2007)
59. Deflorian, F., Rossi, S., Fedrizzi, L.: Silane pre-treatments on copper and aluminium. Electrochim. Acta. **51**, 6097–6103 (2006)
60. Wang, D., Bierwagen, G.: Sol-gel coatings on metals for corrosion protection. Progr. Org. Coat. **64**, 327–338 (2009)
61. Balgude, D., Sabnis, A.: Sol–gel derived hybrid coatings as an environment friendly surface treatment for corrosion protection of metals and their alloys. J. Sol-Gel Sci. Technol. **64**, 124–134 (2012)
62. Zucchi, F., Grassi, V., Frignani, A., Trabanelli, G.: Inhibition of copper corrosion by silane coatings. Corros. Sci. **46**, 2853–2865 (2004)
63. Chen, M.-A., Lu, X.-B., Guo, Z.-H., Huang, R.: Influence of hydrolysis time on the structure and corrosion protective performance of (3-mercaptopropyl)triethoxysilane film on copper. Corros. Sci. **53**, 2793–2802 (2011)
64. Qian, M., Mcintosh Soutar, A., Tan, X.H., Zeng, X.T., Wijesinghe, S.L.: Two part epoxy-siloxane hybrid corrosion protection coating for carbon steel. Thin Solid Film. **517**, 5237–5242 (2009)
65. Pilz, M., Romich, H.: Sol-gel derived coatings for outdoor bronze conservation. J. Sol-Gel Sci. Technol. **8**, 1071–1075 (1997)

Chapter 9

Conservation, Restoration and Reverse Engineering: Technological and Theorical Dimension

Patricia Silvana Carrizo

Restoration is a discipline destined to preserve a certain cultural product for the future. It is a concept that has changed over time with respect to how it was understood in the past. Currently, it has become a scientific activity; it is no longer a particular and subjective intervention of the restorer as an artist. The purpose of the restoration–conservative intervention derives from giving an object a particular, artistic, documentary, aesthetic, historical, and cultural value to recognize the object as a material witness of an era, of a society, and of a civilization. The abundant and prolific character of the restoration has been enriching the process of diagnostic process execution.

For this reason, restoration becomes a broad discipline rich in reflections on the safeguarding of our assets, where the different disciplinary territories and the progressive technological development make possible the approach and the common principles that guide all restoration–conservation activity and constitute a punctual tool for the performance of engineers mostly in specialties: chemistry, metallurgy, materials, specialists in finite element calculation, etc., playing key roles in the study and restoration processes.

In 1970, an international opening began to the problem of the recovery of historical values in historical centers, for this reason a series of definitions of the object arise in the different codices and it is important to list them and give a current explanation. This is very important as it determines the procedures, whether restoration or conservation. The formal study of archeometallurgy began in the 1970s and 1980s and has seen recent growth in techniques, data, and theoretical movements. Archeometallurgy is also known as historical metallurgy and represents an unprecedented technique to measure the past and obtain answers, all this closely linked to the development of laboratory equipment, this is currently more concrete and in line with this idea, since there is a variety of equipment fixed and portable to analyze our

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P. S. Carrizo (✉)
Archaeometallurgy Area/Metallurgy Laboratory, National Technological University, Mendoza, Argentina

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_9

past and be able to transport them to the field that is to say to the place where the objects are and work comfortably. So much so is the implication that more and more engineers are passionate about these issues and are called to get involved to work and research in the area of archeometallurgy and reverse engineering because they come to respond to what was previously unanswered. Thus, it is possible to work in a multidisciplinary way, and teamwork is the task to be accomplished, doing it collaboratively and generating equity and equality for all those involved is essential. So, the issue of conservation and restoration are of the same tenor and requires teams made up of various professions, always putting the work or heritage infrastructure to be conserved or restored first, this in my opinion is essential for collective growth and generation of social conscience for the respect and care of historical objects and works, since they have a legacy to share.

1. **Reversibility:** “The object that is intervened must be able to be brought back to the state prior to the intervention” [1]. Absolute reversibility is impossible; therefore, the concept migrates to retractability, as an example: replacing iron tensioners with new tensioners made of special alloy steel, in the future the object may be portrayed with a more suitable material that fulfills the same functions. This principle must be understood taking into account that there is a future possibility of achieving a technology superior to the present one.
2. **Authenticity:** Based on which the aggregates must be visually recognizable and distinguished from the original (immediate recognition of the aggregates), preserving the figurative unity. This principle also contains a reference to the technique, since the technology is in a position to perfectly imitate the original, but it is not what the conservative proposal proposes as a solution.
3. **Minimum intervention:** According to which interventions not strictly necessary, such as beautification or modernization, must be excluded, since the sign of time constitutes a historical and aesthetic value to be safeguarded.
4. **Compatibility**: By which mechanical and chemical–physical affinity is sought between the new material and the original material.
5. **Durability:** Mechanical and thermal stability, resistance to chemical, and atmospheric agents.
6. **Actuality figurative:** It rejects any form of imitation in the integration of new parts on the pre-existence.

In the nineteenth century, it was restored in the name of historical and aesthetic values. The theory determined the collective existence, giving the work an ideological character. The current reflections operate conservatively, considering the work objectively and scientifically. Subsequently, the two historical attitudes toward the intervention of a work have been outlined, from restoration, as intervention of liberation or reintegration to pure conservation. These express the continuing dichotomy between historicity and aestheticity of the work where the debate is still open.

On the other hand, the scientific-technological development allows an effective approach to the knowledge of the work and also offers a way of dialogue between such different positions, and therefore their approach and gaze have a broad and pluralistic sense. This was expressed first in the possibility of diagnosing pathologies and then in the common principles that should be respected in any restoration. Accepting that restoration is not exclusively identified with artistic practice and that the approach has changed regarding how intervention in heritage should be, then the scientific-technological fields have been of particular interest for some time now.

Cleaning, Conservation, and Electrochemical Restoration of Heritage Metal Objects

The restoration and conservation of archaeological, historical, and heritage metal pieces is an often essential stage in the study of the objects found either in archaeological sites, in museum collections, belonging to the industrial heritage or to the heritage infrastructure.

In the particular case of restoring metal objects, coins, jewelry, musical instruments, metal parts of war uniforms, and, for example, the method (s) normally used are usually chemical and have been characterized as abrasive and long-lasting duration. Due to the very nature of the procedure, it is usually only possible to treat piece by piece; it is not advisable to carry out the processes to a batch of pieces.

Fundamentally, chemical methods are based on the elimination of the layer of oxidized products that cover the piece. However, there is the possibility of reversing the corrosion process, causing deterioration, by electrochemical methods. This possibility forms the basis of cathodic or electrochemical reconstruction or restoration and is the one that will be presented in this chapter.

Deterioration of Metal Parts

Understanding the processes of deterioration of materials is essential for conservation. Two types of deterioration can be considered in metallic objects: mechanical (impact and abrasion) and chemical (corrosion).

There are two forms of chemical deterioration: aqueous corrosion and oxidation. The latter occurs under very dry suitable conditions. The metal combines with oxygen and produces compounds on its surface (patina). The surface itself is very reactive and forms these compounds quickly. Reactions occur more easily, if there is moisture in the medium; however, this oxide layer can also form a protective barrier (passivation) that, at low temperature, prevents subsequent reactions between the metal and the gases in the atmosphere [2].

The corrosion process takes place in several stages: a finished object immediately begins to deteriorate, even in an ordinary atmosphere. Atmospheric corrosion is the most frequent cause of the destruction of metals and alloys, the mechanism by which it occurs is electrochemical. Electrolyte, is called a layer of moisture on the metal surface whose thickness can vary from very thin (invisible) layers to layers that perceptibly wet the metal. During the initial stage of atmospheric corrosion, the deposits are slight, and when the corrosion progresses it moves along the grain boundaries of the metal and converts the metallic crystals into minerals, since all material tends to return to its initial state, that is, when it was a mineral, since to transform it into metal it was necessary to give it a lot of energy, that is, the metal seeks its equilibrium and due to the entropy the system tends to return to the original values.

As the deterioration continues, greater amounts of metal are converted to mineral and this causes growth in volume, the metal swells, swells, gaining volume, but losing body, so to speak so that the process is understood, thus leaving the original layer covered by corrosion products [3]. This layer can progress until all the metal disappears, but within it preserves the layer that represents the original surface of the object, which can retain manufacturing evidence and be recovered and preserved with adequate conservation.

Cathodic restoration: The cathodic restoration process is based on the reversal of the corrosion process, that is, on subjecting the part to an electrolysis process in which the part itself assumes the role of cathode in the electrochemical cell, and using as anode an electrode such as zinc, aluminum, and galvanized steel. All this will depend on the difference in electronegativities of the part to be restored and the material used as a sacrificial anode, since this will be consumed to the benefit of the part that is going to remove the corrosion product or the dirt accumulated in other cases. The anode and cathode assembly are submerged in a conductive solution whose mission is to allow the passage of electric current through the solution between anode and cathode, once a potential difference between them has been established using a direct current source.

In this way, when the anode is connected to the positive pole of the source and the cathode to the negative pole, the oxides are reduced to their metallic state and the formation of hydrogen in the cathode (in this case the part to be restored). This release of hydrogen on the surface to restore favors cleaning, since the bubbles interact with the surface of the pieces and help to remove rust, corrosion products, and dirt that is usually attached, thus avoiding the use of mechanical and abrasive cleaning means that many times they are invasive with parts.

Having to apply cleaning techniques to all kinds of archaeological pieces, museum pieces, private collections, and coins, I have been guided by the electrolytic cleaning technique or also called electrolytic reduction, which is also known as cathodic restoration, and which is basically a chemical reduction. The pieces are treated by total immersion in the electrochemical cell, but if the piece does not need it totally, only the parts that are oxidized or with accumulation of dirt are submerged, and it is even possible to treat small areas without totally submerging the piece or even treating it locally using the appropriate products [4].

In this sense, different electrochemical restoration methods have been developed and perfected with excellent results; they can be grouped into two sections: (a) electrochemical methods and (b) cleaning methods by conventional chemical means.

Electrochemical Methods

Electrolysis in Solution or Electrolytic Reduction or Cathodic Restoration

This method consists of the electrolysis of the part in a conventional cell; it is only a container with the capacity to submerge the parts (Photo 9.1).

The anode consists of a rectangular aluminum, zinc, or galvanized steel bar or sheet that works correctly, and the part to be electrolytically restored is connected as a cathode, and everything is already immersed in the appropriate electrolyte. The circuit is closed, and thus, the electrochemical reduction is carried out or the cleaning of the object as a whole, always work with due caution in handling, using gloves, safety glasses, and in ventilated environments. The space between the electrodes should be small (Fig. 9.1). The electrolyte or electrolyte solution used will depend on the corrosion products that the part has: if they are soluble in water, a conductive solution (electrolyte) of sodium perchlorate (ClO_4Na) in tetrahydrofuran (THF) is used, and if they are not soluble in water, a solution of sodium sulfate (SO_4Na_2) or sodium hydroxide (NaOH). In particular, I have used the latter electrolyte: sodium hydroxide (NaOH), it is cheap, accessible, and I have obtained very good results, especially working on copper parts and their alloys, achieving good results in a short time. The method produces satisfactory results on medium-sized pieces of various shapes (uniform armor, helmets, coins, pots, kettles, cannons, artillery items).

Regarding the optimal electrolysis conditions:

Anode: rectangular sheet of zinc (Zn), galvanized steel, or aluminum (Al).

Photo 9.1 The electrolytic cell working on a piece of brass (cathode) in contact with a piece of galvanized steel sheet (anode) in electrolyte NaOH 0.5 M; Archaeometallurgy area, Metallurgy laboratory, UTN FRM University

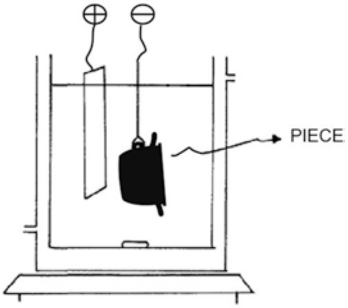

Fig. 9.1 Scheme of the electrochemical cleaning process

Cathode: piece.
Electrolytic solution: 1% NaOH (in aqueous solution) or THF + 10% NaCl (in aqueous solution).
Current density: from 50 mA/dm^2 to 1 A/dm^2 (most of these values depend on the cell equipment used).
Electrolysis time: 2–48 h (depending on the state of the piece).

After this electrolytic reduction process, the process of preserving the treated parts from subsequent corrosion occurs, it is a consolidation stage. Once the cathodic restoration stage is finished, the piece should be washed and rinsed only with plenty of clean water several times until the electrolyte remains from the previous step are eliminated. Then, a thermal drying is carried out (with a hair dryer or similar) and gives very good results. This stage must be detailed since all remaining water from the wash or moisture must be eliminated. Here, carry out the drying of the piece with patience and in detail. (see in Chap. 12: Cases Study: "Conservation of Historical Copper Coin from 1853 Rescued in the Is Fort May 25 Village, Mendoza").

Finally, it is about protecting the part from further corrosion and a product that works very well and is practical is the aerosol metal varnish because it provides a film that protects the part from the environment.

Cleaning Methods by Conventional Chemical Route

A review of the methods of treatment and cleaning of archaeological pieces, or belonging to museum collections or private collections and even industrial heritage by the procedures conventionally used indicate that the cleaning of any object involves carrying out three stages:

(a) Previous treatment of the piece.
(b) Cleaning the object.
(c) Consolidation of the piece.

(a) *In the first phase*, free the piece of products and adhesions foreign to its own nature.

Among the most common procedures is the treatment by rubbing with a small brush (it can be similar to a toothbrush) after having subjected it to a prolonged bath with citric acid that is less invasive. In other cases, adhered materials are removed by using scalpels and steel punches.

Finally, a more sophisticated method requires an ultrasonic bath which, through vibration, helps remove the rust. In all cases, the treatment should be carried out by experts, as there is always the risk of fracture of the piece.

(b) *The second phase* is the cleaning of corrosion products.

There are different cleaning procedures that are used according to the nature of the object to be restored and according to the nature of the corrosion products.

- For iron pieces, the most used methods are:

– Treatment of the piece with oxalic acid. In this way, the oxides dissolve by forming complexes with the oxalate ion.
– Treatment of the piece with semi-neutralized citric acid.

- When the parts are made of bronze, the cleaning procedures are diverse and mainly focus on chloride corrosion. Stand out among them:

– Sodium sesquicarbonate method (mixtures of sodium carbonate and sodium bicarbonate): Allows the elimination of chlorides and protects the piece from humidity by forming a layer of a basic copper carbonate.
– Rosenberg method: It transforms insoluble copper salts into other soluble ones. When the pieces present deposits of calcium and magnesium salts, the Calgon method (sodium hexametaphosphate) is used, which disintegrates the calcareous deposits although very slowly.

- On gold and precious metal pieces: mineral salt stains are removed with mixtures of sulfuric acid (SO_4H_2), hydrochloric acid (ClH), and sodium hypochlorite (ClONa).
- In lead parts, corrosion products are eliminated by dissolving them with ammonium acetate ($C_2H_7NO_2$).
- Silver pieces showing corrosion products such as copper salts or silver sulfides (S_2Ag) are cleaned with formic acid (CH_2O_2) and sodium bicarbonate ($NaHCO_3$), respectively.

(c) The third *phase* is the consolidation of the pieces.

The aim is to preserve these from subsequent corrosion and to try to remedy the fragility of the piece due to the energetic treatment carried out in the previous phase. A first stage would be thermal drying (hair dryer works well) in order to eliminate the water after washing the pieces. Subsequently, it is about protecting the piece from further corrosion, especially in cases where the piece has suffered strong chloride corrosion (bronze pieces). After removing the chlorides, the piece can be protected by treatment with benzotriazole ($C_6H_5N_3$) [5, 6]; if the corrosion has been by pitting, we first clean the foci of chlorides and then fill with silver oxide (Ag_2O) [7, 8]. Finally, a treatment with aerosol resins, acrylic copolymers, and metal varnishes provides a film that protects the part from the environment.

Comparison with Electrochemical Methods

By means of the previous brief exposition, it is easily understood that these methods are expensive and that they have to be carried out by expert hands, being in any case aggressive when they are not harmful to the piece itself but are carried out with special care.

This without taking into account that the piece undergoes various cleaning phases the risk of deterioration increases and with it also the times of completion of the restoration. In short, the latter are aggressive, expensive, and time-consuming methods. However, cathodic restoration (electrolytic reduction) has great advantages over traditional chemical methods that could be summarized as:

1. The use of abrasive products that deteriorate the surface is avoided.
2. Due to the reduction of protons, hydrogen is released and this bubbling is capable of cleaning the surface of the object (there is therefore no need to clean the parts beforehand).
3. There is a great saving of time in the restoration: by these methods, cleaning a coin, a helmet, or a kettle is done in a matter of hours and not days according to traditional methods.
4. The procedure can be easily automated; many parts can be treated simultaneously by using cathodes designed for this purpose, and obviously placing the parts in different trays and considering the differences in potentials that are going to be applied.
5. The procedure is cheap and faster than traditional chemical methods and in my opinion expert personnel are needed to put it into practice, although the part is always protected by the current itself (since it acts as a cathode), that is, there is absence of electric risk. However, it is necessary to know the particular practice and its implications, such as: the type of electrode to be combined, taking into account the electronegativities of the different metals, depending on the piece to be cathodically restored, or that will be subjected to electrolytic reduction.
6. The electrolytic cell can be used both in the laboratory and it can also be transferred to the place where the pieces are located, that is, to work in situ, in the case of objects that, due to their size or museum regulations, do not whether it is allowed to take the piece to the laboratory or, for example, if the case is a monument, the method is reliable and adequate to work on the spot.

Electrolytic Reduction or Cathodic Restoration of a Historical Cuirassier Belonging to the “Governor’s Guard of Honor” (1910)

This electrolytic reduction process was carried out during 2017 by request for cleaning and restoration by the Regional and Americanist Museum of Luján de Cuyo, Mendoza, Argentina. These two pieces of uniforms of French origin (Cuirassier) correspond to one of the 24 uniforms acquired for the mounted police of the province of Mendoza, who were in charge of the bodyguard of Governor Emilio Civit (1910), consisting of a nickel-plated copper helmet, with long white or black ponytail (white for junior staff and black for senior staff) as appropriate, plume with red or white feathers (white for junior staff, red for senior staff) shell consisting of breastplate and lightweight metal back (aluminum) between copper plates and both nickel plated (Photos 9.2, 9.3, 9.4, and 9.5).

General Considerations After Cleaning Historic Metallic Objects

Once the metallic object has been cleaned, it is necessary to protect it against a subsequent attack from its environment, for this there are two possible options:

1. Intervene on the environment: The conditions of temperature, ambient humidity, solar, or artificial irradiation will be controlled.
2. Intervene on the object:
    (a) By creating an inhibition layer, by stabilizing, or modifying the alteration products.
    (b) By the formation of a natural protective layer “patina,” by means of controlled chemical attacks that will react with the metallic substrate.

Photo 9.2 Bodyguards shell before the electrolyte reduction treatment

Photo 9.3 Bodyguards shell after the electrolyte reduction treatment

Photo 9.4 Helmet before the treatment

Photo 9.5 Helmet after the treatment

(c) By forming an artificial protective layer, provision of a protective coating based on natural or artificial products that act as a sacrifice or barrier.

At this point it could be said that conservation–restoration can be divided into two main parts: Preventive Conservation-Restoration and its Treatments.

Preventive Conservation–Restoration

This part is linked to the study and control of the causes of deterioration to prevent or minimize the damage of metallic objects, whether they are museum collections, private collections, or the type of industrial heritage that the latter are currently opening up to society. The community to show and share the working human being, their awareness of work, and their environment. Moisture is the main cause of damage to metals. Its role is very important in most chemical deterioration processes, because it favors their deterioration. The most sensitive are copper and iron; the former usually has small green spots and the latter rusts. Metallic objects are best preserved in a very dry environment, with ambient relative humidity levels below 40%; while iron in particular needs relative humidity levels below 20%. It is important to point out that the ambient relative humidity level is constant since fluctuations are not advisable. Temperature affects relative humidity; therefore, this is the reason why it must be controlled and maintained at a constant level. A desirable temperature would be between 20 and 25 °C.

Treatments

Undoubtedly, methodologies and scientific advances should lead to reaching interventions where professionals from various areas participate and with well-achieved protocols that are applied methodically and appealing to the scientific criteria of the process. The conservation and restoration of cultural property is the set of processes dedicated to the preservation of material, historical, artistic, and cultural aspects implicit in an asset, prolonging its permanence.

The work of conservation of the metallic heritage includes from the legal protection, the registry, the investigation, the cultural management, the restoration, the museography, the diffusion and the investigation on the manufacturing process, the degradation mechanisms, and the improvement of the techniques. Carrying out interdisciplinary and inter-institutional work achieves the best use of human and material resources, making the study and conservation of cultural heritage more profitable.

In addition to what was previously described in the cathodic restoration technique for pieces of copper, bronze, and brass, other restoration protocols are added, and conservation of historical metal pieces manufactured in cast iron such as colonial cannons, bullets, artillery material, statues, and fountains.

Conservation of Artifacts Belonging to the Colonial Artillery: Cannons

The state of conservation of the canyons depends on several factors: their origin and the position in which they were in their original context, whether it was marine or terrestrial; their current location in the exhibition site (presence of vehicular traffic, time of incidence of sunlight, dry or humid climates, proximity of saline atmosphere, pollution, and damage due to contact), as well as the time they have been exhibited, the treatments of stabilization to which they have been subjected and whether or not there was any conservation or prevention process, together all these data make up the history of the piece.

The barrels were manufactured with mostly gray sheet iron also called cast iron. The castings are iron–carbon alloys with a carbon (C) concentration greater than 1.7%. In addition to carbon (C), they contain as constituent elements: silicon (Si), manganese (Mn), sulfur (S), and phosphorus (P) (these last two are considered impurities). The relative amounts of silicon (Si) and manganese (Mn) influence the properties of the cast iron.

As it's explained on Chap. 7: Corrosion on Ancient Metals, metallic materials tend to return to their original state, that is, a state of lower energy, for which they combine with other elements in the generation of iron oxides and hydroxides that form a thick layer, with lower density and greater volume than that originally presented by metallic iron. Some materials will be better preserved than others and this depends on several factors, including: their original origin and their current place and here several variables arise that must be taken into account in a stabilization treatment, conservation, maintenance, as well as conservation preventive in order to avoid greater damage to the colonial historical pieces.

It could happen that the conservation proposal is in a certain way opposed to the restoration theory with regard to the removal of corrosion products, which could be considered as a natural patina of the cultural property. However, the intervention is justified when it is possible to back it up with scientific research that guarantees to prolong the life of the property. In the case of a good manufactured in iron, which thermodynamically tends to deteriorate, the intention of the restorer, conservator, engineer dedicated to reverse engineering, and archaeometallurgy should focus on reducing the kinetics, that is, reducing the rate of degradation of the material since it is well known that corrosive processes are unavoidable and preserving the forms, inscriptions, seals, and engravings on the metal as relevant historical information. In this sense, the most important thing applied to the conservation of canyons from the colonial period is to consider each one as a unique nonrenewable asset and that any minor intervention that seems deserves research and scientific justification prior to its execution.

Generic Direct Conservation Protocol

Direct conservation is based on all those processes and treatments that are carried out directly on the original material in order to delay its degradation. The direct preservation proposal is to create an artificial oxide layer on the healthy metal. This layer will later be stabilized with a rust converter. The treatments are listed in detail below:

1. **Cleaning and removal of corrosion products by mechanical means:** In this process, the objective is to remove all corrosion products that are not well adhered to the barrel, trying to leave only a thin layer of well adhered and compact corrosion products. In these cases, it is necessary to eliminate the thicker areas of oxides following the theoretical guidelines previously proposed and thus respecting the historical evidence regarding the original shape of the canyons.
2. **Washing of the barrel with distilled water under pressure:** For this process, a pressure washer is used to expel the distilled water under pressure. The objective of this washing is to eliminate any pollutant particles and soluble saline compounds that could be deposited on the metal surface during its exposure to the atmosphere.

   In some canyons, it may occur that drops of orange-colored water are formed locally. This pattern is representative of canyons that degrade faster due to having chlorides. The washing can be repeated as many times as necessary until the formation of these drops is not observed. It is necessary to mention that if the barrel core is uncovered, the interior is washed in the same way. It is important that distilled water is always used as it is not harmful as it does not have dissolved anions and salts that can affect the material itself and that could increase the rate of degradation of the barrels.
3. **Drying:** This process consists of eliminating excess moisture from the barrel washing in order to facilitate drying. An industrial vacuum cleaner, industrial cold air dryer, or air compressor can be used for this purpose. The intention is to blow air under pressure on the surface of the barrel, both external and internal (if required) to eliminate excess moisture, especially when the corrosion products present some cracks where moisture can be stored. Subsequently, it is left to dry naturally to proceed to the next treatment.
4. **Elimination of chlorides by electrolytic reduction or cathodic restoration:** According to the bibliography, the elimination of chlorides present in the pores of the corrosion products is pertinent when the layer of corrosion products is greater than 3 mm thick. The treatment consists of connecting a direct electrical current to the barrel as a cathode and a stainless steel sheet as anode. As electrolyte solutions in distilled water can be used, such as 1–5% sodium hydroxide, 5% sodium sesquicarbonate, or 5% sodium carbonate. This treatment can be done by immersion of the barrel or with electrolyte-impregnated cotton pads where the pad separates the barrel from the steel sheet. With the application of current, a reduction reaction is initiated on the surface of the barrel moistened with the electrolyte, releasing hydrogen that is observed as bubbling. This release

of the bubbles causes the detachment of the corrosion products; therefore, doing this stage in a controlled way of its variables does not damage the piece. It is for this reason that in electrolytic reduction the state of conservation of the part, the conductivity of the electrolyte, and the voltage and amperage of the applied current must be considered. The recommended voltage in the literature is 12 V/dm^2 (V) and 10 A/dm^2 (A) at the surface of the iron cathode [9], but it is important to take caution in these values due to the resistance of each cell.

This will also depend on the electrolytic cell equipment available and its limitations in terms of these parameters so as not to damage the equipment, and another very important aspect is that the regulation of the current intensity must be controlled and be taken seriously into account. Since corrosion processes and complex reactions can be generated in the sediments that pass into the electrolyte solution, these reactions are very complex and generate products that damage the material. After the electrolytic reduction or also known as cathodic restoration, it is pertinent that a pressure wash with distilled water is carried out again.

5. **Formation of an oxide layer:** To form a thin oxide layer on the metal surface, apply a 1 M nitric acid solution. This procedure must be carried out by areas of 25 cm^2 and applying nitric acid with a dropper. Once this solution penetrates through the corrosion products, a slight effervescence is observed as a result of the release of hydrogen as part of the oxidation reaction.
6. **Brushing and drying:** The area to which the nitric acid solution was applied is immediately rubbed with a small plastic bristle brush and dried with absorbent paper and/or hot air with a hairdryer for greater homogeneity, and it is even more suitable since it would not leave fiber residues in the material as in the case of paper.
7. **Stabilization of corrosion products:** After the execution of the two previous points, a solution of tannic acid in 5% methanol is applied with a dropper. Corrosion products may change their color to dark gray and purple tones with this process. Tannic acid acts as a rust stabilizer/converter by converting iron oxides into ferric phosphates and tannates that have greater resistance to degradation. Depending on the case, a layer of 2.5 ml phosphoric acid is applied to lower the pH [10].
8. **The chemical procedure:** Described in points 4–6, it is repeated for every 25 cm^2 of the barrel until its entire surface is stabilized.
9. **Final stage of treatment:** Apply a layer of the tannic acid solution with a thin brush. For a preventive restoration of these artillery pieces, it is advisable to apply protective wax with cloths that acts as a barrier between the environment and the material, metal varnish can work well in this case, apply with an aerosol because it generates a homogeneous distribution on the surface and avoids the bristles of the brushes because they would leave marks.

The application time of the wax can be every 2 months, but it will depend on each region, the climate, and other variables where these artillery weapons are exposed. This complete treatment requires full maintenance every 3–5 years.

From the Recommendations to Take into Account for Storage and Exhibition in Museum Rooms

This activity represents a great risk of accidents both for people and for the gun in question, so its execution must be planned and provided with all the necessary human and technical resources.

During handling, you should never exert pressure on projecting areas and avoid placing the piece directly on the ground. The use of work gloves is pertinent for the safety of the worker and the barrel.

The ideal parameters for the conservation of metallic objects oscillate between 20 and 30 °C of temperature and 15–40% of relative humidity.

In spite of this, as a recommendation, it is possible to select a place to display the canyons at a minimum distance of 1 km from the coastline, if applicable, to avoid the contribution of chlorides by breeze and marine aerosols and not exhibit them in a place that is heavily trafficked by motor vehicles that promote the deposit of polluting particles such as sulfates that accelerate corrosion (Photos 9.6 and 9.7).

If the cannons are to be displayed or stored inside a building, it is advisable to take care that the relative humidity does not exceed 70%. The use of dehumidifiers could be useful depending on the case (Photos 9.8 and 9.9).

If the storage room or showroom has air conditioning, it will be necessary to consider the ideal parameters for the conservation of metal objects and that this system works 24 h a day to avoid drastic fluctuations in relative humidity and temperature.

Photos 9.6 and 9.7 Images of historic cannons from San Carlos Fort Museum, (Uco Valley, Mendoza, Argentina) before its restoration

Photo 9.8 Image of one of the cannons. Courtesy of the San Carlos Fort Museum, (Uco Valley, Mendoza, Argentina) after its restoration

Photo 9.9 Cannon restored and on display. Open gallery of the museum as an assigned place for exhibition. The images courtesy of the San Carlos Fort Museum (Uco Valley, Mendoza, Argentina)

Conservation of Statues and Monuments of Foundry

Photographic survey: A photographic survey of the total set of the monument is carried out in detail of all its components and other ornamental, structural and fixing elements. In addition, the different physical, chemical, and biological deteriorations detected are photographed.

Materials testing: If it is necessary to melt missing parts of the monument or statue, the metallographic and chemical analysis of the material that constitutes it must be carried out to determine the chemical composition and metallographic structure of the foundry material. This helps in determining the type of casting. This study must be certified by a qualified institution in order to cast the missing parts with their original materials and determine the type of electrodes to be used in the joint welds.

Analysis and Diagnosis

Deterioration due to degradation of the material: Analyses of the deterioration of chemical (smog and rain) and biological agents (fungi and moss) of the constituent material of the monument or statue must be carried out. The chemical and biological analysis will consist of a microscopic study in order to determine how to eliminate the aforementioned deterioration agents from the casting material, and how to stop their formation by applying certain products that do not affect the casting and that are compatible with the paints and patinas to be made. All the aforementioned studies must be duly certified by institutions or professionals authorized for this purpose.

Protocols of Intervention Properly Said

General cleaning: General cleaning of the entire work will be carried out, removing at this stage the smog, dust, bird droppings and mold accumulated on the surface, ornaments and other elements that make up the set.

This cleaning will be done as follows: A manual system will be used by using cloths of medium weft, moistened with water, being able to add detergent in a proportion of 1–20; soft bristle brushes of different sizes according to the sector of the monument to be cleaned and gouges (double-blade steel stakes) and without awl (the models to be used will depend on the removal to be carried out according to the sector or figure and details of the work to be intervened).

Removal of patinas: An analysis of the different patinas used in the work, monument, statue will be carried out, in order to determine how to remove each one of them. It is totally forbidden to sandblast or treat with chemical solvents in this type of works of art because they directly affect the casting material.

Depending on the types of patinas and the sector to be intervened, they are removed as follows:

1. Cleaning the total surface.
2. Application of liquid or gel remover, leaving to act for 5–20 min. Always using products of recognized quality.
3. Washing with water (in the case of gel remover) or with solvent (for liquid remover), without leaving any residue of remover on the surface.
4. Apply as many coats of stripper as there are coats of paint on the work, carefully removing it, leaving no residue. For this action, the following products can be used, such as detergent diluted in water with a 1:20 ratio, double sheet steel stakes, without a punch, rolls of light steel wool, heat gun from 250 to 500 °C.

Important Clarifications

Remover: It can only be used on surfaces of 0.05 m^2, acting quickly, and removing the remains that could have a negative effect on the cast material of the sculptural work. In vertical and inclined elements, it is advisable to use the gel remover. The liquid stripper can be used on horizontal surfaces, where runoff does not occur and can be controlled. In all cases, the removal mode is done manually.

Removal of Oxides, Agents, Chemicals, and Biologicals

(a) Oxides

- Brush the surface until all loose oxide is removed (a soft bristle brush will be used that does not damage the cast material of the work and thus does not modify the expressions in the figures).
- Clean with a copper-free phosphate deoxidizer and allow to dry (one part of deoxidizer will be dissolved in four parts of water). It is applied on the surfaces of the figures, plates, ornaments, and other integral elements of each work in particular, with a brush or cloth, rubbing until all the rust is removed.
- Rinse the cleaned surfaces with water and dry.

(b) Fungi

- First a chemical analysis to know the type of fungi existing on the surface of sculptural works, as already specified in previous paragraphs.
- Clean the surface by hand rubbing with a fine and medium weft fabric, and using soft bristle brushes.
- The chemical products to be applied (according to the types of fungi detected in the analyses carried out), which should not affect in any way the original casting material of the work, to eliminate all remaining fungi and inhibit the formation of new fungi and other biological agents.
- By manual and gentle friction with water-based sandpaper N°20 or less, the existing remains of fungi will be removed.

The removal products to be applied must be compatible with the paints and finishing patinas to be applied in the sculptural works, in this case of casting, in order to achieve the correct adhesion on the surfaces to be treated. In all cases, the removal method will be manual by using medium-weft cloths moistened with water and the aforementioned products, soft bristle brushes of different sizes depending on the sector of the work to be cleaned, and double-blade steel gouges, without punch. The maximum time that must elapse between the cleaning and removal of fungi, paint and oxides, and then the placement of the first coat of anticorrosive paint, should not exceed 45 min.

Anticorrosive protection: Then, an inhibitor will be applied compatible with the foundry material of the work itself and the finishing paints to be made, as protection against the action of any chemical and/or biological agent. Then, apply a coat of antirust paint (60 μm minimum thickness when dry) using a brush and/or roller (to reach all the corners, moldings, reliefs, and folds of the figures of the sculptural work) letting it dry for a minimum of 12 h or according to the specifications of the material used to then apply a second coat of anticorrosive protection. The maximum time that must elapse between the cleaning operation and the placement of the first coat of anticorrosive paint will not exceed a period of 45 min. Later, the final finishing painting will be done according to specifications.

Finishing painting: The painting works are carried out with all the necessary precautions, and the surfaces to be painted must be sealed, cleaned and neatly prepared, any defects that may occur will be corrected before starting to paint and the work must be carefully retouched once completed. At least three coats of paint will be applied and, if necessary by default, successive coats will be applied until a satisfactory job is obtained. The last coat of paint is done after all the work teams participating in the intervention have completed their respective work. Prior to the execution of the first coat, the samples required for the inspection of the progress of the work are carried out in each and every one of the parts. According to each case, in addition to what has already been specified, the necessary layers are made to achieve a perfect finish.

Materials: The materials to be used will in all cases be of the best quality in their class, and must be brought to the job site in their original containers and provided with their guarantee seal. The time that must elapse between each coat of paint will be strictly 24 h. The ambient temperature should not be less than 10 °C, the relative humidity of the environment not greater than 50%. Paint chambers are built on site to achieve these values. For the preparation of the paint, the manufacturer's instructions will be strictly followed. The curing and commissioning period will not be less than 7 days. For the application of the paint, the Air-Lees system (airless torch) will be used. To cover the joints well, you can use a good quality brush or roller.

Patinas: Based on what has already been specified, patinas are made to highlight figures, details ornaments, lights, and shadows in order to revalue the work. The type of paint used for the patinas will depend on the base paint used.

Finishing lacquer: A final finish will be given by applying two coats of reversible polyurethane satin varnish. The application will be done by brush and/or roller so that it covers the entire surface of the figures, ornaments, and other elements that make up the work and/or sculptural group.

Industrial Museums and Their Relationship with Conservation–Restoration Processes

Industrial heritage: Since the end of the twentieth century, there has been a proliferation of initiatives for the conservation of industrial heritage. These had a double function: on the one hand, to reintegrate this heritage into the leisure cycle of post-industrial society, and on the other, to generate industrial tourism products. In short, activate the cultural consumption of industrial heritage.

Industrial museums as places of memory: The postmodern tourist is interested in the culture, the landscape, and the signs of identity of the places he visits. Thus, cultural heritage becomes the tourist destination within which industrial tourism is framed.

This is a social demand that has caused some of the vestiges inherited from times of industrialization to become witnesses of an era and contributors to the collective memory [11]. This heritage is closely related to the mechanical age and scientific thought of the moment, which gives it a unique character within the historical heritage.

An industrial museum expresses specific characteristics such as: homogenization and standardization, both of objects and construction materials, its massive character and finally contains a strong didactic content.

The industrial museum, therefore, must teach the operation of the machines, the working conditions of the workers, the manufacturing processes used, the materials used in the construction of the artifacts, the way of life of the various social classes, and the role of individuals in the process of production and work.

The industrial museum is an element of revaluation of the cultures of the historical industrialization of the area in which it is located, at the same time that it must reinforce the forms of collective behavior within the territory in which it operates, the industrial museum represents the memory of the industry of an age. The same can be expressed of the new railway museums, many of them located in former train stations of my beloved Latin America, where the towns were abandoned and stagnant in time due to the absence of the train, which at one time symbolized progress and commerce of regional products, as well as the arrival at the port for export of these products from the interior of the country.

Hence, an industrial museum and/or a railway museum. As an example, they are witnesses of times where it is shared and observed making us part of their previous ways of living, of their daily life, with their customs, they even fulfill didactic roles since they teach the tourist, the students of the schools and that the general public know part of its past and all these initiatives must be supported and sustained over time, so that they can last generation after generation.

Ultimately, industrial and railway museums can become the living memory of the cultures of historical industrialization and their implementation does not depend so much on the abundance of economic resources available to the administration for their execution and maintenance, as on a large measure of the will of the latter to bet on more sustainable and social management models.

Acknowledgments The author of this work wants to give special thanks to the staff of the Regional and Americanist Museum “Saint Rose House” from Luján de Cuyo, Mendoza and to San Carlos Fort Museum from Uco Valley, Mendoza, Argentina, for their collaboration in this researching work.

References

1. Gianini, C.: “Dizionario del Restauro”, Firenze, Italy, p. 152 (2003)
2. Bakula, C.: Cleaning and Preservation of Coins. Museum of the Peru Central Reserve Bank, Memoria de ICOMON Proceedings: Stavanger Noruega, (1995); Viena Austria, Museo Casa de la Moneda (1996)
3. Cronyn, J.: The Elements of Archaeological Conservation. Routledge, New York (1990)

4. Aldaz, A., España, T., Montiel, V., López Segura, M.: A simple tool for the electrolytic restoration of archaelogical metallic objects with localized corrosión. Stud. Conserv. **31**, 175 (1986)
5. Fleichsmann, I.: The synergetic effect of benzylamine on the corrosion inhibition of cu by benzotriazole. Electrochim. Acta. **28**(10), 1325–1333 (1983)
6. Genin, G.: Corrosion, nettoyage et protection des structures artistiques. Revue de la Societé Royale Belge de Ingenierie Industríale. **2**, 72–77 (1977)
7. McCroy-Joy, C.: Modification of electrochemical behaviour of cu by azole compounds. J. Electroanal. Chem. **136**, 105–118 (1982)
8. Angelucci, S.: Pitting corrosión in cu and alloys: comparative treatment tests. Stud. Conserv. **23**, 147–156 (1978)
9. Plenderleith, H.: La conservación de antigüedades y obra de arte. Oxford University Press, New York (1967)
10. Novegil-Anleoa, J., Beltrán, J., Minotasa, J., García, K., Moralesa, B., Pérez, G.: Acción de los convertidores de herrumbre en óxidos de hierro. Revista Colombiana de Física. **1**, 37 (2005)
11. Santacreu Soler, J.: La recuperación del patrimonio industrial de la Europa comunitaria: balance actual y perspectivas. In: Campos, C., Ramos, M., Martín, M. (eds.) Arqueología industrial (notas para un debate), pp. 39–70. Universidad de Málaga, Málaga (1992)

Chapter 10
Antique Metal Welding and Reparation

Patricia Silvana Carrizo

Forge Welding

Forge welding is a process of joining two metals by means of heat or pressure and is defined as the metallurgical bond between the atoms of the metal to be joined and the filler metal. The oldest welding process is forge welding [1]. This consists of heating the pieces to be joined in a forge, and then by means of pressure or knocking, the joining of the pieces is achieved. Its limitation is that it can only be applied in small pieces and in the form of a sheet. The union is made from the center of the piece to the outside of the piece and it is important to be careful in order to avoid oxidation by parts or the whole piece, it is in this sense that thick oils are used together with the flux material. To comply with this, the use of borax combined with ammonium salt is common.

History of Forge Welding

Forge welding is the first type of welding to appear in history. The earliest examples of forge welding date from the Bronze Age and Iron Age in Europe and the Middle East. Forge welding was used in the construction of the Iron Pillar of Delhi, India, built around 310 AD. The Middle Ages brought advances in forge welding, with which blacksmiths repeatedly struck and heated metal, until the union occurred.

There was even a joining method that was used in conjunction or combined with forging welding called “embedded”, which is the method of joining by embedding, by which metal pieces were cut from an area and interlaced or embedded with metal pieces from another area, for example, the bottom of a container was embedded and

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P. S. Carrizo (✉)
Archaeometallurgy Area/Metallurgy Laboratory, National Technological University,
Mendoza, Argentina

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_10

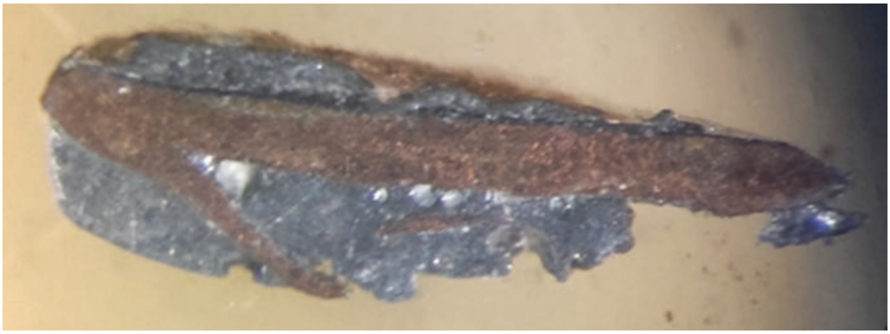


Photo 10.1 Forge welding of the side wall-body of the old pot seen with a stereoscopic magnifying glass. Archaeometallurgy Area, Metallurgy Laboratory, UTN FRM

these cuts of the bottom of the container were embedded with the cuts made in the wall of the container, with this technique it was achieved that the bottom of the container was closed, and in this way the pieces remain united and closed; in this case it is important to note that no third bonding material was included. Then, the sealing was carried out by forging welding and this was the final touch to avoid spills and ensure that there were no liquid leaks (Photos 10.1 and 10.2). (See in Chap. 12: Study of reverse engineering cases: “Metallurgical, historical and patrimonial study of contemporary copper pieces to the Liberation Army of San Martín”).

In 1540, Vannoccio Biringuccio published “De la pirotechnia” [2], which includes descriptions of the forging operation. Renaissance artisans were skilled in the process, and the industry continued to grow over the following centuries. Welding was transformed during the nineteenth century and until the end of that century, the only welding process was forge welding, which was later replaced by other types of welding with the advancement of knowledge and technology.

With this concept, we find that progress continued through rivet joints, especially in railway and bridge structures, both road bridges and railroad bridges, it has been an accepted and used technique over time, which gave very good results and all this prior to the advent of welding and its processes as we know it today. We can cite some examples of these old structures that are still in service, among others: the Eiffel Tower in Paris - France, which was manufactured with puddled iron and mounted with hot rivets, another example is road bridges and railway bridges and rivet-assembled fuel tanks in refineries around the world. (See in Chap. 12: Reverse engineering case study: “Archeometallurgical and heritage study in the Iron Bridge over the Mendoza River”).

Antique Metal Welding

To begin to address this type of old and in-service structures that need maintenance and knowing that welding is a current and versatile resource that helps with their maintenance. The first important factor is to know that each material to be welded is

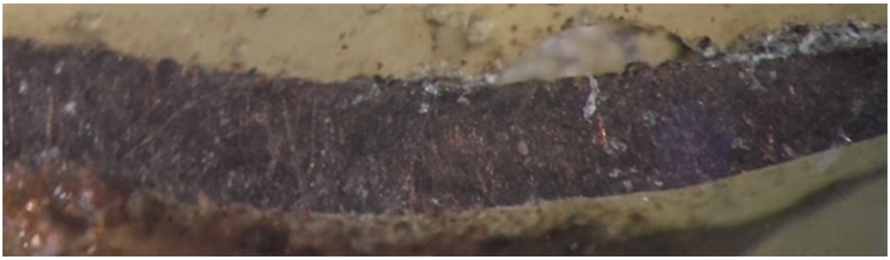


Photo 10.2 Encasting and forge welding technique of the base zone of the old pot, Archaeometallurgy Area, Metallurgy Laboratory, UTN FRM

different from the rest and each matrix must be previously analyzed to answer the following questions: With what base material should I weld? and How should I weld it?

In old or unknown materials, it is first necessary to carry out a chemical test by means of x-ray spectroscopy, it consists of a non-destructive, rapid test and with portable equipment. It is also important to verify the mechanical properties of the material to be welded and what service it provides.

Generally, in the case of cast iron or steel plates and welding contributions, there are currently standardized materials in international codes, predominating the ASME code, both for the materials in Ferrous Bases Section II part A and for the materials in Non-Ferrous Bases Section B, while the contribution materials are specified in Section II part C.

In the case of maintenance of oil tanks manufactured with rivets more than 70 years ago, and their repair by welding is desired, first the chemical composition, service temperatures, cyclical loads, etc., among other variables, must be taken into account. This is why each case must be analyzed in a particular way before starting the welding work, the aforementioned factors must be taken into account. Another significant example of repair by welding, is the repair of a metal road bridge, it must be taken into account when welding the old material damaged by shocks that the material to be replaced is as close to the original material of the bridge as possible. It is essential to carry out a chemical composition test using a portable XRF equipment, in order to avoid the appearance of galvanic corrosion. It is very important to take into account the stresses to which the bridge is subjected, such as: vibrations due to traffic, all this must be taken into account before welding the material. As preventive maintenance and to control the quality of welding, specialized technicians carry out non-destructive tests of penetrating inks, magnetic particles, analysis by X-rays, etc.

As for the welding processes themselves, there is a great variety of alternatives, taking into account the thickness to be welded, the expected performance of the work, type of base material, and so on.

In this way, one of the alternatives if you are working with small thicknesses (up to approximately 5 mm) and with pieces made of bronze and aluminum: the TIG process in alternating current gives good results because it facilitates the regulation of electrical values. As a domestic example of aluminum welding we have: the repair of the kettle for boiling water of the grandmother or the statuette of a souvenir angel of three previous generations, surely manual TIG welding is a good option. While electric arc welding and coated electrodes are not recommended, since it is very difficult to maintain low amperage and the resulting electric arc is more aggressive and could damage the part to be repaired.

Now, if I have to carry out a repair work on the statue of a walk in my city and this statue has a significant thickness, the option to choose for its repair is: normal welding with aluminum-coated electrodes or a recharge with a process semi-automatic continuous wire [3].

This concept is also valid for the brazing of copper, bronze and their alloys. As an example of repair by welding and from everyday life is the repair welding of football championship trophies (perhaps a memory of the grandfather), the bedside table lamp that is a received inheritance. These are thin materials and in these cases low regulation electrical values predominate, and therefore TIG welding is a good alternative.

In this first part of the reading, the objective is to understand that each weld must be analyzed individually.

– Therefore, a good practical guide is to know:

What base material should I weld? (Knowing the base material). I analyze the chemical composition, mechanical properties, the loads and temperatures in service, and all the technical data that can help me know the base material.

With this data I determine: What filler material should I use? (Selecting the filler material). I analyze filler material alternatives, according to the data about the base material and the welding process that I am going to use.

With these data I select: What welding process to use? (I select the process). I analyze the type of base material, thicknesses, welding temperatures, welding access and welding requirements, available equipment (machines), and the ability of the welder to carry out the repair or joining work itself. As an example, a manual welder who does not know how to weld with semi-automatic or automatic is limited to manual welds only.

Dissimilar Metal Welding

This type of material is found in very old pieces that may have been damaged and may have a fracture that is the product of a previous crack. This is important information, since if there is a fracture it means that the part can be welded. It should be clear from the outset that a crack is not admissible in any case.

To develop this task, first, we must have a rectifying machine, which is commonly called an “inverter”; common or old (large) transformers are not useful because we work with special electrodes that work with alternating current, and we need equipment that sends direct current and rectifies it.

Second, we have to have some electrodes that can play with various variables.

Generally, we grind the area, clean it well with a solvent at the beginning, and take care that the solvent evaporates so as not to run the risk of fire on the part or damage to the welder when the electric arc is lit during welding. It is recommended to blow with a blowtorch to aerate, that is, to take the appropriate precautions (using all the safety elements). It is also advisable in these cases to work in the old-fashioned way, that is, with a bucket of dry sand. Once complete cleaning has been carried out and the surface is completely dry, proceed to grinding.

It can be unknown steels, as well as high-, medium-, or low-carbon steels. It may so happen that the percentages of the chemical elements are unknown and perhaps a chemical composition analysis cannot be performed either. Then, in these In cases, proceed as follows: work with a grinder and through the spark test, depending on the color of the spark, the material with which we are working will be identified.

Recognition of the Various Steel Alloys by the Spark Test

The sparks from the grinding of different types of steel that are produced when polishing a piece on an emery stone have well-defined characteristics. Through the spark test it is possible to recognize if it is a high speed steel, low carbon steel, if it is a hard or soft steel, etc. The spark test is therefore a very simple means of determining the quality of steel. This test can also be performed on finished tools, without damaging them and therefore its application is recommended.

Of course, spark testing is not a substitute for chemical analysis, but today it is considered a very effective method for quickly and easily determining the alloy and classification of a steel. By the spark test, mistakes in the determination of the different grades of steel can easily be avoided.

When doing this test, it is recommended to compare the sparks from the grinding of an unknown steel with those of a piece of steel whose class and alloy are known (Table 10.1).

To perform the spark test, it is recommended to use a medium-grained, hard and dry stone, with a medium diameter of 250 mm, which is preferably located in a dark place and rotates at a speed of 1400 rpm, as well. It must be taken into account that the pressure on the disk changes the amount of sparks and with that change the length and quantity of the rays, as well as the size and density of the sparkles. It is advisable to apply light pressure on the disc. In this way, only thin but well-marked bundles are produced; by applying a higher pressure, we get an abundant image of sparks but it becomes difficult to compare. The tempered pieces do not produce sparks of the same characteristics as the tempered ones, nor the clarity and density of the beams.

Therefore, when performing the spark test, it must be taken into account whether the sparks are superficially carbonless or cemented. The luminous appearances of the rays are of light or dark colors.

According to the latest studies, the formation of sparks is due not only to the rise in temperature or friction in the disc, but also the combustion (oxidation) of iron and

Table 10.1 Identification of alloys from spark test

Designation	Images	Alloy	Lightning color	Lightning shape
High Cr alloy tool steels.		2% C 12% Cr 0.8% W	Orange red	Short spikes with many or few spark bursts
Unalloyed tool steel		1% C	Yellow white	Many explosions of sparks beginning at the foot of the highly branched spike
Tool steel alloyed to silicon and manganese		0.55% C 1.0% Si 1.0% Mn	Yellow	Explosions similar to case 2 In front of the spark explosions, swellings in the main beam and many small side branches
Molybdenum alloy tool steel		0.5% C 1.4% Cr 0.7% Mo 0.3% V	Yellow Orange	Analogous to case 2 but the ends of the rays provided at the tip lanceolate
Tool steel alloyed with chromium, tungsten, silicon		0.9% C 1.0% Si 1.2% Cr 2.0% W	Red Orange	Few explosions of sparks, with truncheons, clear and long
Tool steel with chrome and tungsten		1.0% C 1.0% Mn 1.0% Cr 1.2% W	Reddish orange	Very thin rays, image of live sparks, ends of the rays in the form of tongues
Stainless steel		0.45%C	Orange	Short spikes with bursts of bristling sparks
Unalloyed tool steels		0.5% C	Yellow white	Same as case 1, but sharper

also of the other constituent elements of steel (carbon), silicon, manganese, and so on. Due to this combustion (oxidation), the steel particles become incandescent and melt.

Once we know what material it is, we should have a simple electrode such as E-7018, which is very well known and popular, this electrode should be used if the part is not large. It is tested with this E-7018 electrode, the area is heated between 80 °C – 100 °C and we bring the palm of the hand to a maximum of about 5–10 cm from the surface of the piece and if we support the heat in the palm of my hand for a time of 3–4 s then it means that I can start welding. If the case that concerns us is the repair of a crack then the ends of the crack are drilled, that is, at the beginning and at the end (procedure similar to the repair of castings), this is done with a small wick and determining the extremes: at the beginning and end of the fissure, to prevent its propagation. If the opposite occurs, i.e. there is propagation of cracks, then it means that the material is very hard.

How Do I Know Which Is the Beginning and Which Is the End?

A tactic usually practiced by welding technicians, and especially in welding old parts, is after the cleaning and drying stage of the part, this test is carried out to verify if there are still cracks that must be welded and could be unnoticeable. To do this, the piece or part of the piece is impregnated with kerosene (solvent) and then this solvent is dried with a cloth, then ground chalk is placed on where we have impregnated with kerosene, and if there is a problem of cracking that does not visible to the naked eye, then the ground chalk will get wet, revealing the location and length of the crack being repaired, as well as giving us more information about other possible cracks. Once the length of the crack is determined with this method, the filler is extended 10 mm more as a factor of safety.

These procedures try to keep the temperature of the part as low as possible, in these welding protocols the pilgrim step is carried out, that is, short sections, and welded with cords of only 5–6 cm (discontinuously). This task requires some time to complete and a lot of observation, it is generally not done in a single day, since it is done in very short sections and allowing the material to cool as slowly as possible and using a lighter to heat the piece and its temperature, after welding, decreases slowly and evenly until it reaches room temperature. Many times it is convenient to place the part (if its size allows it) previously welded protected from air currents and to place the lighter so that the entire part falls uniformly in temperature. In the case of not having a lighter or if there is no intention of investing in a repair that increases costs, then you can simply cover the welded areas with welding aprons that are made of cowhide, with the only precaution of waiting about 15 min to prevent aprons from burning. Another option is to cover the newly welded part with dry sand or lime and leave it there until the weld cools slowly.

In order to carry out a guaranteed repair job, a visual verification is then carried out or a penetrating ink test is carried out to verify the absence of cracks. Alternatively, the kerosene and chalk test, which was previously used to verify the existence of cracks, is carried out again. If there are still cracks, then the E-7018 electrode is totally discarded. Then we have two electrode alternatives that we could have access to: the AISI E-312 and the AISI E-309.

It is first tested with the AISI E-309 electrode, which is indicated for stainless steel (Chrome-Nickel) and precisely has better elasticity characteristics than the E-7018 electrode, which stands out a lot for its resistance to traction. Then, it is tested with the AISI E-309 electrode and the same procedure described above for the E-7018 electrode is carried out. This process is accompanied with the hammering of the weld immediately after completion, as well as with the foundries, so very gently with a ball hammer so that the tensions are affirmed. This E-309 electrode has the advantage over other stainless electrodes as it has stabilizers such as Niobium (Nb). This alloying does not allow the particles of the material to combine with those of another material, resulting in a less mixed weld between the two. The materials, therefore, do not produce hard or brittle points and you can reach very good results.

Finally, it is checked if there are still cracks, as in the previous case, and if there are no cracks, it is also recommended to follow up as a control and make a record of what is the appropriate electrode and procedure for that kind of material and part.

Suppose that the weldment cracked, after finishing welding or when time has passed, these cracks can occur in the center of the weld bead or at the edges, and generally appear in the heat affected zone: (HAZ), since this is the transition zone most affected by the heat of the filler material and the base material. Then, to make the repair, the test was carried out with the AISI E-312 electrode, which has the same characteristics as the AISI E-309 electrode, but has a higher tensile strength, that is, it better supports the contractions of the material. In addition, it is important as mentioned above, to keep a record of each particular piece, the type of material and with which electrode it was that the repair was finally possible and without forgetting to carry out periodic checks in order to do preventive maintenance.

It is very important in welding repair work on old pieces that are often made of dissimilar metals, to keep a complete record of the activities and protocols followed in each job, since this type of bibliographic information is not always accessible, an this information is often the product of many iterations, also very expensive information that involves the standards of the art of good welding.

Special Weldings: Cast Irons

Cast iron is an alloy of iron (Fe) plus carbon (C) and its most harmful impurities are phosphorus (P) and sulfur (S). Cast iron in its chemical composition, it has at least 1.7 carbon (C). There are several types of castings, but when it comes to manufacturing, we will find two that stand out: white cast iron and gray cast iron.

The white cast iron has a white tone that is soft to the touch and shiny, and is generally considered insolvable and is practically irrecoverable.

Gray cast iron is very porous, dark and to check if there is breakage we clean it with a light cloth, and if it is stained gray-black it is due to the large amount of graphite in the cast iron. The welding of the cast iron requires certain precautions and experience since it may happen that in the welding of a certain gray cast iron we are successful, but with another gray cast iron we do not succeed in the welding process, this means that each case is particular. Cast iron weldability can be done in two ways: Cold welding and Hot welding.

Hot welding takes the part to be welded to 600 °C and that temperature is maintained throughout the welding process. This operation requires great effort on the part of the welder, especially with elevated ambient temperatures above 40 °C, and one must be very careful with temperature changes since we cannot have a temperature difference between the different points of the piece to be welded. It is a very difficult task to control in the workshop and, therefore, this method is not recommended.

Cold welding: there are two types of cold welding. The first type, which is not precisely a weld, but rather a union by mechanical means of two broken pieces by means of threaded rods, which make up the union elements. The second type is a weld where it is a question of welding but keeping the temperature values low.

Cold welding is a valid procedure either for when we have a total break or simply a crack; it is very important to know that any crack in a weld is unacceptable not only in a material such as cast iron but in any type of weld.

Procedure for Cold Welding

1. Locate the crack with a penetrating ink test in the workshop. Although this test is often not available, there is a fairly accurate alternative: with kerosene and ground chalk, the piece to be welded is washed, dried, and then ground chalk which is moistened is placed in the area of the crack.
2. The ends of the crack are drilled so that the crack does not spread during welding.
3. Then proceed to weld with the pilgrim step, which consists of short sections and welded with cords of approximately 5–6 cm discontinuously, the sequence is established ensuring that the entire welded area is heated uniformly, distributing the temperature.

4. Small sections welded at 50 mm are made and then another bead is made as far away as possible. Then another bead is made at the center and the sequence is followed until the weld is completed.
5. Do not weld above 80 °C, if you do not have special pyrometers, for this reason there is a practical way to evaluate the temperature instinctively, and it is about removing the welding glove and bringing the palm of the hand closer to about 10–15 cm of the welding bead, and if the palm of the hand supports the heat, it means that the temperature is close to 80 °C. But you have to be very careful.
6. Hammer immediately after having welded the weld bead with a ball-type hammer, taking care to only hit the weld to flatten the weld and relieve stress.

There are other more complex and safe techniques, for example doing this welding procedure but without joining the part, it is done by making a bicell grinding in "V" 60°, and weld only in one part of the bicell near the joint and then repeat on the other side respecting all the previous steps and alternating on each side of the (Graphics 10.1 and 10.2).

It is advisable to alternate the welding of both sides of the joint, but without joining the pieces and finally finish with this method between the two beads, thus in this way the welding stresses between the two provided beads, and if a large number of pores appear in the welding it is necessary to carry out a cleaning treatment of impurities such as: Phosphorus (P) and Sulfur (S).

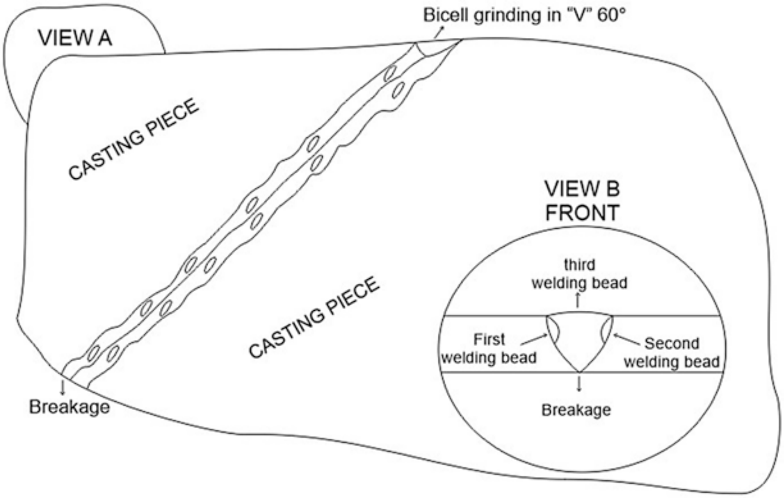
This treatment consists of welding without joining, with the previous sections with a basic electrode E-7016, because its slag attracts impurities, this being one of its main advantages of this electrode. This weld can be started with a short iron or simply run through the grinder and then welded. If many pores still appear in the weld, repeat the technique to remove impurities and then proceed to weld with the appropriate electrode for the material.

The last step is to let the piece cool as slowly as possible in a special oven, covered with special canvases that insulate the piece and allow slow cooling because this step is essential.

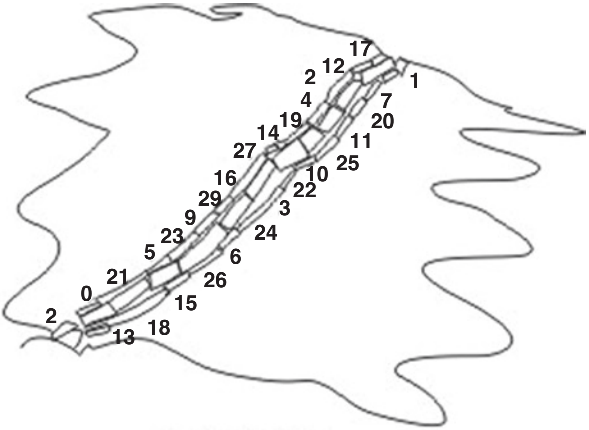
There is a simple and practical method called the "hammer test or method" and it is done to give you some confidence in the welding procedure of cast iron. A necessary and important clarification is that the "hammer test or method" has no bearing on the hammering action of stress relieving welds.

Cast Iron Weldability Test

Often, it would be ideal to have prior chemical analysis from the laboratory, but in many cases it is not possible or on other occasions even with these data it is very difficult to find the so-called "consumables": this refers to the electrode, the rod or ideal roll of wire for welding. For that reason there is a very simple and practical workshop test that allows us to know if the material is weldable or not and what degree of weldability the material has, this test is called: "hammer test or method" and was developed by a company Argentine electrode manufacturer.



Graphic 10.1 Procedure for cold welding

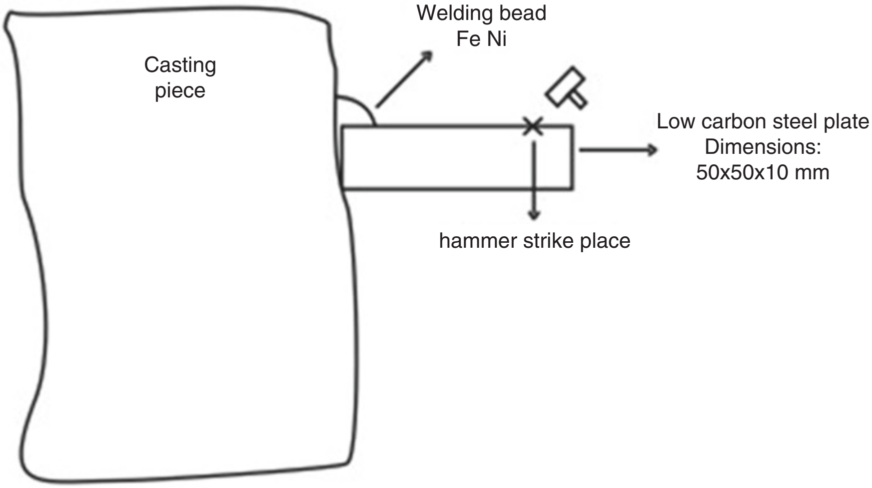


1- Start at the ends

2- Weld in pilgrim step in interleaved way

Graphic 10.2 Detailed procedure for cold welding

The "hammer test" method involves welding a mild steel, low carbon steel sheet approximately to SAE 1015 of the following lengths: 50 mm long × 50 mm wide × 10 mm thick or similar measurements, but making sure that it is made of low-quality carbon steel, for example: the slabs for the manufacture of garden fences, (Graphic 10.3).



Graphic 10.3 Cast iron Weldability Test

The electrode to use would be a Conarco E-Ni55, it is an electrode of 55% of Nickel (Ni) and the rest of Iron (Fe). The piece to be welded must be previously clean and without traces of oil or paint.

A normal weld bead is made by melting both the plate and the casting in equal parts in a flat position without a bevel, simply a weld bead is made on the upper part of the plate.

A blow is made with a medium hammer on the upper part, that is, on the same side of the weld, but at the end of the test piece close to the welder, the blow must be very soft, since dropping the hammer abruptly It could happen that it breaks suddenly, generating confusion and it would take away the confidence of this test.

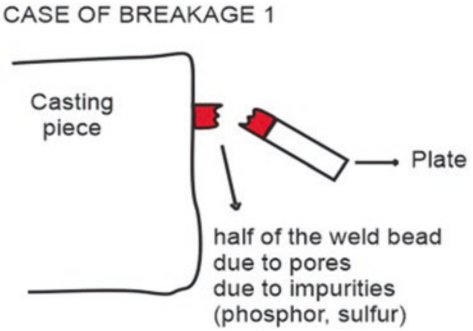
It may happen that it does not break, so we hit it with greater pressure. And so it is, that as the impact increases the weldability increases. In some cases, it can even deform the plate, this means that the cast iron is not very feasible to be welded.

If it breaks, then the cast iron is moderately weldable, the cast iron is difficult to weld and if there is no other alternative, try to reinforce with plates or rods threaded to this piece and we must be aware that it will be very fragile.

- We have several options of the ways that the cord can break:

  The logical thing is that it breaks in the center, this is because this area is the last to solidify and is the most fragile point due to the large formation of pores produced by impurities such as: phosphorus (P) and sulfur (S) (Graphic 10.4).

  This casting should undergo a cleaning treatment before welding and that consists of performing a procedure as explained above with an electrode ("cleaning electrode") much cheaper than Nickel and is more effective in terms of



Graphic 10.4 Case of breakage 1

extraction. of impurities that cause pores. Due to the type of slag and is designed exclusively for this purpose.

- Some brief mention about the cleaning electrode is the Conarco E-16 AWS E-7016 electrode:

  This electrode is designed to clean the casting because with many pores the casting is prone to breaking. Small sections are made in the cords on the sides of the break, these cords must be made in an interleaved way trying not to get the piece too hot.

- Sometimes it is necessary to leave a few minutes without welding so as not to overheat the piece. This weld will remove the most pores.

  The bead must be pulled out with an iron cutting tool and hammer, literally detaching the bead and / or grinding until the weld is completely removed and if the number of pores is too great, the operation is repeated taking care not to join the piece.

  In this way, the piece will be in the best possible condition to be joined by welding, although it should be clarified that this condition is not ideal.

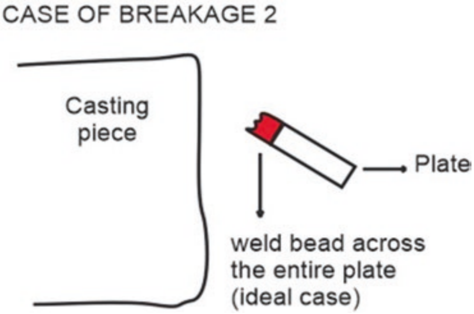
- Another option of breakage is that after the great impact of the hammer blow, the plate breaks and the cord remains completely in the plate and this means that the weldability is very good (Graphic 10.5).
- Finally, it may happen that when breaking the cord remains in the casting, this is not logical and is exclusively due to a failure of the welder due to lack of ability to weld these materials (Graphic 10.6).

  This “hammer test” (Graphic 10.7), will give us some security when welding and we will save time and money on expensive welding consumables [4].

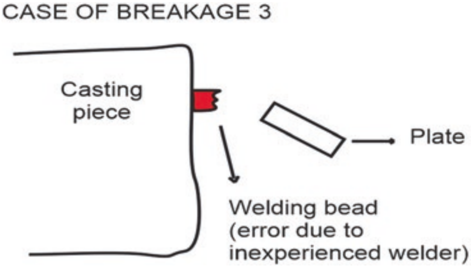
Welding as an Effective Maintenance Tool

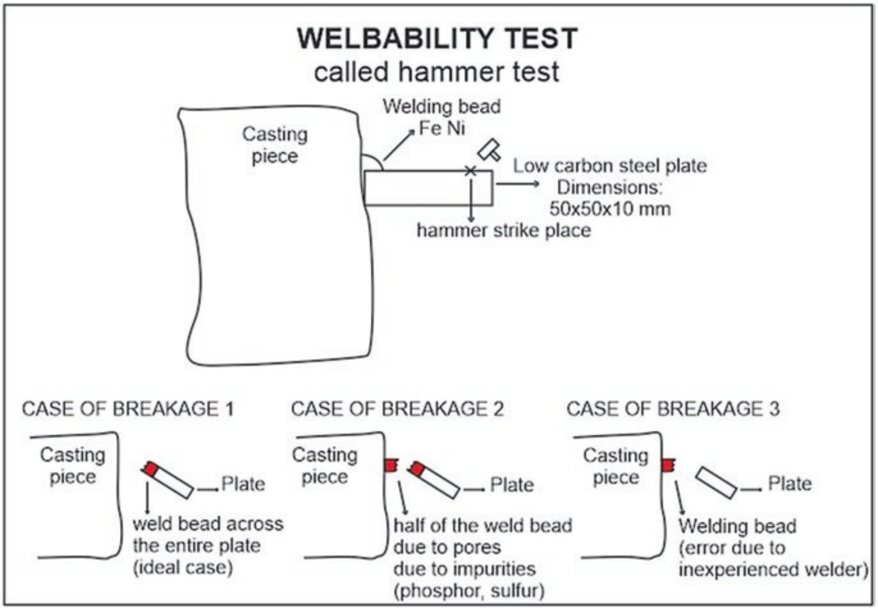
Among the alternatives for maintenance repairs is “maintenance welding”, and if it is used effectively, it generates practical, fast and low-cost solutions, allowing the reactivation of the equipment or component in failure, thus avoiding greater

Graphic 10.5 Case of breakage 2



Graphic 10.6 Case of breakage 3





Graphic 10.7 Compendium of weldability testing by "hammer test" and possible breakage cases

production losses and that it can also offer a certain time for planning the new maintenance intervention.

Based on these basic principles of engineering, large corporations and world-class companies invest in equipment, service contracts and personnel specialized in welding, seeking economic and rational solutions that minimize risks, as well as time and costs, which would take the change of a part or component, thus leaving only the use of special alloys and welds in those equipment or parts thereof, which are very expensive and are subject to extreme but controlled wear, that is, the mechanical integrity of the equipment is restored or recovered. Parts and components locally by means of cheap and ductile alloys or ordinary steels, but in a controlled and programmed way.

“Maintenance welding”are temporary or permanent alterations and repairs under the criteria of operating practices or standardized welding procedures that are made to a piece of equipment, component or metal parts that has a failure (wear, fractures, corrosion or deformations) in order to give it back, its operation, operability and aesthetics while maintaining the same stable design conditions [5].

However, you will seldom repeat the maintenance welding technique when performing a repair, since; metals failure cases are always different, but you will often perform prequalified fillet and butt welded joints to develop a standardized practice or a technical procedure in support of an operational practice.

Therefore, the human resources that make up a maintenance team must be highly organized and technically very competent in both engineering and resource management, since it is very common to see the application of palliative with reactive management, better known as the “theory of firefighter puts out fires”.

In the quest to develop a dynamic and proactive administration of maintenance and risk management plans, they must be organized and based on “inspection follow-ups”. This is the way to reduce the stress level of the maintenance team, while at the same time increasing its effectiveness, with obvious advantages for all. Applying this work philosophy allows assertive and coherent decisions to be made to maintain maintenance welding operations with acceptable risk levels based on engineering management and objective evidence.

The best welding repair practice is the one that gives the best results in terms of its execution oriented to three factors: risk reduction, production losses and the profitability of a process. The following are the main points of attention to develop the best operational practice for welding repair of a static equipment in metallic heritage repairs.

Many of the initial problems and consequences of maintenance repairs with welding, is not fully knowing the part that is being treated. It is essential to know the components to be repaired, their identification, engineering drawings, technical specifications of materials and equipment failure records, etc. This will provide first-hand, formal information, which will avoid additional costs for checks and shorten investigation times.

Design of the Repairment

This involves engineering the repair with welding. Once the antecedents and history of the bridge, monument or heritage element to be repaired have been reviewed, the repair methodology is developed, that is; The scope of the repair is specified: Is this repair temporary or permanent? The materials to be used, the process and type of welding are defined, execution activities are scheduled, resources are defined, risks are evaluated and times are estimated for the new commissioning.

Technical Support

Any repair without technical support or carried out without taking into consideration normative references is a crude palliative ("firefighter theory puts out fires").

Technical support is the stage of development of operational practice, which includes engineering calculation, under standardized criteria. This is the technical basis of a repair; involves the technical capacity of the work team in the execution, the verifying calculations of the procedure (empirical method or specialized software) and its application, based on regular trade practices (internal procedures, lessons learned, cases studied or shared experiences) and recommendations of technical standards (national and international standards and laws that impose a penalty).

Security, Speed and Effectiveness in Execution

An unscheduled repair enters emergency maintenance, and this is the high point where maintenance work intensifies, to which is added the emotional pressure exerted by many bosses on the execution staff and rational thinking is lost at times.

Undoubtedly, these are circumstantial agents that put aside the safety and effectiveness of a welding repair trying to do everything quickly, without measuring in advance the consequences or risks of something going wrong. Therefore, the safety, speed and effectiveness of a weld repair is of vital importance.

In the execution activities these three principles intersect and go hand in hand, because they represent the success of the commissioning of the equipment, infrastructure or monument in failure, avoiding security risks in people and facilities, production losses and profitability of a process.

Conclusions

Review inspection plans, verify that equipment that is prone to or indicates recurring failures involving welding repairs is included. Inspection is the spearhead of maintenance, it throws the first alerts that something is wrong and many times they are overlooked.

The risks in maintenance welding are indisputably controlled when it is not improvised. It is forbidden to leave the responsibility for a welding repair to a single welder, you must work collaboratively and as a team. Maintenance welding repair jobs should be operating practices or work procedures under proven standards and technical engineering guidelines.

In a plant stoppage and more when it involves an unscheduled repair (emergency), the action plan and the times to achieve the commissioning are managerial impatience. Designing a repair, having technical support and being able to establish inspection follow-up plans, guarantees risk control (safety-production-time) and in turn offers the balance of making rational decisions that in the end always represent money.

Lessons learned must be recorded. Having tested and qualified welding processes and procedures allows an advantage. It is essential for welding maintenance activities to have prequalified design manuals and procedures that have been previously studied, this offers the certainty that a repair with welding of similar characteristics will work properly.

The quality of the work depends largely on a qualified staff. This human resource must be conserved at a high level. By achieving a high-performance, high-commitment maintenance team, you will undoubtedly enhance current trends in strategic maintenance, provide inspection and monitoring strategies, paying attention to potential risks.

Acknowledgments The autor wants to give special thanks for the support and the assesments to Mr. José Luis Fernández (Welding Teacher), and to Miss Rocío Algañaraz (student involved in the Area of Archeometallurgy) for the collaboration with the welding graphics for this chapter.

References

1. History of welding. http://www.ehowenespanol.com/historia-equipos-soldada-hechos_101201/. eHow in Spanish
2. Biringuccio, Vannoccio. De la pirotechnia. https://www.worldcat.org/oclc/476529707 (1559)
3. Sánchez, C.: Welding Advisor at Ex Industrias Metalúrgica Pescarmona S.A. (IMPSA), Mendoza, Argentina
4. Information Source CONARCO Electrodes
5. Marquez, A.: Static Equipment Mechanical Integrity Analyst. Maintenance Engineering Department (PDVSA CGO), Maturín, Venezuela

Chapter 11

Advanced Analytical Techniques Applied to Reverse Engineering Studies

Patricia Silvana Carrizo

Applied Analytical Techniques

The studies on metallurgical technology are supported by a series of analytical techniques in order to obtain information that is subsequently interpreted from a technical, metallurgical, chemical, manufacturing point of view and everything is linked to important historical and anthropological references. This analytical vision of the material culture of human societies constitutes an inverse engineering in an important area of knowledge, which could have limitations only due to the accessibility to the archaeological and historical object, although not always.

Through the traces that tools leave on the surface of metallic objects, metallic structures that arise from various manufacturing processes, degradation in an archaeological site or even if the piece belongs to a museum or a private collector, from here the researcher considers the reconstruction of the manufacturing processes by performing the reverse path, deconstructing the material history of the object.

In this way, in the beginning, the inverted optical microscope was used for metallographic analysis, which is still used today with increasing performance (Chap. 6). Then, the advent of scanning electron microscopy with microprobe (SEM-EDS) which has played a fundamental and revolutionary role in the studies of materials since it allows simultaneously in the same equipment, the topographic observation of the object at high magnifications and with great depth of focus in addition to performing non-destructive microanalysis (Figs. 11.1 and 11.2).

Another very useful and highly impactful technique is X-Ray Fluorescence spectrometry (XRF). Equipment specifically oriented to the analysis of metals has been developed, which allow the identification of the chemical elements present in a

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P. S. Carrizo (✉)
Archaeometallurgy Area/Metallurgy Laboratory, National Technological University, Mendoza, Argentina

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_11

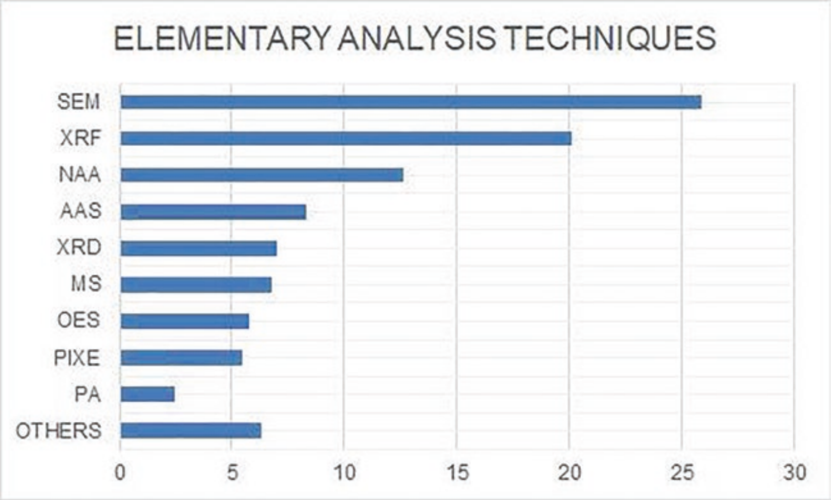


Fig. 11.1 Analysis techniques most used in archaeometallurgy studies (period 1975–2000)

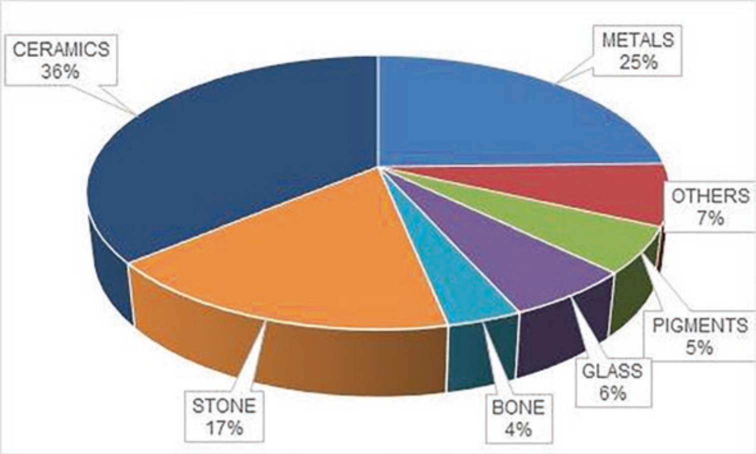


Fig. 11.2 Distribution of the type of archaeological material studied in articles according to an analyzed sample (period 1975–2000) [1]

sample from the atomic number $Z = 11$ onwards in the case of our laboratory equipment. The development of portable and precise equipment has meant a great advantage, since it allows measurements to be made in the place where the piece or element to be studied is located, this quality being highly valued since sometimes it does not have the permission of the authorities pertinent to carry out the transfer of the piece to the laboratory and therefore the best thing is to carry out the measurements in situ.

In this way the components of non-ferrous metal alloys can be identified (qualitative analysis) and quantified (quantitative analysis). Although the XRF equipment has a limitation in ferrous materials because it does not measure the carbon content (% C), it has a great advantage, as will be described later, since it can identify light elements ($Z = 11$) generated in metallurgical production (mainly in slags) data that collaborate in provenance studies. The previously mentioned "limitation" should not always be considered in this way, since when the researcher has experience in metallographic analysis, the carbon content (% C) can be inferred through the observed metallographic structure. The XRF portable equipment brings with it a complete database or library to identify metals and alloys and details the chemical elements present, expressed in percentages.

And other equipment that is described in this chapter is the Atomic Force Microscope (AFM) for its acronym in English, it is a mechano-optical instrument capable of detecting forces of the order of nano newtons. By tracking a sample, it is able to continuously record its topography using a sharp pyramidal or conical shaped probe or tip. The probe is attached to a very flexible microscopic stick or lever of only about 200 μm. The atomic force microscope has been fundamental in the development of nanotechnology studies for the characterization of materials. It has applications to facilitate the visualization of scanned samples of materials from various fields of knowledge such as: life sciences, material sciences, electrochemistry, polymers, biophysics, nanotechnology and biotechnology. Is well indicated for thick and thin films, ceramics, composites, glasses, metals, membranes, conductor, semi-conductor and insulator materials.

Handheld X-Ray Fluorescence Spectrometer (XRF-P)

X-rays are part of the electromagnetic spectrum (Fig. 11.3) which includes radiowaves, microwaves, infrared radiation, visible and ultraviolet light, at higher energies X-rays and gamma rays. Shor wavelength ultraviolet light, X-rays, and gamma

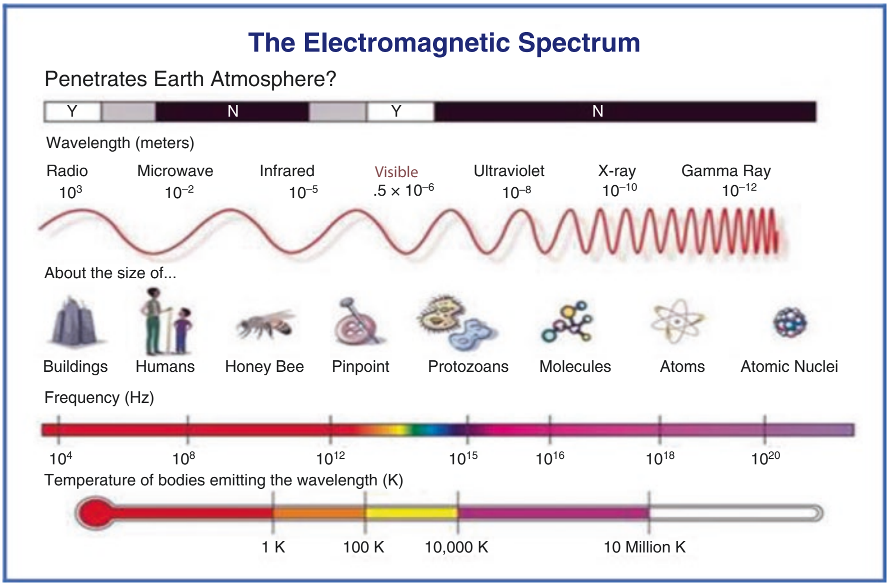


Fig. 11.3 The electromagnetic spectrum

rays produce ionizing radiation capable of causing damage to organic compounds and living tissue. In a vacuum, all of these different forms of radiation travel at 3.00×10^8 m/s (the speed of light) and differ only on their wavelength/energy. R-rays radiation have wavelengths ranging from 0.01 to 10 nm, which corresponds to a wide range of energies from 124 to 0.124 KeV, respectively. In practice, handheld XRF spectroscopy utilizes a much smaller range of energies from about 1 KeV to slightly over 30 KeV.

Technique Basic Concepts

X-ray fluorescence (XRF) is a non-destructive instrumental analytical technique that measures the elemental composition of a generally solid substance when exposed to X-ray radiation (Fig. 11.4). X-rays have such energy that by striking the sample they can ionize it, expelling electrons from the innermost layers. These ions are highly unstable, and those vacancies are filled by cascaded upper shell electrons. These jumps of electrons from a higher energy level to a lower one gives off a characteristic radiation that is X-ray fluorescence (Fig. 11.3a). The set of electronic jumps between layers of an element forms the characteristic spectrum of the element and is unique.

Measurement of Chemical Composition

Figure 11.5a, b, shows the X-ray fluorescence analysis, which consists of three steps

- Excitation of the atoms that make up the sample.
- X-ray emission characteristic of the sample.
- Detection of the characteristic X-rays emitted.

The qualitative analysis is obtained from the characteristic energy, or its wavelength, of the emitted X-ray fluorescence radiation. The quantitative analysis is

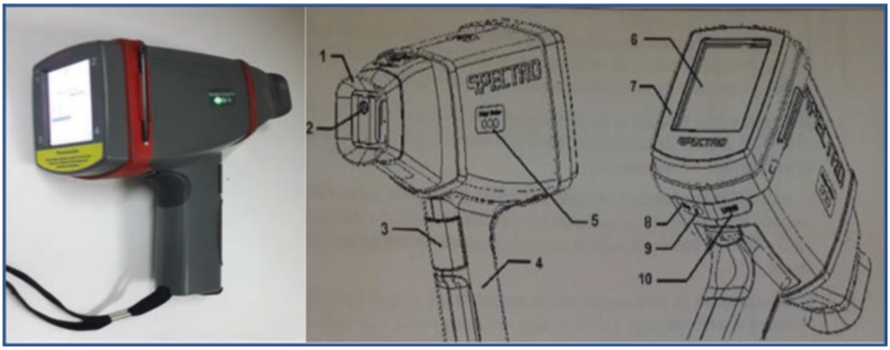


Fig. 11.4 Spectro XSORT Handheld X-Ray Spectrometer

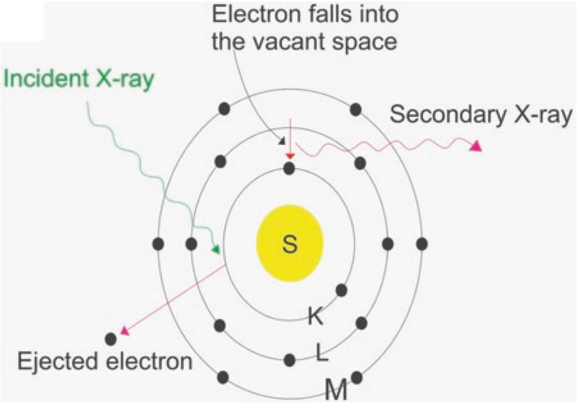


Fig. 11.5 (**a**) Scheme of X-ray fluorescence radiation emission and (**b**) Scheme of a spectrometer

obtained by counting the X-rays for a determined wavelength. The elemental contents are total contents, without distinction of oxidation states.

When X-rays hit the atoms of the elements, their electrons change their orbital, which is recorded in a continuous spectrum consisting of characteristic energy peaks of each detected chemical element, the equipment shown in the following images shows the chemical composition results expressed in percentages (%) of each chemical element detected, although there are other equipment models that draw the respective peaks for each detected chemical element, the property of these percentages and / or peaks is that they always appear in perfectly fixed and determined at the wavelength (λ) for the same element.

An XRF spectrometer consists of three fundamental parts: the source that generates the X-rays (a tube or a radioactive source); a detector that converts the X-rays emitted by the sample into an electronic signal capable of being measured; and a processing unit that registers the signal and calculates the elemental concentration in the sample (Fig. 11.6 and Table 11.1).

The time of exposure of the sample to radiation depends on the quality required in the analysis, the usual being between 30 and 600 s. Detection limits also decrease with increasing measurement time. Regarding the detection limit, this is not the only factor, but there are others of greater incidence: physical effect of the matrix (physical properties of the sample, such as particle size); the chemical effect of the matrix (effects of absorption of the radiation emitted by another element in the environment; overlapping of lines of different elements) and the contents of various components around 10% that affect the transmission of X-rays.

Detecting this fluorescence and the way it is scattered gives rise to different analytical techniques. Those that disperse the different wavelengths through crystals require a sufficient physical size to house the optical part, so they are laboratory techniques. The dispersion of energies, on the other hand, is done through the same detector that works as a pulse height discriminator.

Fig. 11.6 (**a**) On-site chemical composition measurement with portable spectrometer on a historical canyon of the San Carlos Museum and (**b**) Pigments chemical composition measurement on wall oil paintings of Emiliano Guiñazú Fader's House Museum, Archaeometallurgy Area

Table 11.1 Constituents parts of X-ray spectrometer

Number	Component
1	Protection washer (radiological protection)
2	Measurement window with shutter and window cover
3	Measurement initiator button
4	Battery pack
5	Indicator: -shutter open/closed X-ray tubes ON/OFF
6	Touch sensitive screen
7	Pressure sensitive display frame
8	Helium connection
9	Connector / Disconnector for power supply
10	USB and mini-USB connection (e.g.: To use a USB stick or the connection on the PC)

How to Measuring. The Surface Preparation

There are two alternatives depending mainly on the shape of the piece:

(a) Sand with 80 or 100 grit sandpaper to remove dirt, paint or impurities from the surface, which may affect the result of the analysis.
(b) Use a grinder, in which case we must make sure that we have roughly identified grinding discs and sandpaper of 80 or 100 as indicated below.
(c) Clean the sanded surface with cotton and alcohol.

Preparing for the Measurement

1. Make sure that the adapter and sample show no signs of moisture.
2. Make sure the adapter is clean.
3. Prepare the sample surface.
4. Make sure the X-ray shield is mounted.
    - In case of incorrect placement of the sampling radiographic protection, the equipment will check error.

Chemical Composition Measurement

1. Select the area to be measured, the equipment has several security points, radiographic protection and as a second security point is that for its operation the equipment requires that both hands be on the equipment, the second hand is free, there are than press part 1 and 2 (Fig. 11.5) on the piece.
2. When pressed on the screen displays a countdown of 30 s. This time is the one that is prepared for the measurement.
3. Hold the equipment steady on the part 1, avoid moving it at the time of measurement. The measurement results are indicated on the screen, if the material is within the standard, the equipment will indicate the material or a reference standard, or in the case of ancient metals, it searches its library for the closest thing today to the material being measured analyzing. This equipment does not measure Carbon (%C), therefore for non-ferrous metal studies it is a great ally, it is fast, non-invasive, non-destructive and easy to handle with the only care to be taken with regard to radiation [2] (Fig. 11.7).

Scanning Electron Microscopy with EDS Detector (SEM-EDS)

Since ancient times, man has sought a way to increase his resolving power and to make the invisible visible.

For this purpose, the lenses are discovered and with the combination of them higher resolution images are obtained. The optical microscope was born and one began to venture into the microscopic world of nature. In order to surpass the resolution limit of an optical microscope, it is necessary to design instruments that use radiation other than visible light to form the image (Fig. 11.8).

In the 1920s, various discoveries found that a beam of electrons accelerated in a vacuum, in addition to traveling straight paths, also behaved like a wave similar to visible light characterized by a wavelength 100.00 times smaller. It was even found that the behavior of electrons against electric and magnetic fields was similar to that of visible light in mirrors and lenses. Precisely, a beam of electrons accelerated by

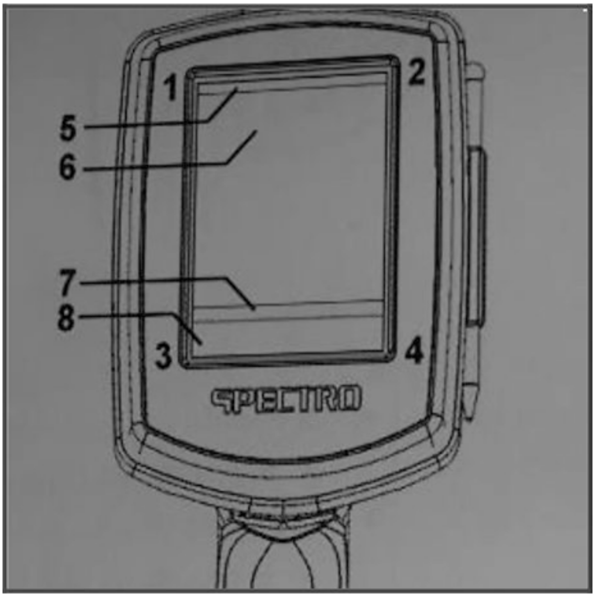


Fig. 11.7 Control panel of portable X-ray spectrometer

a high electrical potential (25,000 Volts) constitutes the radiation source of a Scanning Electron Microscope (SEM). Although these microscopes began to be developed commercially around 1960, their performance and ease of operation were continually improving.

A modern instrument can observe samples with a resolution of about 4 nm with magnifications of up to ×300,000. In this way, images of all types of structural materials can be obtained with a minimum of previous preparation and directly observe all types of surfaces with a great depth of focus. This is a unique characteristic of electronic instruments that allows obtaining in-focus micrographs of irregular surfaces such as a fracture surface. For this, it is only necessary to ensure that the samples are clean, dry, resistant to the high vacuum of the instrument and good electrical conductors. If it is a question of observing a non-conductive material, the samples are normally covered with a thin metallic layer, for example: gold (Au), or by pre-drying the samples that have high contents of water vapor [3] (Fig. 11.9).

All scanning electron microscopes consist of an electron gun in a high vacuum column, on the order of 10^{-5} mmHg, in which a high-energy electron beam (5–30 kV) is generated. This beam is collimated by a series of electronic lenses and focused on the analyzed sample.

The detectors record the signals originated by the interaction between the electron beam and the sample, which are processed and displayed in the final observation system (monitor or computer screen).

The electron gun is the first component of the column of the microscope and is the one that produces the electron beam. It consists of a filament emitting electrons that are then accelerated by a positively polarized anode at a variable voltage

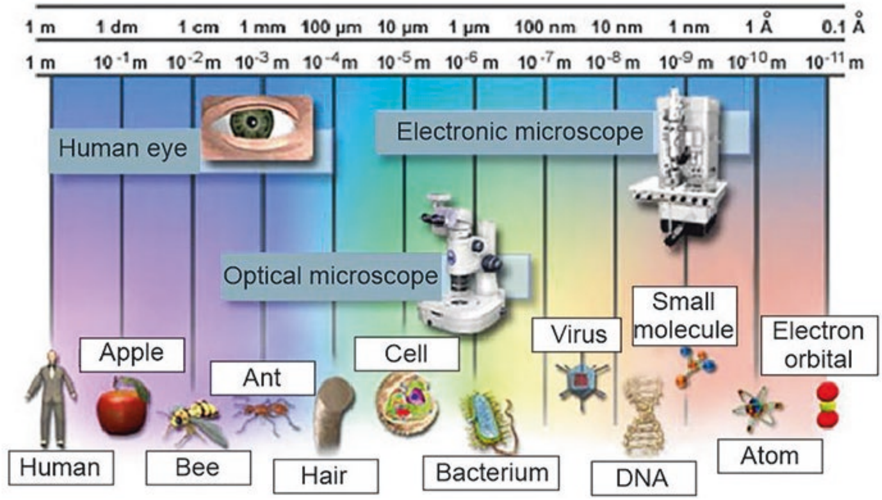


Fig. 11.8 The figure shows the relative sizes of different objects (including humans) and the instruments needed to detect them

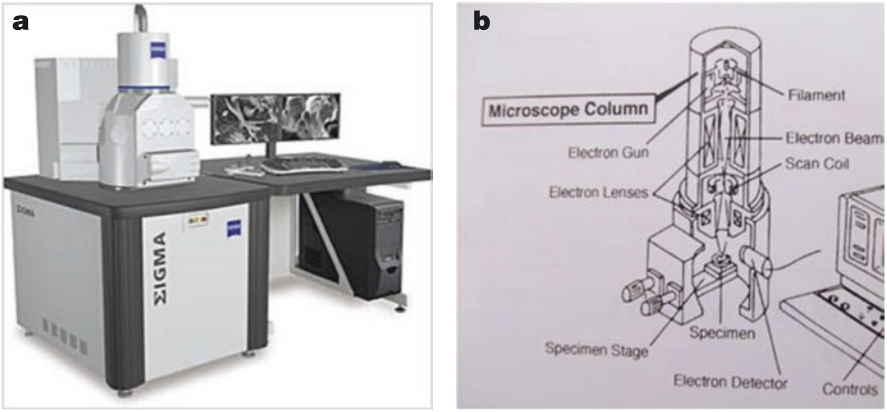


Fig. 11.9 (**a**) Electron microscope diagram showing the main components and (**b**) detail of the column

between about 5 and 30 kV. Currently there are different types of electronic guns. The corresponding gun designs are certainly different, but they all constitute the first part of the electronic optical system that originates the electron beam.

This beam is then collimated by a series of electronic lenses and small apertures until it is focused on the surface of the sample. It is intuitive that the diameter of this electron beam is one of the factors that determines the final resolution of the image. A coil system deflects this beam in such a way that an area of the sample surface is continuously scanned and the resulting signals are recorded by the detectors.

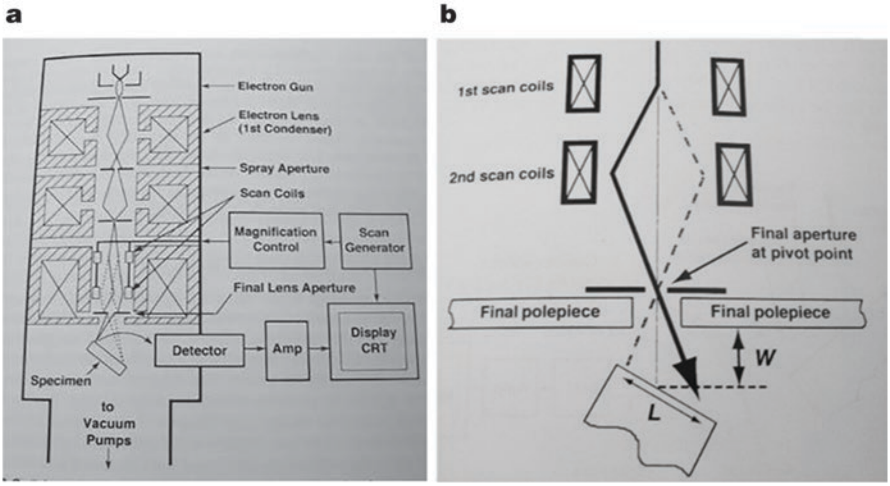


Fig. 11.10 (**a**) SEM Column and (**b**) Final lens opening detail

The final part of the electron microscope column is the vacuum-sealed chamber that contains the stage where the sample is placed. A set of external controls makes it possible to move this stage along the three x, y and z axes and vary its orientation along two axes of rotation. Detectors are placed in this chamber to record the different signals emitted by the sample (Fig. 11.10).

Imaging

The images of an electron microscope are obtained by detecting, processing and visualizing the signals resulting from the interactions between a high-energy electron beam with matter. These interactions can provide information on topography, composition, and crystallographic structure.

In a scanning electron microscope, the image is obtained from the signals emitted by the sample and is formed as the electron beam moves over a portion of its surface. This scanning is performed line by line over a small rectangular area (raster). This area is the one that is viewed magnified in the final image.

As the beam explores the sample in this way, the intensity of the generated signal varies according to the particular point analyzed at each instant. The detected signal can then be analyzed and amplified, both in its analogue and digital form, and finally suitably processed.

Unlike an optical image, the scanning electron microscope does not form a real image of the object, but builds a virtual image from some of the signals emitted by the sample (Figs. 11.11, 11.12, and 11.13).

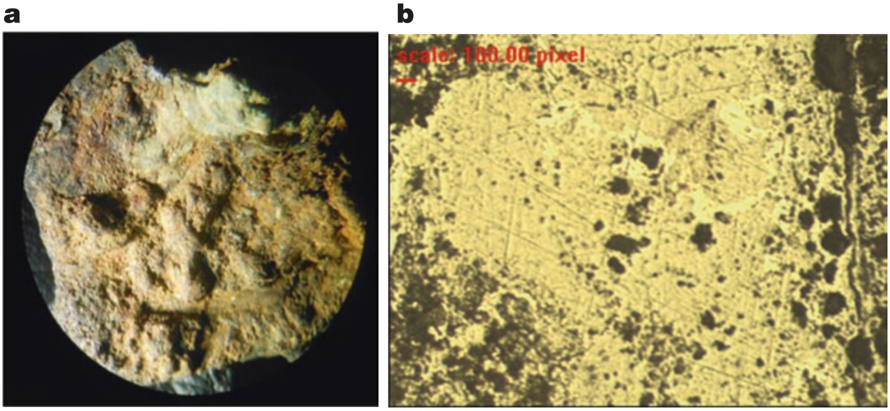


Fig. 11.11 (**a**) Military uniform button from the garbage dump of Fort May 25 Village Museum, San Rafael, Mendoza, Argentina (Border Archaeometallurgy Project) [4] and (**b**) Its metallography shows a ferritic matrix and corrosive damage of the chloride type is observed. Magnification: ×100. Reactive: Nital 1%

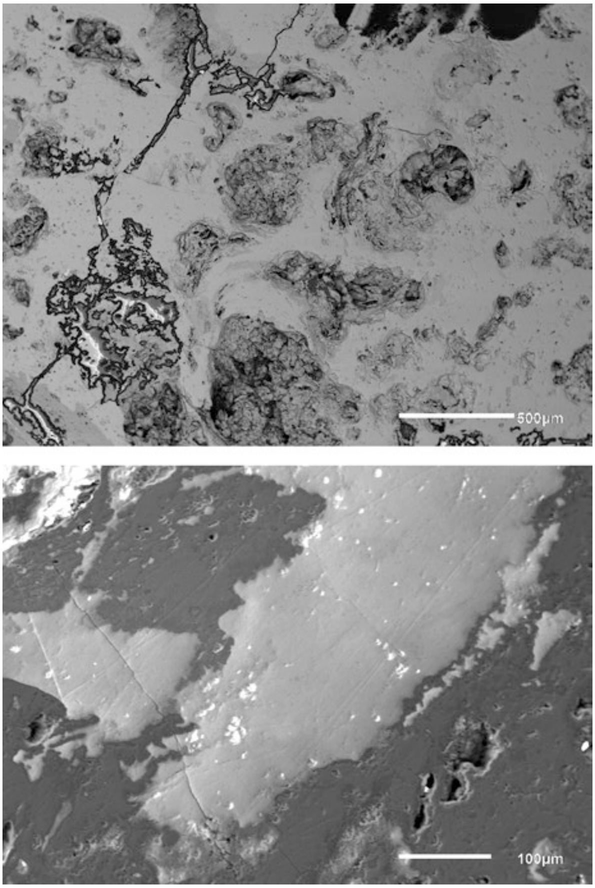
The image is displayed on a cathode ray tube where the deflection coils of the beam are synchronized with the scanning of the electron beam in the microscope. By modulating the intensity of the cathode ray tube beam, a point-to-point recording is finally obtained on the screen, which is precisely the electronic image provided by the microscope. Currently the visualization is done on a computer screen.

Secondary and Backscattered Electrons

Secondary electrons are electrons that have been inelastically scattered by the interaction of the electrons in the incident beam with the sample. They are characterized by a low energy of the order of 20–50 eV. Given this low energy, the secondary electron signal is formed in a thin surface layer, on the order of 50–100 Å. They are electrons that can be easily diverted from their initial emergent trajectory and allow information to be obtained from areas that are not in view of the detector. This particularity gives this sign the possibility of providing information “in relief” (Fig. 11.14).

Backscattered Electrons are electrons in the incident beam that have been elastically scattered by the atoms in the sample. Its energy is close to that of the incident beam: 10–30 keV. They originate in deeper areas of the interaction volume and the spatial resolution of the corresponding images is worse.

But given the strong dependence of the emission of backscattered electrons on the atomic number Z of the sample, this display mode allows to detect variations in the elemental chemical composition.



Figs. 11.12 and 11.13 Images of the same sample of military uniform button with Scanning Electron Microscopy (SEM)

Areas of higher atomic number are more efficient in emitting backscattered electrons and therefore appear brighter in the image. This implies that two parts of the sample that have different composition are revealed with different intensity, although there is no difference in topography between them. The X-rays that are generated in a sample subjected to electronic bombardment allow the elements present to be identified and their concentration established (Fig. 11.15).

Atomic Force Microscope (AFM)

The Atomic Force Microscope was invented in 1982, by scientists working in IBM, just after the invention of the Scanning tunneling Microscope in 1980 by Gerd Binnig and Heinrich Rohler by IBM Research in Zurich. That is when Binnig later

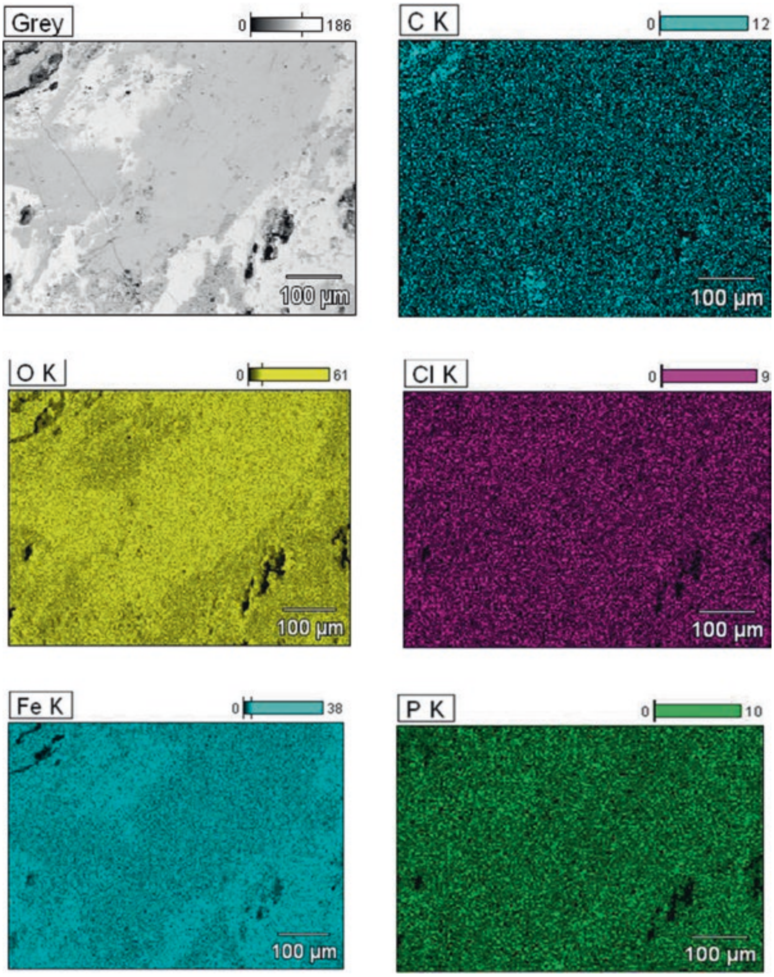


Fig. 11.14 Mapping of the same sample (military uniform button) with SEM-EDS

invented the Atomic Force Microscope, and it was first used experimentally in 1986. It was put on the market for commercial sale in 1989. The atomic force microscope (AFM) is a type of scanning probe microscope whose primary roles include measuring properties such as magnetism, height, friction [5] (Fig. 11.16).

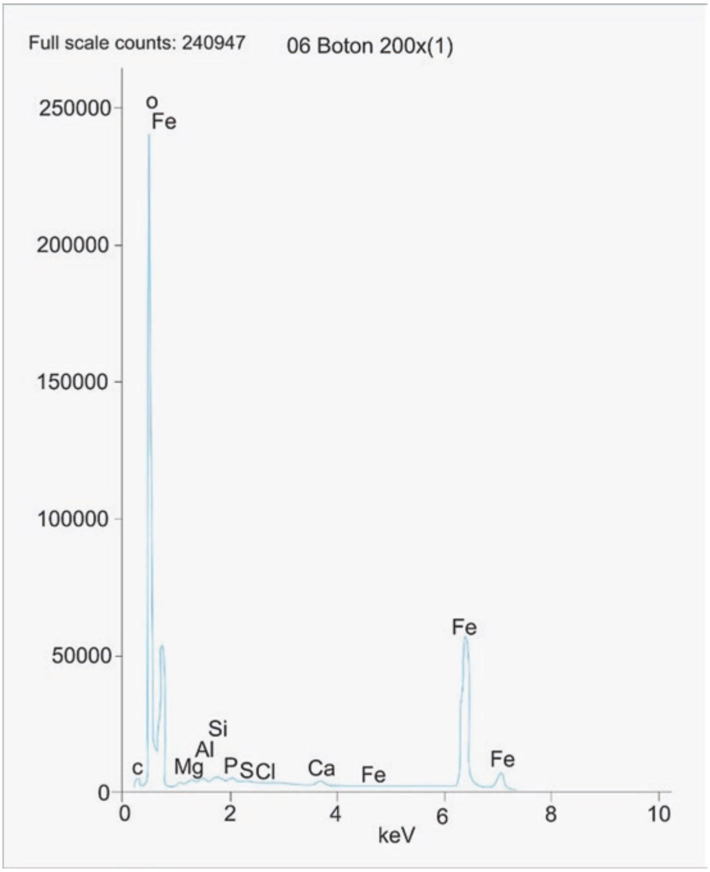


Fig. 11.15 Chemical composition of the same sample by EDS (military uniform button)

The Working Principle of the Atomic Force Microscope

The Atomic Force Microscope works on the principle measuring intermolecular forces and sees atoms by using probed surfaces of the specimen in nanoscale. Its functioning is enabled by three of its major working principles that include surface sensing, detection and imaging.

The Atomic Force Microscope (AFM) performs surface sensing by using a cantilever (an element that is made of a rigid block like a beam or plate, that attaches to the end of support, from which it protrudes making a perpendicularly flat connection that is vertical like a wall). The cantilever has a sharp tip which scans over the sample surface, by forming an attractive force between the surface and the tip when

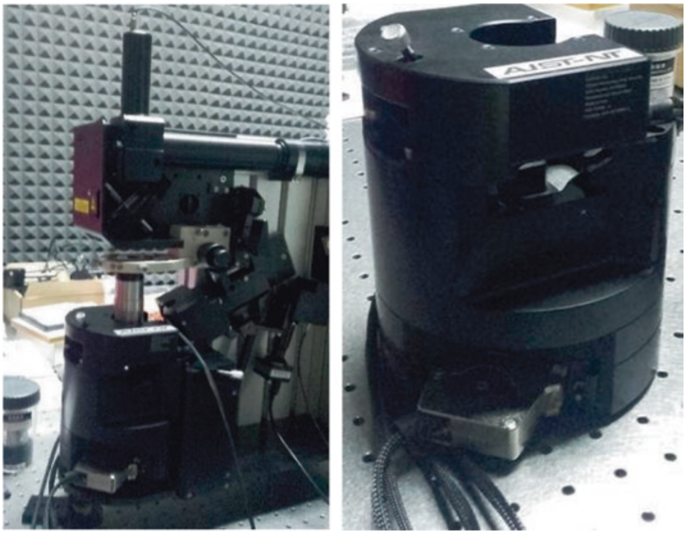


Fig. 11.16 Atomic Force Microscope (AFM)

it draws closer to the sample surface. When it draws very close making contact with the surface of the sample, a repulsive force gradually takes control making the cantilever avert from the surface (Fig. 11.17).

During the deflection of the cantilever away from the sample surface, there is a change in direction of reflection of the beam and a laser beam detects the aversion, by reflecting off a beam from the flat surface of the cantilever. Using a positive-sensitive photo-diode (PSPD—a component that is based on silicon PIN diode technology and is used to measure the position of the integral focus of an incoming light signal), it tracks these changes of deflection and change in direction of the reflected beam and records them (Figs. 11.18 and 11.19).

The Atomic Force Microscope (AFM) takes the image of the surface topography of the sample by force by scanning the cantilever over a section of interest. Depending on how raised or how low the surface of the sample is, it determines the deflection of the beam, which is monitored by the Positive-sensitive photo-diode (PSDP).

The microscope has a feedback loop that controls the length of the cantilever tip just above the sample surface, therefore, it will maintain the laser position thus generating an accurate imaging map of the surface of the image.

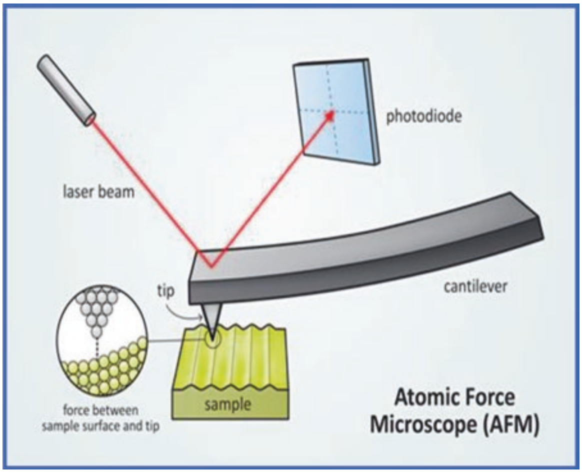


Fig. 11.17 (**a**) Detail of the cantilever and its operation and (**b**) General components (AFM) and their functions

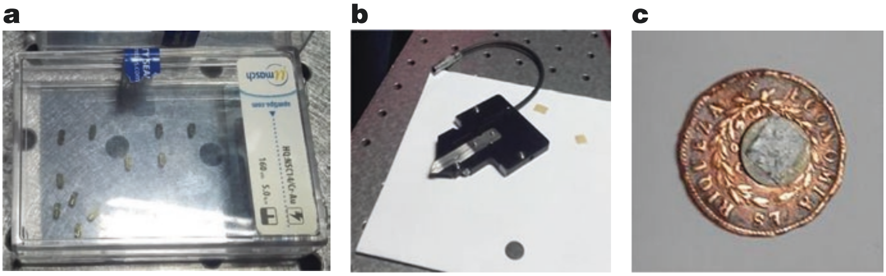


Fig. 11.18 (**a**) Details of tips used in AFM, (**b**) Cantilever detail, (**c**) Preparation for AFM studies of historical copper coin (1853) found in Fort May 25 Village Museum, San Rafael, Mendoza, Argentina (Border Archaeometallurgy Project)

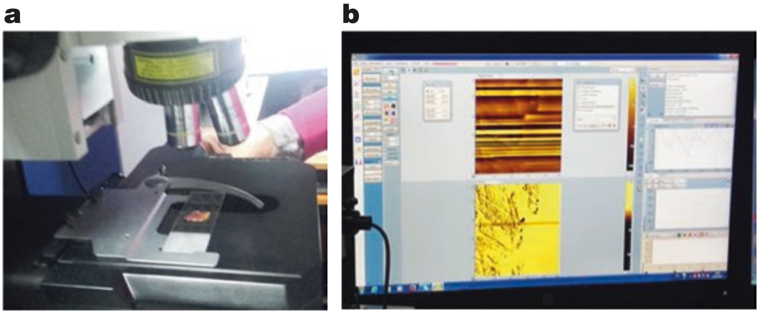


Fig. 11.19 (**a**) Observation of the historical copper coin and (**b**) topographic mapping of the coin

References

1. Montero Ruiz, I.: Arqueometría: Cambios y Tendencias Actuales, [“Archaeometry: Current Changes and Trends”], Trabajos de Prehistoria **64**(1), enero-julio, 23–40, ISSN: 0082-5638 (2007)
2. Instruction Manual Spectro XSort Handsheld X-Ray Spectrometer. Laboratory of Metallurgy, UTNFRM (2013)
3. Riberos, A.: Curso de Posgrado Básico de Microscopía Electrónica de Barrido y Procesamiento de Imágenes, [“Basic Postgraduate Course in Scanning Electron Microscopy and Image Processing”], Laboratory of Electron Microscopy and Analysis of Materials by X-rays (LAMARX). Faculty of Mathematics¸Astronomy and Physics (FaMAF), National University of Córdoba (UNC), Argentina (2016)
4. Carrizo, P.: Border Archeometallurgy Project (MATUNME; Code: 0004308). Archaeometallurgy Area, Metallurgy Laboratory (UTN FRM), Mendoza (2016–2017)
5. Menchaca, J.: Curso de Posgrado Caracterización Espectroscópica y Morfológica de Materiales, [“Postgraduate Course in Spectroscopic and Morphological Characterization of Materials”]. Mexico, Faculty of Physical-Mathematical Sciences, Autonomous University of Nueva León (2017)

Chapter 12
Case Studies on Reverse Engineering on Ancient Metals

Patricia Silvana Carrizo, Rafael Colás, Hugo Ricardo Dengra, Luisa Vetter, Augusto Bazán, Rocío Algañaraz, Marcos Guipponi, and Noelia Ibañez

Introduction

This chapter includes case studies with the purpose of showing real cases investigated in historical metallic materials belonging to museum collections, heritage sites, historical metallic infrastructure, means of transport, archaeological-ceremonial sites and antique industrial production systems, which are developed theoretically in the previous chapters. In addition, it has the very important sense of pedagogical support to teachers, students and readers in general interested in the subject, providing images and concepts that make the work enjoyable. This chapter shows the application of the scientific method to develop research in Reverse Engineering, in which take part concepts previously adquired in chairs such as Materials Sciences, Chemistry, Strength of Materials, Metallurgy, Metallographic Techniques, Prospecting, Archeology and History intervene and how all these concepts let us to get results. Finally, this penultimate chapter of the book is proposed as a compendium of concepts and practical application.

P. S. Carrizo
Archaeometallurgy Area/Metallurgy Laboratory, National Technological University,
Mendoza, Argentina
e-mail: patricia.carrizo@frm.utn.edu.ar

R. Colás
Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León,
San Nicolás de los Garza, México
e-mail: rafael.colas@uanl.edu.mx

H. R. Dengra
Department of Museums, San Carlos Fort Museum, Mendoza, Argentina
e-mail: hrdengra@gmail.com

L. Vetter (✉)
Pontificia Universidad Católica del Perú, Academia Nacional de Ciencias, Lima, Peru
e-mail: luisa.vetter@pucp.edu.pe

A. Bazán
Fundación Augusto N. Wiese, Lima, Peru
e-mail: abazan@elbrujo.pe

N. Ibañez · R. Algañaraz · M. Guipponi
Area Archaeometallurgy, Metallurgy Laboratory, Electromechanics Department, National
Technological University Mendoza Regional Faulty (UTN FRM), Mendoza, Argentina

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_12

Cleaning and Conservation of a Historical Copper Coin from 1853 rescued in the Fortín Villa 25 De Mayo-Mendoza

Patricia Silvana Carrizo

Abstract

This article deals with the cleaning treatment of an old copper coin (1853) and the conservation problems. The objective of the research was to study metallographically the coin found in archaeological rescue in Fort Villa May 25 Village in San Rafael-Mendoza and apply an appropriate method of cleaning and subsequent conservation of it. To achieve this, the specimen was cleaned in an electrolytic cell, the adequate oxidation potential of the sacrificial anode to be combined with the coin material was studied, a good practical and economical cleaning method was found. Then, the composition of the metal is analyzed with X-ray fluorescence equipment (XRF), subsequent study of microhardness and the structure of the material was studied by metallographic microscope. Finally, an additional work is done for its conservation and exhibition in the Narciso Sosa Morales Museum.

Keywords

Copper coin; Conservation; Cleaning method

Introduction

This work is part of the studies carried out on historical materials within the Border Archaeometallurgy Project of which I am an author and which was developed during 2016–2017; the objective was to study metallic materials belonging to the forts of southern Mendoza such as San Carlos and May 25 Village. Precisely the protagonist of this investigation is a copper coin belonging to the Narciso Sosa Morales Museum that works in front of the Fort Villa May 25 and has been declared of national heritage site interest. The copper coin of 1853 is from the Republic of Chile, stage independence, and value of half a cent, and it exhibits as part of the history of the southern zone of Mendoza. The purpose of this study was to clean the coin rescued from an archaeological site and now belonging to the Narciso Sosa Morales Museum. After this, the study of the material in terms of chemical composition, microhardness, and metallographic studies was continued.

Through the study of currencies, the relationship between money and the nation can be observed, these are a material testimony of the identity of people, of an era and of the monetary policies that have animated the economy. Engravers and artisans have captured in metal many of the most significant features of the history of a nation, as well as its artistic development. The rich iconographic heritage allows us to read the symbols that have become the historical imaginary of our societies and that today give us a look of identity in front of the celebration of the bicentennial of the American nations. The installation of these new nations required another image, and for this purpose, the telluric image of America was resorted to, with new symbols such as volcanoes erupting; the range; the Sun; the eagle and the condor; the Andean camelids; the hands swearing the constitution; the figures of the Republic and Minerva, as representations of freedom; the education of the people by the school; the party or other symbols against the monarchical tyranny of which the new American nations had been liberated. In the eighteenth century, the idea of a nation began to slowly form itself as a group made up of individuals who associate freely. With the fragmentation of the old Spanish empire in America, the new nations required symbols that would give a homogeneous identity to these new countries. These symbols, representative of the power of a new nation, were given in the context of the war process of the independence revolution and the new republican scaffolding that structured these new nations. Not only were symbols required to identify themselves as a nation in reference to their former ruler. The idea of nation-territory meant the adoption of emblems and symbols of their own, for this resorted to republican allegories: stars, tree of freedom, among others, which allowed to replace the image of the sovereign by symbols that appealed to a new political order, becoming an effective vehicle for the visual construction of the nascent American republics. In accordance with the prevailing style of the time, it was resorted to ancient symbols of the republican Rome like the lictores, the Phrygian cap, the pileus. The use of this symbology responded to the pedagogical need to print a republican seal in the town, literally dethroning the old monarchical order. The symbols used were in line with the independence ideas, with clear inspiration in the French Revolution and the independence of the United States of America; for this reason, the inscriptions of freedom, union, strength, and independence represented the new order. In the country of Chile by the enactment of the law of January 9, 1851, turned the Chilean monetary system, passing the Royals and Shields to Pesos and Cents, with the following equivalence 1 Peso = 8 Reales. The mentioned law, in the fourth article said: "There will be two kinds of copper coins, called cents and half cents of copper refined without mixing of another metal." And the law of March 19, 1851, established that: "The copper coins will bear on the obverse the central star of the coat of arms with the inscription: Republic of Chile and the year in which they are issued; and on the reverse the expression of its value, a circular laurel bouquet, and the slogan: Economy is wealth." Throughout the numismatic history of Chile, different versions of shields have been used in the coins, initially, when Chile was a Spanish colony, the arms of Spain were used. Then, when independence arrived, a shield representing the Earth on a pillar was used, and later, it was changed to the current shield. There was also an even more simplified version of the shield, in which only the central star is shown.

Experimental

Cleaning Method: Electrolytic Reduction

When observing that the coin to be treated presented good conditions, not only metallic core but the original surface was covered with non-deforming corrosion products that could be reduced back to the metallic state (malachite, or something similar in green), it was decided to clean electrochemistry through an electrolytic reduction. This treatment consists of the creation of a galvanic battery in which the metallic object to be treated acts as a cathode and a galvanized steel sheet (zinc) or an aluminum sheet acts as an anode, with a sodium hydroxide electrolyte at 1% M. When the galvanic reaction takes place, the less noble metal, in this case the aluminum or zinc loses electrons in favor of the most noble (copper) producing a reduction of some corrosion products back to the metallic state. At the same time, the reaction produces hydrogen, which when released in the form of bubbles, mechanically removes some corrosion products from the metal surface. The results were very satisfactory, being achieved in a fraction of the time very short (2 h), to the employee usually in a metal cleaning, a degree of cleanliness that allowed to appreciate all the details of the copper coin surface. Cleaning by electrolytic reduction is a reaction that is caused by the application of an electric current. To do this, an electrolytic cell is created with the object to clean treated as cathode and an aluminum or galvanized sheet as a sacrificial anode, both submerged in an electrolyte that is usually 1 M sodium hydroxide [1]. A continuous current is applied to the electrolytic cell with an intensity that is a function of the surface of the object to be treated and which is usually expressed in A/cm^2. The reaction is more uniform than in basic electrochemical cleaning. Different results can be obtained and depending on the intensity of the applied current can affect the rate of reduction of corrosion products to the metallic state and mechanical cleaning by the action of bubbles of hydrogen on the surface. But in general, it is advisable not to work with very high currents, due to the complexity of the chemical reactions that could occur, and could affect the cleaning process sought. In my case of study and with the electrolytic cell equipment that I have, for reasons of careful use of the equipment, it is not possible to go beyond the 6 A/cm^2, for security of this equipment, it is advisable not to reach to full scale. But according to several investigations, it has been demonstrated that intensities of the order of 50 A/cm^2 result in a greater and faster extraction of corrosion products [2]. The great advantage of this method is the possibility of controlling the reaction by the magnitude of the potential that is supplied to the reaction to develop the electrolytic reduction.

Fig. 12.1 Sequence of evolution in the cleaning of the copper coin

In Fig. 12.1, the state in which the coin was received is macroscopically observed, to make the chemical cleaning, as well as the sequence of evolution as it progressed in cleaning and subsequent polishing. It is possible to appreciate the clean and polished coin, where you can read correctly its origin, year of issue, and in contrast you can see its monetary value, legend, and two laurels. The material is mostly copper (Cu), with alloying elements that do not have a primary role in the chemical composition of this historical element. Due to the formed calamine (green), on its surface, which behaves as a protective barrier over time and corrosion, that is why the coin has an almost perfect state of preservation. Coin minted in 1853, Republic of Chile, simple and flat shield, value: half a cent, legend: economy is wealth (Fig. 12.2).

According to a numismatic catalog, we find in collection the same currency in a better state of preservation in order to share data that indicate that it is a legitimate currency (Table 12.1).

To carry out this law, copper was commissioned to Carlos Lambert's smelter in Coquimbo. The plates produced were taken to Santiago where they proceeded to mint in the *Casa de Moneda*. Defects in the plates led to many coins were defective in their weight, which ranged between 8388 and 9400 mg, which added to technical deficiencies of the Mint for the minting of copper coins (it was the first time he did in large quantities), led to stop the production of these coins in the country. There is no complete information regarding which variant was coined in which country, except for the one presented below:

Fig. 12.2 Half a cent 1853. Design used in 1851 and 1853

Table 12.1 Coin characteristics by Krause catalog

Material	Copper
Weight	4.6–5.0 g
KM #	126
Diameter	22 mm
Edge	Smooth
Year	1853
Print	2,667,000
Coined	The Heaton Mint, Birmingham, England

This coin, cataloged like KM #126 was coined by The Heaton Mint, located in Birmingham, England. It is mainly identified by:

Inverse: REPUBLICA DE CHILE, Star of five points and year of minting 1853 between two points. Number 1 of the date with straight top.

Reverse: ECONOMY IS WEALTH. Denomination in words surrounded by laurels. Four-pointed star on bottom. Letter Q of "*RIQUEZA*" with short outer tilde. Laurels united by double loop.

To perform the metallography and see the microstructure of this coin was used as a reagent: alcoholic solution of 2% ferric chloride ($FeCl_3$), which shows the grain structure worked in cold or hot and annealed with some visible twin grains, variable grain size, and some porosity seen as dark holes due to corrosion (Fig. 12.3). Some intracrystalline cracks have also occurred due to copper corrosion [3] (Tables 12.2 and 12.3).

According to the manufacturing method used at that time, a rail was prepared where the molten metal, which was obtained from a coal furnace and later gasoline, was poured, the metal contained in crucibles was melted and then cast in molds to obtain solid ingots (Fig. 12.4).

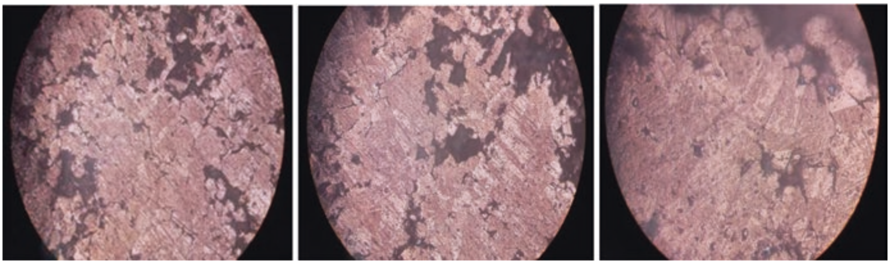


Fig. 12.3 Micrograph of the historical copper coin. Detail corrosion by pitting. Reagent: alcoholic solution of 2% ferric chloride ($FeCl_3$). Magnification: 100×

Table 12.2 Chemistry composition

% Zn	% Ni	% Fe	% Mn	% Cu	% Pb	% Si	% As	% Bi
<0.076	0.099	<0.090	<0.015	96.2	<0.10	<0.26	0.091	0.11

Table 12.3 Vickers microhardness

1°	146 HV	138.7 HBr
2°	132 HV	125.4 HBr
3°	121 HV	114.95 HBr
Average	133 HV	126.35 HBr

Fig. 12.4 The molten metal was poured into the rail, with molds in the shape of ingots

Fig. 12.5 Rails laminator

The ingot did not have an adequate thickness to obtain the blanks and needed to pass several times through the mill, in which the ingots passed between two rollers that pressed the metal strip, stretching it until obtaining the required thickness. When the rail hardened, it was necessary to anneal it to re-laminate it. If the rail was too long, it would be cut into smaller pieces (Fig. 12.5).

Once the rail with a thickness equal to the blanks was obtained, this is annealed in ovens to soften it internally and thus be able to work more easily. A great protection against oxidation that could arise in the annealing process was needed, and the rails were put in the oven in sealed boxes.

The first automatic machinery appeared to drill the rail and obtain the blanks, these machines were manually fed, and the operator had to move the metal strip forward to the rhythm of the machine. The freshly cut blanks then went through the press that created a pre-listel, which, among other things, favored the minting of the listel in the coin, which avoided its wear. The press was formed by a conduit through which the flange passed and while this coin was pressed in its edge, raising it and creating its pre-listel and eliminating the burrs left by the cut of the coin. After the coin was to be annealed to soften it, eliminate internal tensions to facilitate its coinage. Rotary annealing furnaces for blanks appeared in the early twentieth century as in the following illustration (Fig. 12.6). The annealing of the blanks was followed by washing, since in the annealing, rust was formed in the blanks, and these had to be cleaned, first in a chemical solution and then with a bath of soap and water that left its surface shiny. Later they were dried, at first trays were used with hot sawdust and years later drying machines [4].

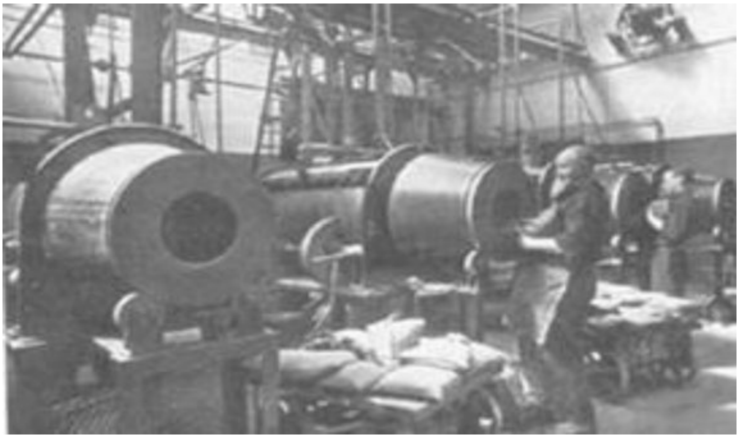


Fig. 12.6 Rotary annealing furnaces for blanks

Discussion

The use of sodium hydroxide for electrolytic cleaning is highly recommended or suitable for cleaning copper, bronze and brass coins. All the corrosion products (greenish malachite layer) had been separated in a time of about 60 min. After washing the coin, its entire surface could be seen in detail. In addition, the good state of conservation of this old coin was verified.

Information from coin collectors' catalogs (numismatic) was also used and it was verified that the coin is legitimate and numerical data of minting and of the company in charge of its manufacture were obtained. It was even verified that there are several models of coins, although they are of the same value, in this case Half Cent since they vary in the shape of the laurel bow since it can be single or double, although other models differ in the shape of the Q of the word RIQUEZA of the Spanish language, or in the form of the number 1 of the date.

Results

This method was applied to the cleaning of museum copper pieces such as teapots and pots, including a historic breastplate belonging to the Mendoza police, that is, the cleaning method works well for both small and large pieces. Thus, the photographs show the result of the treatment in the historical coin. Finally, it should be noted that in the case that the pieces need some type of restoration, it is very suitable to do by means of electrolytic cleaning or galvanic cleaning because it presents great advantages to the piece (coin) through the use of strong oxidizing chemical agents:

1. The use of abrasive products that deteriorate the surface is avoided.
2. Due to the reduction of the protons, there is a hydrogen evolution that is able to clean the surface of the object (there is therefore no need to clean the parts beforehand). This also translates into speed in cleaning method speed, helping to reduce contact time easily.
3. A great saving of time in the restoration takes place: by these methods, the cleaning of a coin is done in a matter of hours and not in days according to the traditional methods.
4. The procedure can be easily automated. Many pieces can be treated simultaneously using cathodes designed for this purpose.
5. The procedure is cheap and does not require expert hands to put it into practice since the piece is always protected by the current itself, being cathode.

Conclusions

This method was applied to the cleaning of museum copper pieces such as teapots and pots, including a historic breastplate belonging to the Mendoza police, that is, the cleaning method works well for both small and large pieces. Thus, the photographs show the result of the treatment in the historical coin. Electrolytic cleaning is a quite effective method for the removal of the corrosion layer; in the case of copper coins, galvanic and electrolytic cleaning should be perfectly usable. The 1 M concentration sodium hydroxide cleaning agent is quite suitable and also not expensive and in these cases sodium hydroxide (NaOH) of pro-analysis quality has not been used, instead sodium hydroxide in flakes for industrial use was used, and very adequate and interesting results were obtained. A suitable, cheap and easily acquired material such as aluminum sheets was placed as sacrificial anode (also called galvanic cleaning). The potentials of the electrochemical series were considered to verify the best pair of materials for copper in this electrochemical circuit, for which aluminum was chosen, with $Al = -1.062$ V being more anodic and with a greater tendency to corrosion, while the copper potential, $(Cu) = +0.337$ V being more cathodic and with less tendency to corrosion [5].

Finally, it should be noted that in the case that the pieces present some type of fracture, it is not advisable to use large current intensities, since due to the appearance of a large hydrogen bubbling, in some cases you could get to the break of the piece.

Border Archaeometallurgy: Pieces found at the “Cerro Mesa” Mapuche Cemetery, Malargüe, Mendoza

Patricia Silvana Carrizo

Abstract

Metallic pieces from the archaeological site of the Mapuche Cemetery of Cerro. Mesa de Malargüe, located in the southern region of Mendoza, Argentina, were studied. These pieces were made of raw and alloyed copper and can be described as a notched quadrangular hoop, three cones, and the hemisphere of a spherical rattle. This study allows us to glimpse that a developed society was inserted south of the Salado River before the arrival of the Spanish colonizers. The studies consisted of metallographic analysis with the help of a portable microscope, analysis of the chemical composition carried out with portable X-ray fluorescence equipment and the evaluation of microhardness. The samples were further characterized by scanning electron microscopy (SEM) and X-ray energy dispersion spectrometry (EDS). There was evidence of changes in metal working methods, as well as in the use of raw materials, and this can be linked to the processes of social transformation that occurred within Mapuche society. These historic metal pieces were studied as part of the Border Archeometallurgy Project carried out between 2016 and 2017.

Introduction

This work is part of the studies conducted on historical materials within the Border Archaeometallurgy Project, of which I am an author, and this project was developed during 2016–2017. A series of metallic pieces found at the “*Cerro Mesa*” Mapuche Cemetery located at the southern region of Malargüe, Mendoza, Argentina, were studied to obtain information related to their processing and technological evolution [6]. The historical material as a whole consists of a quadrangular hoop with notch, three cones, and a hemisphere of a rattle. It may be possible that the hoop, due to its morphology, raw material used and in agreement with the bibliographic review [7] corresponds to the metalworking known as “El Vergel,” which would exist prior to the arrival of the Spanish to these lands of the southern hemisphere, while that the analyzed cones and the hemisphere of the rattle could come from more recent times and may be post-Hispanic in nature. Therefore, the hoop piece would be located within a period of time between 1000 and 1500 AD, and for the rest of the pieces from 1700 AD. As Mapuche people were divided by the Andes mountain range, those ones who occupied the Argentine pampas were called Puwelches, particularly those south of the Salado River. Those who lived in Chile were called Guluches, and occupied the region from the Bíobio River to the south in the Araucania area, maintaining a great exchange across both sides of the Andes mountain range, an ideal mechanism to expand families and strengthen commercial transfer to the marketing points on the banks of the Bíobio River and to assure the mountain passages in their commercial and war trips to the Puwel Mapu in the actual pampa zone to the south of Argentina.

Through the study of historical pieces of Mapuche origin, it is possible to find connections and links of great importance between the invasions of the Inca Empire to the Mapuche lands, but even besides prior to the expansion of the Inca Empire, it is already known that a tradition of metal work would have existed in southern regions of Chile and Argentina. In the same way, the arrival of Spanish to these latitudes left their mark with respect to the use of other techniques for metal-working and in the supply mode of raw materials as well as internal processes dynamics of Mapuche people had influence in the work of metals. The metal pieces of adornment would be linked to the feminine world. In turn, the change in raw materials is linked to the processes of social and political transformations, which, responding to internal dynamics—of prehistoric origin—was powerfully fed by the European arrival and the creation of the Frontier. In this process, both Indigenous and Hispanic-Criollos (Creole) metal craftsmen would participate, following and adapting to the aesthetic guidelines of both worlds, and would produce the changes in the universe of the manufactured pieces. All this can be studied, explained, and perhaps not be able to reach all the answers, but it is possible to add and contribute to the current knowledge.

The purpose of this work is to understand the manufacturing methods and to establish a temporal chronology with the help of applied technology to the study of historical pieces, such as chemical composition studies, hardness, microhardness, and metallography, together with scanning electronic microscopy (SEM) and studies of X-ray energy dispersion spectrometry (EDS) and bibliographic review for greater approach.

Experimental Procedure

The work was carried out on a copper-arsenic alloy quadrangular hoop with notch, three cones and an alloyed bronze bell hemisphere. These pieces come from the Mapuche Cemetery "Cerro Mesa" located in Malargüe, Mendoza, Argentina. The purpose of this work is to evaluate the manufacturing methods used and establish a temporal chronology with the help of technology applied to the study of historical pieces, such as studies of chemical composition, hardness, microhardness and metallography, together with scanning electron microscopy (SEM) and X-ray energy dispersion spectrometry (EDS) studies and literature review for further focus.

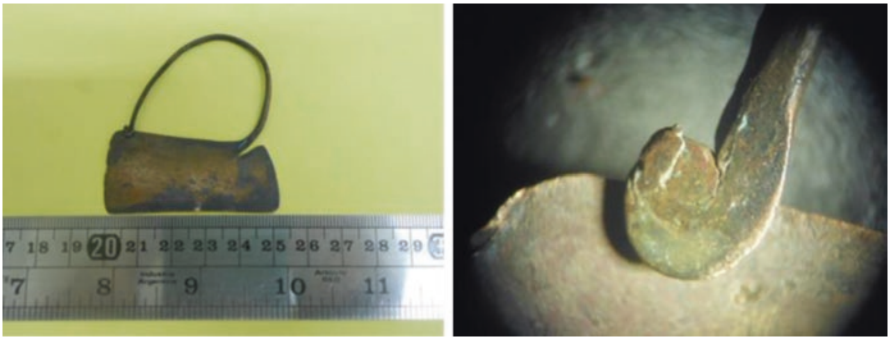


Fig. 12.7 (**a**, **b**) Quadrangular hoop with notch belonging to Mapuche Cemetery of Cerro Mesa ("El Vergel" metal working tradition)

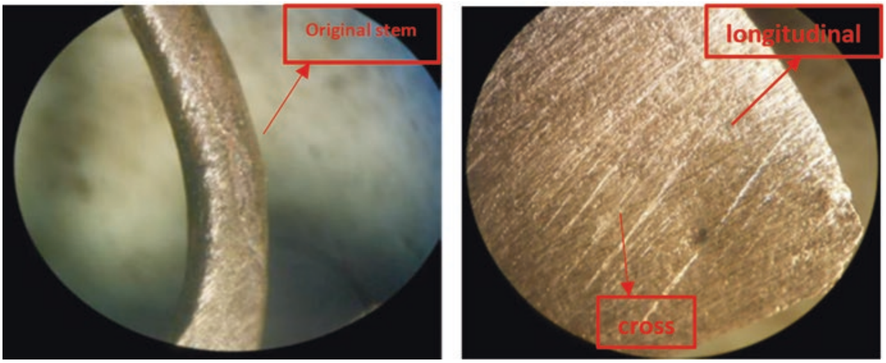


Fig. 12.8 (**a**, **b**) Reduction of thickness by forging and successive reheating of the original stem, in order to stretch it in the longitudinal and transverse directions, respectively

Hoop Quadrangular Hoop with Notch ["Chawai Chapel"]

The quadrangular hoop with notch presents, macroscopically, a good state of preservation and a gentle cleaning was required to begin its studies (Fig. 12.7). From the metallographic and microhardness studies, it is evident that the manufacturing procedure followed was the reduction in thickness by forging and successive reheating of the original stem to stretch it in both the longitudinal and cross-section directions (Figs. 12.8 and 12.9a–c).

Microhardness

Microhardness determination was carried out with a Microdurometer Brand Shimadzu series 344-04152-02 with system microvickers with ISO Standard 6507. The indentation system microvickers 136° with ISO 6507 certificate.

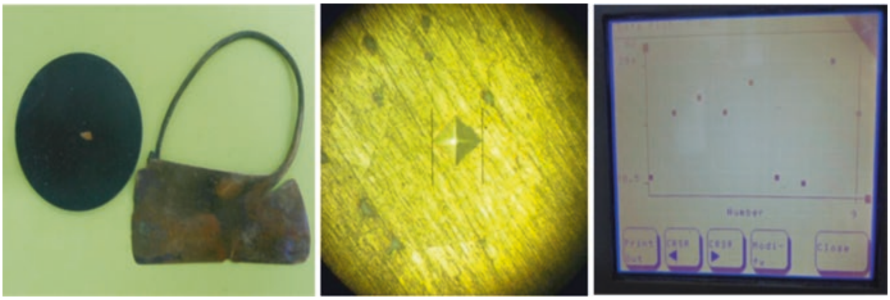


Fig. 12.9 (**a**) Hoop area where the microhardness was taken. (**b**) 50× Indentation. (**c**) Distribution of the indentations taken from the microdurometer screen

Table 12.4 Vickers microhardness

Longitudinal 1°	158 HV	81.2 HBr
Longitudinal 2°	158 HV	81.2 HBr
Longitudinal 3°	173 HV	–
Longitudinal 4°	186 HV	–
Longitudinal 5°	95.2 HV	52.4 HBr
Transversal 1°	90.3 HV	48.2 HBr
Transversal 2°	156 HV	80.5 HBr
Transversal 3°	204 HV	–

Table 12.5 Chemistry composition (mass%) of the Hoop with notch

Zn	P	Si	S	Pb	Fe	Mn	A	Cu
<0.057	0.38	≪0.30	0.012	<0.064	<0.020	<0.014	4.32	Balance

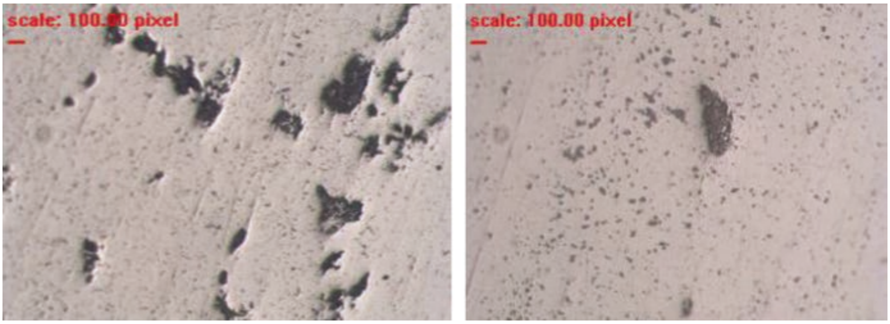
The load applied in the test is 1961 N (HV = 0.2), with an loading time of 15 s (Table 12.4).

Chemical Composition

The metallic elements of the sample were determined in a portable spectrometer for analysis of non-ferrous materials, SPECTRO XSORT Handheld X-Ray Spectrometer brand. Method: X-ray fluorescence emission. The values are shown in Table 12.5.

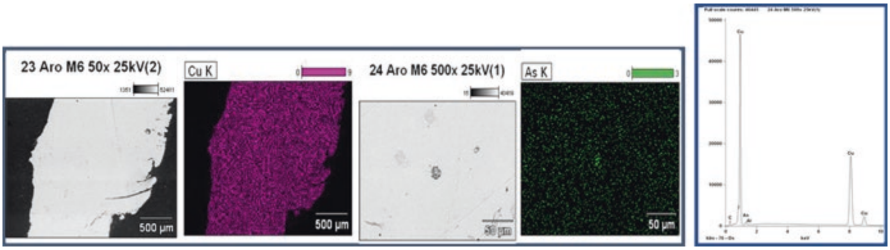
Metallographic Study

Observations: The simultaneous concurrence of an approximately constant composition by a single phase and an adequate proportion of arsenic, from the metallurgical point of view, supports the hypothesis that it was intentionally used and that



Micrographs 12.1 and 12.2 Typical structure of solid solution of arsenical-copper constituted by a single phase. Reagent: ferric chloride. Magnification: 200×

its content in the alloys was controlled in some way. The arsenic (As) alloy with copper (Cu) improves properties such as strength, hardness, malleability, and ease of melting. The contents of trace elements analyzed are low. If the proportion by weight of arsenic in the alloy is less than 8% w/w [8], we can see this typical structure of solid solution of arsenical-copper constituted by a single phase (Micrographs 12.1 and 12.2).



Observations: Filter fit chi-squared value: 47.479 errors: ±2 Sigma. Correction method: Proza (Phi-Rho-Z). Acc. voltage: 25.0 kV. Take off angle: 37.4°. Friday August 12, 15:30:52, 2016.

From the metallographic and microhardness studies, it is evident in this piece that the procedure followed was to reduce its thickness by forging and successive reheating to the original stem, in order to stretch it in both the longitudinal and transverse directions [9].

This is deduced by the presence of shear lines and annealing twins, a deficiency of the recrystallization annealing is denoted due to the complexity of calculating based on scores the exact temperature that must be applied to the piece after having been plastically deformed. Despite the limitations mentioned, they knew how to maintain the fine grain, whose advantage is to enhance the mechanical resistance to the object.

Observing the micrographs can be deduced that they did not reach beyond 600 °C since the dendrites just disappear at 700 °C, and with this, to prevent the grains from increasing in size and therefore the piece losing mechanical resistance.

Arsenic sublimates around 603 °C; so to avoid its volatilization, it is possible that this chemical element has been added to the liquid by previously encapsulating it in a copper flake, its fusion being rapid and/or although there is also the possibility that arsenic was already present in the native copper.

The average value of microhardness in the longitudinal direction is **154 HV,** and in the transverse direction it is **150 HV**. The microhardness value of a current alloy of copper-arsenic (Cu-As) has a value of **151 HV**, which indicates the degree of technological development of the Mapuches to achieve a resistant material.

The copper-arsenic alloy is atypical, but if may come from the different mineral sources such as enargite ($CuAsS_4$) and tennantite (Cu_3AsS_3) that are present in common form in the region, it could be considered a fortuitous event and can be considered valid.

However, this does not mean that the artisans have not deliberately selected certain ores to be treated, after noting that the product obtained had appreciable advantages over the products obtained from other ores.

In other words, although they could not know that, “technically,” they made an arsenical copper, if they could take into account that processing enargite they had a metal of better qualities and the color even more reddish than the result of processing, for example, malachite [Cu_2 ($OH_2 \cdot CO_3$)].

Indeed, the square hoop with notch is from the pre-Hispanic tradition called “*El Vergel,*” and we must consider that this type of hoop corresponds to this morphology, that is to say quadrangular with notch, stopped being manufactured surely at some time of the eighteenth century, but this does not prevent these pieces have continued use, perhaps inheriting from generation to generation. The data of the alloy copper-arsenic (Cu-As) is very interesting, since it allows us to place this piece in the timeline, because this alloy tends to be the dominant alloy during the pre-Hispanic time.

Alloy Brass Cones (They Integrated Pectoral Pendants Called “Sikil”)

Macroscopically observing the three cones, their morphology is very similar, as well as its chemical composition and microhardness values (Fig. 12.10a–c). It is possible these cones integrated the Pectoral Pendants called “Sikil,” this type of pendants also have tubes in another versions. According to this, cones or tubes they fulfilled the function of a type of ornament according to the model of pendant to be manufactured. And according to ref. [10], these pendants seem to emerge after the nineteenth century, approximately 1860 AD (Fig. 12.11a–c).

Fig. 12.10 (**a–c**) Cone 1, Cone 2, and Cone 3 belonging to the "*Cerro Mesa*" Mapuche Cemetery

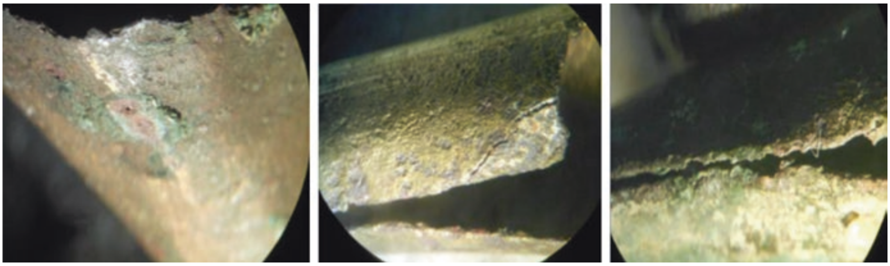


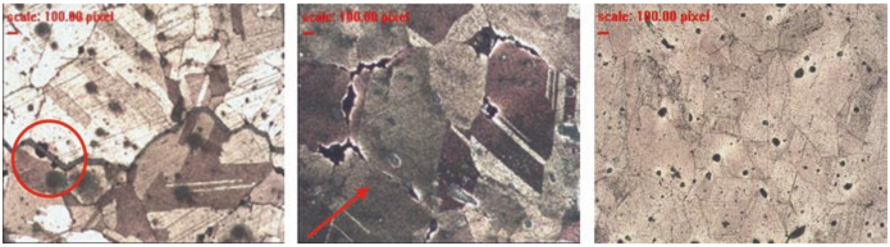
Fig. 12.11 (**a–c**) Macrographic images of the three Cones belonging to the "Cerro Mesa" Mapuche Cemetery

Table 12.6 Vickers microhardness

Measurements	Depth (mm)	Microhardness value HV	Equivalent HRB
Cone 1			
1	0.10	125	69
2	0.20	119	66
3	0.50	119	66
Cone 2			
1	0.10	103	58
2	0.20	112	63.2
3	0.50	112	63.2
Cone 3			
1	0.10	138	74
2	0.20	147	77.5
3	0.50	157	81

Microhardness

The determination was carried out with a Microdurometer Brand Shimadzu series 344-04152-02 with system microvickers with ISO Standard 6507. The indentation microvickers system 136°, ISO 6507 certificate. The load applied in the test is 1961 N (HV = 0.2), with an application time of 15 s (Table 12.6).



Micrographs 12.3–12.5 Typical structure of forged brass α for cartridges, showing a corrosion's crack (red circle). Reagent: ferric chloride (Cl_3Fe). Magnification: 100× and 200×

Table 12.7 Chemistry composition (%)

Piece	Zn	Ni	Si	S	Pb	Fe	Cu
Cone 1	24.4	0.060	0.73	0.15	2.91	0.34	Balance
C 26000	≡ 31.3				0.07	0.05	68.5–71.5

Table 12.8 Chemistry composition (%)

Piece	Zn	Ni	Si	S	Pb	Fe	Co	Cu
Cone 2	27.9	0.042	1.42	0.25	3.28	0.33	0.030	Balance
C36000	≡ 34.3				2.5–3.7	0.35		60–63

Table 12.9 Chemistry composition (%)

Piece	Zn	Ni	Si	S	Pb	Fe	P	Sn	Cu
Cone 3	26.2	0.040	2.92	0.43	2.6	0.51	0.39	0.12	Balance
C36000	≡34.3				2.5–3.7	0.35			60–63

From the microhardness studies, it is possible to suggest the manufacturing process of the receptacle, it could be that the original ingot had a greater plastic deformation in one of its ends until forming a thin sheet, which was rolled using for example a wood as a guide (Micrographs 12.3–12.5).

Chemical Composition

The metallic elements of the sample were determined in a portable spectrometer for analysis of non-ferrous materials, SPECTRO XSORT Handheld X-ray Spectrometer brand. Method: X-ray fluorescence emission (Table 12.7).

Observations: The chemical analysis of the piece corresponds to what is currently a commercial alloy for forged brass: Brass for cartouche 70% C26000 [11] (Table 12.8).

Observations: The chemical analysis indicates that it could correspond to one of the commercial alloys for forged brass, as it is: Brass α for cartouche 70% C36000 (Table 12.9).

Observations: The chemical analysis corresponds to one of the alloys for forged brass α: Brass α type with lead (Cu-Zn-Pb) for cartouche 70% C36000. The addition of lead (Pb) increases the machinability, although mechanical strength decreases

From the microscopic study, the images show structures consistent with α-brass and of leaded brass (Cu-Zn-Pb). The metallographic structure is very similar to the Cu-Zn alloy, lead appears as small dark particles in grain boundaries. Manufacturing process consists of alternating processes of hot rolling, subsequent annealing, to be then again rolled but cold at this time and final annealing to increase the grain size.

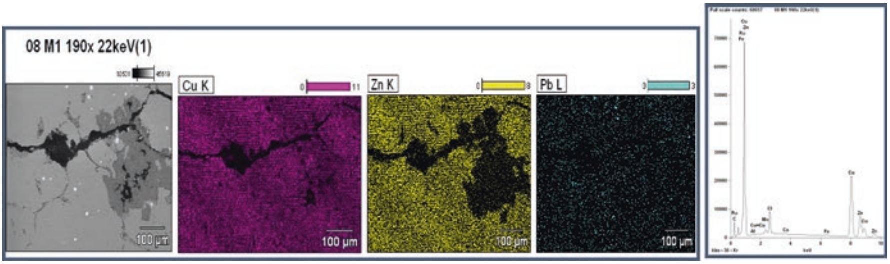
Arrow in the lower left corner of the micrograph indicates the direction relative to the tread plane of the sheet. The images show equiaxial grains, polygonal, annealed twins, sliding lines, and some casting segregations; this reveals the process that took place in the material to give it the desired shape.

The addition of lead increases machinability, although mechanical strength decreases. Ferric chloride was used as reagent. Magnification: 100× and 200×, respectively.

The results to the pieces in study suggest that they are objects worked by deformation from an ingot, whose form seems to have been quite similar to the finished piece.

It is possible to suggest an approximation of the manufacturing process of the receptacle, and it could be that the original ingot had a greater plastic deformation in one of its ends until arriving to form a thin sheet, that possibly having this sheet the shape of a truncated triangle, and then they proceeded to place a wooden stick or other material, which serves as a "guide" in the center of the sheet. Then the sheet was folded by forging until its ends were joined, thus obtaining the cone shape.

In the micrographs you can see, after being polished, the lines that indicate the process to which they were subjected. In addition, to soften the material and give it the desired shape, the process that took place alternately consisted of hot rolled and forged, followed by successive stages of annealing accompanied by cold rolling and forging. The micrographs show equiaxial grains, polygonal, annealed twins, sliding lines, and casting segregation.



Alloy Bronze Rattle Was Part of a Pin Piece ("Tupu" or "Katawe")

Macroscopically observing this Bronze Rattle could be admitted that the metal artisans reached the knowledge that in order for the metal not to be broken by the continuous forging, it needs successive reheating, making the material return to its stress-free state by means of heat application (Fig. 12.12). The surface of the piece has grooves, which can be seen when observing with a stereoscopic magnifying glass where the lines are evident in the material on the outer side, corresponding to the surface where the material was supported and struck and inside the interior of the hemisphere, as can be seen in Fig. 12.13a, b, the internal area where the forge developed became soft and smooth.

Fig. 12.12 Image of the Alloy Bronze Bell that could be part of a pin piece, called "Tupu" or "Katawe," respectively, depending on the model

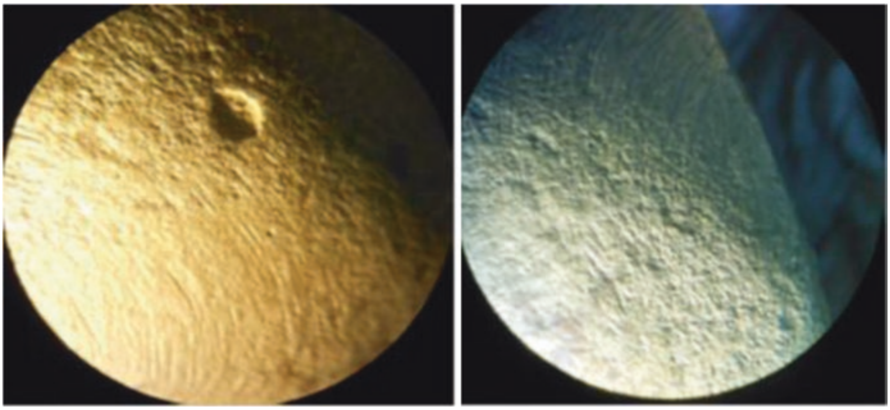
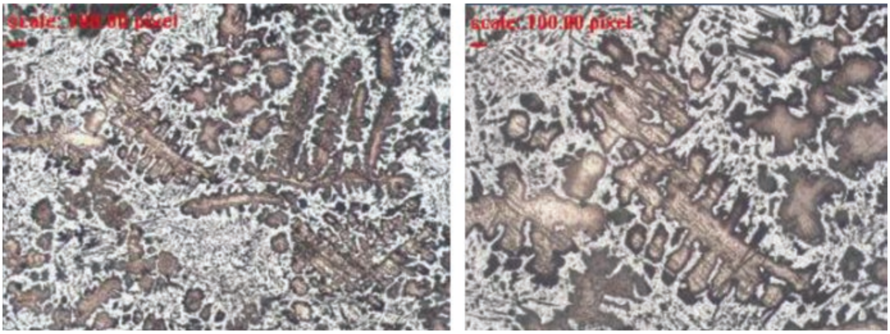


Fig. 12.13 (**a**, **b**) Macrographic images of the alloy Bronze Rattle from the "*Cerro Mesa*" Mapuche Cemetery

Table 12.10 Vickers microhardness

Point	Depth (mm)	Microhardness value HV	Equivalent HRB
1	0.10	147	77.5
2	0.20	118	65.5
3	0.50	129	70.5



Micrographs 12.6 and 12.7 Corresponds to Bronze alloyed with zinc, silicon. Reagent: 3% ferric chloride (Cl_3Fe). Magnification: 100× and 200×

Table 12.11 Chemistry composition

Piece	%Zn	%Sn	%Si	%S	%Pb	%Fe	%Ni	%Sb	%Cu
Bronze rattle	6.46	8.65	*7.87*	0.11	*6.35*	0.71	0.13	0.11	*63.2*

Microhardness

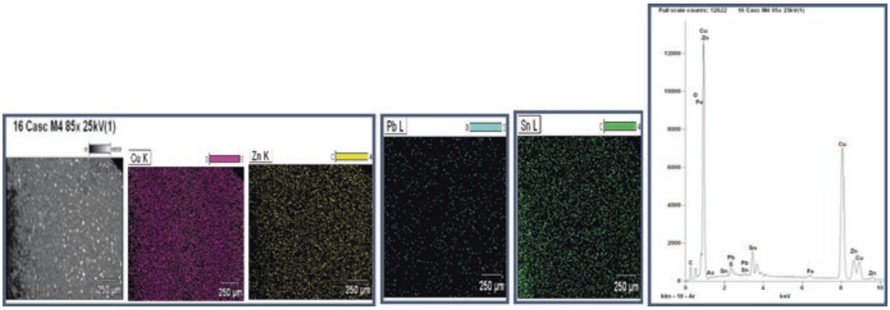
The determination was carried out with a Microdurometer Brand Shimadzu series 344-04152-02 with system microvickers with ISO Standard 6507. The indentation microvickers system 136°, with ISO 6507 certificate. The load applied in the test is 1.961 N (HV = 0.2), with an application time of 15 s (Table 12.10).

The metallographic structure corresponds to an alloy of the bronze type alloyed with silicon and zinc. The lead (Pb) surely comes from the welding process of joining both hemispheres. It is a bronze (Cu-Sn). The dendritic structure from the cold-worked of cored grains (Micrographs 12.6 and 12.7).

Chemical Composition

The metallic elements of the sample were determined in a portable spectrometer for analysis of non-ferrous materials, SPECTRO XSORT Handheld X-ray Spectrometer brand. Method: X-ray Fluorescence Emission.

The chemical analysis of the sample corresponds to bronze alloyed with silicon and zinc. The Lead corresponds to the union by welding of both hemispheres which gave form to the pin called "*Tupu*" or "*Katawe*" (Table 12.11).



Manufacturing Process of the Bronze Rattle Pin Called "TUPU" or "KATAWE"

For the construction of this pin, two equal discs are used, which are hammered to create two hemispheres. In this particular case, the hemispheres are flattened at their poles and, however, like all models of punches or pins, are joined by welding at its equatorial center. Decoratively, a fluted fret was used that allows the visual division of two poles of the cap where two holes were made to put a large needle. In the upper part stands a piece that is sculpted with various motifs, whether medals, crosses, or anthropomorphic forms.

In late 1700s, Morris [12] mentioned the use of metal artifacts by the puwelches, so it could be post Hispanic. This copper tupu (pin) could be placed in the eighteenth century and it distances it from the paradigm of the Mapuche Silverware precisely because it is spheroidal, as well as being made of alloyed bronze.

Finally, since they are the four metals most referred (copper, silver, iron, and gold), it is possible that each one has had a historical origin of different and independent supplies.

In the case of copper, it is feasible to propose that two modes of raw material supply coexisted in the early post-contact period: first from local mines, possibly involving the reduction of minerals, and therefore continuing with the pre-Hispanic tradition, and the second, where the Hispanic presence was articulated and obtaining the raw material through exchange and looting

Other mode of supply goes through the phenomenon of fusion of existing copper pieces. On the other hand, it is important to bear in mind that, although in historical times the knowledge about the reduction of minerals would have been lost, this does not imply that the knowledge of fire management has been lost precisely, for example: "the fusion of existing metals again and recycling."

Precisely, the historical record would be supported by the statement of [13] that until 1840, "*the trousseau of the Mapuche woman is composed of only three pieces: the pins (tupu/katawe), the tendrils (upul) and rings (iwelkuc),*" then it is considered that the vast majority of the complex and large pieces that are part of the Mapuche Silverware must be after 1840.

Metallurgical, Historical, and Heritage Study of Copper Pieces Contemporaries to the Liberating Army of San Martin

Patricia Silvana Carrizo

Abstract

The following article offers an interdisciplinary study in which Argentina's history, archaeology, and engineering are once again a common point: it presents an essay that has as its protagonists two pieces of copper that could belong to the San Martin's liberation campaign. One of the pieces is a little teapot while the second is a pot, and both are assets of the Regional Museum and Americanist "Saint Rose" House, belonging to the Town Hill of Luján de Cuyo, Mendoza, Argentina.

Unfortunately, it has an unknown provenance or site where they were found, and for this reason, one cannot assert, but we can say it is very possible that they could have belonged to the army of General San Martín, which is why it is proposed to find some characteristics of its origin for these objects and to establish a relative chronology, using the characteristics of its production methods, and these data place these parts in the story corroborating it with the studies and to say that it is likely they belong to equipment manufactured by Friar Luis Beltran for the army of San Martin. This will use historical sources and metallurgical and chemical information derived from studies in the laboratory.

Keywords

Army San Martin; Ammunition; Friar Luis Beltrán; Copper; Forge welding

Introduction

General José de San Martín planned a liberating campaign that had to stock up with cannons, bullets, and grenades and other projectiles, gun carriages, rifle cartridges, backpacks, saddles, troop shoes, gear, and other war supplies for the Argentine hosts [14]. With the aim of overcoming this lack, San Martín found the right person and appointed him on March 1, 1815, to Friar Luis Beltrán as second Lieutenant of the third Artillery Battalion, entrusting him to take charge of the assembly of the Army Park and Maestranza. Expressly asking him that the weapons he manufactured should be strong but at the same time light in order to be able to rise up the

Andean peaks, that is why the friar manufactured the vast majority of copper foundry supplies (light and soft material), and to give it resistance, he used alloying metals such as beryllium, which gives copper a hardness and resistance similar to steel but with the advantage of being light.

With 700 men in their workshops under their care, they manufactured from spark stones for rifles and fittings for horses, to footwear for the troops. "*Understood in all the manual arts, what he did not know he learned"* as recounted by General Bartolomé Mitre [15].

Thus, according to history, he is credited with the effective and active creation of an entire manufacturing organization that allowed the Army of the Andes to be supplied with the necessary objects and weapons. After improvising his staff with creoles and countrymen of good will, he cast cannons, bullets, and grenades using the metal of the temple bells and the bronze utensils he obtained from the families, that is, he looked for raw materials in all the metal artifacts that he could find. Not even the church bells were spared and of the seven that existed in the Convent of San Francisco, six went to their ovens, after lowering them with rigging of his own invention. All molten metal would be transformed into campaign elements and would cross the Andes being participants in the feat. It was all under strict discipline, enthusiasm, control, and economies, which have taken from General Mitre, the expression of Archimedes of the Los Andes Army, for the glorious friar. With good reason, it has been possible to say in happy and inspiring phrases:

> *At Priest Beltrán's breath, the forges were lit and the metals that he modeled into war artifacts melted like wax. Like a Vulcan dressed in talar habits, he forged the weapons of the revolution.*

Development

Friar Luis Beltrán: Great Craftsman of the Liberating Armies

He was born in the vicinity of Mendoza, on September 7, 1784, the son of Luis Bertrand and Manuela Bustos. He was educated in the San Francisco's Convent and when he turned 16 years old, he decided on an ecclesiastical career. Transferred to Chile, he was Vicar of the choir in the Santiago's Convent (Image 12.1).

In 1811, he began in the Chilean Army's Maestranza, and the following year, he served as Chaplain of the Carrera's Army. In 1814, he returned on foot to Mendoza through the Los Andes Mountain Range, carrying his bag of tools and instruments to isolate himself in his Convent.

He was incorporated into the troops of San Martín as Chaplain of the Los Andes's Army, who enlisted in the *Plumerillo* Camp and later in 1815 General San Martín entrusted him with the Maestrance of the Liberation's Army. In 1816, he was promoted to first Lieutenant with the rank of captain, this decision caused conflict in Buenos Aires, but nevertheless he received the authorization from the Canon Diego Estanislao Zabaleta and the incorporation of the friar-soldier figure status to the fighting forces was achieved [16, 17].

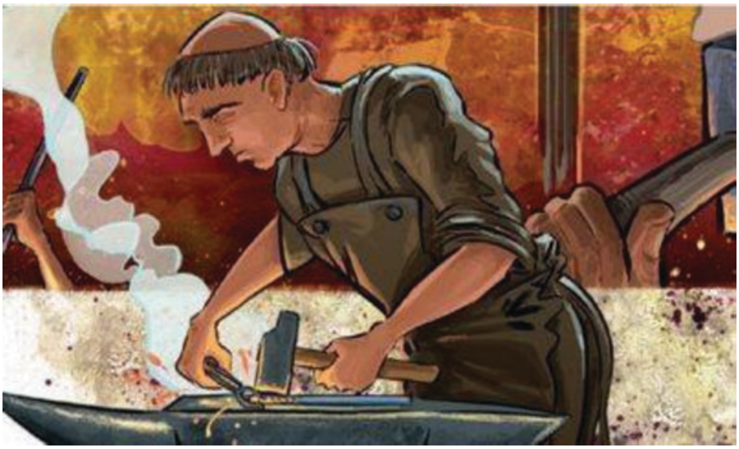


Image 12.1 Friar Luis Beltrán: "the metallurgical priest"

Bartolomé Mitre qualifies it like this: "Every wealth of science he had acquired by himself in his readings, or by observation and practice. Thus he became a mathematician, physicist and chemist by intuition; gunner, pyrotechnic, carpenter, architect, blacksmith, draftsman, an embroiderer and a doctor by observation and practice, understood in all the manual arts and what he did not know he learned just by applying his extraordinary mental faculties to it."

After the Chacabuco's battle, on February 12, he obtained a silver medal. The *Cancha Rayada's* defeat cost him the loss of almost all the ammunition prepared materials. This forced him to work day and night, for 17 days to remake the weapons that would allow the brilliant triumph of Maipo, on April 5, 1818. Then the government of Chile decorated him with a silver medal and the from that Buenos Aires declares him as "Heroic defender of the Nation."

He participated in the Liberation Campaign to Peru, where he acted until 1824. In 1823 he received the dispatches of Lieutenant Colonel Graduate. In 1824, faced with an unjust reprimand from Simón Bolívar, who plunged him into despair, losing his mind, he returned to Buenos Aires. In 1827, installed in Buenos Aires, and feeling that his end was coming, he renounced his arms and spent his last life months concentrated only on religious practices. He died on December 8, 1827, wearing his talar habit and was buried in the *Recoleta* Cemetery, Buenos Aires, in priest class.

Metallography of Archaeological Alloys

On the occasion of illustrating situations where metallography has contributed to the metallurgical study in archaeology; an example is the primitive use of metallic materials. Although the exact date of when man began to use metals is unknown, it is clear that the primitive metals used were native metals, that is, those that are in their metallic form in nature were then available and ready to use without the need for smelting from minerals.

Only a few metals appear or are in the native state, copper being the most important and it is thus that this native copper was the first metal used by humanity approximately 8000 years BC. Later, it took several million years for the development of copper smelting techniques. It is of great importance to be able to find a connection between these developments, but in order to do this by analysis of archaeological objects, it is very necessary to be able to distinguish between native copper and early molten copper. This is not difficult to achieve by compositional analysis as native copper is of high purity but has traces of other elements and can therefore be distinguished from molten copper, early molten copper has high purity compared to copper native [18].

The high purity is a consequence of the minerals being chosen by hand and then melted, so it has a high grade in small quantities and low furnace temperatures, so there was little opportunity for it to be contaminated with impurities. The microstructure of native copper is usually distinguished by large grain size and contains very low density of nonmetallic inclusions (a clean structure) and in some cases abundant long, thin equiaxed twin grains. Furthermore, the inclusions that are present are typically silica and silicates in greater quantity than the oxides or sulfides that are more present in molten coppers. The upshot of all this is that metallography is of great use for the differentiation between native copper and molten copper.

Methods and Materials

Methodology

This historical research is approached through the use of scientific analysis techniques such as metallographies, chemical composition, and manufacturing process of these two archaeological pieces, and with this, it seeks to provide the necessary information that certifies their origin within the context historical record and thus provide important heritage information.

Due to the characteristics of its elaboration, it could be said that the pieces are within the temporal range covered by the San Martín campaign, that is, they are contemporary to the Liberating Campaign, covering a period that goes from 1740 to 1840.

Pieces Studied

Copper Teapot

Metallography and Microstructures of Copper and Its Alloys

Copper and its alloys have played an integral role in the human advancement of technology since ancient times. Native copper and later copper alloys, even bronze, were first used as tools and for decoration. The combination of electrical and

Image 12.2 Molten copper teapot belonging to the Regional and Americanist Museum

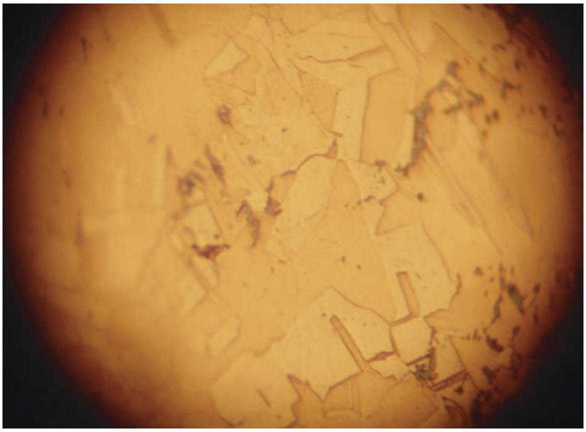
thermal conductivity, workability, corrosion, resistance, and their abundance have made this family of metals important to the entire industry.

It corresponds to an alloy with a high content of recycled molten copper, with a copper content close to 94%, it would be almost pure copper, which corroborates with what was explained above about the need to see the difference between native copper and molten copper.

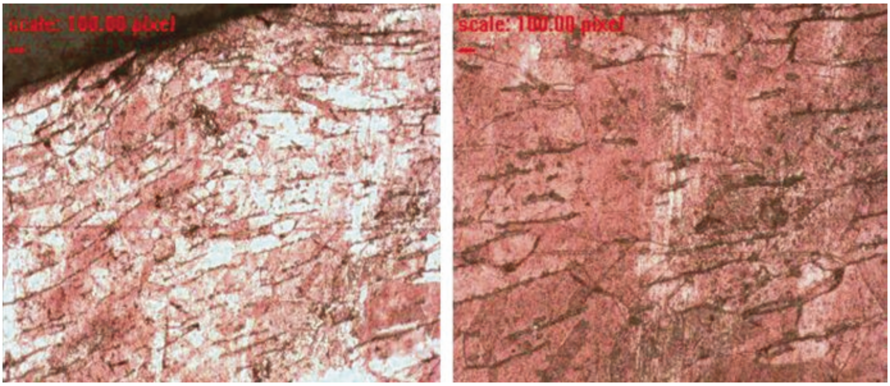
The teapot (Image 12.2) is a piece made of molten copper due to the characteristics of its high purity, which indicates that it was manufactured with copper mineral native to the region (which occurs in the absence of impurities in its chemical composition), as well as with recycled and melted copper metal objects, which were obtained from the donations of families and churches in Mendoza for the liberation campaign of General San Martin that did not initially have the support of Buenos Aires (here it is useful to remember that San Martín created and instructed his liberating army in Mendoza).

Notes About Gas Solubility: The oxygen content must be carefully controlled, so that copper oxide is not formed, which is harmful and reduces workability. In molten copper, oxygen can react with dissolved hydrogen to form water vapor that later on solidification remains in the form of bubbles, making the material weak (Micrograph 12.8).

In the teapot piece, according to the analyses carried out, this information can be extracted, since it is molten copper (there is presence of green sulfides), it is almost pure copper and the absence of oxygen in its structure tells us that it was fused with charcoal; this is also explained by the forge that Priest Luis Beltrán used which is located in "*El Plumerillo*" Maestrance Camp. This shows that these smelting procedures with charcoal used to eliminate the oxygen present, due to its harmfulness, are consistent with the historical facts and the chemical analyses carried out.



Micrograph 12.8 Metallography of the bottom of the pot directly taken with a metallographic microscope



Micrographs 12.9 and 12.10 Metallographs of teapot fragment, details of inclusions and lines indicating forging

As well as the metallographic structure of this piece [19], which has long equiaxed grains, and which highlights the evidence that there was cold work to make this piece, that is, it was worked with blows, hammer blows to give resistance to the material by hardening it, before it had completely cooled down. This is verified with the naked eye in this historical piece (Micrographs 12.9 and 12.10).

Description of Micrograph 12.8: Oxygen-free copper structure. Large, twin, equiaxial grains. Cold rolled and forged. Presence of sulfides (green color) which indicates that it is a practically pure molten copper. Magnification: 100×, Reagent: 3% ferric chloride ($FeCl_3$).

High Copper Alloy Pot

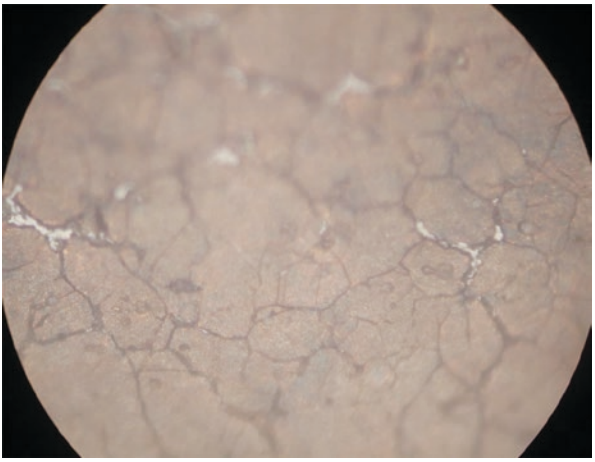
The largest amount of copper alloys are those that consist of solid alloys. Copper-rich alloys are copper-beryllium, copper-chromium, and copper-zirconium, but they have limited solubility. These systems can be hardened by precipitation, and this phenomenon is also known as precipitation strengthening and aging hardening.

The pot part is a copper-beryllium alloy, which is shown by the analyses carried out that it was treated at high temperatures. Beryllium is an alloy that is added to copper to harden, that is, to increase the hardness of the material and also its resistance, making it similar to steel but light (Images 12.3 and 12.4).

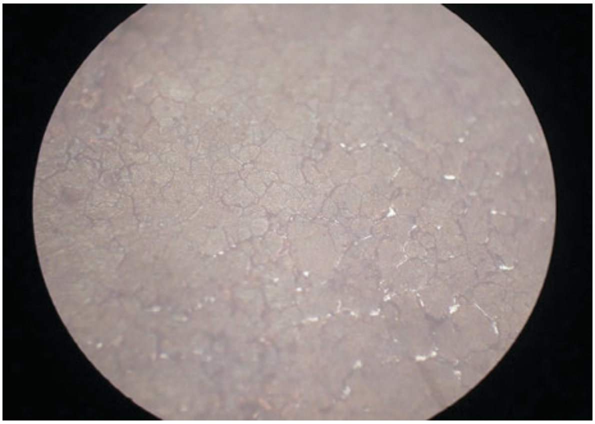
> *"If cannons have to have wings, they will,"* Friar Beltrán told to San Martín.

In the metallographic structure of the pot piece, equiaxed grains of a supersaturated solid solution of beryllium in copper can be seen.

Images 12.3 and 12.4 Copper-beryllium alloy pot. Belonging to the Regional and Americanist Museum, Luján de Cuyo Town Hill, Mendoza, Argentina



Micrograph 12.11 Equiaxed grains, 11% reduction due to cold rolling. Alpha grains elongated in the direction of rolling. Magnification: 200×. Reagent: 3% ferric chloride ($FeCl_3$)



Micrograph 12.12 Copper-beryllium alloy, solid solution. Magnification: 100×

A reduction in grain size by 11% is also observed by cold rolling, elongated alpha grains are observed in the determined rolling direction (Micrograph 12.11). This rolling and forging work can be seen with the naked eye in the piece, where it can be seen that it was made from a hammered copper-beryllium alloy sheet and joined at its opposite ends by lead welding (Micrograph 12.12).

Forge Welding

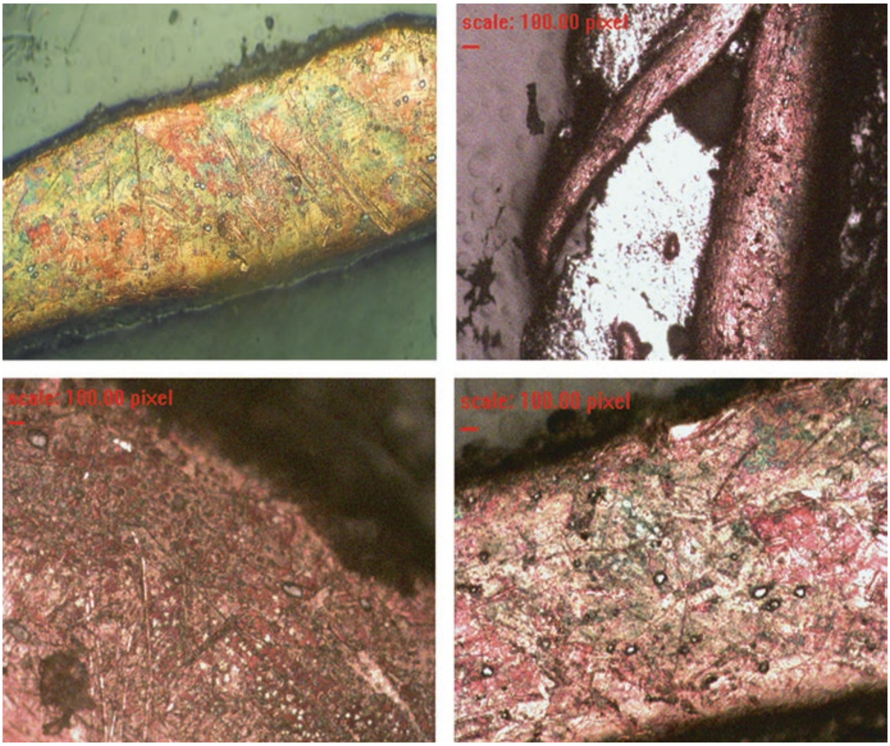
Forge welding is a process for joining two metals by means of heat or pressure and is defined as the metallurgical bond between the atoms of the metal to be joined and the filler metal. The oldest welding process is forge welding [20]. This consists of heating the pieces to be joined in a forge, and then by means of pressure or knocking, the joining of the pieces is achieved. Its limitation is that it can only be applied in small pieces and in the form of a sheet. The union is made from the center of the pieces outwards and oxidation must be avoided, for this thick oils with a flux are used, and usually borax combined with ammonium salt is used.

History of Forge Welding

Forging welding is the first type of welding to appear in history. The earliest examples of forging welding date from the Bronze Age and Iron Age in Europe and the Middle East. Forge welding was used in the construction of the Iron Pillar of Delhi, India, built around 310 AD. The Middle Ages brought advances in forge welding, with which blacksmiths repeatedly struck and heated metal until the union occurred.

There was even a joining method that was used in conjunction or combined with forge welding called "encasting," which is the joining method by means of inserts, by which tabs or inserts were cut from the metal of an area with the inserts made of metal from another area, for example, the bottom of a container and these cuts or tabs were embedded, which were thus locked, in this way it was achieved that the parts remained united and closed, in this case a third material was not included, then these tabs were worked by forging welding, and this was the final touch to avoid spillage (Images 12.5 and 12.6, Micrographs 12.13–12.16).

Images 12.5 and 12.6 Pot body and pot base zone forge welding piece



Micrographs 12.13–12.16 Forge welding metallographic picture set: pot base zone and pot body zone

Conclusions

With this investigation, it has been possible to affirmatively determine that these historical pieces could have belonged to the supplies of the Liberation Army of San Martín since, due to the scientific analysis of the procedure of their manufacture, it was verified that they certify the origin of the same within the historical context noted, covering a period from 1740 to 1840. It has also been possible to corroborate through a review of Argentine history on how the preparations for the provision of ammunition and supplies for the Liberation Army were carried out by the Friar Luis Beltrán (Images 12.7 and 12.8).

Through this work, an attempt is also made to rescue the hero and praise the work of this metallurgical friar, Patron of Argentine Metallurgy, who was the owner of an exemplary nobility, a great personality characterized by his typical optimism, a self-taught being, an endearing and disinterested collaborator of the emancipatory deed of America, in addition to providing interested parties with important patrimonial information.

Image 12.7 Panoramic view of the Forge of the Friar Luis Beltrán, Maestrance Place, Historic Camp *"El Plumerill*o", Las Heras, Mendoza, Argentina

Image 12.8 Top view of the Friar Luis Beltrán's Forge, Maestrance Place, Historic Camp "*El Plumerillo*", Las Heras, Mendoza, Argentina

Acknowledgments

The author Patricia Silvana Carrizo wants to thank: Mayor of Luján de Cuyo, Lic. Omar Parisi (with completed mandate), Ms. Professor Marisa Garnica director of Human Development, Family and Community (with completed mandate), Mr. Omar Giunta† director (with completed mandate), and the staff of the Regional and Americanist Museum "Saint Rose House," Eng. Miguel Ángel Franetovich, director of the Metallurgy Laboratory (with completed mandate) of the National Technological University Mendoza Regional Faculty, the Alberdi Library staff, the San Martín Library staff, the staff from the *"El Plumerillo"* Historical Camp belonging to Las Heras Town Hill, and the staff of the Mendoza Province Historical Archive, who all very kindly collaborated and provided historical information for this work.

Gold Artifact Production During the Central Andean Formative Period: New Evidence from Chavín De Huántar and Caballete, Perú

Luisa Vetter and Augusto Bazán

Abstract

Current knowledge on the beginnings of metallurgy in the Andean area is still scarce. Some new findings have been reported from tombs belonging to the Late Archaic and Middle Formative Periods, in the form of small pieces of laminated gold. In this article, we will study two gold beads scientifically excavated from contexts associated with the Middle and Late Formative Periods of the North Central coast and highlands. These gold pieces have been chemically analyzed via Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS), and the results have been compared with the available databases of pieces belonging to these periods, with the objective of unveiling the characteristics of the raw material from which they were fabricated and the changes made from one period to the next.

Keywords

Central Andes; North Central Coast; North Central Highlands; Middle Formative Period; Late Formative Period; Gold

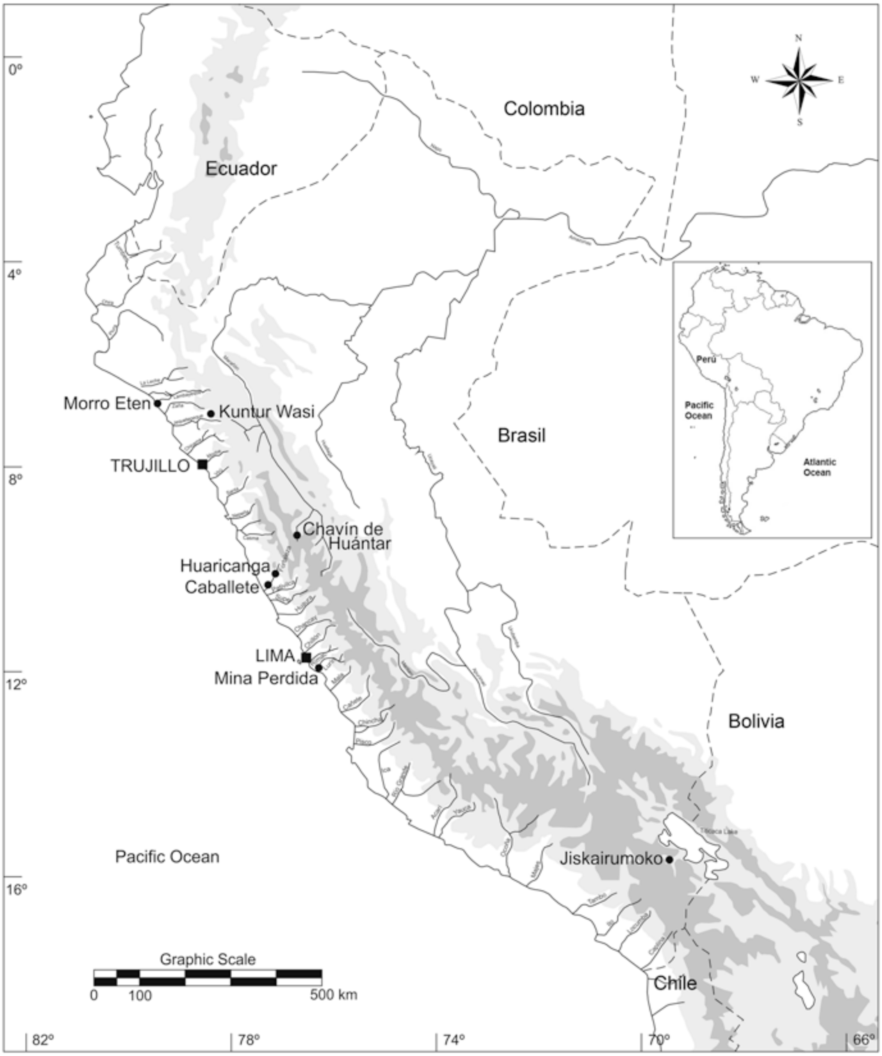
Introduction

Two small gold beads, from two different Formative Period contexts in the Central Andes, were found on the North Central Coast and in the North Central Highlands of present-day Peru. The find from the North Central Coast was made in the Fortaleza Valley, at the archaeological site of Caballete, in the funerary context of two individuals, an infant and an adult. The bead was found in association with the adult, along with other objects such as *mates* (gourd vessels), *piruros* (mace heads), obsidian tools and flakes, mollusk-shell beads, bone and reed implement probably related to textile production, and concentrations of small pyrite beads among many other loose beads. This burial yielded a radiocarbon date of 897–419 BCE.

The second find was made in the North Central highlands, at the site of Chavín de Huántar, specifically in a fill layer from natural depositional processes after the abandonment of the recently discovered Galería de la Explanada (Gallery of the

Esplanade). The discovery consists of a necklace composed of 40 beads, 24 of which are made from gold and 16 of which are made from shell. The necklace was found in association with a semiprecious stone, three shells, and carbon fragments, and the find has been dated to 800–500 BCE.

The metal beads from these two different sites were made with gold sheets that were subjected to a process of plastic deformation until they reached their final thickness. They were deposited in a funerary context and an architectonical context, similarly to other metal pieces found in sites from the same time periods (Map 12.1).



Map 12.1 Map of Peru showing the location of the archaeological sites mentioned in this article (Elaborate by A. Bazán)

This evidence allows us to expand our scarce knowledge of metallurgy during the early periods in the Andean region.

The Contexts: Caballete and Chavín de Huántar

Two objects were analyzed, from two different archaeological sites: the renowned ceremonial center of Chavín de Huántar, located in the southern part of the Callejon de Conchucos in the North Central Highlands, and the site of Caballete, located in the lower section of the Fortaleza Valley, on the North Central Coast. Both occupations date to the Formative Period.[1] However, a study of their specific contexts allows for a better understanding of their chronological location within this long period.

Caballete, Fortaleza Valley

This site is located on the right bank of the Fortaleza River, approximately 9 km to the Northeast of the city of Paramonga. The site is made up of multiple components and is located at the bottom of the La Empedrada ravine, toward its lower end, adjacent to the lower alluvial terraces along the Fortaleza river.

The site consists of twelve mounds belonging to the Late Archaic Period (3000–1700 BCE) [22–24]. In addition to this main occupation at the site, there is a Late Period cemetery extending to the South. Some looter pits in this area reveal pottery with brown and red paste and Pativilca Impreso-type of decoration, textiles, and skeletal remains [25, p. 59]. There is also a group of irregular depressions and stone accumulations associated with a big quadrangular space sunken into the southern end of the site, in which ceramic fragments can be observed. Judging by the characteristics of the dispersed materials, Perales postulates that these reoccupations belong to the Initial and Middle Horizon.[2]

The Preceramic mounds surround a wide-open space, which has recently been partially disturbed and excavated with heavy machinery for agricultural purposes, exposing extensive areas that have brought various objects to the surface, such as mollusk shells, ashes, thermo-fractured stones, and related objects. Two of the six mounds present sunken circular plazas.

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[1] We use the chronology for the Formative Period proposed by Kaulicke [21] as a reference, which divides this period into five phases: Early Formative (1700–1200 BCE), Middle Formative (1200–800 BF), Late Formative (800–600/500 BCE), Final Formative (500/400–200 BCE), and Epiformative (200–100/200 ACE).

[2] Considering the chronological terminology used by Perales.

Gold Bead Associated with a Funerary Context

Haas and his team intervened at the site of Caballete during multiple research seasons. First, they cleaned profiles and dug test pits before beginning larger excavations. In 2003, the posterior part of Sector F was explored, referring to the back part of the EA 6[3] mound (see Plan 12.1), by way of Test Pit 1.

A funerary context, consisting of an infant and an adult, was found intruding into the sterile sediment. The infant was positioned above the adult, and although they were separated by sediment, both were clearly buried together. The pit was later filled with fine, light brown mud.

The infant was wrapped in textiles and placed over a concentration of plant fibers, used as a base. A sample of these fibers (*Tilandsia sp.*) was extracted from near the cranium, and it showed a date of cal. 1292–842 BCE.[4] Some of the cranial bones and textile pieces were painted with a red pigment. The infant was buried in a flexed position, laying on the right side.

Individual 2, buried underneath the infant, corresponds to an adult individual wrapped in a simple reed mat. The individual was buried in a dorsal decubitus position, hyper-flexed with the knees to the chest and the arms grabbing the lower legs. Three *mate* containers were found, two of which were located near the feet of the individual, close to a piece of metal found beneath the feet; this is the object we will later discuss in detail. The third *mate* contained cotton and was located below a basket (or possibly a headdress) that was partially covering the individual's head. Toward the southern side, large, intentionally placed stones were documented. On top of the reed mat, beneath the individual, five obsidian tools and flakes, and four mollusk-shell beads, one of which was complete, were found. Toward the right side, a concentration of artifacts was found, including bone and reed implements presumably related to textile production. On the same side, but not within the same concentration, four *piruros* were found. In another space, three concentrations of small pyrite beads were found among other loose beads. This burial has a radiocarbon date of cal. 897–419 BCE,[5] taken from a mixture of samples belonging to the plant fibers coming from a thin level of botanic material to the south of the individual.

The individual was female and died when she was between 55 and 60 years old. Her height was around 151.13 ± 3.42 cm [28, p. 178, Fig. 7.6]. (Fig. 12.14).

Intrusive contexts belonging to posterior periods are not unusual within archaeological sites of the Late Archaic Period. Seasonal occupations and offerings have been found at this same site and at Huaricanga, in the Fortaleza Basin. We can deduce that seasonal occupations represent populations who revisit sites considered "abandoned" or "ancestors' lands." Furthermore, bioanthropological analysis has

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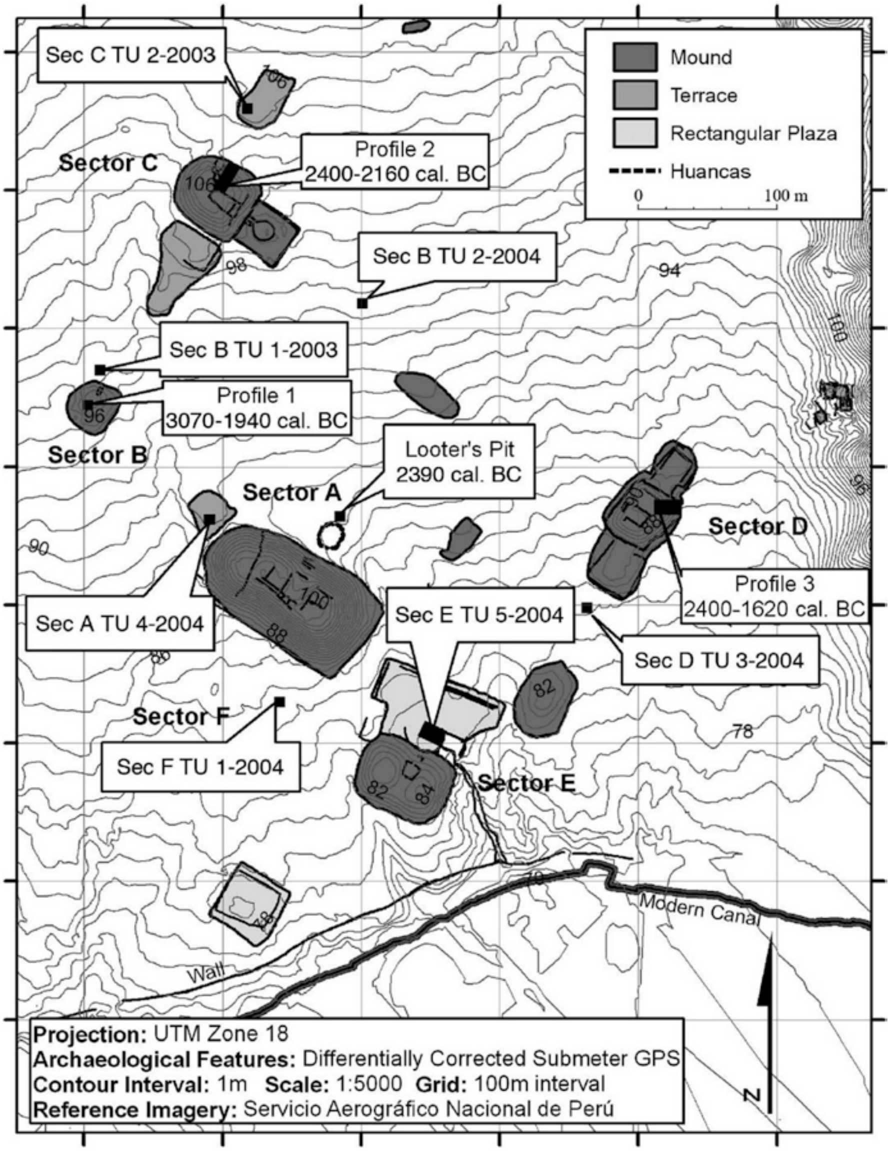
[3] Haas and his team identify and denominate the sectors at the complex [24, 26], while Vega-Centeno [27] names the mounds inside them.

[4] ISGS-5724 (2870 ± 80).

[5] ISGS-5729 (2580 ± 70).



Plan 12.1 Distribution of archaeological interventions at Caballete in 2003. Note the intervention located in Sector F, where the context described in this article was found. Taken from Creamer, Ruiz, Perales, & Haas [24, Figure 11]

Fig. 12.14 Recreation of individual 2. Taken from Bazán [28, p. 178, Figure 7.6]. Drawn by Miguel Ortiz Mestanza

determined that these individuals died from non-natural causes, with peri-mortem contusions on their bodies. Human sacrifice is the hypothesis proposed to explain this kind of sacralized space from the Formative Period [28].

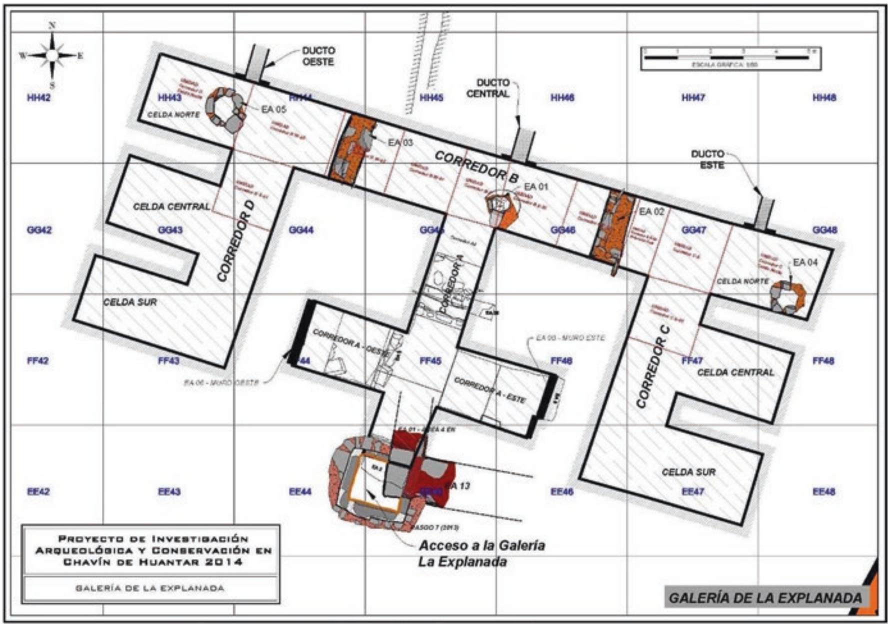
The Esplanade of Chavín de Huántar

The site of Chavín de Huántar, located in the North Central Highlands of the Central Andes, at the juncture of the Mosna and Wacheqsa Rivers, in the southern section of the Callejón de Conchucos, is the ceremonial center that dominated the political and religious scenes during the Middle and Late Formative Periods. John Rick and his team's studies have defined an occupation period of at least 700 years, between 1200 and 500 (BCE). Silvia Rodriguez-Kembel [29] has identified 25 constructive events grouped into five architectonic phases, of which the "White and Black Phase" is seen as the classic example, during which the settlement reached its maximum dimensions.

During the excavations which have been carried out since 2009 in the sector of the esplanade of Buildings C and D, located immediately to the North of the structures and not previously excavated, researchers were able to identify an architectonic complex of medium scale. This complex consists of multiple plazas, platforms, and floors that were modified over time. The final phase of this sector, the Late Chavín Phase, is represented by a plaza (called the Plaza de la Explanada) located adjacent to a platform that was continuously being remodeled until its current configuration was attained. In 2013, underneath the plaza, a gallery known as the Galeria de la Explanada was discovered [30] (see Plan 12.2).

The gallery is found underneath the previously mentioned plaza, whose floor is composed of a layer of flagstones, a trademark of Chavín occupation. The same plaza extends southward, toward Building C, with a series of small-scale platforms associated with the large platform and perimetric corridors located immediately to the West. The gallery has a formal entrance located in the floor of the plaza: an L-shaped opening leading to a staircase composed of two inclines descending to the principal corridor (A) which has two cells. This corridor ends as it joins another perpendicular one, Corridor B, with an East-West orientation. The ends of this corridor are the beginnings of two lateral corridors, C and D, that lead to the South. Three symmetric cells are attached to each of these corridors (see Plan 12.2).

As with most of the architecture found at the site, the structure was built with flat-faced stones joined together with mud mortar. The roof, as is typical, is composed of large elongate boulders placed transversally along the corridors. Evidence



Plan 12.2 Plan view of the Galería de la Explanada. Note the corridor sequence, cells, and architectonic features linked to the construction of this underground structure

of the architectural development are visible, especially in Corridor A and its cells, as well as the ends of Corridor B. It is evident that this space did not originally have this configuration and was not always an underground space. The gallery's floor was made out of clay, and excavations below the floor have revealed small structures, little rocks associated with a "stove," with a date of cal. 1410–1192 BCE [31, pp. 76–77].

The closure of the underground structure was intentional and not violated by later occupations. This has been demonstrated by the absence of ulterior intrusions or intrusions into the roof or entrance. At the time of abandonment, the people of Chavín deposited a mixture of clay and soil fill over the floor, which in general was clean. This, with the addition of natural deposits from sediment filtration, filled the gallery to at least two thirds of its height, with scarce cultural material.

Despite this, an isolated find was discovered in the natural deposits which consisted of 40 beads, making up a necklace (Fig. 12.15), a semiprecious stone (probably *crisocola*), three shells (*Oliva* sp.), and small carbon fragments. Apparently, this layer was a product of natural deposition via gallery filtration, and it was located 50 cm underneath the surface of the sedimentation and 70 cm above the gallery floor. Twenty-four beads, from what was possibly a necklace, seem to have been made from laminated gold, and 16 beads from shell. Both the types of bead show evidence of reddish pigmentation, seemingly cinnabar, according to the results of the Energy Dispersive Spectroscopy (EDS), in which sulfur and mercury were detected (Fig. 12.26), although more was present in the shell beads (Fig. 12.15). Since no depositional layer inside the gallery shows Post-Chavín alterations, the objects described here seem to be offerings placed after the closure or sealing of the gallery, when it was no longer possible to move about except by crawling or remaining in the corridors.

Fig. 12.15 Collection of metal and shell beads. (Photo: A. Bazán)

It is hard to assign an accurate date to the previously mentioned find, especially as it is part of a fill and intrusion during Chavín times. Nevertheless, it is clear that the find cannot be from the century previous to eighth century BCE. Excavations underneath Unit 3 of Corridor A, where there was a depression or missing part of the clay floor of the gallery, discovered a canal made with parallelly aligned angled stones, that was covered by a layer possibly corresponding to a burn event, and its radiocarbon date was approximately cal. 1300 BCE.

Considering that the chronological placement of the object cannot exceed the Support Phase of the architectonic sequence, which ends around 500 BCE, this find corresponds to the Formative Period. However, a refinement of its chronological placement remains pending, since the architectural development of the gallery, as well as the activities that occurred above it in the Plaza de la Explanada and its associated platforms and corridors, are also being refined. Nevertheless, the construction of the gallery seems to have occurred during the White and Black phase—that of classic Chavín development—while the closure of this space took place during the Late Formative Period (800–600/500 BCE).

Analytical techniques

Three beads were analyzed with a Scanning Electron Microscope Quanta 200 with dispersive X-ray analyzer (EDS 4i), made by FEI Company from MyAP SAC. The beads from the Galería de la Explanada were analyzed in an initiative by the Chavín de Huántar Archaeological Project, led by John Rick. The pieces were analyzed to determine their elemental chemical composition with the EDS. For area and point analysis of the sample, a secondary electron detector (LFD) was used as well as the backscattered electron detector (SDD) under low vacuum (LV). This is a non-destructive and repetitive elemental analysis (it simultaneously analyzes 85 elements between bohrium and uranium), and the values are given by percentage of their respective atomic weights (wt%). The accelerated tension was 30 kV for gold, and the X-ray lines used for the determined elements were $K\alpha$Cu, $L\alpha$ Au, and $K\alpha$ Ag.

Results

The results of the elemental chemical composition for the bead recovered at Caballete indicate that its nature is electrum gold (see Table 12.12).

According to the macro and microscopic observations, we can reconstruct the way in which the oval bead from Caballete was produced (Figs. 12.16 and 12.17). This piece was made with two gold sheets that were embedded in matrixes, which could have been wood, with a semispherical shape. Two perforations were made on one of these sheets with a puncturing tool. These perforations were then polished, and the remaining notches that may have been left in the cavity were removed

Table 12.12 Information about the mentioned pieces

Archaeologic site and piece	Gold	Silver	Copper	Iron	Platinum	Region	References	Context[a]
Caballete, bead	68.08	28.36	2.68	0.88		Costa	[28]	CF F
Mina Perdida, sheets	92.7	7.3				Costa	[32]	C Arqt
Mina Perdida, sheets	95.8	4.2				Costa	[32]	C Arqt.
Morro de Éten, thin sheets	67.3	30.2	2.2		0.34	Costa	[33]	CF
Morro de Éten, circular pendant	79.6	19	1.4			Costa	[33]	CF
Morro de Éten, tubular bead	93	5	1		1	Costa	[33]	CF
Morro de Éten, small tubular sheets	92	4.6	1.1		2.3	Costa	[33]	CF
Morro de Éten, ring	70.3	26	3		0.7	Costa	[33]	CF
Chongoyape, pin	26	74				Costa	[34]	CF F
Chongoyape, sheet	100	0				Costa	[34]	CF F
Chongoyape, disk	100	0				Costa	[34]	CF F
Chongoyape, crown	100	0				Costa	[34]	CF M
Chongoyape, plate	68.8	28.8	2.3			Costa	[35]	CF M
Lambayeque, feline plate	78.4	20.4	1.2			Costa	[35]	?
Maltina, Huarmey, disk	60.6	17.5	21.9			Costa	[35]	?
Maltina, Huarmey, pectoral	79.6	12.8	6.9			Costa	[35]	?
Explanada Chavín, bead	92.53	6.37	1.1			Sierra	[31]	C Arqt.
Explanada Chavín, bead	96.78	2.95	0.27			Sierra	[31]	C Arqt.
Chavín? Dalmau Collection, snuff spoon	72	24.5	3.6			Sierra	[35]	?
Chavín? Dalmau Collection, disk	74.9	22.4	2.7			Sierra	[35]	?
Chavín? Dalmau Collection, cruciform disk	72.5	23.7	3.8			Sierra	[35]	?
Chavín? Dalmau Collection, *nariguera*	71.6	24.2	4.2			Sierra	[35]	?
Chavín? Dalmau Collection, *nariguera* in the form of a ring	71	22	6.8			Sierra	[35]	?
Chavín, ornament	70.4	26.3	2.9			Sierra	[35]	?
Chavín, cone-shaped laminated piece	70.36	26.31	2.93			Sierra	[36]	?
Jiskairumoko, tubular bead	95.5	4.3	0.28			Sierra	[37]	CF F
Kuntur Wasi T1, crown	85	15				Sierra	[38]	CF M

(continued)

Table 12.12 (continued)

Archaeologic site and piece	Gold	Silver	Copper	Iron	Platinum	Region	References	Context[a]
Kuntur Wasi T1, ring	91	9				Sierra	[38]	CF M
Kuntur Wasi T2, crown	63	37				Sierra	[38]	CF M
Kuntur Wasi T2, plates	73	27				Sierra	[38]	CF M
Kuntur Wasi T2, *nariguera* H	76	24				Sierra	[38]	CF M
Kuntur Wasi T2, jaguar *nariguera*	79	21				Sierra	[38]	CF M
Kuntur Wasi T3, earring a	65	35				Sierra	[38]	CF M
Kuntur Wasi T3, earring b	63	37				Sierra	[38]	CF M
Kuntur Wasi T4, cone shaped	89	11				Sierra	[38]	CF F
Kuntur Wasi T4, pendant	90	10				Sierra	[38]	CF F

[a] Key: *CF* funerary context, *CF F* female funerary context, *CF M* male funerary context, *C Arqt* Architectonic Context

Fig. 12.16 Oval bead from Caballete. (Photo: A. Bazán)

(Figs. 12.18, 12.19, and 12.20). In the photomicrograph in Fig. 12.21, the finish on the orifice's borders can be clearly observed, with a diameter of approximately 2.2 mm. Finally, two hemispheres were mechanically united by pressure, resulting in the oval bead (Figs. 12.18, 12.19, and 12.22).

From the other context, two of the 24 metal beads from La Explanada of Chavín de Huántar, belonging to the Late Formative (800–600/500 BCE), were analyzed.

The elemental chemical analysis indicates that the beads are 22-karat gold with minor concentrations of 3% silver and 1.1% copper (Figs. 12.23, 12.24 and 12.25).

Fig. 12.17 Superior view of the bead, showing the orifice where the “thread” or cord would have been placed, so that the piece could be hung. (Photo: A. Bazán)

Fig. 12.18 Details of the mechanical union of the hemispheres viewed through a stereoscopic magnifying glass. (Photo S. Petrick)

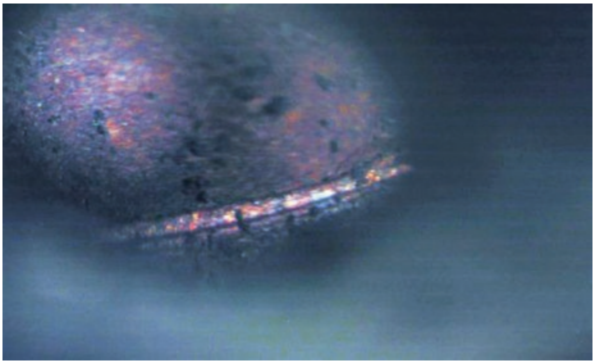


Fig. 12.19 View in detail of the union with a stereoscopic magnifying glass and guided LED light. (Photo S. Petrick)

Fig. 12.20 Details of one of the bead orifices. (Photo S. Petrick)

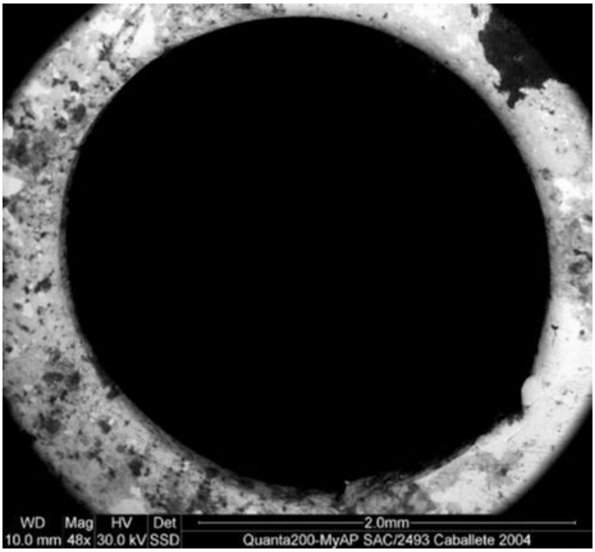


Fig. 12.21 Photomicrograph of one of the orifices. Note the very regular borders. (Photo: G. Ocharán)

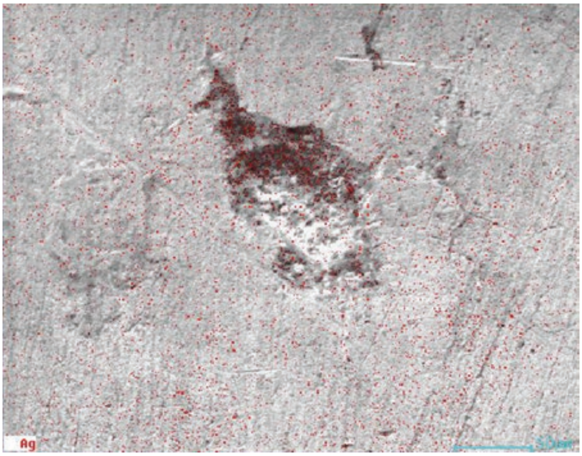


Fig. 12.22 SEM image in secondary electrons which shows the analysis for silver performed on the area on the surface of the sample. The results show that it is *electrum* gold. (Photo: G. Ocharán)

Fig. 12.23 Part of the necklace made from 40 cylindrical shell and metal beads. (Photo L. Vetter)

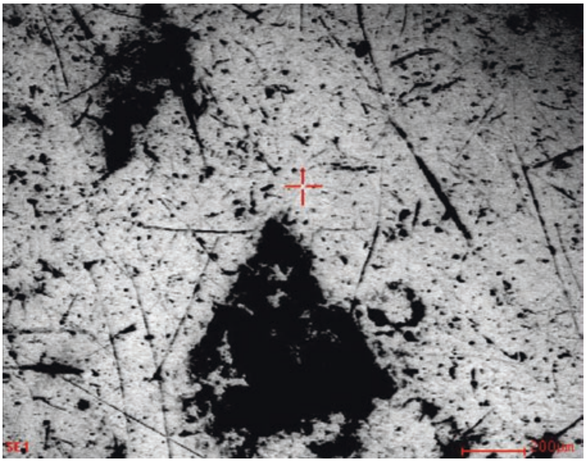


Fig. 12.24 The cross indicates the point where the chemical analysis (body) was performed, reporting the result of 22-karat gold. (Photo: G. Ocharán)

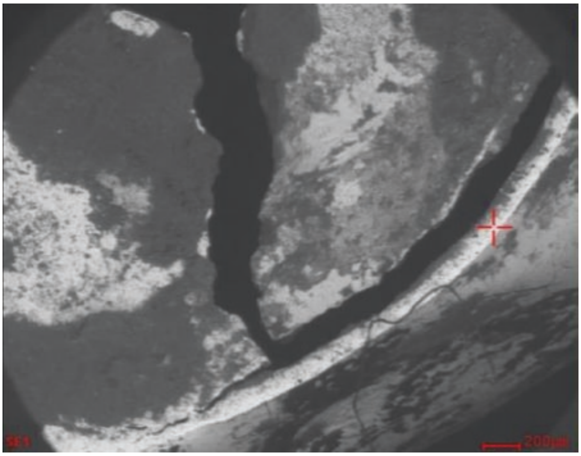


Fig. 12.25 The cross indicates the point at which the chemical analysis was performed (upper border), with the result of 22-karat gold (Twenty-four karats is pure gold. The lower the measure in karats, the less gold it contains; 22-karat gold contains 91.7% gold and 8.3% other metals, usually cooper or silver). (Photo: G. Ocharán)

The Chavín beads, unlike the one from Caballete, are cylindrical in shape. The manufacture of these beads is similar to that of the Caballete bead, with two halves made from a sheet embedded in a matrix shaped like half a cylinder. Later, the orifice was made in each half cylinder with a puncturing tool. The marks caused by the pressure of this tool on the sheet were cut and filed, thereby achieving the polished

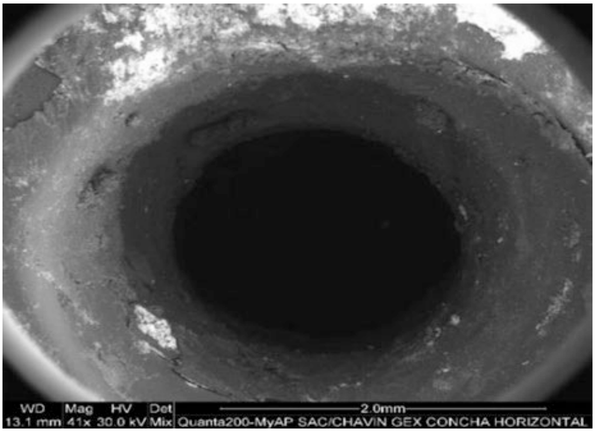


Fig. 12.26 Photomicrograph of the orifice of the cylindrical bead. The gray zone has 38.45% mercury, which indicates that this bead was partially covered by cinnabar (Photo: G. Ocharán)

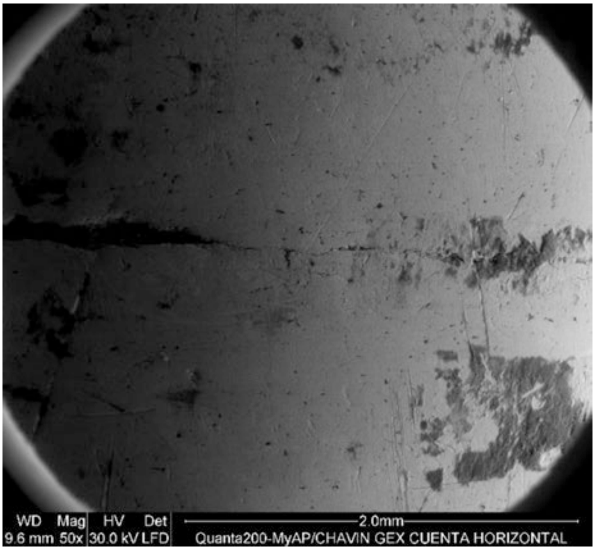


Fig. 12.27 SEM image in secondary electrons. View of the mechanical joint in the middle of the object. (Photo: G. Ocharán)

border observed in Fig. 12.26. Just like the one in the bead from Caballete, these orifices have an approximate diameter of 2.2 mm.

The two parts of the bead have been mechanically united under pressure, as is shown in the photomicrograph in Fig. 12.27. Although the majority of the beads were found in a good state of conservation, some bases show a certain amount of fracturing, as can be observed in Fig. 12.28.

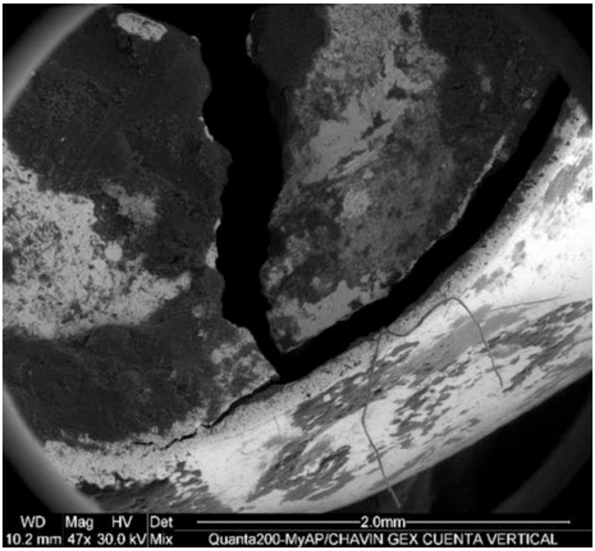


Fig. 12.28 Fragmented zone of the bead near the base. (Photo: G. Ocharán)

Discussion

The analyzed beads, the oval one from the site Caballete on the North Central Coast, and the ones from Chavín de Huántar in the North Central highlands, show a clear difference in the percentage of gold in their composition. The oval bead is electrum gold and its gold content averages around 70%, while the cylindrical beads from Chavín de Huántar have a higher gold content, reaching 96% as 22-karat gold.

Both of these kinds of beads seem to have had the same manufacturing process, starting with the lamination, followed by the embedding in a stone or wood matrix, and the preparation of the orifice with a puncturing tool. In particular, the polishing work observed on the orifices of both beads, the oval one as well as the cylindrical ones, stands out, along with the diameter of the orifices being nearly 2.2 mm in both cases; this indicates that the puncturing tool used to penetrate the sheet and to make the orifice had basically the same width.

However, there is a difference between the cases that we must point out: that the contexts in which the beads were found are different. The oval bead from Caballete was associated with the funerary context of an adult female, and the necklace of cylindrical beads was placed during the activities related to the closure and abandonment of the Galería de la Explanada, possibly as an offering for the closure of the structure.

To better understand the development of metallurgy, especially that of gold, in the Late Archaic and Formative Periods, we reviewed various writings and compared these objects to other findings, as well as the contexts from which they were excavated and the metal compositions of the pieces. In this article, only the pieces which were chemically analyzed have been taken into account.

According to the archaeological investigations carried out to date, the first metal used to make a metallic object in the Andean region was gold. This first evidence was found in a funerary context belonging to a female individual in Jiskairumoko, an archaeological site located in the Jachicachi community, in the district of Ilave, province of El Collao, in Puno, in the Titicaca basin. It consisted of a tubular bead necklace of gold sheets and light blue semiprecious stone *chaquiras*. This context has been dated cal. 2155–1936 BCE, placing it in the Late Archaic Period [37]. Chemical analyses were performed on the nine tubular beads using a portable XRF, the results of which indicated that the average composition of the beads was 95.5% gold, 4.3% silver, and 0.28% copper, and the authors concluded that these beads were probably made out of native gold nuggets mined from quartz streaks. The source of this gold could be in the Sandia River basin, to the north of Jiskairumoko, on the Andes' western flank in the department of Madre de Dios. The analysis performed on the Sandia source, from the data presented by Petersen [39], shows a chemical composition of gold varying from 98.5 to 91.6% and silver ranging from 1.85 to 5.6% [37, p. 5004]. In his travels through the Peruvian territory, Lechtman identified a large number of mines that were exploited during pre-Hispanic times. One of them is La Rinconada San Francisco mine, located at 5000 m above sea level, on the peak of Ananea, in Sandia, which is a gold mine possibly utilized since the pre-Hispanic era which continues to be exploited to this day [40]. Even though the necklace in question is not from the northern region (coast or highlands), it is important to mention, as it is the first evidence in the Andean region of a piece worked in metal.

On the South Coast, the pieces that have been analyzed belong to the Paracas Necropolis phase, posterior to the periods involved in this study, which is why we will not take this data into account.

On the Central Coast, there is some evidence of metallurgy, though it is scarce. At Mina Perdida (Valley of Lurín), there is evidence of gold and copper work dated between 1500 and 1100 BCE [32]. The objects were excavated from one of the main pyramids of the site's terraces. The gold pieces had a chemical composition of 92.7% gold and 7.3% silver, and 95.8% gold and 4.2% silver, with no registry of any other element such as copper, even in trace amounts. According to the authors of that analysis, early examples demonstrate three patterns that characterize the metal work of the Central Andes during the following three millennia: laminate, golden copper, and the association between the metallurgical work, religious ritual, and the supernatural world. Thus, technological development in the Central Andes arose in a sociopolitical context preceding the appearance of strong social ties, stratification, and state organization [32, pp. 1109–1110]. However, this is not accurate when considering the contexts from the Early Formative. The rise of social relationships, stratification, and social organization precedes the Formative and even the Late Archaic.

On the North Coast, the first evidence of gold work consists of pieces dated to the Late Formative (800–600/500 BCE) from a cemetery at the site of Morro de Eten in Lambayeque. Many thin sheets (E10), a laminated circular pendant (U8-D), a laminated tubular roll (U13-D), small tubular sheets, and a ring made from tied wires were found [41]. These pieces were analyzed by SEM, FRX, and Neutronic Activation; the results are shown in Table 12.12 [33].

At the Almendral hacienda, located at Chongoyape (400–300 BCE), Lambayeque, two sets of pieces belonging to two funerary contexts were found fortuitously. The first context belongs to a male individual who was found accompanied by crowns, ear pieces, and tweezers, while the second corresponds to a male individual accompanied by two females associated with ceramic vessels, lithic pieces, and some *tupus*, or metal cloak pins, as well as rings, beads of various shapes, and embossed and punctured metal plaques. According to Lothrop, the gold pieces from the second context were thinner and chronologically later, as indicated by the more advanced metallurgical processes employed for their fabrication, as well as the fact that the design of the ornaments was more complex [42, p. 259]. The chemical composition analysis performed on one of the crowns from the first find gave a result of 100% gold with platinum impurity. From the second tomb, a small sheet was analyzed with a result of 100% gold, a disk with 100% gold, and a pin with 74% silver and 26% gold [34, p. 238].

The first evidence of gold work in the Northern Highlands comes from Chavín de Huántar, where Burger found a cone-shaped piece made from a gold sheet, which was found broken in two parts and dates to 1200 BCE. Lechtman analyzed this object and found it to be 73.6% gold, 26.31% silver, and 2.93% copper [36].

During the Middle Formative (1200–800 BCE) and Late Formative (800–600/500 BCE) Periods, with which the pieces from Caballete and Chavín de Huántar, respectively, are associated, metal objects continued to be small sheets, except at Chongoyape, where larger pieces were found with more elaborate iconography, such as the crowns from the first tomb or the crab-shaped plaques from the second one. The latter are chronologically placed closer to the end of the period, coming later than the former, though the context's specific date is uncertain.

Onuki [38] presents the data on metal pieces excavated from the eight tombs at Kuntur Wasi, as well as the results of analysis by X-ray fluorescence (XRF). Although they do not include the percentages of chemical elements in their paper, the researchers report traces of copper and in some cases iron. These results had been previously presented [35, 43, 44]. The first six tombs belong to the Kuntur Wasi Phase (800–500 BCE). The first tomb (A-Tm1) belonged to a male individual around 50–60 years old at the time of death, found with a crown with 14 metal plaques, each representing a human face. This object contained 85% gold and 15% silver, except for a small ring-shaped sheet with 91% gold and 9% silver.

The second tomb (A-Tm2) belonged to a 60-year-old male. Along with the individual, researchers found a crown with five embossed jaguar faces, with a composition of 63% gold and 37% silver, two plaques with inverted symmetrical designs of two faces in profile and jaguar claws with 73% gold and 27% silver, a nose piece shaped like an H with 76% gold and 24% silver, and a *nariguera* featuring a jaguar face with four limbs and two snakes with 79% gold and 21% silver.

In the third tomb (A-Tm3), researchers found a 30- to 40-year-old male individual with a pair of earpieces with compositions of 65% gold and 35% silver, and 63% gold and 37% of silver.

A 60-year-old female individual was found in the fourth tomb (A-Tm4) in association with gold and silver objects including a cone-shaped with 89% gold and 11% silver, and another pendant composed of 21 bird-shaped sheets with 90% gold and 10% silver, and parts containing 30% gold and 70% silver.

Tombs 5 and 6 belong to the Kuntur Wasi Phase and Tombs 7 and 8 to the Copa Phase (500–250 BCE); an elemental chemical composition analysis was not performed on the "gold" pieces coming from these contexts, so we will limit ourselves to descriptions of the objects found in the tombs presented by Onuki [38].

Tomb 6 (G-Tm6) contained a male individual with a gold pectoral, while Tomb 7 (B-Tm 1) had a 40-year-old male individual with a gold crown with a design of twelve jaguar profiles, a pair of cylindrical golden *orejeras* with bird figure designs, a pair of golden pendant ornaments with jaguar profile designs, and a pair of golden pendants shaped like a squash.

In Tomb 7 (G-Tm5), a male individual was found in association with a gold crown, metal tweezers shaped like an *Argopecten* shell, a pair of circular earpieces, cylindrical golden beads, rounded golden *chaquiras* with four divisions, fretted golden beads, and spherical golden *chaquiras*.

Lastly, in Tomb 8 (G-Tm 4), a female individual was found in association with eight golden beads decorated with a feline-like faces, 18 golden beads shaped like large balls with three trapezoidal pendants, spherical golden *chaquiras* both small and medium size, and 13 small cylindrical golden beads.

Burger did a study of Chavín art as represented in metal pieces found in the highlands and on the North Coast. Elemental chemical analyses were performed on a series of objects from influential areas such as Chavín, and from archaeological excavations as well as *huaquería*, or looting [35]. The first piece is a plaque presented by Lothrop; according to Burger, its iconography is related to the deity depicted on the Raimondi Stela, and it probably belonged to the first tomb of Chongoyape. However, it was not recovered with the looted group because it was separated from the original [42]. This plaque was analyzed by XRF with a result 68.8% gold, 28.8% silver, and 2.3% copper [35, p. 52]. The next piece is a sheet cut in the shape of a feline that Burger dates to between 400 and 300 BCE; it comes from a *huaqueo* in Lambayeque. This plaque was also analyzed by XRF with a result of 78.4% gold, 20.4% silver, and 1.2% copper [35, p. 54]. The next piece is a bimetallic effigy spoon, made for inhalation of snuff and dated to between 400 and 200 BCE, which indicates—according to Burger—that it could come from Chavín de Huántar. It was analyzed by XRF with a result of 72% gold, 24.5% silver and 3.6% copper [35, p. 60]. Also, a disk originating from Chavín de Huántar was analyzed; like the previous piece, it belonged to the Juan Dalmau Collection. It was analyzed by XRF with a result of 74.9% gold, 22.4% silver, and 2.7% copper [35, p. 69]. A second disk was analyzed, but this one was from Maltina,[6] near Huarmey,

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[6] Among the looted pieces from Maltina, there were at least 26 golden objects: ten or eleven disks, seven pectoral ornaments, six feathers, and two stirrup-spout bottles. Apparently, Moreno, the looter, melted at least three of the feathers and three of the pectoral ornaments for the value of the raw metal, and the other objects may have been scattered without being recorded [35, p. 72].

and Burger dates it to between 400 and 200 BCE. It is composed of 60.6% gold, 17.5% silver, and 21.9% copper. According to Burger, this alloy was intentional [35, p. 73]. From this same group, a pectoral ornament, which some researchers believe could be chronologically later than the aforementioned disks, was analyzed. Burger presents the results of the analysis by scanning electron microscope (SEM) performed on the pectoral ornament, which is composed of golden and silver bands. The former contains 79.6% gold, 12.8% silver, and 6.9% copper, while the latter contains 46.7% gold, 43.9% silver, and 8.5% copper [35, p. 74].

Other pieces that Burger presents as coming from Chavín or of Chavín style that were analyzed include: an ornament excavated by Burger from Chavín de Huántar, assigned to the Janabarriu Phase, that is composed of 70.4% gold, 26.3% silver, and 2.9% copper; a cruciform disk that belonged to the Juan Dalmau Collection and is composed of 72.5% gold, 23.7% silver, and 3.8% copper; a *nariguera* from the Dalmau Collection that contains 71.6% gold, 24.2% silver, and 4.2% copper; and another *nariguera* from the Dalmau Collection, this one ring-shaped, with 71% gold, 22% silver, and 6.8% copper. Burger identifies the objects from the Juan Dalmau Collection as coming from Chavín de Huántar [35, pp. 60–61].

Hirao, Ohnishi, Onuki, and Kato mention that ten golden objects from Kuntur Wasi were analyzed, and the results indicate that they contained between 10 and 40% silver, indicating that the objects were not pure gold. The alloy of gold and silver contained small amounts of copper and even iron. Apart from the copper and iron, no other trace elements were found. The researchers state that the gold's composition indicates that the objects were manufactured using the metals in their natural composition, not by melting the minerals together. Furthermore, they claim that the copper content is related to the silver concentration, with at least two different systematic relationships, in the golden objects. All these indicate that there were probably more than two sources for obtaining the silver [43, p. 30].

Although the gold pieces that we have analyzed have a silver composition below 30%, there are two objects from Kuntur Wasi that present compositions higher than 35%. According to Burger, this is because some of the Kuntur Wasi alloys were fabricated by melting gold and silver together, since the compositions of the placer gold deposits recorded in the north of Peru show silver content around 25% [35, p. 61].

According to Onuki, the metal pieces from the Kuntur Wasi Phase have no precedents at the site. Their style and technology show an uncanny likeness to the objects from the Cupisnique culture from the North Coast of Peru, just like the pieces found at Chongoyape. This coastal region may have been the place of origin for the ideas and practices found later at Kuntur Wasi and may have been the center for the development of gold-working technology. However, to date, gold ornaments of the magnitude of those found at Kuntur Wasi have not been found in archaeological excavations on the North Coast, making the objects from the Kuntur Wasi Phase the oldest gold pieces known to the American continent [45, p. 17]. Although it can be said that the objects from the Kuntur Wasi Phase and the pieces from Chongoyape show the same technological advances in the production of alloys and new decoration techniques, we must also consider evidence of earlier gold work, from the controlled archaeological excavations described above, to be the beginning of what would later develop into this grandeur.

As for the source of the gold, Viladevall Solé, in his study of placer gold, states that chemical alteration involves the breakup, by chemical means, of rocks and minerals, as well as the dispersal of the released elements, generally by water and up to considerable distances from the source area, as well neoformation of minerals. He also mentions that very large amounts of oxygen, carbon dioxide, and water are necessary for this to occur. Physical alteration will take place on this selective chemical change by means of remobilization and transport of resistant material, especially oxides and silicates, with almost no modification of their structure and mineral composition. On the other hand, the physical processes are fundamentally carried out by water, in its different states, and wind, both of which cause the disintegration and/or desegregation of a rock or mineral, helping to release resistant minerals for their subsequent transport and deposition [46, pp. 5–6]. As a result of these processes, fine gold particles vary depending on the type of deposit; placer has higher-grade gold than seams, which have silver and quartz in accompaniment. Seams or veins allow the entrance of different minerals, which is why it is possible to find different elements. Gold has a high density, so when it is carried and transported by water, the accompanying minerals are sorted out along the way and the gold settles into the sand and heavier gravel, remaining trapped in river banks and on the riverbed as alluvial deposits, forming what are known as placer deposits.

Georg Petersen [39, p. 49] presents the chemical analysis performed on gold recovered from rivers in the south of Ecuador and in the north and northeast of Peru. These sources are the Tumbes River (Northwest Peru) with 72.95% gold, 26.34% silver, and 0.73% copper; the Chinchipe River (Northern Peru) with 81% gold silver and no copper registered; and the Ucayali River (Northern Peru) with 75% gold, and the rest silver.

Burger, using Petersen's studies as his basis, mentions that in the Central Andes, placer gold is typically high in silver and can contain small traces of copper; this gold is usually known as *electrum.* Furthermore, he says that these compositions are similar to the Chavín or Chavín-like objects presented in his reports [35, pp. 60–61].

Root mentions that, even though there is not an exact differentiation among the varieties of gold, three types can be found more frequently than others: Type A, almost pure (0–5% silver); Type B, gold rich in silver (15–30% silver); and Type C, gold-silver alloy (35–50% silver). Furthermore, he indicates that this considerable variation could be predicted, especially coming from gold placers. A gold nugget rich in silver can lose almost all of the silver found on its surface while being transported along the course of the river, making the nugget almost pure gold. Likewise, Root states that the composition of natural gold can vary notably from one place to another in the same tributary river. Finally, he indicates that the silver-gold alloy, which has a percentage larger than 35%, is artificially made [47, p. 11].

Lechtman, who carried out the analysis of the Chavín and Chavín-like pieces, including those from Chongoyape, mentions that the results reveal the existence of two groups: a) The first group is composed of objects that have a natural three-way alloy of gold, silver, and copper and whose silver percentage is around 25%,

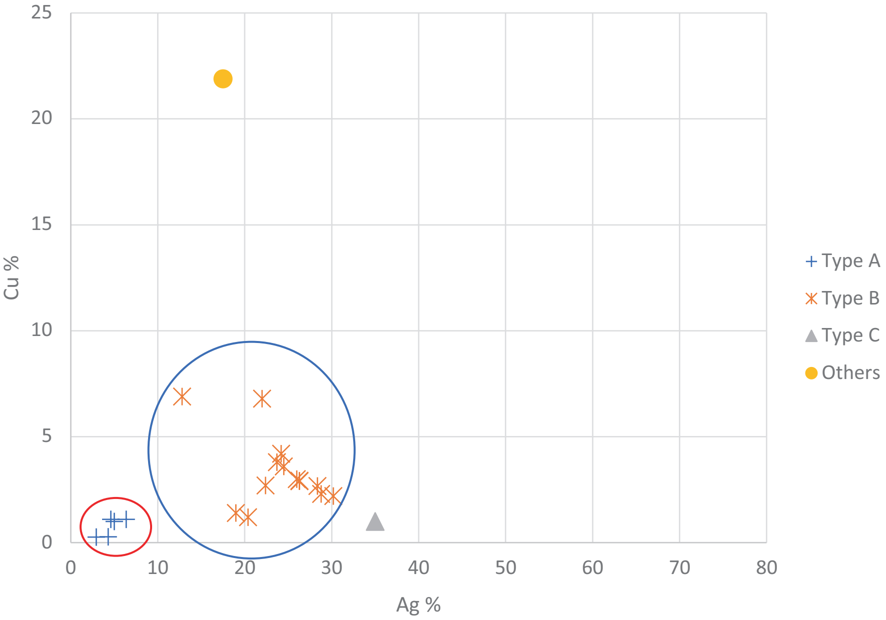

Fig. 12.29 Scatter plot showing silver composition in relation to copper, forming four well-defined groups, according to the types presented by Root [47]. The figure shows that the objects in the “others” category are not made of gold; one was made with *tumbaga*, and the other seems to be golden silver. It should be noted that all the pieces are laminated, which is why we can say that the use of different techniques, like hammering or casting, is not the reason for the percentages of types A and B (Elaborate by L. Vetter)

meaning it is *electrum*; b) The second group is characterized by some Kuntur Wasi pieces that were excavated analyzed by the Japanese Mission, which are composed of an intentional alloy of gold and silver in which the silver composition is 35–37% [35, p. 61]. These groups can be clearly observed in the dispersal diagram in Fig. 12.29, where we have plotted all the pieces described in this research, though with the addition of a few more groups based on Root [47].

In some of the pieces from Morro de Eten and Chongoyape, the element platinum was found. According to Klein and Hurlbut, the gold chemically contains approximately 10% other metals, which, in addition to silver, include iron and traces of bismuth, lead, tin, zinc, and elements from the platinum group [48]. As mentioned by one of the authors in a previous study, Elera uses the evidence from Morro de Éten to determine that native gold has been exploited and worked since the Late Formative, and the objects created from it could have been transported to nearby areas. To support his hypothesis, Elera points out the meaning of the place name Éten, which is associated with a type of gold (characterized by the karat amount), because of the color of the glow from the sunrise behind the Morro. In addition, he mentions that near the temple and the ritual road of Morro de Éten, there is a mine whose minerals were associated with tertiary gold. Also, the rock outcrop contains basic to ultrabasic rocks, registering the presence of platinum. Furthermore, Elera states that the pieces from Chongoyape could have been manufactured in Morro de Éten due to its closeness to the site, as well as there is evidence of platinum in the chemical composition of at least one of the pieces, and the marine iconography has been depicted on these pieces [41, 49].

Table 12.12 presents all of the pieces mentioned in this study with their chemical composition, the region to which they belong, and the type of context. The pieces come from funerary or architectonic contexts, but some cases are lacking information because they were looted, and even in the case that there is some information available for these pieces, it is not necessarily accurate. It has not been possible to establish the relationship between the type of object and the sex of the associated individual because there is no information about the latter.

Conclusions

To date, the data available in the archaeological record does not allow us to determine the development of metallurgy from the Late Archaic to the Final Formative in the northern part of the territory that is present-day Peru. There are gaps in the information that must be filled in to understand how, during the Final Formative, there are large, laminated pieces with a rich iconography in Chongoyape on the North Coast and, while in the Northern Highlands, the Kuntur Wasi pieces from the Middle and Final Formative Periods are also large in size, laminated, and present rich iconography, but additionally show embedment or collets, as well as welding. Moreover, if we compare these findings with the ones from Caballete on the North Central Coast and the Gallery of the Esplanade at Chavín de Huántar in the North Central Highlands, dated between the Middle and Late Formative Periods, we can see a great difference in the development of metallurgy. When, and how, did the technology advance from elaborating small laminated pieces with mechanical union to large laminated pieces that were embossed, colleted, and welded? The archaeological evidence is insufficient because it does not explain the transition to pieces of great quantity and size. Also, it should be noted that some pieces come from illegal excavations, so the timeline was assigned based on iconography and style.

It is clear that the beginning of metal work is related to native gold, the representative metal of the early periods. The pieces are laminated objects with no evidence of casted objects. Furthermore, we wonder where these objects would have been produced. The only evidence for gold working in this era is the funerary context of Waywaka, where Grossman reports that the individual was a goldsmith because he was accompanied by a toolbox that contained three hammers and an anvil used for these tasks [50, 51]. Nonetheless, we still lack information about goldsmith workshops in the early periods, which is why we still do not know if the pieces were made in ceremonial centers such as Chavín de Huántar or Kuntur Wasi, as occurred in later periods,[7] or if perhaps they were fabricated elsewhere and taken there as

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[7] For more on this, review [52, 53].

offerings. These are questions that the archaeological record is bound to answer at some point.

Another pending matter is to identify the sources of the gold used in the pieces we have presented. They were made with *electrum* gold and 22-karat gold, except for two pieces that are outliers in the scatter plot presented in Fig. 12.29 because one was made of *tumbaga* and the other seems to be golden silver. It is important to begin prospecting research and deposit analysis to determine the sources so that we can understand the process that these specialists employed to make the pieces we see today.

The radionuclide analysis of lead could yield answers about the origin of the prime materials from which these ornaments were produced; this would also contribute to knowledge about possible trade routes and relationships between different populations.

Acknowledgments

We would like to express our gratitude to Dr. John Rick, head of the Proyecto de Investigación Arqueológica y Conservación en Chavín de Huántar, for allowing us to use the data obtained from SEM-EDS; to Dr. Gladys Ocharán from the Laboratorio de Microscopia y Aplicaciones en el Perú for carrying out the SEM-EDS analysis; and Dr. Susana Petrick from the Dating Laboratory of the Faculty of Sciences from the National University of Engineering for the analysis performed by stereoscopic magnifying glass with LED light.

Archaeometallurgical Study of Pieces from Buenos Aires to Pacific Railway (BA&P) in Mendoza, Argentina

Patricia Silvana Carrizo, Marcos Guipponi, Rocío Algañaraz and Noelia Ibañez

Abstract

The railroads have been of great importance for the growth and prosperity of Cuyo region. The objective of this study is the metallographic and historical analysis of two pieces from the Buenos Aires to Pacific Railroad (BA&P). The main elements of this research are a threaded bolt and a fixing nail both kindly assigned for this study by the San Rafael Railway Museum, Mendoza, Argentina. These pieces are not the result of an excavation process, they are typical of the place where the Museum is located, that is, the old train station. Through studies on these railway parts, it is feasible to find out about the possible manufacturing techniques of the parts in question. This information collected is useful for comparison with the techniques and materials used at that time with current techniques and inquire as to whether the material itself has varied or evolved from the metallurgical point of view, as well as knowing the quality of the raw material used for the construction of the historic railway line that linked the capital of Mendoza with the south of the province in San Rafael. The information obtained on this occasion puts light on how the pieces were manufactured and also that this metallic material resembles some steels that are currently also used for the same purposes, that is, to support large loads. In this process, historical bibliographical sources, information from metallurgical, metallographic, chemical, and hardness tests derived from the studies developed in the archaeometallurgy area that depends on the metallurgy laboratory, located in units of the Department of Electromechanics of the National Technological University of the Mendoza Regional Faculty.

Keywords

Railways; Threaded bolt; Fixing nail; San Rafael railway museum

Introduction

The Buenos Aires Pacific Railway (FCBA&P) was the British capital company that operated a network of wide gauge railways (1.676 m) in Argentina during the latter part of the nineteenth century and the first half of the twentieth century. Its objective

Image 12.9 The emblematic Palermo station in Buenos Aires, Argentina capital city in 1930. Note the inscription "BAP" after the name

was to unite the city of Buenos Aires with the Pacific Ocean, specifically, the Port of Valparaíso, Chile. For this, it acquired the existing company of the Great Western Argentine Railroad (FCGOA) in 1907. The Great Western Argentine Railway was created in 1887, the same year in which it acquired the state-owned Andean Railroad, which owned 518 km of railways between San Luis and Mendoza. Until the twentieth century, the Argentine Grand West Railway (FCGOA) did not build or acquire more railroads. In 1901, the Luján de Cuyo line is enabled and in 1903 the Branch of the Catitas to San Rafael. On the 8th of November, 1903, for the first time, a locomotive arrives at the San Rafael station. This is the N°315 locomotive from FCGOA, nicknamed "*La Constructora*" or "The Builder." The main promoter for the rail network expansion in this region was Don Rodolfo Iselín. Born in France, he arrived Argentina in 1884 with that objective, and thus allowing for an easier way to transport regional fruits and vegetables products. In this way, it manages to transform itself into a regional system that met the needs of the area. During all this period of time, there was a tough competition against the Buenos Aires Railroad to the Pacific, this last achievement absorbing the Argentine Grand West Railroad (FCGOA) and by administration of the national government its administration is granted for a period of 20 years [54, 55] (Images 12.9 and 12.10).

Introduction to the Concepts Related to Railways and Their Component Elements

This research work consists of studying two typical railway elements: threaded bolt and fixing nail, both are a constitutive part of any railway track, in this case the railroad tracks were built by the Argentine Great Western Railway (FCGOA), a

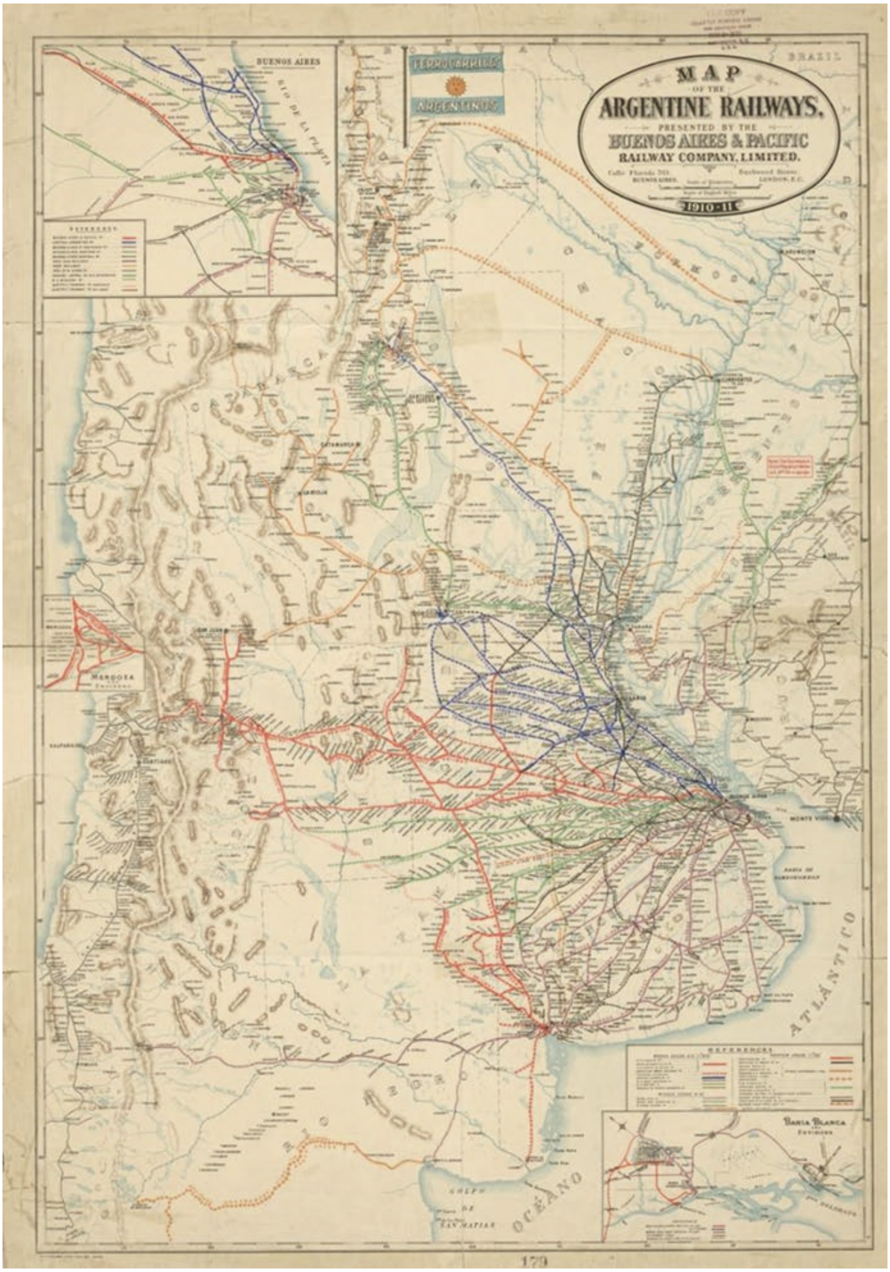


Image 12.10 Map of the Argentine rail network in the years 1910–1911 by Buenos Aires & Pacific Railway Company Limited [56]

company that was later acquired by as Buenos Aires to Pacific Railways (FCBA&P), and nowadays, these pieces (threaded bolt and fixing nail) belong to the San Rafael Railway Museum, Mendoza, Argentina.

- **Fixings**
- Fixing is the main small material used for fixing the rails to the sleepers. The main functions that must be performed by rail fasteners are as follows:
  - Fix the rails to the sleepers.
  - Ensure the invariability of the trail.
  - Facilitate the transfer to the infrastructure of the track (platform) of the static and dynamic efforts exerted by the rolling stock on the structure of the track (railway package).
  - Possess mechanical strength and constant elasticity throughout the long life of the fixation.
  - Contribute to good electrical insulation between both rails.
  - Small number of pieces, which will facilitate their manufacture, placement and conservation.
  - Have low cost.
  - The fixings for wooden sleepers can be divided into rigid and elastic by the way of carrying out the support and by the type of support in direct (without saddles) and indirect (with saddles).
  - Rigid fixings (without saddles): the nail hook and the screw (Image 12.11).
  - Elastic fixings (without saddles): we have the single and double elastic nail, the shun, gauge-lock (Pandrol clip), etc. (Image 12.12).
- **Bolts or Bolts for Tracks**
  The bolts are cylindrical body screws with a threaded or threaded end and very varied heads, which serve to secure the plates to the rails. It tends to give the head of the bolts a square or quadrangular design, and some with a diamond-shaped

Image 12.11 Hook type fixing nail

Image 12.12 Gauge-lock (Pandrol clip)

Images 12.13 and 12.14 Fixing elements for tracks. On the left are the bolts that secure the rails to the rails. On the right are two elements for fixing the rails to the sleepers [57]

Table 12.13 Chemical composition of fixing nails currently [57]

% C	% Mn	% Si	% P	% S
0.37–0.75	0.86–1.74	0.30 Max	Less than 0.05	Less than 0.05

upper face. IRAM-FA Standard L 70-06 June 84 BULONS FOR ROAD defines the technical requirements that must meet the track bolts in their material, manufacturing tolerances and requirements for approval. Not only bolts are used for joints but also for other uses such as component of track apparatus.

The fixing parts for the rails are manufactured following a variety of standards that consider dimensions, materials, and tolerances. They are usually manufactured from a single solid piece which, through different machining, is given the required shape. In the case of bolts, one of the processes is that by which the thread is formed. The pieces that are used are treated superficially to give them better properties. Several of the features will depend on the manufacturer (Images 12.13 and 12.14, Table 12.13).

Experimental Methodology

- **Methodology of Study**
  This historical and metallographic research on railroad parts is addressed through the use of scientific analysis techniques such as metallographic analysis techniques, hardness analysis, chemical composition study, and manufacturing process of the parts, all this is done by studying under a microscope the pieces with the acquired technical knowledge, it is possible to interpret "read" the message that the piece has to transmit and using historical, geographical, chronic bibliographies to be able to bridge and make a cross of information that approximates us a little more and is useful for Museums, schools, students, and teachers.
- **Pieces Studied**
  The pieces received to investigate are: bolt of the threaded type and fixing nail used in the section of the BAP railroad that connected Las Catitas with San Rafael. Both pieces belong to the San Rafael Railway Museum. The bolt would have as a function of distribution of the efforts on the rails. The nail would have as main application the subjection of the rails to avoid variations of the gauge width or separation of the railway tracks (Images 12.15 and 12.16).

Image 12.15 Threaded bolt, where the print of a letter B (BAP) is seen

Image 12.16 Fixing or clamping nail

Experimental Results

- Metallography: Threaded Bolt (Images 12.17 and 12.18, Micrographs 12.17 and 12.18)
  - Chemical Composition of the Threaded Bolt (Table 12.14)
    In the metallography of the bolt head, a ferrite-perlite structure is observed. It is observed in the photomicrographs that there is a decrease in the grain size of the constitutive raw material due to the machining work performed on the piece. The machining that would have been carried out is of the head type "drop of bait," due to its final shape, typical of the first epochs of railways.

Image 12.17 Bolt head

Image 12.18 Threaded bolt

Micrograph 12.17 Metallography obtained, 200× magnification

Micrograph 12.18 Stem zone metallography, 100× magnification

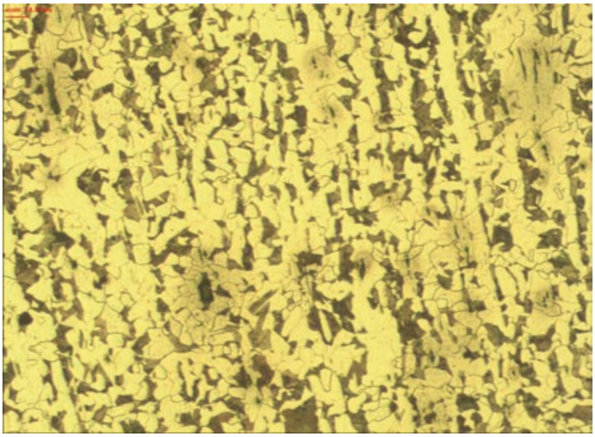
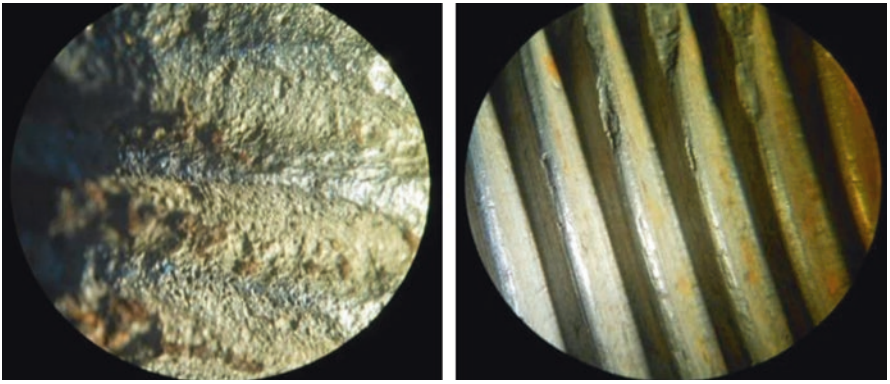


Table 12.14 Chemical composition of the threaded bolt

% C	% Si	% Mn	% P	% S	% Mo	% Ni	% Al	% Cu	% Fe
0.28	0.043	0.83	0.017	0.042	0.003	0.014	0.004	0.03	98.6

In the photomicrograph of the threaded bolt rod, a cast iron structure of high strength of low alloy and low carbon content (0.28%) is observed. It is a structure of the ferritic-perlitic type. Which would have received a hot rolling or forging work with successive tempering treatments, through which the piece is shaped and to give greater resistance to the material of the piece itself. According to the chemical composition obtained by means of the Spectro Sort

Images 12.19 and 12.20 The bolt that was studied. Proper way to measure the type of thread using the thread comb



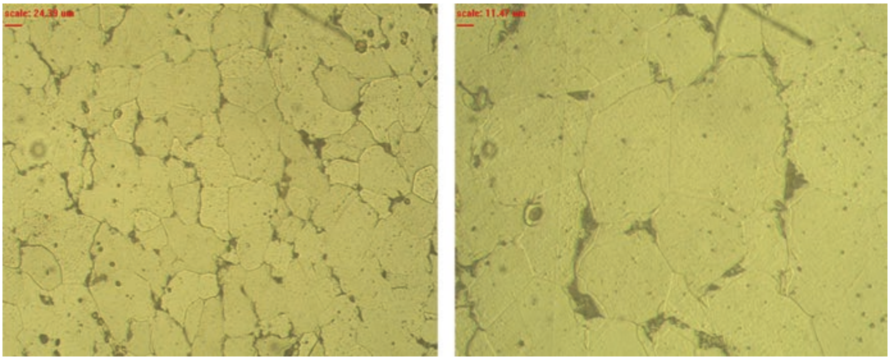
Images 12.21 and 12.22 Corrosive damage to thread steaks, thread steaks detail with stereoscopic magnifying glass

Spectrometer of argon spark, it can be said that it is similar to a SAE 1030 steel [58, p. 27] of those currently used. The hardness value of the material obtained was 80 HB [59, 60].

- **Bolt Thread**
  At that time, the types of standardized or specified threads were not yet, so the thread comb does not match the sample under study (Images 12.19 and 12.20). However, the one that most closely resembles is the 9 G 7/8″ of the current metric system. By means of the stereoscopic magnifying glass, the corrosion on the thread can also be observed in greater detail (Images 12.21 and 12.22). In this sense, it is observed that the corrosive damage has not been very serious and is mainly due to atmospheric type corrosion (Image 12.23).
- **Metallography**: Fixation or Fixation Nail (Image 12.24, Micrographs 12.19 and 12.20))

Image 12.23 Function of the threaded bolts is to join rails

Image 12.24 Fixing nail



Micrographs 12.19 and 12.20 Nail metallographs. 100× magnification (left) and 200× magnification (right)

Table 12.15 Chemical composition of the fixing nail

% C	% Si	% Mn	% P	% S	% Mo	% Co	% Cu	%Al	%Fe
0.083	0.005	0.61	0.026	0.062	0.003	0.014	0.017	<0.003	98.6

- **Chemical Composition** (Table 12.15)
- At present, the chemical composition of the parts of a railroad is as described below:
  - Carbon (C): (0.37–0.73%). It increases hardness and wear resistance, but also influences fragility.
  - Manganese (Mn): (0.86–1.74%). It has an influence on hardness, wear resistance, and toughness (not fragile), but decreases weldability.
  - Silicon (Si): (0.30%). Increases hardness, wear resistance, and facilitates rail rolling.
  - Sulfur (S) and phosphorus (P): (less than 0.05%). They are not desirable because they give fragility, but their elimination is very expensive.

From the metallographic images, it is observed that it is a ferrite-perlite structure, that is, it is low carbon (0.08%) cast iron. The ferric carbide deposited in the limits of the grain edge of the ferrite structure is observed in order to give it hardness. It would correspond nowadays with a SAE 1008 steel [58, p. 11]. The hardness value obtained by the tests performed gave 90 HB [59, 60].

Conclusions

The Buenos Aires Pacific Railroad (FCBAP) was called to be prosperous, its objective was to link the City of Buenos Aires with the Pacific Ocean, crossing the provinces of Buenos Aires, Santa Fe, Córdoba, San Luis, and Mendoza. I play a key role in the emergence of dozens of towns and cities, in agricultural activity and, especially, in the wine industry of the province of Mendoza. The arrival of the railroad contributed to the colonization of the provincial south and its development due to a fast and economic connection with the rest of the country which expedited the movement of goods and people and the expansion of the market through the insertion of regional products. Prior to the expansion of the railways in Argentina, the main means of transport consisted of carts that circulated on roads to transport the products of the country and also from other places. It took approximately 60 days to get from Mendoza to Buenos Aires. The trains on the other hand allowed to shorten these times to 36 h, and also the international transit between Chile and Argentina was accelerated. In addition, having reduced transport times for passengers, another way in which trains managed to integrate the localities was through postal services. These services also included the distribution of the most important newspapers of that time, such as the newspaper *La Nación*, and thus the information became more accessible. Beginning in 1860, the railroads experienced rapid growth, connecting several capitals in the provinces of Buenos Aires and other production points with Buenos Aires. The system was not if its obvious disadvantages, being one of the main ones the fact that the ends of its most important lines did not join, and several important points were out of the connections. The rail system in Argentina consisted, by 1910, of four main lines, all of which had as their starting point the port of Buenos Aires. These four lines were the Ferrocarril Oeste, Ferrocarril del Sur, F.C. Argentine Central, and the Buenos Aires Railroad to the Pacific. Due to the large investment of British capital in the construction and expansion of the railroads in Argentina, these were representative of the close ties between the two nations [61].

As for the threaded bolt, it is a connecting element, in which there is a difference in the size of grain between the parts of the head and the stem. These differences are due to the different types of machining in the production process. These production processes mentioned, give the pieces the necessary strength to withstand the mechanical stresses to which they would be subjected. Manganese, one of the chemical elements with the greatest presence, provides greater and better ductility characteristics.

On the other hand, the fixing nail has a metallographic structure where the carbon is deposited at the borders of the grain edge which gives it strength and functional characteristics; this deposited carbon would be forming a kind of shell or shield to protect the material and make it more resistant. Similar to what is achieved are a heat treatment of today called cemented, where the material retains a soft heart and its surroundings are hardened, as a protective shield. Being a clamping piece, to behave elastically, therefore the present Mn provides these characteristics with greater ductility and therefore elastic behavior, that is, the material is liable to support loads, bending, without breaking, to then remove the load or mechanical effort, returns to its original form. In this way, a fixing nail transmits efforts, deforms and recovers, maintaining the invariability of the gauge width, the fixing of the sleepers and the electrical insulation.

Acknowledgments

The main author wants to thank:

- Metallurgy Laboratory, Electromechanical Department—UTN FRM, Rodríguez 273, Mendoza, Argentina.
- Department of Chemical Engineering—UTN FRM, Rodríguez 273, Mendoza, Argentina.
- Trasandino Mendoza, Mr. President: Rubén Adrián Lepez, Benegas Park, Godoy Cruz Town Hill, Mendoza, Argentina.

Archaeometallurgy Study from Guido Station Belonging to Trans Andean Railway

Patricia Silvana Carrizo, Marcos Guipponi, Rocío Algañaraz and Noelia Ibañez

Keywords

Rail; Guido's station; Trans Andean railway

Introduction

This study was carried out for reasons of interest in rail, property issues, and to contribute to the studies carried out at the museum with whom we work in collaboration. The idea came up during a walk to the *Guido* Station organized by the Ferroclub Benegas Station Museum in 2018. The objective is to enrich the heritage information and then to disseminate visitors to the museum, schools, tourists, presentations for dissemination in Congresses, etc.; with this type of studies, archaeometallurgy has given added value to museum pieces in general and is approaching the university and researchers to society.

To carry out this study, metallographic techniques were used, an inverted stage microscope was used to observe the structure, a mass spectrometer was also used to obtain the chemical composition of the pieces, and the hardness of the material was measured. Then, the results obtained were analyzed to reach the conclusions.

Trasandino *Railway's History*

The "*Trasandino*" railway was a project devised by the brothers Juan and Mateo Clark [62], born in Chile with English descent. The objective of such an undertaking was the vision of being able to facilitate the transport of cargo and passengers between the oceans, through the construction of railroads 248 km long and a tunnel in the 3 km mountain range.

The first steps between the countries involved, Chile and Argentina, began in 1870; however, construction was hindered by several factors, both political and technical. In 1887 the construction by the company Clark's Trans Andean Railway Cia. Limited was approved. In 1889 construction began, but it was isolated to the city of Los Andes. By 1891, the new drilling machines began to be used in a project that already accumulated a lot of delay [63]. In 1896, due to delays in the work, a new English company took over the construction. The work was finished in 1909, and the transportation was opened on April 5, 1910.

New technologies were used at the time for the drilling of the tunnels, which would be of great help due to the difficulties that the terrain and the climate offered. ABT zipper rail sections were also installed, which would allow locomotives to generate more traction. The width of the trail in the areas between the city of the Andes and Mendoza was 1.00 m, then cargo and passengers were forced to transfer to a 1676 m trail. For that period, it was the highest railway tunnel in the world, with an average daily progress of 2.50 m [63], and it is considered by some a success of railway engineering, and for others, it serves as an example of weaknesses in terms of planning and operation.

One of the FFCC *Trasandino* stations is the Guido station, located at an altitude of 1500 m above the km 1101 of the national route 7, from which there are two railway bridges that cross the Mendoza River, one at 5 km and one at 12 km This station is now in decent condition compared to other stations on the same route. It is currently a destination for trekking and hiking fans.

Rail Technical Information

General Concepts

1. Rail: The rail is a reinforced steel element consisting of the following parts (Diagram 12.1):
2. Sleeper: Its purpose is to provide the rail with adequate support. The sleepers are separated from each other at a distance that varies between 55 and 60 cm depending on the track and can be composed of wood, pre-stressed concrete, or metal, where the latter is in disuse.
3. Track gauge: It is the distance that separates the inner faces of the rails.
4. Ballast: It constitutes the base of the railroad tracks, and they are composed of thick aggregates which give a good stability to the ground (Diagram 12.2).

Rail Types

1. Light rail: It is one whose weight does not exceed 40 kg per linear meter. It is used on lines that run trains without excessive weight or that carry light loads, and whose speed is not high.

Diagram 12.1 Rail parts: head, web, and foot

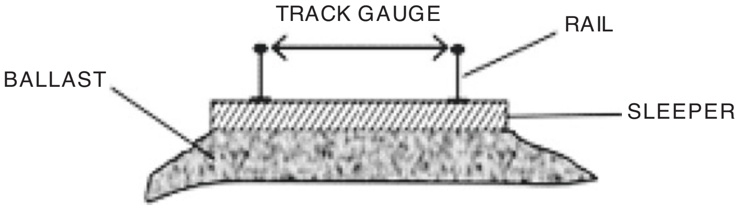


Diagram 12.2 Principal components

2. Heavy rail: Its weight ranges between 40 and 60 kg per linear meter. They are used when the requirements for speed, safety, and maximum load to be transported increase. It is mainly used in freight or passenger railways and metropolitan railways, as well as high-speed lines [64].

Requirements

1. Directly resist the tensions it receives from rolling stock and transmit them, in turn, to the other elements that make up the road infrastructure.
2. Carry out the guidance of the wheels in their movement.
3. Serve as a conductor of the electric current for signaling and traction on the electrified lines.

Qualities Searched on the Rails

1. The tread surface should be as smooth as possible to reduce friction, but at the same time, it has roughness to improve the wheel rail adhesion.
2. Geometric characteristics must be within the range defined by a road of good quality, with high rigidity, but must absorb energy in the form of elastic deformation.
3. Its weight is desirable to have high axle loads and speeds and to maintain safety, but the cost increases, although maintenance costs, longer life, and lower resistance to wheel travel are also reduced.

Experimental Methodology

Object of the Study

This historical and metallographic research is approached through the use of scientific analysis techniques: metallography, hardness analysis, chemical composition study, and manufacturing process.

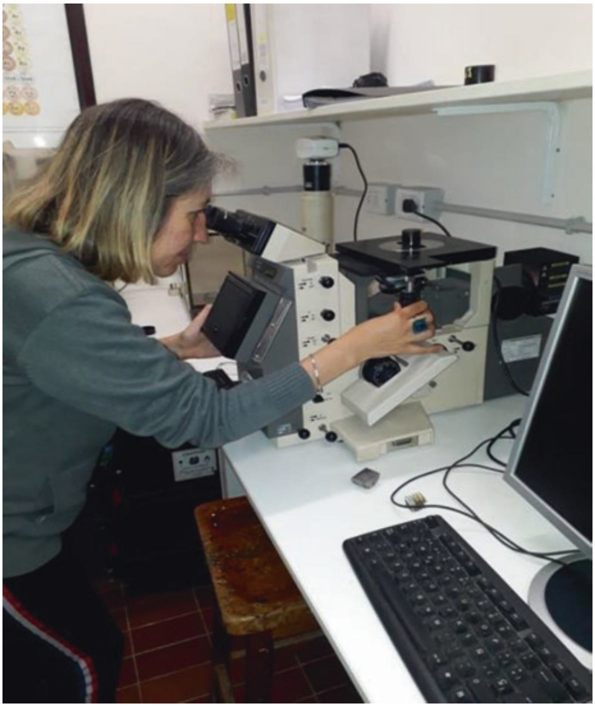
Pieces Studied

A section of rail extracted from the Guido Trasandino Railway Station mentioned above was studied (Photograph 12.1).

First, a macroscopic study of the rail piece was carried out where its surface was observed with magnifying glass (Photograph 12.2).

Two samples were extracted, one belonging to the "web" and the other to the "foot," to then perform the scientific analyzes mentioned above.

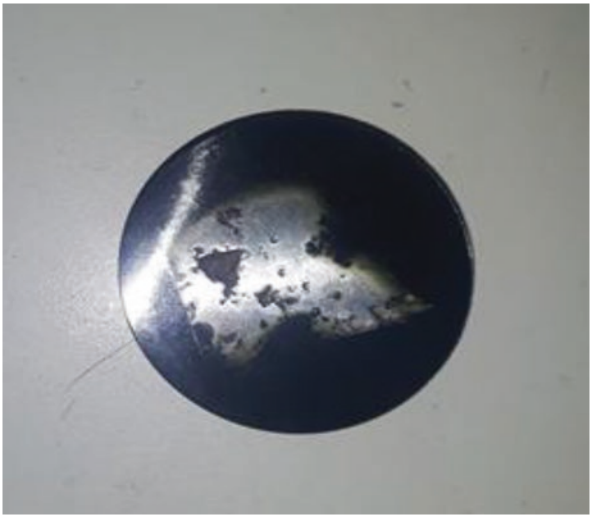
1. Foot (Photographs 12.3, 12.4, and 12.5)
2. Web (Photographs 12.6, 12.7, and 12.8)

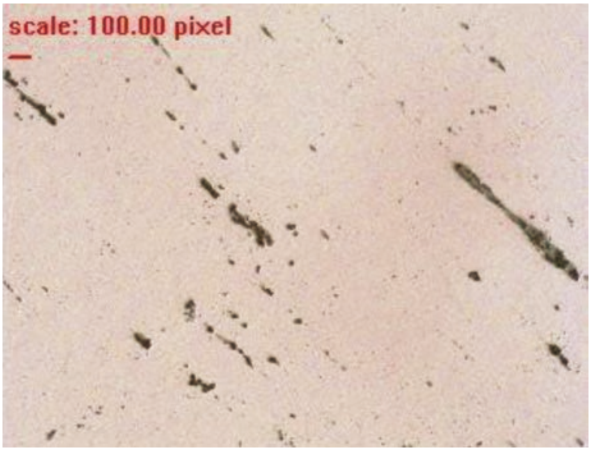


Photograph 12.1 Eng. Carrizo is working with metallographic microscope

Photograph 12.2 Piece of rail cut transversely

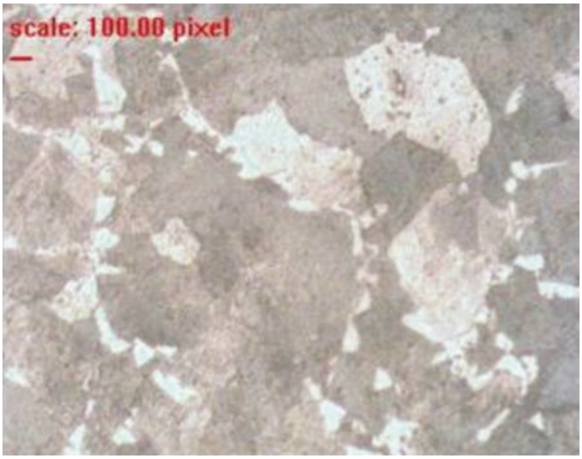
Photograph 12.3 Sample "foot" embedded in phenolic resin tablet



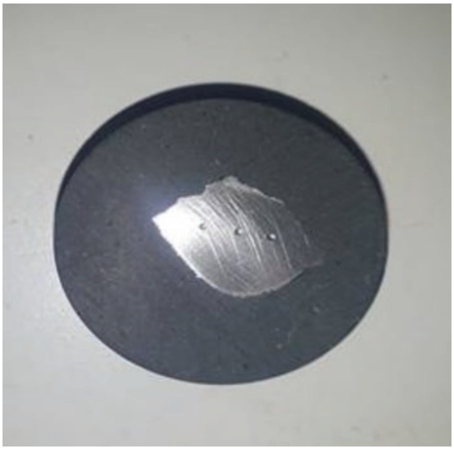


Photograph 12.4 Micrograph of the foot sample before performing the chemical attack

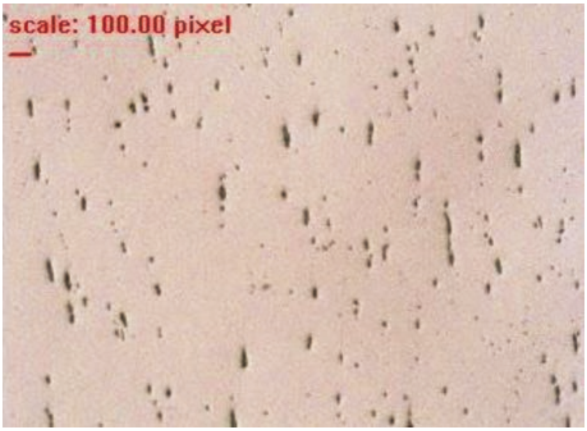
Photograph 12.5 Metallography of the foot sample. Ferrite -perlite structure is observed



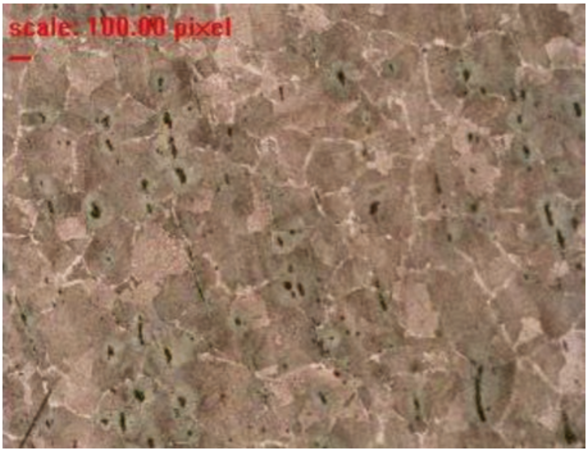
Photograph 12.6 Sample "web" embedded in phenolic resin tablet



Photograph 12.7 Microscope view of web sample before chemical attack. Sting corrosion damage is observed



Photograph 12.8 Metallography of the "web" sample. Ferrite - perlite structure is observed



Chemical Composition

The chemical composition is the same for both the samples since they are the same piece. The results are shown in Table 12.16.

Table 12.16 Chemical composition obtained by Argon Spark Spectrometer

Component	Composition (%)
Fe	97.3
C	0.49
Si	0.49
Mn	1.54
P	0.003
S	<0.002
Mo	0.003

Hardness Test

The Brinell hardness test was performed. The results obtained are detailed in Table 12.17.

Table 12.17 Results of the Brinell hardness test

Sample	Foot	Web
Hardness (HB)	259	275

Discussion of the Results

The macroscopic analyses show us some pitting corrosion damage due to carelessness and the passage of time in unfavorable conditions.

From the results of the metallographs, we can see that it is ferrite-perlite structures where perlite predominates, and it is also observed that the grain size of the foot is smaller than that of the web, this indicates that the foot is more resistant.

The chemical composition indicates that it is a hypo eutectic iron, with manganese (Mn) and silicon (Si) as main alloys, which act as good deoxidants, also neutralize the harmful effects of sulfur, facilitating lamination, molding, and other hot work operations. In addition, the Mn increases the penetration of tempering and contributes to its resistance and hardness.

It is cast iron, obtained by "puddling method," which was a material of great importance and quality, which was present in large infrastructure works in its time. What happened was that the technological current of steel advanced very steeply, providing more development opportunities, and that is why steel left behind molten cast iron.

The hardness of the web is greater because this part of the rail is the most exposed, that is, it has been hardening with the passage of the railroad. This behavior is typical of this type of iron.

Conclusions

It is a rail of excellent quality, with very low impurity content, obtained by the puddling process (process prior to the Bessemer furnace).

When comparing its chemical composition and hardness with a standardized steel, we can estimate that it would be a SAE 1548 steel. This material is used in conditions where high hardness, resistance and toughness are required. They are steels that can be used to manufacture forged parts.

With the analysis carried out, bibliography consulted, and documents validated by the Museum, it is concluded that this piece of rail extracted from the old Guido Station belongs to the time when the Trasandino Railway worked.

Archeometallurgical and Heritage Study on the Old Iron Bridge over the Mendoza River

Patricia Silvana Carrizo

Abstract

This chapter arises from the intention by the Town Hall of Lujan de Cuyo, declared heritage sites of the old Iron Bridge, which is in full use to be an important means of communication for vehicles up to 4000 kg. Thus, the relevant historical research of the origin of the bridge in the Municipal Archives were performed, with installation in 1898 decreed by President Roca. It consists of seven sections of 40.6 m each, and the center to center distance of the main beams is 5.80 m. Metallographic studies confirm that the bridge structure is wrought iron or hot rolling, and the chemical composition was determined, besides thickness measurement, hardness. Tensile tests corresponding to the complete characterization of the manufacturing material of the bridge were made. Its survey allowed observing its state of conservation, evaluating its corrosive state and analyzing vibrations with six sensors of the triaxial accelerometer type with a frequency of 200Hz for little traffic on the bridge. In this first instance, the direction in which the acceleration is greater was obtained.

Keywords

Iron; Heritage; Vibrations; Composition; Strength; Oven Bloomery

Introduction

On the occasion of the construction of the Iron Bridge, a camp was established on the north bank of the Mendoza River, before the creation of the National Highway Directorate. The “River Bridge” was authorized by Law Decree No. 1889 of October 18, 1886, signed by President Roca with a budget of \$171,021.46, along with two other bridges in San Juan and Neuquén; they are the first iron bridges built in the provinces and the first of its kind in Mendoza with an extension of 284.20 m long and 5 m wide, built in seven sections of 40.6 m, a work that in its time was monumental and fundamental. For development, it was a National Rail that with the modern bridge facilitated communication with the south of Mendoza, another testimony to the historical flow that the center of Luján keeps [65] (Fig. 12.30).

According to the original and primitive project submitted for approval by the government in 1885, the beams had to be of mixed construction; “Hard wood,” for

Fig. 12.30 Panoramic view of the iron bridge over the Mendoza River in its North-South direction

the pieces that will work in compression and of laminated iron those that will undergo tensile stress. The public tender is held on March 18, 1887, and a contract is signed with the company Andrés Braly y Cía. For the sum of $178,391.00. The works are finished in September 1890.

Its cost was very high, and it is enough to compare with other works of the time to understand the effort of acquiring this material that was imported from England to which had to be added the cost of transport from the port of Buenos Aires to Mendoza by railroad. Being one of the first works of these characteristics, there were construction failures, in 1890 considerable repairs were made. It is common to find in all the departments crossed by mighty rivers hiring of boats and "river passers" in times of flood; in 1889, it was still hired in Luján, which proves the serious shortcomings that the construction had. Reviewing the international publications of studies carried out on this subject, it is found that C. Gentili and A. Saisi [66] made studies monitoring the vibrations for a period of 1 year in an iron bridge of 100 years; the San Michele bridge built in 1889 being the most important monument of the nineteenth century of iron architecture in Italy, and it is still in operation for vehicular traffic as well as maintaining its status as a railway bridge, and by way of conclusion, they determined that the frequencies The natural characteristics of all models tend to decrease with increasing traffic and cross-sectional models are generally more sensitive to traffic acceleration compared to vertical models. They even determined that temperature affects almost all natural frequencies, but this effect is nonlinear for several of the frequencies, although a decrease in frequency was not characterized with increasing temperature.

Regarding the area of historical metallurgy, no antecedents have been found that specifically speak of this issue regarding the iron bridge.

It is noteworthy that the bridge was built based on a new project, making the sections entirely metal. In the archives of the Department of Civil Engineers of the Argentine Republic, in documents of the time it is reported that there are no decrees or any resolution that authorized the change of project. Between 1889 and 1890, during the final part of the execution of the work, Eng. Nicolás Rosetti, in charge of the Mendoza Section in several notes, to the inspection of Bridges and Roads, stated that he was accompanying sketches showing how many diagonals they had to work the traction was loose, but it was not given importance, and the bridge was received without requiring the contractors to correct the poor assembly. In addition to the bad assembly, the sections as they were built were weak to safely withstand the overload of 400 kg/m^2 and that the defects are the same as they were noticed 7 years ago (inauguration), aggravated naturally by use, to such a degree that the passage of an insignificant moving load, such as being a rider, for example, made the tremble in an alarming way. Therefore, in this report of February 3, 1898, the consolidation works were proposed. Among them the main ones were: placement of transverse beams, where they have been omitted; reduction of the permanent load, by lightening the gravel layer of the deck; reinforcement of uprights, such as diagonal and horizontal bars; and their resistant moments, the bars Diagonals that were loose bent should be cut and reattached. Seventy-six tons of rolled iron were used, in plates, reinforced beams, and the necessary rivets.

On March 17, 1898, the then Governor of Mendoza Emilio Civit and the Minister of Public Works Enrique Day required an urgent solution given the importance that the Bridge service lends because the southern departments of Mendoza and the Government of Mendoza are linked to this city Neuquén. If you are late, there is a danger of catastrophe. Then on April 30, 1898 (second presidency), the president of the Roca Nation with the agreement of ministers authorized the repair. On October 19, 1898, Pedro Vassena was contracted to produce 76 tons of rolled iron. Put into service, the work worked relatively well with only repair and/or maintenance work, on the wooden deck and its components, notable works being carried out in 1957, and especially in 1972, where by means of wheel guards, it was limited to a single track the circulation. With this background and added to a worsening of the traffic conditions due to increasingly pronounced pavement defects over time, a new intervention was undertaken to study and reformulate the deck of the bridge, a true Achilles heel. Work began in October 1990.

The following were considered fundamental solutions: to support a maximum vehicle load of 4000 kg that would originate 1000 kg/wheel and increased by a coefficient of 50%, possibility of the simultaneous transit of two tracks for vehicles of the indicated characteristics, which would reduce the weight of the own existing deck (whose value was 450 kg/m^2), use of pre-molded pieces and supplemental beams for the deck construction, then there was a significant reduction in deck weight to 380 kg/m^2, dismantling of the road and wooden wheel guards, review of the entire metallic structure, repair of the support mechanism, cleaning and painting of the bridge, repair and reconditioning of the pedestrian walkway, placement of metallic defenses, lighting, signaling, construction, and placement of maximum permitted height limiters for vehicles [67].

Experimental

The metallographic and historical study of the Iron Bridge belongs to the Archeometallurgy Area, which works within the Metallurgy Laboratory, the Electromechanical Department, belonging to the National Technological University

Table 12.18 Chemical composition and hardness

Chemical composition	Hardness
%Si = 0.73	115.33 HB
%Cr = 0.019	
%Ni = 0.017	
%Ni = 0.017	
%P = 0.35	
% S = 0.37	
%Fe = 97.6	
%Mn = 0.031	

Table 12.19 Results of mechanical test on samples from the old iron bridge over Mendoza river, carried out at IMPSA Company

Flat tensile test	Impact test
Breaking load: 66,770 N	Sample 1: 13 J
Breaking strain: 352 N/mm^2	Sample 2: 12 J
Yield load: 50,409 N	Sample 3: 10 J
Yield stress: 266 N/mm^2	Average: 11.7 J
Elongation: 11.5%	

Fig. 12.31 View of the bridge infrastructure consisting of seven sections of 40.6 m each

Mendoza Regional College and was carried out in 2014, at the request of the Directorate of Culture of the Municipality of Luján de Cuyo, with the aim of subsequently carrying out the enhancement and declaration of patrimonial interest. The corresponding metallographies were carried out that allowed observing the structure of the bridge, knowing the manufacturing process, measurements of chemical composition, hardness (Table 12.18), tensile and impact tests (Table 12.19), and so on with all this information. Once gathered, perform the characterization of the material (Fig. 12.31).

The constituent material of the bridge is iron in its entirety rolled or hot forged. Wrought iron is a material whose microstructure consists of slag inclusions of silicates, sulfates, and even phosphates embedded in a matrix that can vary from being fully ferritic to inclusion of large quantities of perlite, frequently distributed in a very heterogeneous way. Slag inclusions are normally elongated in the working direction by hot forging processes used to process molten material and shape wrought iron objects [68].

Wrought iron, also called laminate, has been produced in many countries of the world over a period of time ranging from the Iron Age (second millennium BC) until well into the twentieth century.

It was initially produced by two distinctly different technologies: direct Blommery furnace smelting and alternative indirect smelting [69]. Wrought iron is an iron alloy with a very low carbon content in contrast to cast iron, and it has fibrous inclusions, known as slag. It is strong, malleable, ductile, and easy to weld. Historically known as “commercially pure iron,” however, it no longer qualifies because current commercially pure standards require a carbon content of less than 0.008% by weight. Wrought iron has been used for many centuries, and it is the “iron” that is known in Western history.

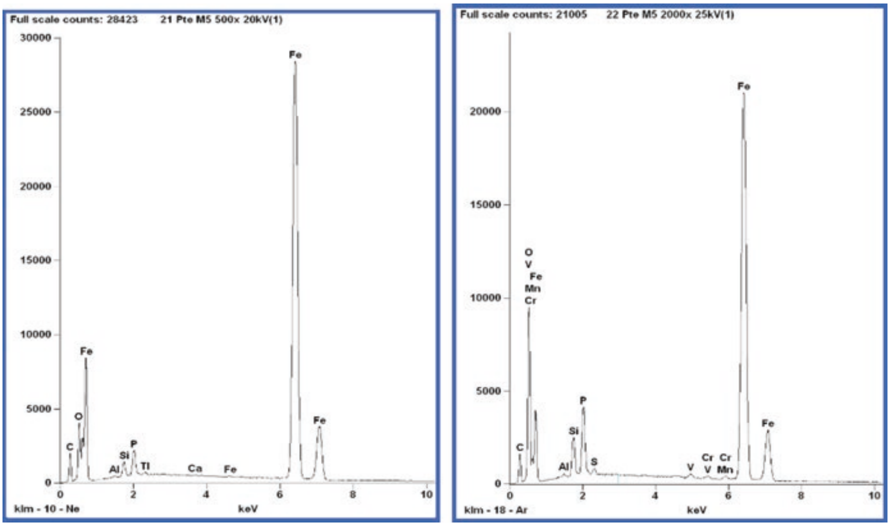
The other form of iron, cast iron, was not introduced into Western Europe until the fifteenth century, even then, due to its brittleness, it could only be used for certain purposes. Throughout much of the Middle Ages, iron was produced by the direct reduction of minerals in a manually operated Bloomery kiln. Hydraulic energy to give movement to the mechanisms began to be used in 1104. The raw material obtained by the method of indirect melting is pig iron, and it has a high carbon content and therefore is fragile, and the raw material obtained by direct melting is of better quality. The Bloomery process continued in many places, but depended on the development of the blast furnace, of which medieval examples have been discovered in Lapphyttan, Sweden, and in Germany.

The process consisted of loading coal and iron ore and then igniting, air was blown through a nozzle to heat to a temperature below the melting point of iron. During the melting, the slag melted and the carbon monoxide in the charcoal fulfilled the function of reducing the iron ore, which was transformed into a spongy mass without passing through the liquid state.

Furthermore, as a result of the process, the material used to include a large amount of slag, which could later be removed or expelled to a greater or lesser extent by hammering. During the Middle Ages, the force of water was applied to the process, mainly to feed the bellows and then to move the forging hammers. And this was the culmination of the direct process for making iron, which survived in Spain and southern France as Forjas Catalanas in the mid-nineteenth century, in Austria as Stuckofen in 1775, and near Garstang in England until around 1770.

The Bloomery process produced the so-called coal iron and continued until the end of the eighteenth century. Also with the successive inventions and improvements to the process, wrought iron was produced from pig iron with Gallic forges or from the industrial revolution in a Lancashire home, the resulting metal was highly variable, from both the chemical and the slag contents.

Already at the end of the eighteenth century, there was a demand for pig iron (an impure form of iron), to be refined with coal as fuel. This allowed the passage to puddle iron, which contained less slag, less sulfur, and very low carbon content. Here the iron was kept separated from the fire in a reverberatory furnace to prevent harmful sulfur and phosphorus from entering the finished iron, this puddled iron was also highly variable in its properties, it was more consistent than previously produced irons and the method it lends itself to the production of much larger quantities (Fig. 12.32). In 1876, the annual production of pudding iron in the UK alone was four million tons [70].



It is observed in the macroscopic examination which exemplifies the typical damages induced by external corrosion, observed in a large number of structural elements both on the downstream sides and on the upstream sides (Fig. 12.33).

It should be noted that the large separation of the rivets is not suitable for the thickness of the iron plates (10.05 mm), this easily allows the penetration of moisture between the contact planes so that the expansion of oxide, due to the subsequent volume increase, it includes the deformation of the iron plates and sections in the connections of the composite struts [66].

The study of chemical composition, hardness, tensile tests (universal testing machine, Wolpert-Amsler brand, range 0–100 ton) and impact (Impact machine, Wolpert-Amsler brand, range 0–300 J) were carried out. The vibration measurements were made with triaxial accelerometers and thereby identify the vibration frequency of the bridge (Figs. 12.34 and 12.35).

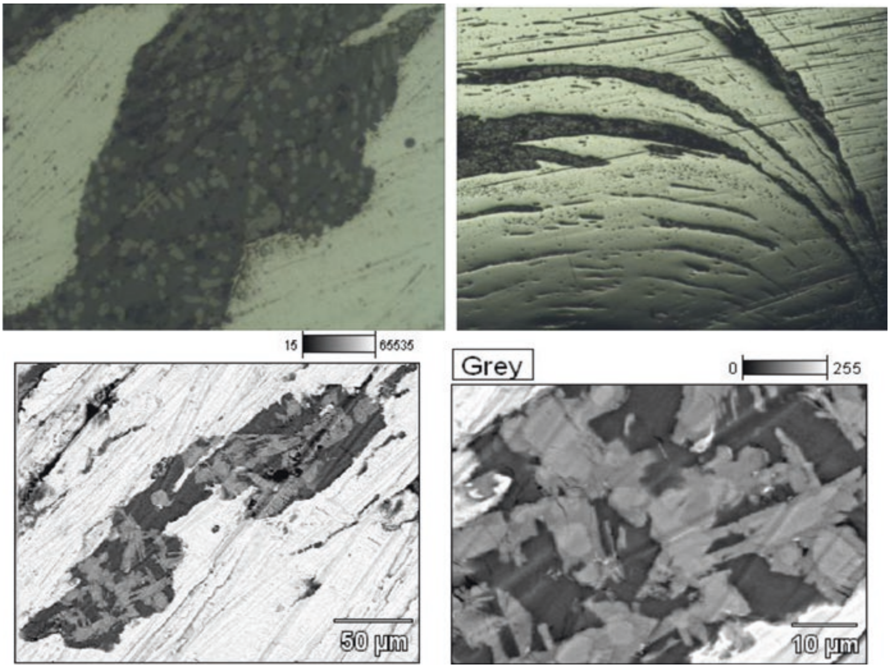


Fig. 12.32 Historical wrought iron microstructure, equiaxed grains of ferrite are observed with a certain amount of inclusions of the type silicates, sulfides, phosphates, and iron oxides present in dendritic form. Detail of the forging lines. Reagent: Nital 2%. Magnification: 50×. Corresponding images with SEM-EDS

Fig. 12.33 Macroscopic observation of the bridge structure, column detail of the third section and the external corrosive damage produced

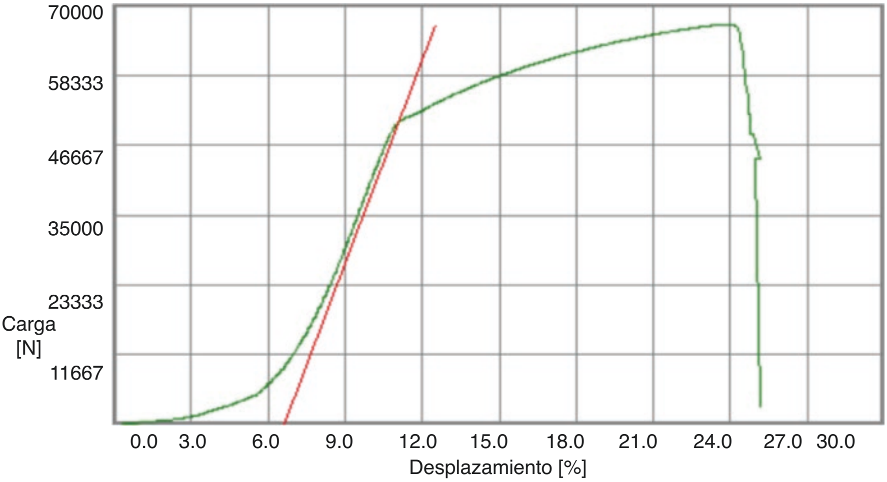


Fig. 12.34 Stress curve—unit strain in an iron bridge specimen

Fig. 12.35 Placement of triaxial accelerometers powered by their corresponding batteries

Regarding the study of vibrations of the bridge, six sensors of the triaxial accelerometer type with a frequency of 200Hz were placed for little traffic on the bridge. The resolution of the accelerometers is 2×10^{-8} m/s^2 for all three directions. The objective of these measurements is to determine the dynamic properties of the first span of the bridge. This study has two fundamental purposes in the process of conservation and recovery of heritage. The first of them is to be able to evaluate the state of the construction by means of the contrast with a computational model of the construction. The second reason is to be able to establish a baseline for monitoring the bridge in future interventions, even earthquakes that could damage it.

In the case of the present study, the dynamic property that will be useful and will be used is the fundamental frequency of the bridge, which is composed of six equal sections, so that the measurements are also useful to compare section to section and to be able to establish a level of relative damage between sections. For this present study, the dynamic property that was determined and will be useful is the fundamental frequency of the bridge. In this case, the bridge is made up of seven equal spans, so the measurements are also useful to compare span to span and to establish a level of relative damage between spans. Currently the measurements of the first and second section have been carried out. Next, the fundamental frequencies of the first section with traffic enabled and without traffic are presented, which implies an approximate mass increase of nine tons with respect to the empty bridge. Figure 12.36 presents the Fourier spectrum and Table 12.20 shows the oscillation frequencies of the bridge in the vertical direction. Each frequency indicates a different way of vibrating.

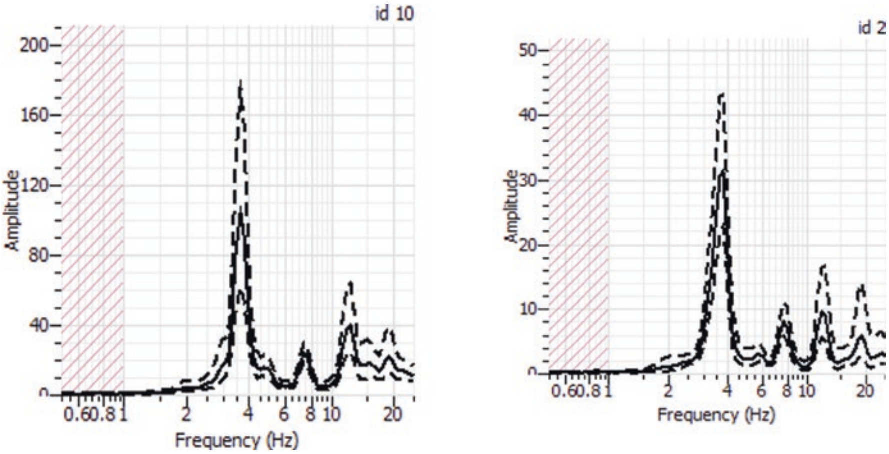


Fig. 12.36 Fourier spectrum of measurements with and without transit. Each peak indicates a different vibrating frequency

Table 12.20 Vertical oscillation frequencies values of the bridge

Frequency values [Hz]		
	With traffic	Without traffic
1	3.64	3.72
2	4.89	5.79
3	7.47	7.79
4	12.12	12.16
5	15.51	15.75
6	19.05	19.14

Results and Discussion

In the metallographic examinations, elongated inclusions of the type of silicates and iron oxide are observed, which were morphologically ascribed to fayalite (Fe_2SiO_4) and wüstite (FeO). Iron oxide is not liquid at temperatures around 1200 °C and is considered the maximum obtainable in primitive furnaces: therefore, silica (SiO_2) had to be added, which binds to FeO to generate fayalite, which is liquid to the indicated temperatures.

This reaction can also occur spontaneously when in contact with the natural fused silica that forms the refractory base material of early furnaces. The availability of an iron silicate as a waste product of copper metallurgy, which is one of the first metals discovered by mankind, and was seen by some as the reason for the birth of the iron and later steel industry.

The micrographs also show small globular oxides that would be associated with heating at high temperatures (estimated to be above 1100 °C) during the forging process. In addition to pointing out that due to the manufacturing process: puddling, a lot of sulfur was left in the pasty iron, proof of this is in the micrographs made, that there is a significant presence of sulfates, sulfides as inclusions and little diffusion [71]. But there is also the presence of phosphates that retard corrosive processes. Slag inclusions, or stringers, in wrought iron give it properties not found in other types of ferrous metals.

There are approximately 250,000 inclusions per square inch. A fresh fracture is light bluish in color with a high silky shine and stringy appearance. Manganese (Mn) is present in the chemical composition analysis, which is the element that gives it the important characteristic of ductility. For most purposes, ductility is a very important measure of the quality of wrought iron with respect to tensile strength. In tensile strength tests, the best irons are capable of undergoing considerable elongation before failure, in our case the elongation value was 11.5%. At the end of the nineteenth century, when the metallurgists of the time were able to better understand properties such as traction, ductility, processes were then improved and good iron began to be manufactured, only a little late, since iron was displaced by steel.

With the tensile test values (Table 12.19), the material's modulus of elasticity (Eq. 12.1) was calculated, which is the relationship between the stress to which it is subjected and its unit deformation and represents the rigidity of the material before a load imposed on it. When the relationship between the stress and the unit strain to which the material is subjected is linear, constant, and the applied stresses do not reach the limit of proportionality, the material has an elastic behavior that complies with Hooke's law (Fig. 12.34).

Also, wrought iron is ductile and tends to give way slowly, giving warning signs. From the tensile and Charpy tests carried out, it appears that it is a ductile material, which admits elastic deformation forces; therefore, this low value of the modulus of elasticity indicates that it is easy to bend under loads. It does not present stricture, so it is possible that, due to the passage of time, the structure of the bridge has developed some fragile behavior. The low value of the Charpy impact test (11.7 J) assures us that it is a ductile material.

$$E = \frac{\sigma_f}{\varepsilon} = 2313 \ MPa \tag{12.1}$$

σ_f: yield stress, ε: percentage elongation.

As regards the study of the vibrations of the bridge, the measurements carried out have allowed us to generate a spectrum of frequencies. Each peak in this frequency spectrum indicates a different vibrating frequency. Each way of vibrating takes on a different physical configuration. The variation of the frequency between the two states: with traffic and without traffic, respectively, represents the increase in mass due to vehicular traffic (Eq. 12.2). If the first frequency from Table 12.20 is taken, the frequency with transit is 3.64 Hz and without transit is 3.72 Hz, which gives a difference of 2.15%, which implies a variation of the mass of 4.62% (10.3 tons) that it is approximately the mass of the vehicles in circulation relative to the mass of the structure of 224 tons. Therefore, in principle, the bridge would have a linear elastic behavior, which corroborates what was evaluated in the tensile tests and would not present structural damage.

$$f = 2\pi\sqrt{k / m} \tag{12.2}$$

f: frecuencia [Hz], k: rigidez [N], m: masa [kg]

Conclusions

The manufacturing material of the historic bridge, as anticipated by the Municipal Archives documents, is wrought iron or hot rolled; this material lacks the necessary carbon content for its hardening by heat treatment, but it was hot worked or forged after hardening it; before it cooled down, the rivets were placed by blows, that is why the set of plates and rivets form a single structure and therefore its corrosive process is external and added that the environmental humidity does not represent a problem due to the dry climate of Mendoza. Its metallographic structure is composed of a ferritic matrix with dendritic inclusions. Sulfur impurities in wrought iron decrease corrosion resistance, but the presence of phosphorous increases corrosion resistance. According to the chemical composition of wrought iron and according to the Bloomery manufacturing process, initially, but with the advancement of technology and knowledge, iron began to be produced in large quantities and continuously by the pudding process. The presence of manganese in its composition gives it ductility characteristics, which was also verified by the low value of the Charpy test. The calculation of the modulus of elasticity reports that the wrought iron constituting the bridge behaves as an elastic material, complying with Hooke's law, which tells us that the material can be subjected to linear elastic stresses. The vibration measurements with the triaxial accelerometers give us the values in the vertical direction, these values also corroborate the elastic behavior of the bridge structure and affirm that it does not present any damage. The iron bridge continues to provide service today, it is 123 years old since its inauguration, and it lacks its own name and with proper maintenance it can continue in controlled use. It is a true treasure, the third bridge being that installed in Argentina and the first of its kind in Mendoza and should be declared of heritage interest.

Acknowledgments

The author of this work, Engineer Patricia Silvana Carrizo wishes to express her gratitude to: Mr. Rubén Carrizo for their selfless collaboration, Engineers Miguel Ángel Franetovich, and Carlos Bello for their collaboration, staff of the Municipal Archive, staff of the National Library of the Mendoza Highway, staff of the Police and Preventers of the Municipality of Luján de Cuyo, Deputy Director (with completed mandate) of the Americanist Museum Lic. Omar Giunta†, to Mr. David Piraces, technician of the IMPSA company, to colleague Roger Chung for their collaboration.

Archaeometallurgical and Historical Study of Metallic Defense Elements Belonging to the San Carlos Fort in the Uco Valley, Mendoza-Argentina

Patricia Silvana Carrizo and Hugo Ricardo Dengra

Abstract

The Fort of San Carlos, installed in the Uco Valley in 1770 to stop the attacks that native enemies and bandits carried out on the farms of the Valley, was the nucleus of the emergence of the Villa de San Carlos, founded in 1772. From hence, as a meeting place, it effectively served to pacify the border and allow the development of the region. The objective of this research is to study the raw material and the metallographic structure of two cannons and of the metal-tipped tacuara cane spear on permanent display at the San Carlos Fort Museum. This site was declared a National Historic Site and preserves some archaeological remains and ruins of the Fort. The studies related to the chemical composition of historical metals were carried out with an X-ray fluorescence spectrometer and subsequent study of the metallographic structure using a metallographic microscope and finally the measurement of hardness, all these studies were carried out in situ with portable equipment and with the obvious limitations of the case. These investigations are part of the Border Archaeometallurgy Project (2016–2017) where the studies developed on historical metallic materials, raw materials, and manufacturing processes were correlated with the history of the two most important Forts of the Southern Border of Mendoza.

Keywords

Canyon; Cast iron; *Tacuara* cane spear; Metallography; Historical fort; Southern border

Introduction

Since the mid-1600s, Cuyan settlers, who are affected by the theft of animals, began to insist that a border fort be installed to defend their properties. Likewise, the authorities of Santiago of Chile needed to protect the animals that had to pass into that territory, to provide in particular to the Spanish army. On the other hand, the risk of the threat and the damage caused by the gangs of non-allied tribes in the Uco Valley made the inhabitants of the city of Mendoza constantly threatened [72].

In February 1770, the Mendoza City Council decided to build an advanced fort for the protection of Mendoza, which was to be installed in *La Isla or Real de San Carlos*. The design and construction were entrusted to the Master of Field Juan Martínez de Soto y Rosas. By the end of February, he had the tools and the personnel, and the work began. The Fort was completed in August 1770 [73].

The Cabildo indicated that a "double-staked fort" should be built, with wood, but, as this material is lacking, the existing is used: stone, clay, reeds, and cane. With about 50 m of side and a wall of more than 3 m high, it had four towers for surveillance. A wooden gate closed the access on the east side; a moat more than 2 m deep surrounded it. A garrison of 24 men was installed there, with a commander. The Fort was equipped with some artillery pieces [74]. Under the protection of the Fort, ranches immediately began to rise, generating a small frontier village. It must be assumed that those muleteers who camped for months near the Fort, more confident, even brought their families, or became a family, and the installation was more permanent. Furthermore, it is possible that the aborigines were also bringing their villages closer together. Thus, on October 3, 1772, Mayor Juan Manuel Ruiz founded the San Carlos Village, arranging the plots to the west of the Fort [75].

It should be noted that, since the Fort was installed and due to the hard work of the local commanders, who called to hold Parliaments with the aborigines, in order to solve difficulties, plan actions, enter into agreements, the threat of invasions decreased. Only the attacks organized by tribes that did not sit down to agree, generally more distant to loot the estates, occurred. Even the friendly aborigines, being also affected by these attacks, supported the colonial authorities.

The Sketch from 1775

In 1776 Don Jacobo Badarán y Bustillo, Mayor of Cuyo region, was transferred to *Santiago de la Nueva Extremadura*, capital of the General Captaincy of Chile. Among the documents he carries is the sketch of Fort San Carlos, with references to its surroundings, dated by the Chilean National Archive as 1775 (Photo 12.1, Table 12.21). It is the oldest documentation of the first Fort [76].

A document from 1779, kept in the General Archive of the Province of Mendoza, states:

> The Fort's armament includes: a front-mounted cannon that shoots nails, pellets, and pieces of iron; four *pedreros* (small and short artillery pieces that shoot stones), which are fixed at each angle of the building. Subsequently, the number of cannons is raised to ten, more effective than the quarriers. They fire eight rounds per hour and overheat easily, so they need time to cool down. Its handling is complicated, they require several people, so they are not very useful to fight against a highly mobile enemy like the aborigines. Other equipment they use are: rifles, carbines, bayonets, emery boards (very old artillery pieces), sabers and spears. These, four meters long, are the most widely used weapon to fight against the indigenous in open terrain. [77]

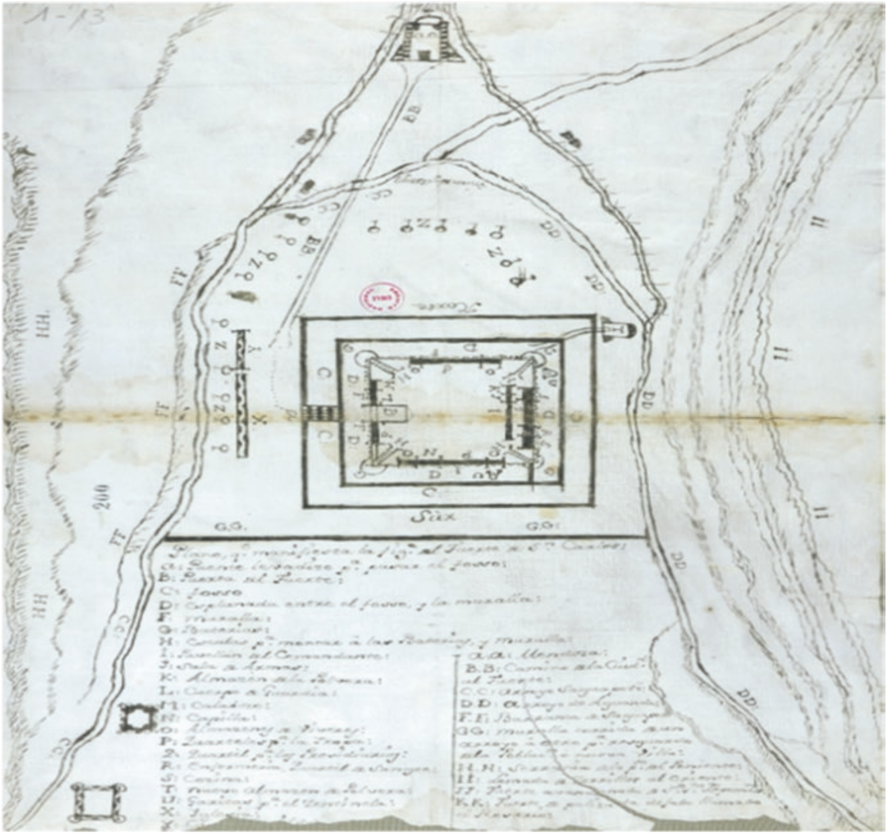


Photo 12.1 Sketch San Carlos Fort (1775), Chile National Archive, map_anh 0377

The cannons are made of iron, although we know that in America the Spanish artillery also had them made of bronze and even quebracho [78] (due to the hardness of this wood, being lined with leather to achieve greater resistance and prevent cracking): they were loaded with stones, pieces of iron, nails, bullets..., which when fired formed a wall of highly effective shrapnel at short distances and against an “enemy” who mostly went on foot or on horseback with rudimentary weapons such as spears, bows, arrows, and knives. Both the cannons and the stones took their place in the bastions or towers to have a greater angle of fire and reach a greater distance; although the reality was that they were used more as dissuasive weapons than for their clear effectiveness [79].

Rafael de Sobremonte, during his administration at the head of the Córdoba Government of Tucumán [80], maintained an effective strategy to generate a series and chain of forts on the southern border of his Province. The forts were also endowed with “outstanding armament and he arranged battalion cannons on light carriages, so that in the early departures these means would supply the short number of people who can join in the invasions of the Indians” (Punta y Rustán 103) [81].

Table 12.21 Sketch references from 1775

A: Drawbridge to pass the moat	S: Kitchen
B: Gate of the Fort	T: New Gunpowder Warehouse
C: Pit	U: Sentry Boxes
D: Esplanade between the moat and the wall	X: Church
F: Wall	AND:
G: Batteries	Z:
H: Scales to mount to the batteries and walls	A.A: Mendoza
I: Commander's Pavilion	B.B: Road from the City to the Fort
J: Weapons Room	C.C: Creek Saguapoto—Yaucha
K: Gunpowder Warehouse	D.D: Creek of Aguanda
L: Guard Corps	F.F: Gully of Saguapoto
M: Dungeon	G.G: Wall run from one stream to another to protect the population of the new town
N: Chapel	H.H: Mountain range of the western part
O: Grocery Stores	I.I: Hill of cerrillos to the east
P: Barracks for the Troop	J.J: Abandoned Fort of San Juan Nepomuceno
Q: Inmate Barracks	K.K: Strong, wooden palisade, called del Rosario
R: First Aid, Blood Barracks	

Photo 12.2 Model of the Fort around 1780

In 1787, José Francisco de Amigorena detailed the state of Fort San Carlos. With the data from this document, a model of the set is designed (Photo 12.2) [82].

In 1805, the Marquis of Sobremonte, already Viceroy of the Río de la Plata, agreed to create Fort San Rafael del Diamante and a town next to it. It is from San Carlos that the colonists' column for that foundation departs. There was then the intention of dismantling Fort San Carlos, but later it was deemed convenient to support it.

During the Independence War, Fort of San Carlos also witnessed important events. In September 1816, General José de San Martín held a long and effective Parliament with the aboriginal *Pehuenches*, in which he managed to ally them as participants in the Crossing of the Andes Mountains. And in January 1817, it was the column of Captain José León Lemos that left Fort of San Carlos marching through the passes of *Portillo* and *Piuquenes* to attack the San Gabriel Fort, and distract the Spanish troops in a risky mission.

The Fort Around 1860

During the independent period the building is modified and expanded. It is called THE BARRACK. They continue to be the place from which defense and protection parties depart, from attacks by both aborigines (the *malones*) and outlaws [83].

The space is shared by the military commander, the policeman, the judge, the political delegate. Also the person in charge of the Civil Registry, the Revenue Registry, the doctor, and the teacher (Photo 12.3).

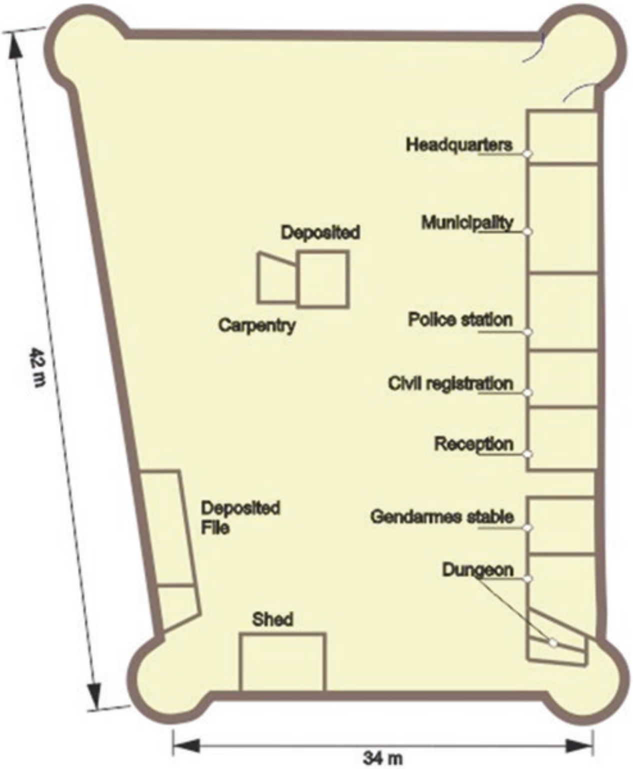


Photo 12.3 The political headquarters of San Carlos, 1904

Attacks by the Pincheira, bandits from Chile, since the 1820s, threatened the Uco Valley. On October 14, 1931, a group of Gral. Quiroga's squads, led by officers José Ramírez, Estanislao Recabarren and Florencio Videla, confronted the bandits in Chilecito. Commander Florencio Videla dies on this occasion. On October 16, General José Albino Gutiérrez left again and confronted them in Paso de las Carretas (battle of Aguanda), where he died. But the group reorganizes and finally defeats the Pincheira. In 1833, parties against the southern Indians left the Fort, organized during the government of Juan Manuel de Rosas to extend the southern border.

At this stage, particularly during the Desert Campaigns of both Presidents: Rosas and Mitre, the garrisons did not have sophisticated weapons, since the most common were the outings or "games" to the field, in outposts and attacks against tribes, hostile, or persecution of bandits. Short firearms, easy to carry on horseback, and bayonet-mounted rifles were used. In addition, the soldiers and militiamen used sabers and the particular tacuara cane spear with a metal tip. Already the aborigines used them previously to attack and defend themselves. During the Desert Campaign the Army also used them, adapting its structure by mounting two sections (about 2 m each) with metal socket union or inserts.

It is this building that sees how the old department of San Carlos is subdivided, giving rise to the departments of Tupungato (1858) and Tunuyán (1880).

The Political Headquarters

In 1895 the Municipalities Law was enacted in Mendoza, by which each principal Villa of each Department should have its own municipality [84], and the neighbors could choose their own authorities and manage themselves [85].

From that period we find a sketch, dated 1904. It once again has its rounded towers and still preserves some of the walls of the old fort. The measurements of the building are indicated (Photo 12.4).

The building is occupied by police, judicial, and municipal units. Later, while they were moving to their own places, the building was gradually abandoned. By 1910 it was only occupied by the 18th Police Station of the Provincial Police [86].

The last preserved image of the Fort is a photograph (Photo 12.6) that appeared in the *Los Andes Newspaper* in January 1920, taken by Benjamin Buttini (father) from the roof of the old municipal building (to the west).

When the old fort was definitively demolished, in 1927 the new building of Section 18 of the Police was erected on the same site. This one was also demolished around 1980.

The Remains of the Fort

The site of the Fort was declared a National Historic Site, by Decree 4592/51. Several buildings have been built on the large site (School 4-045 from General Schools Direction; Museum and other departments of the Municipality of San

Photo 12.4 Photograph published in Los Andes Newspaper, January 1920

Photos 12.5 and 12.6 Current photographs of the remains of the Fort and today view of the San Carlos Fort Museum

Carlos). A section of the northwest tower is preserved (Photos 12.5 and 12.6). In some archaeological excavations, buried foundations and remains of walls have been found, in addition to various elements that allow the recovery of historical data.

Studied Materials

In this stage of the investigation, metallic pieces belonging to the Museum of the Fort of San Carlos are studied. This set of historical metal pieces is represented by two cannons: one of English origin and the other of French origin, and the study of the metal tip of the tacuara cane spear used as a defense element.

These metallographic studies, chemical composition, and hardness of these historical metals that belong to the Fort San Carlos Museum, located in Villa San Carlos, Mendoza, Argentina were carried out within the framework of the "Border Archeometallurgy" Project [87].

Photos 12.7 and 12.8 Images of the English cannon belonging to the San Carlos Fort Museum, Mendoza, Argentina

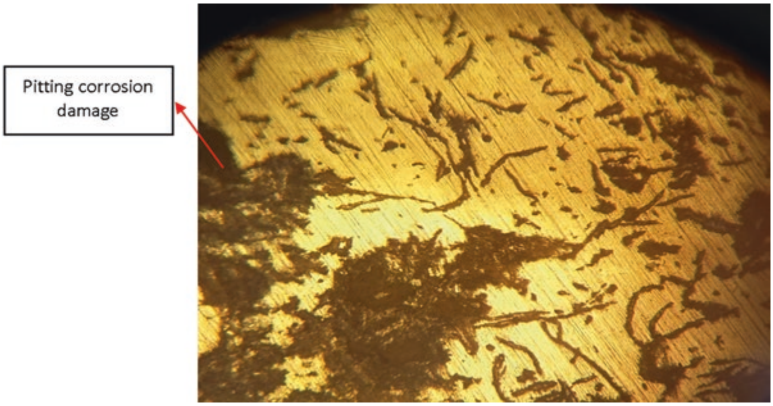
Photo 12.9 Metallography with portable

English Canyon (Photos 12.7 and 12.8)

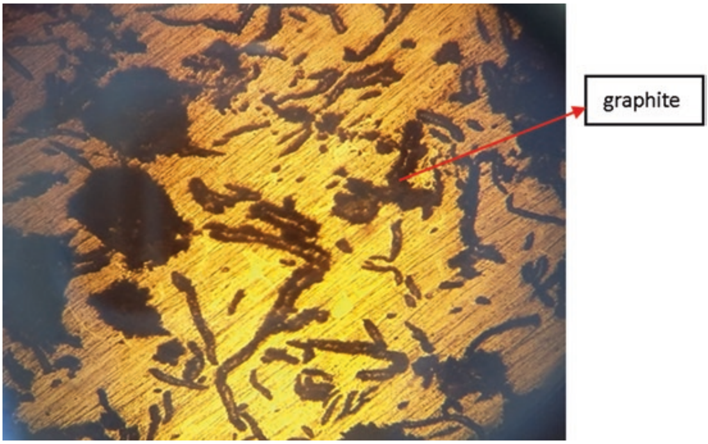
Metallographic Study (Photo 12.9, Photomicrographs 12.1 and 12.2)

Observations: From the studies carried out, it appears that the manufacturing material of the guns is *gray laminar cast iron*, although it is a known fact that the raw material for the manufacture of this type of weapon is cast iron, it is important for this research to find what type of foundry it is. Metallographic studies (Photos 12.1 and 12.2) indicate that it is a gray lamellar cast iron.

The chemical composition (Table 12.22) was measured with a portable X-ray fluorescence spectrometer (portable XRF), which has the limitation of not measuring the carbon (C) content, for this reason it could be said that the carbon content is approximate (that is, 3% C); it would be hypoeutectic cast iron). With the study of



Photomicrograph 12.1 Structure in laminar gray cast iron. Magnification: 100×



Photomicrograph 12.2 Lamellar gray cast iron. Magnification: 200× microscope

Table 12.22 Chemical composition

S %	Mn %	Si %	P %	Ti %	Fe %
0.60	1.11	1.87	0.85	0.071	96.4

metallographic analysis, this data could be inferred, but it is clarified that it is not precise; due to the limitation of available equipment, the data can be asserted with an electron emission equipment, for example, but the impossibility also arises in this context to move the canyon to a local research facility. All measurements were noninvasive and were carried out at the Fortín de San Carlos Museum, and these pieces studied in the present work are part of the permanent exhibition collection.

The basic structure of gray iron can be altered by changing the cooling rate of the cast iron. Cooling too fast is likely to produce free cementite. Key slow cooling

Table 12.23 Hardness measurement

266 HB	270 HB	225 HB	251 HB	283 HB	Average: 259 HB

Table 12.24 English Canyon Caliber

Internal diameter	6 cm
External diameter	10 cm

generally produces free ferrite. The castings are iron-carbon alloys with a carbon concentration greater than 1.7%. In addition to carbon, they contain as constituent elements: silicon (Si), manganese (Mn), sulfur (S), and phosphorus (P), the latter two are considered impurities. The relative amounts of silicon and manganese influence the properties of the cast iron.

In *gray cast iron*, part of the carbon is in free form: as graphite, it solidifies according to the stable diagram, that is, iron-graphite. Its formation is catalyzed by the presence of higher amounts of silicon (±2%) and with slow cooling.

Gray cast iron is widely used in the industry due to its low cost and its mechanical properties such as good machinability, good vibration absorption, good castability, and hardness value between 150 and 250 Brinell (Table 12.23).

Its chemical composition is very well achieved, it contains a corresponding amount of graphitizing agent silicon (Si) and manganese (Mn) that gives it ductility for the best machining of the piece.

These properties mentioned, together with the metallographic study and the hardness value measured in the canyon of English origin (Table 12.24), correspond to values of current castings, what is very important to highlight in this piece that it meets the standardized specifications [88].

French Canyon (Photos 12.10, 12.11, and 12.12)

Photo 12.10 French Canyon

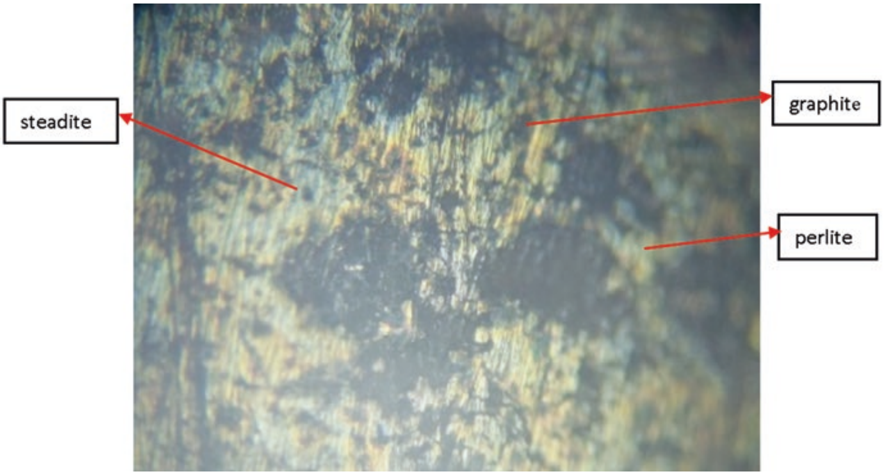
Photo 12.11 Chemical composition test

Photo 12.12 French Canyon with portable XRF

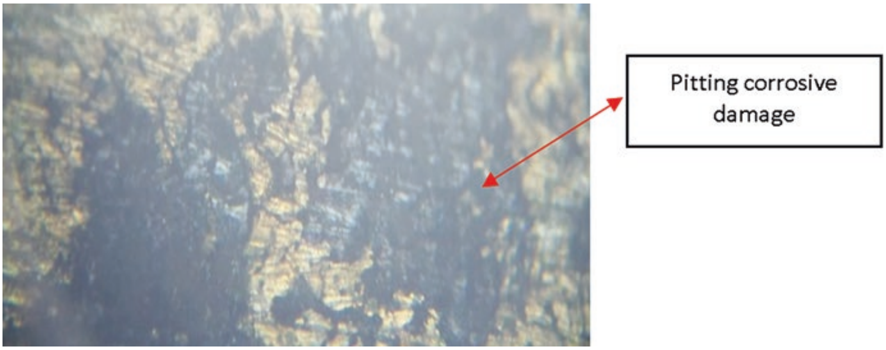
Metallographic Structure Evaluation

Observations: The image shows the gray lamellar cast iron structure with a pearlitic matrix (Photomicrographs 12.3 and 12.4). As in the previous case, the study is based on the metallographic study, the hardness measurements, therefore the chemical composition has the limitation that the equipment that is available: portable X-ray fluorescence spectrometer does not measure the carbon content (%C). With a bibliographic review [88], it could be stated that it corresponds to a hypoeutectoid laminar gray iron with a pearlitic matrix, but the percentage of carbon should be ensured with equipment such as electron emission spectrometer or similar.

Another limitation is the impossibility of transferring the canyon to a research center and in a similar way the impossibility of transferring a sophisticated measurement equipment to the San Carlos Fort Museum; therefore, the carbon content



Photomicrograph 12.3 Gray lamellar cast iron. Magnification: 100×



Photomicrograph 12.4 Corrosive damage. Magnification: 200×

Table 12.25 Chemical composition

Si %	P %	Mn %	S %	Fe %
1.47	1.30	0.91	0.24	96.0

Table 12.26 Hardness measurement

268 HB	277 HB	236 HB	258 HB	Average: 254.8 HB

Table 12.27 French Canyon Caliber

External diameter	13 cm
Internal diameter	6 cm

cannot be ensured; however, an approximate value of the carbon content (%C) can be given in accordance with the studies carried out and mentioned above (Table 12.25).

Due to the slow cooling, characteristic of gray cast iron, starting from the liquid line in the stable diagram (Fe-graphite), it begins to solidify, separating dendrites of austenites of variable compositions as the temperature decreases, as it is cooling very slow, the compositions have to do with the diffusion of carbon. The precipitated austenite homogenizes by diffusion and gradually loses carbon reaching the composition of the eutectoid perlite (sheets of ferrite and cementite). The carbon that austenite has lost during its cooling has gone to form graphite sheets. During this slow cooling, part of the perlite can decompose due to graphitizing agents such as silicon (Si), which decomposes some C_3Fe (cementite) sheets into ferrite and graphite. This graphite will thicken existing sheets of graphite, and a polygonal grain of ferrite appears next to some sheets of graphite.

For this reason, these castings that contain pearlite, some ferrite, and graphite are called hypo-eutectoid gray laminar cast iron (since it looks like hypo-eutectoid steel with graphite aggregate). Another constituent called stedite may also appear in the cast irons, it is a phosphorous eutectic formed by iron phosphide (FeP or Fe_3P_2, depending on the chemical valence) and ferrite.

The dark areas in the form of small globules correspond to steadite, the light areas correspond to the pearlite matrix, the larger dark areas correspond to graphite, and at some ends of the graphite, you can see polygonal forms of ferrite. Large, almost circular, dark areas correspond to corrosion damage. Reagent: Nital 2% (Photomicrographs 12.3 and 12.4).

Its chemical composition is very well achieved because it contains a corresponding amount of graphitizing agent silicon (Si) as well as manganese (Mn) that gives it ductility for the best machining of the piece. Approximate content of 3% carbon. Both foundries, from both the English and the French cannon, also contain S (sulfur) and P (phosphorus), which are considered impurities. The gray cast iron that partially responds to this diagram corresponds to the most used alloy in the industry due to its low cost and its mechanical properties (good machinability, good vibration absorption, good castability, hardness between 150 and 250 Brinell) (Table 12.26).

Gray cast irons solidify according to the evolution of iron-graphite (stable diagram), their formation is catalyzed with higher amounts of silicon (* / - 2%) and with slow cooling [89] (Table 12.27).

Tacuara Cane Spear with Metal Tip

Metallographic Study (Table 12.28)

Observations: The images or photos 12.13, 12.14–12.16, and 12.17 show details of the metal tip and the tacuara cane spear used at that time as a defense element. The spears were 4 m long, with an union socket to reach the length, and it was the most used and most practical weapon to fight against the indigenous people in open terrain, who were extremely fast.

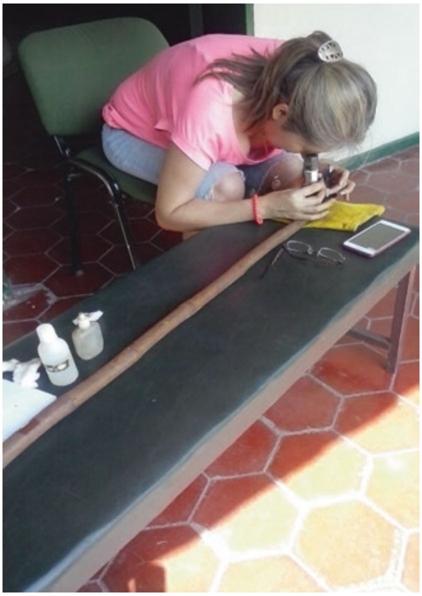
Table 12.28 Chemical composition

Si %	P %	Cr %	Ni %	Pb %	Mn %	S %	Mo %	Cu %	Fe %
0.35	0.10	0.042	<0.054	<0.058	0.40	0.30	<0.014	0.12	98.6

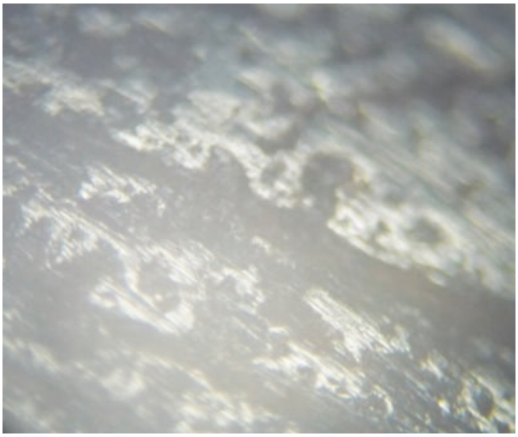
Photo 12.13 Tacuara cane spear with metal tip

Photos 12.14–12.16 Details from metal tip of tacuara cane spear and the metal union socket

Photo 12.17
Metallography of metal tip



Photomicrograph 12.5
Laminated wrought iron structure. Magnification: 100× of tacuara cane spear



In these metallographics, the laminated or forge iron structure is observed (Photomicrograph 12.5), and the orientation of the forging lines denotes in which direction the material was drawn. Ferrite-pearlite structure. Reagent: Nital 2%.

Although it has always been said that the Homeland was made on horseback (an idea to which I adhere), it should be added that this history was built with spears, because “the spear,” until the appearance of the Remingtons, the Gotling machine guns, and the Krupp canyons (this back in 1870 and so on), was the weapon most available to the people, the lowest cost and the easiest to build.

It could almost be assured that it is the oldest tool and weapon of humanity, which remained in force century after century while the weapons of war, in the warlike zeal of man, were being surpassed [90].

Every straight and long stick, or similar rod, at the end of which a metal blade was secured, was considered a "polearm," that is, a "spear." In its origins, the sharp-pointed element at its end was a carved stone and also a well-sharpened piece of hard wood, for this reason, this spear corresponds to the colonial era since the arrival of the Spaniards is also represented in the sheet of wrought iron that was used as the tip of this tacuara cane to be an element of defense.

The "cavalry spear," with an extension of 2.50 m, carries the moharra at one end, that is, the sharp-pointed blade; and in the opposite, the regatón. Yamandú Rodríguez said in "Romance de Pumas": "The regatón of the spears/is turning the dead…" [91].

The "*gaucho"*, at the call of his "*caudillo"* (chieftain), improvised his "spear" with a long tacuara cane mounted with an old knife, or a half-scissors of tusar, or a pointed iron; hence, many times just by saying "*la tacuara*" it was known that they spoke of "the spear."

All the indigenous groups used it in some of its variants. The one from the Pampas region formed a skilled warrior hoisting a very long one, up to 6 m. The indigenous knew how to brandish it over his head, practicing a pinwheel, which made it difficult for the soldiers to attack them with a saber or with the shorter military spear, and sometimes he carried it under his arm at the moment of the tremendous spear.

This "*Pampeana*" weapon (meaning originally from the Argentine pampas), was never intended to be thrown, as is sometimes seen in some representations, in which well-mounted Indians, standing in stirrups, throw a short spear.

Another popular and common way of naming it was "*chuza,*" and this expression perhaps derives from the old Spanish expression "*chuzo,"* which designates a short, throwing spear, which did take place in the Northern Chaco region (Northeast area) from Argentina close to the border with Paraguay.

Acknowledgments

The authors would like to especially thank the Secretary of Culture and Tourism of San Carlos: Mrs. Professor Sandra Martelossi for allowing us to analyze the historical pieces and also for the support received from Mr. Luciano Ruiz of the Culture staff of the Municipality of San Carlos.

Also give recognition for the support received to Eng. Cristián Aguilera and Rocío Algañaraz, intern of the Archeometallurgy Area at UTN FRM for their contribution with some graphics.

Ferreria, a Case Study of Ironmaking

Rafael Colás

Abstract

Iron was one of the metals known in antiquity being associated to the Roman god and planet Mars. Ceremonial and ornamental objects were manufactured from meteorites that were reserved for upper echelon of society. Iron weapons were made from early times to conquer and destroy various cultures and civilizations and evolved into steel over a period of close to 5000 years. The case study of ironmaking known as *Ferrería* took place in the North of Spain from around the eleventh to mid-nineteenth centuries.

Introduction

It is not clear where and when the development of iron took place. It is recognized that ancient civilizations knew of seven metals that were associated with seven gods and seven celestial bodies. One of the metals was iron, which was associated with the planet Mars and Roman God of the same name, who took the Greek name of Ares [92]. Ironmaking has retained the celestial connotation in the languages derived from Latin, such as *sidérurgie* in French or *siderurgia* in Spanish, as it is derived from the Latin term *sidereus*, from *sider-*, *sidus* star, which refers to the meteoritical origin ancient iron objects. It can be considered that the meteorites were a divine gift in ancient cultures. It is generally accepted that civilizations around the world used meteoritic iron to produce small tools and ceremonial objects [93–95]. The quality of the iron dagger found in Tutankhamun's tomb (fourteenth Century BCE) attest for the degree of ironworking in ancient Egypt [95]. Small iron lumps found in the Sinai desert as early as 3000 BCE suggest their accidental production while smelting copper ores [96, 97].

Pliny the Elder expresses his concerns about the use of iron in Chapter XXXIX on iron ores of *The Natural History* [98]: "Next to copper we must give an account of the metal known as iron, at the same time the most useful and the most fatal instrument in the hand of mankind. For by the aid of iron we lay open the ground, we plant trees, we prepare our vineyard-trees, and we force our vines each year to resume their youthful state, by cutting away their decayed branches. It is by the aid of iron that we construct houses, cleave rocks, and perform so many other useful offices of life. But it is with iron also that wars, murders, and robberies are effected, and this, not only hand to hand, but from a distance even, by the aid of missiles and winged weapons, now launched from engines, now hurled by the human arm, and now furnished with feathery wings. This last I regard as the most criminal artifice that has been devised by the human mind; for, as if to bring death upon man with still greater rapidity, we have given wings to iron and taught it to fly. Let us therefore acquit Nature of a charge that here belongs to man himself."

Iron

Iron is a metallic element with symbol Fe (from Latin *ferrum*) and atomic number 26. It belongs to group 8 of the first transition series and group 8 of the periodic table. Iron forms three allotropes at ordinary pressure. It crystallizes from the liquid state into a body centered cubic at 1538 °C, δ, which transform into the denser face centered cubic, γ, at 1394 °C. Reversion to the body centered cubic allotrope, stable at room temperature, takes place at 912 °C, α. Iron exhibits a Curie point, paramagnetic to ferromagnetic transformation at the temperature of Curie, 768 °C [99]. Iron is the fourth most common element in Earth's crust [100]. Most of iron in the crust is combined with other elements to form ores of which hematite (Fe_2O_3), magnetite (Fe_3O_4), and siderite ($FeCO_3$) are the most common; iron is also found in igneous rocks that leach into sulfides and sulfates [101].

Iron has been present in the history of humanity for a long time; its predominance over other materials at a given time promoted the use of the term "Iron Age" over that period of time, although iron was produced during the Bronze Age, and bronze was cast during the Iron Age [96, 102]. Such overlapping confused early researchers as it is pointed out elsewhere [103]. The superiority of iron as a material for weaponry [98] is identified as one of the many causes for the demise of civilizations such as the Achaeans, Aztecs and Incas [104]. The development of iron into steel can be found elsewhere [96, 102, 105, 106].

Ferreria

The European region of the Pyrenees includes the South of France, North of Spain, and Andorra. It is a region rich in minerals and has a long tradition in ironmaking that has been recognized as a Cultural Route of the Council of Europe [107]. These activities have left a huge imprint in both landscape and urban communities. Iron production in the Basque Country had a paramount importance from the Low Middle Age up to the nineteenth century due to the abundant iron-making facilities. The relevance or ironmaking in the Basque Country is reflected by the archaeological sites in the Basque provinces of Gipuzkoa and Bizkaia [108–114].

Iron in the Basque provinces was produced in *ferrerias*, ironworks, that reduced iron mixed with charcoal at high temperature and was then hammered to obtain useful shapes and utensils [115]. The Iron Valley, or *Burdin Harana* in Basque or *Valle* *del Hierro* in Spanish, forms part of the Municipality of Legazpi in Gipuzkoa; ironmaking in this municipality dates from the eleventh century when the first charcoal furnaces were installed, and iron was obtained from the direct reduction of available iron ores. A major energetic revolution occurred by the fourteenth century with the use of hydraulic wheels to drive bellows and hammers. *Ferrería Mirandaola* is an example of a major *Ferrería* that was in operation as early as 1400 and that it was still working in 1832, being one of the last *Ferrerías* to shot down due to the lack of competition with the iron produced by blast furnaces constructed all over Europe as a result of the Industrial Revolution. The iron produced in the Basque country was shipped and commercialized in different parts of Europe and America by the sixteenth century [108–114].

Iron implements were produced at *Mirandaola* by reducing iron ores with charcoal, which were then forged. The complex was more than a simple workshop, as the owner lived there and had various buildings that provided storage and other different facilities. The *Ferrería* had five full-time working people from September to June, as the river will have enough flow to sustain the wheels. Each person will have its specific tasks. The foundrymen, *urtzileak* in Basque, were assigned to control the reduction of the iron ores as they will have to balance the amount of charcoal and keep operating the bellows that provided the flow of air to obtain the temperatures required for the reduction. This stage was carried out in the darkest part of the *Ferrería*, for the operators to follow and control the process.

Forging was conducted by the foreman, *iele*, who commanded the other operators, *gatzamaileak*. Reduction and forging proceeded by driving the water from the Urola River into channels that provided the power to drive two waterwheels, one for the bellows to reduce and heat up the iron, and the second for forging the iron into bars and other shapes. Use of water wheels allowed the production of 180 kg of iron in 1 h, compared to the 5 kg obtained by hand. The *Ferrería* provided work and income to the population of the Iron Valley during those months. The iron workers will then tend the fields during summer, as the water flow of the river was reduced. Life expectancy of the *ferrones*, iron workers, was of 30–40 years, but the paid compensated the hardships of the work as they will be able to sustain a better diet than that of the peasants, even having the opportunity for luxuries such as cheese, wine, and meat.

The *Ferrería* was shot down and neglected toward the second half of the nineteenth century; it was not until May 3, 1952, that the *Ferrería* was reconstructed with the direct support from Mr. Patricio Echeverría, Figs. 12.37, 12.38, 12.39, 12.40, and 12.41. *Lenbur Fundazioa*, Lenbur Foundation, was created in 1997 by the Legazpi municipality with support from private companies to organize and manage the archaeological and historical remains of the Iron Valley and to recover the historical and cultural identities of the region. The Foundation has promoted research and recovery works for the past 20 years. Among the works that the Foundation has accomplished are the maintenance of the *Ferrería*, and the construction of a neighboring Museum, Basque Iron Museum.

Fig. 12.37 State of *Mirandaola* in 1952

Fig. 12.38 Buildings erected in 1952; forging equipment is shown before installing it

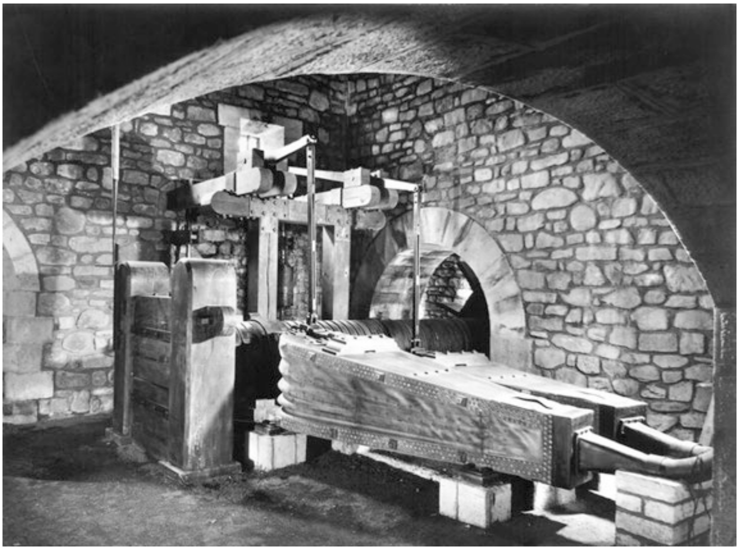


Fig. 12.39 Bellows being recently installed

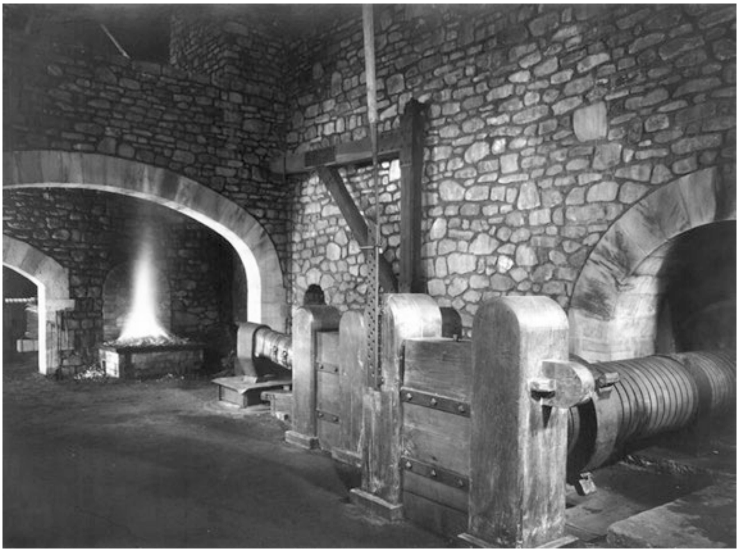


Fig. 12.40 Hearth located at the darker site of the *Ferrería* and the forging hammer

Fig. 12.41 Present-day state of *Ferrería Mirandaola*

Concluding Remarks

The Pyrenees region is situated at the North of Spain and South of France is rich of mineral deposits and forested. The *Ferrería* process was developed due to the wealth of iron ore deposits and wood to make charcoal to be used to provide energy and reducing the iron to make tools and other type of utensils. Bellows and tooling used to reduce and forge iron was provided by waterwheels. This limited the manufacture of iron during the summer months due to water limitations.

Restoration works and Preservation Study of the Iron Bridge over Mendoza River

Patricia Silvana Carrizo

Abstract

The present work arises from the intention on the part of the Town Hall of Luján de Cuyo, Mendoza, Argentina, to restore the Iron Bridge (1898) previously declared of patrimonial interest, which is in full use being an important means of communication. It consists of seven sections of 40.6 m each and the distance of the main beams is 5.80 m. Metallographic studies confirm that the structure of the bridge is made of forged iron; the chemical composition, thickness measurement, and hardness were determined. The corresponding tensile and Charpy tests were carried out for the exhaustive characterization of the material with which the bridge was manufactured. This survey allowed to observe the state of conservation and evaluation of the corrosive state. This work deals with the tasks carried out for its restoration and preservation, from the corrosive state to the welding or replacement with similar material and the protocol of surface preparation and painting of the same.

Keywords

Restoration; Iron; Heritage; Composition; Traction

Introduction

On the occasion of the construction of the Iron Bridge, a camp was established on the north bank of the Mendoza River, before the creation of the National Road Administration. The "Bridge of the River" was authorized by decree of law Number 1889, of October 18, 1886, signed by President Roca with a budget of $171,021.46, along with two other bridges in the provinces of San Juan and Neuquén, which are the first three iron bridges built in the interior of this country and this is the first of this type in Mendoza with an extension of 284.20 m long and 5 m wide, built seven sections of 40.6 m, a work that was monumental and fundamental for the development. It was a National Route that with the modern bridge facilitated the communication with the south of Mendoza, one more testimony of the historical volume that the center of Luján keeps [116] (Fig. 12.42).

From the original and primitive project submitted for approval by the Government in 1885, the beams had to be of mixed construction; "Of hard wood," for the pieces

Fig. 12.42 Panoramic view of the Iron Bridge over the Mendoza River in its north-south direction

that worked to compression and of iron laminated those that underwent effort of traction. The public tender was held on March 18, 1887, and a contract was signed with Andrés Braly y Cía for the sum of $178,391.00. The works were finished in September 1890. Its cost was very high just compare with other works of the time to understand the effort of the acquisition of this material that was imported from England to which the cost of transport from the port of Buenos Aires to Mendoza had to be added by means of the railroad, being one of the first works of these characteristics there were faults in the construction, in 1890 considerable repairs were made. It is common to find in all the departments crossed by mighty rivers hiring boats and "river passers" in times of flood, in 1889 was still hired in Luján, which proves the serious flaws that the construction had. Reviewing the international publications of studies carried out on this subject, it is found that C. Gentili and A. Saisi [117] did studies monitoring the vibrations for the period of 1 year in a 100-year-old iron bridge San Michele and was built in 1889 being the most important monument of the nineteenth century of iron architecture in Italy and still continues to operate for vehicular traffic as well as maintaining its status as a railway bridge, and as a conclusion determined that the frequencies Natural models of all models tend to decrease with increased traffic and cross-sectional models are generally more sensitive to traffic acceleration compared to vertical models. They even determined that the temperature affects almost all-natural frequencies but this effect is non-linear for several of the frequencies, although a decrease in frequency with the increase in temperature was not characterized. Regarding the Area of Historical Metallurgy, no background has been found that specifically discusses this topic related to iron bridge. It is noteworthy that the bridge was built based on a new project, making the sections entirely metallic. In the files of the Department of Civil Engineers of the Argentine Republic, in documents of the time it is reported that no decrees or resolutions are found that authorize the change of project. Between 1889 and 1890 during the final part of the execution of the work, Mr. Nicolás Rosetti, in charge of the Mendoza Section in several notes, to the inspection of bridges and roads, said that he accompanied sketches showing how many diagonals they had to work. The traction was loose, but it was not given importance and the bridge was received without requiring the contractors to correct the poor assembly. In addition to the bad assembly, the sections as they were built were weak to safely support the overload of 400 kg/m^2 and that the defects are the same as they were noted 7 years ago (inauguration), aggravated as is natural by the use to such a degree that the passage of a negligible moving load, such as being a rider for example, shook alarmingly. Therefore, in this report of February 3, 1898, consolidation work was proposed. Among them the main ones were: placement of transversal beams: where they have been omitted, decrease of the permanent load: by means of lightening of the layer of gravel of the board, reinforcement of uprights: like being diagonal and horizontal bars, and their resistant moments: the bars diagonals that were loose and bent, should be cut and rejoined, 76 tons of laminated iron were used, in sheets, reinforced beams, and the necessary rivets.

On March 17, 1898 Dr. Emilio Civit (the Mendoza's Governor) and Enrique Day (Minister of Development) required an urgent solution given the importance that the service of the Bridge provides to the region, for being linked to the southern departments of Mendoza and the provinces of Neuquén. "*So If there is a delay, there is a danger of a catastrophe*…" Then on April 30, 1898, the President of the Nation Julio A. Roca (2nd presidency of Roca), with the agreement of ministers, authorized the reparation. On October 19, 1898 is contracted with Pedro Vassena, the production of 76 tons of rolled iron. Put into service the bridge worked relatively well with only repair work and/or maintenance, on the wooden board and its components, highlighting works made in 1957, and especially in 1972, where by guardrails was limited to a single path the circulation.

With these antecedents previously reported here and due to the worsening of the traffic conditions because of the increasingly pronounced pavement defects over time, a new intervention was carried out for the study and reformulation of the bridge deck. Intervention works on the bridge began in October 1990. The following were considered as fundamental solutions: to support a maximum vehicle load of 4000 kg that would originate 1000 kg/wheel and increased by a coefficient of 50%, possibility of the simultaneous transit of two gauges for vehicles of the indicated characteristics, which would reduce the weight of the vehicle board itself (whose value was 450 kg/m^2), use of pre-molded pieces and beams supplement for the construction of the new board, then there was a significant reduction in the weight of the board to 380 kg/m^2, dismantling of the road and guardrails in wood, revision of the entire metallic structure, repair of the support mechanism, cleaning and painting of the bridge, repair and reconditioning of the pedestrian walkway, placement of metal fences, lighting, signaling, construction, and laying of limiters of maximum height allowed for vehicles [118].

Experimental

The metallographic and historical-patrimonial study of the Iron Bridge belongs to the Archeometallurgy Area, which works within the Metallurgy Laboratory of the Electromechanical Department, belonging to the National Technological University of the Mendoza Regional Faculty and was carried out in 2014, at the request of the

Department of Culture of the Municipality of Luján de Cuyo, with the objective of realizing the value and declaration of heritage interest. The corresponding metallographies were carried out which allowed observing the structure of the bridge, knowing its manufacturing process, measurements of chemical composition, hardness (Table 12.29), tensile and impact test (Table 12.30), and so on–with all this information collected–to be able to perform a fairly complete characterization of the bridge material (Fig. 12.43).

The constituent material of the bridge is iron in its entirety laminated or hot forged. Wrought iron is a material whose microstructure consists of silicate slag,

Table 12.29 Chemical composition and hardness

Chemical composition	
Si	0.73%
Ni	0.019%
P	0.35%
Ni	0.017%
S	0.37%
Fe	97.6%
Mn	0.031%
Hardness:	115.33 HB

Table 12.30 Results of mechanical samples from the old iron bridge over Mendoza river, carreid out at IMPSA Company

Flat tensile test	Impact test
Breaking load: 66770 N	Sample 1: 13J
Breaking strain: 352 N/mm^2	Sample 2: 12J
Yield load: 50409 N	Sample 3: 10J
Yield stress: 266 N/mm^2	Average: 11,7J
Elongation: 11.5%	

Fig. 12.43 View of the bridge structure consisting of seven sections of 40.6 m

sulfates, and even phosphates embedded in a matrix that can vary from being totally ferritic to the inclusion of large amounts of perlite, often distributed in a very heterogeneous way. Slag inclusions are usually lengthened in the working direction by the hot forging processes that are used to process the molten material and shape the wrought iron objects [68]. Wrought iron, also called laminate, has been produced in many countries of the world during a period of time that goes from the Iron Age (second millennium BC) until well into the twentieth century. It was initially produced by two clearly different technologies: direct fusion in Bloomery furnace and alternative indirect fusion [119]. Wrought iron is an iron alloy with very low carbon content in contrast to molten iron and has fibrous inclusions, known as slag. It is resistant, malleable, ductile, and easy to weld. Historically known as “commercially pure iron,” however, it no longer qualifies because current commercially pure standards require a carbon content of less than 0.008% by weight. Wrought iron has been used for many centuries and is the “iron” that is known in Western history. The other form of iron, cast iron, was not introduced into Western Europe until the fifteenth century, even then, due to its fragility, it could only be used for certain purposes. Throughout much of the Middle Ages was the iron produced by the direct reduction of minerals in Bloomery oven operated manually, the hydraulic energy to give movement to the mechanisms began to be used in 1104. The raw material obtained by the method of indirect fusion is the pig iron and it has high carbon content and, therefore, is fragile; therefore the raw material obtained by direct fusion is of better quality. The Bloomery process continued in many places, but depended on the development of the blast furnace, of which medieval examples have been discovered in Lapphyttan, Sweden, and in Germany.

The process consisted of charging coal and iron ore and then igniting, blowing air through a nozzle to heat to a temperature below the melting point of the iron. During the fusion, the slag melt and the carbon monoxide in charcoal serve the purpose of reducing the iron ore, which was transformed into a spongy mass without passing through the liquid state. In addition, as a result of the process, the material used to include a large amount of slag, which could be further eliminated or expelled to a greater or lesser extent by hammering. During the Middle Ages, the force of water was applied to the process, mainly for feeding the bellows and then for the movement of hammers for forging. And this was the culmination of the direct process for the manufacture of iron, which survived in Spain and southern France as Forges Catalan in the mid-nineteenth century, in Austria as Stuckofen in 1775, and near Garstang in England until around 1770. The process Bloomery produced the so-called coal iron and continued until the end of the eighteenth century. Also, with the successive inventions and improvements to the process, wrought iron was produced from pig iron with gallic or Gallic forges or since the industrial revolution in a home in Lancashire, the resulting metal was highly variable, both from the chemical and the slag content. Already at the end of the eighteenth century there was a demand for pig iron (an impure form of iron) to be refined with coal as fuel. This allowed the passage to puddling iron, which contained less slag, less sulfur, and very low carbon content. Here the iron was kept separate from the fire in a reverberatory furnace to prevent harmful sulfur and phosphorus from entering the finished iron, this puddled iron was also very variable in its properties, it was more

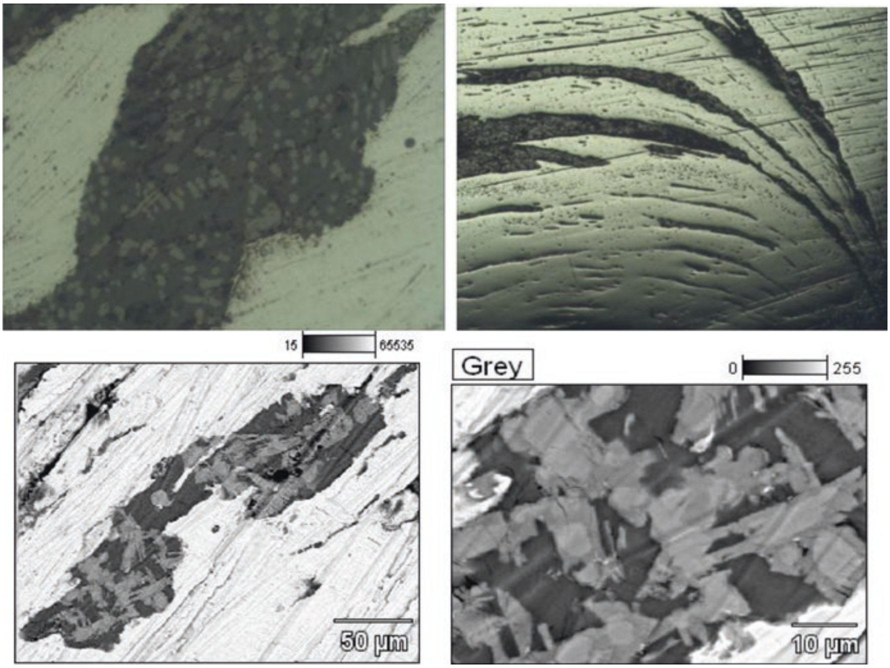


Fig. 12.44 Microstructure of historical forged iron, equiaxed ferrite grains with a certain number of inclusions of the silicates, sulfides, phosphates, and iron oxides present in dendritic form. Detail of the forging lines. Reagent Attack: Nital 2%. Increase 50×

consistent than the irons produced previously, and the method it lends itself to the production of much larger quantities. In 1876, the annual production of puddled iron in the United Kingdom alone was four million tons [120] (Fig. 12.44).

Examples of typical damage induced by external corrosion can be observed in the macroscopic examination; they have been observed in a large number of structural elements both on the downstream sides and on the upstream sides (Figs. 12.45 and 12.46). It must be taken into account that the large separation of the rivets is not adequate according to the thickness of the iron plates that make up the columns of the bridge (thickness: 10.05 mm). This aspect would allow the penetration of moisture easily between the contact planes and in such a way that the expansion of the oxide due to the subsequent increase in volume that it causes; it is what induces the deformation of the iron plates and profiles in the connections [117]. The studies of chemical composition, hardness, tensile tests (Universal testing machine, Wolpert-Amsler brand, range of 0–100 ton), and impact (Impact machine, Wolpert-Amsler brand, range of 0–300 J) were carried out.

All these tests and characterization studies were carried out prior to the works concerning preservation, which is precisely what this paper is about. With regard to the issue of preservation specifically, firstly, the damage was repaired in the metal parts damaged either by vehicle collisions or due to corrosion problems or previous welding errors or all of the above together. Next, the surface preparation of the

Fig. 12.45 Macroscopic observation of the structure of the bridge, column detail from third section and external corrosive damage

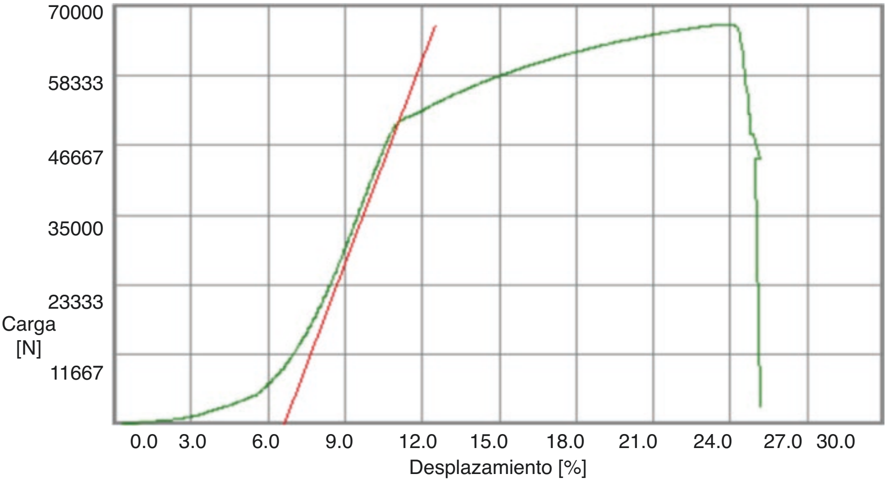


Fig. 12.46 Stress curve-unitary deformation of an iron specimen

metal plates of the bridge is carried out, by sanding and with this all the remains or layers of old paint are removed, until the bare iron is observed. This procedure is a priority and extremely important stage during the preservation works, because all the remains of previous paintings must be removed so the new painting scheme for the bridge is successfully completed (Fig. 12.47).

Fig. 12.47 Details of repair work, surface preparation, welding, and painting of the old iron bridge over the Mendoza River

Results and Discussion

In the metallographic examinations, elongated inclusions of the type of silicates and iron oxide were observed, which morphologically were ascribed to fayalite (Fe_2SiO_4) and wüstite (FeO). Iron oxide is not liquid at temperatures around 1200 °C and is considered the maximum temperature obtainable in primitive furnaces: therefore silica (SiO_2) must be added which binds to OFe to generate fayalite, which is liquid at the indicated temperatures. This reaction can also occur spontaneously when in contact with the natural fused silica that forms the base material of the refractory type of the primitive furnaces. The availability of an iron silicate as a waste product of copper metallurgy, which is one of the first metals discovered by mankind, was seen by some as the reason for the birth of the iron industry and later steel. The micrographs also show small globular oxides that would be associated with heating at high temperature (estimated above 1100 °C) during the forging process. In addition to pointing out that due to the manufacturing process: puddling, it left a lot of sulfur in the pasty iron, sample of it is in the micrographs made, that there is an important presence of sulfates, sulfides by way of inclusions and little diffusion [121]. But there is also the presence of phosphates that retard corrosive processes. The inclusions of slag, or stringers, in the forged iron give properties that are not found in other types of ferrous metals. There are approximately 250,000 inclusions per square inch. A fresh fracture has a clear bluish color with a high silky luster and fibrous appearance. Manganese (Mn) is present in the analysis of the chemical composition, which is a chemical element that gives the bridge material the important characteristic of ductility. For most purposes, ductility is a very important measure of the quality of the forged iron with respect to tensile strength. In tensile strength tests, the best irons are capable of undergoing considerable elongation before failure; in our case, the elongation value was 11.5%. At the end of the nineteenth century, when the metallurgists of the time were able to better understand properties such as traction and ductility, processes were then improved and good iron was started, only a little late, as iron was being used displaced by steel.

With the values of the tensile test (Table 12.30), the calculation of the modulus of elasticity of the material (Ec. 1) was made, which is the relationship between the stress to which it is subjected and its unit deformation represents the rigidity of the material before a load imposed on it. In addition, wrought iron is ductile and tends to yield slowly, giving warning signals. From the results of traction and Charpy tests carried out, it is clear that it is ductile material, which admits elastic deformation efforts; therefore this low value of the modulus of elasticity indicates that it is easy to bend under loads. There is no stricture, so it is possible that due to the passage of time, the structure of the bridge has developed some fragile behavior. The low value of the Charpy impact test (11.7 J) assures us that it is ductile material.

$$E = \frac{\sigma_f}{\varepsilon} = 2313 \text{ MPa}$$

$\sigma_{f:}$ tensión de fluencia, ε: elongación porcentual

Conclusions

The constituent material of the historic bridge, as anticipated by the Municipal Archives documents, is forged or hot rolled iron. This material lacks the necessary carbon content for its hardening by heat treatment, but it was worked or hot forged to harden it and before the plates cool down, the rivets were placed with blows, therefore the set of plates and rivets. They form a united structure; this way of joining pieces in structures and infrastructures was characteristic of the time, that is, it was the traditional thing for this moment in history and corresponds to the technology developed at that time and therefore its corrosive process of the material of the bridge is external and humidity does not represent a problem due to the dry climate of Mendoza. Its metallographic structure is composed of a ferritic matrix with dendritic inclusions. Sulfur impurities in the forged iron decrease the corrosion resistance, but the presence of phosphorus increases the resistance to corrosion. According to the chemical composition of the forged iron and according to the Bloomery manufacturing process, initially, but with the advance of technology and knowledge, iron was produced in large quantities and continuously by the pudding process. The presence of manganese in its composition gives this material important ductility characteristics, which was also verified by the low value of the Charpy test. The calculation of the modulus of elasticity reports that the wrought iron that constitutes the bridge behaves as an elastic material, which complies with Hooke's Law; therefore, the constituent material of the bridge can be subjected to stresses of the linear elastic type. The iron bridge continues to provide service, has been 120 years since its inauguration, lacks its own name, and with proper maintenance can continue in controlled use. It is a real treasure, being the third bridge that was installed in Argentina and the first in its style in Mendoza and deservedly it has been declared of patrimonial interest.

Historical Horseshoes: Connection with the Origins of the “Villa del Río”

Patricia Silvana Carrizo

Abstract

In the current province of Mendoza, two regions or geographical areas are established: the northern one where the Huarpes lived, who were later linked to the Inca empire and later to the Spanish conquerors, and the southern one where the Puelches and Pehuenches lived. In the sixteenth century, the Spanish conquerors, who arrived from Chile and Peru, made the first explorations in lands where docile and industrious indigenous families lived: the Huarpes. Cacique Oliunta was the owner of the territory that includes the current Luján de Cuyo and had his tolderías on both the banks of the Mendoza River. After the Foundation of Mendoza (1561), lands were delivered by decree to the Spanish captains, and the distribution was made in the first stage to the Mendoza River to the south. With the creation of the royal road approximately in 1747, the fixed post system was established, preceding the “post regulation” that arose with the creation of the Viceroyalty of the Río de la Plata (1776), as well as the improvement of the roads and greater comforts for travelers. Thus, at the “Postas,” the horses had to be changed and the travelers accompanied to the next post. In Luján de Cuyo, there has been a Posta on the north bank of the Mendoza River that, due to its irregular flow, travelers had to stay to rest and tend to the horses and mules. In this way, different populations settled, and later the hamlets that were installed around the posts to become the Villa de Río and with the passing of time in the current “Luján de Cuyo.” Two horseshoes from the colonial era are studied in this work, belonging to a set of horseshoes found in the historic area where the first posts and hamlets took place. Chemical composition measurements, hardness studies, and metallographic studies were carried out to know the manufacturing process and SEM-EDS studies to deepen and corroborate the previous studies.

Introduction

The Spanish Conquerors on Lujan Soil

A year after the founding of Mendoza (1561), by decree of the Captain of Cuyo Don Juan Jufré, distant lands were distributed up to six leagues around the city of Mendoza that included up to the Mendoza River in the South. Lands were handed over to the Spanish captains and the distribution was made, in a first stage, up to the Mendoza River to the south, then effectively the Spanish conquerors arrived in the Lujan lands in the year 1562 and the lands, until then, of property of the natives were distributed by decree. This distribution of land resulted in the birth of ranches that, over time, gave rise to the districts and departments of the province. In the distribution of lands, Captain Don Diego de Velasco was responsible for the neighboring territories to the coast of said river, where in 1562 he established an "Encomienda" there.

They gave Captain Juan de Coria y Bohorquez lands that the natives called "*Lanyení*" that later, when a farm was established, became "Chacras de Coria." With the passing of time, they handed over to Captain Juan Hilario de Bohorquez the lands of Cacique Tar-Tar, which later constituted what is now "El Carrizal." The objective was for the captains (*encomenderos*) to initiate agricultural and livestock activities.

Later they went more toward the provincial south and the limit of the incursion of the Spanish conquerors was the Diamante river, to the south of the said river, the territoriality of the conquerors was not manifested, being dominated by the original peoples: *Puelches* and *Pehuenches*.

Royal Road

Between the years 1747 and 1748, the Spanish crown established the system of "fixed post," which had the function of transporting correspondence between Buenos Aires, Santiago de Chile, Lima (Peru), and Potosí (Bolivia). In 1762, the ordinance that post and road officials had to observe was established. When the Viceroyalty of the Río de La Plata was created (1776), the roads were improved, and greater comforts were guaranteed to travelers. As time went by, the "Post Regulations" would become the antecedent of transport, mail, and customs. The regulations established that they had to change the horses between the different posts or stops, have spare oxen and mules, had to be attended by a "Master of Post" appointed by the government and the "*Postillón*" who accompanied the travelers, until the next post, to return with the animals.

Royal Road in Mendoza

It linked the three foothills of Mendoza with the eastern and southern plains. To do this, he had to cross the *Huentata* Valley (Capital of Mendoza), heading southwest toward the Mendoza River, arriving at Luján, crossing La Pampa Blanca, El Pedregal, and Los Cerrillos, by the Alfalfar, going down to the Uco Valley by the Portezuelo de Guevara. Along the banks of the Tunuyán river, they went to the other towns of the Uco Valley and from there to the southern province. The road adapted its route to the course of the Mendoza and Tunuyán rivers to, in this way, supply water to animals and travelers; thus, the first "*Postas*" were defined [122].

Origins of "La Villa del Río"

These royal roads gave rise to the different populations that settled on the banks of the water courses and later the hamlets that were installed in the surroundings of "Las Postas."

The traces of the roads were directed toward the points of the course of the rivers where the flow was less or not so fast. In the case of the Mendoza River, its irregular flow made it impossible to cross with carts and animals in considerable periods of time. Due to this need of the travelers, "Las Ramadas" arose in order to mitigate the long waits until the water went down. In this way were born the blacksmiths, grocery stores, accommodation and other services that were offered to travelers. On the north bank of the Mendoza River, "*La Villa del Río*" (today Luján de Cuyo) was formed along one of the most important roads of the conquest. The "Villa del Río" was an obligatory stop before crossing the Mendoza River. Those who came from the North (today the capital city of Mendoza) stopped before crossing the Mendoza River and those who came from the south (San Carlos) stopped after crossing it. In those years, the "Villa del Río" ("The River Village") ended at the river, since from there San Carlos began (i.e., Uco Valley area), and it took many years for the department of Luján de Cuyo to be formed as it is today.

Experimental

The metallographic and historical study of these horseshoes was carried out in the Archaeometallurgy Area, which operates within the Metallurgy Laboratory of the Electromechanical Department, belonging to the National Technological University of the Regional Faculty of Mendoza and was carried out at the request of the Directorate of Culture and Tourism of the Municipality of Luján de Cuyo, Mendoza, Argentina with the aim of making related studies of the raw material, its manufacturing techniques, chemical composition to make a relationship with history by crossing the information obtained, so that with the information collected it is planned to carry out a work to enhance the initial site where the first settlers of what was then called "Villa del Río," today Luján de Cuyo, settled (Fig. 12.48).

The corresponding metallographs were made that allowed observing the structure of the horseshoes, knowing the manufacturing process, measurements of chemical composition, and hardness, and for a more complete study, SEM and EDS studies were carried out, with all this information collected to perform the characterization and the manufacturing processes of the material (Fig. 12.49).

- Mule hand previuos to the word horseshoe (Inventory No. 0137) (Fig. 12.50, Tables 12.31 and 12.32)

  Observations: The structure of the historic horseshoe would correspond to a current SAE 1008 type edged steel. Forging or hot rolling process, alternating hot and cold finishing, with the presence of silicate-type inclusions (Fig. 12.51).

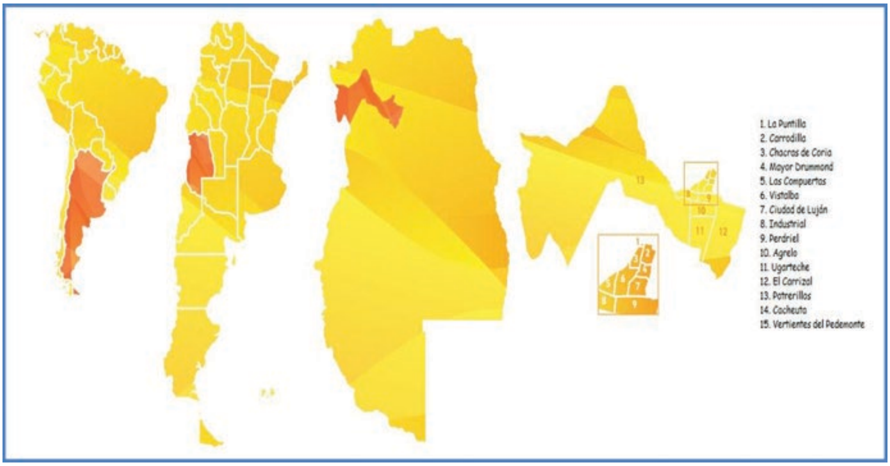


Fig. 12.48 Argentina in South America, Mendoza in Argentina, Lujan de Cuyo in Mendoza, and finally 15 districts that configurate Luján de Cuyo region, N°7 in the map is Luján de Cuyo capital city where the horseshoes were found

Fig. 12.49 Images of the two mule horseshoes analyzed

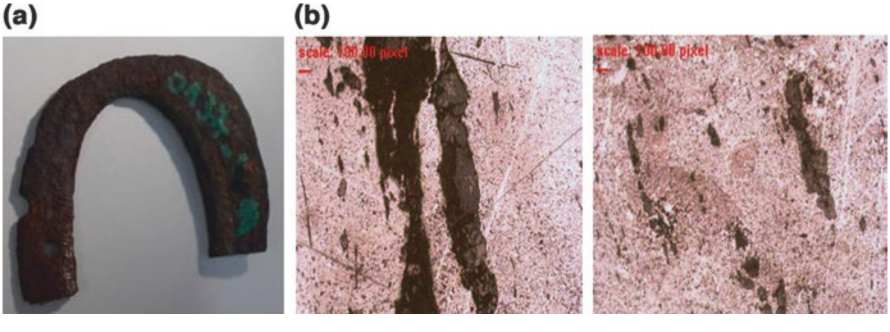


Fig. 12.50 (**a**) Macrograph of hand horseshoe for mule. (**b**) Metallography of the hand horseshoe piece. Magnification: 100×X. Reagent: Nital 2%

Table 12.31 Chemical composition

%Si	%P	%Cr	%Ni	%Pb	%Mn	%S	%Mo	%Cu	%Fe
0.20	>0.43	<0.020	<0.25	<0.053	0.22	0.031	<0.013	<0.031	99.1

Table 12.32 Brinell hardness measurements (HBr)

Sample 0137/HBr hardness measurement
66.5
64.5
Average: 65.5 HBr

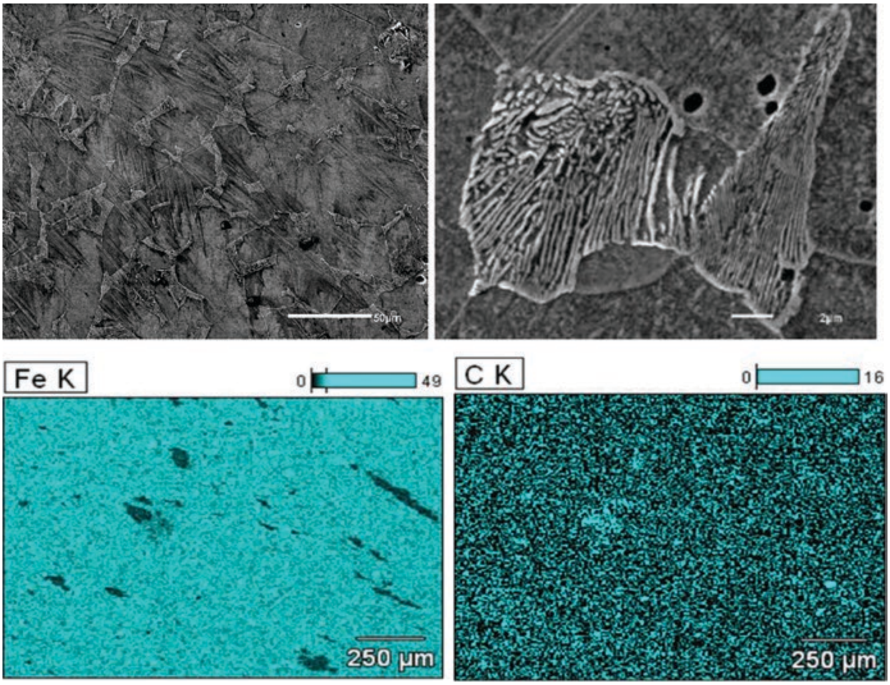


Fig. 12.51 SEM-EDX images for a mule hand horseshoe

Take into account the increase in grain elongation as the reduction increases. The structure corresponds to ferrite and pearlite [119] (Table 12.33).

- **Mule foot horseshoe (Inventory No. 0136)** (Fig. 12.52, Table 12.34 and 12.35)

  Observations: The structure of the historic horseshoe would correspond to a current SAE 1008 type edged steel. Forging or hot rolling process, alternating hot and cold finishing (Fig. 12.53). Easy machining steel, few dendritic colonies on a ferritic matrix with lead and silicate inclusions (Table 12.36).

Table 12.33 Chemical composition from SEM-EDX study

Element	Line	Element weight (%)	Weight (%) error
C	K	1.61	±0.06
Al	K	0.10	±0.03
Si	K	0.36	±0.02
Si	L	–	–
P	L	–	–
P	K	0.43	±0.02
Ca	K	0.09	±0.02
Ca	L	–	–
Mn	L	–	–
Mn	K	0.19	±0.05
Fe	K	97.22	±0.38
Fe	L	–	–
Total		100.00	

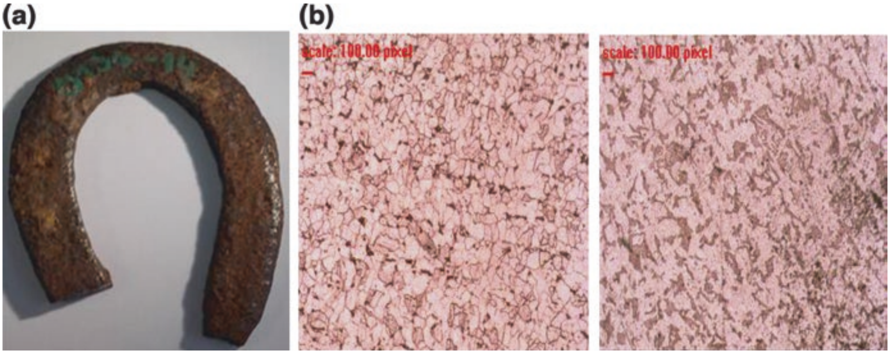


Fig. 12.52 (**a**) Macrograph of foot horseshoe for mule. (**b**) Metallographies of the foot horseshoe for mule piece. Magnification: 100×. Reagent: Nital 2%

Forging the Horseshoes

Traditionally, farriers forged their own horseshoes and it was even common for them to combine the shoeing of cows, mules and horses with the manufacture and repair of farm tools. Hence, the figure of the blacksmith has enjoyed great prestige throughout history. His office, which dominated the elements of nature, fire, water, and air, endowed him with an almost magical aura. On the other hand, his figure became essential in the agricultural and livestock communities, since they depended on his art and work to be able to sow the fields and manage the livestock and, in the case of the “Postas” located along the royal road, he relates the story that they had to have horses and mules in conditions to take over from the travelers.

Table 12.34 Chemical composition

%Si	%P	%Cr	%Ni	%Pb	%Mn	%S	%Mo	%Cu	%Fe
<0.12	<0.040	<0.019	<0.015	<0.054	0.36	0.058	<0.012	0.082	99.4

Table 12.35 Brinell hardness measurement (HBr)

Sample 0136/HBr hardness measurement
58
62
Average: 60 HBr

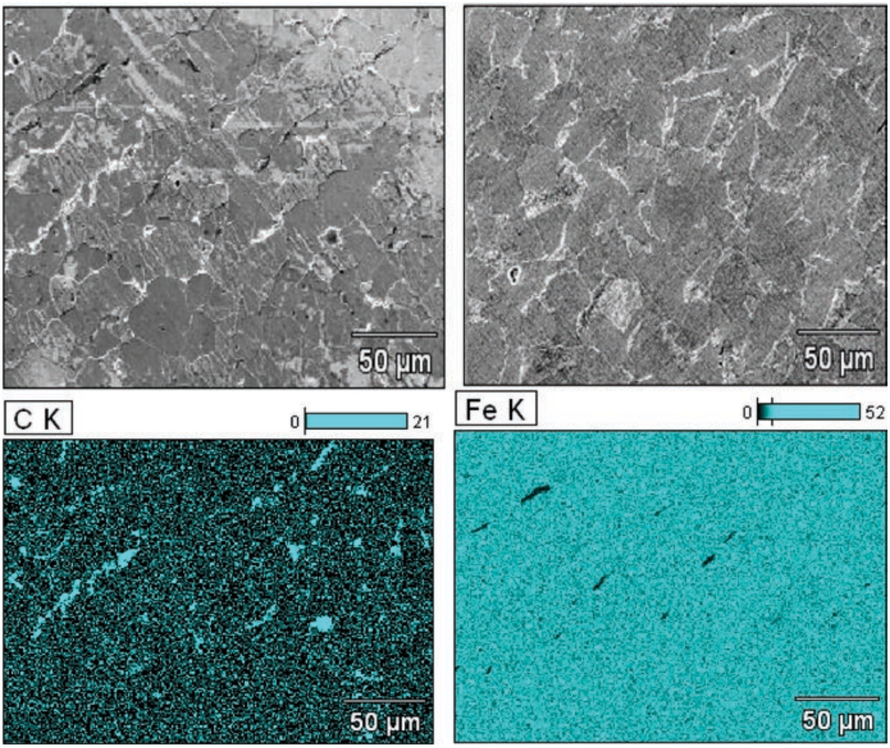


Fig. 12.53 SEM-EDX images for mule foot horseshoe

Although mules are used less today, there are still many mules that have horseshoes fitted (Fig. 12.54). Traditionally, horseshoes intended for mules were crude and the shoeing of animals was done in an unscientific and careless manner. At present, the recovery of these animals for hooking has returned mule shoeing to the place it deserves, comparable to the shoeing of sport horses.

Table 12.36 Chemical composition from SEM-EDX study

Element	Line	Element weight (%)	Weight (%) error
C	K	2.26	±0.06
Si	L	–	–
Si	K	0.11	±0.03
P	K	0.15	±0.04
P	L	–	–
Mn	K	0.57	±0.05
Mn	L	–	–
Fe	K	96.7	±0.37
Fe	L	–	–
Mo	L	0.22	±0.06
Mo	M	–	–
Total		100.00	

Fig. 12.54 Making the horseshoes

The mule's hoof, inherited from its donkey part, has characteristics that differentiate it from the horse's hoof. Therefore, the shape of the horseshoe is also different, to adapt to the shape of the animal. In general, the mule hoof is characterized by having more or less straight branches, with strong bars, and they are wider than the horseshoes intended for horses, hence the distinction of these historical horseshoes. It has the same shape as the foot, although it is wider in the openings. Mules' hands are generally braced with a wide, low flange, while the feet are braced without a flange. Mule shoes are usually small in size.

Comparing hand shoes with foot shoes, we can see that the hand shoe is generally wider than the foot shoe. The inner branch is always a little straighter than the outer, more rounded. In addition, the outer heel can be left more pronounced than the inner one.

In general, mules and donkeys are tightly fitted with horseshoes, due to the roughness of the work and the terrain where they move; it was customary to rest mules destined to pull carts or those used to tow barges in canals (tow mules), but their horseshoes were finished with a good bevel on the inner edge [123].

Acknowledgments

The author wants to give special thanks to Mr. Pablo Tahan, owner of "Los Carrizales" Cabin Criollos Horses, and to the Blacksmith Mr. Ezequiel Osorio for their contributions and advice.

References

1. Aldaz, A. et al.: A simple tool for the electrolytic restoration of archaeological metallic objects with localized corrosion. (Studies in Conservation, in press)
2. Birchenall, C.: Principies of gaseous reduction of corrosión producís. NBS special publication, Nº 479, pp 39–57 (1977)
3. Angelucci, S.: Pitting corrosion in Cu and alloys: comparative treatment tests. Stud. Conserv. **23**, 147–156
4. Muñiz García, B.: Fabricación de la moneda a través de los tiempos ["Manufacture of the currency through the times"], versión October 2005-2008
5. Evans, U.: The corrosion and oxidation of metáis. E. Arnold (pub), London. (1968) (First supplementary volume. London, (1975): Second supplementary volume)
6. Carrizo, P.: "Border Archeometallurgy" Project (MATUNME; Code: 0004308). Archaeometallurgy Area, Metallurgy Laboratory, (UTN FRM), Mendoza (2016–2017)
7. Campbell, R.: Entre el Vergel y la Platería Mapuche: El trabajo de los metales en la araucanía post contacto (1550-1850 D.C.) [Between the Vergel and the Mapuche Silverware: Metalworking in post-contact Araucanía (1550-1850 A.D.)] (2004)
8. Hansen, M.: 'Constitution of binary alloys'. Metallurgy and Metallurgical Series. MacGraw-Hill Book. Segunda Edición (1958)
9. ASM: ASM Handbook, vol. 9: Metallography and Microstructures. Edition 1985 (Last revision: Edition 2004)
10. Antinao, J.: Sociedad y Cosmovisión en la Platería Mapuche [Society and Cosmovision in Mapuche Silverware]. Universidad Católica de Temuco, Temuco (2010)
11. ASM: ASM Handbook, vol. 2: Properties and selection: Nonferrous alloys and special-purpose materials'. Edition 1990 (Last revision: Edition 1990)
12. Morris, R.: "Plata de la Araucanía: Colección Raul Morris von Bennerwitz", [Silver from Araucanía: Raúl Morris von Bennerwitz Collection]. SAF, Santiago de Chile (1987)
13. Morris, R.: Los Plateros de la Frontera y la Platería Araucana: en el Contexto Caratulado: Salteo al Cacique Huemul (1856-1860), [The Border Silver artisans and the Araucana Silverware: in the Context entitled "Salteo al Cacique Huemul" (1856-1860)]. Editorial Universidad de la Frontera, Temuco (1997)

14. Castro, A.: El Paso de Los Andes, ["The Crossing of Los Andes Mountain"]. Alberdi Library (January 1918)
15. Mitre, B.: History of San Martín and the Emancipation of South America. San Martín Library (1887)
16. Hudson, D.: Historical memories about the province of Cuyo, vol. I. San Martín Library (1852-1875)
17. Favaloro, R.: Do you know San Martín?. Editorial Sudamericana (2009)
18. Thompson, F.: The Early Metallurgy of Copper and Bronze (1958)
19. George F. Vander Voort, Publisher: ASM International, Year of Published: 2004, Pages: 1184. ISBN: 978-0-87170-706-2
20. History of welding. http://www.ehowenespanol.com/historia-equipos-soldada-hechos_101201/. eHow in Spanish
21. Kaulicke, P.: Las cronologías del Formativo. 50 años de investigaciones japonesas en perspectiva. Fondo Editorial de la Pontificia Universidad Católica del Perú, Lima (2010)
22. Haas, J., Creamer, W., Ruiz, A.: Dating the Late Archaic occupation of the Norte Chico Region in Peru. Nature. **432**, 1020–1023 (2004)
23. Haas, J., Creamer, W.: Crucible of Andean civilization. The Peruvian coast from 3000 to 1800 BC. Curr. Anthropol. **47**(5), 745–775 (2006)
24. Creamer, W., Ruiz, A., Perales, M., Haas, J.: The Fortaleza Valley, Peru: Archaeological Investigation of Late Archaic Sites (3000–1800 BC). Fieldiana Anthropol. **44**, 1–108 (2013)
25. Perales, M.: Proyecto de Investigación: Reconocimiento Arqueológico en el Valle de Fortaleza (Lima-Áncash, Perú). Informe Final presentado al Instituto Nacional de Cultura, Lima (2007)
26. Haas, J., Perales, M.: Proyecto de Investigación Arqueológica en el Norte Chico: Excavaciones en Caballete, Valle de Fortaleza, Perú. Informe Final presentado al Instituto Nacional de Cultura, Lima (2004)
27. Vega-Centeno, R.: Arquitectura pública del Arcaico Tardío en el valle de Fortaleza. Reflexiones sobre las sociedades complejas tempranas en la Costa Nor-Central. Arqueología y Sociedad. **15**, 31–58 (2004)
28. Bazán, A.: Reocupaciones de complejos monumentales del Periodo Arcaico Tardío en el valle de Fortaleza, Costa Nor Central del Perú. Tesis de Licenciatura. Lima, Universidad Nacional Mayor de San Marcos (2012)
29. Rodriguez-Kembel, S.: Architectural Sequence and Chronology at Chavín de Huántar, Perú. Tesis Doctoral, Stanford University, Stanford, California, EE.UU (2001)
30. Rick, J., Lumbreras, L.G., Bazán, A., Mendoza, R.: Cambiando la percepción sobre Chavín: las últimas campañas del Proyecto de Investigación y Conservación en Chavín de Huántar. In: Actas del I Congreso Nacional de Arqueología, vol. II, pp. 5–20. Ministerio de Cultura, Lima (2016)
31. Rick, J., Bazán, A.: Reporte de la Campaña de Excavaciones Arqueológicas 2014 en Chavín de Huántar. Develando y entendiendo Nuevos Espacios Rituales en la Explanada Norte del Edificio C. In: Actas del II Congreso Nacional de Arqueología, vol. II, pp. 67–87. Ministerio de Cultura, Lima (2017)
32. Burger, R., Gordon, R.B.: Early Central Andean Metalworking from Mina Perdida, Peru. Science. **282**(5391), 1108–1111 (1998)
33. Vetter, L., Petrick, S., Olivera, P.: Estudio arqueométrico de piezas de oro de Morro de Éten, Perú. In: Vetter, L., Vega-Centeno, R., Olivera, P., Petrick, S. (eds.) Actas del II Congreso Latinoamericano de Arqueometría. Lima, 19 al 21 de octubre de 2009, (pp. 73-86). Fondo Universidad Nacional de Ingeniería/ rganización de Estados Iberoamericanos/Instituto Peruano de Energía Nuclear, Lima (2011)
34. Lothrop, S.K.: Gold artifacts of Chavín style. Am. Antiq. **3**, 226–239 (1951)
35. Burger, R.: Chavín. In: Boone, E.H. (ed.) Andean Art at Dumbarton Oaks, vol. 1, pp. 45–85. Dumbarton Oaks Research Library and Collection, Estados Unidos, Washington, DC (1996)
36. Lechtman, H.: Technical examination of a gold-alloy object from Chavín de Huántar. In: Burger, R. (ed.) The Prehistoric Occupation of Chavín de Huántar, Peru, pp. 271–276. University of California Press, Estados Unidos, California (1984)

37. Aldenderfer, M., Craig, N., Speakman, R., Popelka-Filcoff, R.: Four-thousand-year-old gold artifacts from the Lake Titicaca basin, southern Peru. Proc. Natl. Acad. Sci. **105**(13), 5002–5005 (2008)
38. Onuki, Y.: Ocho tumbas especiales de Kuntur Wasi. Boletín de Arqueología PUCP. **1**, 79–114 (1997)
39. Petersen, G.: Minería y metalurgia en el antiguo Perú. Arqueológicas 12 (1970)
40. Lechtman, H.: A metallurgical Site Survey in the Peruvian Andes. J. Field Archaeol. **3**(1), 1–42 (1976)
41. Elera, C.: Investigaciones sobre patrones funerarios en el sitio formativo de Morro de Éten, valle de Lambayeque, costa norte del Perú. Memoria de Bachillerato en Arqueología. Pontificia Universidad Católica del Perú, Lima (1986)
42. Lothrop, S.K.: Gold ornaments of Chavín Style from Chongoyape, Peru. Am. Antiq. **3**, 250–262 (1941)
43. Hirao, Y., Ohnishi, J., Onuki, Y., Kato, Y.: Chemical composition of samples excavated from Kuntur Wasi archaeological site. Peru. Archaeology and Natural Science. **25**, 13–30 (1992)
44. Kato, Y.: Resultados de las excavaciones en Kuntur Wasi, Cajamarca. Senri Ethnological Studies. **37**, 203–228 (1993)
45. Onuki, Y.: Kuntur Wasi. In: Pillsbury, J., Potts, T., Richter, K.N. (eds.) Golden Kingdoms. Luxury Arts in the Ancient Americas, (pp. 17). The J. Paul Getty Museum & The Getty Research Institute, Estados Unidos, Los Angeles (2017)
46. Viladevall Solé, M.: La prospección de placeres de oro y otros minerales densos. https://www.academia.edu/26764009/LA_PROSPECCI%C3%93N_DE_PLACERES_DE_ORO_Y_OTROS_MINERALES_DENSOS (2004). Accessed 13 Oct 2019
47. Root, W.: The metallurgy of the Southern Coast of Peru. Am. Antiq. **15**(1), 10–37 (1949)
48. Klein, C., Hurlbut Jr., C.: Manual of Mineralogy. Wiley, Estados Unidos, New Jersey (1993)
49. Vetter, L., Mac Kay, M.: Tumbas y oro: Evidencias de cambios sociales y tecnológicos en el Formativo Tardío. In: Melgar, E. Solís, R., González, E. (eds.) Producción de bienes de prestigio ornamentales y votivos de la América antigua, pp. 50–69. Publicación electrónica de Syllaba Press, 7. www.syllabapress.com/temp (2010)
50. Grossman, J.: An ancient gold worker's tool kit: the earliest metal technology in Peru. Archaeology. **25**(4), 270–275 (1972)
51. Grossman, J.: The Waywaka gold: new chronometric evidence. Andean Past. **11**, 123–138 (2013)
52. Shimada, I., Szumilewicz, A., Valdez, R., Merkel, J.: La producción artesanal a gran escala y el centro religioso andino: una reconsideración. In: Ponencia presentada en el VI Congreso Nacional de Arqueología organizado por el Ministerio de Cultura del Perú (2019)
53. Uceda, S., Rengifo, C.: La especialización del trabajo: Teoría y arqueología. El caso de los orfebres mochicas. Bulletin de l'Institut Français d'Études Andines. **35**(2), 149–185 (2006)
54. Lewis, C.M.: British Railways in Argentina 1857-1914: A Case Study of Foreign Investment. Athlone Press, Londres (1983)
55. Vicuña, S.M.: Los Hermanos Clark. Establecimientos Gráficos Balcells, Santiago de Chile (1929)
56. World Digital Library. (29 May 2013). https://www.wdl.org/es/item/11313/
57. Agico Group. http://www.railroadpart.com/
58. Instituto Argentino de Siderurgia, Aceros para Construcciones Mecánicas Hojas de Caracteristicas (1981)
59. William, S.F., Hashemi, J.: Fundamentos de la ciencia e ingeniería de materiales. McGraw-Hill, Mexico (2006)
60. Hayden, H.W., Moffatt, W.G., Wulff, J.: Introducción a la Ciencia de los Materiales, vol. III. Mexico, Editorial Limusa-Wiley, S.A. (1968)
61. Lacoste, P.: El Ferrocarril Trasandino y el desarrollo de los Andes Centrales argentino-chilenos. Editorial IDEA, Santiago (2013)
62. Vargas, E.: Amigos del Tren. https://www.amigosdeltren.cl/el-trasandino-los-andes-mendoza (2017). Accessed 15 August 2019.

63. Martin, G.: Centro Cultural Argentino de Montaña. http://culturademontania.org.ar/Noticias/historia-ferrocarril-trasandino-mendoza.htm. 2018. Accessed 15 August 2019
64. Fundamentos de Ingeniería. http://ing.unne.edu.ar/dep/eol/fundamento/tema/T11F.pdf
65. Archivo Histórico de Mendoza, ["Historical Archive of Mendoza"], Folder 543 bis, D.3.
66. Gentili, C., Saisi, A.: One-year dynamic monitoring of a centenary iron arch bridge. In: Experimental Vibration Analysis for Civil Engineering Structures, Ouro Preto, Brazil (2013)
67. Datos de expediente de Archivo Municipalidad de Luján de Cuyo, ["File data of the Municipality of Luján de Cuyo Archive"] (1990)
68. Scott, D.: Metallography and Microstructure of Ancient and Historical Metals, Chapters 2, 12. The Getty Conservatory Institute. ISBN 0-899236-195-6 (1991)
69. ASM. ASM Handbook, vol. 9: Metallography and Microstructures, (2004)
70. Mattolini, M., En: Apuntes de clase y disertación sobre "Historia de la Metalurgia", ["Class notes and dissertation on History of Metallurgy"], Mendoza, Argentina (2013)
71. Cavallini, M.: La Scoperta dei metalli: Mitología e Termodinamica, ["The Discovery of Metals: Mythology and Thermodynamics"], Enco-journal, Roma, Italia (2007)
72. De Paula, F.: La conquista y la colonización. pág. 43 y ss, en San Carlos es futuro, Municipalidad de San Carlos (1987)
73. Pérez, F.I.: El Fuerte y el Cuartel de San Carlos. Crónicas de la Frontera y de la Campaña. Pág. 16. En Serie Investigaciones Nº 7. Archivo Histórico de Mendoza (1987)
74. De Paula, F.: OP.CIT. pág. 45 y ss
75. Chaca, D.: Síntesis histórica del Departamento Mendocino de San Carlos, Buenos Aires (1964)
76. Pérez, F.: El Fuerte y el Cuartel de San Carlos, Crónicas de la Frontera y de la Campaña. En Serie Investigaciones Nº7. Archivo Histórico de Mendoza, Mendoza (1997)
77. Pérez, F.I. OP.CIT. Pág. 34
78. Gullón Abao, A.: La Artillería de los fuertes del Chaco en el siglo XVIII. En MILITARIA. Revista de Cultura Militar, Nº10 Servicio de Publicaciones, UCM, Madrid (1997)
79. See Gullón Abao, Alberto José, "La Artillería de los fuertes del Chaco en el siglo XVIII," page 112
80. Torrejón Chaves, J.: La Artillería en la Marina española del siglo XVIII. En MILITARIA. Revista de Cultura Militar, Nº10 Servicio de Publicaciones, UCM, Madrid (1997)
81. See "Relación de las medidas dictadas por el marqués de Sobremonte en Córdoba (1785-1788)". Transcripción de Quesada, V. G. en la Revista de Buenos Aires, año II, tomo IX, N°33, 1866, pp. 89–104
82. Archivo Histórico de Mendoza, 77/2 y 33/23
83. Pérez, Francisco I. OP.CIT. Pág. 50 y ss
84. Olmedo, E., Tamagnini, M.: La frontera sur de Córdoba a fines de la Colonia (1780-1809): Guerra, saber geográfico y ordenamiento territorial. En FRONTERAS de la HISTORIA. Vol. 24, N.˚ 1 (2019)
85. Pérez, Francisco I. OP.CIT. Pág. 74 y ss
86. San Carlos es futuro. Municipalidad de San Carlos, Mendoza (1987)
87. Carrizo, P.S.: "Border Archeometallurgy" Project (MATUNME; code 0004308). Archaeometallurgu Area, Metallurgy Laboratory, Mendoza (2016–2017)
88. Notes on Metallurgy and Metallography for Students. Student Center, UTN FRM, (1980)
89. ASM. ASM Handbook, vol. 9: Metallography and Microstructures, 1985 edn. (Última revisión: Edition 2004)
90. Risso, C.: SPEAR. LR11 University Radio, Blog: SONG IN BLUE AND WHITE. Micro N°011 (2017)
91. Rodríguez, Y.: "Romance de pumas", Vinil LP, Category: Recitations, Folklore (1891–1957)
92. Habashi, F.: The seven metals of antiquity. Min. Proc. Extract. Metall. **117**, 190–191 (2008)
93. Buchwald, V.F.: On the use of iron by the Eskimos in Greenland. Mat. Char. **29**, 139–176 (1992)
94. Buchner, E., Schmieder, M., Kurat, G., Brandstätter, F., Kramar, U., Ntaflos, T., Kröchert, J.: Buddha from space - An ancient object of art made of a China iron meteorite fragment. Meteor. Planet. Sci. **47**, 1491–1501 (2012)

95. Comelli, D., D'orazio, M., Folco, L., El-Halwagy, M., Frizzi, T., Alberti, R., Capogrosso, V., Elnaggar, A., Hassan, H., Nevin, A., Porcelli, F., Rashed, M.G., Valentini, G.: The meteoritic origin of Tutankhamun's iron dagger blade. Meteor. Planet. Sci. **51**, 1301–1309 (2016)
96. Pense, A.W.: Iron through the ages. Mat. Char. **45**, 353–363 (2000)
97. Ogden, J.: Metals. In: Nicholson, P.T., Shaw, I. (eds.) Ancient Egyptian Materials and Technology, pp. 148–176. Cambridge University Press, Cambridge (2000)
98. Pliny the Elder, The Natural History. https://www.perseus.tufts.edu/hopper/text?doc=Perseus%3atext%3a1999.02.0137
99. Haynes, W.M., Lide, D.R., Bruno, T.J. (eds.): CRC handbook of chemistry and physics, 97th edn. CRC Press, Boca Raton (2016)
100. http://periodictable.com/Properties/A/CrustAbundance.html
101. Klein, C., Dutrow, B., Dana, J.D.: Manual of Mineral Science, 23rd edn. Wiley, New York (2007)
102. Tylecote, R.F.: History of Metallurgy. Institute of Materials, London (1992)
103. Read, T.T.: Metallurgical fallacies in archaeological literature. Am. J. Archeol. **38**, 382–389 (1934)
104. Diamond, J.: Guns, Germs and Steel: A Short History of Everybody for the Last 13,000 Years. W.W. Norton, New York (1997)
105. Camp, J.M., Francis, C.B.: The Making, Shaping and Treating of Steel, 2nd edn. Carnegie Steel Co., Pittsburgh (1920)
106. Lang, J.: Roman iron and steel: A review. Mater. Manuf. Process. **32**, 857–866 (2017)
107. https://www.coe.int/es/web/cultural-routes/the-pyrenean-iron-route
108. Carrión-Arregui, I.M.: Tecnología tradicional y desarrollo de una industria pesada: La fabricación de anclas en Guipúzcoa (siglos XVI-XVIII). Rev. Hist. Ind. **7**, 199–214 (1995)
109. Dacosta, A.: El hierro y los linajes de Vizcaya en el siglo XV: Fuentes de renta y competencia económica. Studia Hist. **15**, 69–102 (1997)
110. Florén, A., Rydén, G.: Convergencia tecnológica y diversidad social. Mercados, centros de producción y cambio tecnológico en la industria del hierro europea, 1600-1850. Rev. Hist. Ind. **12**, 75–111 (1997)
111. García-de-Cortázar, J.A.: Alava, Guipúzcoa y Vizcaya en los siglos XIII a XV: De los valles a las provincias. Rev. Int. Estud. Vascos. **45**, 197–234 (2000)
112. Erdozáin-Azpilicueta, P., Mikelarena-Peña, F.: Siderurgia tradicional y comunidad campesina. La gestión de las ferrerías municipales de Lesaka y Etxalar en 1750-1850. Vasconia. **32**, 491–515 (2002)
113. Sancho, M.: El hierro en la Edad Media: Desarrollo social y tecnología productiva. An. Est. Med. **41**, 645–671 (2011)
114. Aragón-Ruano, A.: Las ferrerías guipuzcoanas ante la crisis del siglo XVII. Cuad. Hist. Mod. **37**(2012), 73–102
115. Gil, P.P., Yusta, I., Orue-Etxebarria, X., Herrero, J.M., Baceta, J.I., Artaraz, J., Madina, E., Mintegui, J.M.: Caracterización mineralógica y química de escorias de ferrerías de monte ("haizeolas") en el entorno de Galdakao (Vizcaya). Macla. **9**, 117–118 (2008)
116. Mendoza's Historical Archives, Binder 543 bis, D.3
117. Gentili, C., Saisi, A.: One-Year Dynamic Monitoring of a Centenary Iron Arch Bridge Experimental Vibration Analysis for Civil Engineering Structures. Ouro Preto, Brazil (2013)
118. File data of the Municipality of Luján de Cuyo
119. ASM Handbook, vol. 9: Metallography and Microstructures (2004)
120. Mattolini, M.: Class Notes and Dissertation About the History of Metallurgy, Mendoza, Argentina (2013)
121. Cavallini, M.: La Scoperta dei metalli: Mitología e Termodinamica. Enco-journal, Roma, Italia (2007)
122. Gattás, O.: Historia de Luján de Cuyo relación e integración con la región, Argentina y el mundo, ["History of Luján de Cuyo relationship and integration with the region, Argentina and the world"]. Digital Format, D10 Productions (2017)
123. Tahan, P.: Owner of *"Los Carrizales*" Cabin Criollos Horses. Luján de Cuyo, Mendoza

Chapter 13
Special Case Studies on Reverse Engineering

Patricia Silvana Carrizo, Julio Rubén Ortigala, Cristian José Aguilera, Luisa Vetter, Jessica Carneiro, Yezeña Huaypar, Erika Gabriel, and Jesús Ruiz

Introduction

This Special Case Study chapter aims to show two cases investigated in historical nonmetallic materials. The first case study represents a novelty for the Area of Archaeometallurgy since it is the study of pigments in pictorial works of the plastic artist Fernando Fader (1882–1935) and found in the Museo Emiliano Guiñazú Casa de Fader where they remained hidden from the viewer behind insulating panels. It is a study of the chemical composition of pigments where known works of the artist

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P. S. Carrizo (✉)
Archaeometallurgy Area/Metallurgy Laboratory, National Technological University, Mendoza, Argentina

J. R. Ortigala
Sciences Basics Department, National Technological University, Mendoza, Argentina
e-mail: julioortigala@yahoo.com.ar

C. J. Aguilera
Industrial Metallurgy Laboratory, Electromechanical Department, National Technological University, Mendoza, Argentina
e-mail: cristianaguilera76@yahoo.com.ar

L. Vetter
Pontificia Universidad Católica del Perú, Academia Nacional de Ciencias, Lima, Peru
e-mail: luisa.vetter@pucp.edu.pe

J. Carneiro
Kullasiri S.A.C., Lima, Peru

Y. Huaypar · E. Gabriel
Laboratorio BIZALAB S.A.C., La Victoria, Peru
e-mail: yezena.huaypar@bizalab.com.pe; erika.gabriel@bizalab.com.pe

J. Ruiz
Metallurgy and Materials Consulting, Lima, Peru
e-mail: jruiz@metallurgy-materialsconsulting.com

P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7_13

are compared with these recently found works; statistical studies were carried out on the collection of measured data. It confirms that the portable X-ray spectrometry technique is optimal, being a technique that currently provides all the information prior to the start of work by professional restorers in the world, since it is noninvasive, fast, and reliable. The second case study presented in this chapter deals with Antimony (Sb), a metalloid that occurs in the form of oxides and in native form, of which there is very little or no dedicated bibliography on its use in pre-Columbian Peru, due to the shortage of deposits. Two elite tombs of the Sicán culture (750–1375 AD) were studied and the excavation found antimony beads, which were part of pectorals and necklaces. Characterization techniques were applied such as, for example, X-ray diffraction, X-ray spectroscopy, and scanning electron microscopy; and two mines have been studied to study the origin of the raw material for the manufacture of these necklaces and pectorals. This special chapter even implies showing the scientific method applied to develop research in Reverse Engineering, where a large number of concepts acquired in chairs are involved such as Materials Sciences, Chemistry, Strength of Materials, Metallurgy, Metallographic Techniques, Prospecting, Provenance, Archeology, and History and how all these are combined as well as tools to obtain research results, and that is why the chapter is proposed as a special chapter, since both works are interesting, novel, and deserve to be disseminated.

Analysis of Inorganic Pigments in Unknown Works by Painter Fernando Fader Through X-Ray Fluorescence (XRF)

Patricia Silvana Carrizo, Julio Ortigala, and Cristián Aguilera

Abstract

Since the last decades of the last century, noninvasive and portable analytical techniques have been developed for the study of patrimonial works. One of the techniques that have evolved is the fluorescence of X-rays. It is a procedure to be carried out at the moment of carrying out a study prior to an intervention or an authentication of a work of art. The results help to determine the type of pigments used, how they were combined (palette of a painter). Through this technique, it was possible to identify the pigments used in pictorial works known by the Argentine painter Fernando Fader and which served to make the corresponding contrast of a variety of unknown works recently found on the walls of the Emiliano Guiñazú Museum Fader's House. The test study of hypothesis of difference of means between the different chemical elements read by XRF showed for reds and blues there is no significant difference with a level of significance of 0.05 and a value of p greater than 0.2.

Keywords

Inorganic pigments; X-ray spectrometer; Statistical analysis; Oil painting

Introduction

A new painting that will take the name of "Impressionism" in 1874 arose in France, between the years 1860 and 1890. This evolution does not constitute an isolated movement, the independent pictorial art evolves throughout Europe during the second half of the nineteenth century towards a painting faster and more contemporary, corresponding to a world in which progress is accelerated and where lifestyles evolve rapidly. Several painters who will be called first "independent," then "intransigent," and finally "impressionists" will carry out a struggle initiated by Monet in 1860, against the established conventions, definitively rejecting the search in the classics of perfect beauty and the eternal essence of things. If it took 30 years for the contemporaries to get used to the painting of the impressionists, it was because they criticized centuries of academic and codified painting. The impressionist painters established a link with the painting of the real world; they moved away from the past and achieved a completely new way of pictorial representation. The connection with the real world will allow to choose subjects not addressed in the painting until those moments and to invent a new pictorial technique, responding to the desire to privilege in painting the instantaneous impression on the construction of the spirit. The impressionist generation was born between 1830 and 1841. Two groups were formed: one in the Swiss Academy, grouped around Pisarro, and another in the Atelier Gleyre, around Monet [1]. An editor of a publication of the time and from a painting by Monet baptizes him in a mocking "impressionist," that is, impressionist, to the group of painters. Monet, far from being offended adopts the name as an emblem. The fact officially confirms Monet's place as head of the new school. This new school was defined and was separated from the rest of the pictorial schools existing until that moment by certain characteristics such as: the battle against academicism and the need to express modernity, the progressive conquest of light, chosen as the dominant principle and its natural field of expansion is the landscape where the contours are blurred under the vibration of the atmosphere, the revolutionary idea of painting the landscape outdoors and not already within the walls of an atelier. The treatment of light and the triumph of color, never seen before, new technique thanks to which the painter will not represent the forms any more than they are but as the painter sees them and feels them, at a precise moment, bathed by light or by the shadow of the fleeting moment. Critics of Argentine art agree in indicating that it was in 1920 when the modernization of the plastic language reached Argentina. In the late nineteenth and early twentieth century, Argentine painting seemed engrossed in a naturalistic academicism. Impressionism, like all foreign artistic and literary currents, arrives late in the country embodied in the work of Martín Malharro (1902) [2]. Fernando Fader being another artist who influenced the Argentine painting and who is very loved on Mendoza soil. He was born in Bordeaux, France, on April 11, 1882 and died on February 25, 1935 in Ischilín, Córdoba, Argentina. Son of a French mother and a German father, he receives his artistic training in Europe. However, in his heart, he declares his love for Mendoza and says he feels that he is originally from this land. His work demonstrates the concern for light, its fusion in forms. He travels in 1900 to study painting at the Munich Academy with Heinrich Zügel. Returns to Argentina in 1904 and since 1905 occupies a prominent place in Argentine painting. He is only 23 years old and fortunate. He made his first exhibition in the "Salón Costa" and then in Müller. Its success is fulminating. His painting offers us family portraits, still lives, animals, and landscapes made in Germany, Holland, and Mendoza. For a few years, from 1909 to 1914 above all, it eclipses the artistic scene. He will return to him being another man: mature, poor, and tired of failures. Soon the disease will be added and suffering will be his companion until the end. He will dedicate himself to painting in an absolute, almost devotional way. That is why his work is nourished by a measured and peaceful landscape. Everything is peace and silence. In this stage, Fernando Fader begins with a concern for the native, and affirms: "Open your eyes and see your homeland. That's what I call great art. Be so strong that your works represent only that which can be your homeland. That is art." For Fader, art is the homeland. Fader paints landscapes with light colors and emphasizes the atmosphere. He wants painting to be the vehicle of the states of the soul. He wishes to convey the loneliness and silence of the Argentine countryside in his canvases.

In the Emiliano Guiñazú Museum—Casa de Fader, in Luján de Cuyo, one can appreciate how this renowned painter was influenced by Degas in the paintings "Nude back" (1917), "Nude, roses" (1921), and "Lavanderas" (1925), regarding the subject and the invoice of his paintings. In the same way, in "In the pond or the ducks" (1920), "The visit" (1922), and "Las Dalias" (1928), the presence of Claude Monet is felt in the fabrics by the theme, the light, and colors. Thanks to the influence exerted by the great impressionist painters on the Argentine painters, the luminous landscape becomes the center of Argentine painting, marking in this way the beginning of modern painting in our country. Although his creations are scarce, since he could only make less than 800 paintings in the 23 years that he dedicated himself, overcoming his illness and economic breakdowns. Fader is the favorite artist and most desired by international collectors. Undoubtedly, Fernando Fader is one of the pillars of Argentine painting [3].

Experimental

The analysis of pigments by X-ray fluorescence (XRF) is a procedure to perform at the time of making a study prior to an intervention or conservation of a work of art, can help us determine the time in which the work was made, based on the type of materials used or to verify possible interventions carried out later on the work. The technique of analysis of pigments by XRF is transportable and noninvasive, expressed as a percentage (%) to each chemical element identified, and by this help to determine the type of pigment used by the artist, also to know the way which were combined, that is to say, to identify the "palette of a painter." A strength is the analysis of inorganic pigments that correspond to 70% of the pigments used worldwide. X-ray fluorescence (XRF) is an analytical technique that enjoys great popularity to perform studies of elementary composition of cultural goods, which allows to perform qualitative and semiquantitative multielemental analyses in a short period of time and with a high sensitivity, which also allows the detection of minor elements and traces whose concentration is less than 0.01%. On the other hand, it allows to analyze the works without establishing physical contact with them and without causing material alterations in the analysis areas during the measurement process with the experimental conditions usually used [4]. In principle, this technique allows the identification of all the elements of the periodic table, with the exception of hydrogen and helium, covering an energy range between 50 electron volts (eV) and 100 kiloelectronvolts (keV). However, light elements can be difficult to measure, which limits practical work to the study of atomic number elements greater than 13 (Al) although, if a helium current is used between the sample and the X-ray detector, the analysis up to sodium ($Z = 11$) [5]. The product of the technique is a list that identifies the chemical elements that form the pigments of a certain color not only of the surface layer of the work but also of the arrangement, proportion, and composition of pigments and other constituent materials used in the preparation of the support and primer of the painting. Through this study, we came to have a fairly consistent approximation of what was the palette and technique used by the teacher and artist Fernando Fader.

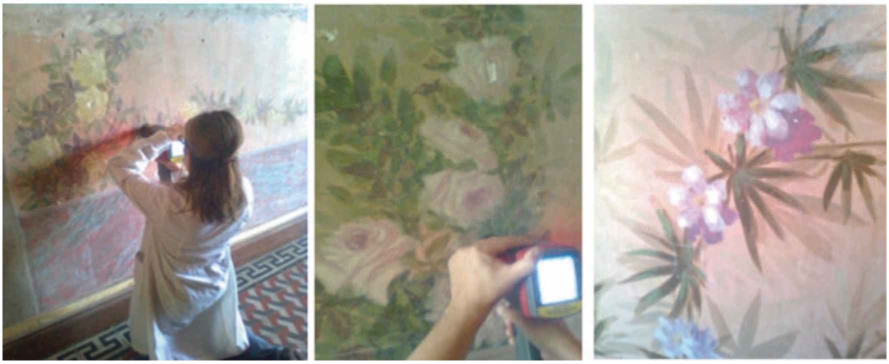
Development of the Method

The purpose of this study was to determine the chemical composition of the pictorial pigments of works and validate their belonging to the famous painter Fernando Fader; these works have remained hidden and were found on the walls in Emiliano

Guiñazú Museum Fader's House under plates of insulating material. It should be noted that this was our first experience in the subject (2013); therefore, an intensive review of the state of the art was carried out, and the methodology to be followed was adapted according to the equipment available. In this way, the development of the technique was based on the measurements of chemical composition in the walls where the new pictorial works are found, correctly designing each work for the area of location. Then these data are contrasted with the murals already known by the painter Fernando Fader, and which are in the room where the pool is located. Three colors were studied: green, red, and blue, because they are the colors that dominate the most. It begins with the study of the greens in the paintings recently found, and they are contrasted with the greens of the well-known works of the famous painter, such as Mural Paseo en Bote, Los Bañistas, Las Garzas. It continues in the same way with the study of the blues and finally with the study of the red ones.

Sampling in Works of Art

The data collection of the works was carried out in the facilities of the Emiliano Guiñazú Museum Fader's House located in the district of Mayor Drummond, Luján de Cuyo department, Province of Mendoza, Argentina. The chemical elements were determined by a portable X-ray fluorescence spectrometer for material analysis, SPECTRO × SORT Handheld X-Ray Spectrometer (XRF-Portable), test conditions: voltage 50 kV, current 0.050 mA. The chemical composition, expressed in percentage of chemical element, associated with the pigments analyzed is detailed in each table ordered by color and depending on whether it is a chemical element belonging to the known and unknown pigments of the painter, six measurements were made for each zone and in other areas four measurements for each of the pigment studies (green, blue, and red). The portable spectrometer is placed perpendicular to the work, between four and six measurements are made for each sampling point, the time for each measurement is 30 s, this portable equipment has output for USB port, allows connection of Wi-Fi and connection of data, and these characteristics allow us to save measurements in files and print. In the green tones of the unknown works, we work with very low green tones and in the known works of the painter the range of tonalities is wider for the greens. In the blues and reds, we find higher tonalities in both unknown and known works. The selection of sampling points was made under the technical criteria of a conservator-curator of heritage assets [6]. Statistical methods are used as a tool to validate our study of XRF spectroscopy (Figs. 13.1–13.3), since there is no sample of the murals and additional equipment to carry out stratigraphic and advanced studies. With these measurements made with the portable spectrometer, a statistical study was carried out, for which it was started by calculating the average values and variances for each color studied both for those belonging to the known works and those belonging to the unknown works and which are the ones that are wanted to validate to Fernando Fader [7] (Tables 13.1, 13.2, and 13.3).



Figs. 13.1–13.3 Data collection with XRF spectrometer. Measurements of green pigments in unknown works found in the north side corridor west wall of the Fader Museum

Figs. 13.4–13.5 Contrast of greens and reds pigments in the mural: “Las Grazas”, a well-known work of the plastic artist Fernando Fader

Figs. 13.6–13.7 Contrast of red pigments in the mural: “Bañistas”, well-known work of the plastic artist Fernando Fader

Fig. 13.8 Measurement of green and blue pigments in unknown work discovered in the Entrance Hall of the Fader Museum

Figs. 13.9–13.10 Measurement of green and blue pigments in the Mural: "Paseo en Bote", a well-known work of the plastic artist Fernando Fader

Table 13.1 Known and unknown reds: mean and standard deviation

Known reds	Mean	Standard deviation	Unknown reds	Mean	Standard deviation
Ag	0.29	0.058	Ag	0.282	0.056
Fe	6.11	4.92	Fe	7.22	3.01
Cr	4.11	3.88	Cr	6.04	0.68
Ti	4.13	1.61	Ti	4.16	0.46
V	1.59	0.62	V	1.54	0.19
Pb	78	12.43	Pb	76.67	4.03

Table 13.2 Known and unknown blues: mean and standard deviation

Known blues	Mean	Standard deviation	Unknown blues	Mean	Standard deviation
Ag	0.38	0.11	Ag	0.34	0.046
Fe	7.58	3.42	Fe	7.30	5.72
Cr	1.87	0.99	Cr	1.42	0.88
Ti	5.58	0.88	Ti	4.87	0.59
V	2.19	0.35	V	1.86	0.19
Pb	79.26	2.67	Pb	72.9	5.24

Table 13.3 Known and unknown greens: mean and standard deviation

Known greens	Mean	Standard deviation	Unknown greens	Mean	Standard deviation
Ag	0.4	0.095	Ag	0.49	0.34
Fe	5.66	3.32	Fe	0.88	0.42
Cr	8.44	2.86	Cr	7.32	1.69
Ti	3.82	1.15	Ti	2.64	2.17
V	1.03	0.49	V	1.17	0.95
Pb	77.33	7.7	Pb	93.33	4.12

Interpretation of Data

A normality test was performed to know the probability distribution of the data of the percentages of chemical elements associated with the colors: green, blue, and red. Then, hypothesis tests were performed among the studied colors: green, blue, and red known versus unknown.

Shapiro–Wilks Test for Normality

We consider a random sample of data $x_1, x_2, \ldots, x_n$ that come from a certain unknown distribution denoted by $f(x)$. We want to verify if said data were generated by a process that has a normal probability distribution, by means of statistical hypotheses:

H_0: the data come from a normal distribution
H_A: the data do not come from a normal distribution

The steps for the Shapiro–Wilks test are:

1. The data is ordered from least to greatest. Denote the data by $X_{(1)}, X_{(2)}, \ldots, X_{(n)}$
2. From the corresponding table, we obtain the coefficients $a_1, a_2, \ldots, a_k$, where k equals $n/2$
3. The W statistic defined as:

$$W = \frac{1}{(n-1)S^2}\left[\sum_{i=1}^{k} a_i \left(X_{(n-i+1)} - X_{(i)}\right)\right]^2$$

4. If the statistic W is greater than its critical value at the selected α level of the table, the normality of the data of a normal distribution is rejected. From the table of quartiles, for $n = 24$; the critical value is read for an alpha of 0.05; critical value = 0.984

$$W = \frac{1}{(24-1)20^2}[89.38]^2 = 0.86$$

Since W is smaller (0.86) than the critical value (0.984), the hypothesis that the data come from a normal distribution is accepted.

Bartlett Test for Variance Homogeneity

Suppose we have k populations or independent treatments, each with a normal distribution, where the variances are unknown. We want to test the hypothesis of equality of variances given by:

$$H_o : \sigma_1^2 = \sigma_2^2 = \cdots = \sigma_k^2 = \sigma^2$$
$$H_A : \sigma_i^2 \neq \sigma_j^2 \cdots, \text{for some } i \neq j$$

The test statistic for the proposed hypothesis is:

$$\chi_o^2 = 2.3026\frac{q}{c}$$

where

$$q = (N-k)\log_{10} S_P^2 - \sum_{i=1}^{k}(n_i - 1)\log_{10} S_i^2$$

where S_i^2 is the sample variance of the treatment *i*

$$c = 1 + \frac{1}{3(k-1)}\left(\sum_{i=1}^{k}(n_i - 1)^{-1} - (N-k)^{-1}\right)$$

$$S_p^2 = \frac{\sum_{i=1}^{k}(n_i - 1)S_i^2}{N-k}$$

If *q* is zero or negative, it is considered that it cannot be rejected.

$$c = 1 + \frac{1}{3(k-1)}\left(\sum_{i=1}^{k}(n_i - 1)^{-1} - (N-k)^{-1}\right) = 1.083$$

$$\chi_o^2 = 2.3026\frac{q}{c} = 2.3026\frac{0.89}{1.083} = 1.89$$

The critical value for a chi-square distribution with $K - 1 = 4 - 1 = 3$ degrees of freedom and alpha = 0.05; it is 7.81. So, the null hypothesis cannot be rejected and it is concluded that they are all the same.

Hypothesis Tests

Hypothesis tests were performed among known and unknown green, blue, and red. It was preferred to use the technique of hypothesis testing before the design of experiments, even at the risk of increasing the type I error, since some correlation was observed between the values of the percentages of chemical elements associated with the pigments.

The statistic was used: $T_o = \dfrac{\bar{X}_1 - \bar{X}_2}{\sqrt{\dfrac{S_1^2}{n_1} + \dfrac{S_2^2}{n_2}}}$

This statistic follows a Student's *t* distribution with $v = n_1 + n_2 - 2$, degrees of freedom.

We worked with a level of significance $\alpha = 0.05$ [8].

In all cases, the null hypothesis could not be rejected, and it was concluded that there was no statistically significant difference between the percentages (%) of the chemical elements: Pb, V, Ti, Cr, Fe, Cu, Ag for both known and unknown works for the study of blue and red colors. A statistically significant difference is observed in the case of the percentage of the chemical element Fe between the known and unknown greens, although the *p*-value is 0.01. This indicates that if we had worked with a larger alpha (α) the null hypothesis would have been accepted. The *p*-value in all cases where the null hypothesis was accepted was greater than 0.15.

Discussion

The use of the different chemical elements expressed in percentages (%): Pb, V, Ti, Cr, Fe, Cu, Ag, in the known and unknown green, red, and blue colors led us to perform an analysis based on hypothesis tests to know if the percentages of chemical elements associated with the pigments used in the different colors used by the plastic artist were the same or different. A test of normality and constant variances was carried out, both of which were positive. A certain correlation was observed in the values, so that the design of experiments designed even at the risk of suffering an increase in the type I error was rejected. It was found that there is no statistically significant difference between the percentages used of the different chemical elements which form each pigment, except in the case of Fe between known and unknown greens, although the *p*-value is 0.1. In the other cases, where the null hypothesis could not be rejected that both means were equal, the *p*-value obtained was greater than 0.2.

For the interpretation of the results, besides the support by statistical methods, we worked taking into account the K lines of the elements from the aluminum ($Z = 13$) to the barium ($Z = 56$), and the L lines from the molybdenum ($Z = 42$) to bismuth ($Z = 83$). Each of the readings made on each sampling point related to each of the studied colors was analyzed separately and the variations that could be between each measurement were determined. Emphasis was placed on the highest elemental concentrations, expressed as a percentage by our portable equipment. When interpreting the values of the chemical elements of greater concentration or percentage were related to the chemical compound that forms each pigment, it is possible to determine the pigments and remains of the constituent materials. The oxides of iron (Fe_2O_3) were found in all the range of colors studied: red, green, and blue, the difference between some of them is the lowest proportion in which are some chemical elements such as potassium (K) or manganese (Mn). Many times, the use of materials seemed to be to lower costs, so it sometimes uses iron oxides to reach the same tonalities, using the dark clearing technique [9].

Another chemical element that appears in a high percentage in general in all measurements is lead (Pb) from the lead white, $CO_3Pb\ (OH)_2$, or basic lead carbonate, which corresponds to the white pigment used by the painter, and in this case the Lead element, in the form of carbonates, is not associated as a type material to complete and level the pictorial layers, since using the white color as the basis for other colors is a characteristic technique of Fernando Fader's work. In a first reading of all the data collected, it can be inferred that the element Pb (lead) is present in a high percentage with respect to the other chemical elements and is a constant that occurs in all measurements. This undoubtedly gives us a clue, because the plastic artist Fader used a palette of colors of an almost spectral simplicity, for example, one or two yellows, two reds, two or three blue, one green and white is fundamental [10]. Another element that was found forming different compounds is copper (Cu), which was associated with pigments such as verdigris, malachite, azurite. We did not find the chemical element calcium (Ca), from the chemical compound calcium carbonate, CO_3Ca, which could reach 70%, and depending on the color, this would be telling us that there was no previous intervention-restoration. However, higher percentages of titanium (Ti) related to titanium oxides (TiO_2) were found, to achieve titanium white, these would be a more modern type of pigments and could indicate previous intervention-restoration. And that in some areas and certain color there was intervention but that titanium was used as target of titanium and not calcium carbonates to achieve the same effect. This reading is very useful because white paint helps to date the restoration, because some white pigments are very characteristic of certain times. It is what titanium white reveals according to an article published in 2009 in X-ray spectrometry, only in 1921 was a suitable painting for artistic purposes based on this pigment, indicating that the works were retouched in the twentieth century.

Conclusions

The proposed method for the non-destructive examination of paints from in situ analysis by XRF-P; it allows to characterize the painting of an artist through the identification of pigments and a quantitative classification model for attribution, which was demonstrated with the study of the paintings of the outstanding Argentine artist Fader. The method works correctly, the established conditions help us determine pigments that have compounds from aluminum (Al) to bismuth (Bi). After the studies carried out in the known and unknown works of art recently found in the walls of the Emiliano Guiñazú Museum Fader's House, in Luján de Cuyo, Mendoza, in a first reading of all the data collected, it can be inferred that the element Pb (lead) is present in a high percentage with respect to the other chemical elements and is a constant that occurs in all measurements. This undoubtedly gives us a clue, because the plastic artist Fader used a palette of colors of an almost spectral simplicity, took from the spectrum what is fundamental, for example, one or two yellows, two reds, two or three blue, one green and white is fundamental. It was verified that there is no statistically significant difference between the percentages used of the different chemical elements that form each pigment, except in the case of Fe between known and unknown greens, although the p-value is 0.1. That is, if a p-value less than 0.1 had been used in known and unknown green tones, there would be no statistically significant difference. In the other cases, where the null hypothesis could not be rejected that both means were equal, the p-value obtained was greater than 0.2. The presence of titanium, in the measurements of works known as unknown, indicates that there were previous interventions-restorations, because the adequate paint for artistic purposes based on this pigment of titanium oxide was marketed around 1921.

Antimony as a Luxury Good in the Sicán Culture on the North Coast of Peru

Luisa Vetter, Jessica Carneiro, Yezeña Huaypar, Erika Gabriel, and Jesús Ruiz

Abstract

In two elite tombs of the Sicán culture (750–1375 AD), archaeologists uncovered antimony (Sb) beads from pectoral ornaments and necklaces. Antimony is a non-metal or metalloid which comes in the form of native antimony or oxides. There is little to no bibliographic information referring to the use of antimony in pre-Columbian Peru.

In this chapter, the Barranco Colorado and Cerro Mellizo mines, located in the research area at the Batán Grande National Historic Sanctuary, Lambayeque on the North Coast of Peru, were visited in search of the source of the antimony used for the production of the beads found in the Sicán tombs. Both the beads and the minerals extracted from the mines were analyzed by scanning electron microscopy with EDS (SEM-EDS), X-ray fluorescence (XRF), and X-ray diffraction (XRD). The beads from the tombs have a high antimony content and, according to their mineralogy as determined by XRD analyses, they appear to mainly consist of native antimony and oxide (senarmontite and stibiconite). From the XRD results for the samples collected from the Barranco Colorado Mine, we can identify a local source for some antimony minerals, such as senarmontite and stibnite. In the samples from Cerro Mellizo, we found tetrahedrite, which is an antimony sulfide of iron and copper.

Keywords

Antimony; X-ray diffraction; X-ray fluorescence; SEM-EDS

Introduction

Antimony (Sb) is a non-metal or metalloid that has been found in the form of worked beads in the elite tombs of the Sicán, a culture that developed on the North Coast of Peru between 750 and 1375 AD and whose political, economic, and administrative center was located in the Pomac Forest. These beads were part of pectoral ornaments or necklaces that were found in association with the funerary contexts of elite individuals excavated at Huaca Loro [11] and Huaca Las Ventanas [12], which had been deposited as offerings. In addition, necklaces and pectoral ornaments were made with beads from various other materials, such as mollusk shells and semi-precious stones.

Antimony can appear as native antimony or as oxides; moreover, in Peru it is related to arsenic and copper ore, an alloy that allows for identification of the deposit. However, the use of antimony as a luxury metal or material for offerings is essentially unknown from other archaeological research or ethnohistorical sources regarding pre-Columbian Peru. In the register of pre-Hispanic objects achieved to date, there are no other cases like the one discussed in this research. For this reason, there is little or no bibliographical information referring to the use of antimony in pre-Columbian Peru.

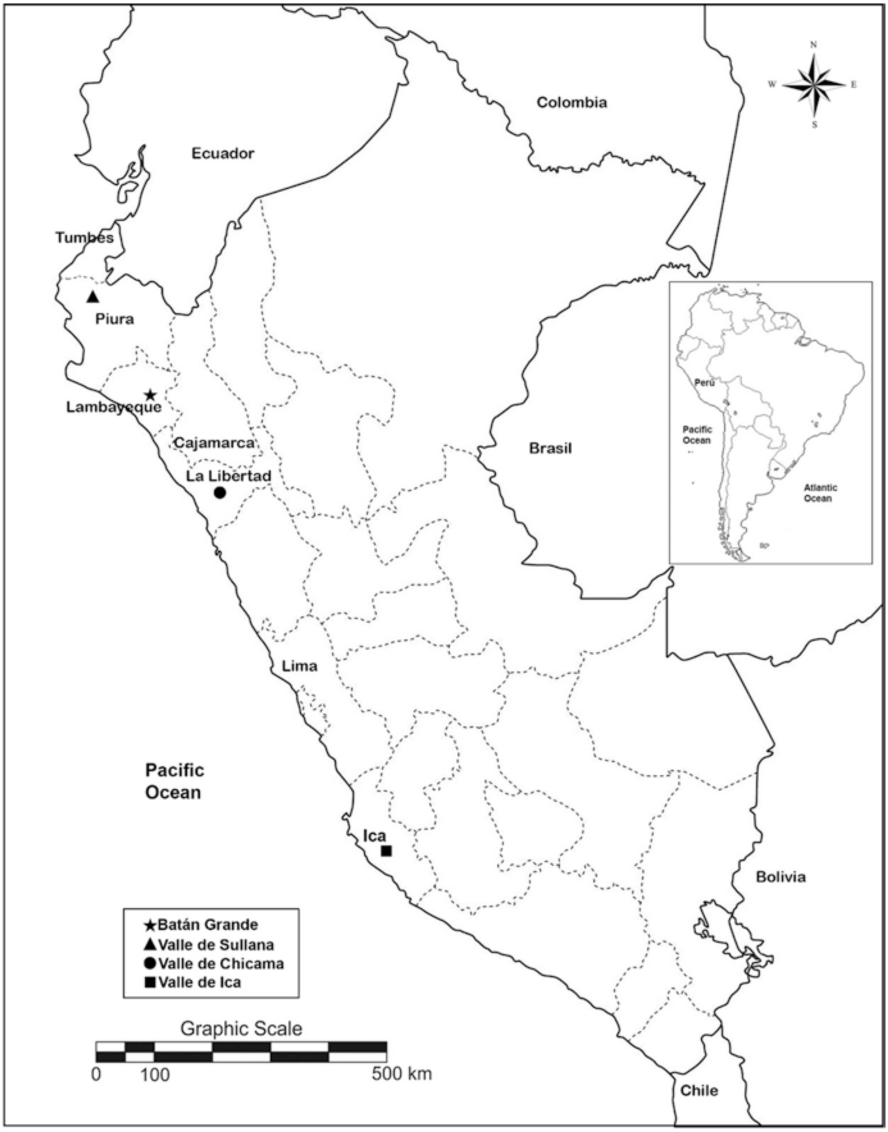
In the research presented in this chapter, antimony beads were identified using several analytical techniques, such as scanning electron microscopy with EDS (SEM-EDS), X-ray fluorescence (XRF), and X-ray diffraction (XRD), in order to determine their mineralogical and elemental chemical compositions.

In addition, the mines located at the Batán Grande Archaeological Reserve were surveyed to identify the site from which the mineral had been exploited. This was done performing XRD analyses of the mineral samples collected at the Barranco Colorado and Cerro Mellizo mines, and comparing the results with those from the beads found in funerary contexts. Based on these analyses, similar mineralogy was identified (with respect to minerals containing Sb) in the beads and the minerals extracted from mines, which may link them to local sources. This is in contrast to the many Sicán luxury and exotic funerary goods that were obtained from farther sources and locations, such as *Spondylus* sp., amber or cinnabar. This could indicate that source exploited for antimony was nearer to the site of research rather than to neighboring regions.

Geographical Location and Provenance

The Sicán culture, also known as the Lambayeque culture, has been studied by I. Shimada for over 40 years. This culture developed on the North Coast of Peru in the Lambayeque region about 700 km to the north of Lima. Its political, economic, and religious center was Batán Grande, at the Pomac Historical Sanctuary, in the middle valley of La Leche. The Sicán culture was not limited to this area, but also extended to the north up to Sullana (Piura) and to the south down to the Chicama Valley (Trujillo); furthermore, its sphere of cultural influence reached Ecuador and Columbia to the north, and the Ica Valley on the South Coast of Peru [13] (Map 13.1).

This culture is divided into three periods. The Early Sicán period (800–900 CE) developed due to the agricultural capacity of the Lambayeque region, joined with the cultural antecedents of the northern Moche culture and the inclusion of religious concepts from the Wari culture. During the Middle Sicán period (900–1100 CE), political and economic connections were established between



Map 13.1 Territory of influence of the Sicán culture. (Map created by L. Vetter)

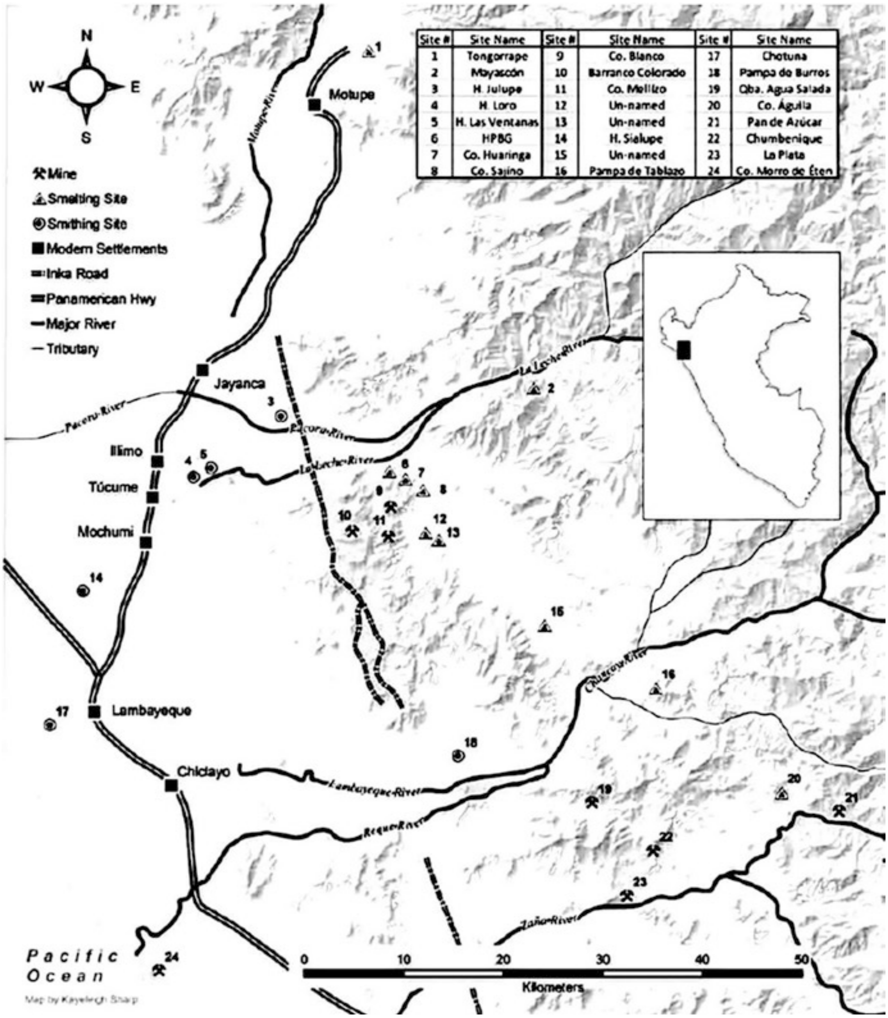
Cajamarca and Batán Grande. At that time, the Lambayeque area would receive pilgrimages from Cajamarca with intense trade between the two areas. In addition, a trade network with Ecuador and Colombia to the north and the Amazon to the east was established, guaranteeing the obtainment of prestige items (*Spondylus sp.*, *Conus sp.*, amber, emeralds, feathers, and other valuable objects), which were exchanged for agricultural and metallurgical products, the latter of which became very important as Sicán developed manufacture of arsenical bronze objects at an industrial scale. An important characteristic of the culture is its burials with large quantities of funerary goods, such as ceramics, metal objects (gold, silver, copper, arsenical bronze, *tumbaga*), textiles, shell, semi-precious and precious stones, and wood objects; tombs of up to 20 m deep have been excavated, containing over a ton of offerings accompanying the main individual. Cinnabar (mercury sulfide) has been found in the tombs of the elite in association with metal objects such as the famous Sicán mask; this pigment has been found in funerary contexts since the Formative. It is important to note that around 20 adobe pyramids are found at Batán Grande, such as Botija, Colorada, Ingenieros, Huaca Loro (or El Oro), Merced, Sontillo, Abejas, Ventanas, Rodillona, Facho, Cholote, Arena, and Corte, among others. For all these reasons, the prestige and reputation of Batán Grande as a religious and funerary center were established. The beads studied in this research came from this apogee of the Sicán culture and were excavated in some of the impressive tombs mentioned above [13].

In approximately 1100 CE (Late Sicán period), many of the religious and funerary spaces of Batán Grande were abandoned, with the new center of power moving to Túcume. By the year 1375 CE, the Sicán's era ended when the Chimú Kingdom, with its base at Chan-Chan, conquered the Lambayeque region [13].

Mineral and metallurgical development was an important part of the Sicán culture, allowing for a great accumulation of objects made from metal and semi-precious stones, which have been found as funerary offerings. Shimada and Craig have done research on the organization of mining and metallurgy during the Middle and Late Sicán periods, which revealed the integral nature of local mining and autochthonous production of arsenical copper at nearby foundries (see Map 13.2). The samples of minerals, products, and by-products of smelting analyzed by the researchers were obtained from local mines and production centers. These analyses showed how the alloys of arsenical copper were designed and smelted locally, and the arsenic was derived from scorodite (arsenopyrite oxide) and/or eroded sulfurous minerals available close to the surface of the local mines [14]. Based on this information, and knowing that in Peru, antimony is found in association with arsenic and copper minerals, alloys which allow for the determination of provenance, we proceeded to investigate the local mines to find the possible source of antimony deposited as beads from necklaces and pectoral ornaments in some Middle Sicán tombs.

Antimony Beads

The antimony beads analyzed here were part of necklaces and pectoral ornaments found in two tombs belonging to the Sicán elite. They were excavated at Huaca Loro and Huaca Las Ventanas in different years.



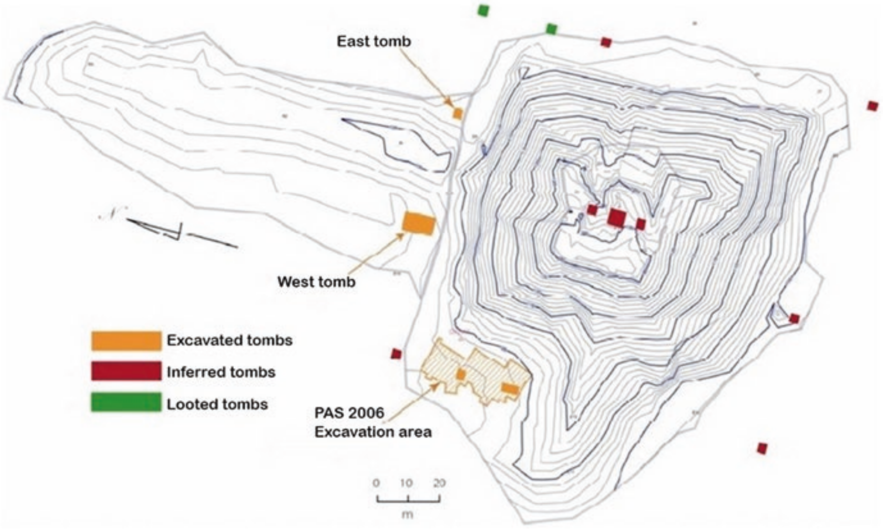
Site #	Site Name	Site #	Site Name	Site #	Site Name
1	Tongorrape	9	Co. Blanco	17	Chotuna
2	Mayascón	10	Barranco Colorado	18	Pampa do Burros
3	H. Julupe	11	Co. Mellizo	19	Qba. Agua Salada
4	H. Loro	12	Un-named	20	Co. Águila
5	H. Las Ventanas	13	Un-named	21	Pan de Azúcar
6	HPBG	14	H. Sialupe	22	Chumbenique
7	Co. Huaringa	15	Un-named	23	La Plata
8	Co. Sajino	16	Pampa de Tablazo	24	Co. Morro de Éten

Map 13.2 Area of study indicating the locations of the mines, foundries, associated roads, and the *huacas.* (Taken from [14])

Context of the Pectoral Ornament from Huaca Loro

The pectoral ornament from the Huaca Loro tomb was found next to two other pectoral ornaments made from different materials, such as semi-precious stones and mollusk shells, and arranged one above the other.

All of these objects were removed from the tomb as a single block of excavated earth for conservation reasons and in order to prevent them from being damaged (Plan 13.1).



Plan 13.1 Location of the intact cemetery where the excavation was carried out in 2006. (Taken from [11])

The block of earth with the pectoral ornament and necklace came from excavations carried out in 2006 by the Sicán Archaeological Project, co-directed by Dr. Izumi Shimada and Dr. Carlos Elera. This project was carried out in order to obtain information about an intact cemetery from the Middle Sicán period (900–1100 AD), excavated for the first time at the northeast base of the monumental temple of Huaca Loro. Tomb 12, which contained one of the pectoral ornaments with antimony beads, did not contain an individual, but it did have a semicircular niche used as a deposit for valuable offerings. The information recovered suggested the predominance of high status or elite women, showing the importance of women in this northern society.

According to Shimada and Elera, "two sets of offerings containing only luxury objects were discovered in two quadrangular graves, each with a niche. Moreover, a rectangular grave was found containing 70 fine ceramic vessels, among other offerings, but lacking human remains." It is precisely in West Cemetery Burial 12 (lacking human remains) where the pectoral ornaments and necklaces that are analyzed in this study were found (Figs. 13.4, 13.5, and 13.6). Furthermore, the excavators pointed out that "next to the east side of the pectoral ornament, in the eastern edge of the niche, there is a large greenish cluster of corroded 'metallic chips' (copper alloys), approximately 45 cm long (N-S), 18 cm wide and over 16 cm high; and towards the southwest corner of the niche, there is some black pottery. To the west of the pectoral ornament there are small deposits of different-colored pigments (such as white, pink, red, yellow, and orange) and some golden copper wires. Almost 30 cm below the pectoral there is a set of rusted metal objects, four rattle-type cups (copper and silver alloy, and copper, gold and silver alloy), a cylindrical golden copper crown and a golden mask" [11].

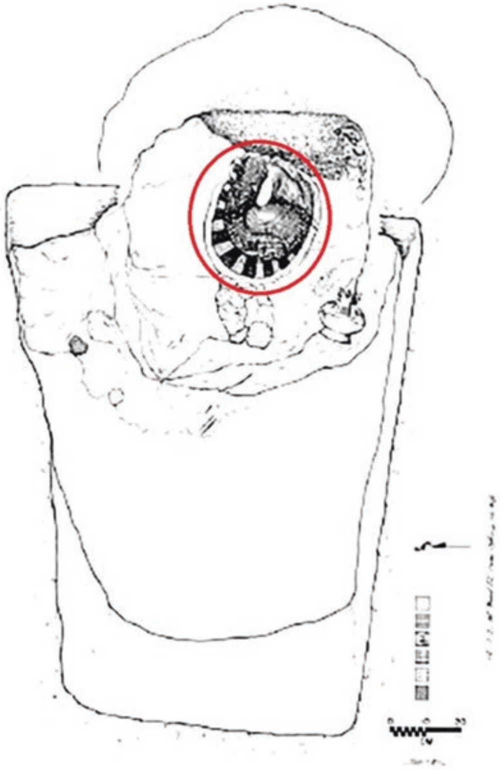


Fig. 13.4 Burial 12, Huaca Loro. Block of earth with pectoral ornaments associated with the burial can be observed. (Taken from [11])

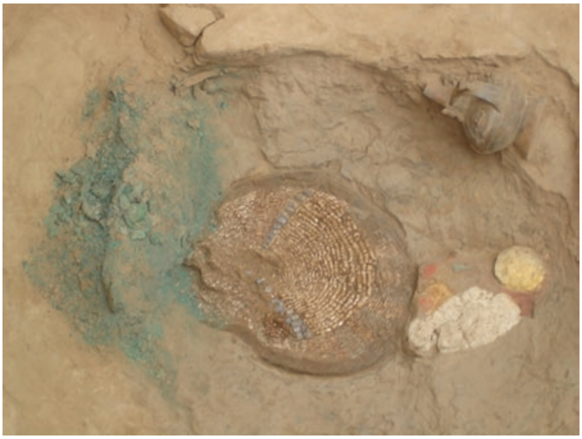


Fig. 13.5 Block of earth with pectoral ornaments made from beads of different materials, including antimony. Located inside the tomb of Burial 12. (Photo provided by the Sicán National Museum)

Fig. 13.6 Conserved pectoral ornament of beads made from antimony from Burial 12. (Photo by J. Carneiro)

Context of the Necklace from Huaca Las Ventanas

The other object was excavated as part of an archaeological rescue project at Huaca Las Ventanas in 2007 by Dr. Carlos Elera. At this site, a necklace was found as part of Burial 35, which was located on the river bank in the southern sector of the monumental zone. This funerary context was discovered on the northern bank of the La Leche River, which was reinforced with large rocks to prevent river erosion and flooding in rainy seasons. Burial 35 contained a 7- or 8-year-old child placed on his or her back and with both arms spread out. This child was holding small packets of copper feathers in each hand. In addition, the child was accompanied by various funerary offerings such as a *tumbaga* alloy mask adorned with cinnabar paint, light blue feathers, copper feathers, Huaco Rey-type (Sicán Deity) ceramic vessels, a set of unfired clay miniatures representing characters and funerary masks, a golden copper knife, and the necklace, which was found around the neck. According to the report provided by the Sicán National Museum, this burial shows evidence of having been revisited, since most of the offerings were not found in their original positions. Some of the fragments of offerings placed next to the body were even found several meters above it. As for the necklace, since it was found around the neck of the child it could be removed *in situ* [12] (Figs. 13.7 and 13.8).

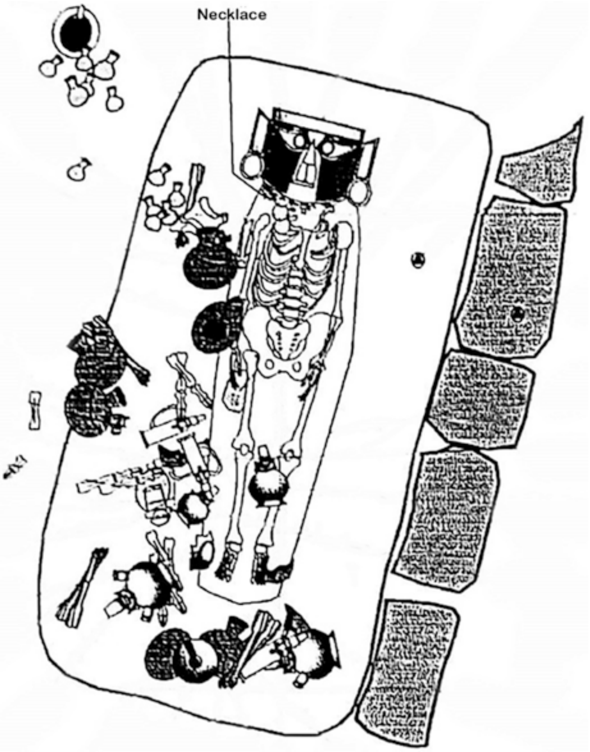


Fig. 13.7 Burial 35 (child). Huaca Las Ventanas. (Taken from [12])

Fig. 13.8 Child's necklace. Huaca Las Ventanas. (Photo provided by the Sicán National Museum)

Analytical Techniques

Three analytical techniques were applied to study the samples: scanning electron microscopy, X-ray diffraction, and X-ray fluorescence.

Scanning Electron Microscopy (SEM)

A Jeol scanning electron microscope, ITSM 300 model JSM-IT300ITSM with: accelerating voltage 0.3–30 kV; resolution (HV) 3.0 nm (30 kV) 15.0 nm (1 kV); resolution (LV) 4.0 nm (30 kV) BED; magnification ×5 to ×300,000; probe current 1 pA to 1 uA or more; maximum sample diameter: 200 mm; maximum sample height: 100 mm; eucentric stage with 5 axes, *X*/*Y*/*Z* (mm) 125/100/80, tilt (degrees) −10 to 90, rotation (degrees) 360; secondary electron detectors (SED) and low vacuum secondary electron detector (LVSED), and backscattered electron detectors (BED). OXFORD EDS detector: LK-AESTDP20 AZTEC ENERGY STANDARD MICROANALYSIS SYSTEM, X-MAX 20 AZtecEnergy Standard Microanalysis System with X-MaxN 20. Large Area Analytical Silicon Drift Detector, X-MaxN 20 SDD detector with PentaFET Precision 20 mm^2 active area. Resolution guaranteed on Mn K 127 eV at 50,000 cps. Includes SATW window for detection of elements from Beryllium WDS: LK-IW500/int. INCA WAVE 500i WDX SYSTEM. A fully focusing wavelength dispersive X-ray spectrometer system for analysis of all elements down to boron ($z = 5$), integrated into the Inca Energy SEM EDS system y EBSD: LK-NORMAXADVINT HKL NORDLYS-MAX EBSD INTEGRATED WITH AZTEC EDS.

X-Ray Fluorescence (XRF)

A portable Olympus computer (Professional Delta model) was used, including an alloy and metal analyzer. Excitation source: X-Ray Pipe of 40 kV, 4 W, 200 uA, Rh Anode, SDD Detector, Service Temperature: −10 to 50 °C. A portable AMPTEK XR-100CR model was used, with an Ag tube, solid state detector with Si crystal and 2048 channel analyzer. The calibration of the equipment was determined with the reference material NIST_ SMR 2709.

X-Ray Diffraction (XRD)

Measurements were carried out with a BRUKER X-ray diffractometer, D4-Endeavor model, at 40 kV, 40 mA, with Cu-Kα radiation (Kα1: 1.54060 Å and Kα2: 1.54439 Å), and Ni filter for radiation Kβ; under a measuring range from 5 to 70° (2theta), angular pitch of 0.02° and a count time of 2 s/step. Approximately 500 mg of powdered sample was used. In order to identify mineralogical phases, the ICDD PDF2 2012 database was used, and phase quantification was performed using the Rietveld refinement method [15, pp. 524–544]. As a previous stage to the measurement, the instrumental verification of the equipment was carried out with control of the position and relative intensity parameters of the peaks of the reference material NIST_SMR1976.

Results

Huaca Las Ventanas

A total of four beads were analyzed by MEB-EDX (Fig. 13.9a, b). From the analyses, it is clear that these beads were designed with precision, despite their small size (internal diameter approximately 1 mm and external diameter approximately 3 mm). Figure 13.10 shows the image obtained by SEM. Table 13.4 describes the results of point chemical analyses, which reveal a high antimony (Sb) content, followed by oxygen (O), a low silicon (Si) content, and, in some areas (presenting reddish color), mercury (Hg).

In order to analyze the internal composition of the bead, it was cut along its transverse axis. Figure 13.5 shows that the interior consists only of native Sb (Fig. 13.11a), while a scan of the external area reveals Sb oxide distributed across the entire area (Fig. 13.11b).

A total of three beads were analyzed by X-ray fluorescence. The quantitative results show a very similar composition to the one obtained by SEM-EDX trials. However, there are some differences, such as the presence of lead (Pb), copper (Cu), and iron (Fe). In one region of Bead 1 (Fig. 13.12a), high content of Pb and Sb was recorded, as well as Cu and Fe in smaller concentrations. In Bead 2 (Fig. 13.12b), the major component is Sb, while Hg, Cu, and Fe appear as minor components. Bead 3 presents Sb as a major component and Hg, Pb, Cu, and Fe as minor components. Figure 13.12a and b shows the XRF spectra obtained from the point analyses of Beads 1 and 2.

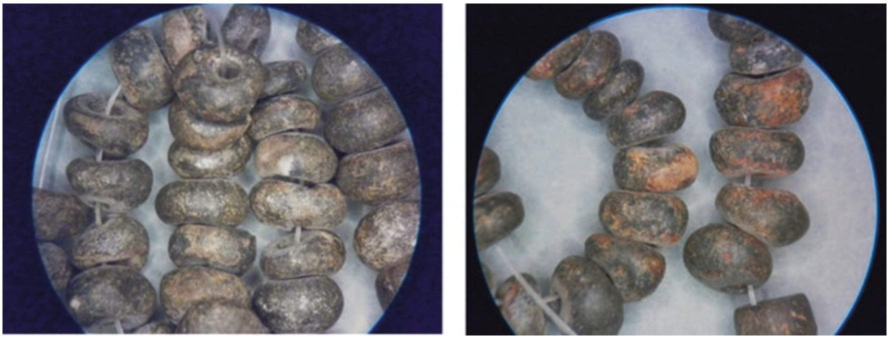


Fig. 13.9 (**a**, **b**) Beads from the child's necklace under stereoscope. In (**b**), it can be noted that some of the beads have spots of red pigment. (Photos by J. Carneiro)

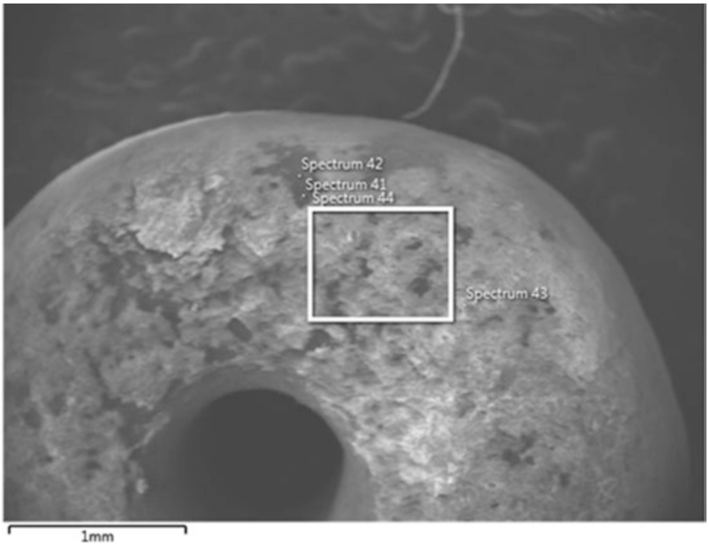


Fig. 13.10 SEM image of Bead 1, Huaca Las Ventanas. Burial 35. (J. Ruiz)

Table 13.4 Chemical composition obtained from EDX point analysis for Huaca Las Ventanas and Huaca Loro beads

			Chemical composition (%)			
Sample	Sb	Si	O	Hg	Fe	Ca
Huaca	75.8	3.8	20.4			
Las Ventanas	75.7	2.8	19.1	2.4		
Huaca	72.4	6.6			1.5	16.4
Loro	82.2				1.7	16.1

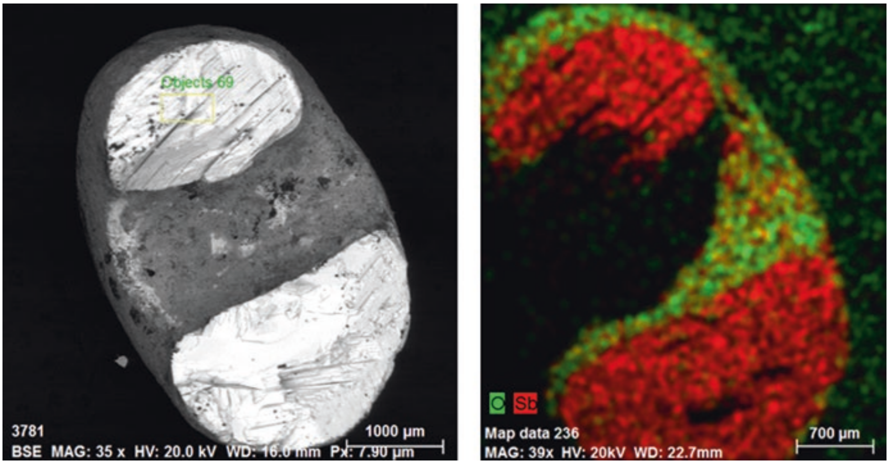


Fig. 13.11 (**a**, **b**) Image of a transverse cut of Huaca Las Ventanas bead and its chemical area analysis by EDX. (BIZALAB)

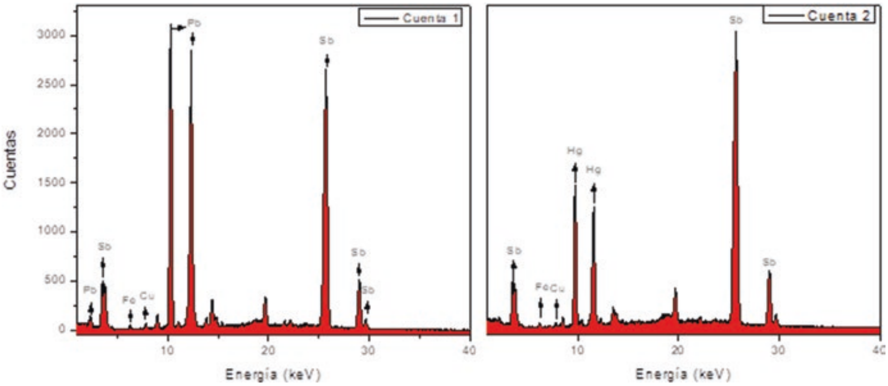


Fig. 13.12 (**a**, **b**) XRF spectra for Beads 1 (left) and 2 (right) from Huaca Las Ventanas, with respective detected elements. (BIZALAB)

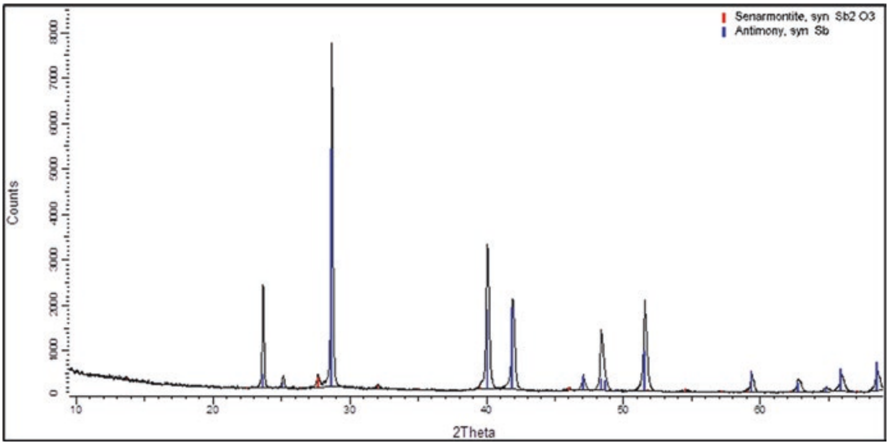


Fig. 13.13 X-ray diffractogram of the Huaca Las Ventanas beads, with identified mineral phases (BIZALAB)

XRD results are shown in Fig. 13.13. The analysis identified two crystalline phases: native antimony and senarmontite (Sb oxide). Table 13.5 summarizes the mineralogical analysis obtained for the beads.

Huaca Loro

Only two beads were analyzed by SEM-EDX (Fig. 13.14). The images reveal the poor state of preservation of the beads, unlike the Huaca Las Ventanas samples (the images show parts of the beads with Paraloid B-72 resin applied in places). The point analyses of the beads show a high content of Sb, followed by calcium (Ca), as

Table 13.5 XRD mineralogical result for Huaca Las Ventanas and Huaca Loro beads

Sample	Identified mineral	General formula	Approximate result (%)
Huaca Las Ventanas	Antimony	Sb	96
	Senarmontite	Sb_2O_3	3
Huaca Loro	Stibiconite	$Sb_3O_6(OH)$	55
	Senarmontite	Sb_2O_3	34
	Quartz	SiO_2	5
	Antimony	Sb	4

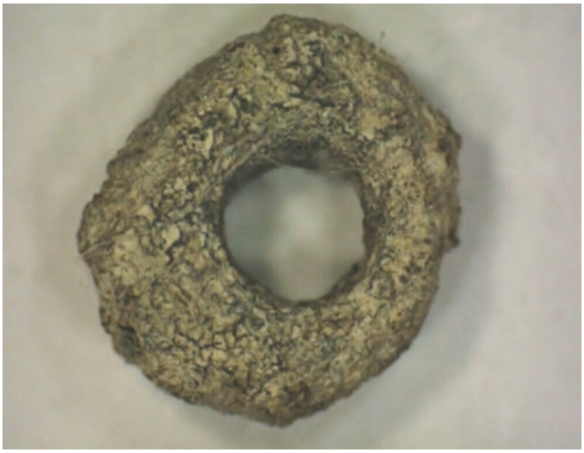


Fig. 13.14 Bead from Pectoral Ornament 2 seen in stereoscope. (Photo by J. Carneiro)

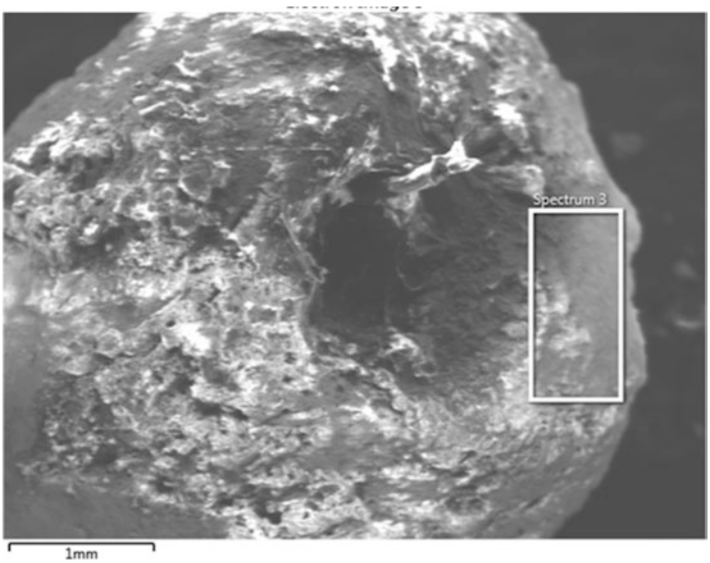


Fig. 13.15 SEM image of one of the Huaca Loro beads. (J. Ruiz)

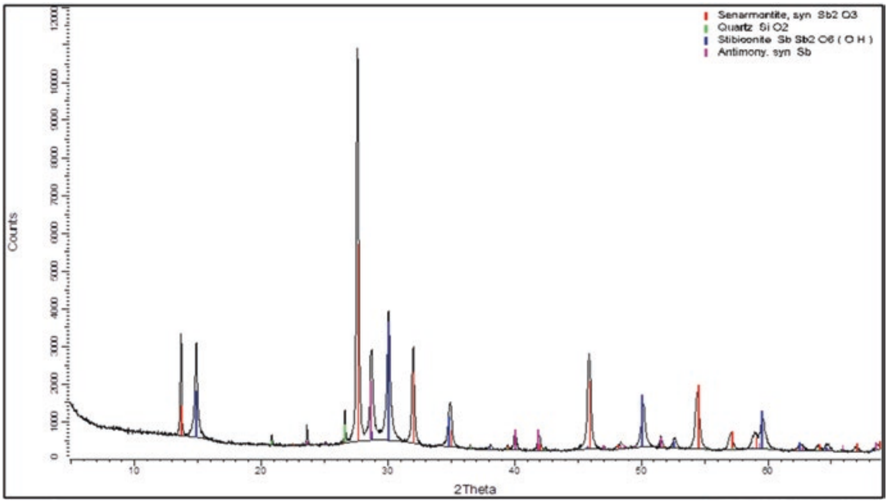


Fig. 13.16 X-ray diffractogram of Huaca Loro beads, with mineral phases identified. (BIZALAB)

well as a low content of Si and Fe. Figure 13.15 shows the image obtained by SEM, while the EDX elemental point analyses are summarized in Table 13.4.

The XRF analysis was performed on the powdered sample, which was prepared after the XRD tests were completed. The quantitative result shows a very similar composition to that of the Huaca Las Ventanas beads, with a majority presence of Sb and minority presence of Fe, Pb, Cu, Hg, and Ag.

The XRD analysis results shown in Fig. 13.16 for the Huaca Loro beads show two types of Sb oxides (stibiconite and senarmontite) as major compounds and, in lower concentrations, native antimony and quartz. Table 13.5 shows the percentages obtained for each of the phases identified.

In Search of the Antimony Source

To achieve a better understanding of the use and importance of antimony in Middle Sicán culture and funerary rites, in March of 2017 we decided to look for possible sources of this non-metallic mineral. To these ends, we went to the Mining and Metallurgical Geological Institute (INGEMMET by its Spanish acronym) to look for the location of antimony mines in our area of study, i.e., the Batán Grande National Historic Sanctuary. We located the Barranco Colorado mine and inspected it with a geologist, Daniel Plasencia, as well as the Sicán National Museum team. The mine is located at 647444 E, 9274134 S, at 331 m above sea level, very close to the Doña Celinda mine, where the presence of Sb minerals has also been documented. Upon arriving at the Barranco Colorado mine, we found that the entrance was partially destroyed; however, this obstacle did not prevent us from collecting

Fig. 13.17 Satellite image of expedition route (L1), showing the path taken up to the pit and sampling place (L9 a)

samples. Figure 13.17 is a satellite image showing the route of the expedition up to the pit and the sampling place.

Eight samples of minerals were taken from different points near the mine, all of which were analyzed by XRD in order to determine their composition. Figure 13.18 shows the pit from which samples for analysis were obtained.

XRD results show different mineralogical contents for the eight samples. However, it should be pointed out that two of the samples revealed Sb minerals, although in low concentrations: senarmontite (Sb_2O_3) and stibnite (Sb_2S_3). Table 13.6 summarizes the mineralogy found in the Barranco Colorado samples.

After reviewing the results obtained by XRD from the mineral samples collected at the Cerro Barranco Colorado mine, in July 2019 we decided to carry out a new prospection at another mine and possible source of antimony mineral deposits. Thus, we carried out a bibliographic search to locate mines exploited for antimony minerals in pre-Columbian times that had been prospected by archaeologists and geologists. Shimada and Craig identified the Cerro Mellizo mine, where they found malachite, arsenopyrite, and scorodite [14]. This mine is located to the south of the Cerro Blanco mine (6°33′39.39″ S, 79°39′34.74″ W; elevation approx. 420–480 masl). At the Cerro Mellizo mine, we collected samples from four shafts (Figs. 13.19, 13.20, 13.21, and 13.22), which were analyzed by XRD; the results are shown in Table 13.7.

Fig. 13.18 Image of pit at Barranco Colorado Mine from which samples were obtained. (Photo by L. Vetter)

Table 13.6 Summary of phases identified in Barranco Colorado samples

Sample	Mineralogical composition
1	Quartz, jarosite, goethite, K-Na feldspar, and clays
2	Quartz, K-Na feldspar, and clays
3	Quartz, jarosite, goethite, senarmontite, hedenbergite, and hematite
4	Quartz and dravite
5	Quartz and dravite
6	Biotite, magnetite, antigorite, and stibnite
7	Quartz, magnetite, calcite, chlorite, forsterite, apatite, and calcite
8	Magnetite, goethite, chlorite, and clay

Fig. 13.19 Shaft 2 at Cerro Mellizo. (Photo by L. Vetter)

Fig. 13.20 Shaft 3 at Cerro Mellizo. (Photo by L. Vetter)

Fig. 13.21 Sample collected from Shaft 2. (Photo by L. Vetter)

Fig. 13.22 Sample collected from Shaft 3. (Photo by L. Vetter)

Discussion

The results of our analyses indicate that the beads from both tombs have an antimony content greater than 75%. Silicon is found in both groups, whereas calcium, iron, copper, and mercury are minor elements that differentiate them. The Huaca

Table 13.7 Summary of the minerals identified in the Cerro Mellizo samples

Name of mineral	General formula	Approximate result (%)
Sample shaft 1		
Scorodite	$Fe(AsO_4)(H_2O)_2$	54
Arsenopyrite	FeAsS	20
Quartz	SiO_2	18
Jarosite	$KFe_3(SO_4)_2(OH)_6$	3
Mica (muscovite)	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	2
Cast	$CaSO_4 \cdot 2(H_2O)$	<L.D.
Sample shaft 2		
Quartz	SiO_2	37
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	28
Arsenopyrite	FeAsS	22
Chalcopyrite	$CuFeS_2$	10
Mica (muscovite)	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	<L.D.
Sample shaft 3		
Quartz	SiO_2	50
Arsenopyrite	FeAsS	18
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	20
Mica (muscovite)	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	5
Chalcopyrite	$CuFeS_2$	5
Sample Shaft 4		
Scorodite	$Fe(AsO_4)(H_2O)_2$	70
Quartz	SiO_2	17
Chalcanthite	$Cu(SO_4) \cdot 5(H_2O)$	6
Jarosite	$KFe_3(SO_4)_2(OH)_6$	4
Cast	$CaSO_4 \cdot 2(H_2O)$	<L.D.

Las Ventanas beads are the ones with the higher percentage of native antimony.

On the one hand, results from SEM-EDX and XRF show a high Sb content. These results are complemented by the phases identified by XRD, identifying antimony oxide and native antimony. On the other hand, no Sb sulfides have been identified (such as stibnite, Sb_2S_3), which are among the most common minerals in Peru. Sb oxides are products of the alteration of stibnite, with the most common being stibiconite, which is often observed covering stibnite. According to INGEMMET [16, p. 102] the Doña Celinda mine located in Chiclayo, Lambayeque, Batán Grande, at 652015E 9272103S, is characterized by ore consisting of galena and stibnite, among other minerals. There, the antimony percentage is estimated at 12%.

The mineralogy of the samples collected at the Barranco Colorado and Cerro Mellizo mines does not directly correspond to that of the beads studied. However, some antimony minerals were found. Thus, it cannot be ruled out that there may be other areas with antimony minerals similar to those found in the beads analyzed here.

Regarding the red pigment found on the beads from Huaca Las Ventanas, it was determined to be mercury, which could be cinnabar (mercury sulfide), taking into account the ancient Peruvians' custom of depositing this mineral in tombs. However, due to the small quantity of the red pigment found on the beads, it was impossible to carry out an XRD analysis to determine for certain if it is mercury sulfide.

Published sources regarding antimony mineral deposits in Peru are quite limited. Nevertheless, based on a review of Raimondi's studies, we can say that the elements that appear along with antimony in the Huaca Loro and Huaca Las Ventanas beads are consistent with the items studied by this illustrious Italian scholar.

From a historical intellectual point of view, Raimondi states that antimony is a constant companion of metallic ores. For this reason, he infers, antimony combinations are very abundant. Furthermore, he notes that native antimony can be found, though this form is scarce. He mentions that sulfur and stibnite can be found in different areas of Peru, although they are known simply as antimony, and that there are a few combinations of antimony with silver and arsenic [17, p. 171]. However, in our research we have not been able to find this combination.

The Italian researcher also mentions that double sulfides of antimony and lead, such as jamesonite, zinkenite, boulangerite, etc., are abundant antimony ores; these have not been found in our research. It is important to highlight Raimondi's statements about a mineral that is rare in Europe but common in Peru, called stiblite or antimony oxide antimoniate, which can be found together with stibnite. Oxidation of antimony in stibnite turns into antimony oxide and antimonic acid, which combine and give rise to this mineral. The author mentions a location known as Chayramonte, in the province of Cajamarca, where large pieces of stiblite can be found, still containing the fibrous structure of stibnite. This place is called Hueso de Muerto (Dead Man's Bone) [17, p. 172].

Raimondi also mentioned that the transformation of stibnite (antimony sulfide) into stiblite (antimony oxide antimoniate) is neither the result of the action of external agents, in which all the sulfur in the stibnite is eliminated, nor the work of natural calcination. Instead, the data seem to indicate that this mineral was formed by the great oxidation phenomenon that took place in Peru during the volcanic period [17, pp. 171–172].

Recent studies on the mechanism and kinetics of stibnite show that oxidation of stibnite (Sb_2S_3) is completed at temperatures between 300 and 500 °C. Between 700 and 1000 °C, stibnite oxidation results in the sequential formation of Sb_2O_3 with its partial volatilization, leaving a trace of SbO_2, while above 1000 °C, stibnite oxidizes to form Sb_2S_3, which then decomposes to form metallic antimony [18, pp. 32–49].

In Peru, there is still no archaeological or archaeometric interest in studying the diverse types of materials, minerals, and precious and semi-precious stones found in the form of beads from necklaces and pectoral ornaments and embedded in wooden objects, ceramics, and metals. As a consequence, comparative mineralogical information is extremely scarce. Furthermore, there is little information regarding the technology used for the manufacture of these objects, since no instruments have been found that could provide insight into whether these beads were produced in the area or brought from other regions to be placed in the tombs.

Future work must emphasize the importance of studying metal and rock collections in museum collections to identify possible manufacturing instruments. A similar study, whose approach and methods can be applied and emulated to these ends, was Carcedo's [19] research that successfully identified lithic, metallic, and wooden goldsmithing instruments used in the manufacture and decoration of metal objects.

Another set of questions must address why the Sicán people used antimony at all. What did they see in this mineral, which currently is not considered a precious or semi-precious stone, that they would use it to make luxury objects used only by their elite? An a priori could be that antimony has a metallic shine that could have enhanced ancient lapidaries by its perceived beauty. Due to the oxidation from the burial environment in which they were found, today it is not possible to observe the original shine these objects once had.

Conclusions

The beads from both huacas have high antimony contents and, according to mineralogical compositions determined by XRD assays, this appears mainly in the form of native antimony and oxide (senarmontite and stibiconite). It should be noted that the Huaca Las Ventanas beads have a higher native antimony content than the Huaca Loro ones, in which more than one antimony oxide mineral were found.

According to the results of SEM studies of the Huaca Las Ventanas beads, their interiors consist of native Sb, and their exteriors are antimony oxide. Thus, we can infer that the Sb oxide may have been formed as part of an oxidation process involving the native Sb, with the latter being the main material for the production of the beads. In the case of the Huaca Loro beads, a more intense oxidation was observed, which gave rise to other Sb oxides, such as stibiconite. This can be seen reflected in the state of conservation of these beads.

From the results obtained by XRD for the samples collected at the Barranco Colorado Mine, we can determine that there was a local source for some antimony minerals, such as senarmontite and stibnite. From the samples from Cerro Mellizo, we found tetrahedrite, which is an antimony sulfide of iron and copper. This mineral was not found in the beads. However, this information suggests the presence of antimony sources in the area, which is close to the *huacas*, as has been documented by other sources.

According to research on the Sicán culture, there is no other evidence to indicate the use of antimony as a luxury object. The same can be said about the rest of the pre-Columbian Peruvian cultures, as it is not present in the existing bibliography. As for ancient societies in other parts of the world, such as Europe, the bibliography is also extremely scarce.

Perhaps the inexistence of other objects or necklace beads made from antimony in ancient Peru could be explained by a confusion in the identification of objects made from antimony with those made from lead, since up till the present these are the first objects identified as being made from antimony within the pre-Hispanic cultures of Peru.

It is well known, and has been the focus of studies, that in the Sicán culture, antimony in trace amounts in some minerals and replacing arsenic in others, and that the alloy Cu-As is distinctive of our area of study. However, in the absence of other evidence indicating the use of antimony, the present study and identification of this element has allowed us to provide new knowledge on the manufacture of beads for luxury objects in Sicán culture.

It remains for future research to continue investigating and touring the mines of the Pomac Forest to find the deposit of native antimony and antimony minerals (stibiconite and senarmontite) from which the beads of these luxury objects were made. In addition, analyses with radioisotope techniques to determine the origin of the mineral used, for example, lead, are a pending possibility, as they are a new trend in archaeology and paleontology.

Acknowledgments We would like to offer a special thanks to Carlos Elera, Director of the Sicán National Museum, for providing the antimony beads for the archaeometric study; to Izumi Shimada, Director of the Sicán Archaeological Project, for providing us with his accurate comments; to geologists Daniel Plasencia and Charly Asto, and architect Saúl Castro Racchumí for their contributions and for guiding us, along with the team of museum workers, especially Henry Diaz, to the Cerro Barranco Colorado and Cerro Mellizo mines to obtain the antimony mineral samples that were analyzed in this study.

References

1. de Onofri, R.G.: Impressionism in Argentina. Inca Editorial, Mendoza (1996)
2. Canal Encuentro TDA Argentina, Huellas del Arte argentino: Fernando Fader I y II, Canal Educativo y cultural del Sistema Federal de Medios y contenidos públicos, Abril (2012)
3. Gutiérrez, I.Z.: Fader, 1st ed. Editorial Zurbarán (1993)
4. Mantler, M., Schneider, M.: X-ray fluorescence spectrometry in art and archeology. X-Ray Spectron. **29**, 3–17 (2001)
5. Lindgren, E.: X-Ray spectrom. In: Guest (ed.) Special Millennium Issue on Cultural Heritage, vol. 29, No. 1 (2000)
6. Doménech-Carbó, M.: Principios físico-químicos de los materiales integrantes de los bienes culturales. Universitat Politècnica de València (2013)
7. Mendoza, A., et al.: Identificación de pigmentos y obtención de un modelo cuantitativo para la atribución de pinturas artísticas por fluorescencia de rayos x portátil. Revista Cubana de Física, pp. 46–51 (2011)
8. Montgomery, E.: Probability and Statistics applied to engineering, Chap. 8, pp. 370–390. Limusa Edition, Mexico (2006)
9. Klockenkämper, R., et al.: Analytical characterization of artists pigments used in old and modern paintings by total-reflection X-ray fluorescence. Spectrochim. Acta. **48B**(2), 239–246 (1993)
10. Arechaga, C.: Editorial Note from The Freedom Newspaper Editorial, 11 May 1935
11. Shimada, I., Elera, C.: Informe sobre los trabajos arqueológicos desarrollados por el Proyecto Arqueológico Sicán, Temporada 2006, presentado al Instituto Nacional de Cultura. Lima, Perú (2006)

12. Elera, C., Pinilla, J.: Informe sobre el Proyecto de Puesta en Valor Huaca Las Ventanas, Temporada 2007, presentado al Instituto Nacional de Cultura. Lima, Perú (2007)
13. Shimada, I.: Detrás de la máscara de oro: la cultura Sicán. In: Shimada, I. (ed.) Cultura Sicán: esplendor preincaico de la costa norte, pp. 15–90. Fondo Editorial del Congreso del Perú, Lima (2014)
14. Shimada, I., Craig, A.: The style, technology and organization of Sicán mining and metallurgy, northern Perú: insights from holistic study. Chungara, Revista de Antropología Chilena. **45**(1), 3–31 (2013)
15. Pecharsky, V., Zavalij, P.: Fundamentals of power diffraction and structural characterization of materials. Springer, New York (2009)
16. Wilson, J.: Geología de los cuadrángulos de Jayanca, Inkahuasi, Cutervo, Chiclayo, Chongoyape, Chota, Celendín, Pacasmayo and Chepén. Boletín del Instituto Geológico Minero y Metalúrgico 38. Lima, Perú (1984)
17. Raimondi, A.: Minerales del Perú o catálogo razonado de una colección que representa los principales tipos minerals de la República con muestras de huano y restos de aves que lo han producido. Imprenta del Estado, Lima, Perú (1878)
18. Aracena, A.: Mechanism and oxidation kinetics of enargite (Cu3AsS4) and stibnite (Sb2S3) at high temperatures. Faculty of Engineering - Doctoral Program in Metallurgical Engineering, Universidad de Concepción, Concepción, Chile (2013)
19. Carcedo, P.: Instruments used in the manufacture of metal parts that are found in the museums. In: Lithic and metal, pp. 44–45, 241–270. Boletín Museo del Oro, Bogotá, Colombia (1998)

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P. S. Carrizo (ed.), *Reverse Engineering of Ancient Metals*,
https://doi.org/10.1007/978-3-030-72842-7