EARLY TECHNOLOGIES FOR METAL PRODUCTION IN THE IBERIAN PENINSULA

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Abstract

This paper focuses on the characterization of technological processes used for producing copper, tin-bronze and silver in the Prehistory and Protohistory of the Iberian Peninsula. To this purpose, slags and slaggy materials have been analyzed by optical microscopy (OM) and scanning electron microscopy (SEM-EDS). In particular, the results obtained allow us to characterize the main technological features for smelting copper ores since the 3rd millennium BCE, a process that was performed in simple fire structures by using a non-slagging process. Regarding tin-bronze, the analytical data suggest that prehistoric bronzes were obtained by co-smelting copper and tin oxidic ores or by cementation of copper with cassiterite. Finally, some metallurgical debris dated to the Phoenician time, in the early 1st millennium BCE, points to the extraction of silver from argentiferous copper ores employing a method similar to the 15th century liquation process. This is a unique discovery up to now as this type of materials is unknown in any other Mediterranean region settled by the Phoenicians.

KEYWORDS: Archaeometallurgy, Iberian Peninsula, slags, crucibles, copper, bronze, tin, silver, OM, SEM-EDX

1.0 INTRODUCTION

In the early ‘80s, the Institute of History of the Spanish National Research Council (IH, CSIC) and the National Archaeological Museum (MAN) of Madrid started a pioneer lab-based project with the title “Archaeometallurgy of the Iberian Peninsula” (*Arqueometalurgia de la Península Ibérica*) project, dedicated to the study of ancient metal objects and metallurgical by-products.

Throughout its many years of activity, this still ongoing research has built a large analytical database including mostly prehistoric materials, with a special attention to the study of slags; furthermore, this project produced a large number of scientific publications and PhD dissertations.

Metal production in the Iberian Peninsula had a very early start, with its earliest evidence dating back to the Neolithic period, namely in the first half of 5th millennium BCE (1), when copper begun to be obtained from ores. However, only over thousand years later, copper metallurgy reached maturity and started to spread across the western part of the European peninsula in the cultural period called Chalcolithic that lasted roughly until the 3rd millennium BCE.

As it is well known, slags are key archaeological materials for the investigation of the most relevant technological aspects of metal production. Although archaeological excavations provided a large number of metal objects dated to the 3rd millennium BCE, the amount of slag found is surprisingly small, only a few kilograms. On the contrary, crucible fragments are a quite common finds and, as discussed further on in this paper, they were also used for smelting copper ores. According to Paul T. Craddock (2), those fragments of metallurgical vessels are the remains of a primitive metallurgy based on the use of a non-slagging process that was sufficiently effective for the metal demand of the time.

Up to now, it has not been clearly established when copper-tin alloys make their first appearance in the Iberian Peninsula. Traditionally, the Bronze Age is considered to begin in the late 3rd millennium BCE, coinciding with the Bell-Beaker Horizon. However, so far the only archaeological evidence for bronze production in this period comes from an archaeological site in Catalonia, with a chronology confirmed by radiocarbon dates: La Bauma del Serrat del Pont (Tortellá, Girona) (3). Here, some slagged fragments of crucibles and a few bronze objects were collected but, due to the low tin content of those artefacts, it was suggested that this alloy could have been the result of smelting the mixed copper-tin ores documented in the region (4).

In general, finds of tin are very scarce for the Bronze Age, not only in the Iberian Peninsula, but also in the rest of Europe (5). Sound evidence for ancient tin smelting slags has not been found either. Regarding this current lack of data, we have to bear in mind the general assumption that bronze alloys were made by melting tin and copper metals in a crucible, but archaeological investigations suggest that the technology for making bronzes in ancient Iberia was more complex and varied. In fact, some Iberian Bronze and Iron Age sites excavated in the last fifteen years have provided metallurgical waste that points to the use of tin ores, mainly cassiterite, instead of tin, for producing bronze (6).

Finally, silver started to be used in the Iberian Peninsula since the early 2nd millennium BCE, in the cultural period known as El Argar. Both the composition of the earliest silver objects and the meagre metallurgical remains of its production suggest that native silver and/or chlorargyrite were used at that time. These mineral deposits were an important source of silver in Spain and have been only recently exhausted (7).

Since the 9th century BCE, among other important technological novelties that characterized the beginning of the Iron Age, the Phoenician presence in the Iberian Peninsula led to the exploitation of a peculiar source for silver, the argentiferous jarosite extracted in the large mining area of the Iberian Pyrite Belt, mainly in the Huelva province. To extract silver from those ores, it was necessary to add lead during the smelting process so that it would act as a collector for the noble metal. The typical slags associated to this process for extracting silver, improperly called “free-silica” slags and unknown in other parts of the ancient world, have been a topic of debate since many years. There is a large number of publications dedicated to this type of slags (8, 9, 10), therefore we will not include this discussion.

Our research brought to light interesting evidence that suggest the use in antiquity of a novel method for producing silver by exploiting cupro-argentiferous ores. Copper-silver resources are scarce but their existence did not go unnoticed by late medieval metallurgists, as documented in the works of some scholars such as V. Biringuccio, G. Agricola, L. Ercker and M.A. Della Fratta. According to their description, the method used to extract silver from this type of ores is known as liquation and consists in a smelting process that has a copper-silver *regulus* as final product. Subsequently, this alloy is de-silvered by adding lead and, finally, the resulting argentiferous lead is cupellated to separate the silver. However, although this method might have derived from a technique for refining mostly debased silver known since ancient times (11, 12), there is no clear archaeological evidence for the use of liquation for exploiting silver-rich copper ores.

Yet, recent studies of the metallurgical materials from two Phoenician settlements in Spain, La Fonteta (Alicante) and El Cerro del Villar (Malaga) (13), allowed us the identification of some debris, dated approximately to the 8th century BCE, possibly related to a process for de-silvering argentiferous copper ores, similar to the liquation process described above. This debris consists mainly of copper-lead slags, fragments of cupels rich in copper-lead oxides, and silver droplets containing high impurities of both copper and lead.

2.0 MATERIALS AND METHODS

This study is based on the analyses of ores, slags and fragments of crucibles with a slaggy layer adhering to the inner surface by using scanning electron microscopy (SEM-EDS). This investigation was carried out in two different laboratories: some samples were analyzed at the Interdepartmental Service of Research (*Servicio Interdepartamental de Investigación*) of the Autonomous University of Madrid with a Philips XL30 SEM equipped with an EDAX micro-analyzer DX41 operated by E. Salvador; while some other were examined at the Microscopy Laboratory of the National Museum of Natural Sciences in Madrid by using a FEI Inspect environmental SEM with an Oxford Instruments Analytical-Inca analysis system, operated by L. Tormo and M.M. Furió.

Prior to analysis, the samples were embedded in epoxy resin, ground and polished following the usual method for metallography. A number of samples were also observed under an optical microscope Leica DFC480 DML with digital camera.

2.1 EARLY COPPER SLAGS FROM THE IBERIAN PENINSULA: ANALYSIS AND DISCUSSION

Theoretically, the metallurgical process for a successful smelting of high-quality secondary copper ores, such as carbonates or oxides, does not leave any slaggy debris; every chemical element present in the ore, except copper, forms volatile compounds and the only solid product left is the metal. Nevertheless, in practice ores are rarely pure. They are often formed by association with other minerals, and cupriferous compounds are predominant, but they can also contain iron minerals, manganese, arsenic, antimony, nickel, tin, lead and a long list of other possible accompanying elements. Table 1 shows some examples of ores found in Chalcolithic archaeological contexts. In those samples, iron and arsenic compounds are both quantitatively and qualitatively significant impurities. Moreover, the ores can include portions of host rock, in general quartz and silicates that contribute to the formation, apart from the metal, of other solid debris during the smelting process.

The amount of slags recovered from Chalcolithic metallurgical sites is surprisingly small. On the contrary, fragments of crucibles with a strongly slagged inner surface are relatively abundant. In general, the external wall of these vessels does not present any evidence of being affected by fire (Fig. 1). The chemical and mineralogical composition of the slag adhering to the crucibles walls shows that strong reactions occurred among the charge of the vessel, the ceramic body and the fuel ashes.

The kinetic and the thermodynamics of the formation of such slags have been the focus of recent investigations (14, 15, 16). This is not-in-equilibrium debris, where minerals reached high temperature without coming to a completely liquid state. As a consequence of this viscous texture, partially or fully melted host rocks inclusions can be trapped in the matrix of the slag, resulting in heterogeneous materials where different petrographic phases can coexist. These slags may also retain plenty of copper, both as residual ores and entrapped metal prills. The existence inside the slag of micro-regions in which the melted material tends to equilibrium conditions, suggests that the smelting was performed with quite high firing temperatures, but for a too short period of time to successfully complete the reaction (Fig. 2).

It is not surprising that the composition of the slags resulting from such direct smelting processes of copper ores is closely related to that of the original ores. Therefore, as shown in table 2, the bulk compositions of these slags can be as variable as the mineral resources exploited. The copper retained in the slag can be also very variable, ranging from approximately 8% to 68% CuO. Usually the melted material forming the slag matrix is a complex silica glass with noticeable amounts of metal oxides (Tab. 3), showing significant mineral losses during the metallurgical process that was not fully efficient.

Among the minerals that can form in the slags, a wide range of silicates, such as wollastonite, different types of olivine, plagioclase, pyroxene, feldspar, melilite, spinels, etc. is normally identified. In some occasions, when the mineral charge contains enough iron and the redox conditions in the chamber are suitable, some fayalite crystals can be observed. Their presence indicates the formation of low melting point slag that facilitates a better separation of the metal. These minerals are frequently found in smelting slags from contemporary sites, as for example at Faynan (Jordan), but are less common in crucible slags due to the variability of the reducing/oxidizing episodes within the vessel (16).

The formation of magnetite (see Fig. 2) and delafossite occurs frequently in these very ancient slags. The presence of these minerals gives important insight into the working conditions of the smelting process. In both magnetite and delafossite the iron is in the oxidation state Fe^{+3}, indicating that some oxidizing episodes occurred in the vessel. Moreover, delafossite is stable at temperatures of around 1,150ºC, and this fact provides further information on the thermal pattern of the pyrometallurgical process. Slaggy layers on the smelting crucibles walls show characteristics similar to those of “detached” slags, although the composition can be affected by the reaction of the charge with the components of the ceramic. SEM-EDS studies of sections of the crucibles show quite a wide range of thermal and chemical impact.

The composition of these ancient Iberian slags was plotted on a $CaO\text{-}FeO\text{-}SiO_2$ ternary diagram to observe the variability of the theoretical temperature ranges reached during the metallurgical process (Fig. 3). Interestingly, the diagram shows a dispersion similar to that of the earliest slags from the Near East where, according to Andreas Hauptmann (16, 17), a primitive technology was also used for smelting copper ores in the 4th-3th mill. BCE.

2.2 CHEMICAL AND MINERALOGICAL CHARACTERISTICS OF COPPER-TIN SLAGS: ANALYSIS AND DISCUSSION

Bronze and Iron Age slags from tin smelting have not been found so far, despite the large deposits of cassiterite existing in the north-western part of the Iberian Peninsula and the dispersed mineralizations in other areas. The systematic surveys carried out by Craig Merideth to explore the tin resources available in Iberia (18) did not give any positive results in this regard. Fortunately, the archaeological excavations of the past fifteen years have yielded some finds, mostly dated to the Bronze Age-Iron Age transition period (8th-7th centuries BCE) and to the Iron Age (6th-2nd centuries BCE), which were examined in the laboratory (19). These few finds are copper-tin slags, small in size and characterized by complex mineralogical compositions. Often, unreacted or partially reacted minerals can be observed in the samples, and the material reached a molten state only in limited areas of the slag. Complex silicates are the most common components of the slag matrix that, in general, is a glassy material with variable amounts of copper and tin (Tab. 4). In these pyroxenic slags small globules of the original cassiterite, as well as rhombohedral and acicular crystals of secondary tin oxide can often be identified (Fig. 4). In addition, calcium-tin oxides and calcium-tin silicates have been detected, with compositions of ~30% SiO_2, ~20% CaO, ~50% SnO_2, normally accompanied by wollastonite or other calcium-rich pyroxenes. Such compounds form in calcium-rich areas of the slag during highly oxidizing episodes that cause the reaction of the tin/cassiterite with the clay and the fuel ash, and produce first Ca-Sn oxide and then more complex Ca-Sn compounds. A nucleus of tin oxide is often still visible in these formations (Fig. 5).

A large amount of the tin oxide present in the system is retained in the slag as euhedral needles produced by tin secondary oxidation. Part of the tin obtained by smelting the cassiterite is quickly re-oxidized to SnO_2 crystals. Generally, tin oxide needles have a copper core, preserved because of the deoxidizing power that tin has over copper, when the conditions inside the crucible are not sufficiently reducing (Fig. 6). When iron oxide is present in the system, the often poor reducing conditions in the vessel lead to the formation of delafossite in some samples. These characteristics clearly indicate a process carried out in a crucible heated from above, under a not too thick charcoal layer. When the working conditions are sufficiently reducing and the composition of the ore charge allows it, we observe the formation of some fayalite crystals (Fig. 7). In these cases, silica dissolves and reacts with the iron oxide to form fayalite. Due to their regular morphology, great part of the iron oxide crystals in the samples (partially dissolved in the matrix) can be identified as spinels, suggesting that short alternating reducing-oxidizing episodes occurred during the metallurgical process, providing the oxygen fugacity needed for these reactions.

As those slags could not fully reach the free running temperature, their viscosity was rather high and most of the produced metal was retained in the matrix (see Fig. 7). Interestingly, the composition of the metal trapped in the slags can be very variable. A wide range of compositions, going from pure copper to highly tin-rich prills, is often detected within the same sample (Tab. 5). In general, despite the formation of biphasic tin-rich nodules (see Fig. 6), no pure tin prills are observed; this is probably due to the fact that tin is “collected” by copper (that is predominant in the system) and/or oxidized to secondary needles.

Experiments reproducing co-smelting and cementation processes to make bronze have turned to be a very helpful tool to gain a better understanding of the structure and composition of these archaeometallurgical materials. For example, a co-smelting experiment carried out by using a complex copper ore, with approximately 70% gangue, and almost pure cassiterite, produced the formation of slag and metal with microstructure and composition similar to that of the materials described above (20). As shown in figure 8, in the experimental slags we could identified (Ca,Sn) silicates with tin oxide nucleation in a glassy matrix in which precipitation of wollastonite can be observed.

The cementation of copper with cassiterite to obtain bronze does not produce slag but only a slaggy layer on the inner wall of the crucible as a result of the vitrification of the ceramic components. This slaggy layer can retain part of the crucible charge, as shown in figure 8 in which relics of cassiterite and metal prills are trapped in the glassy matrix. The experimental replication of this method (21) also provided results consistent with the main chemo-physical characteristics of the archaeological samples analyzed so far.

2.3 BY-PRODUCTS OF COPPER-SILVER METALLURGY: ANALYSIS AND DISCUSSION

A peculiar metallurgical process for extracting silver from copper-silver bearing ores was documented so far only in two Iberian Phoenician sites: La Fonteta (Alicante) and Cerro del Villar (Malaga). Copper-lead slags and cupellation debris, characterized by high amounts of copper and lead oxides, are the typical by-products from this process.

The copper-lead slags were found in small fragments of few centimeters in size (4-5 cm); the surface has a grey-greenish color with clayey concretions and patches of copper-salts. In general, in the cut section, with compact texture and dark greenish color, metal prills are visible to the naked eye. The chemo-mineralogical composition of these slags is heterogeneous, characterized by the formation of glassy matrix and complex silicates, often of the feldspar and melilite groups.

Occasionally, in some portions of these slags, relicts of metalliferous minerals can be still detected as mainly copper and lead oxides that in the metallurgical process partially reacted with silicates forming glasses. It is still unclear whether this type of metallurgical waste is the result of co-smelting of copper and lead ores/litharge or of smelting of mixed copper-lead ores, whose existence is well documented in some Iberian mines.

A further type of by-product or cupellation debris, associated with this method for producing silver, are fragments of vessels in which the copper and lead oxides penetrated so deeply into the vessel’s walls as to replace almost completely the ceramic components by forming different complex compounds. However, their chemical and mineralogical composition is similar to that of the slags described above.

In lead-silver metallurgy, litharge, i.e. lead oxide, is the by-product from cupellation operations. However, when a copper-lead-silver alloy as the one produced by smelting cupro-argentiferous ores using lead as silver collector, is cupellated, this “litharge” will not only consist of lead oxide, but also contain high amounts of copper oxide, as shown by the analysis of some highly reacted cupellation debris (Tab. 6).

Figure 9 shows the mineralogical complexity of these materials: the striped matrix consists of lead and copper oxides. Occasionally, different type of silicates can react with the ceramic vessel (the cupel) and the calcium oxide of the fuel ash. When during the cupellation process temperatures in the range of 1,200ºC are reached, dendrites of copper oxide can also be observed (Fig. 10).

At high temperature the clayey components of the cupel react with the “litharge” forming in its interior, and progressively transform into lead silicates, partially dispersed in the litharge. Consequently, distinguishing fragments of cupels and litharge when they are small in size, can be difficult. From the analytical point of view, we expect cupels fragments to contain higher percentages of silica, as shown by the comparison of tables 6 and 7. However, debris with less silica might also be portions of the upper layers formed on the inner walls of the cupels, as lead oxide penetrates progressively into the vessel from the inside. In fact, the microstructure of the cupels is quite similar to that of the possible “litharge” fragments (Fig. 11).

The product of the cupellation of a copper-lead-silver alloy is a raw silver *regulus* with high lead and copper impurities. The *regulus* has a complex microstructure due to the mutual insolubility of the three metals. Copper impurities are predominantly allocated in the grain’s boundaries, while lead usually forms spherical segregates in the silver matrix (Fig. 12).

In the light of the analysis results of such materials, we first interpreted them as by-products of refining activities of recycled objects made of a silver-copper alloy. However, this hypothesis did not explain the copper-lead slags, as metal recycling in a crucible does not produce significant amounts of slag. Furthermore, silver objects from the Iberian Peninsula dated to the Phoenician period do not contain high amounts of copper (22), therefore the recycling of this metal would not produce cupellation debris rich in lead-copper oxides as the ones presented here (see Tables 6 and 7).

Archaeological evidence for the extraction of silver from cupro-argentiferous ores is still scarce. At present, the only mention known in the literature is the existence at the Late Bronze Age industrial area of Ras Ibn Hani northern palace (Syria), of an installation possibly related to the use of this technique (23). However, the data provided so far are insufficient to prove this interpretation. Copper-lead-silver metallurgical activities are also mentioned in the Phoenician site of Morro de Mezquitilla (Malaga) but, unfortunately, no description or analyses of the debris, possibly related to this process, are currently available (24).

3.0 CONCLUSIONS

The chemical and mineralogical characteristics of the slags from the Iberian Peninsula, dated to the 3rd mill. BCE, suggest that copper production was carried out in simple open fire structures, often by using ceramic vessels as reactors for the smelting of the ores. In general, the charcoal layer used to cover the hearths was quite scarce and the redox conditions were often variable. Consequently, highly oxidizing episodes favored the formation of minerals such as magnetite and delafossite, while formations of fayalite are less common as it requires a more reducing atmosphere and a sufficient presence of iron in the system (25).

With firing temperatures in the range of 1,000-1,200ºC, these complex slags do not reach a fully molten state and their high viscosity renders the separation of the forming copper from the slag rather difficult. The consequence is a slag with noticeable amounts of copper retained both as microscopic metal prills and partially smelted minerals, (cfr. table 2) and documented in early slags from other geographical areas (16, 26). After smelting, the slag must be mechanically crushed to separate metal prills by hand sorting. The complete labor flow diagram suggested by Paul Ambert and his team (27), reproduced in figure 13, is perfectly applicable to the ancient copper-based metallurgy described here.

With regard to the production of bronze, the slags and the crucibles examined until now suggest the use of two main methods employed in the production of this alloy in Iberian prehistory, i.e. co-smelting of ores and cementation of copper with cassiterite. This idea was already suggested by William Gowland (28), but it is still not fully accepted by scholars, due to current insufficient analytical data. In fact, only few publications have been dedicated to this topic so far (see for example 29).

Finally, out of the production waste presented here, we want to especially underline the novel interpretation of the cupellation debris rich in copper-lead oxides recovered at the Phoenician settlements of La Fonteta (Alicante) and Cerro del Villar (Malaga) (13). This debris has been interpreted as possible by-product of the extraction of silver from cupro-argentiferous ores using a method similar to medieval liquation. Up to date, this process has never been clearly documented in any other archaeological site.

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FIGURE CAPTIONS

Fig. 1. Fragment of a smelting crucible from the Chalcolithic site of Almizaraque (Cuevas, Almeria, Spain), with a heavily slagged layer on the inner surface (Photo: S. Rovira).

Fig. 2. Copper slag from the Chalcolithic site of Almizaraque (Cuevas del Almanzora, Almeria, Spain): melted matrix of pyroxene (Px) entrapping copper prills (Cu); remaining quartz grains (Qz) and several magnetite formations (Mt). SEM image, backscattered electron mode (Photo S. Rovira).

Fig. 3. Chemical composition of slags (shown in table 2) plotted on the $Ca(+K_2O+TiO_2)-SiO_2(+Al_2O_3)-FeO(+MnO)$ system. Note the large dispersion of points.

Fig. 4. Copper-tin slag from the Iron Age site of Sant Jaume-Mas Serra (Catalonia, Spain): globular and acicular tin oxide (white) crystals. SEM image, backscattered electron mode (Photo: S. Rovira).

Fig. 5. Copper-tin slag from the Late Bronze-Early Iron Age site of El Castro (Leon, Spain): pyroxene (Px) matrix with black leucite (Lc) and (Cu, Sn) silicate crystals; abundant cassiterite (Cas) crystals. A bronze (Bz) prill is located in the upper right corner. SEM image, backscattered electron mode (Photo: S. Rovira).

Fig. 6. Copper-tin slag from the Early Iron Age site of El Castillo (Zamora, Spain): glassy matrix (Gl) showing biphasic tin-rich prills close to secondary tin oxide (SnO_2) crystals and cuprite (Cp). OM, bright field (Photo S. Rovira).

Fig. 7. Copper-tin slag from the Early Iron Age site of El Carambolo (Seville, Spain): fayalite laths (Fay) in a field with free silica (Qz) and iron oxide (Fe-ox). White spots are metal prills. SEM image, backscattered electron mode (Photo S. Rovira).

Fig. 8. Slaggy layer of a crucible used for experimental copper-cassiterite cementation: complex Ca,Al-silicate containing some Cu and Sn (glassy matrix, Gl); bronze (Br)

prills with tin contents ranging 1-59% Sn; (Cas) cassiterite (light grey). SEM image, backscattered electron mode (Photo S. Rovira).

Fig. 9. Cupellation debris from the Phoenician site of La Fonteta (Alicante, Spain): striped matrix of copper (light-grey strips) and lead oxides (white strips); crystals of akermanite (Ak) and wollastonite (Wol). SEM image, backscattered electron mode (Photo S. Rovira & M. Renzi).

Fig. 10. Cupellation debris from the Phoenician site of La Fonteta (Alicante, Spain); dendrites of cuprite (black) in a lead-oxide matrix (white). SEM image, backscattered electron mode (Photo S. Rovira & M. Renzi).

Fig. 11. Cupellation debris from the Phoenician site of Cerro del Villar (Malaga, Spain): striped matrix of lead (white) and copper (light-grey) silicates with cuprite dendrites (medium-grey) and augite needles (black). SEM image, backscattered electron mode (Photo S. Rovira & M. Renzi).

Fig. 12. Lead-copper rich silver nodule from the Phoenician site of Cerro del Villar (Malaga, Spain): silver matrix with copper (black) allocated predominantly in the grains boundaries and dispersed lead prills (white). SEM image, backscattered electron mode (Photo S. Rovira & M. Renzi).

Fig. 13. Simplified labor flow diagram applied to earliest Iberian copper metallurgy, after (28).