



Smelting and recycling evidences from the Late Bronze Age habitat site of Baiões (Viseu, Portugal)

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ARTICLE INFO

Article history:

Received 22 June 2009

Received in revised form

7 January 2010

Accepted 19 January 2010

Keywords:

Late Bronze Age

Archaeometallurgy

Smelting

Microstructure

EDXRF

SEM-EDS

Iberian Peninsula

ABSTRACT

Many aspects of bronze production during Late Bronze Age in Western Europe are so far unknown. In the present study selected artefact fragments and metallurgical debris, which include a slag fragment, from the emblematic Late Bronze Age habitat site of Castro da Senhora da Guia de Baiões (Viseu, Portugal) have been studied by optical microscopy, micro-EDXRF, SEM-EDS and XRD. Evidences were found for bronze production involving smelting and recycling. Compositional analysis showed that the artefacts are made of a bronze with 13 ± 3 wt.% Sn (average and one standard deviation) and a low impurity pattern, namely <0.1 wt.% Pb, being comparable with the composition of other bronzes from the same region (the Central Portuguese Beiras). This alloy is generally different from elsewhere Atlantic and Mediterranean bronzes, which show frequently slightly lower Sn contents and higher impurity patterns, namely Pb which is often present as an alloying element. The present study gives further support to early proposals suggesting the exploration of the Western Iberian tin resources during Late Bronze Age, and besides that, it indicates that metalworking and smelting could have been a commonplace activity requiring no specific facilities, being bronze produced at a domestic scale in this Western extreme of Europe.

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1. Introduction

During Late Bronze Age (LBA) the circulation and consumption of bronze increased, as evidenced by the numerous metal artefacts and deposits found all over Europe (Huth, 2000). This period is also characterized by the full adoption of bronze in many regions, namely in the Iberian Peninsula, as well as a significant diversification in artefacts typologies (Melo, 2000).

Although the high number of metal artefacts dating to LBA all over Europe, many aspects of prehistoric technologies for Cu–Sn production are so far unknown. Three hypotheses for bronze production have been proposed in literature (Coghan, 1975; Rovira, 2007): (1) smelting ores of tin and copper together, in a co-smelting operation; (2) adding one of the metals to the other still as ore, in

a partial smelting operation; (3) smelting the ores separately and then alloying the metals in a melting operation.

Slags are a crucial evidence for the study of the technology involved in bronze production. Nevertheless, these are very scarce in Western European contexts, namely in the so called Atlantic areas (Craddock, 2007; Faoláin, 2004; Pendleton, 1999). Most of the latest works on the topic are based on some copper–tin slags that have been found in a number of settlements in the Iberian Peninsula, particularly in the Spanish territory, having the earliest ones been found in north-eastern regions, and later ones (dating to LBA and Early Iron Age) all over the Spanish territory (Gómez Ramos, 1999; Rovira, 2007). Studies on these slags and associated metallurgical debris (e.g. reduction vessels) has conducted to the proposal that bronze was initially obtained by co-smelting (option 1), a technique that was still in use during LBA and Early Iron Age in many settlements. They also showed some possible evidences of smelting cassiterite (tin oxide, as it appears in nature) with metallic copper (option 2) during the transition from LBA to EIA, being the earliest evidences of copper and tin alloying (option 3) dated to

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VIII–VII century B.C., probably as a result of Mediterranean contacts (Rovira, 2002).

In the Iberian Peninsula, the adoption of bronze did not seem to change the extractive technology; bronze was obtained in a similar way as was previously done in Chalcolithic times for copper, with a direct smelting of ores in reducing vessels (Gómez Ramos, 1999). Such primitive smelting process involved a very simple infrastructure, as those composed by a small pit excavated in the soil where a vessel containing the ores was placed, with charcoal, being heated from above. The resulting smelt was completely fragmented to recover the metallic lumps and prills (also called smelting droplets) (Hauptmann, 2007) leaving scarce evidences (e.g. slags) in the archaeological record.

Significant changes in extractive metallurgy in the Iberian Peninsula just happened at the beginning of Iron Age in those regions better connected with the Eastern Mediterranean (frequently called the Orientalising period) as has been indicated by the content of iron in copper-based metals which increased to values >0.05 wt.% (iron is most dependent on the smelting process and primitive relatively mild reducing conditions prevented iron minerals to be reduced to metal) (Craddock and Meeks, 1987).

The employ of a primitive and simple method for smelting for such a long period of time in the Iberian Peninsula (about 3 millennia) has been related to its adequacy to the kind of minerals being worked – rich minerals, such as copper carbonates, achieving acceptable efficient rates of metal recovery – and to the social adequacy – serving the metal requirements of the immediate local community (Rovira, 2002).

A different reality existed in most Eastern regions, as in Central and Alpine regions of Europe, Eastern Mediterranean and Middle East, that experienced important developments in technological knowledge and skills between Chalcolithic and LBA, i.e. a transition from simple primitive, crucible based, small scale domestic production to mass production involving slag heaps and complex furnaces, the existence of large smelting sites distributing ingots, sites specialized in producing copper and sites specialized in producing tin (Adriaens et al., 1999; Burger et al., 2007; Rothenberg, 1985).

These differences may rely mostly in the Iberian Peninsula (and generally Western Europe) social landscape, which was very different from the one in the Eastern Mediterranean, which saw the development of early states which controlled large territories and populations (Whittaker, 2008).

In the Iberian Peninsula almost all the recently excavated habitat sites, including some of very small size, from Chalcolithic in most southern regions to LBA sites in Northwest regions record metallurgical activities (Bettencourt, 2000; Rovira, 2002; Senna-Martinez and Pedro, 2000a; Vilaça, 2004). This reality indicates disseminated metallurgical knowledge since early times, and substantiates absence of any monopoly controlling production. It also suggests regular supply of ores and metals for a long period of time, probably a reflection of the exploration of the Iberian minerals.

The Iberian Peninsula is very rich in both copper and tin ores, having one of the major tin deposits of the European Old World. The geographical distribution of the copper and tin deposits is different, with a general dispersion of the former ones and a concentration of the latter ones mainly in the northwestern region. During the last quarter of the second millennium B.C., with the advent of full adoption of bronze and the increase in metallic artefacts production, the Central Portuguese Beiras witnessed an emergence of many sites, most of them with vestiges of metallurgical activities. This emergence has been suggested to be related to the control and exploitation of gold and cassiterite (Senna-Martinez and Pedro, 2000a), the latest an essential ore for bronze

fabrication. The collapse of most of those sites in the middle of the 1st millennium B.C. (Vilaça, 1995a) has been explained as a possible result of the rupture on metal circulation, which happened with the crisis of the Phoenician settlements in Iberian coastal areas (Senna-Martinez, 1998).

The development of local elites during the LBA has been linked to the role of metallurgy in producing status enhancing artefacts (archaeologically expressed by the higher number of metallic artefact productions, their more complex shapes as well as and new techniques of production). So an easy access to the minerals must have been seen as an advantage, and can also be taken into account in the positioning of some emerging sites (Senna-Martinez, 1996; Vilaça, 1995b).

While the exploitation of Iberian copper resources seems to be widely accepted, the exploitation of the local tin resources is more discussed, and rather difficult to prove due to the scarcity of evidence. Old mines can be difficult to find due to posterior mining works and due to the possibility that most of the tin explorations would occur in alluvial placers. Nevertheless, in the Central Portuguese Beiras – a region with abundant tin and gold resources (Garcia, 1963) – during the reopening of the ancient gallery of the S. Martinho mine (Orgens, Viseu), during the World War Two, a bronze dagger of “Porto de Mós” type was found at the bottom of the rubble which filled its shaft, proving its original opening and posterior infilling during the Late Bronze Age, probably for cassiterite exploration (Correia et al., 1979). Other Iberian evidences of tin exploration come from the Spanish area of Cáceres, from the LBA settlement of Cerro de Logrosan (Caceres, Spain) (Merideth, 1998; Rovira, 2002).

An LBA Iberian production of bronze, based on the exploitation of the local ores and independent of the most Atlantic and Mediterranean areas has been previously suggested based on the composition of many Iberian bronzes. While comparing the composition of bronzes from the Ria de Huelva LBA hoard with contemporaneous bronzes from external peninsular regions, Rovira and Gómez-Ramos (1998) have stressed the low impurity pattern (namely of Pb) and the slightly higher Sn content that seem to differentiate the Huelva bronzes from other bronzes in Atlantic and Eastern Mediterranean areas (Fig. 1). Analysis of bronzes from various emerging sites in the Central Portuguese Beiras has also showed compositions similar to the Ria de Huelva hoard, mostly ~8–15 wt.% Sn and <1 wt.% Pb (Figueiredo et al., in press; Valério et al., 2007; Vilaça, 1997). If these bronzes were made just by recycling imported bronzes, lower contents in tin were to be expected since tin is lost preferentially to copper after remelting (Rovira and Montero, 2003).

In the present work we will discuss the analytical results of a study made on selected items – that include a slag fragment – recovered at the Castro de Nossa Senhora da Guia de Baiões LBA archaeological site, situated in the Central Portuguese Beiras.

2. Baiões site and its artefact collection

The Castro de Nossa Senhora da Guia de Baiões (CSG) site is placed on a granitic hilltop in the county of S. Pedro do Sul, Viseu, in central Portugal, part of a series of residual reliefs which dominate the Vouga river valley (Fig. 2A and B). In modern times, a sanctuary (Senhora da Guia Sanctuary) has been constructed which provoked the destruction of most of the archaeological site (Fig. 2C).

The site has a great domain over the involving landscape and controls the old road going west through the passes of the Gralheira massif, alongside the northern margin of the Vouga river that was navigable just some 20 km ahead (until middle of XIX century), allowing a good access to the Atlantic waters (Fig. 2B). Its

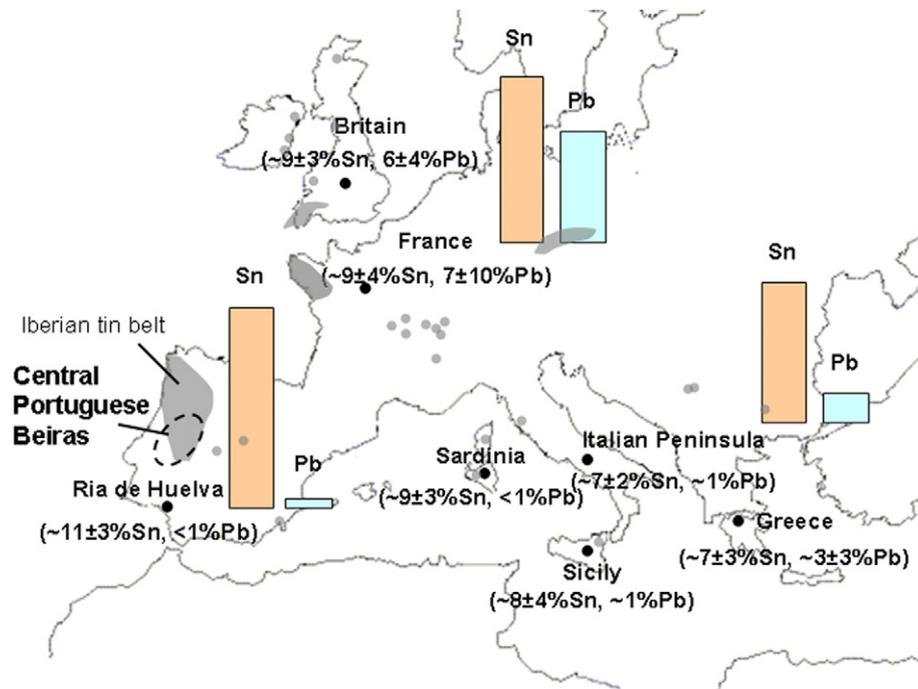


Fig. 1. Approximate location of the Central Portuguese Beiras and the Ria de Huelva hoard in Iberian Peninsula; location of tin deposits (grey areas) in European areas based on illustrated in Merideth (1998); and average of bronze compositions in different regions (indicative of general trends) based on Rovira and Gómez-Ramos (1998). A decrease in Sn and an increase in Pb content occur when moving from Iberian Peninsula towards Atlantic and Mediterranean territories.

prehistoric occupation is estimated to lay in between the 13th and the 8th centuries B.C. (Senna-Martinez and Pedro, 2000a).

The site's archaeological interest was first acknowledged in the XVIII century when Friar Agostinho de Santa Maria mentioned that "...digging in the same place, worked gold has been found such as bracelets and similar things..." (Santa Maria, 1716).

In 1947 during some road construction to improve the access to the sanctuary the so called "treasure of Baiões", comprising two gold torcs and a bracelet, was found. Later works in 1971 revealed an important group of pottery and bronze artefacts (Silva, 1979).

The first archaeological excavations took place in 1973 conducted by Celso Tavares da Silva (Silva, 1979) followed in 1977 by a campaign directed by Kalb (1978). All these interventions confirmed the concentration of metal findings in the general area of the old ones. Although most of those interventions are poorly published, Kalb (1995) describes that numerous metallic nodules

were found in the surroundings of a fireplace, interpreting this area as a melting place (being the nodules a result of some spilled metal during a pouring operation), and Baiões as a habitat site.

In 1983, when the construction of the actual layout surrounding the chapel of Senhora da Guia began, the finding of a series of bronze artefacts lead to an urgent archaeological excavation resulting in the finding of the so called "Baiões Hoard" (Silva et al., 1984). Since then, the gold and bronze artefacts from the Castro da Senhora da Guia de Baiões have been presented as a "hoard" or "foundry deposit".

The majority of the metal finds of Baiões comprise bronze foundry leftovers, scrap, bits of wire and bars to forge, as well as moulds in clay, stone and bronze together with brand new artefacts still with casting seams. All the collection – c. 400 pieces – was made public, for the first time, at the 2000–2001 exhibition "Walking along Viriato's land: The Archaeology of Viseu's Region",

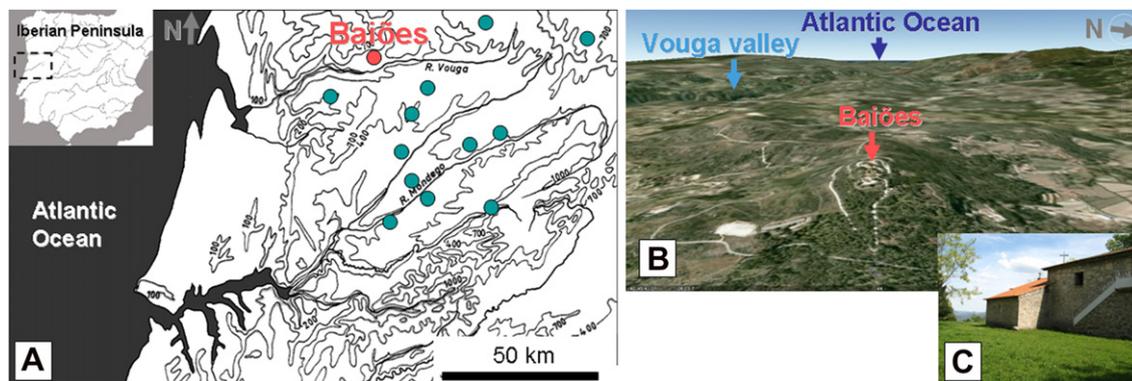


Fig. 2. (A) Approximate location of Senhora da Guia de Baiões and other LBA sites in the proximities – the Baiões/Santa Luzia cultural group (Senna-Martinez and Pedro, 2000a); the sea level and palaeo-estuarine systems during Bronze Age are depicted. (B) Google Earth image (<http://earth.google.com>) showing the hilltop of Baiões and surroundings. (C) Modern sanctuary on the archaeological site.

presented at the National Museum of Archaeology, Lisbon (Senna-Martinez and Pedro, 2000a). Since then, the existence of a metal-working area at Baiões site (and not a “hoard” or “foundry deposit”) similarly to what had been recently exposed through excavation in other sites at the proximities, namely the sites of S. Romão and Outeiro dos Castelos de Beijós (Senna-Martinez and Pedro, 2000b), was strengthened.

Although the widespread metallurgical evidences in LBA sites, including those in the proximities of Baiões which compose the Baiões/Santa Luzia cultural group (Fig. 2A), the Baiões collection, with its metal and metallurgy related artefacts, has a strong expression amongst the latest as well as amongst other contemporaneous sites from the Iberian Peninsula. Its collection has been reported in several studies, related with typological (e.g. Atlantic and Mediterranean features) and production issues (Ambruster, 2004; Coffyn, 1985; Giardino, 1995; Senna-Martinez and Pedro, 2000a; Ruiz-Gálvez, 1998). Despite the richness and importance of the collection, analytical studies are very scarce. The most significant investigation carried out until now were the energy dispersive x-ray fluorescence (EDXRF) analyses recently performed by Valério et al. (2006) over 54 bronze artefacts (complete or semi-complete), which showed that the alloy employed was a bronze, occasionally with lead and arsenic as impurities. Once this study was performed in artefacts with museological interest the analyses were performed over non-cleaned patinated surfaces, not allowing the determination of the bulk composition.

For the present study a multi-method approach was adopted and other items were selected, most of them metallurgical debris. The items include one vitrified fragment, later recognized as a slag fragment, sixteen artefacts and artefact fragments and twelve minute roundish or irregular fragments of metal named “metallic nodules”, for the sake of simplicity (Fig. 3). The latest were selected owing their high number amongst the collection and since their study could provide information about processing techniques. Some of the selected artefact fragments showed partially heat-distorted areas. Accordingly, the microstructure examination could help in their classification as faulty castings or partial melting of artefacts, e.g. during an incomplete recycling operation. Overall, the main purposes of the present study were to: attain the metal compositions; describe the thermomechanical sequences performed on the artefacts; and infer about the metallurgical processes undergoing at the site, to which a significant contribution of the slag fragment was expected.

3. Experimental

In order to cause the minimum damage in the collection, all the metallic items were analysed by micro-energy dispersive x-ray fluorescence spectrometry (micro-EDXRF) for elemental composition determination in a small area (frequently $<25 \text{ mm}^2$), which had been cleaned (by removing the superficial corrosion patina) and polished (until $1 \mu\text{m}$ diamond paste). These prepared areas were afterwards observed under an optical microscope (OM) for



Fig. 3. The twenty-nine items selected for analyses: (A) metallic nodules; (B) slag fragment; and (C) fragments of artefacts and artefacts.

microstructure examination, under bright field (BF) and polarized light (Pol) illumination, in unetched and etched conditions. Etching was performed with an aqueous ferric chloride solution.

The slag fragment was sectioned into two parts that were analysed by scanning electron microscope (SEM–EDS) without a conductive coating (metallic oxides were conductive enough for backscattering electron observations and elemental analysis) and one of the parts was analysed by x-ray diffraction (XRD).

The OM observations were conducted in a Leica DMI5000M microscope, coupled to a computer with the LAS V2.6 software.

The micro-EDXRF analyses were performed in an ArtTAX Pro spectrometer, with a low-power X-ray tube (30 W), a molybdenum anode and a set of polycapillary lens that generate a microspot of primary radiation, of $\sim 70\ \mu\text{m}$ in diameter. The quantification analyses involved the WinAxil software. Details on quantification procedures have been recently described (Figueiredo et al., 2007; Valério et al., 2007). Three analyses were made on different spots of the prepared area of the artefacts, being considered the average values.

The SEM analyses were performed in Zeiss model DSM 962, with a backscattered electrons detector (BSE) and an energy dispersive spectrometer (EDS) from Oxford Instruments model INCAx-sight with an ultra thin window which extends the detection to light elements, as oxygen and carbon. Semi-quantifications were made using ZAF correction procedure.

The XRD analyses were conducted in a Siemens D5000 diffractometer, with Cu $K\alpha$ radiation. This analysis has been carried out on the cross section of the slag part.

4. Results and discussion

Results are presented in the following sections, accordingly to the nature of the analysed items.

4.1. Slag fragment

In Fig. 4 are presented the main results from the SEM–EDS analyses made on the cross-sections of the fragment (1.28 g). These revealed a heterogeneous structure, essentially composed by: a vitreous matrix (aluminium silicate) with the regular presence of O, Cu, Al, Si and irregular presences of K, Fe, Pb, Mg and Ti; large globular inclusions of malachite (surrounded by cuprite) (Fig. 4A), cuprite and metallic copper (surrounded by cuprite) (Fig. 4B); occasionally some small inclusions of metallic lead (Fig. 4B); cuprite in coarse dendritic (image embedded in Fig. 4A) or small globular form (Fig. 5B); and the presence of cassiterite, frequently in needle like crystals with a rhombohedral form enclosing cuprite (Fig. 5A, B and C). The morphologies of the cassiterite and dendritic cuprite among the vitreous matrix suggest that they formed during the solidification process.

Many of these features have been described previously for Bronze Age and Early Iron Age slags from the neighbouring Spanish territory and regarding some particularities, they have been related with co-smelting processes, “cementation” of copper with cassiterite or an alloying of copper with metallic tin (in later times) (Rovira, 2007).

The XRD analyses showed peaks related to cassiterite, cuprite and magnetite (Supplementary online material). The formation of magnetite (Fe [II/III]) instead of fayalite (Fe [II]) is frequent in early

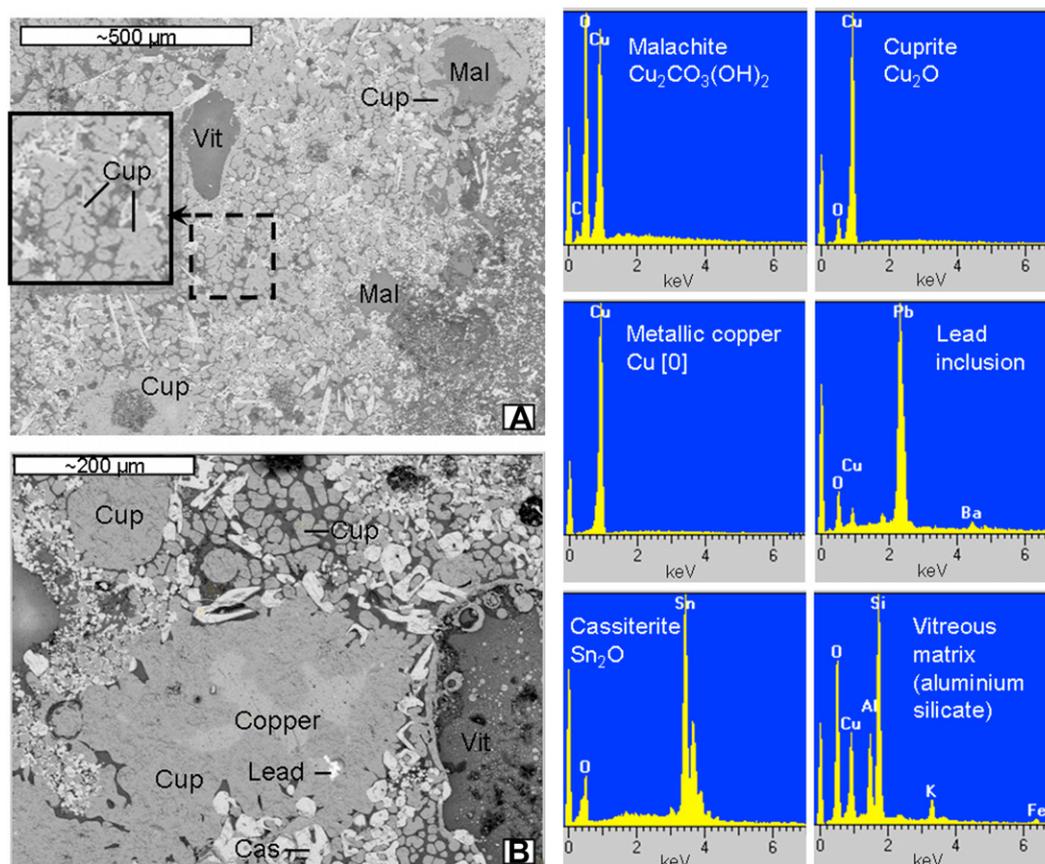


Fig. 4. SEM (BSE) images (A–B) of CSG-315 slag fragment at lower magnifications (Mal – malachite; Vit – vitreous matrix; Cup – cuprite; Cas – cassiterite). At right some representative examples of EDS spectra of different compounds present in the slag.

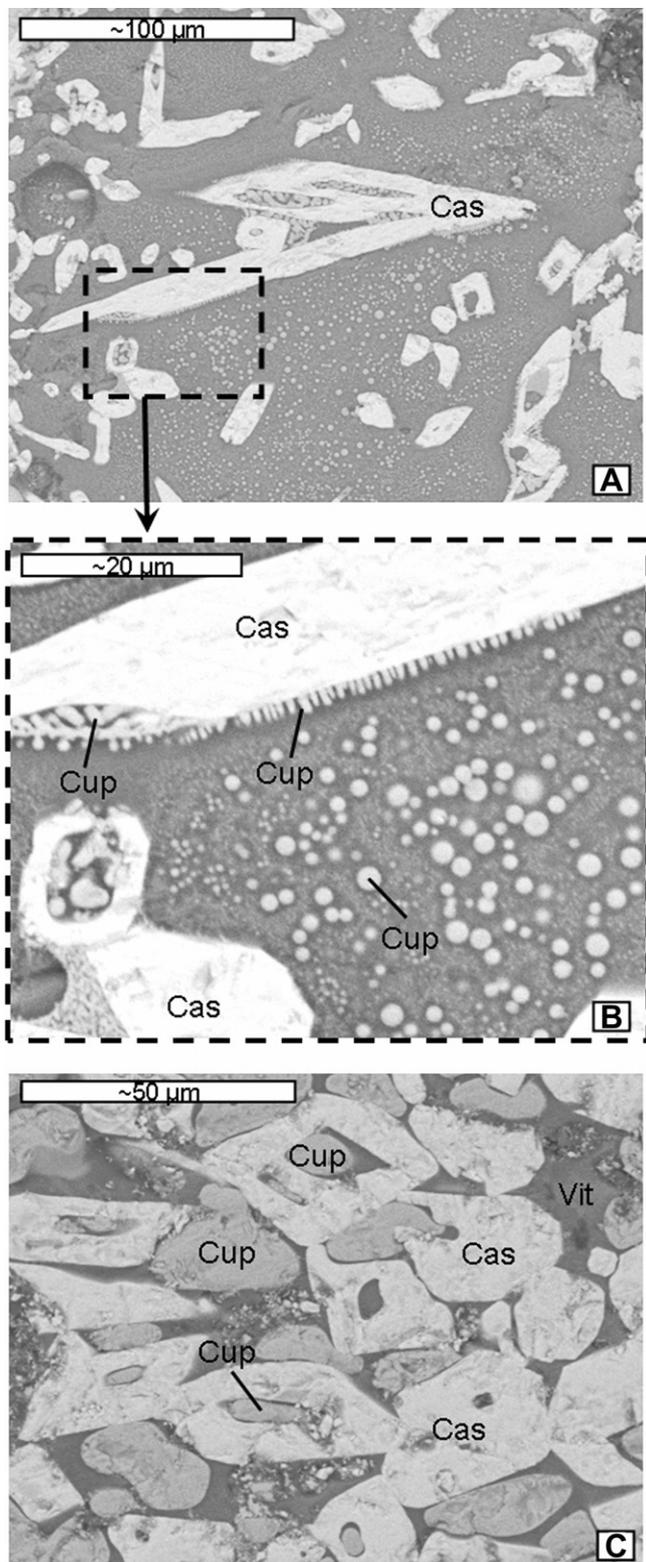


Fig. 5. SEM (BSE) images (A–C) of CSG-315 slag fragment at higher magnifications (Vit – vitreous matrix; Cup – cuprite; Cas – cassiterite).

Iberian smelting slags (before the Iron Age). This is a consequence of the smelting being normally conducted in open shape reaction vessels with heat from above (Rovira, 2004), producing very heterogeneous conditions inside the vessels, and thus frequently weak reducing atmospheres in many parts.

The studied fragment is most likely only one small part of the whole product that resulted from a metallurgical operation. The weak reducing atmosphere that this particular fragment experienced, at least in the last stage before solidification, was only enough to keep some Cu in metallic form, but clearly not enough to allow Sn exist in the metallic solid solution (Sn is preferentially oxidised in respect to Cu). The interpretation of such a microstructure is rather difficult, more over since we lack other vitrified fragments and any ceramic body that served as reaction vessel, which could give additional information. This fragment could be a result of an oxidation process, e.g. during a bronze recycling or an alloying of metallic copper and metallic tin, or it could be a result of an extractive operation, such as a smelting operation to reduce copper and tin ores. All these possibilities can be considered since ancient firing techniques, as using blow pipes, did not create constant or uniform conditions inside the reaction vessel (Hauptmann, 2007). Thus, this fragment does most probably not represent the thermodynamic conditions reached in other parts of the reaction vessel, sufficient to retain or produce bronze. It has been shown that in a recycling or alloying operation some oxidation could occur (e.g. Klein and Hauptmann, 1999) and in ancient smelting operations all the transitional stages between thermal decomposition of the original material up to the formation of proper melts can be present in the slag (e.g. Hauptmann, 2007). These heterogeneities might even explain why this fragment stayed behind in the archaeographic record: it was probably recognized as “waste” part that enclosed no metallic bronze.

Regardless all the possibilities, some particularities in the microstructure may suggest that the fragment is a slag resulting from a reduction operation. The presence of malachite inclusions in areas without external corrosion evidences, as the malachite inclusion (Cu [II]) that is totally surrounded by cuprite (Cu [I]) (Fig. 4A top right) suggests that this malachite is not a secondary corrosion product. Most likely, it was originally present in the mixture, and was partially decomposed at some stage of the process into CuO, CO₂ and H₂O (decomposition of malachite can continue to temperatures greater than 600 °C (Simpson et al., 1964)), and the resultant tenorite was reduced into cuprite.

Although copper may initially been present as ore, the initial state of tin is more difficult to accomplish. In the fragment, tin is only present as cassiterite that resulted from the slag’s solidification process. Thus, it is impossible to determine if tin was added as metal or ore. Additionally, the lack of archaeological evidences of metallic tin items or cassiterite fragments in Baiões and other local LBA sites, does not provide additional information on the subject – both can be very difficult to recognize in the archaeographic records, due to “tin pest” in the first case, and due to the not expressive colour of cassiterite when compared with copper ores in the second case. So, future studies on other materials and sites are needed to help answering this last question.

4.2. Nodules

The main results on the elemental composition and microstructural features of the nodules are summarized in Table 1. Relative standard deviations (RSD) calculated for alloying elements and impurities ($RSD = SD \times 100 / \text{average}$) show disperse values: in the alloying element Sn, RSD is mainly <10%, except for 3 items; in minor elements, RSD is mainly <50%, except for Pb in one item. These values are expected due to micro-heterogeneities on the analysed areas (Northover and Rychner, 1998), namely different metallic phases and some intergranular corrosion (Figueiredo et al., 2010). Fig. 6 comprises micrographs of the microstructures of the items examined in this section with the exception of the nodule CSG-327 that is described later in more detail.

Table 1

Summary of the experimental results on the copper-base metallic nodules. Composition for each nodule is given by average of three micro-EDXRF analyses \pm one standard deviation (SD).

No.	Weight (g)	Composition (wt.%)				Phases present
		Sn	Pb	As	Fe	
CSG-153	0.99	12.0 \pm 1.0	n.d.	<0.1	<0.05	α
CSG-154	0.90	12.9 \pm 1.2	n.d.	0.13 \pm 0.05	<0.05	α
CSG-159	1.02	13.6 \pm 0.6	0.44 \pm 0.21	0.21 \pm 0.02	<0.05	α , δ
CSG-186	1.50	12.9 \pm 0.9	n.d.	0.18 \pm 0.02	<0.05	α , δ ↓
CSG-187	1.03	10.9 \pm 0.6	0.11 \pm 0.08	<0.1	<0.05	α , δ
CSG-210	2.73	12.6 \pm 0.1	n.d.	<0.1	<0.05	α , δ ↑
CSG-227	0.54	12.5 \pm 2.8	n.d.	<0.1	<0.05	α , δ
CSG-317	3.73	14.2 \pm 2.2	n.d.	0.10 \pm 0.01	0.08	α
CSG-320	2.93	9.7 \pm 0.2	n.d.	<0.1	<0.05	α
CSG-325	2.91	14.3 \pm 2.8	<0.1	<0.1	0.05	α , δ
CSG-327	1.93	14.3 \pm 0.5	n.d.	n.d.	<0.05	α , δ , ϵ , η
CSG-329	0.42	15.5 \pm 4.6	n.d.	0.11 \pm 0.03	<0.05	α , δ ↓
Total	21.7	13.0 \pm 1.6	–	–	–	

n.d., not detected; ↓, low amount; ↑, high amount.

The micro-EDXRF analyses indicated that all the nodules are made of bronze with Sn in the range of 9.7–15.5% and Pb and As frequently present in low contents.

The microstructures of the nodules CSG-154, 186 and 320 (with Sn contents between 9.7 and 12.9%) are composed by twinned equiaxed grains, a result from a mechanical deformation followed by annealing, and exhibit deep intergranular corrosion. Among these, the CSG-186 nodule shows the smallest recrystallized grains which are superimposed in an earlier dendritic structure, pictured by the corrosion along preferential paths. These paths are given by the interdendritic regions that show a concentration of Cu–S inclusions and ($\alpha + \delta$) eutectoid. Their microstructures suggest that they are probably remains of artefacts.

The other nodules, show coarse microstructures with grain twinning absent or very low (CSG-153, 187, 317, 325 and 329) or cored dendrites with ($\alpha + \delta$) eutectoid in the interdendritic areas (CSG-159, 210 and 227). Cu–S inclusions are frequently observed. The nodules with coarse microstructures suggest a very slow cooling rate or a heat-treatment after solidification (it is difficult to distinguish between both) and the nodules with cored dendrites suggest faster cooling and absence of a heat-treatment. It can be proposed that some of those with coarse (more homogenised) microstructures and rounded shapes (CSG-317, 325, 187, 327 and 329, with Sn contents between 10.9 and 15.5%) are smelting droplets. Smelting droplets are expected to show coarse microstructures due to the rather slow cooling of the smelt. Nevertheless, if this is so, one has to question their narrow range of Sn content, since dispersed Sn contents among lumps and prills recovered from a smelt are expected (Rodríguez Diaz et al., 2001; Rovira, 2007). The existence of some melting droplets, as suggested by Kalb (1995), cannot be rejected within those that show a faster cooling microstructure.

The CSG-327 nodule has a distinct microstructure of the previous nodules and was thus also analysed in SEM–EDS. The bulk is composed by primary α phase grains and ($\alpha + \delta$) eutectoid. Near to the nodule surface two clear layers of the intermetallic compounds δ and ϵ were observed, followed by an irregular outer layer of η phase which had small amounts of a tin rich constituent amongst it (Fig. 7). These features suggest two independent events: one at higher temperatures (>520 °C), to allow the formation of ($\alpha + \delta$) eutectoid from γ decomposition in the bronze bulk; and another, at lower temperatures (<415 °C), to allow a thermally activated solid interdiffusion of Sn from metallic tin and Cu from the pre-existing bronze. For this last stage the system temperature should be between 350 and 415 °C, since only at this temperature

range, and accordingly with the Cu–Sn equilibrium phase diagram, all the three monophasic layers (δ , ϵ , η) could coexist, without an ($\alpha + \delta$) eutectoid layer resulting from γ decomposition during cooling.

The archaeometallurgical explanation of this nodule is not simple. The absence of conventional tinned artefacts during Bronze Age – tinned artefacts have a eutectoid or delta (Rovira, 2005) layer formed by in situ cassiterite reduction or by inverse segregation during solidification (Meeks, 1986) – seems to rule out the possibility of this being a fragment of a tinned artefact. As a result, the nodule might have been formed during a smelting or alloying operation, where at a stage of cooling of the reaction vessel some metallic Sn (formed over strong reduction conditions if cassiterite was initially added), still in a liquid state, moved through fissures and cracks ending up in contact with a bronze nodule already in a solid state, starting the interdiffusion process. On the other hand, if this nodule is a result of some recycling operation, then one can only suppose that metallic tin or cassiterite was intentionally added to balance the loss in tin due to its preferential oxidation in respect to copper. Either way, the presence of metallic tin adds the information that the local metallurgists were capable of creating reducing conditions sufficient to preserve tin in a metallic state or reduce cassiterite into metallic tin in the course of their metallurgical operations. This should bear no surprise, since Timberlake (2007) was successful in reducing cassiterite to tin, by smelting high grade ores within small, low-temperature, poorly reducing open hearths, and thus in a comparable way as bronze could have been produced in LBA Iberian Peninsula.

4.3. Artefacts and fragments

The main results on the elemental composition, microstructural features as well as possible thermomechanical treatments applied are summarized in Table 2. Fig. 8 comprises micrographs with the microstructures of all the items examined in this section.

The micro-EDXRF analyses indicated that the artefacts and fragments are made of bronze, except for the bar CSG-293 that is made of unalloyed copper. Pb, As and Fe are frequently present, although in low contents – sometimes in concentrations lower than the quantification limits (Pb and As <0.1 and Fe <0.05%). The presence of Cu–S inclusions is also recurrent, similarly to the nodules.

The copper bar CSG-293 has equiaxed twinned grains and numerous Cu–S inclusions. Its microstructure indicates that it has been shaped through thermomechanical work to the final semi-quadrangular section. The composition and typology of this artefact suggests that it might be a semi-finished product. It could have served to provide small amounts of metal, that were cut-off, to manufacture small simple copper items, such as rivets, cramps, etc., or to melt to produce more complex shaped copper artefacts. The thermomechanical work detected can be explained as a result of shaping and softening it for easier transport, handling and posterior cutting. There are evidences for use of copper during LBA to the manufacture of specific objects such as two rivets in Ria de Huelva (Rovira, 1995), a belt hook fragment from Fraga dos Corvos (Figueiredo et al., 2009), a cramp (possibly another belt hook fragment?) from Canedotes (Valério et al., 2007) and a gilded nail in Castro de São Romão (Figueiredo et al., in press). Another hypothesis could be that the copper bar was used for bronze production, to be joined to cassiterite in a partial smelting operation (option 2 in introduction), as a copper ingot. Some copper ingots attributed to LBA have been found in the Iberian territory. However, these are scarce, and a clear connection to metallurgical activities is lacking since most of them were found in hoards with finished palstaves and not among metallurgical debris (Gómez Ramos, 1993).

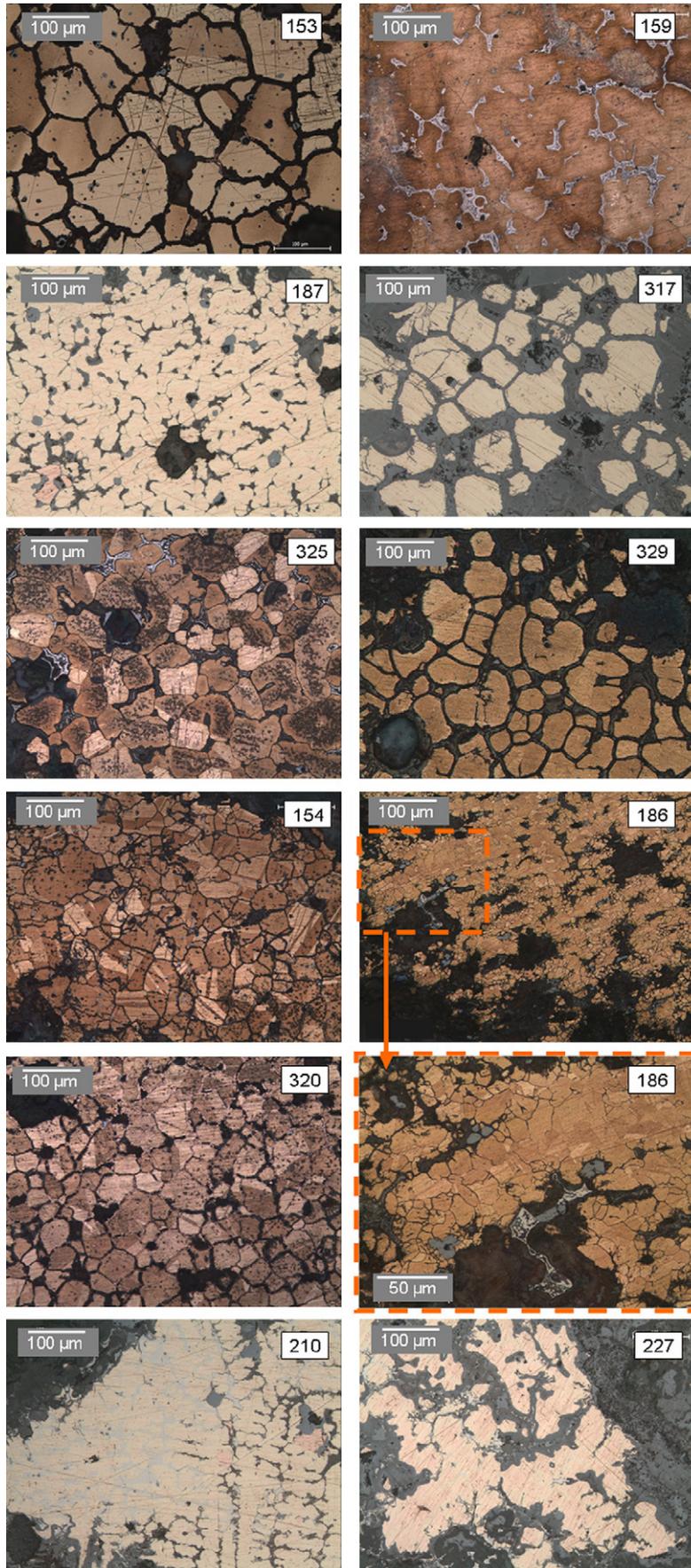


Fig. 6. OM (BF) images of some nodules, showing various microstructures. All images were taken at the same magnification (200 \times) except 186 which has a second image taken at 500 \times . All surfaces are etched except for CSG-187, 317, and 210.

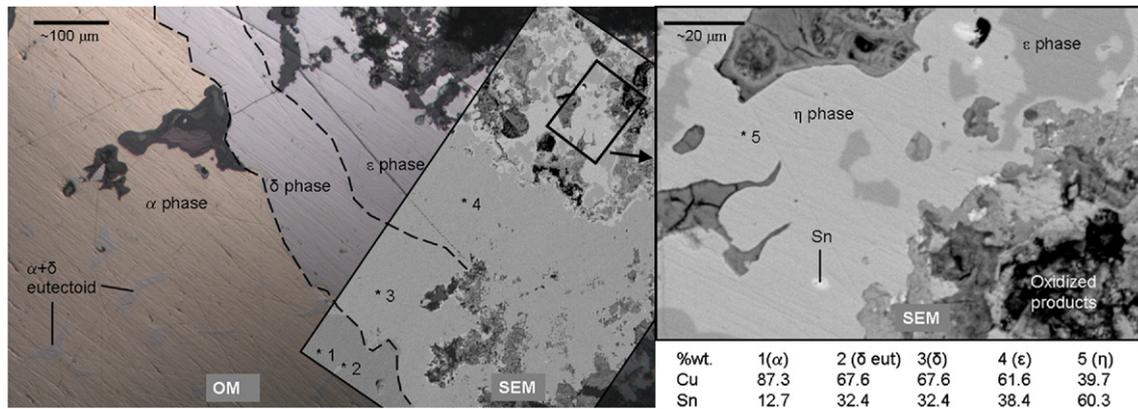


Fig. 7. OM (BF) (left) and SEM (BSE) (centre and right) images of CSG-327 nodule. The table shows the results of the EDS analyses on the different Cu–Sn intermetallic compounds.

Among the bronzes, tin contents are in the range of 9.6–15.4%, except for two items: socket fragment CSG-139 and pin head CSG-162, which have >15% (17.1 and 18.8%, respectively). These two items show as-cast microstructures, with the formation of cored dendrites and a high amount of interdendritic ($\alpha + \delta$) eutectoid. Increasing Sn content in bronze increases the hardness but decreases its ductility. Therefore, it seems reasonable that these artefacts were not subjected to mechanical works.

The use of a ~10–15% Sn bronze on all the other items suggests that its optimum mechanical properties were appreciated. Besides, the absence of low tin bronzes suggest that some “control” in the bronze composition was accomplished.

The microstructures of the heat-distorted blade fragments CSG-318 and CSG-335 and the sickle fragment CSG-400 show equiaxed α -grains, with varying (although low) amount of twinning and low amount of ($\alpha + \delta$) eutectoid taking into account the Sn contents. These features represent a typical recrystallized microstructure, indicating a post-casting work, which suggests that they were not faulty castings. If they were faulty castings a dendritic microstructure composed by α -cored dendrites with interdendritic ($\alpha + \delta$) eutectoid would be expected. They are most likely artefacts that suffered high temperatures, perhaps during a recycling operation interrupted at an initial stage or during a larger fire involving

the settlement. However, the occurrence of artefacts in the collection with microstructures that show absence of a final heat-treatment, as well as the relatively small number of artefacts showing heat-distorted shapes, does rather point out to some intentional metallurgical operation, such as a recycling operation.

The amalgam of four bar fragments, CSG-312, joined by corrosion products or partially melted together, also suggests recycling operations at the site since they appear to be scrap fragments gathered for melt. Microstructures of two analysed bar fragments are similar to the sickle (CSG-400).

The microstructures of the artefact fragments CSG-314 and CSG-316, scabbard chape fragment CSG-346, buckle element CSG-407 and bracelet fragment CSG-408 show absence of high deformations. They have a dendritic (CSG-314) or an annealed microstructure with large grains (CSG-316, 346, 407 and 408), without annealing twins, and presenting various amounts of ($\alpha + \delta$) eutectoid. They have only been subjected to an annealing and/or to a slight final cold work – evidenced by corrosion along slip bands (CSG-314 and 407). Their shapes were most probably obtained by cast, with some posterior mechanical work applied for surface finishing.

The unifacial palstave butt fragment CSG-308 has a microstructure composed by large equiaxed grains with a small amount of twinning. Its primary shape was most likely obtained by cast

Table 2

Summary of the experimental results on the copper-base artefacts and fragments of artefacts. Composition for each artefact is given by average of three micro-EDXRF analyses \pm one standard deviation (SD).

No.	Item	Weight (g)	Composition (wt.%)				Method of fabrication	Phases present
			Sn	Pb	As	Fe		
CSG-139	Socket fragment	4.12	17.1 \pm 1.8	<0.1	0.17 \pm 0.06	<0.05	C	α , δ \uparrow
CSG-162	Pin head	2.29	18.8 \pm 2.1	n.d.	0.16 \pm 0.03	<0.05	C	α , δ \uparrow
CSG-179	Spatula fragment	1.10	10.9 \pm 0.1	n.d.	0.12 \pm 0.06	<0.05	C + F + A	α
CSG-293	Bar	83.0	n.d.	n.d.	0.16 \pm 0.02	<0.05	C + F + A	α -copper
CSG-308	Unifacial palstave butt fragment	57.1	13.6 \pm 1.7	n.d.	<0.1	<0.05	C + F \downarrow ? + A	α
CSG-312	Amalgam of 4 bar fragments	12.3	13.2 \pm 3.2	n.d.	0.12 \pm 0.04	<0.05	C + A	α
			9.9 \pm 1.7	n.d.	0.11 \pm 0.01	<0.05	C + F \downarrow ? + A	α
CSG-314	Fragment	8.47	13.7 \pm 2.9	<0.1	0.13 \pm 0.01	<0.05	C + F \downarrow ?	α , δ
CSG-316	Fragment	16.8	14.8 \pm 0.7	n.d.	0.18 \pm 0.01	<0.05	C + A \downarrow	α , δ
CSG-318	Blade fragment partially remelted?	20.7	9.7 \pm 2.3	n.d.	n.d.	<0.05	C + F \downarrow + A	α , δ \downarrow
CSG-330	Spatula fragment	0.64	11.7 \pm 0.9	n.d.	<0.1	<0.05	C + F + A + F	α
CSG-335	Blade fragment partially remelted?	20.7	11.1 \pm 0.6	n.d.	<0.1	<0.05	C + F \downarrow + A	α
CSG-383	Double spatula	3.29	10.8 \pm 3.0	n.d.	<0.1	<0.05	C + F + A + F \downarrow ?	α
CSG-346	Scabbard chape fragment	6.02	15.4 \pm 1.0	<0.1	0.15 \pm 0.02	<0.05	C + A	α , δ \downarrow
CSG-400	Sickle fragment partially remelted?	44.1	14.4 \pm 2.0	n.d.	0.15 \pm 0.03	<0.05	C + A	α , δ \downarrow
CSG-407	Buckle element	9.98	9.6 \pm 1.7	n.d.	<0.1	<0.05	C + A + F	α
CSG-408	Bracelet fragment	11.1	10.6 \pm 0.7	n.d.	<0.1	<0.05	C + A + F \downarrow ?	α
Total		301.7	12.8 \pm 2.8	–	–	–		

n.d., not detected; C, cast; F, forged/deformed; A, annealed; \downarrow , low amount; \uparrow , high amount.

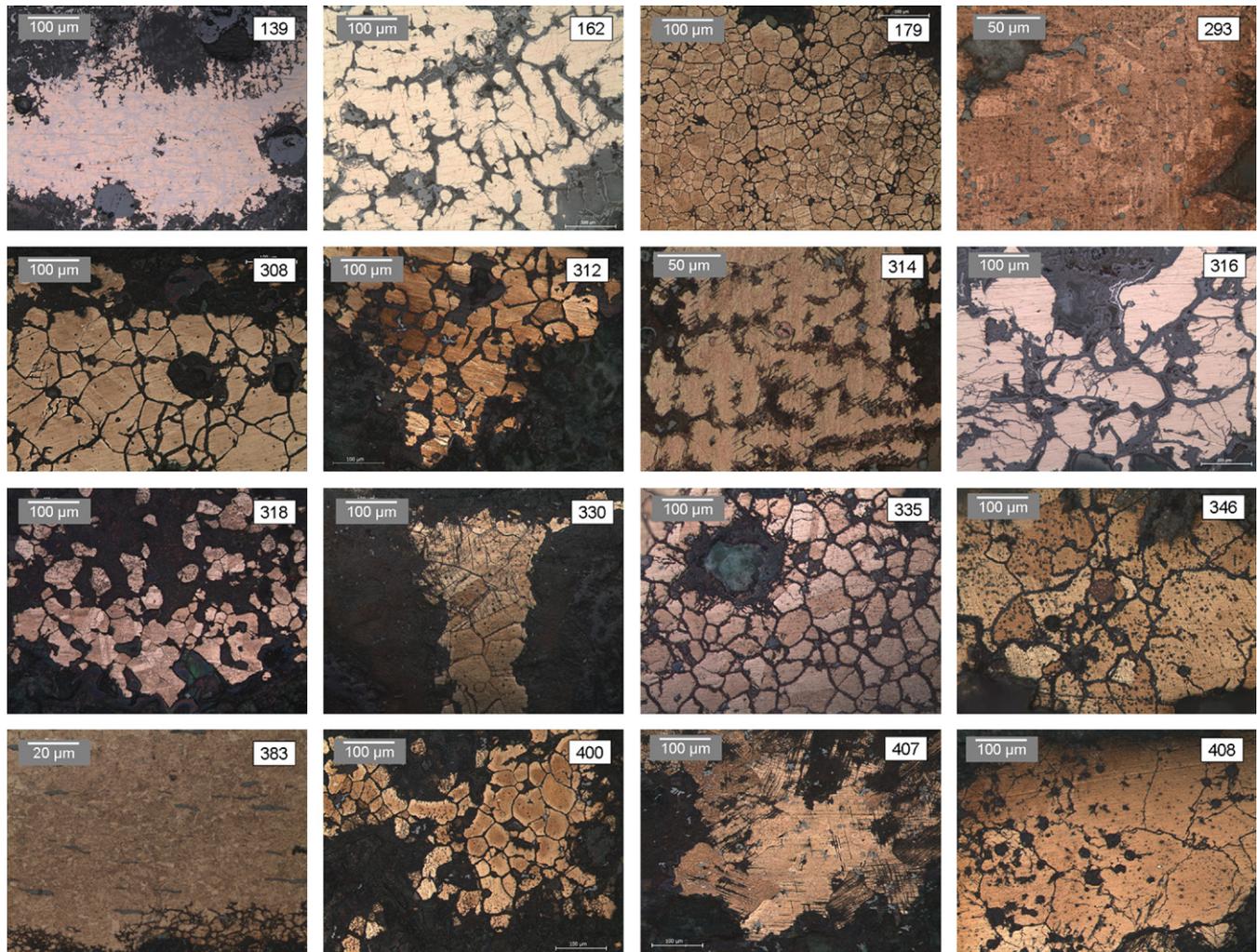


Fig. 8. OM (BF) images of the artefacts and fragments of artefacts. All images were taken with a magnification of 200× except CSG-293, 314 (500×) and 383 (1000×). All surfaces are etched except CSG-139, 162 and 316.

(a mould to produce such a palstave was found at the site). Its microstructure suggests that after casting it was subjected to some cycles of deformation and annealing possibly for the cutting of the casting sprue and finishing of the surface.

The two spatula fragments CSG-179 and CSG-330 and the double spatula CSG-383 are those which show the most pronounced thermomechanical worked microstructures. They are composed by equiaxed grains totally twinned and CSG-383 show clear elongated Cu–S inclusions. They also have slip bands indicative of a final cold work, probably performed to provide a strain hardening effect. The shape and microstructure of these artefacts is thus consistent with a cast bar fragment that was subject to thermomechanical cycles until its final shape.

5. Final discussion

Baiões collection has showed that there is more about the archaeological site than just an LBA foundry place with good examples of Late Bronze Age artefacts with Atlantic or Mediterranean typological features. The presence of a slag fragment gives evidences for the local production of bronze – and this happens for the first time in the studied region – offering new expectations to the early proposals of a local exploration of ores, as cassiterite. Also, it suggests that smelting was still performed inside the settlement,

similarly to what happened in earlier periods in the Iberian Peninsula, and differing from what happened in many contemporaneous LBA metallurgical sites in more Eastern/Mediterranean territories where smelting was done exclusively at the vicinity of the mine. The analysis of the slag fragment suggests smelting of copper ores with cassiterite or metallic tin by a rather primitive smelting process (as in a reaction vessel/crucible) leading to incomplete ore reduction and resulting in a heterogeneous microstructure with fine grained mixture of different phases. The low Fe content (<0.05%) in the analysed bronze artefacts does also point out to their fabrication in this kind of primitive smelting technology.

The metal worked in the site was mainly bronze – just a copper bar being identified – with an average composition of 13% Sn, with Pb and As absent or present as impurity. This alloy shows closest resemblances with other bronzes from the Central Portuguese Beiras and the bronzes from the Ria de Huelva hoard, rather than with bronzes from external Iberian regions (that show generally lower Sn contents and higher impurity patterns, specifically Pb). The extension of the area where this bronze is present, from Huelva to the cassiterite-rich areas of the Iberian Peninsula, might give some clues to LBA interactions among different regions of Iberian Peninsula, as well as give further support to the early proposals of a peninsular origin of the Huelva bronzes.

The presence of partially heat-distorted fragments of artefacts with equiaxed grain microstructure suggests recycling operations rather than faulty castings. Also, the assemblage of metallic nodules with worked microstructures and tin contents similar to the artefacts suggests that these might be parts of artefacts or other metallurgical remains (e.g. seams and splashing droplets) gathered for recycling. The coarse microstructure of some nodules suggests the presence of smelting droplets, or, due to their narrow Sn content range comparable to the Sn contents in the artefacts, heat altered fragments of artefact. If they were smelting droplets, their narrow Sn content can only be explained by previously selected prills that were being gathered with the aim of melting them together, perhaps with fragments of artefacts (recycling) to produce new artefacts with the proper Sn content. If the second hypothesis is to be true, these nodules might be, similarly to the partially heat-distorted fragments of artefacts, a result of a recycling operation. All these evidences pointing out to recycling operations, suggests that recycling was a normal procedure, even in sites where smelting, and thus production of new bronze, was performed.

The absence of low tin bronzes suggests that the loss in tin that occurs in regular recycling operations must have been compensated. Possibly, recycling was conducted with the addition of tin metal or tin ores, being the nodule CSG-327 an evidence of such an operation.

The “control” over Sn content in the artefacts, could possibly be achieved by the awareness of the colour (and hardness?) of the metals. The Sn content range of ~10–15% (most of the artefacts) produces a metal with a yellowish “gold like” colour that was probably appreciated, besides its good thermomechanical properties. The manufacture of two items with a higher Sn content (17–19%) could be intentional, to produce a more “silver like” colour, or, if unintentional, these artefacts could just be waiting for recycling. Most probably, among these LBA communities, “control” must be understood in the basis of a trial and error practical experience, which nevertheless, led to an empirical deep understanding of the materials behaviours and characteristics. This can somewhat be reflected in the various thermomechanical works that were applied in the artefacts, regarding their shape and composition. Long cycles of forging and annealing were more evident in the spatula fragments, suggesting the shaping of cast bars. Others, of larger size and more complex shapes, such as the scabbard chape, buckle element and bracelet fragment, were shaped by casting being needed just some final works. On the other hand, the socket fragment and the pin head, with the higher Sn compositions, were not subjected to any mechanical treatment.

The presence in Baiões of some items that can be a result of more than one operation, e.g. the nodule CSG-327 (smelting or recycling of bronze with addition of tin metal or cassiterite?), or items that could have had more than one function, e.g. the copper bar (to produce copper items or to be alloyed with tin metal or cassiterite in a partial smelting operation?), points out to the possibility of bronze being produced by various methods, regarding the needs and materials available. Certainly, more studies on metallurgical remains from other LBA sites of the region and from the Portuguese territory will be needed to fully understand the variety of the metallurgical operations that could have been undertaken at these small size LBA settlements.

Generally, the Baiões evidences suggest that smelting and metalworking could have been a commonplace activity requiring no special facilities (as complex furnaces and large infrastructures), no task specialization (various metallurgical procedures could be performed in one place possibly by the same people), being thus perfectly adequate to be performed inside the settlements, at a domestic part-time(?) level.

The relatively high Sn content among the studied items (~13 ± 3%) and absence of low tin bronzes may suggest that the exploitation of local tin ores was a reality (although in a relative low scale), resulting in an constant tin supply, and thus enforcing the role of metallurgy and associated activities in the site/region.

Finally, the present study suggests that the neat separation among smelting and melting sites, mostly based on Mediterranean models, does not seem to be adequate to the central Portuguese LBA reality, namely to the Baiões/Santa Luzia cultural group. Sharing the problem of slags scarcity, as generally happens for the Atlantic areas, this study suggests that the problem might rely mostly in the different archaeological visibilities that exist between large, specialized smelting sites (as those present in many Eastern/Mediterranean areas) and small bronze producing settlements (maybe with simple smelting processes), whose activities are not so perceptible in the archaeological records. Perhaps, the increase in bronze circulation during the LBA in Western Europe could have had a significant contribution from (numerous?) small habitat sites like Baiões that were also smelting to produce bronze.

Acknowledgements

The authors are thankful to Prof. Thilo Rehren and the anonymous reviewers for their valuable comments and suggestions to an early version of the manuscript. This work has been carried out in the framework of the project METABRONZE (Metallurgy and Society in Central Portugal Late Bronze Age) financed by the Portuguese Science Foundation (FCT) (POCTI/HAR/58678/2004). The first author acknowledges the FCT for the SFRH/BD/27358/2006 grant. CENIMAT/I3N funding by FCT/MCTES is acknowledged by RJCS and FMBF.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the on-line version, at doi:10.1016/j.jas.2010.01.023.

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