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Metallographic studies of copper based scraps from the Late Bronze Age Santa Luzia archaeological site (Viseu, Portugal)

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ABSTRACT: Once metal was recognized as a new material in prehistorical times metallic artifacts began to be made and the metallurgical skills started to develop. Metallurgical scraps found in archaeological sites normally evidence metallurgical production of artifacts *in situ*. Studies of metal scraps can reveal the different stages of thermo-mechanical treatments that the artifacts were subjected to in order to obtain a selected shape and hardness. While for metal artifacts sample taking can be problematic, sample taking in metallurgical scraps can be easier since scraps have normally no artistic/esthetical display value. Additionally, corrosion phenomena can be evaluated in scraps that frequently have not been subjected to any conservation treatment. This paper deals with metallographic (optical and electron microscopy), EDS-SEM and EDXRF studies that have been undertaken in copper based metallurgical bars of circular and square sections from Santa Luzia site, in central Portugal.

1 INTRODUCTION

1.1 *Santa Luzia archaeological site*

The Santa Luzia site is one of the archaeological sites that form the Baiões/Santa Luzia cultural group. It is located near Viseu (central Portugal), in the Beira Alta region. Four ^{14}C dates were obtained for the site, relating the site earliest occupation between 1270–1030 cal BC (Senna-Martinez 2000a).

The metallurgical findings in the Baiões/Santa Luzia archaeological sites have first been described as a "hoard" or "foundry deposit". In the Santa Luzia site bronze artifacts have been found, as well as fragments of scrap and a mould for casting chisels with a square section. More recently the material recovered has been re-analyzed and a new interpretation for the metal findings has been developed. Since the majority of the metal recovered from the sites are not artifacts but fragments of scraps, wire, bars and leftovers, the metallurgical findings are now related with the existence of foundry areas (Senna-Martinez & Pedro 2000). If this is to be true, all the sites from the Baiões/Santa Luzia cultural group show small familiar type foundry areas. This contradicts the traditional model for Atlantic Late Bronze Age where it was thought that all the metallurgical work was made in a centralized workshop that would produce for an entire surrounding area.

This preliminary work involving non-destructive chemical analysis and metallographic studies of scrap bars aims to improve the understanding of the metallurgical processes during the Late Bronze Age in central Portugal.

1.2 *Archaeometalurgical studies*

The use of copper alloyed with tin within the Portuguese territory becomes generalized just in the beginning of the Late Bronze Age (1250/1100 BC). The addition of lead to the alloy happens by the ending of the Late Bronze Age and is essentially restricted to the northern region (Senna-Martinez 2000b).

Adding tin to copper lowers the melting temperature of the metal and allows a higher hardness after cold work when compared to unalloyed copper. Lead also improves the castability of the metal (Mohen 1992).

When a metal is cold worked its internal structure is deformed increasing the metal's hardness. A piece of metal with extensive cold work will get fragile and very brittle. But after cold work, if the metal is heated during enough time (annealing) its microstructure will suffer a recrystallization allowing the metal to be cold worked again.

During solidification some alloying elements and impurities are segregated by the solid phase into the remaining liquid. As the solidification progress, and volume contraction takes place, the remaining liquid will experience a greater difficulty to flow along the interdendritic channels; in the final crystal interstices some liquid could become trapped between first solidified crystals leading to the formation of high solute concentrate regions. Pores are then frequently formed in the place of metal in the last parts to solidify (Smith 1982).

Metallographic studies of metal artifacts from Portuguese archaeological sites are very rare (Soares et al. 1996). Most of the work done in Portugal recently, in the archaeometallurgical field, has concerned the elemental characterization, mainly through EDXRF analytical techniques (Araújo et al. 2004, Figueiredo & Araújo 2005, Soares et al. 1994).

Regarding the entire Iberian Peninsula the recent published work from the authors S.R. Llorens & P.G. Ramos (2003) has given a vital contribution for the development of archaeometallurgical studies, namely metallographic studies.

In their work the authors studied different metal artifacts covering a chronology that goes from the Copper Age to the Middle Bronze Age. In their conclusion they observe that during the Copper Age most of the objects analyzed were cold worked without annealing after casting, and just some suffered an annealing after cold work. Even less suffered no mechanical work at all after casting. The Early Bronze Age broadens the number of sequences of work to be carried on the metal artifacts. Most of the objects were still just cold worked after the cast but some others show a new sequence, where annealing was made after the casting with no mechanical working in between. The number of objects that were cold worked after a sequence of cold work and annealing also increase compared to the Copper Age. It has not been analyzed as-cast artifacts from the Middle Bronze Age. Some further mechanical work after casting has always been observed; most of the analyzed artifacts were cold worked, annealed and cold worked again or just cold worked after casting. It is interesting to observe that the majority of the analyzed objects had cold working as the final operation while the majority of the copper-tin awls show the annealing as the last operation.

2 EXPERIMENTAL DETAILS

2.1 *Scrap samples*

For this study six scrap bars were chosen with similar sizes but different sections (Fig. 1). Three bars have a square section (SL1, SL2 and SL3), two a circular section (SL4 and SL5), and one an oval section (SL6) (Table 1). Their original functionality is unknown, but the shape can show similarities with known forms e.g. chisels, awls or bracelets.

All the samples show a greenish surface corrosion color.

2.2 *Sample preparation and analytical techniques*

To avoid taking a sample of an already very small sized object the complete bars were mounted in the mould with a metallographic preparation resin that

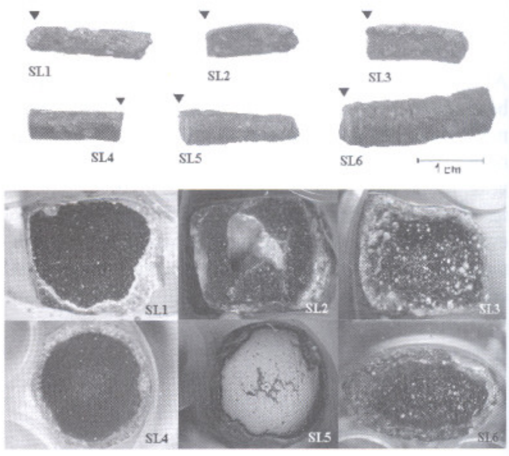

Figure 1. Scrap bars studied (on top) and the corresponding cross-sections (on bottom). The black arrows point out the localization of the studied cross-sections.

Table 1. Description of archaeological metal scrap bars studied.

Scrap bar	Section*	Weight (g)	Length (cm)	Section** (cm)
SL1	square	0.8	2.0	0.3 × 0.3
SL2	square	1.1	1.5	0.3 × 0.3
SL3	square	1.6	1.7	0.5 × 0.5
SL4	circular	1.3	1.5	0.5
SL5	circular	1.9	1.7	0.5
SL6	oval	2.7	2.5	0.5 × 0.4

* Geometry of the bars cross-section.
** Side lengths for square sections; maximum and minimum diameter for oval sections; diameter for the circular sections.

allows the recovery of the bars after the study. The bars were positioned in such a way that their cross-section could be analyzed.

All the mounted bars were first polished in SiC abrasive paper from 240 to the 2400 grit size and then polished with a diamond suspension in a rotary polishing wheel (until one-quarter micron size diamond).

The etching was made using an aqueous ferric chloride solution. Samples were examined both in unetched and etched conditions.

Before the scrap bars were mounted in the mould a surface elemental characterization was made using the analytical technique energy dispersive X-ray fluorescence spectrometry (EDXRF). The equipment used was a Kevex 771 installed in Departamento de Química do Instituto Tecnológico e Nuclear, with secondary targets that allow the optimization of the analytical conditions. With this technique the corroded surface was analyzed and quantification for metallic elements was performed. Quantification was made using calibration lines recorded on standard phosphor bronzes certificated by Burial of Analysed Samples LTD. Detailed descriptions of the equipment as well as quantification procedures were previously described in Araújo et al. (2004).

The scrap bars cross-sections unetched and etched were analyzed in a reflected polarized light microscope with a digital photographic camera attached.

A selected sample (SL5) was studied under the scanning electron microscope (SEM), Zeiss model DSM 962, with a secondary electrons detector (SE), backscattered electrons detector (BSE) and an energy dispersive spectrometer (EDS) from Oxford Instruments model INCAx-sight with a ultra thin window. This equipment is installed in CENIMAT/DCM Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa.

The sample was previously sputtered with a thin layer of gold. Semi-quantitative analyses were performed using a calibration line recorded on a pure cobalt reference standard.

3 RESULTS AND DISCUSSION

The corroded surfaces were analyzed by EDXRF, showing that the scrap bars were made of a copper-tin alloy, having the most of them small amounts of lead and/or arsenic (Table 2). The EDXRF analyses show a high value of tin as a result of corrosion phenomena (Figueiredo & Araújo 2005, Meeks 1986).

In unetched conditions all the scrap bars show the existence of small inclusions of copper sulfide. The copper sulfide has a gray color very similar to the grey color of copper oxides under reflected light in the microscope.

But these can be distinguished under reflected polarized light microscope by the fact that the grey sulfide inclusions get a darker grey color, while the copper oxides get a red color. The presence of copper sulfides in a high content, over 0.1%, has been related to the use of sulfide ores for smelting (Rapp 1989). Data for the Iberia Peninsula points out that in the early ages the metal was obtained by smelting oxide and carbonated copper rich ores producing a small amount of slag (Rovira 2002). The smelting of sulfide copper ores would probably just begin in the Iron Age for some sites.

Table 2. Elemental composition of the corroded surfaces obtained by EDXRF. *

	Cu	Sn	Pb	As	Sb	Fe
Scrap bar	wt% (normalized)					
SL1	34.6	63.7	0.11	nd	nd	1.27
SL2	44.7	52.3	1.43	0.29	0.26	0.75
SL3	44.8	46.2	0.09	3.32	1.50	3.69
SL4	49.6	49.5	nd	0.26	nd	0.66
SL5**	44.5	53.3	0.33	0.57	nd	0.97
SL6	49.6	48.2	0.56	0.43	0.27	0.68

* nd = not detected.
** this scrap bar has also been analyzed by EDS-SEM giving the following values: Cu 83.1%; Sn 16.9%.

All the bars show pores, but in different number and sizes. In the circular cross-section bars SL4 and SL5 the pores are present mainly in the center of the bar and are small sized.

The SL5 circular bar shows corrosion coming from the center of the cross-section. The corrosion has probably developed along the center of the bar where the impurities concentration was higher due to normal segregation that occurred during solidification.

The oval section bar SL6 has many large size pores distributed in the entire cross-section surface, even in the more superficial corroded metal. The SL3 square bar has a similar number, distribution and size of pores.

The square section bars SL1 and SL2 have some pores, but small. The bar SL2 has a big lack of metal in its center, possibly due to corrosion progress that has developed further than in the SL5 bar.

In the bars SL1, SL2, SL3 and SL5 the $\alpha + \delta$ eutectoid phase from the bronze (Cu-Sn alloy) can be seen (Fig. 2). Under the reflected light microscope eutectoid phase has a light blue color which becomes gray under polarized light.

The eutectoid (α copper rich phase + δ tin rich phase) could be distinguished under large magnifications.

The bar SL5 is the one which has more eutectoid phase present. This bar was analyzed by EDS-SEM and a semi-quantification was made under a $\times 200$ magnification, with no corrosion products in the analyzed area.

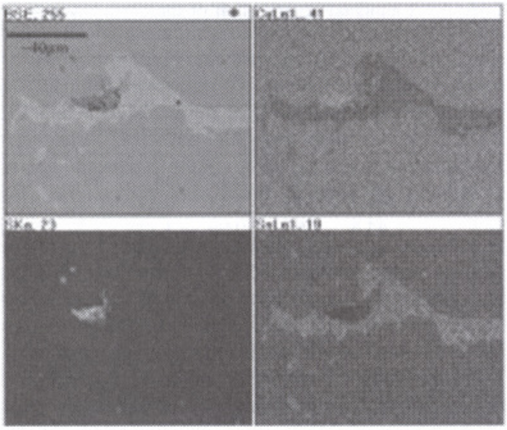

Figure 2. Elemental mapping of a section from the SL5 bar showing the δ tin rich phase in the eutectoid phase and copper sulfide inclusions. SEM image (scale bar = 40 μm).

The SEM-EDS microanalysis revealed a bronze with 16.9 wt% of Sn. The results from the EDXRF analysis on the corroded surface show a greater tin content (53.3 wt% Sn) probably as a result of copper being leached out of the surface as part of the corrosion phenomena.

The loss of copper on the corroded areas is demonstrated on Figure 3 were an SEM-EDS line scan was made over the SL5 cross-section, from the exterior corrosion layer to the central corrosion.

When corrosion reaches an eutectoid region the α copper rich phase that is preferentially corroded leaving the δ tin rich phase frequently surrounded by copper oxides (Fig. 4).

Intergranular corrosion is present in greater or lesser extent near the surface of the metal in contact with the external corrosion layer.

In the bars SL2, SL4 and SL5 there is also an intergranular corrosion starting from the center of the cross-section. The bar where intergranular corrosion is more pronounced is the SL6 bar. In this bar the corrosion travels along the grain boundaries and reaches the pores that begin to get filled with the copper oxides corrosion product (Fig. 5).

Lead spherical droplets are very small and difficult to distinguish under reflected light microscope even with large magnifications. They become visible under the SEM atomic number contrast image (BSE) where they appear close to the eutectoid phase, frequently inside a pore (Fig. 6). Since lead has a low solidification temperature, the last liquid to solidify is lead rich.

When etched, the bars show different microstructures. The bars SL1, SL2 and SL5 evidence along all the cross-section recrystallized grains (twinned). These bars have been cold worked and annealed or have been shaped by hot working. It is not possible to

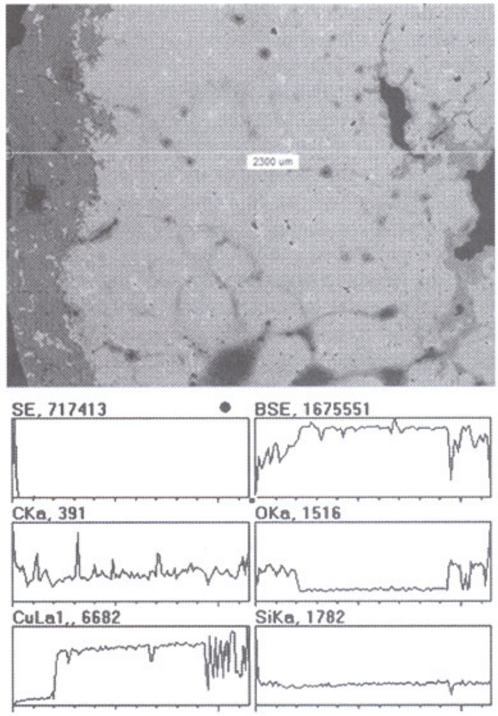

Figure 3. Line scan analyze of 2300 μm made along the cross-section of the SL5 circular scrap bar with EDS-SEM. Top: cross-section of the SL5 scrap bar from the corroded surface layer (at left) until the corrosion on the center of the section (at right) (SEM image obtained by BSE). Bottom: morphology line scan (SE); atomic contrast line scan (BSE); carbon elemental line scan (C); oxygen elemental line scan (O); copper elemental line scan (Cu); silicon elemental line scan (Si).

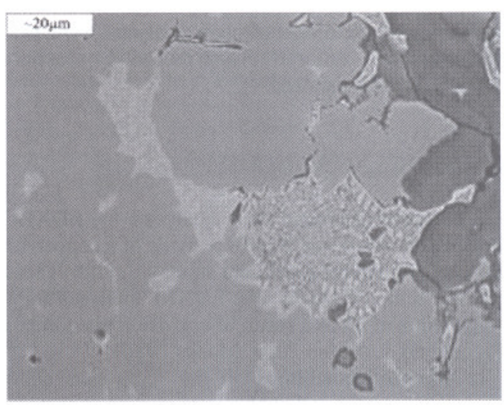

Figure 4. Section of the SL5 bar near the corroded surface layer (at right, dark grey color). A $\alpha + \delta$ eutectoid phase begins to be attacked by corrosion. Selective corrosion takes place as the corrosion attacks first the α copper rich phase within the eutectoid phase. BSE image (scale bar = 20 μm).

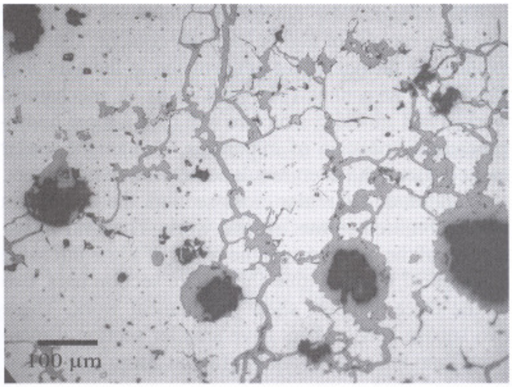

Figure 5. Section of the SL6 bar unetched. Intergranular corrosion reaches the pores which begin to get filled with copper oxides corrosion products. Reflected light microscope.

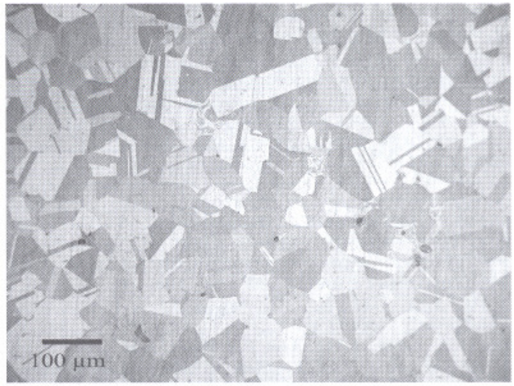

Figure 7. Etched section of the SL1 bar showing well developed recrystallized grains (twinned). Reflected light microscope.

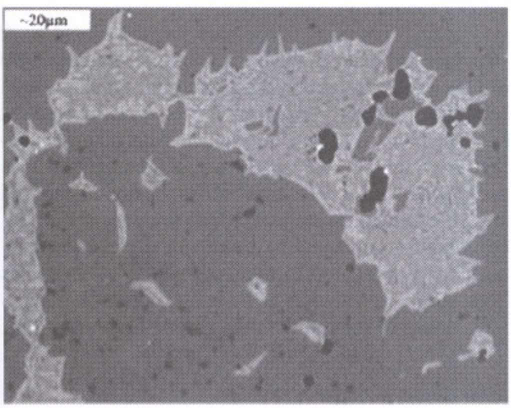

Figure 6. Section of the SL5 bar with a $\alpha + \delta$ eutectoid phase filled with pores (black) and lead spherical droplets (white). SEM image obtained by BSE (scale bar = 20 μm).

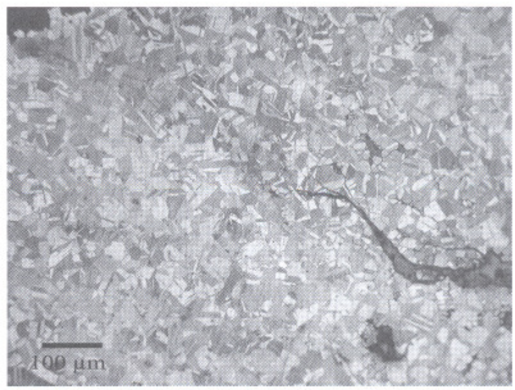

Figure 8. Etched section of the SL2 bar showing the recrystallized grains (twinned). A crack penetrates from the center of the cross-section towards a corner of the square section. Reflected light microscope.

distinguish between these processes, but tools used by metal smiths to manipulate and fasten the hot objects haven't been found for these periods in prehistoric archaeological sites leading some authors to allege that the metal was cold worked followed by annealing (Llorens & Ramos 2003). The two square section bars SL1 and SL2 show well-developed twinned grains which demonstrate a large amount of cold work and a long annealing treatment, specially for bar SL1 where the average grain size is larger (Fig. 7).

The bar SL2 has some cracks that come from the interior of the cross-section and go towards the square corners (Fig. 8). Midsection cracking is often associated with over-working at some stage during manufacture. These cracks in the worked alloy are not removed with further annealing and working (Scott 1991).

The SL4 bar has a very distorted microstructure possibly owing to extensive cold working. Grain boundaries are difficult to recognize possibly for the reason that the bar has not suffered any annealing for recrystallization. The shape of the porosities evidence hard working since they are small sized and have deformed shapes.

The square bar SL3 has a typical as-cast microstructure showing well defined dendrites (Fig. 9). Possibly, some annealing has taken place in order to increase the grain size.

The oval bar SL6 has an as-cast microstructure on the center and evidence of work in the areas nearer to the surface, probably for some shape finishing. The bar has been annealed since the outer grains are recrystallized (Fig. 10).

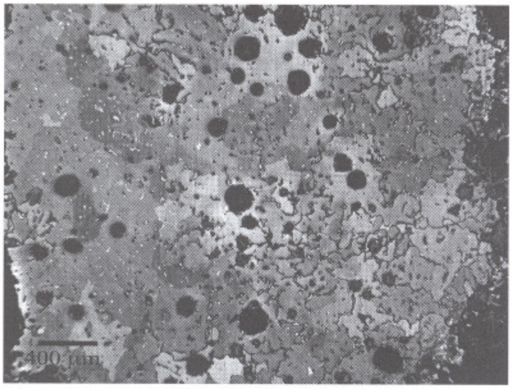

Figure 9. Etched section of the square SL3 bar showing a as-cast microstructure. Reflected light microscope.

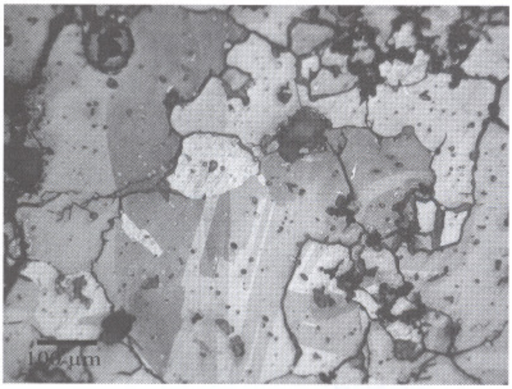

Figure 10. Etched section of the oval bar SL6 showing recrystallized grains (twinned) just on areas near to the surface. The bar was cast, worked just on the surface and annealed. Reflected light microscope.

4 CONCLUSIONS

All the bars were worked after casting except for the S3 square section bar.

The two bars that show a significantly major size and number of pores (SL6 oval bar and the SL3 square bar) are the only scrap bars studied which show an as-cast microstructure. One can then suppose that the small size pores on the other scrap bars result from larger pores that have been compressed and probably elongated along the bar length due to the mechanical deformation.

The SL3 square section bar microstructure is as cast and has probably just suffered some annealing treatment. This kind of square section has probably been obtained from a chisel mould as the one that has been found also in the Santa Luzia site.

The intergranular corrosion path tends to follow along the regions of higher impurity content. That may explain the further extent of corrosion in the bars with the as-cast structures (SL3 and SL6). A mechanical worked and annealed structure will have a more homogeneous distribution of impurities. This might render more difficult the intergranular corrosion development.

To produce a circular cross-section, the metal bars were submitted to mechanical work. The oval cross-section of the bar SL6 was the result of a less intensive mechanical work. Within the square section bars, two of the three samples show mechanical work. These two square section bars have smaller section dimensions than the cast square bar (about 2 mm less each).

Probably, the metal bars have begun as a cast awl or chisel with a square section. For chapping the cast to a circular section cold work and annealing has been applied. For improving the appearance of a square section, changing the size or making the object harder, some mechanical work and annealing could also be made.

The fact that none of the bars showed a cold work structure over an annealed microstructure can have different interpretations. The bars might just be some leftovers that did not receive the final treatment because none of them achieved the final stage of artifact making. The bars or some of them might have made part of an artifact that had not been cold worked after the annealing stage. Copper-tin alloy show predominantly the annealing treatment as final processing (when compared to the unalloyed copper) as has been shown for objects as awls by Llorens & Ramos (2003) maybe related with the spread of a new alloy.

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