Microstructure Interpretation of Copper and Bronze Archaeological Artefacts from Portugal

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Abstract. In the present paper, a selection of micrographs showing some typical microstructures and corrosion layers developed in copper and bronze alloys from different archaeological contexts will be discussed. Metallurgic interpretation of the microstructures observed, based in the proper binary equilibrium phase diagrams is presented. Micro-EDXRF and SEM-EDS analysis were carried out to assess the alloy composition and to contribute to the understanding of the corrosion processes occurred during the long periods of burial of the archaeological metals. Examples of surface decuprification, strong intergranular corrosion, cuprite under green corrosion layers and copper redeposition indicate particular corrosion processes. The presence of copper oxides, sulphides inclusions, lead globules and porosities is also documented.

Introduction

Metal has been used to produce artefacts since pre-historical times. Different periods in History may be characterised by the use of different alloys.

Copper was one of the first and most important metals used in pre-history and more recent times. The Chalcolithic period, when copper metallurgy appeared, starts at 3rd millennium BC in the Portuguese territory. Later on, the introduction of the alloy of copper and tin proceeded to the Bronze Age. During Late Bronze Age (~1200-450 BC in Portuguese territory) bronze became common [1] and a new alloy, leaded bronze, came to use. From Roman times onwards other copper alloys became common.

Due to the historical/artistic value of archaeological artefacts, some archaeometallurgical studies regarding destructive or invasive techniques are not recommended since these can lead to change in the appearance of the artefact as changes in physical and chemical properties. Archaeometallurgical studies in the Portuguese territory have been carried out during the last decades based mainly on non-invasive analytical techniques. This has allowed collecting information about the surface composition of artefacts, often presenting thick corrosion layers resulting in high tin contents [2] but information about the microstructure, internal corrosion and on the metallurgical processes used in the manufacture of artefacts is still very scarce (nearly not available).

More recently, due to the importance of these data in the comprehension of ancient metallurgy and corrosion phenomenon, archaeological broken artefacts, small fragments and scraps that have no strong artistic value have been sampled for metallographic studies using optical and electronic microscopy. A series of metallographic micrographs has been collected, especially those regarding to copper based alloys, particularly bronzes.

This gathered data, complemented with micro-EDXRF and SEM-EDS experiments, is of a major importance in archaeometallurgical and conservation science studies since it gives information about the thermo-mechanical chain work, metal inclusions and corrosion phenomena in artefacts of different periods and metal compositions.

Experimental Details

Artefacts and fragments. The artefacts and metal fragments studied cover a wide frame of time, since Chalcolithic (3rd millennium AC) until Middle Ages (XIII century). They are as following:

  – a fragment of the edge of an axe, from the Chalcolithic site of "Vila Nova de São Pedro" (Azambuja, Central Portugal) [3];

  – a bar fragment with unknown function, recovered in Late Bronze Age archaeological layers (1270-1030 BC) in site of "Castro de Santa Luzia" (Viseu, Central Portugal) [4];

  – a bar fragment with unknown function, attributed to a late period of Late Bronze Age, from "Fraga dos Corvos" (Macedo de Cavaleiros, North Portugal) [5];

  – a sample of a broken ancient bell, dated to 1287, from Coruche (Central Portugal).

Sample preparation and analytical techniques. Small samples from the metal artefacts and fragments were mounted for metallographic preparation. The samples were positioned in such a way that their cross-sections could be analysed. All the mounted samples were first polished with SiC abrasive paper and then polished with a ½ μm diamond suspension. Samples were examined by light microscope (OM) in bright field and polarized light, both in unetched and etched conditions. The etching was made using an aqueous ferric chloride solution.

Micro-EDXRF analyses were made over the metal core of the cross-section of the mounted and polished samples (unetched) in order to obtain the metal alloy composition. The micro-EDXRF equipment used was an ArtTAX Pro spectrometer which comprises a low-power X-ray tube with a molybdenum anode. The system includes a set of polycapillary lenses that generates a micro spot, smaller than 100 μm in diameter, of primary radiation [6].

For analysis under the scanning electron microscope (SEM) the equipment used was a Zeiss DSM 962, with a secondary electrons detector (SE), backscattered electrons detector (BSE) and an energy dispersive spectrometer (EDS) from Oxford Instruments INCAx-sight.

Results and Discussion

Figure 1 shows a Chalcolithic copper micro-structure belonging to a fragment of the edge of an axe, recovered from the site of "Vila Nova de São Pedro". The microstructure consists of a primary α-Cu phase and (α+Cu_2O) eutectic. According to the Cu-O binary phase diagram this eutectic reaction occurs around 1066 ºC for oxygen contents in the melt higher than 0.004 wt%. The presence of cuprite, Cu_2O, in the metal core is typical of copper melted under normal oxidizing conditions. Annealing twins in the α-Cu phase reveal the practice of a recrystallization heat treatment. The eutectoid regions envelop the primary α-Cu grains, evidencing its shape and allowing the evaluation of previous deformation. A central crack, probably

Fig. 1 Micrograph of the edge of the Chalcolithic axe from "Vila Nova de São Pedro". Optical microscope, bright field, etched sample.

formed during burial corrosion, crosses all the micrograph. Intergranular corrosion, observable in both sides of the crack, seems to prefer the path along the grain boundaries between the primary grains and the eutectoid.
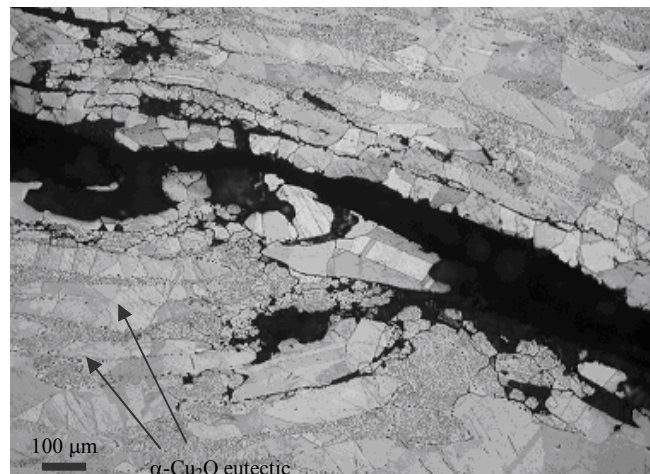
The next micrograph (unetched), in Fig. 2, shows the central section of the bar fragment from "Castro de Santa Luzia" (Late Bronze Age), made of a "binary" bronze, with 8 wt% Sn. The presence of sulphide inclusions was identified by OM and SEM-EDS although sulphur content could not be determined. During solidification, according to the Cu-S binary phase diagram, a

sulphur content higher than 0.84 wt% leads to a monotectic reaction ($L_1 \rightarrow L_2$+solid), with formation of a solid Cu_2S phase. The remaining liquid results in an eutectic, α-Cu+Cu_2S. This eutectic has a composition close to 99.2 wt% Cu, and it is mainly composed by a very pure α-Cu phase. In this ancient bronze, those compositions were attained in the interdendritic regions of the primary α-Cu grains, due to sulphur segregation during solidification. This leads to the formation of Cu_2S (dark grey colour in MO) and a much pure α-Cu (pink colour in MO) phases in the microstructure. In this micrograph it is also visible some intergranular corrosion along the interdendritic regions.
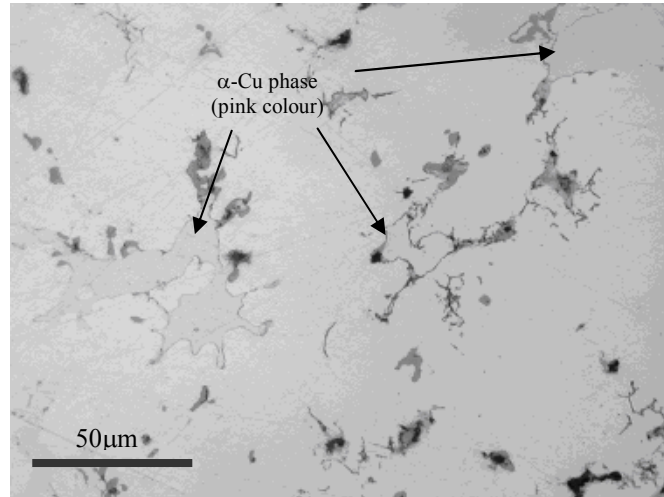

Fig. 2 Micrograph of the central region in the cross-section of the "Santa Luzia" bar fragment. Optical microscope, bright field, unetched sample.

Figure 3 shows the microstructure (unetched) of the Late Bronze Age metal artefact from "Fraga dos Corvos", north of Portugal. The average bronze composition is 8.6 wt% Sn and 2.1 wt% Pb. The bronze exhibits a uniform distribution of small globules and micropores in the matrix. The regular distribution and rounded forms of the micropores is attributed to its interdentritic formation. Figure 3-b shows an X-ray elemental map for the main chemical elements present in the metal core and in the corrosion layers. Those SEM-EDS results show that regularly distributed globules in the metal core are from a Pb rich microconstituent. According to the Cu-Pb binary phase diagram, this lead rich constituent, with a Pb content of approximately 99.9 wt%, is formed at a low temperature eutectic (326 °C). In the X-ray map it is clear that, near the corrosion layer, the Pb content in the globules is replaced by Cu and O. The X-ray map and polarized light microscopy observations, also performed for these samples, suggest that leaching of Pb phase during burial is mainly replaced by Cu_2O (red colour under polarized light).
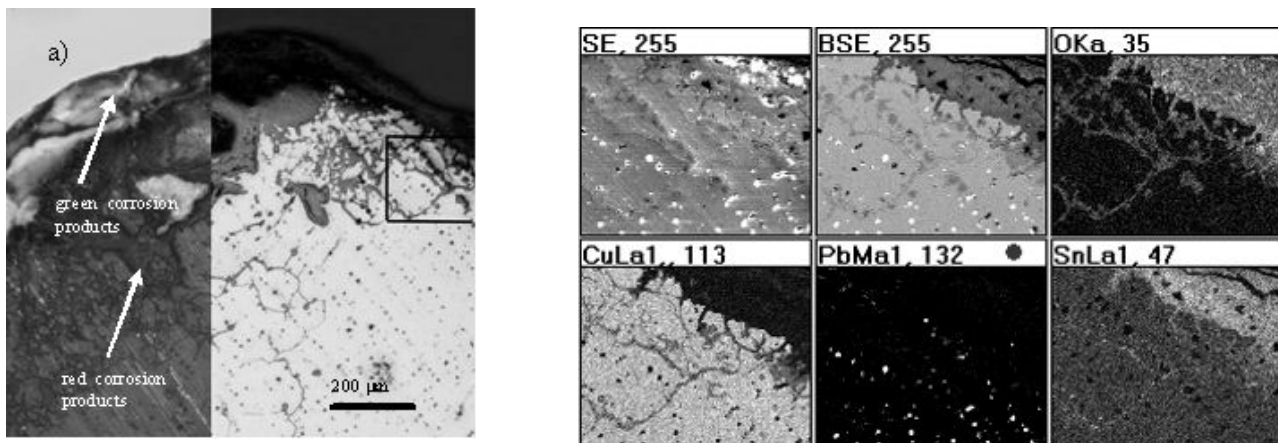

Fig. 3 a) Micrograph from the cross-section, unetched, of the "Fraga dos Corvos" bar fragment. This picture is a combination of observations under polarized light (on left) and bright field (on right) image. Corrosion developed from the surface of the bar (at left and top) to metal core (bottom and right). b) Elemental mapping of the area marked at top. From left to right, top to bottom: secondary electrons image (SE); backscattering electrons image (BSE) and oxygen (O), copper (Cu), lead (Pb) and tin (Sn) X-ray maps.

The same set of observations also shows a deep intergranular corrosion with Cu_2O precipitate. At the outer corrosion layers, the X-ray map shows a relative enrichment in Sn. This is attributed to the formation of high solubility copper corrosion products in the highly aerated regions - as copper carbonates that give a green colour under polarized light - comparatively with the formation of a stable and not soluble tin oxide, SnO_2.

Figure 4 shows a high tin bronze, around 21 wt% Sn and 3 wt% Pb, belonging to the ancient bell from Coruche. The metal core comprises a primary α and (α+δ) eutectoid microstructure. Intergranular corrosion developed during the burial and transgranular cracks, parallel to the bell surface and filled with corrosion products, are easily observed. This peculiar corroded microstructure shows the result of the low oxygen content in the deeper corrosion regions. Oxidation of δ-eutectoid Sn rich phase (light grey colour in MO) to tin oxide (black) was accomplished with the redeposition of its copper content into empty places, like cracks and globule holes - left behind by the leaching of the lead rich phase - to form a copper rich phase (pink colour in MO). On the other hand, at the more superficial regions, oxygen remains at a potential level high enough

Fig. 4 Micrograph from the bell cross-section. Corrosion developed from the surface of the bell (on right) to the metal core (on left). Optical microscope, bright field, unetched sample.

to oxidize the copper existing in the primary α phase, and in the eutectoid α phase, to cuprite (grey colour). In those regions the δ-eutectoid phase seems to be unaffected. This preferential corrosion of copper rich phases in the outer regions could be understood taking into account that tin, although less noble metal than copper, passivates more efficiently at high oxidizing conditions.
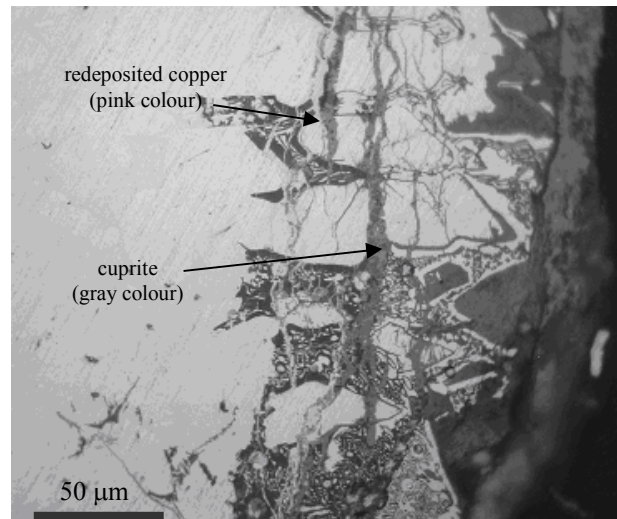
Conclusions

Metallographic studies have been of great value in archaeometallurgical studies since different inclusions and metal phases between the primary α-Cu phase could be identified in the samples: eutectoid (α+Cu_2O) in the Chalcolitic copper from "Vila Nova de São Pedro"; a eutectic (α-Cu+Cu_2S) in the bronze alloy from Late Bronze Age "Castro de Santa Luzia" site; small Pb globules and micropores in the Late Bronze Age "Fraga dos Corvos" site; and a significant quantities of (α+δ) eutectoid in the Middle Age bell from Coruche due to its high tin content.

The metallographic analysis has allowed an evaluation of the corrosion process undergoing archaeological metallic artefacts. Intergranular corrosion is present in all metal fragments, as a result of long term corrosion. This corrosion follows preferentially the interdendritic regions, with higher impurities content. Although copper is a more noble metal than tin in oxidizing conditions copper rich phases suffer preferential corrosion, since tin passivates more efficiently, forming not soluble tin oxide, SnO_2. This leads to a superficial enrichment in tin that is not representative of the core composition of the artefact. When present, lead globules are lixiviated near the surface resulting in the precipitation of Cu_2O in their place. Redeposition of copper in empty spaces forming copper "inclusions" has also been observed.

Acknowledgements

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