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The Early Metallurgy in Southwestern Iberia: Metals from the Chalcolithic Settlement of São Pedro (Redondo)

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para o meu pai.

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Abstract

Archaeological excavations carried out in the archaeological site of São Pedro (Southern Portugal) revealed a Chalcolithic settlement occupied in different moments of the 3rd millennium BC. The material culture recovered includes different types of materials, such as ceramics, lithics and metals. The later comprises about 30 artefacts with different typologies such as tools (e.g. awls, chisels and a saw) and weapons (e.g. daggers and arrowheads) mostly belonging to the 2nd and 3rd quarter of the 3rd millennium BC.

In the present work the collection of chalcolithic metallic artefacts recovered in São Pedro was characterized. Analytical studies involved micro energy dispersive X-ray fluorescence spectrometry (micro-EDXRF) to determine elemental composition, together with optical microscopy and Vickers microhardness testing for microstructural characterisation and hardness determination.

Main results show copper with variable amounts of arsenic and very low content of other impurities, such as iron. Moreover, nearly half of the collection is composed by arsenical copper alloys (As > 2 wt.%) and an association was found between arsenic content and typology since the weapons group (mostly daggers) present higher values than tools (mostly awls). These results suggest some criteria in the selection of arsenic-rich copper ores or smelting products. Furthermore, after casting an artefact would have been hammered, annealed and sometimes, finished with a hammering operation. Additionally, microstructural variations in this collection reveal somewhat different operational conditions during casting, annealing and forging, as expected in such a primitive metallurgy. Moreover the operational sequence seems to be used to achieve the required shape to the object, rather than to intentionally make the alloy harder.

Overall, this study suggests that Chalcolithic metallurgists might have a poor control of the addition of arsenic and/or were unable to use this element to increase the hardness of tools and weapons.

Finally, the compositions, manufacturing processes and hardness were compared to those from neighbouring regions and different chronological periods.

Keywords: Archaeometallurgy; Chalcolithic; Southern Portugal; Copper; Arsenic

Resumo

Escavações arqueológicas realizadas em São Pedro (Sul de Portugal) revelaram um povoado Calcolítico ocupado em diferentes momentos do 3º milénio a.C.. Durante a escavação foram recuperados diversos tipos de materiais tais como cerâmicos, líticos e metálicos. O conjunto de metais compreende uma coleção de cerca de 30 artefactos com diferentes tipologias, tais como ferramentas (punções, cinzeis, espátulas e uma serra) e armas (punhais e pontas) na sua maioria pertencentes ao 2º e 3º quartel do 3º milénio a.C..

O presente trabalho centra-se na caracterização dos artefactos metálicos calcolíticos recuperados em São Pedro. Os estudos analíticos envolveram a determinação da composição elementar por espectrometria de fluorescência de raios X, dispersiva de energias e a caracterização microestrutural e determinação da dureza, obtidas por microscopia óptica e ensaios de micro dureza de Vickers.

Os principais resultados revelam um conjunto de artefactos constituídos por cobre com quantidades variáveis de arsénio e baixo teor de impurezas, nomeadamente de ferro. Verificou-se que cerca de metade da coleção é composta por ligas de cobre arsenical (As > 2 %), tendo sido encontrada uma associação entre o teor de arsénio e a tipologia, uma vez que o conjunto das armas (maioritariamente punhais) apresenta valores mais elevados de arsénio quando comparado com o conjunto das ferramentas (maioritariamente punções). Estes resultados podem sugerir algum critério na seleção de minérios de cobre ou produtos de fundição ricos em arsénio. A manufatura dos artefactos incluiu operações de martelagem e recozimento, sendo pontualmente finalizada com uma martelagem. No entanto, diferentes características microstruturais revelam a utilização de condições operacionais distintas durante o vazamento, recozimento e martelagem, como seria de esperar numa metalurgia primitiva. Além disso, a cadeia operativa parece ter sido usada para dar forma ao objeto em vez de aumentar a sua dureza. De uma forma geral, este estudo sugere que os metalurgistas do período Calcolítico teriam um fraco controlo sobre a adição de arsénio e/ou que estes não aproveitavam a vantagem desta adição para aumentar a dureza das ferramentas e armas.

Por fim, as composições, processos de fabrico e durezas foram comparados com estudos semelhantes de regiões vizinhas e de diferentes períodos cronológicos.

Palavras-chave: Arqueometalurgia; Calcolítico; Sul de Portugal; Cobre; Arsénio

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Contents

List of Figures

List of Tables

Acronyms

BA Bronze Age.

BC Before Christ.

BCS British Chemical Standards.

BF Bright field (in OM observations).

BTA Benzotriazol.

C^{2}TN/IST Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico.

CA Chalcolithic.

CENIMAT Centro de Investigação em Materiais.

DCR Departamento de Conservação e Restauro.

DF Dark field (in OM observations).

EDXRF Energy Dispersive X-Ray Fluorescence.

FCT Faculdade de Ciências e Tecnologia.

FCT Fundação para a Ciência e a Tecnologia.

I3N Instituto de Nanoestruturas, Nanomodelação e Nanofabricação.

IA Iron Age.

IDLF Industries de la Fonderie.

MBA Middle Bronze Age.

OM Optical Microscopy.

PA Proyecto Arqueometalúrgico de la Península Ibérica.

Pol Polarized light (in respect to OM observations).

SAM Studien zu den Anfängen der Mettalurgie (project).

SEM-EDS Scanning Electron Microscope - Energy Dispersive Spectrometer.

SP São Pedro.

UNL Universidade Nova de Lisboa.

VHN Vickers Hardness Number.

Chapter 1

Introduction

The study of ancient metallurgy (archaeometallurgy) can provide important information regarding the technological progress of prehistoric societies. Archaeometallurgical studies were only possible with the development of chemical analysis in the eighteenth century, being the first study made in 1779 in two Bronze Age swords from Ireland (Pownall 1786). By this time, the main purpose of these studies was to determine the composition of the artefacts as well as the technology used in their production.

The idea of correlating the composition of artefacts with their provenance to provide information on their chronology and usage, was suggested by J.E. Wocel in the mid-nineteenth century (Craddock 1995). The progress of physical analytical techniques in the twentieth century, allowed large-scale analytical projects to become achievable as the analysis could be carried out much more efficiently and with reduced samples (Craddock 1995). Hence, interdisciplinary Archaeometallurgical studies started to connect analytical studies with the historical and cultural background, involving significant material culture such as artefacts and metallurgical remains (slags, crucibles, moulds, tuyeres etc.). This allowed to understand the evolution of metallurgical activities of ancient societies as well as their culture, economy and technological capacities (Craddock 1995). One of the early projects in this field was the "Sumerian Copper Committee of the British Association for the Advancement of Science in the Middle Eastern", by Otto and Witter, related to Bronze Age metallurgy in Europe, which was reported annually in the British Association from the 1920's through to the 1930's (Otto and Witter 1952). After that, other large scale projects have taken place, such as the "Studien zu den Anfängen der Metallurgie" (SAM), where numerous prehistoric copper-based artefacts from Europe were studied (Junghans et al. 1968; Junghans et al. 1974) or the "Proyecto de Arqueometalurgia de la Península Ibérica" (PA) which has focused on the elemental and microstructural analysis of artefacts, ores and by-products (Delibes and Montero 1999; Rovira and Gómez-Ramos 2003; Rovira et al. 1997).

The development of the archaeometallurgy in Portugal has improved significantly since the seventies due to the installation of non-destructive analytical techniques in

Portuguese research centres. Recently, archaeometallurgical research involving the Portuguese territory has provided significant contributions in the study of the production and use of metals and artefacts from the Chalcolithic (CA) to the Iron Age (IA), especially with the project "Early Metallurgy in the Portuguese Territory" (Araújo et al. 2013).

"The division of the history of the world in different periods named after metals is probably of Iranian origin" but Greeks poets and philosophers as well as Christians have also used this idea as the development of metallurgy allowed the transition from Stone to Metal Age (Forbes 1950) and is considered to have an important role in societal development (Lull et al. 2011). Therefore, the European prehistory is commonly divided in three different periods: Copper Age or Chalcolithic, Bronze Age (BA) and Iron Age. Each one of these stages corresponds to a different chronological period that differs from one region to another, e.g. the Chalcolithic in the Portuguese territory corresponds roughly to the third millennium BC (~3000-2000 BC). Moreover, the advance of time implies increasingly higher metallurgical knowledge, which comprises the use of native copper, the reduction of metallic ores and the production of alloys.

Native copper was surely more common than other native metals, thus being probably the first metal used in prehistory (Craddock 1995; Killick and Fenn 2012). As pre-historic communities realized that native copper could be reshaped by heating, they soon started to apply the processes that were used to work bone, clay or stone. These processes included hammering, annealing, cutting and grinding and some of them remain in use nowadays. Often, the work of native copper consisted in hammering it into sheets and then rolling these into tubes for smaller artefacts, such as awls (Craddock 1995; Tylecote 1992). Alternatively, forging and annealing could be used to prevent stress cracking (Killick and Fenn 2012) as annealing at moderate temperatures (easily obtained in a charcoal fire) leads to the removal of residual stresses introduced during forging. Sometimes, cold-working and annealing could be combined into one operation named hot-working (Scott 1991).

Although native copper tends to be extremely pure, it could present considerable amounts of arsenic, nickel, lead, antimony and iron (Craddock 1995; Tylecote 1992) as well as silver (Ortiz 2003), thus being very difficult to distinguish between native and smelted copper. In fact, it seems that the composition of native copper largely reflects the deposit in which it occurs (Tylecote 1992).

It is usually considered that the metallurgy begins with the discovery of the reduction of copper ores as well as the possibility of casting and melting (Killick and Fenn 2012). The process of copper smelting consisted in the reduction of the copper ore (previously crushed and hand sorted) through the application of heat in a reducing atmosphere (Ottaway 2001). During the copper smelting the unwanted minerals (gangue) were removed to the slag, which is mostly composed by oxides of iron and silica (Craddock 1995).

During the Chalcolithic, the ores were possibly smelted in a small non-conventional clay furnace with no bottom, placed on or half-buried in the ground and the fuel would have been charcoal with air provided from bellows (Ortiz 2003). However, due to the relatively low temperatures and low reducing conditions in the furnace, only small sized copper prills embedded in some poorly fused slag would have been formed during this process. Smelted copper was obtained by crushing the slag and removing the copper prills by hand, which were then melted to obtain the copper mass (Craddock and Meeks 1987; Ortiz 2003; Ottaway 2001). For that, a crucible usually in the form of a bowl, ideally covered with charcoal to provide reducing conditions and often heated from above could have been used (Ottaway 2001; Tylecote 1992).

According to Rovira (2002), in the Iberian Peninsula the process of ore reduction was conducted in open ceramic vases from the Copper Age to the pre-Roman period. This could be justified by the efficient rates of copper recovery from copper carbonates, which are easier to reduce and common in this region. Additionally, the social need for metal in this region was small, therefore, there was no need to use more complex and efficient smelting furnaces (Rovira 2002).

The ore smelting conditions in those primitive operations (poor reducing conditions and relatively low temperatures) did not allow the iron impurities from the ore to reduce and become incorporated in the copper, resulting in artefacts with very low iron contents (Craddock and Meeks 1987). Therefore, the iron content of ancient copper provides a good indication of the smelting process used.

Studies have shown that copper with variable amounts of arsenic and low concentrations of other impurities was the dominant metallurgical production in Iberian Peninsula from Chalcolithic till Middle Bronze Age (Rovira and Montero-Ruiz 2013; Soares et al. 1996). During many years it has been thought that arsenical copper (usually defined as copper with more than 2 wt.% arsenic) was an important step forward in alloying techniques to obtain better metals (Craddock 1995). Nevertheless, the true significance of arsenical copper as an alloy, intentional or not, is still uncertain and subject of many discussions.

Overall, the term alloy is referent to the combination of at least two components (of which one has to be a metal) in order to change or improve the properties of the material (Junk 2003). It is recognized that the addition of arsenic to copper leads to a lower melting temperature, colour changes (into a silvery colour) and, in certain conditions, to an increase of hardness and toughness. However, another matter is if prehistoric Man was aware of the advantages of arsenical copper alloys (Ottaway 2001).

The easiest way to obtain arsenical-copper alloys would be by smelting copper ores with natural proportions of arsenic. Metallic arsenic is a volatile element, with a boiling point of 613 ºC, but under reducing conditions, it is retained in metallic copper, having little affinity for the slag (Ortiz 2003). On the other hand, some authors defend that another way to produce arsenical copper alloys would be the addition of arsenical-rich minerals or speiss (a mixture of arsenical iron and iron arsenides) (Rehren et al. 2012; Thornton et al. 2009).

In relation to the Portuguese territory, only a few studies have been carried out regarding the Chalcolithic metallurgy and, for the most part, concerning metallurgical evidences from the Portuguese Estremadura (Pereira et al. 2013) and Northern Portugal (Valério et al. 2014b). The research reveals that artefacts are made of copper with low and variable arsenic contents, suggesting that even though no significant association between the arsenic amount and mechanical properties was found, there is some correlation between some artefact typologies and the arsenical copper alloy (considered as copper with more than 2 wt.% As). However, it should be emphasized that there are no modern analytical studies regarding the understanding of Chalcolithic metallurgy in the southern region of the Portuguese territory.

To cover this lack of knowledge, a group of 31 artefacts from the Chalcolithic site of São Pedro (Redondo, Southern Portugal) was selected for elemental and microstructural study. Artefacts include different typologies such as tools and weapons, with a chronology from the 2nd half of the 3rd millennium BC (Mataloto 2010). Materials were analysed with micro energy dispersive X-ray fluorescence (micro-EDXRF) to identify their major and trace elements composition. The microstructural characterisation comprising the identification of different phases, inclusions and casting defects, in addition to the manufacturing evidences (e.g. grain size, annealing twins and deformation bands) from operations used to produce these artefacts involved optical microscopy (OM) observations. Lastly, the microhardness was determined by Vickers microhardness testing on selected artefacts to establish the efficiency of the working sequence.

Besides the identification of the composition, manufacturing and hardness of the metals used in São Pedro during the Chalcolithic period, a comparison with artefacts from neighbouring regions and different chronological periods was made to better understand the ancient metallurgy in the southwestern end of the Iberian Peninsula.

Chapter 2

Experimental Procedure

2.1 Materials

2.1.1 *The Archaeological Site of São Pedro*

Manuel Calado first referred the archaeological site of São Pedro (SP) in 1993. This pre-historic site is located in Central Alentejo (Redondo), district of Évora, between Évora plains and the Guadiana valley, near Serra d'Ossa (Costeira and Mataloto 2013; Mataloto 2010; Mataloto and Boaventura 2009; Mataloto et al. 2013) (*Figure 2.1A*). The settlement is positioned on a small hill (318 meters above sea level), which allowed an ample visual dominance to South and West, over the surrounding territory (Davis and Mataloto 2012; Mataloto 2010).

Archaeological excavations carried out in 2004 revealed a Chalcolithic settlement (*Figure 2.1B*) occupied between the end of the 4th millennium and during different moments of the 3rd millennium BC (Mataloto 2010). The material culture recovered included ceramics, lithics and metals. The later comprises 31 artefacts with different typologies such as tools (e.g. awls, chisels and saw) and weapons (e.g. daggers and arrowheads) mostly belonging to the 2nd half of the 3rd millennium BC (Mataloto 2010).

Figure 2.1: A)Location of São Pedro in the Iberian Peninsula (adapted from (Mataloto et al. n.d.); (B)São Pedro settlement (courtesy of Rui Mataloto).

2.1.2 *Artefact Collection*

The weapons group comprise arrowheads and daggers, which could serve many general purposes. Some consider them as tools related with everyday life tasks or ceremonial practices, as for instance the case of daggers (Skak-Nielsen and Rundkvist 2009) (*Figure 2.2*).

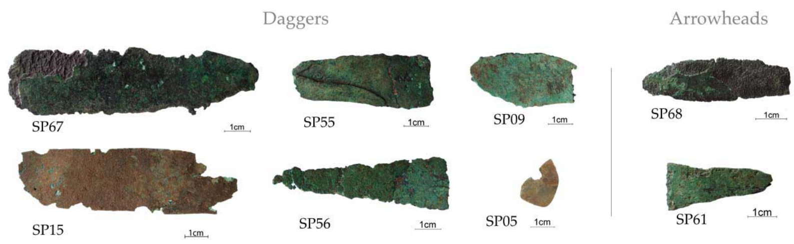

Figure 2.2: Weapons recovered from SP.

Tools include different types (awls, chisels, spatulas, a needle and a saw) that were used by Chalcolithic communities to work with different materials, such as wood, leather or ceramics. One of the spatulas from São Pedro settlement (SP58) presents a peculiar shape resembling a large spoon (*Figure 2.3*).

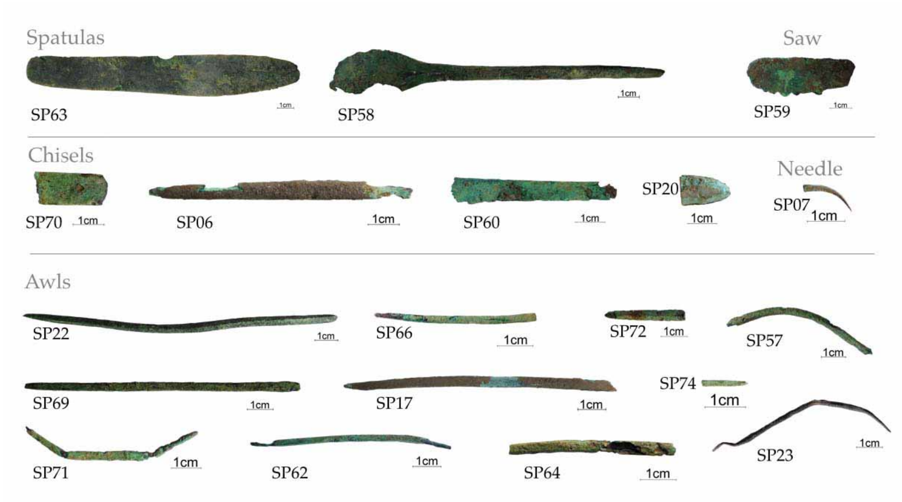

Figure 2.3: Tools recovered from SP.

Finally, other artefacts have an indeterminate function since at the time of recovery they were too fragmented and shapeless to enable a correct identification (*Figure 2.4*).

Figure 2.4: Objects with indeterminate function recovered from SP.

In the first stages of Iberian metallurgy, copper was used in order to build tools (Valério 2005) and tool-weapons (Murillo-Barroso and Montero-Ruiz 2012), as well as personal objects of religious nature (Costa 1985). Nevertheless, copper ornaments in reliable archaeological contexts form Iberian Peninsula are almost absent during this period, being usually made of bone, stone, ivory, gold, etc. perhaps, suggesting that copper ornaments had not reached an aesthetic and prestige value like those made of gold. For this reason, an absence of ornaments in this collection is considered normal.

2.2 Methodology

Due to the cultural and archaeological significance of these artefacts, the methodology used in the present work involves non-invasive and microanalytical techniques. Such techniques aim to establish the elemental compositions, microstructural characteristics and microhardness values of the metallic collection. Due to the chemical alteration of the surface during the long depositional time of artefacts, it was necessary to remove the superficial corrosion in a very small area or to cut a small sample (in the case of fragmented artefacts), always considering the minimum impact to the object.

Initially, the elemental composition of artefacts was determined by micro-energy dispersive X-ray fluorescence spectrometry (micro-EDXRF). After that, the artefacts were characterised by optical microscopy (OM) in order to determine the metallurgical operations. As a way to establish the actual efficiency of the thermomechanical processes in the hardness of the artefacts, Vickers microhardness testing was performed on selected samples. Figure 2.5 summarises the methodology used to characterize the artefacts studied in the present work.

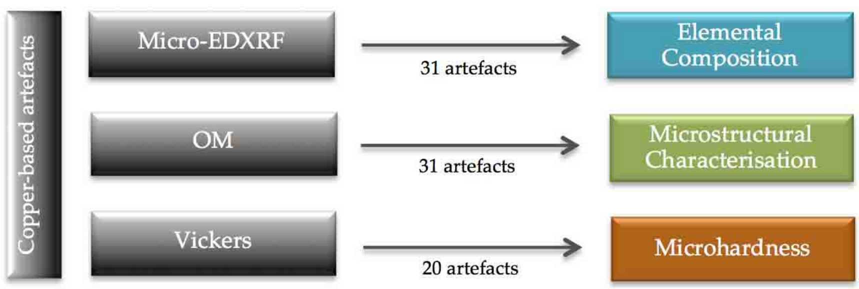

Figure 2.5: Methodology used to characterize artefacts from SP.

2.2.1 *Sample Preparation*

Archaeological copper-based artefacts that remained buried in the soil for a long period present a notable corrosion layer enriched in specific elements. For that reason, the elemental composition of copper-based archaeological artefacts can only be determined by the analysis of a surface previously cleaned from the corrosion layer.

Due to the cultural and archaeological significance of these materials, the sample preparation involved the cleaning of a very small area (about 3-5 mm diameter) at the surface, which was latter polished with diamond pastes of increasingly smaller grit size (6 μm to 1 μm). In the few artefacts that were already broken it was easier and had a lower impact on the artefact to cut a small section (~1-3 mm long). These analyses were done in the small sampled cross-section previously mounted in epoxy resin, polished with SiC abrasive papers (P1000, P2500 and P4000 grit sizes) and finished with 3 μm and 1 μm diamond pastes (see appendix A).

2.2.2 *Micro-Energy Dispersive X-Ray Fluorescence Spectrometry*

EDXRF is one of the firsts analytical techniques used in cultural objects studies providing a fast, multi-elemental and non-destructive quantitative analysis of elements (Mantler and Schreiner 2000; Musílek et al. 2012). In the last decades, micro-EDXRF systems have been developed to have minimum lateral resolutions (typically, the spot size is <300 μm) (Bronk et al. 2001; Buzanich et al. 2007) thus allowing the analysis of minute areas and becoming essential to study different types of cultural materials.

Micro-EDXRF analyses were performed using an ArtTAX Pro spectrometer from Bruker (Germany), installed at DCR-FCT/UNL, operating with a low power molybdenum X-ray tube, focusing polycapillary lens and a silicon drift electrothermally cooled detector with a resolution of 160 eV at 5.9 keV (Mn-Kα). The accurate positioning system and polycapillary optics enable a small area of primary radiation at the sample, ~70 μm diameter (Bronk et al. 2001). Artefacts were analysed with a tube voltage of 40 kV, a current intensity of 600 μA and a live time of 100 s. Three analyses were made in different places, to take into account possible sample heterogeneity, being considered the average value.

Quantitative determinations were made with WinAxil software involving secondary fluorescence corrections and experimental calibration factors calculated with the analysis of the certified reference material British Chemical Standards (BCS) Phosphor Bronze 551. In order to calculate the uncertainty associated to the analytical technique another certified reference material was used: Phosphor Bronze BCS 552 (*Table 2.1*). Overall, the method presents relative errors below 10%. The higher error for zinc results from the spectral interference between the characteristic lines of zinc and copper (Zn-Kα with Cu-Kβ). In the case of iron, the lower accuracy is due to the proximity to the detection limit, in addition to the overlapping of Fe-Kα and Cu-Kα escape peak.

Table 2.1: Micro-EDXRF analysis of certified standard reference material BCS 552 (average ± standard deviation).

	Cu (wt.%)	Sn (wt.%)	Pb (wt.%)	Ni (wt.%)	Zn (wt.%)	Fe (wt.%)
Certified	87.7	9.78	0.63	0.56	0.35	0.12
Obtained	88.1±0.1	10.0±0.06	0.64±0.04	0.60±0.02	0.46±0.03	0.10±0.01
Uncertainty	0.4 %	2.2 %	1.6 %	7.1 %	31 %	20 %

Quantification limits for the elements usually detected in this type of artefacts were determined with the analysis of certified reference materials BCS Phosphor Bronze 551 and Industries de la Fonderie (IDLF) 5: 0.33 wt.% Sb, 0.10 wt.% Pb, 0.05 wt.% Fe, 0.04 wt.% Cu and 0.10 wt.% As (calculated as 10/3×detection limit). The remaining elements that sometimes are found in this type of archaeological materials were below the detection limit, namely 0.15 wt.% Sn, 0.01 wt.% Ni and 0.01 wt.% Zn (calculated as 3×background$^{0.5}$/sensitivity). Sn and Sb exhibit higher values when compared to other elements due to the lower fluorescence yield of the Sn-L and Sb-L lines.

2.2.3 *Optical Microscopy*

Optical microscopy has been used in the study of archaeological metallic artefacts as way to deliver information concerning ancient manufacturing techniques, as well as about corrosion/degradation processes (Loureiro et al. 2014). This technique allows the observation of microstructural features like grain sizes, annealing twins and slip bands, which are important to characterize specific thermomechanical treatments that have been performed to shape the artefacts.

Microstructural characterizations were performed using an optical microscope Leica DMI 5000M installed at CENIMAT/I3N-FCT-UNL coupled to a computer with the LAS V2.6 software. The optical lenses of this microscope are set in an inverted position that allows the observation of large sized artefacts. This optical microscope is equipped with numerous objectives allowing a wide range of magnifications (50x to 1000x) under bright field illumination (BF), dark field illumination (DF) and polarised light (Pol). Dark field illumination allows the observation of topographic features such as pores and cracks. Polarised light allows differentiating some components due to their specific colours under this type of illumination (e.g. copper oxides from copper sulphides). The microscope includes a motorized z-focus with parfocal function (automatic compensation of different focus level) that allows obtaining an image of slightly irregular areas. This is very important in the observation of artefacts that cannot be sampled, since the preparation of this type of materials always leaves a somewhat irregular surface.

Initially, all samples were observed without etching, being afterwards etched with an aqueous ferric chloride solution (prepared according to Scott (1991): 120 ml of distilled water, H_2O; 30 ml of hydrochloric acid, HCl; and 10 g of ferric chloride, $FeCl_3$) to enhance microstructural details.

2.2.4 *Vickers Microhardness Testing*

The hardness of a material is connected to its resistance to deformation under permanent or plastic deformation. The Vickers microhardness test uses a square-base diamond pyramid to apply a load over a surface, creating an impression on the incident area. The hardness is given by the Vickers Hardness number (VHN), which is defined as the applied load (F) divided by the surface area of the indentation (L). In practice, it is calculated from the measurements of the lengths of the diagonals of the impression made by the diamond pyramid over the surface (Dieter 1987).

The microhardness was determined in a Zwick-Roell Indentec testing equipment installed at CENIMAT/I3N-FCT-UNL. The mounted artefacts were indented for 10 s with a low force of 0.2 kgf. At least 3 indentations were made, being considered the average value of several measurements with a relative standard deviation better than 5%.

2.2.5 *Minimizing the Impact of the Study*

After analysis, it was necessary to protect the artefacts in order to prevent the increase of the corrosion processes. For that reason, the application of a corrosion inhibitor in the areas of exposed metal was essential.

When applied over a copper surface, the corrosion inhibitor forms a complex with copper, which results in the creation of a polymeric layer. This layer creates a barrier between the metallic substrate and the environment that surrounds it. Therefore, this layer must be denser, thicker and without interruptions, in order to prevent further oxidation of the metal. It has yet to be resistant to water and organic solvents and should not change the object's color (Faltermeier 1998). Thus, the exposed area of the artefact was protected with benzotriazol (BTA) dissolved in ethanol (3% m/v).

BTA has been widely used in the stabilization of copper and copper alloys. It has been proposed for the conservation of archaeological metals based on an extensive research made on the basis of its use at an industrial level and its satisfactory results (Faltermeier 1998).

Afterwards, the exposed areas were covered with an acrylic layer of Paraloid B-72 dissolved in acetone.

In order to replicate the coloration of the surrounding patina, a mixture of pigments dissolved in the Paraloid B-72 solution was used.

CHAPTER 3

Results and Discussion

3.1 Elemental Characterization

Micro-EDXRF analyses of Chalcolithic artefacts allowed a preliminary identification of two main compositional groups comprising pure copper and copper with variable arsenic contents (*Figure 3.1*).

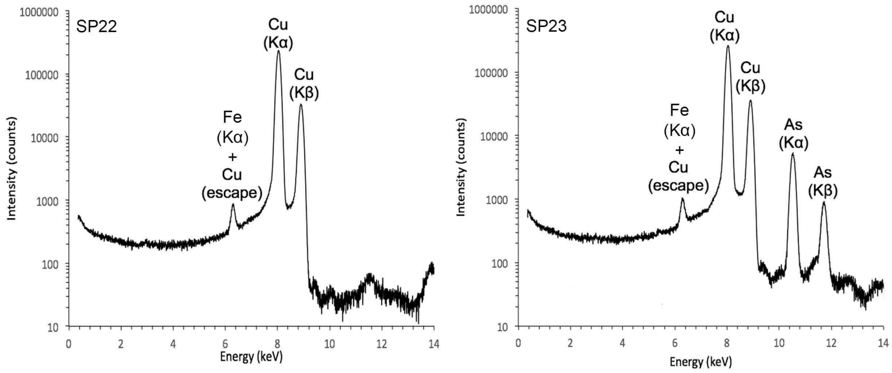

Figure 3.1: Micro-EDXRF spectra of Chalcolithic awls from São Pedro: (SP22) pure copper and (SP23) arsenical copper (note the logarithmic scale on y-axis).

Quantitative results show that the arsenic content is variable reaching values up to 5.08 wt.%, the iron content is always very low (<0.05 wt.%) and only one example has measurable amounts of other elements, namely 0.14 wt.% Pb (plaque SP14) (*Table 3.1*). These differences on arsenic contents confer different properties to the alloy, including the decreasing of melting temperature and casting defects, in addition to hardening effects and colour modifications.

Table 3.1: Elemental composition of artefacts from SP; n.d. – not detected.

Type	Artefact	Code	Cu (wt.%)	As (wt.%)	Pb (wt.%)	Fe (wt.%)
Weapons	Arrowhead	SP61	96.3±0.5	3.65±0.46	n.d.	<0.05
	Arrowhead	SP68	94.8±0.5	4.92±0.08	n.d.	<0.05
	Dagger	SP05	99.9±0.1	0.10±0.01	n.d.	<0.05
	Dagger	SP09	97.0±0.1	2.89±0.20	n.d.	<0.05
	Dagger (?)	SP15	98.7±0.3	1.22±0.35	n.d.	<0.05
	Dagger	SP55	96.8±0.4	3.15±0.35	n.d.	<0.05
	Dagger	SP56	96.1±0.2	3.86±0.25	n.d.	<0.05
	Dagger	SP67	96.5±0.1	3.45±0.83	n.d.	<0.05
Tools	Awl	SP17	96.4±0.5	3.54±0.44	n.d.	<0.05
	Awl	SP22	99.9±0.1	0.10±0.01	n.d.	<0.05
	Awl	SP23	95.5±0.6	4.41±0.57	n.d.	<0.05
	Awl	SP57	97.5±0.2	2.46±0.16	n.d.	<0.05
	Awl	SP62	96.3±0.1	3.62±0.21	n.d.	<0.05
	Awl	SP64	98.7±0.1	1.27±0.05	n.d.	<0.05
	Awl	SP66	98.6±0.1	1.40±0.12	n.d.	<0.05
	Awl	SP69	97.7±0.1	2.23±0.01	n.d.	<0.05
	Awl	SP71	99.3±0.1	0.62±0.01	n.d.	<0.05
	Awl	SP72	94.9±0.5	5.08±0.50	n.d.	<0.05
	Awl (?)	SP74	99.9±0.2	0.10±0.01	n.d.	<0.05
	Chisel	SP06	98.5±0.2	0.10±0.01	n.d.	<0.05
	Chisel	SP20	96.1±0.1	3.84±0.12	n.d.	<0.05
	Chisel	SP60	99.9±0.1	0.10±0.01	n.d.	<0.05
	Chisel	SP70	99.1±0.1	0.84±0.01	n.d.	<0.05
	Needle	SP07	99.0±0.1	0.96±0.12	n.d.	<0.05
	Saw	SP59	97.1±0.1	2.89±1.00	n.d.	<0.05
	Spatula	SP58	95.3±0.1	4.38±0.01	n.d.	<0.05
	Spatula	SP63	97.6±0.4	2.37±0.37	n.d.	<0.05
Others	Plaque	SP14	99.4±0.2	0.10±0.01	0.45	<0.05
	Fragment	SP02	98.1±0.3	1.87±0.29	n.d.	<0.05
	Fragment	SP13	98.4±0.1	1.54±0.14	n.d.	<0.05
	Fragment	SP65	99.7±0.1	0.29±0.04	n.d.	<0.05

A slight difference was verified in the arsenic content distribution between the group of weapons (average of 3.3 ± 1.1 wt.% As, n = 7) and tools (average of 2.6 ± 1.5 wt.% As, n = 15) (*Figure 3.2*).

The higher frequency of arsenical copper alloys from weapons may indicate some criteria in the selection of arsenic-rich copper ores or smelting products (arsenic-rich copper prills). The rational for this may be related to increase the object hardness, as the addition of arsenic leads to an improvement of mechanical properties, especially upon cold work. However, the addition of As to copper also allows turning reddish-copper into silvery-copper. The colour change of Chalcolithic weapons was already referred as a way to revert the object functionality to a more prestige or aesthetic role (Pereira et al. 2013). In another example, at Tepe Yahya (Iran) the tools are made from low-As copper (1-2 wt.% As) while a number of decorative items is made of high-As copper (3-7 wt.% As), possibly because the value of an object was determined by its colour, and thus the more arsenic-rich material with its silvery sheen would be desirable for decorative items (Thornton et al. 2002). However, the relation between type and function is often complex, e.g. the use-wear analysis of Chalcolithic artefacts from the Italian peninsula shows that most classes embody both utilitarian and non-utilitarian values: axes were primarily used for practical tasks, but were mostly withdrawn from circulation when still usable, while daggers were employed in a range of symbolical practices that left little wear on cutting edges (Dolfini 2011).

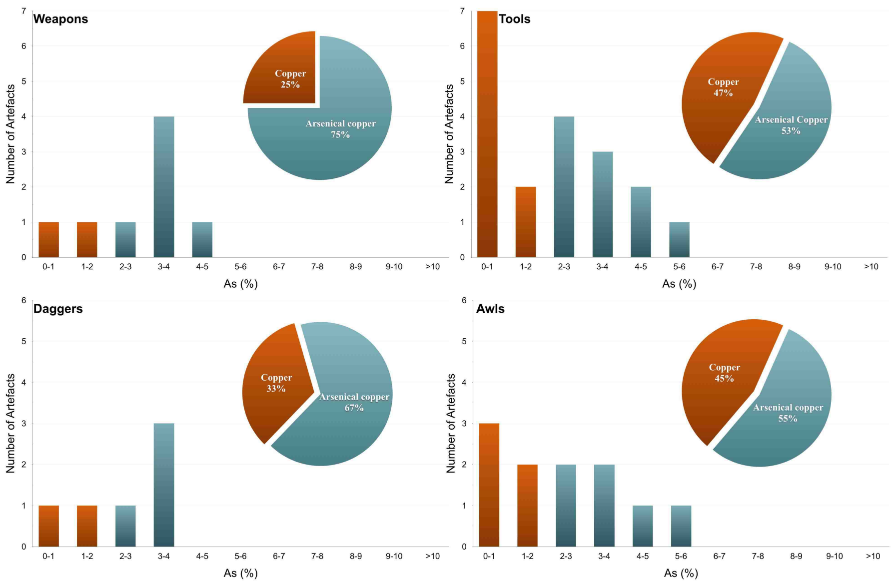

Figure 3.2: Histograms of arsenic contents and distributions of Chalcolithic copper and arsenical copper weapons, tools, daggers and awls from SP.

The low-arsenic content of some artefacts may be related with a possible metal recycling, if we consider that these items could result from a reutilisation of broken artefacts reconditioned by thermomechanical operations. The use of scrap made of arsenical copper under prehistoric conditions (oxidising atmosphere) leads to arsenic losses by evaporation of As_2O_3 fumes. Experiments made on arsenical copper ingots showed an arsenic reduction from 4.2 wt.% to 0.8 wt.% after a single melting and several hot workings under oxidising conditions (McKerrell and Tylecote 1972).

The comparison between daggers and awls (the only types with a significant number of examples) also identified a tendency to higher amounts of arsenic on daggers (*Figure 3.2*). However, the small number of artefacts precludes a firm conclusion. The relation of arsenical copper alloy with some typologies such as Palmela points, saws, long awls and tanged daggers was already identified at the Chalcolithic settlement of Zambujal (Müller et al. 2007). Authors suggested that arsenic copper alloys could be obtained by the selection by colour of arsenic-rich copper prills obtained through the smelting of arsenic bearing copper ores.

Studies on Chalcolithic artefacts from Vila Nova de São Pedro (Pereira et al. 2013) and Leceia (Müller and Cardoso 2008), located in the neighbouring region of Southern Portugal to the North (Portuguese Estremadura), reveal a somewhat lower frequency of arsenical copper alloys (*Figure 3.3*). Moreover, the arsenic contents distribution has been interpreted as resulting from the natural variability of arsenic impurities in the smelted copper ores. In the nearby region to the East (Western Andalusia), the study of Chalcolithic artefacts (Bayona 2008) has identified a similar situation although with a percentage of arsenical copper alloys that is closer to the obtained for Southern Portugal (*Figure 3.3*) . The arsenic variability in several sites of Western Andalusia was associated to the thermomechanical treatments because the lower arsenic amounts were often detected in worked artefacts.

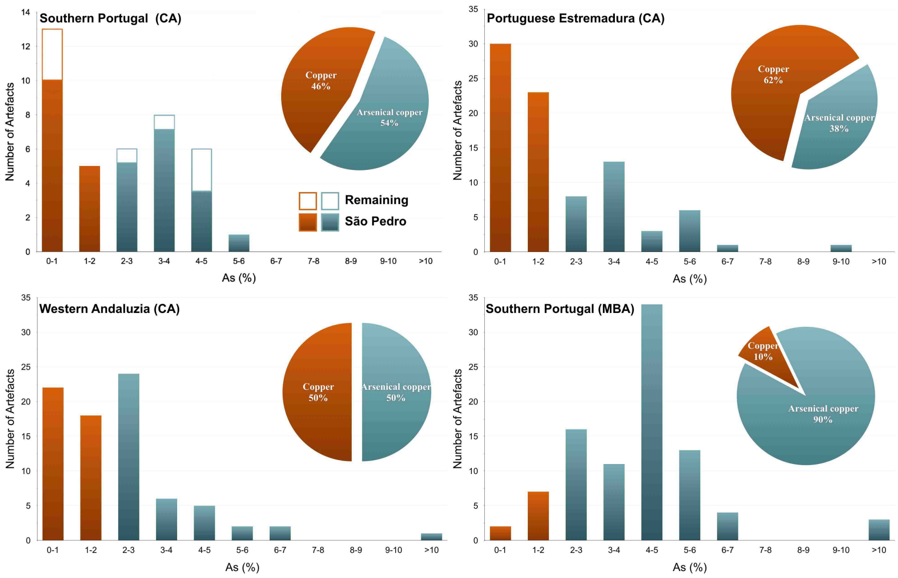

Figure 3.3: Histograms of arsenic contents and distributions of Chalcolithic copper and arsenical copper artefacts in Southern Portugal (Vidigal et al. 2015), Portuguese Estremadura (Müller and Cardoso 2008; Pereira et al. 2013) and Western Andaluzia (Bayona 2008), in addition to Middle Bronze Age (MBA) copper and arsenical copper artefacts from Southern Portugal (Valério et al. 2015; Valério et al. 2014a).

In the Southeastern Iberian Peninsula the high arsenic content was associated, not only with the ores utilised, but also as an indirect indicator of the low use of scrap metal due to the arsenic losses during thermal recycling processes (Montero-Ruiz et al. 2014). Contrary, in other regions like the Levant such regional differences were attributed to the existence of maritime and overland trade routes that facilitate the access to raw materials (Kaufman 2013). Overall, the differences in the frequency of Chalcolithic arsenical coppers are often attributed to the different copper mines. However, in the Portuguese Estremadura the Pb isotopic compositions strongly suggest the use of copper from the Ossa Morena Zone (Müller and Soares 2008; Müller et al. 2007) covering part of Western Andalusia and Southern Portugal.

Chronologically speaking, the circumstances become even more interesting because

Middle Bronze Age (MBA) (~2000-1200 BC) artefacts from Southern Portugal have a distinctively higher proportion of arsenical copper alloys (Rehren et al. 2012; Valério et al. 2014a) (*Figure 3.3*). In the Eastern Mediterranean, an estimated 20 tons of slag from the Early Bronze Age site of Arisman provided evidence of large-scale production of metal including arsenical coppers that could have been produced by smelting a mixture of speiss with copper ore or metallic copper (Rehren et al. 2012). Nevertheless, such archaeological evidences do not exist in the Iberian Peninsula and the arsenic-rich alloys from this incipient stage of metallurgical technology could be obtained by picking arsenic-rich smelting prills, as suggested for other Chalcolithic sites located in near (Zambujal (Müller et al. 2007) or distant regions (Shiqmim, Israel (Golden et al. 2001)).

3.2 Microstructural Characterization

Optical microscopy observation allowed the identification of the artefacts common features, such as segregation bands, equiaxial grains, annealing twins, inclusions and, more rarely, slip bands. Overall, the manufacture of prehistoric artefacts included mechanical and thermal operations, specifically: cycles of forging and annealing and, sometimes, the occurrence of final forging procedure, which was applied with different intensities, evident in deformed twins and, especially in slip bands densities. Annealing allows softening the metal and permits an additional deformation; several sequences of hammering and annealing might be used to achieve the required shape. The final hammering operation would be used to increase the hardness, to sharpen specific areas of an artefact (i.e. the edge of a dagger or awl) or as a final smoothing of the surface.

The presence of a dendritic structure (type of segregation that looks like an open tree structure or a snowflake) is the most common form of “compositional separation” in cast alloys. This sort of segregation usually appears in alloys in which one of the components has a lower melting point than the other. As the size of the dendrites is influenced by the rate at which the metal is cooled and/or by the metal concentrations, larger dendrites with coarser grain morphology would indicate a slower cooling of the alloy. Nevertheless, depending on the cooling conditions, other types of segregation could occur in addition to dendritic segregation (also named as cored). Those are named normal and inverse segregation. In practice, segregation results from the difficulties of attaining equilibrium cooling conditions from the melt (i.e., achieving a homogeneous metal alloy) (Scott 1991).

According to Northover (1989) in order to fully homogenize the as-cast dendritic segregation of arsenical coppers, the alloy must be heated at 600-700 °C. If an alloy was fully homogenized, in etched samples it would be visible an initial grain structure of equiaxed hexagonal grains (recrystallization). As the annealing of ancient arsenical coppers was probably conducted between 300-400 °C (Northover 1989), it is common to observe the relics of dendritic segregation with α-grains (i.e. segregation bands).

In fact, some microstructures from São Pedro artefacts indicate that the prehistoric metallurgists did not control the cooling conditions of the artefacts and that they had no concern in homogenizing the alloys. The presence of segregation bands with equiaxed grains is clearly visible in some areas of the artefact SP72 (*Figure 3.4*). In this, the brighter areas correspond to the regions that are richer in arsenic and were last to solidify during casting.

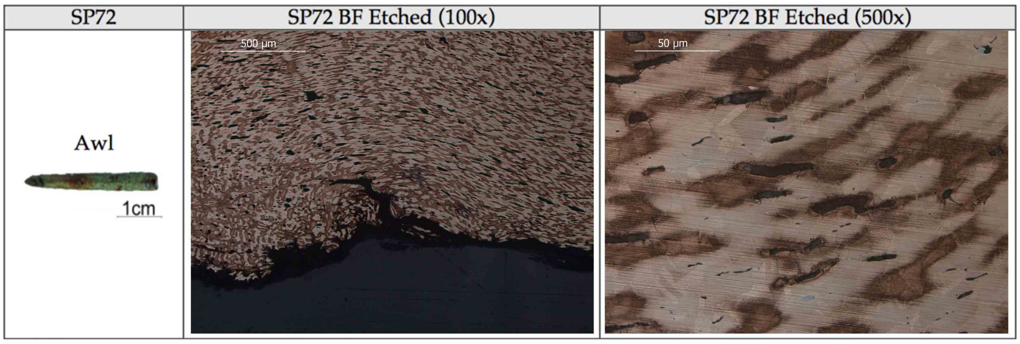

Figure 3.4: Microstructure of awl SP72 showing segregation bands (OM-BF, etched).

If intense mechanical work was applied in non-homogenized alloys, the segregation bands would present an elongated shape. Moreover, as the segregation intensity influences the homogenization of arsenical coppers, heavily segregated microstructures require higher temperatures to be homogenized (Budd 1991).

The microstructures of the artefacts SP23, SP62, SP63 and SP69, show highly deformed segregation bands. Furthermore, these artefacts present different grain shapes and sizes, which indicate different intensities of hammering and annealing. Considering equivalent annealing conditions, a more intense hammering results in smaller and more deformed grains, as sometimes observed in sharpened areas of the artefacts. It was not possible to sample several areas on each awl however, some awls were observed on the tip, while others were seen on the central section. In fact, as the awl SP69 was sampled near the worked edge, it presents a smaller grain size than the awl SP23 that was sampled in a larger and less worked zone (*Figure 3.5*). These differences were observed in the grain size between tips and central sections of other awls. Therefore, it is possible that those edges were sharpened by mechanical deformation.

Concerning the daggers and the chisels groups, no association was found between the grains size of the sampled zones of the artefacts.

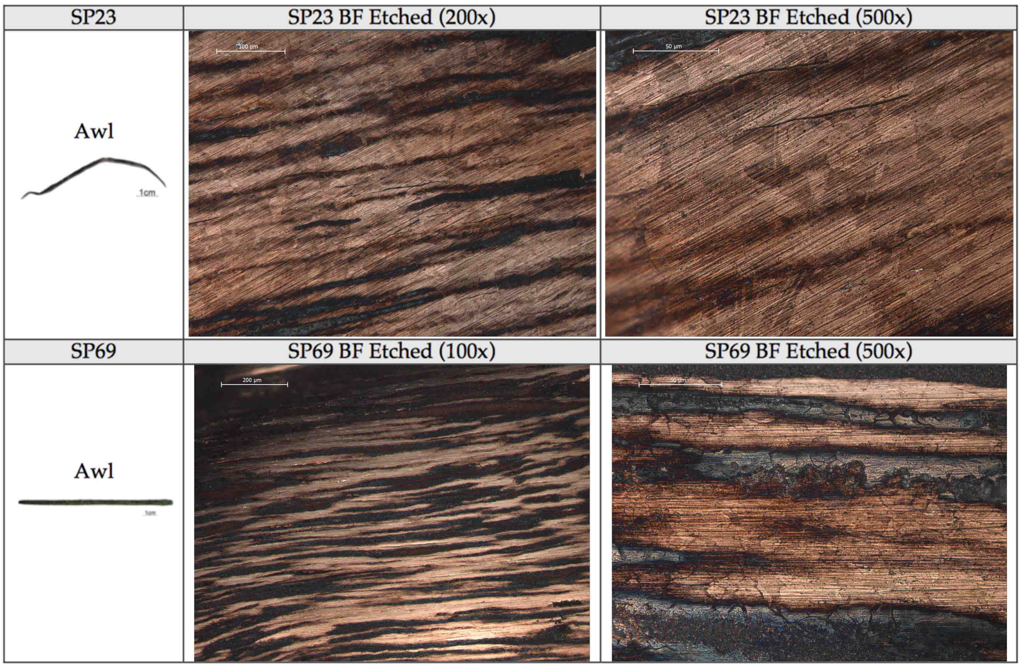

Figure 3.5: Microstructures of awls SP23 and SP69 showing heavily segregated microstructures and different grains sizes (OM-BF, etched).

The plastic deformation of metals through hammering and annealing, or by hot-working, origins changes to the inner structure of the metals. These two processes will produce roughly the same microstructure, therefore, it is not always possible to distinguish between the process that was used in a particular case (Scott 1991). These microstructural features include not only grain boundaries but also annealing twins (parallel strips longitudinally bounded by the α-phase grains) and slip/strain lines in different intensities depending on the amount of deformation.

After recristalization, the annealing twins are perfectly straight, but if the grains are deformed through hammering, the twin lines will also be deformed (Scott 2014).

An example of cold worked and annealed artefacts are shown in figure 3.6. In the artefact SP17 is possible to observe slightly straighter twin lines when comparing to the artefact SP14 however, a similar overall manufacture is present in both artefacts.

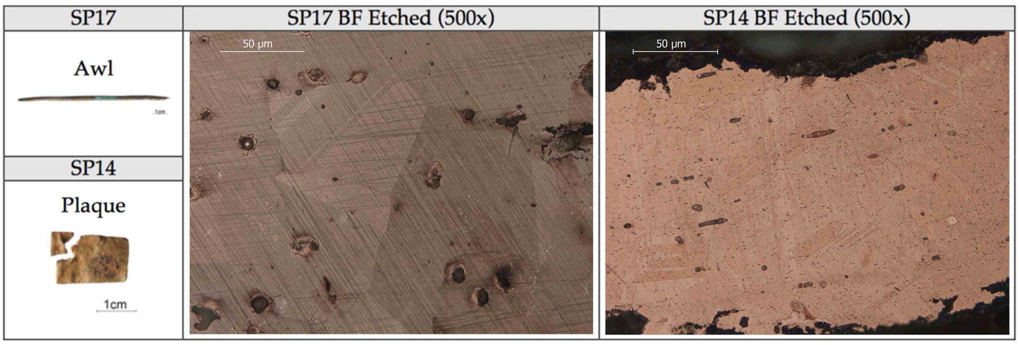

Figure 3.6: Microstructures of SP55 and SP61 evidencing final forging work trough the presence of slip bands (OM-BF, etched).

Additional features that indicate a final cold-working step after annealing include the presence of slip bands within the grains as a result of excessive hammering without a following annealing step (Scott 1991).

Only three artefacts show a higher density of slip bands evidencing a significant posterior mechanical work. Two examples of final forged artefacts are shown in figure 3.7. Further hammering without annealing will increase the metal hardness, however, it takes a skilled metallurgist to significantly strain the metal without fracture.

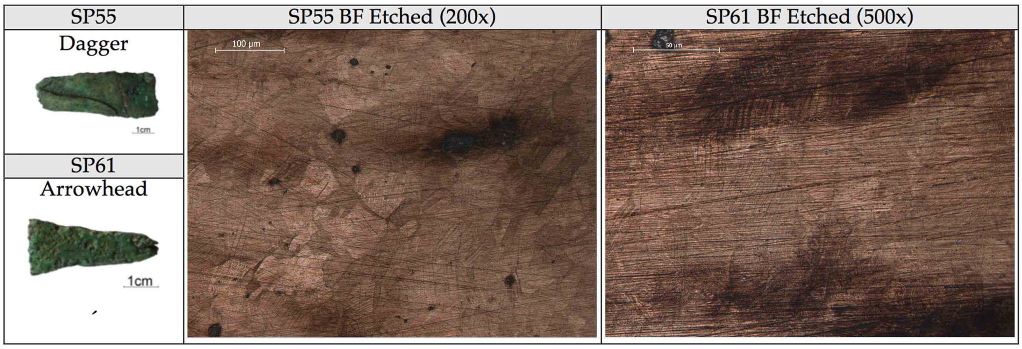

Figure 3.7: Microstructures of Awl SP17 and plaque SP14 revealing annealing twins (OM-BF, etched).

Other common feature in prehistoric metals is the presence of Cu-O reddish inclusions at OM under Pol illumination (*Figure 3.8*). With BF illumination they are usually dark round forms dispersed in the α phase background.

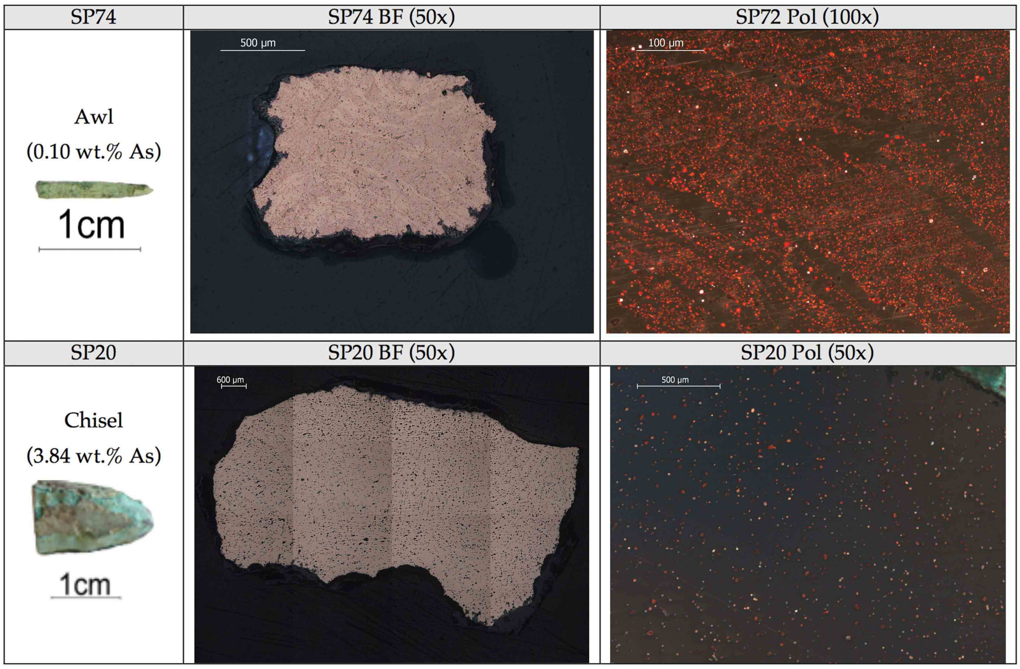

Figure 3.8: Microstructures of artefacts SP74 and SP20 showing different intensities of Cu-O inclusions (Left: OM-BF, non-etched; Right: OM-Pol, non-etched).

These inclusions can occur during solidification, when dissolved gases, such as oxygen, react with the liquid metal to form oxides (e.g., cuprous oxide [Cu_2O]) (see binary phase diagram Cu-Cu_2O - Appendix B) (Scott 1991).

In the collection from São Pedro, 20 artefacts with different contents of arsenic presented Cu-O inclusions of the characteristic eutectic (α + Cu_2O) (see some examples in figure 3.8). The use of a reducing atmosphere (e.g. a layer of charcoal) minimizes the up-take of oxygen. Moreover, arsenic will act as a deoxidizer and detain oxygen (lost as As_2O_3 fumes), therefore, also minimizing the formation of copper oxides. In the São Pedro collection the inclusions were observed not only in artefacts with lower amounts of arsenic (such as the chisel SP60, with 0.10 wt.% As) but also in artefacts with higher amounts of arsenic (such as the chisel SP20, with 3.84 wt.% As), pointing to the use of different/uncontrolled casting conditions.

The presence of Cu-O inclusions in higher quantities is visible in the chisel SP20 (3.84 wt.% As) and in the awl SP74 (0.10 wt.% As) (*Figure 3.8*).

In some artefacts, such as SP07 and SP14, some elongated shapes of the above-mentioned oxides as well as deformed grains are visible (*Figure 3.9*). Those indicate the preferential direction of deformation of those artefacts before annealing.

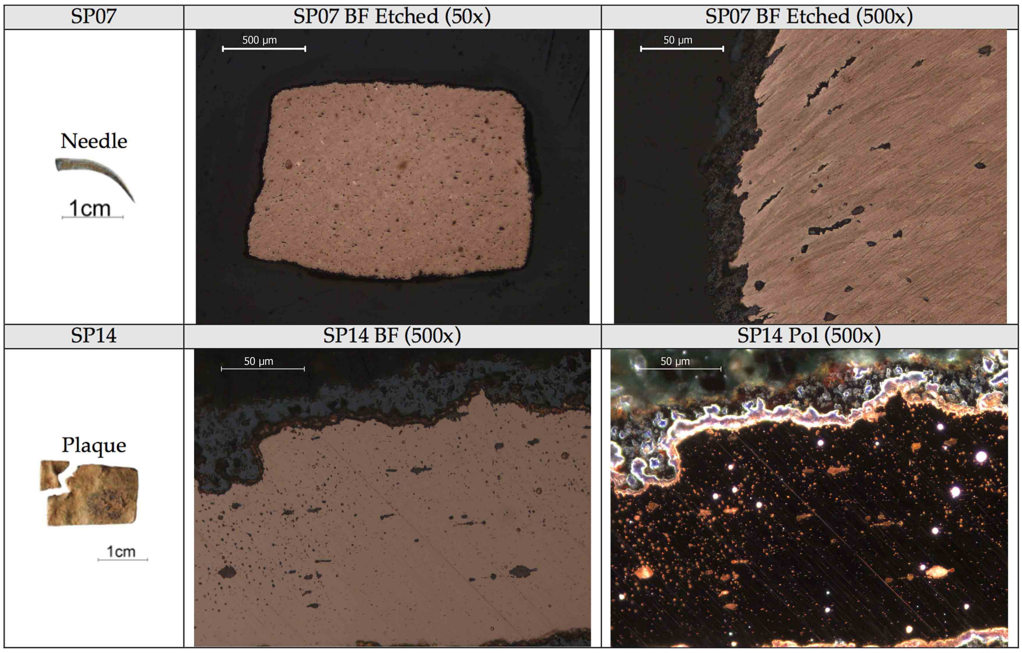

Figure 3.9: Microstructures of artefacts SP07 and SP14, revealing deformed grains and elongation of Cu-O (SP07: OM-BF, etched; SP14: OM-Pol, non.etched).

Besides the presence of Cu-O, it is possible to observe some small dark-blue inclusions (*Figure 3.10*). Studies regarding the prehistoric bronze metallurgy (Valério et al. 2010) have detected these inclusions and identified them by SEM-EDS as Cu-S, a common inclusion in bronze artefacts which probably result from copper ores impurities.

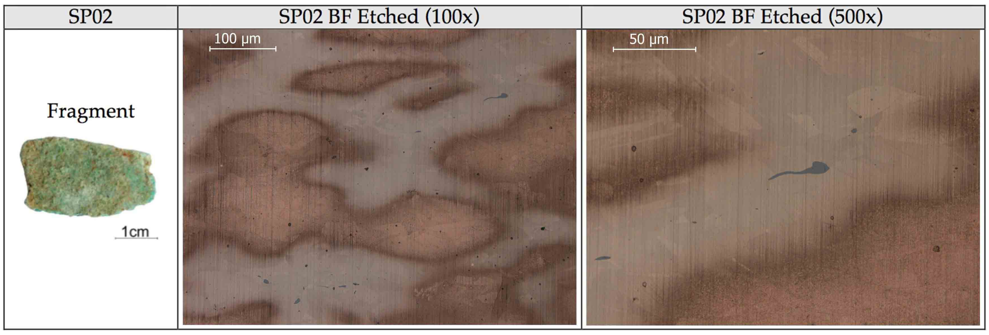

Figure 3.10: Microstructures of fragment SP02 revealing Cu-S inclusions (OM-BF, etched)

In some artefacts the occurrence of a blue-grey phase in intergranular α-Cu regions was found under BF illumination (*Figure 3.11*). Studies on Chalcolithic artefacts from Vila Nova de São Pedro (Pereira et al. 2013) identified the blue-grey phase by SEM-EDS as being an As-rich (γ) phase.

The formation of As-rich phase in equilibrium conditions is observed in alloys with higher arsenic contents (α-Cu phase can dissolve around 8 % of arsenic before the formation of the arsenic rich phase) however, it is possible to detect this feature in alloys with lower arsenic due to the fast cooling rates during casting (Northover 1989).

Furthermore, the As-rich phase visible at the intergranular regions should be due to a precipitation from solid solution at ambient temperatures over archaeological times, thus being the result of post depositional alteration (Pereira et al. (in press)).

Such intergranular segregation is visible in the arrowhead SP68 and in the dagger SP56 (*Figure 3.11*) with a high arsenic content (4.92 and 3.86 wt.% As, respectively) but below the arsenic solubility limit in equilibrium. This indicates a cooling rate away from equilibrium conditions and suggests that there was no intention to control its cooling.

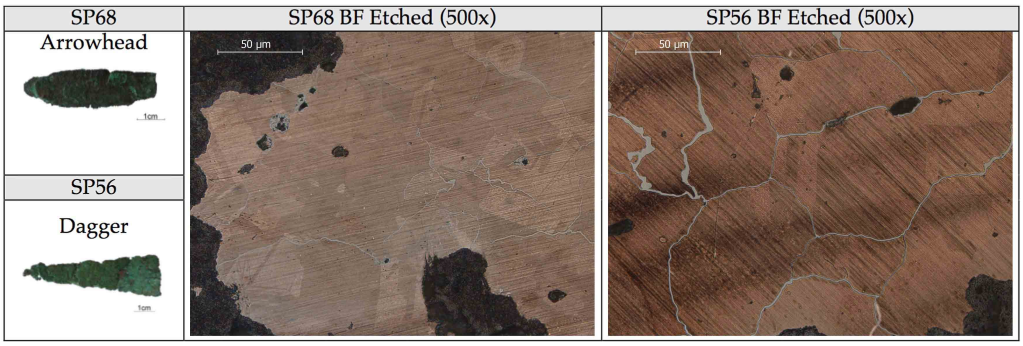

Figure 3.11: Microstructures of weapon SP68 and SP56 revealing an arsenic-rich phase following the grain boundaries (OM-BF, etched).

Despite the overall similarity of São Pedro artefacts manufacturing operations, this collection reveals somewhat different operational conditions, as expected in such a primitive metallurgy. Variances are visible on the size and deformation of inclusions, frequency of segregation bands, grain size and concentration of slip bands (*Table 3.2*). No significant association between the presence of slip bands and the arsenic contents was found, therefore, the metallurgists might have given priority to the aesthetics of these artefacts rather than to improve the properties of the alloy. Thus, as the arsenic content does not seem to have a relation with the manufacturing features, the overall results suggests that Chalcolithic metallurgists were not taking advantage of arsenic to increase the hardness of tools and weapons.

Table 3.2: Microstructural features of São Pedro artefacts (s: segregation bands; t: annealing twins; sb: slip bands; d: deformed inclusions; A: Annealing; F: Forging; FF: Final forging; ↓: low amount; ↑: high amount).

Type	Artefact	Code	As (wt.%)	~grain size (μm)	Phases	Inclusions	Features	Manufacture
Weapons	Arrowhead	SP61	3.65	20-50	α	-	s,t,sb	(F+A)+FF
	Arrowhead	SP68	4.92	50-100	$\alpha;\gamma$	-	s,t	F+A
	Dagger	SP05	0.10	20-50	α	Cu-O↓; Cu-S	t	F+A
	Dagger	SP09	2.89	20	α	Cu-O	s,t,d	F+A↓
	Dagger(?)	SP15	1.22	10-20	α	Cu-O	s,t,d	F↑+A↓
	Dagger	SP55	3.15	50	α	-	s,t,sb	(F+A↓)+FF↑
	Dagger	SP56	3.86	50	$\alpha;\gamma$	Cu-O↓	s,t	F+A
	Dagger	SP67	3.45	50	$\alpha;\gamma$	-	t	F+A
Tools	Awl	SP17	3.54	50-100	α	Cu-O	t	F+A↑
	Awl	SP22	0.10	50-100	α	Cu-O	s,t	F+A
	Awl	SP23	4.41	20-50	α	-	s,t	F↑+A
	Awl	SP57	2.46	20	α	-	s,t	F+A↓
	Awl	SP62	3.62	20-50	α	-	s,t	F↑+A↓
	Awl	SP64	1.27	100-150	α	Cu-O	t	F+A↑
	Awl	SP66	1.40	100	α	Cu-O↓	t	F+A↑
	Awl	SP69	2.23	20	α	-	s,t	F↑+A↓
	Awl	SP71	0.62	10-20	α	Cu-O	s,t	F+A↓
	Awl	SP72	5.08	10	$\alpha;\gamma$	Cu-O	s,td	F+A↓
	Awl (?)	SP74	0.10	50-100	α	Cu-O↑	t	F+A↑
	Chisel	SP06	0.10	20	α	Cu-O↓	s,t	F+A↓
	Chisel	SP20	3.84	50	α	Cu-O↑	s,t	F+A
	Chisel	SP60	0.10	20	α	Cu-O↑	t	F+A↓
	Chisel	SP70	0.84	50	α	Cu-O	s,t	F+A↓
	Needle	SP07	0.96	50	α	Cu-O	t,d	F+A↓
	Saw	SP59	2.89	20-50	$\alpha;\gamma$	-	s,t	F+A↓
	Spatula	SP58	2.89	20/100	α	-	t,sb	(F+A)+FF
	Spatula	SP63	2.37	20-40	α	Cu-O↓	s,t,d	F↑+A↓
Others	Plaque	SP14	0.10	+50	α	Cu-O	t,d	F+A
	Fragment	SP02	1.87	20-50	α	Cu-O↓; Cu-S	s,t	F+A↓
	Fragment	SP13	1.54	+50	α	Cu-O	s,t	F+A↓

Among the collection the existence of non-homogenised microstructures is common, however, as this would not have a visible influence in the alloy properties, this was unimportant to those ancient metallurgists.

Overall the optical microscopy observations indicate that all the artefacts from São Pedro were produced with one or more cycles of forging and annealing (F+A) and only three artefacts present the occurrence of final forging operation (SP55; SP58 and SP61) (*Figure 3.12*). A summary of the results is presented in Appendix C.

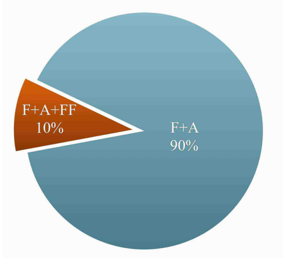

Figure 3.12: Distribution of manufactured procedures in SP artefacts.

There are no general differences between operational sequences applied in the production of arsenical coppers from São Pedro and Vila Nova de São Pedro (Estremadura), where almost all artefacts (96%) were subjected to thermomechanical operations, i.e. F+A: 73% and F+A+FF: 23% (Pereira et al. 2013). However, in the nearby region to the East (Western Andalusia), the study of Chalcolithic artefacts (Bayona 2008) reveal a similar production of arsenical-copper artefacts but a higher incidence in artefacts with final forging procedure was observed. Moreover, in this region an association was found between the arsenic variability of the artefacts with the thermomechanical treatments as lower arsenic amounts were often detected in worked artefacts.

3.3 Vickers MicroHardness Measurements

The hardness of copper-based artefacts is influenced by numerous factors, such as the composition of the α phase (solid solution hardening), precipitation of different phases (precipitation hardening), grain size and degree of deformation (strain hardening).

The addition of arsenic to copper will increase the hardness of the metal, however, according to Budd (1991) if the arsenic content is inferior to 1.5-2 wt.% it will not increase significantly the hardness. Furthermore, it was recorded a main increase in hardness in alloys with about 7 wt.% As, while the metal becomes brittle with arsenic contents above 8 wt.%(Lechtman 1996). Nevertheless, other authors consider that arsenical-copper alloys only become brittle when the arsenic level outdoes 10-13 wt.% (Budd and Ottaway 1995).

The significant presence of the As-rich phase, observed in alloys with low arsenic due to non-equilibrium cooling conditions, will lead to the increase of the alloy hardness of mainly due to precipitation of a higher fraction of the intermetallic γ and the establishment of strain fields in the matrix (Pereira et al. 2013).

According to Hall-Petch (HP) equation, which describes the relation between yield strength and grain size in conventional metal alloys, the presence of smaller grains will result in the increase of the alloy hardness (Nieh and Wadsworth 1991). When compared to pure copper, arsenical copper is more ductile and can be further shaped by cold working (Pereira et al. 2013). The cold hammering operation will result in the strengthening of the alloy due to the increasing number of dislocations (Junk 2003). If exposed to forging and annealing cycles, arsenical copper alloys quickly increase hardness, mainly in the

0-50% decrease in thickness (Lechtman 1996).

The study of the metallic artefacts hardness allows the understanding of the efficiency of operational sequences. Unfortunately, these measurements can only be applied to mounted samples, so it was not possible to measure the hardness of the 3 artefacts with a final forging operation, which is one of the key factors concerning the hardness of prehistoric artefacts.

Table 3.3: Vickers microhardness results made in mounted cross-sections (HV0.2, 10 s).

Type	Artefact	Code	As (wt.%)	~grain size (μm)	Phases	HV0.2
Weapons	Arrowhead	SP68	4.92	50-100	α, γ	**142**
	Dagger	SP05	0.10	20-50	α	105
	Dagger	SP09	2.89	20	α	104
	Dagger (?)	SP15	1.22	10-20	α	**140**
	Dagger	SP56	3.86	50	α, γ	98
Tools	Awl	SP17	3.54	50-100	α	86
	Awl	SP57	2.46	20	α	59
	Awl	SP64	1.27	100-150	α	97
	Awl	SP66	1.40	100	α	85
	Awl	SP71	0.62	10-20	α	**126**
	Awl	SP72	5.08	10	α, γ	**120**
	Awl (?)	SP74	0.10	50-100	α	86
	Chisel	SP06	0.10	20	α	107
	Chisel	SP20	3.84	50	α	52
	Chisel	SP70	0.84	50	α	97
	Needle	SP07	0.96	50	α	99
Others	Plaque	SP14	0.10	+50	α	82
	Fragment	SP02	1.87	20-50	α	**126**
	Fragment	SP13	1.54	+50	α	86

Overall the obtained results (*Table 3.3*) indicate that the arsenic content does not have a major impact on the hardness of São Pedro's artefacts (*Figure 3.13*). For instance, artefacts with similar arsenic contents, such as chisel SP20 (3.84 wt.% As) and dagger SP56 (3.86 wt.% As), reveal different hardness values, i.e. 52 and 98 HV0.2, respectively. On the other hand, it is possible to observe artefacts with higher arsenic contents with high hardness values. Artefacts SP68 (4.92 wt.% As) and SP72 (5.08 wt.% As), show elevated hardness values, i.e. 142 and 120 HV0.2, respectively.

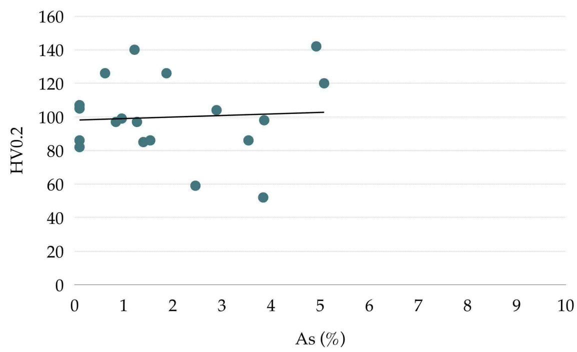

Figure 3.13: Micro-HV measurements (HV0.2, 10 s) in function of arsenic content of the artefacts.

This is due to the fact that hardness is determined not only by the arsenic content but also by the grain size, phase constitution and degree of work hardening. In fact, the higher hardness of the arrowhead SP68 (142 HV0.2) seems to be influenced not simply by the presence of elevated arsenic contents but also by the significant presence of the harder arsenic-rich phase.

Generally, the results suggest that the increase of hardness seems to be mostly related with the grain size. e.g., artefacts with smaller grain sizes such as dagger SP15 (1.22 wt.% As), awl SP71 (0.62 wt.% As) and fragment SP02 (1.87 wt.% As) with approximate grain size of 10-20 μm and 20-50 μm reveal higher values of hardness (140, 126 and 126 HV0.2, respectively). Actually, the smaller grain size is due to the operational sequences applied in the production of these arsenical coppers from São Pedro, i.e. cycles of higher deformation combined with less intense annealing (low temperature or small time of operation).

Overall, despite the small number of samples, it was possible to observe highly variable hardness values (52 – 142 HV0.2), even in typologies that would benefit from a higher hardness, such as daggers and awls. This study suggests that ancient metallurgists may not have control or were not aware of the advantage of the hardening effect of arsenic.

Even though arsenic ought to present an evident influence in the pouring of the alloy, the operational sequences applied in the production of arsenical coppers from São Pedro seem to be used to achieve the required shape to the object, rather than to intentionally make the alloy harder. Similar results were observed in artefacts from Vila Nova de São Pedro (Portuguese Estremadura), where despite the possible visual identification and selection of arsenical copper alloys, evidences suggest that the potential hardness was not exploited and that thermomechanical operations were mainly applied with the intention of shaping and perhaps also producing harder cutting edges (Pereira et al. 2013).

Chapter 4

Conclusions

The use of non-invasive and microanalytical techniques allowed the characterization of São Pedro's artefacts. The selected methodology (micro-EDXRF analysis, OM observations and hardness measurements) allowed obtaining important information concerning the composition and the manufacture techniques of CA artefacts belonging to the southern region of the Portuguese territory.

The present study revealed a collection of 2500-2000 BC artefacts from Southern Portugal comprising from pure copper to arsenical copper alloys with up to 5 wt.% arsenic. Although the true significance of arsenical copper alloys is still a matter of debate, the data collected indicate the preference for higher arsenic-copper alloys for weapons such as daggers, which probably can be considered prestige objects among those communities. This primitive technology is comparable to the Chalcolithic metallurgies found in other regions of the Iberian Peninsula, but has a lower amount of arsenical copper alloys than local Middle Bronze Age archaeological contexts.

Microstructural observations of the studied collection indicate that after casting an artefact would have been hammered, annealed and sometimes, finished with a hammering operation. Furthermore, OM features variations reveal somewhat different operational conditions during casting (i.e. more or less reducing atmosphere), annealing (temperature and operation time) and forging (intensity of deformation) as expected in such a primitive metallurgy. The operational sequences applied in the production of arsenical coppers seems to be used to achieve the required shape to the object, rather than to intentionally make the alloy harder. This technology is comparable to other regions of the Portuguese territory, mainly the Portuguese Estremadura. However, a higher incidence of the final forging procedure was observed in other Iberian regions despite a similar production of arsenical copper alloys. Overall, this study shows that the arsenic content does not seem to have a relation with the manufacture, suggesting that Chalcolithic metallurgists may have a poor control of the addition of arsenic to copper alloys and/or were unable to use it to increase the hardness of tools and weapons.

Finally, additional studies concerning Chalcolithic and Middle Bronze Age artefacts with different functions and typologies are essential to better establish the evolution and use of copper and arsenical copper alloys in this southwestern end of the Iberian Peninsula.

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Appendix A

Artefacts Sampling

A.1 Weapons

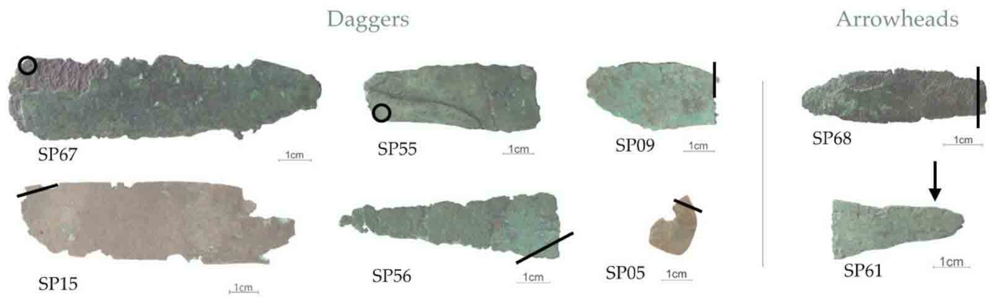


Figure A.1: Summary of weapons sampling.

A.2 Objects with Indeterminate Function

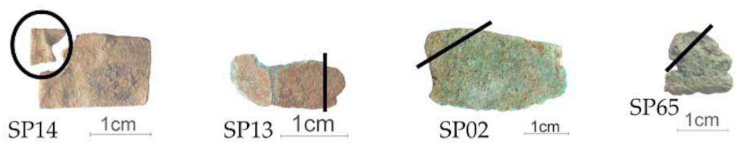


Figure A.2: Summary of objects with indeterminate function sampling.

A.3 Tools

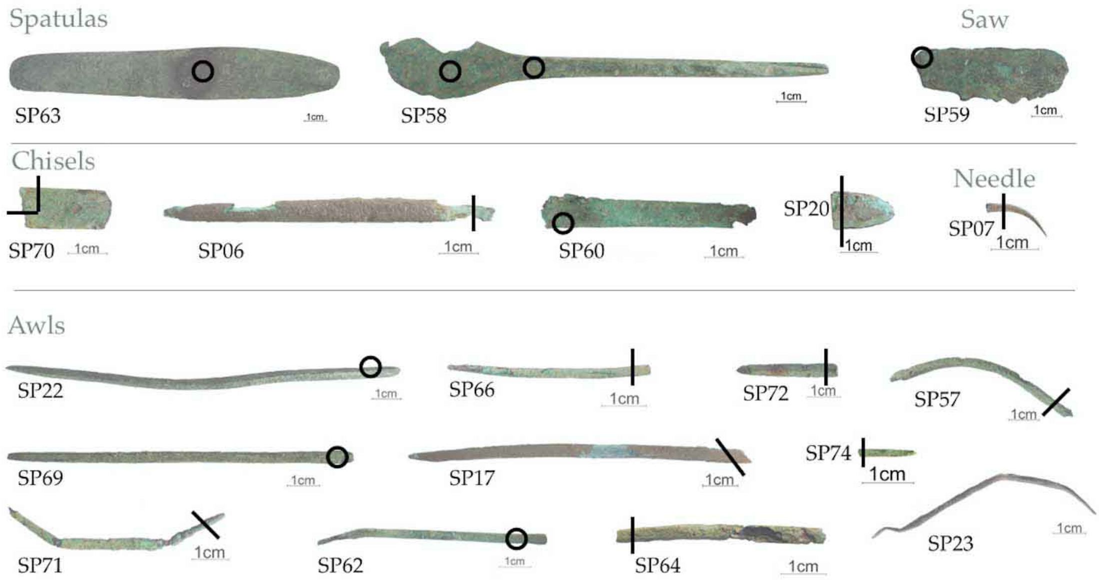


Figure A.3: Summary of tools sampling.

Appendix

B

Phase Diagrams

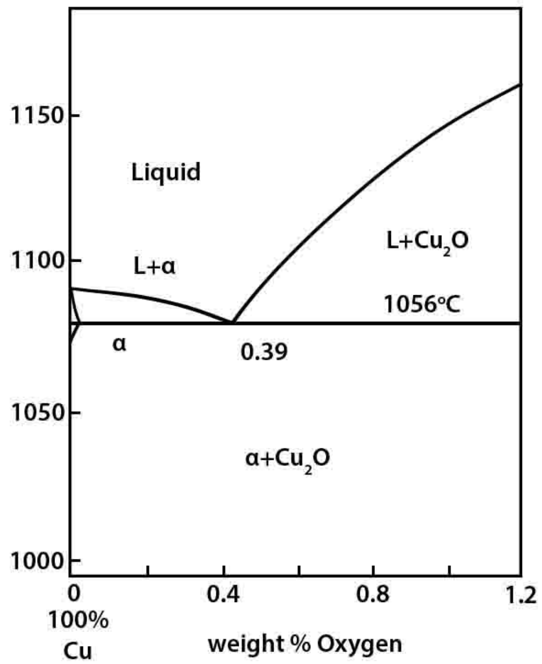


Figure B.1: Binary diagram Cu-Cu_2O (ASM 1973).

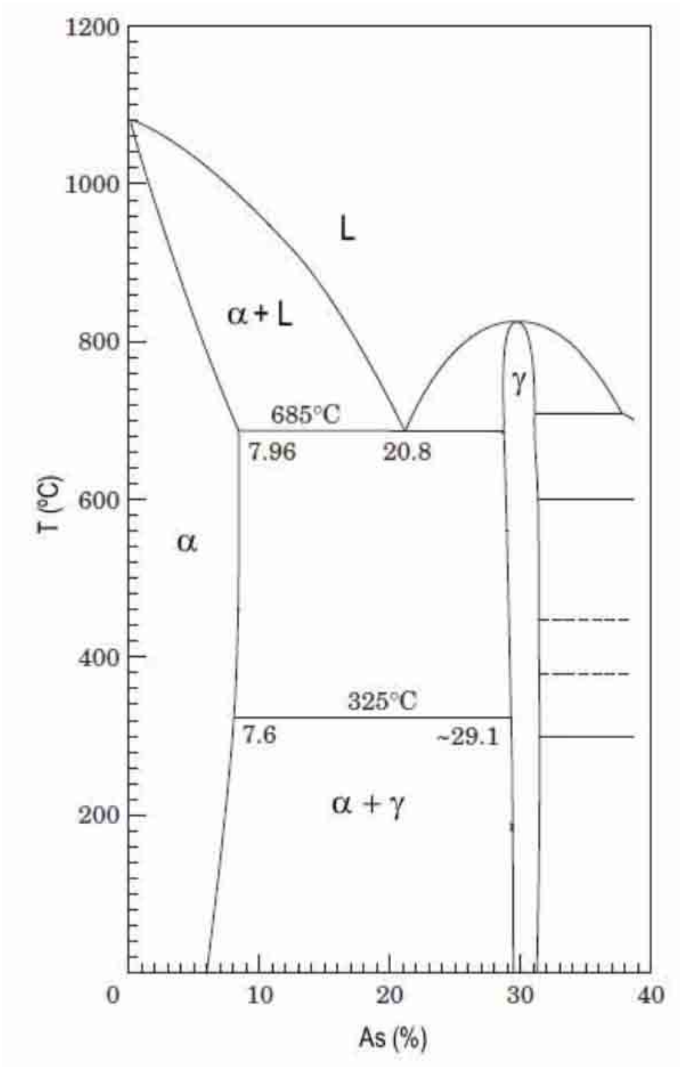


Figure B.2: Section of Cu-As phase diagram in equilibrium conditions (Adapted from Subramanian and Laughlin 1988).

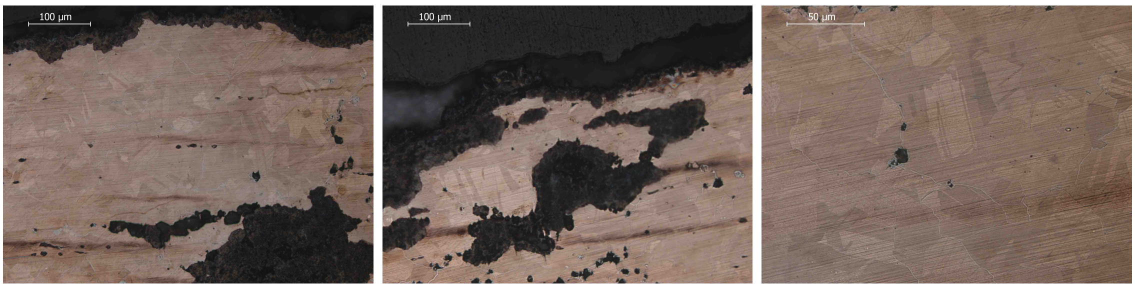
Appendix C

Optical Microscope Summary

C.1 Weapons

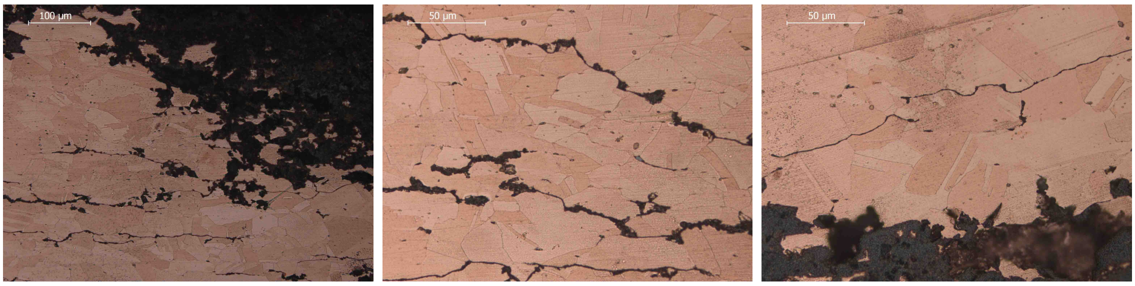
a SP61 - BF; Etched (100x) b SP61 - BF; Etched (200x) c SP61 - BF; Etched (500x)

Figure C.1: Microstructure of arrowhead SP61 (OM-BF, etched)



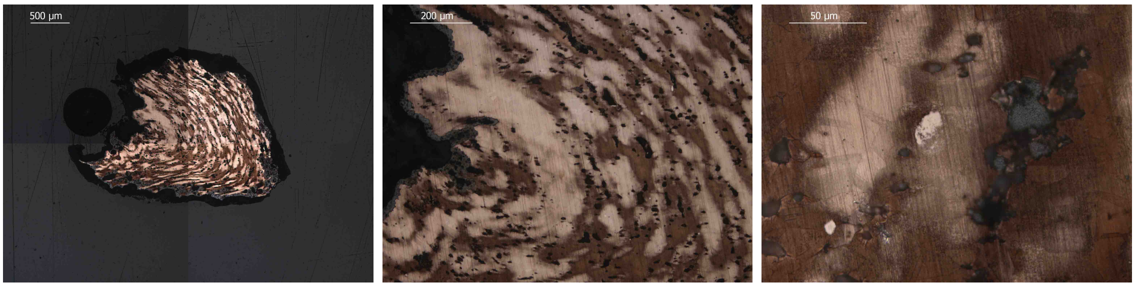
a SP68 - BF; Etched (200x) b SP68 - BF; Etched (200x) c SP68 - BF; Etched (500x)

Figure C.2: Microstructure of arrowhead SP68 (OM-BF, etched)



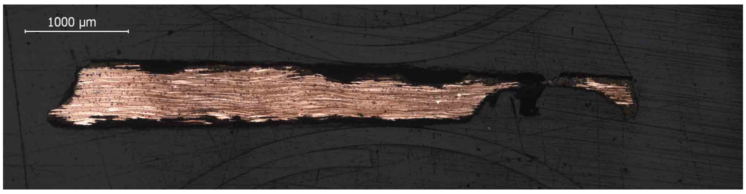
a SP05 - BF; Etched (200x) b SP05 - BF; Etched (500x) c SP05 - BF; Etched (500x)

Figure C.3: Microstructure of dagger SP05 (OM-BF, etched)



a SP09 - BF; Etched (50x) b SP09 - BF; Etched (100x) c SP09 - BF; Etched (500x)

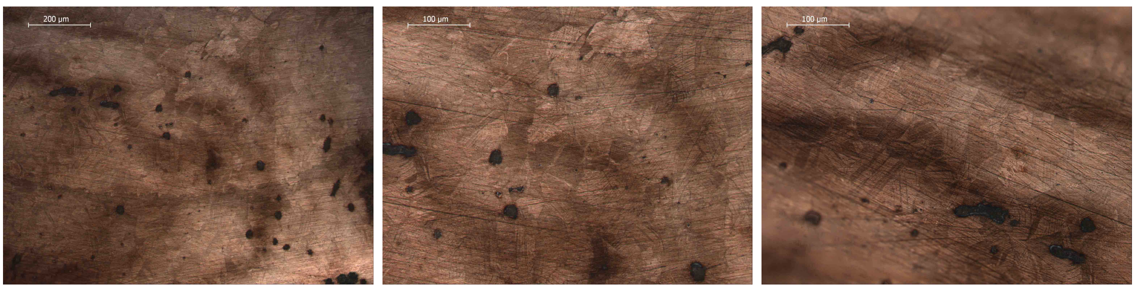
Figure C.4: Microstructure of dagger SP09 (OM-BF, etched)



a SP15 - BF; Etched (50x)

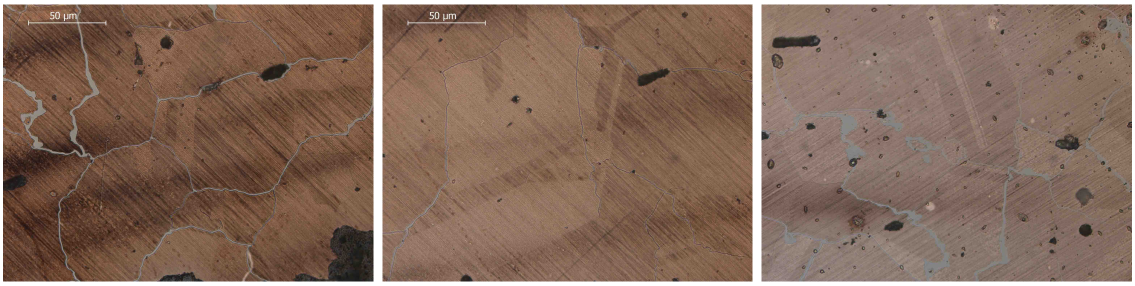
b SP15 - BF; Etched (1000x)

Figure C.5: Microstructure of dagger(?) SP15 (OM-BF, etched)



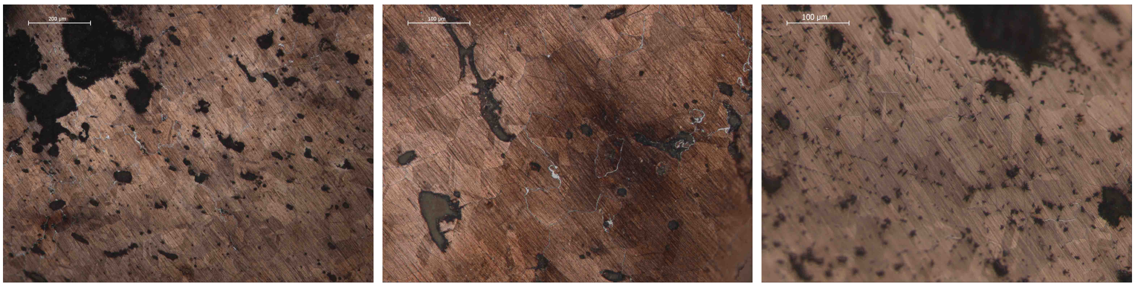
a SP55 - BF; Etched (100x) b SP55 - BF; Etched (200x) c SP55 - BF; Etched (200x)

Figure C.6: Microstructure of dagger SP55 (OM-BF, etched)



a SP56 - BF; Etched (500x) b SP56 - BF; Etched (500x) c SP56 - BF; Etched (500x)

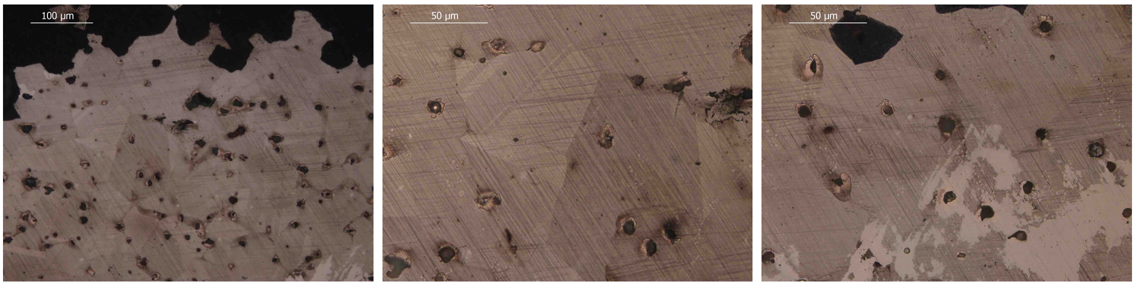
Figure C.7: Microstructure of dagger SP56 (OM-BF, etched)



a SP67 - BF; Etched (100x) b SP67 - BF; Etched (200x) c SP67 - BF; Etched (200x)

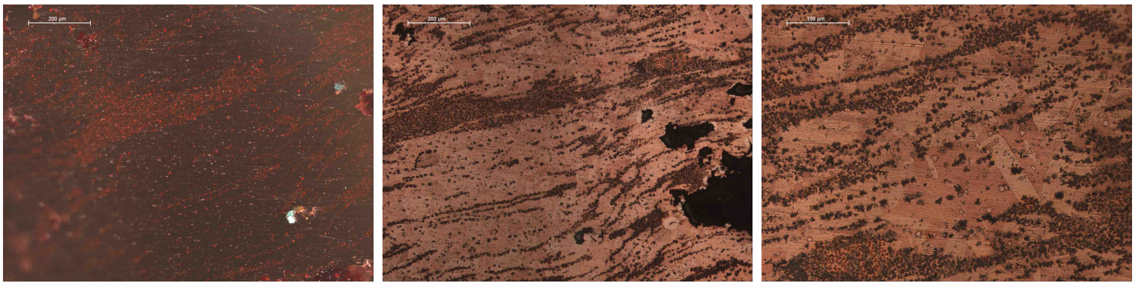
Figure C.8: Microstructure of dagger SP67 (OM-BF, etched)

C.2 Tools



a SP17 - BF; Etched (200x) | b SP17 - BF; Etched (500x) | c SP17 - BF; Etched (500x)

Figure C.9: Microstructure of awl SP17 (OM-BF, etched)

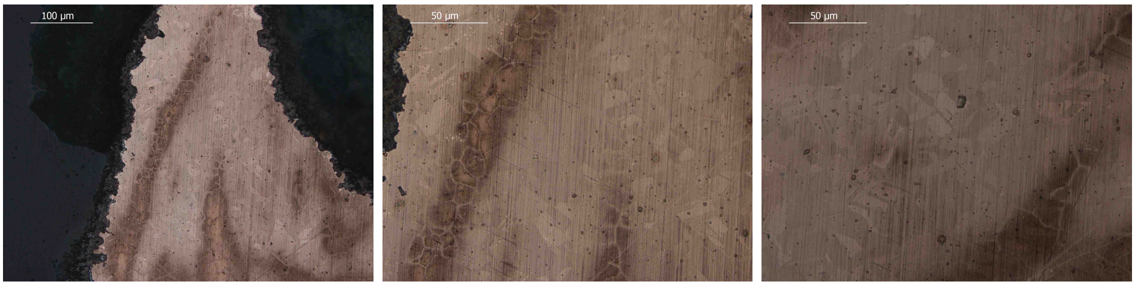


a SP22 - Pol; Non-etched (100x) | b SP22 - BF; Etched (100x) | c SP22 - BF; Etched (200x)

Figure C.10: Microstructure of awl SP22 (a: MO-Pol, non-etched; b and c: OM-BF, etched)

a SP23 - BF; Etched (200x) | b SP23 - BF; Etched (200x) | c SP23 - BF; Etched (500x)

Figure C.11: Microstructure of awl SP23 (OM-BF, etched)

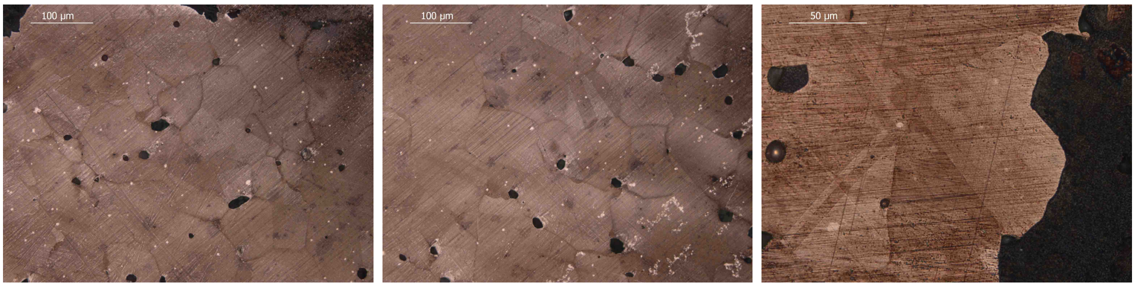


a SP57 - BF; Etched (200x) b SP57 - BF; Etched (500x) c SP57 - BF; Etched (500x)

Figure C.12: Microstructure of awl SP57 (OM-BF, etched)

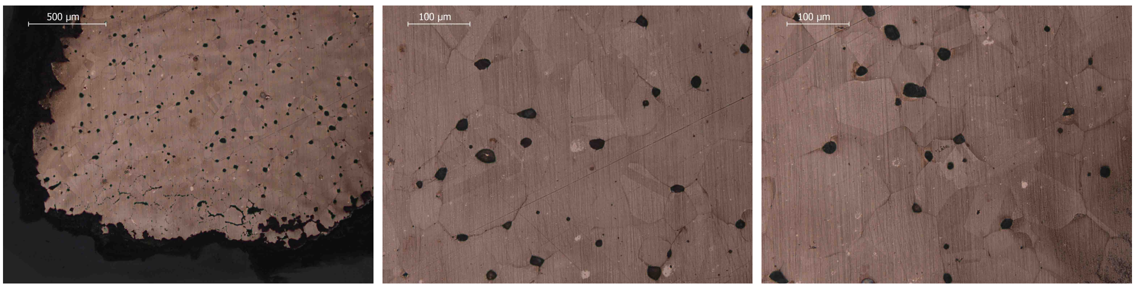
a SP62 - BF; Etched (200x) b SP62 - BF; Etched (200x) c SP62 - BF; Etched (500x)

Figure C.13: Microstructure of awl SP62 (OM-BF, etched)



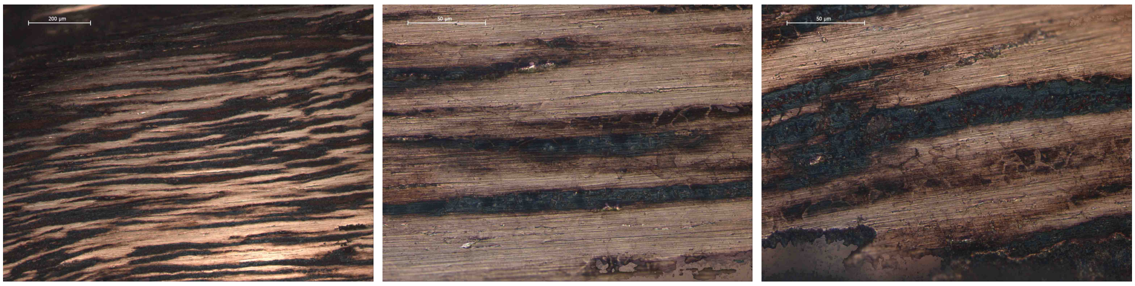
a SP64 - BF; Etched (200x) b SP64 - BF; Etched (200x) c SP64 - BF; Etched (500x)

Figure C.14: Microstructure of awl SP64 (OM-BF, etched)



a SP66 - BF; Etched (50x) b SP66 - BF; Etched (200x) c SP66 - BF; Etched (200x)

Figure C.15: Microstructure of awl SP66 (OM-BF, etched)

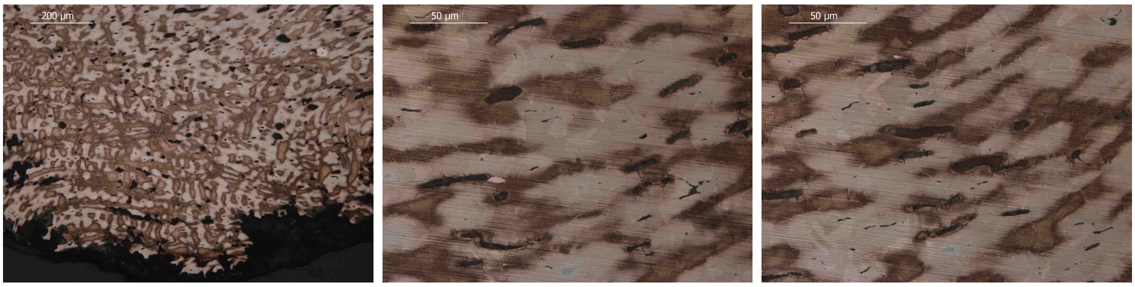


a SP69 - BF; Etched (100x) b SP69 - BF; Etched (500x) c SP69 - BF; Etched (500x)

Figure C.16: Microstructure of awl SP69 (OM-BF, etched)

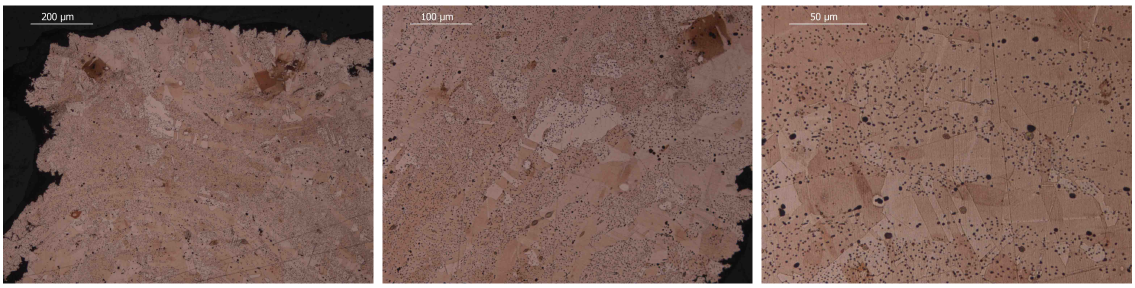
a SP71 - BF; Etched (50x) b SP71 - BF; Etched (1000x) c SP71 - BF; Etched (1000x)

Figure C.17: Microstructure of awl SP71 (OM-BF, etched)



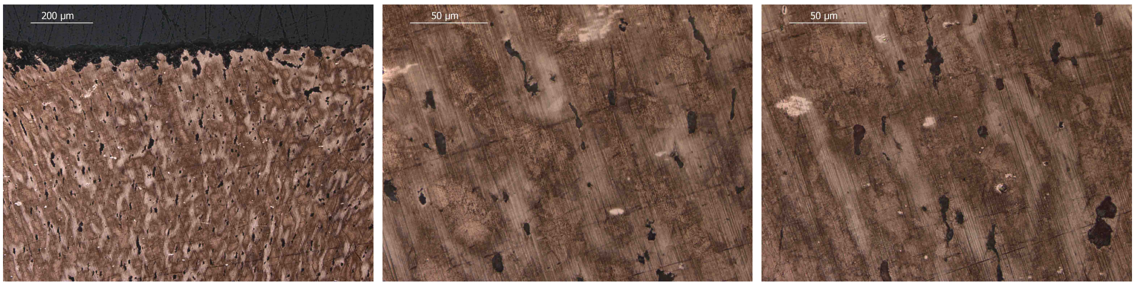
a SP72 - BF; Etched (100x) b SP72 - BF; Etched (500x) c SP72 - BF; Etched (500x)

Figure C.18: Microstructure of awl SP72 (OM-BF, etched)



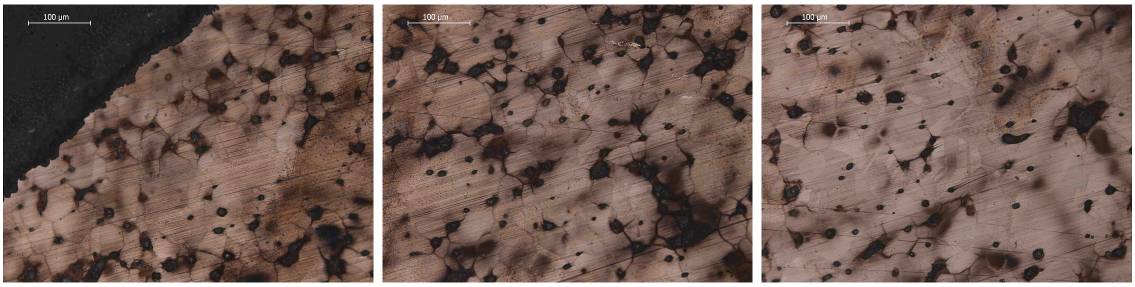
a SP74 - BF; Etched (100x) b SP74 - BF; Etched (200x) c SP74 - BF; Etched (500x)

Figure C.19: Microstructure of awl(?) SP74 (OM-BF, etched)



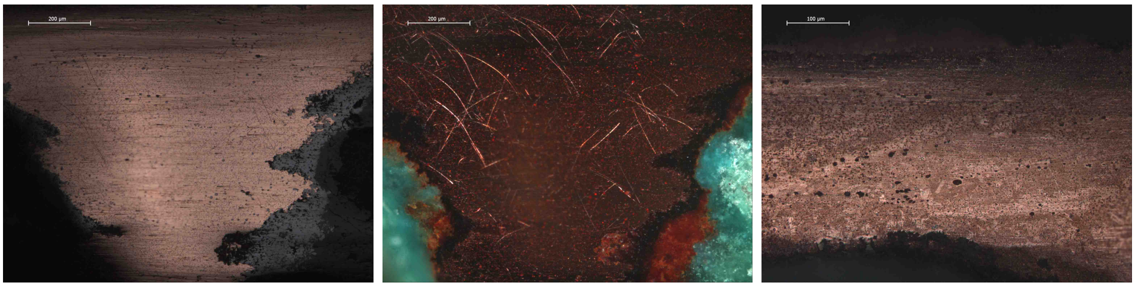
a SP06 - BF; Etched (100x) b SP06 - BF; Etched (500x) c SP06 - BF; Etched (500x)

Figure C.20: Microstructure of chisel SP06 (OM-BF, etched)



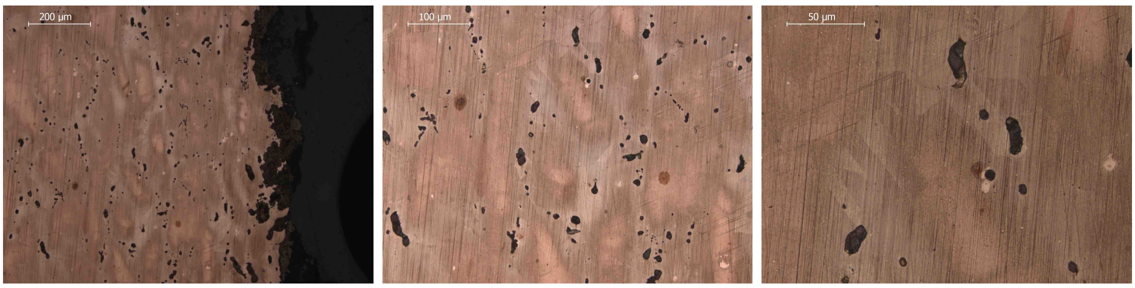
a SP20 - BF; Etched (200x) b SP20 - BF; Etched (200x) c SP20 - BF; Etched (200x)

Figure C.21: Microstructure of chisel SP20 (OM-BF, etched)



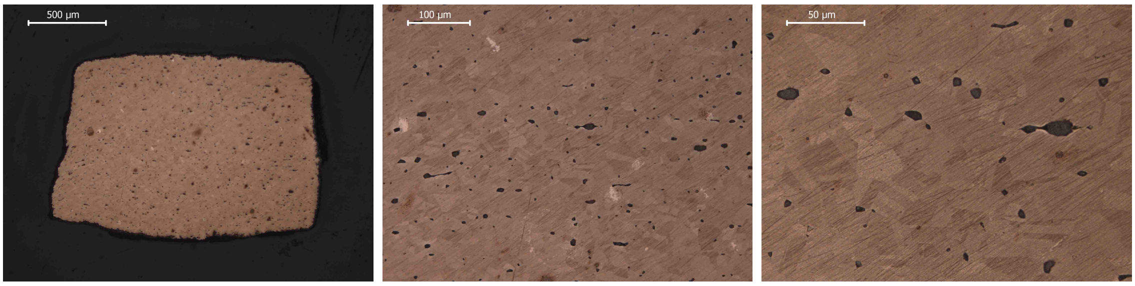
a SP60 - BF; non-tched (100x) b SP60 - Pol; non-etched (100x) c SP60 - BF; Etched (200x)

Figure C.22: Microstructure of chisel SP60 (a: OM-BF, non-etched; b: OM-Pol, non-etched; c: OM-BF, etched)



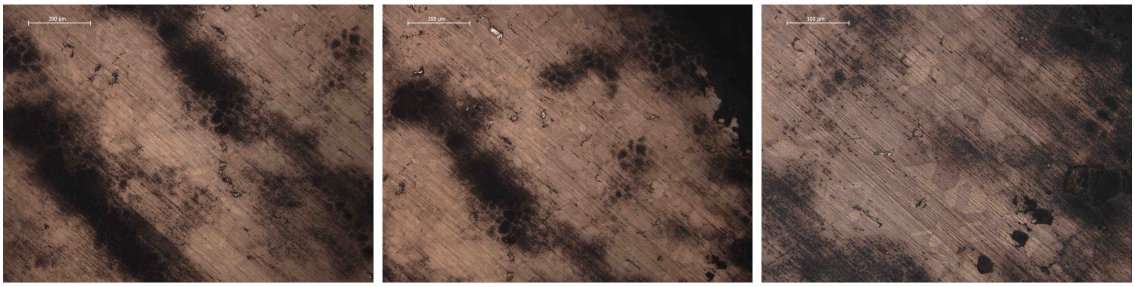
a SP70 - BF; Etched (100x) b SP70 - BF; Etched (200x) c SP70 - BF; Etched (500x)

Figure C.23: Microstructure of chisel SP70 (OM-BF, etched)



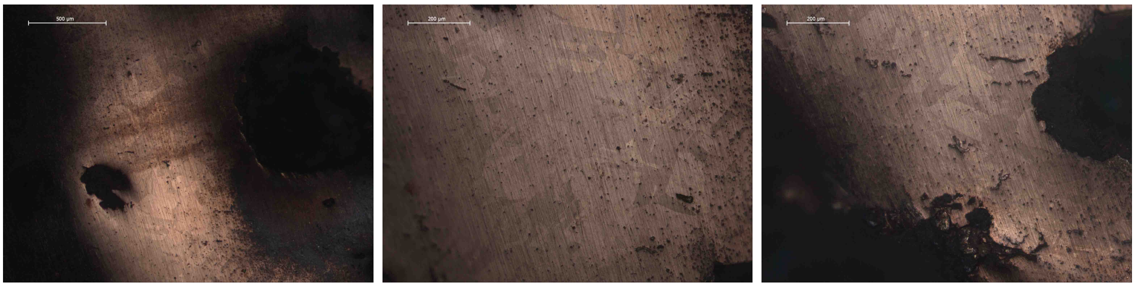
a SP07 - BF; Etched (50x) b SP07 - BF; Etched (200x) c SP07 - BF; Etched (500x)

Figure C.24: Microstructure of needle SP07 (OM-BF, etched)



a SP59 - BF; Etched (100x) b SP59 - BF; Etched (100x) c SP59 - BF; Etched (200x)

Figure C.25: Microstructure of saw SP59 (OM-BF, etched)



a SP58 - BF; Etched (50x) b SP58 - BF; Etched (100x) c SP55 - BF; Etched (100x)

Figure C.26: Microstructure of spatula SP58 (spatula) (OM-BF, etched)

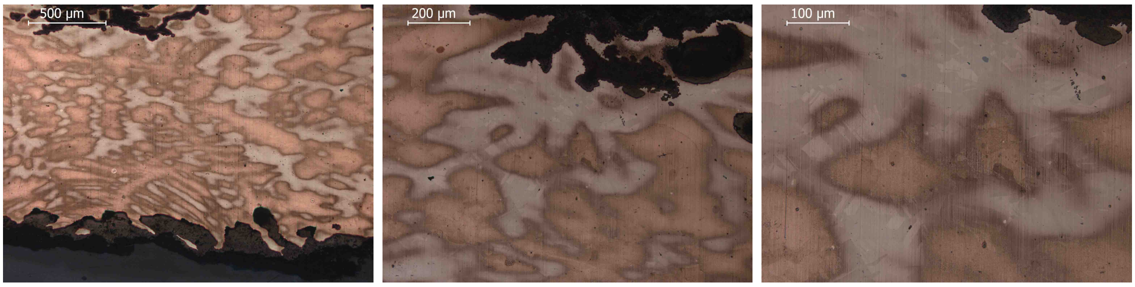
a SP58 - BF; Etched (200x) b SP58 - BF; Etched (200x) c SP55 - BF; Etched (200x)

Figure C.27: Microstructure of spatula SP58 (rod) (OM-BF, etched)

a SP63 - BF; Etched (50x) b SP63 - BF; Etched (100x) c SP63 - BF; Etched (200x)

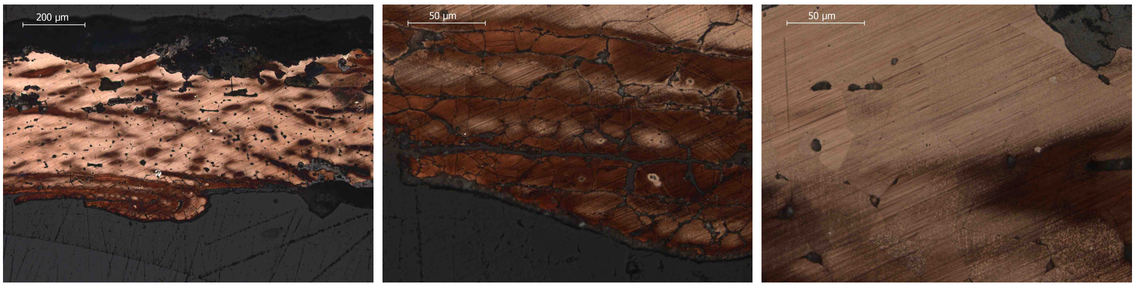
Figure C.28: Microstructure of spatula SP63 (OM-BF, etched)

C.3 Objects with Indeterminate Function



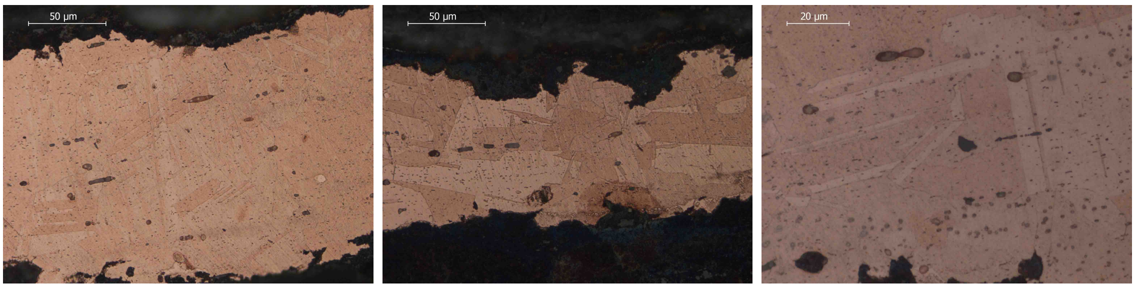
a SP02 - BF; Etched (50x) b SP02 - BF; Etched (100x) c SP02 - BF; Etched (200x)

Figure C.29: Microstructure of artefact SP02 (OM-BF, etched)



a SP13 - BF; Etched (100x) b SP13 - BF; Etched (500x) c SP13 - BF; Etched (500x)

Figure C.30: Microstructure of artefact SP13 (OM-BF, etched)



a SP14 - BF; Etched (500x) b SP14 - BF; Etched (500x) c SP14 - BF; Etched (1000x)

Figure C.31: Microstructure of artefact SP14 (OM-BF, etched)