Archaeometallurgical Study of Copper-Based Artefacts from the Portuguese Territory

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ABSTRACT

In south-central Portugal, the first copper artefacts were emerging in the period from 4th to 3rd millennium BC. The fortified settlement of Vila Nova de São Pedro (VNSP) is internationally known, being one of the best explored Chalcolithic sites of the Portuguese Estremadura. The large collection of VNSP, deposited at Carmo Archaeological Museum (Lisbon), consists of hundreds of metallic artefacts and fragments and thousands of other objects from various materials.
Laboratory project deals with elemental and microstructural characterization of 15 artefacts from the settlement VNSP. Elemental composition was determined by Energy-Dispersive X-Ray Fluorescence spectrometry and microstructure of the artefacts was investigated by optical microscopy and electron scanning microscopy. The work was carried out under the research project Early Metallurgy in the Portuguese Territory - EARLYMETAL (PTDC/HIS-ARQ/110442/2008) at Instituto Tecnológico e Nuclear in Sacavém financed by the Portuguese Science Foundation.
It was discovered that the metallic core of the artefacts is copper or copper - arsenic alloy. The objects have typical structure of cold worked and recrystallized metal with polygonal grains and annealing twins. Samples without arsenic showed structure formed by primary α-Cu grains and network of Cu-Cu2O eutectic. Coarse elliptical shaped non-metallic inclusions of As2O3 are non-uniformly distributed in the samples with arsenic. Microanalysis shows that layer of corrosion products is most probably composed of basic copper carbonates and cuprite.

1 INTRODUCTION

By the end of the 3rd millennium and the beginning of the 4th millennium BC, a series of fortified settlement centre emerged in the Estremadura, south-central Portugal. Three sites of this cultural phenomenon – Vila Nova de São Pedro (Azambuja), Zambujal (Torres Vedras) and Leceia (Oeiras) – were subject to extensive archaeological excavations, which have led to a comprehensive set of data allowing a reasonable definition of the Chalcolithic culture of the region [1, 2].
Vila Nova de São Pedro is the name of an archaeological site in Portuguese Estremadura where thousands of arrowheads were found inside a fortified site. The famous Chalcolithic settlement of VNSP was excavated during successive campaigns between 1937 and 1964 by the Portuguese archaeologist Afonso de Paço. A strong inner enclosure with several semi-circular bastions and two outer lines of defence and particularly the central fortification of the site was discovered. The greatest part of the rich finds is stored and displayed in the Carmo Archaeological Museum, Lisbon [2].
Several hundred of copper and bronze artefacts were discovered at VNSP. First analyses of 10 artefacts were done at 1950s. Later, other analyses of the VNSP collection were made during 1960s and 1970s in the framework of the SAM project (Studien zu den Anfängen der Metallurgie). These

analyses revealed that 35 % of the analysed objects were made of pure copper, 45 % were copper with variable concentrations of arsenic and low concentrations of some other elements [1].

At the beginning copper was utilized in its native state, as reddish brown metal. The first copper treatment was simple hammering of malleable copper into a demand shape. Subsequently, the annealing and tempering included finishing with a cold work were discovered. But annealing temperature (around 800°C) wasn't sufficient for melting of a metal [3].

Development of copper metallurgy from melting of native copper to the smelting of pure oxide ores is probably connected with melting of heavily-weathered pieces of native copper. At different stages, three different processes of copper smelting techniques were used. A crucible smelting was followed by a smelting in non-slag tapping furnaces using fluxes or self-fluxing ores and then by smelting in slag-tapping furnaces [3].

In early times crucibles were often heated from above, and the heat radiated downwards onto the charge. The first type of smelting furnaces was a hole in the ground. The distinction between smelting in a crucible and smelting in a non-tapping furnaces isn't always clear – by inserting a tuyere from the top well down into a crucible it becomes a furnace. Many Cu-based metallic artefacts produced during Chalcolithic age have significant levels of As. There are two possibilities – the ores, that they primary used, contain high level of As or arsenic minerals were intentionally added [3, 4].

2 EXPERIMENT

The set of studied metal artefacts consisted of 15 objects, was preliminary classified into two typologies [5]. The distribution of articles by the typologies is listed in **Tab. 1**.

Tab. 1: Description of types and codes assigned to the set of metal artefacts from VNSP.

Typologies	Pieces	Code	Work number
C - Chisels	6	VNSP261C - VNSP266C	1C – 6C
D - Axes	9	VNSP267D - VNSP275D	7A – 15A

These artefacts (**Fig. 1, Fig. 2**) were subject to a preliminary analysis by Energy-Dispersive X-Ray Fluorescence spectrometry (EDXRF)[1] at non-cleaned surfaces to determine the basic alloy constituents. In a second phase, artefacts elemental compositions were determined by micro-EDXRF (Faculty of Science and Technology, New University of Lisbon), after removing the layer of corrosion products in a small area. At selected artefacts metallographic observations were carried out.

Fig. 1: Parts of chisels (1C – 6C)

Fig. 2: Parts of axes (7A – 15A)

[1] Nuclear and Technological Institute - ITN, Lisbon

3 RESULTS AND DISCUSSION

3.1 ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY

With respect to the fact that study was focused on the oldest copper artefacts, the bronze objects were eliminated on the base of results of energy dispersive non-destructive X-ray spectroscopy. The second goal of this analysis was defined selection of objects into two groups, the objects made from pure copper and objects made from arsenic copper.

3.2 ENERGY DISPERSIVE MICRO - XRF SPECTROMETRY

The division of the artefacts on copper artefacts and arsenic copper artefacts has been confirmed by X-ray energy dispersive micro-analysis performed on the cutting and grinding surfaces of objects. Presence of iron, typical for Chalcolithic age, was shown in several cases. Except iron, bismuth, lead, nickel and zinc were detected (**Tab. 2**).

Tab. 2: micro-XRF spectrometry of 15 artefacts (n.d. = not detected)

Elements / Artefacts	Cu [%]	As [%]	Fe [%]	Zn [%]	Bi [%]	Other (elem.)	Other [%]
Artefacts without or with very low amount of arsenic							
1C	**99.20**	**0.31**	**0.07**	< 0.5	< 0.2	n. d.	-
2C	**99.99**	n. d.	< 0.05	n. d.	n. d.	n. d.	-
3C	**99.43**	**0.26**	< 0.05	< 0.5	n. d.	n. d.	-
4C	**99.67**	**0.06**	< 0.05	< 0.5	n. d.	n. d.	-
6C	**99.60**	**0.02**	< 0.05	< 0.5	< 0.2	n. d.	-
7A	**99.99**	n. d.	< 0.05	n. d.	n. d.	n. d.	-
8A	**99.57**	n. d.	< 0.05	< 0.5	< 0.2	n. d.	-
13A	**99.99**	n. d.	< 0.05	n. d.	n. d.	n. d.	-
Artefacts with arsenic							
5C	**98.97**	**0.67**	< 0.05	< 0.5	< 0.2	n. d.	-
9A	**96.97**	**2.56**	**0.10**	< 0.5	< 0.2	**Pb**	< 0.2
10A	**98.63**	**0.83**	< 0.05	< 0.5	< 0.2	**Ni**	< 0.2
11A	**98.27**	**1.37**	< 0.05	< 0.5	< 0.2	**Pb**	< 0.2
12A	**96.63**	**3.06**	< 0.05	< 0.5	n. d.	n. d.	-
14A	**98.33**	**1.68**	< 0.05	n. d.	n. d.	n. d.	-
15A	**97.43**	**2.30**	n. d.	< 0.5	n. d.	n. d.	-

3.3 OPTICAL MICROSCOPY

Samples without arsenic are characteristic by a presence of Cu – Cu_2O eutectic distributed at boundaries of primary copper dendrites. Arrangement of chains of this eutectic reflects the prevailing direction of metalworking of the artefacts (**Fig. 3**). In microstructure of samples, containing arsenic elliptical inclusions of arsenic oxide were observed sporadically (**Fig. 8**). The presence of arsenic in copper, due to its deoxidizing effect (high oxygen-affinity), is resulted in clearly different structures with respect to samples of pure copper. Microscopy observation in dark field illumination, which uses an oblique lighting, shows Cu_2O in red colour. Pores and superficial impurities are displayed with strong bright contours (**Fig. 4, Fig. 9**).

Samples etching were performed with acid ferric chloride solution. After etching, samples with higher arsenic content show a structural coring effect (**Fig. 10, Fig. 12**). This is a sign that the alloy wasn't efficiently homogenized. Samples without arsenic or with relatively small contents of this element don't exhibit coring (**Fig. 5**). Annealing twins were observed in all samples (**Fig. 6, Fig. 11**). The copper matrix consists of polygonal grains with straight grain boundaries. At one sample (2C) the elongated and slightly bended grains in the cutting edge region were observed (**Fig. 7**).

Artefacts without or with very low amount of arsenic:

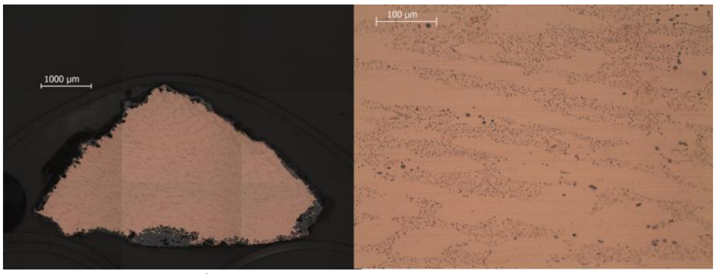

Fig. 3: Distribution of oxide particles in metal matrix without As (3 left - 7A, 50x; 3 right - 13A, 200x)

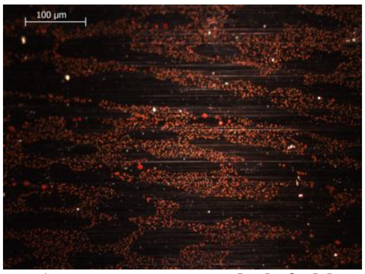

Fig. 4: 13A, 200x, dark field, distribution of oxide particles in metal matrix

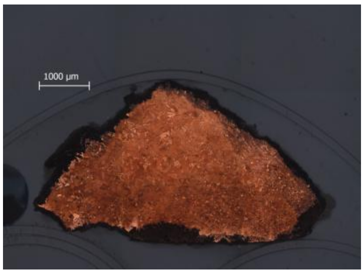

Fig. 5: 7A, $FeCl_3$, 50x, recrystallized structured without coring

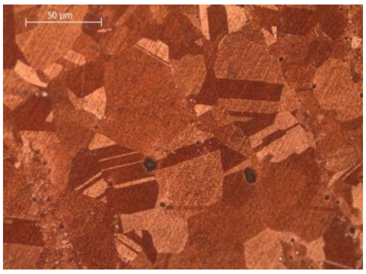

Fig. 6: 7A, $FeCl_3$, 50x, recrystallized structured of Cu without As, annealing twins, polygonal grains

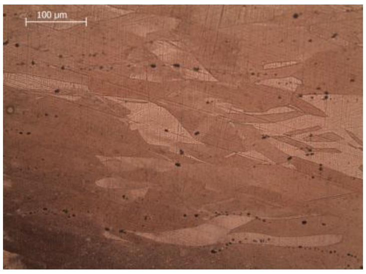

Fig. 7: 2C, $FeCl_3$, 50x, elongation of grains

Artefacts with arsenic:

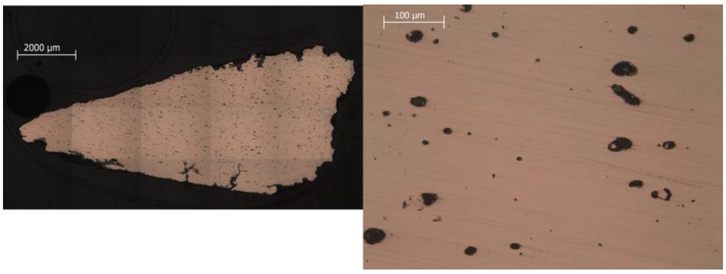

Fig. 8: Distribution of non-metallic particles in metal matrix with As (8 left- 15A, 50x; 8 right - 15A, 200x)

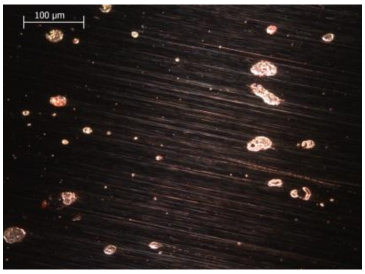

Fig. 9: 15A, 200x, dark field, distribution of non-metallic particles in metal matrix with As

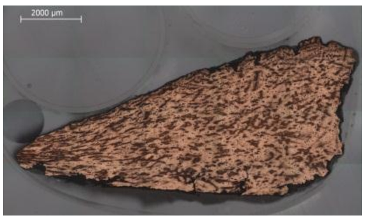

Fig. 10: 15A, $FeCl_3$, 50x, coring effect

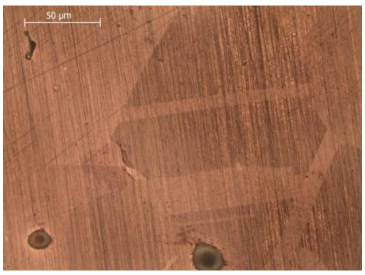

Fig. 11: 14A, $FeCl_3$, 500x, recrystallized structure of Cu with As, annealing twins and non-metallic particles

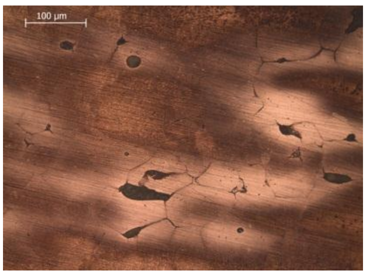

Fig. 12: 11A, FeCl3, 200x, coring effect, non-metallic particles

3.4 Scanning Electron Microscopy – Energy Dispersive Spectroscopy

The composition of corrosion products layer and composition of metallic core was detected with a scanning electron microanalysis.

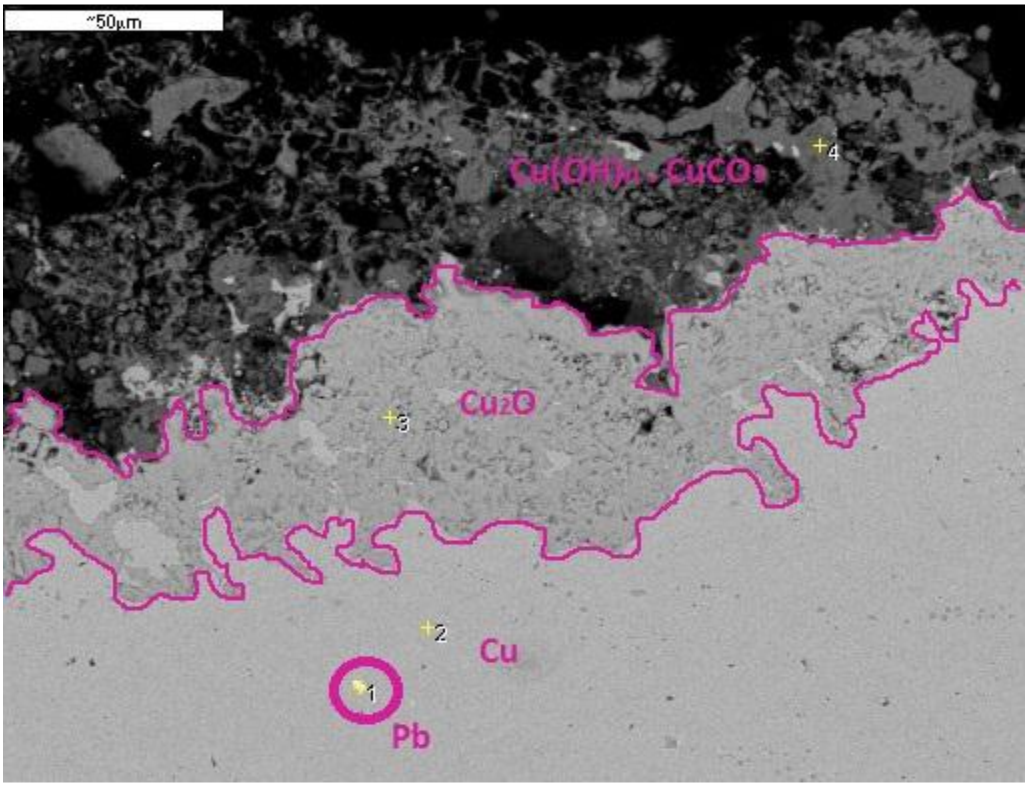

Fig. 13: Stratigraphy of corrosion layers of sample without arsenic

Spectrum of EDS microanalysis reveals the presence of Cu-C-O (basic copper carbonate) in the outer surface corrosion layer, taking into account the relatively high peaks intensities for carbon and oxygen. The inner corrosion layer (**Fig. 13**) is identified as Cu_2O (cuprite). Metallic core is mainly constituted by copper. A presence of lead in the form of globular particle was rarely discovered in the metallic face.

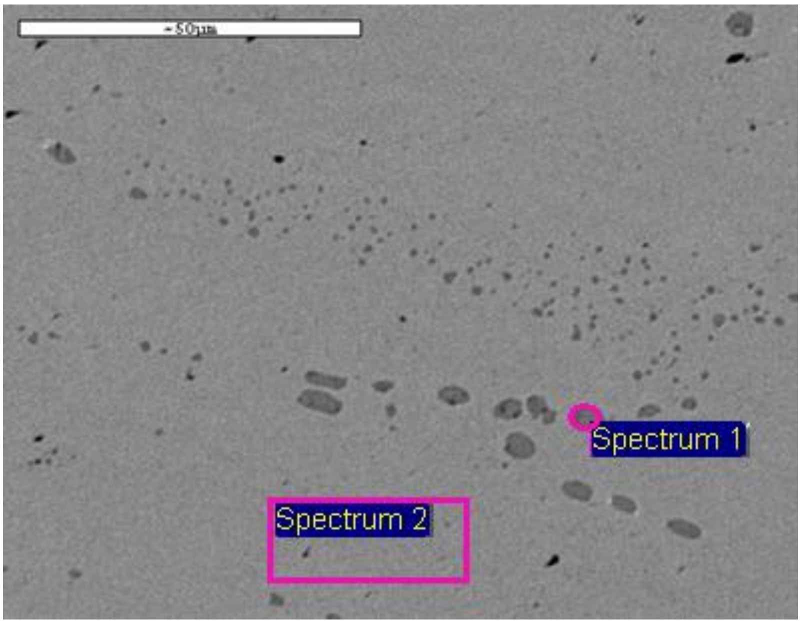

Fig. 14: The area of accumulation non-metallic phase and metal matrix of sample without arsenic

In the metallic area of non-etched pure copper sample nearly continuous network of non-metallic particles was observed (**Fig. 14)**. The non-metallic particles are composed by a cuprous oxide, Cu_2O.

It means that this network represents Cu – Cu_2O eutectic deposited on a pure copper grain's boundaries.
The same analysis of arsenic copper sample reveals a difference of composition of non-metallic particles in comparison with pure copper. The non-metallic particles in this case have complex inner structure (**Fig. 15**). The harder phase **(Fig. 16**) consists of nearly pure arsenic oxide As_2O_3, resembling round homogenous particle. The rest of the particle consists probably of As_2O_3 – Cu_2O eutectic (**Fig. 17**). The metal core shows two areas with a different content of arsenic and copper (**Fig. 18, Fig. 19**). These areas are typical segregations areas (reflecting like a coring effect), that were observed by optical microscope (**Fig. 10, Fig. 12**).
The results of arsenic analysis in the case of electron microanalysis were in a good agreement with the values obtained by micro-XRF analysis.

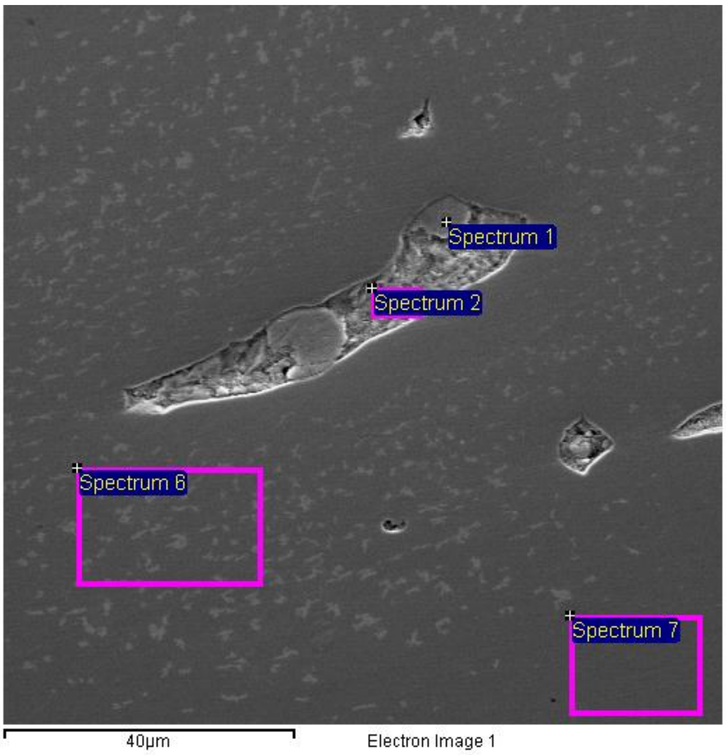

Fig. 15: Complex of non-metallic particle and areas with a different arsenic content at arsenic copper sample

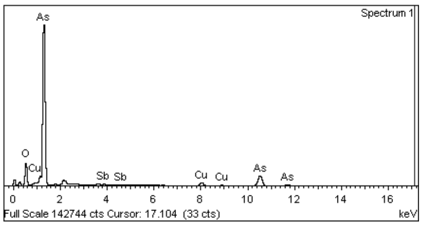

Fig. 16: Spectrum of EDS of non-metallic phase – As_2O_3

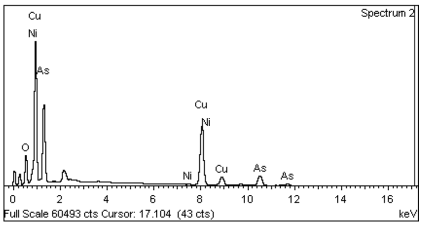

Fig. 17: Spectrum of EDS of non-metallic phase – eutectic As_2O_3 - Cu_2O

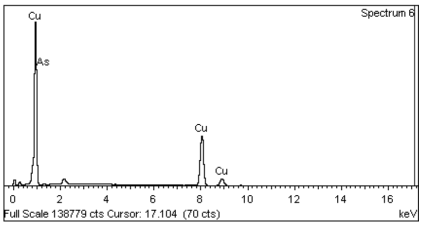

Fig. 18: Spectrum of EDS of metal matrix (As content 1,75 %)

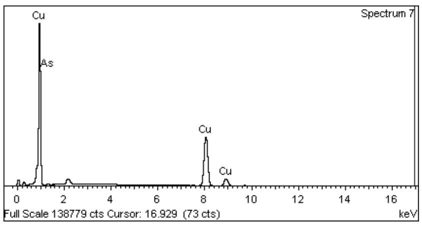

Fig. 19: Spectrum of EDS of metal matrix (As content 1,29 %)

4 CONCLUSIONS

Elemental composition determined by µ-EDXRF at the studied artefacts from Vila Nova de S. Pedro showed that they were constituted by copper or by copper with variable amounts of arsenic (maximum 3.06 %). Besides, some trace elements (Fe, Bi, Zn, Pb and Ni) were also detected. Some differences in the arsenic contents could be related with type of tool. Higher amounts of arsenic, which improves the mechanical properties of the alloys, were detected in axes. These alloy compositions is typical for copper and copper-based alloy in Chalcolithic age.

Metallographical examinations showed that all objects have typical recrystallized structure (annealed twins in a polygonal grain structure). This means that those artefacts were manufactured by cold working and subsequent annealing cycles during its metalworking.

The chisel blade is an example of an artefact with lower arsenic content with presence of the characteristic Cu_2O inclusions in a Cu matrix. The cuprous oxide particles formed a network, outlining the dendritic cells. Corrosion products are constituted of cuprite's layers and basic copper carbonates.

Further work involving the chemical and microstructural characterization of more artefacts of different typologies and variable remains of metallurgical activities (e.g., crucibles, slags) would be important to a more complete understanding of the early metallurgy on Portuguese Estremadura.

5 ACKNOWLEDGEMENT

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