Journal of Archaeological Science 40 (2013) 2045–2056

Contents lists available at SciVerse ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

The role of arsenic in Chalcolithic copper artefacts – insights from Vila Nova de São Pedro (Portugal)

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ARTICLE INFO

Article history:
Received 1 February 2012
Received in revised form
11 December 2012
Accepted 14 December 2012

Keywords:
Chalcolithic
Elemental composition
Arsenic
Microstructure
Vickers microhardness

ABSTRACT

The Castro of Vila Nova de São Pedro (VNSP) is an emblematic settlement located at Azambuja, Portuguese Estremadura. It was occupied during the third and second millennia BC, predominantly during the Chalcolithic period. A diversified collection of 53 copper-based artefacts (most part in a fragmentary condition), belonging to an extensive metallic collection recovered during excavations carried out in VNSP, was studied using micro-EDXRF spectrometry, optical microscopy and SEM-EDS. Additionally, Vickers microhardness measurements were performed to establish the effectiveness of the thermo-mechanical treatment in the hardness of the artefacts. Results show that the Largo do Carmo, artefact collection is mainly composed of copper or arsenical copper, being 37% of the artefacts made of copper alloyed with arsenic (As $>$ 2%). A statistically significant association was found between copper alloyed with arsenic and artefacts classified as tools/weapons (arrowheads, daggers and knives). In several cases, the presence of arsenic rich phases in the microstructure, resulting from an inverse segregation phenomenon, shows no evidence of chemical homogeneity control during the artefact manufacture. Microstructural analyses also show that the majority of this group (73%) was shaped with forging plus annealing operation cycles and 23% of the artefacts received a final cold hammering after the forging and annealing. An association between the presence of a final forging treatment and artefacts presenting higher arsenic contents was also identified. Nevertheless, no direct correlation was found between the arsenic content of the alloy and its hardness. Also no direct correlation was found between the hardness and a final forging operation. However, it was observed that a harder forging was applied to the cutting edge of the artefacts and consequently a high hardness in this area was obtained despite the arsenic content of the alloy. Concerning arsenical copper alloys, all evidences point out that the potential for obtaining a harder material was not recognized by the ancient metallurgists and the selection of the alloy was possibly made based on colour.

1. Introduction

The earliest sites with evidence of metallurgy in the Portuguese territory belong to the transition of the fourth to the third millennium BC (Cardoso and Soares, 1996; Soares and Cabral, 1993). The Portuguese Estremadura is a key region in studies of the Chalcolithic metallurgy in the Iberian Peninsula due to the existence of impressive large settlements with evidences of metal production (Müller and Soares, 2008; Soares and Cabral, 1993; Soares et al., 1996). Within this region, three sites, Vila Nova de São Pedro (Azambuja), Zambujal (Torres Vedras) and Leceia (Oeiras) (Fig. 1), have been subject to extensive archaeological excavations. At the settlement of Vila Nova de São Pedro (VNSP) archaeological digging was carried out from 1937 to 1964 by archaeologist Afonso do Paço with the support of Reverend Eugene Jalhay. Alongside the practice of agriculture and grazing, some evidence of other practices such as hunting, fishing and gathering were found. Apart from the metallurgical collection (artefacts, crucibles and other remains of production), plenty of household utensils, namely pottery and loom weights, were collected in the settlement. Also an important lithic collection of arrowheads, gouges, axes, scrapers and worship idols

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http://dx.doi.org/10.1016/j.jas.2012.12.015

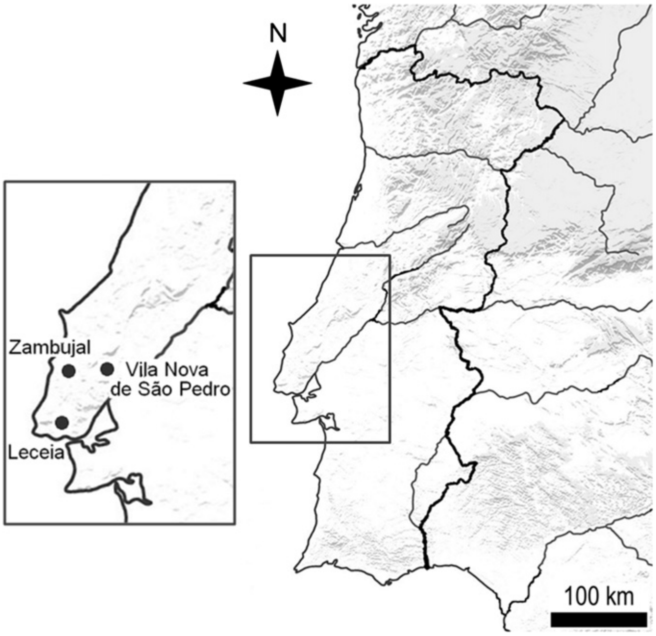

Fig. 1. Location of VNSP and other settlements in Portuguese Estremadura.

were recovered. The majority of the artefacts found in VNSP are currently deposited in the Carmo Archaeological Museum, Lisbon (Arnaud and Fernandes, 2005).

In spite of the extraordinary importance of the recovered metallurgical related materials, only a few studies have been carried out up to the present day regarding the several hundred copper and arsenical copper artefacts and metallurgical remains discovered at VNSP. An earlier study was published in 1952 presenting the elemental composition of few metallic objects found at VNSP (Paço and Arthur, 1952). Other studies carried out by the first author were mainly concerned with descriptions of artefacts or of the settlement (Paço, 1955, 1964).

Nevertheless, some important studies focused on the elemental characterization of artefacts and metallurgical remains led to important results and publications concerning the understanding of the early Iberian metallurgy. It is the case of the analysis carried out by the project “Studien zu den Anfängen der Metallurgie” (SAM; Junghans et al., 1960, 1968, 1974) which form the most comprehensive set of quantitative chemical data of prehistoric copper artefacts from Europe, including Portugal. The SAM programme quantitatively analysed more than 22,000 archaeological copper based artefacts using atomic emission spectroscopy in order to find similar compositionally groups. Of this large dataset, 1700 analysed artefacts were recovered at the Iberian Peninsula, including 87 from VNSP (Müller and Pernicka, 2009; Soares, 2005). A significant conclusion from this programme was that pure copper and arsenical copper were the dominant production during Copper Age to Early Bronze Age in the Iberian Peninsula (Junghans et al., 1968). Later, in order to group artefacts according to their chemical composition, a classification system was developed by Sangmeister using a combination of three two-dimensional element diagrams (showing the content of As–Ni, As–Bi and Sb–Ag) and defined regional groups (Müller and Pernicka, 2009; Sangmeister, 1995). Based on a typological chronology this author concluded that pure copper was primarily used during the Early Copper Age while arsenical copper with low concentrations of other elements was used throughout the Copper Age. Arsenical copper with high concentrations of antinomy, silver and/or nickel tended to occur in Late Copper Age (Müller and Pernicka, 2009; Sangmeister, 1995). Unfortunately, due to the lack of field notes of the early excavations performed in VNSP and the not detailed existing documentation is not possible to match the previous chronology to the materials excavated from VNSP.

In another study, “Bronze Age Metalwork from the Iberian Peninsula”, based on the metallic collection belonging to the British Museum, about 100 metallic artefacts were characterized in terms of trace element patterns using atomic absorption spectrometry (Harrison and Craddock, 1981). An important finding from this study was the observation of a correlation between artefact typology and arsenic content in the alloy including artefacts recovered in Portugal (Müller and Pernicka, 2009). In the same decade, another analytical programme called “Proyecto de Arqueometalurgia” was initiated in Spain. Along this programme more than 10,000 analyses of Chalcolithic and Early Bronze Age copper artefacts were performed using X-ray fluorescence spectrometry in surface cleaned areas and complemented with metallographic analysis (Delibes and Montero, 1999; Rovira et al., 1997; Rovira and Gómez, 2003). This project has provided a comprehensive overview of Copper, Bronze and Iron Age metalwork of Spanish territory. According to their findings, the arsenical copper artefacts from the Chalcolithic period seem to be most likely manufactured from the direct use of the metal obtained during the processing of the ores (Müller and Pernicka, 2009).

More recently, in 2004, a research project was initiated by the German Archaeological Institute in cooperation with the Institute of Archaeometry (University of Mining and Metallurgy in Freiberg, Saxony) in order to characterize chemically and mineralogically the archaeometallurgical findings from Zambujal and other Chalcolithic sites of the Portuguese Estremadura, including VNSP. Several analytical techniques were used: X-ray fluorescence spectrometry and neutron activation analyses of ores, slags and copper objects, combined with lead isotope analyses and mineralogical analyses of ores, crucibles and slags (Müller and Cardoso, 2008; Müller and Soares, 2008; Müller et al., 2007). This project aimed to evaluate the impact of the metallurgical activities in Chalcolithic societies.

Some conclusions and findings from previous studies by several authors make clear that the subject regarding the intentional use of copper with higher arsenic contents to manufacture specific typologies is controversial and still under discussion (Cardoso and Guerra, 1997/1998; Ferreira, 1961; Müller and Cardoso, 2008; Müller and Pernicka, 2009; Müller and Soares, 2008; Müller et al., 2007; Northover, 1989; Rovira, 2004). It must be noted that the production of arsenical copper alloys can be accomplished through several metallurgical processes, namely the smelting of secondary copper ores, rich in arsenic, or co-smelting of these copper ores with oxides or sulphides, also rich in arsenic (Lechtmann and Klein, 1999; Hauptmann et al., 2003). Another possibility is alloying pure copper with a mineral with high content in arsenic (Müller et al., 2004, 2007). The provenance of the arsenic, the technological choices involved in the production of an arsenical copper alloy and how it was recognized and finally used (intentionally or not) are all important issues to be considered and to take into account when analysing the arsenic distribution in prehistoric alloys.

In the present study, a significant number of copper-based artefacts with different typologies, part of the VNSP collection that remained unpublished, were analysed. This study aims to contribute to the understanding of the early metallurgy in the Estremadura area. It was based in the assessment of the arsenic content of copper-based artefacts and its correlation with artefact typologies and functions. A further step concerning the methodologies used in the previous studies mentioned above was the determination of the involved manufacturing operations, “chaîne opératoire”, and the measurement of the artefact hardness in order to understand the choices of the Chalcolithic metallurgist.

2. Metallic collection

The metallic set selected for this study was composed by 53 artefacts, the majority in fragmentary condition, in order to include a variety of typologies and elements that could be sampled.

A classification was established for their typologies, which is summarized in Table 1, using a code that include the label VNSP, followed by a reference number and a letter corresponding to the assigned typology. Some of the fragments were considered to have an indeterminate typology due to the fact that their size is too small and shapeless. Others show intentional sectioning (like axe's cutting edges) and might be scraps from the manufacturing process or parts of ingots, put aside for posterior re-melting or shaping into smaller objects (Müller and Soares, 2008). Parallels of this intentional sectioning process can be found at the settlement of Leceia (Cardoso and Guerra, 1997/1998).

In order to a better systematization and interpretation of the results, the artefact collection was divided in four major groups, according to their probable function: tools (typologies: A + C + F), axes (D), tools/weapons (E) and miscellaneous (B + G + H). Photographic documentation of each group is presented in Fig. 2. The axes were grouped separately because it is assumed they could be used either as tools or ingots (Soares, 2005). The group of tools/weapons include artefacts that could be used in domestic and production activities, in war or for social prestige (Carmé et al., 2010).

3. Methodology

Since most of the selected artefacts were in a fragmentary state, it was possible to apply a small sampling with a minimum impact in the shape of the artefact. The state of conservation of artefacts to be sampled was also taken into account for the sampling location (see Fig. 2). The awls were all sampled in the fracture area. The chisels were also sampled in the fracture area with the exception of the fragments VNSP139C, VNSP140C, VNSP141C and VNSP262C that were transversally cut. Saws VNSP185F and VNSP187F were sampled and polished, respectively, near the teeth, while VNSP186F was sampled in the opposite side of the teeth, since it was the less fragile area. The group of arrowheads, daggers and knifes were all sampled near the cutting edge with the exception of VNSP177E and VNSP189E that corresponds to the shaft area of the artefact. The group of axes were all sampled in the cutting edge area. The final group of wires, socket and indeterminate artefacts were sampled in areas with a minimum impact to the shape of the artefact. Samples were extracted from the corresponding archaeological pieces (in 51 cases) and fixed in an epoxy resin. Mounted cross-sections were polished (until 1 μm diamond paste) using a rotary polishing wheel. Only two artefacts were manually cleaned to remove corrosion products, in a small area (~4 mm^2), and also polished until 1 μm diamond paste.

The analytical techniques used to a complete characterization of the materials are summarised in Table 2.

Table 1
Summary of typologies, quantities and codes attributed.

Typologies	Number	VNSP
A – Awls	10	001A; 021A; 023A; 029A; 031A; 038A; 040A; 047A; 049A; 097A
B – Wires	2	123B; 124B
C – Chisels	11	132C–141C; 262C
D – Axes	12	144D–148D; 150D; 153D–155D; 165D; 178D
E – Arrowheads, daggers, knives	7	177G; 180E-183E; 188E; 189E
F – Saws	3	185F–187F
G – Socket	1	190G
H – Indeterminate	7	025H; 184H; 191H–194H; 196H
Total	53	

3.1. Micro-EDXRF

The 51 cross-sections and the 2 small cleaned surface areas were quantitatively analysed by micro-EDXRF analysis, with an ArtTAX Pro spectrometer. This spectrometer is equipped with a low power 30 W Mo X-ray tube and an electro-thermally cooled silicon drift detector with a resolution of 160 eV (Mn-Kα). Polycapillary lenses collimate the primary X-ray beam enabling a spatial resolution approximately 100 μm. Quantitative determinations were done using WinAxil software with readings performed in 3 different spots on the cleaned areas for each artefact and using experimental calibration factors calculated through the analysis of the standard reference material Phosphor Bronze 551 from British Chemical Standards (BCS).

The quantifications limits for minor elements usually present in archaeological copper and copper-arsenic alloys and the accuracy of the micro-EDXRF analysis were determined with the analysis of two reference materials: Phosphor Bronze 552 (BCS) and IDLF5 (Industries de la Fonderie) (Table 3 and Table 4).

Quantification limits vary according the atomic number of the analyte and the detected X-ray emission line, being less favourable whenever existing strong spectral interferences.

The low standard deviation on the average concentrations obtained for the 3 different spots indicates the good representativeness of the analysed area. The accuracy of the micro-EDXRF is usually better for the major elements, mainly below 5%. The minor elements like lead, iron, zinc and nickel presents higher relative errors. Lead emission peak overlaps with the arsenic and iron with the copper escape peak; zinc and nickel have a strong spectral interference with the alloy main constituent (copper).

3.2. OM

Metallographic observation of the cross-sections and small cleaned areas were carried out with an optical microscope Leica DMI 5000 M, under bright field (BF), dark field (DF) and polarized light (Pol) illumination. Samples were observed in unetched condition and after etching with an aqueous ferric chloride solution.

3.3. SEM-EDS

Microanalyses on the mounted cross-sections were made in a scanning electron microscope Zeiss DSM 962 equipped with secondary electrons (SE) and backscattered electrons (BSE) detectors. The equipment also includes an EDS spectrometer from Oxford Instruments, model INCAx-sight, with a Si(Li) detector with a resolution of 133 eV (Mn-Kα) and an ultrathin window used for semi-quantitative elemental analysis. The SEM working conditions were 20 kV accelerating voltage, 1–2 μm spatial resolution, 70 μA of beam emission current and 25 mm working distance. The EDS spectra were acquired for 60 s lifetime with dead time adjusted to 30–40%. Pure Co sample was used for energy calibration and Co Kα radiation was used to adjust the gain and zero energy level of the detector.

For resin mounted samples the SEM observations were made after the specimen had been sputter coated with carbon.

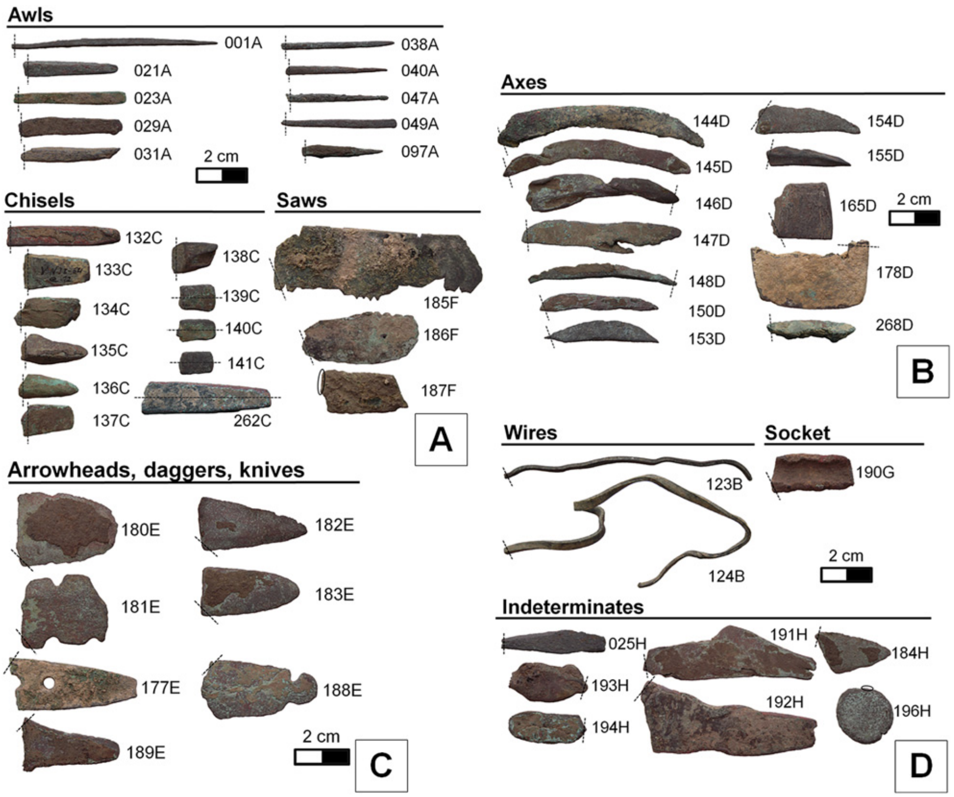

Fig. 2. A: Tools (A + C + F); B: Axes (D); C: Tools/Weapons (E); D: Miscellaneous (B + G + H). The dashed lines indicate the sampled location and elliptical area corrosion cleaned areas for analysis.

3.4. Micro-HV

Vickers microhardness testing was made on the 51 mounted cross-sections after polished up to 1 μm diamond paste to remove the etched layer. The Vickers microhardness, using Zwick-Roell Indentec ZHVμ Micro Hardness testing machine, was measured in the cleaned areas and avoiding the interference of coarser oxide inclusions or other less representative features. At least three indentations were made for each sample with a load of 0.2 Kgf (HV0.2) for 10 s of dwell time. In order to quantify the hardness profiles along a transversal and longitudinal axis, a particular procedure was applied in artefact VNSP262C.

Table 2
Techniques used to characterize metallic artefacts.

Analytical techniques	Number of artefacts analysed	Information expected
Micro-Energy Dispersive X-Ray Fluorescence Spectrometry (micro-EDXRF)	Initial collection : 53 artefacts	Alloy elemental composition.
Optical Microscopy (OM)	53	Identification of different phases, inclusions and the thermomechanical processes applied during artefacts production – the operation chain.
Scanning Electron Microscopy with X-Ray Micro Analysis (SEM-EDS)	2	Determination of main chemical phases present in metal alloy and distribution of the chemicals elements and minerals in the inclusions.
Vickers Microhardness testing (micro-HV)	51	Establishing the actual effectiveness of the thermomechanical processes in the hardness of the artefact.

3.5. Statistical analysis

Statistical analysis was performed using Matlab Version 7.10.0.499 (R2010a) from The Mathworks, Inc (tm). Paired *t*-tests of the hypothesis that two matched samples come from distributions with equal means were performed using the function "*t*-test" from the statistics toolbox. Linear regression analysis was performed by the function "polytool" also from the statistics toolbox. Fisher's exact test was performed using an online tool available at: http://www.graphpad.com/quickcalcs/contingency1.cfm Null hypothesis were rejected at significance levels lower than 5%.

4. Results and discussion

A summary of the elemental composition determined by micro-EDXRF (wt%) and also the results of microstructural characterization and Vickers microhardness measurements of the metallic artefacts are presented in Tables 5–8, according to the established groups of typologies.

Table 3
Quantification limits for micro-EDXRF analyses of copper-based alloys calculated using the standard material Phosphor Bronze 552 and IDLF5 (values in wt%; calculated as 10 × (background)$^{0.5}$/sensitivity (IUPAC, 1978)).

Cu	Sb	Pb	As	Fe	Zn	Ni
0.04	0.50	0.10	0.10	0.05	0.04	0.07

Table 4
Accuracy of the micro-EDXRF analyses of copper-based alloys calculated using the standard material Phosphor Bronze 552 and IDLF5 (values in wt%; average ± standard deviation of 3 independent measurements).

SS552 (wt%)	Cu	Sn	Pb	As	Fe	Zn	Ni
Certified	87.7	9.78	0.63	n.d.	0.10	0.35	0.56
Obtained	88.2 ± 0.4	10.0 ± 0.3	0.56 ± 0.02	n.d.	0.11 ± 0.02	0.41 ± 0.02	0.51 ± 0.02
Accuracy	0.6	2.5	11.1		10.0	17.1	8.9
IDLF5 (wt%)	Cu	Sn	Pb	As	Sb	Zn	Ni
Certified	68.5	19.9	1.42	5.755	2.23	0.94	0.67
Obtained	71.0 ± 0.05	18.9 ± 0.04	1.56 ± 0.03	5.66 ± 0.03	2.12 ± 0.03	0.81 ± 0.02	057 ± 0.02
Accuracy	3.69	5.02	9.86	1.56	4.93	13.8	14.9

4.1. *Alloy composition*

Micro-EDXRF results indicate that the selected artefacts are composed of copper or copper with arsenic (arsenic contents up to 9.13%). As observed in Fig. 3, 23% of the artefacts collection exhibits an arsenic content below the quantification limit (<0.10%) and 37% exhibit an arsenic content that could be considered as an impurity (0.10% < As < 2%). Ultimately, 21 artefacts, representing 40% of the analysed set, present an arsenic content that could be considered an alloy constituent (As > 2%). Iron content is always below the quantification limit (<0.05%) with the exception of two artefacts presenting 0.07% and 0.21% Fe. Other minor elements such as antimony, lead, zinc or nickel were not detected or were under the quantification limit (see Table 3) and, consequently, they were not mentioned in the tables of results.

These results are in accordance with the earlier evidences of copper based metallurgical activities in the Iberian Peninsula where copper and arsenical copper were the only metals used in the manufacture of artefacts (Ruíz Taboada and Montero-Ruíz, 1999).

Emission spectroscopy analyses of 87 copper artefacts from VNSP, conducted under the SAM programme, show that all of them are composed of copper or arsenical copper containing very low concentrations of trace elements (Junghans et al., 1960, 1968, 1974; Soares, 2005): 35% of the artefacts are made of pure copper, 45% of arsenical copper with very low trace element concentration and 20% of arsenical copper with amounts above the quantification limits of antimony, silver and, sometimes, nickel. The arsenic content range from 0.5% to 5% As, and only a dagger presented approximately 9% As. Also, the same analyses show that the artefacts contain a very low amount of iron, less than 0.01% for 98% of the cases and up to 0.2% for the remaining artefacts (Soares, 2005).

Similar results were obtained from the Zambujal settlement concerning the distribution of arsenic and low levels of trace elements. All the artefacts from Zambujal were composed of copper or arsenical copper with very low nickel, bismuth, antimony and silver contents. Later phases of occupation of the settlement were characterized by arsenical coppers with higher amounts of silver, antimony and/or nickel (Müller et al., 2007). In Leceia, another important Chalcolithic settlement located in the same region, not far from Zambujal or VNSP, all the artefacts present an elemental composition similar to those from Zambujal (initial phases of occupation). Artefacts are all made of copper and arsenical copper with low presence of impurities (Müller and Cardoso, 2008).

Table 5
Tools (A + C + F) (P: Present; C: Casting; A: Annealing; F: Forging; FF: Final forging; ↓: Low amount; ↑: High amount).

Tools (A + C + F)	Artefacts	Cu (wt%)	As (wt%)	Fe (wt%)	Phases	Inclusions Cu–O	HV0.2			Operational sequence
							Centre	Blade	Fract.	
A – Awls	VNSP001A	95.4 ± 0.2	4.36 ± 0.23	<0.05	α, As-rich	–	80	–	–	C + (F + A) + FF
	VNSP021A	98.9 ± 0.1	0.90 ± 0.04	<0.05	α	P ↑	40	–	–	C + (F + A)
	VNSP023A	98.7 ± 0.1	0.96 ± 0.08	<0.05	α	P	68	–	–	C + (F + A)
	VNSP029A	96.5 ± 0.2	3.19 ± 0.18	<0.05	α, As-rich	P	59	–	–	C + (F + A)
	VNSP031A	98.3 ± 0.2	1.43 ± 0.20	<0.05	α	P ↑	106	–	–	C + (F + A)
	VNSP038A	98.1 ± 0.2	1.56 ± 0.18	0.07 ± 0.01	α	P	81	–	–	C + (F + A)
	VNSP040A	96.3 ± 0.4	3.39 ± 0.35	0.05 ± 0.01	α	P ↑	60	–	–	C + (F + A) + FF↓
	VNSP047A	99.7 ± 0.1	<0.10	<0.05	α	P ↑	63	–	–	C + (F + A)
	VNSP049A	94.2 ± 0.1	5.59 ± 0.08	<0.05	α, As-rich	–	65	–	–	C + (F + A)
	VNSP097A	93.7 ± 0.1	6.04 ± 0.11	<0.05	α, As-rich	–	86	–	–	C + (F + A) + FF↓
C – Chisels	VNSP132C	94.9 ± 0.4	4.92 ± 0.36	<0.05	α, As-rich	P	53	–	–	C + (F + A)
	VNSP133C	99.5 ± 0.1	0.27 ± 0.04	<0.05	α	P ↑	36	–	–	C + (F + A)
	VNSP134C	99.7 ± 0.1	<0.10	<0.05	α	P ↑	81	–	–	C + (F + A)
	VNSP135C	98.2 ± 0.2	1.53 ± 0.17	<0.05	α	P	42	–	–	C + (F + A)
	VNSP136C	99.7 ± 0.1	<0.10	<0.05	α	P ↑	94	–	–	C + (F + A)
	VNSP137C	99.8 ± 0.1	<0.10	<0.05	α	P ↑	85	–	–	C + (F + A) + FF↓
	VNSP138C	98.7 ± 0.3	1.08 ± 0.28	<0.05	α	P	44	–	–	C + (F + A)
	VNSP139C	98.1 ± 0.1	1.71 ± 0.15	<0.05	α	P	91	115	90	C + (F + A)
	VNSP140C	96.3 ± 0.2	3.43 ± 0.22	<0.05	α	P	80	105	90	C + (F + A) + FF↓
	VNSP141C	97.2 ± 0.1	2.61 ± 0.05	<0.05	α	P	97	123	98	C + (F + A) + FF↓
	VNSP262C	99.8 ± 0.1	<0.10	<0.05	α	P	–[a]	–	–	C + (F + A)
F – Saws	VNSP185F	99.7 ± 0.1	0.10 ± 0.01	<0.05	α	P ↑	53	42	46	C + (F + A)
	VNSP186F	99.7 ± 0.1	<0.10	<0.05	α	P ↑	73	73	73	C + (F + A)
	VNSP187F	99.8 ± 0.1	<0.10	<0.05	α	P ↑	–[b]	–	–	C + (F + A)

[a] Hardness profiles (transversal and longitudinal axis), were determined in artefact VNSP262C.

[b] Vickers microhardness testing was made only in mounted cross-sections (HV0.2, 10 s).

Table 6
Axes (D) (P: Present; C: Casting; A: Annealing; F: Forging; FF: Final forging; ↑: High amount). Vickers microhardness testing was made only in mounted cross-sections (HV0.2, 10 s).

Axes (D)	Artefacts	Cu (%)	As (%)	Fe (%)	Phases	Inclusions Cu–O	HV0.2			Operational sequence
							Centre	Blade	Fract.	
D – Axes	VNSP144D	99.7 ± 0.1	<0.10	0.21 ± 0.02	α	P	44	66	47	C + (F + A)
	VNSP145D	99.8 ± 0.1	<0.10	<0.05	α	P ↑	48	50	49	C + (F + A)
	VNSP146D	97.7 ± 0.1	2.04 ± 0.10	<0.05	α	P	45	47	45	C + (F + A)
	VNSP147D	97.9 ± 0.2	1.85 ± 0.14	<0.05	α	P	65	57	64	C + (F + A)
	VNSP148D	90.6 ± 0.2	9.13 ± 0.23	0.07 ± 0.01	α, As-rich	–	95	95	95	C + (F + A)
	VNSP150D	99.5 ± 0.1	0.24 ± 0.04	<0.05	α	P	45	50	49	C + (F + A)
	VNSP153D	98.6 ± 0.1	1.08 ± 0.13	0.05 ± 0.01	α	P	64	64	65	C + (F + A)
	VNSP154D	98.2 ± 0.3	1.58 ± 0.24	<0.05	α	P	47	46	45	C + (F + A)
	VNSP155D	98.9 ± 0.1	0.79 ± 0.07	<0.05	α	P	42	45	45	C + (F + A)
	VNSP165D	98.4 ± 0.2	1.42 ± 0.24	<0.05	α	P	42	47	46	C + (F + A)
	VNSP178D	99.7 ± 0.1	<0.10	<0.05	α	P ↑	75	–	–	C + (F + A)
	VNSP268D	99.8 ± 0.1	<0.10	<0.05	α	P	41	50	45	C + (F + A)

In this analysed collection from VNSP, the distribution of arsenic content through the groups of typologies shows a tendency for higher levels of this element in the tools/weapons group (Fig. 4).

The question of correlation, in the early metallurgy, between the metal composition and the artefact typology has been discussed by other authors. In the SAM programme (Junghans et al., 1960, 1968, 1974), the study of "Bronze Age Metalwork from the Iberian Peninsula" (Harrison and Craddock, 1981) and in "Proyecto de Arqueometalurgia" (Rovira, 2005) were observed that flat axes and awls tend to be constituted of pure copper, whereas Palmela points and daggers tend to show higher concentrations of arsenic (Müller et al., 2007).

With the artefacts from Zambujal, it was observed that awls and axes present low values of arsenic, while sheet metal fragments, saws, Palmela points and tanged daggers have more frequently higher amounts of arsenic. Long awls from Zambujal are made of copper with more than 2% arsenic (Müller et al., 2007). Also in Leceia settlement, arsenical copper was reserved for long awls, sheet metal objects, Palmela points and tanged daggers (Müller and Cardoso, 2008). Regarding an earlier study of VNSP artefacts, based in the SAM programme, it was argued that weapons (spearheads, arrowheads and daggers) systematically contain higher amounts of arsenic than tools (punches, awls and axes) (Soares, 2005). Therefore it was observed a general tendency for artefacts with thinner shapes, like blades and sheet metal fragments, as well as elongated objects like the long awls, to have higher arsenic content than other tools like axes, chisels and shorter awls.

In the present study, in order to determine if there is an association between the presence or absence of arsenic and the artefact typology, three groups were tested: tools (A + C + F), tools including axes (A + C + D + F) and tools/weapons (E + G). In the first group it was assumed the hypothesis that axes could be used as ingots.

A statistically significant association was found between the tools/weapons and the presence of arsenic (As > 2%) (Fisher exact test $p = 0.0058$ when comparing tools including axes and $p = 0.0131$ when comparing tools excluding axes). Consequently, it can be hypothesized that for the manufacture of this set of tools/weapons there was an intentional selection of an arsenical copper alloy. The correlation found between artefact typology/function and arsenic content point to some degree of control over the selection of the alloys used in VNSP.

4.2. *Microstructural characterization*

Near-equiaxial α-Cu grains with annealing twins (Fig. 5A) and, more rarely, slip bands (Fig. 8B) were the most common microstructural characteristics found. The annealing twins appear after a metal has been mechanically cold worked and softened by posterior heat treatment. Annealing restores the ductility lost during hammering, enabling further deformation. Slip bands appear in the cold work condition without posterior heat treatment.

Therefore, from the microstructural analysis, it can be inferred that the majority of the artefacts from VNSP (73%) were manufactured with forging plus annealing operations (Fig. 6). The operational sequence of forging plus annealing, followed by final forging operation was applied to 23% of the artefacts and only two exemplars of indeterminate typology (VNSP194H and VNSP196H) present as-cast microstructures with some mechanical deformation (possibly incomplete artefacts that were left out before being finished).

The results also point out to an association between the presence of final forging treatment and artefacts presenting higher arsenic content (As > 2%) (Fig. 7). A statistically significant association was found in the tested group, comprising tools and tools/

Table 7
Tools/Weapons (E) (P: Present; C: Casting; A: Annealing; F: Forging; FF: Final forging; ↓: Low amount; ↑: High amount). Vickers microhardness testing was made only in mounted cross-sections (HV0.2, 10 s).

Tools/weapons (E)	Artefacts	Cu (wt%)	As (wt%)	Fe (wt%)	Phases	Inclusions Cu–O	HV0.2			Operational sequence
							Centre	Blade	Fract.	
E – Arrowheads, daggers, knives	VNSP177E	99.8 ± 0.1	<0.10	<0.05	α	P ↑	43	44	46	C + (F + A)
	VNSP180E	94.2 ± 0.4	5.57 ± 0.38	<0.05	α, As-rich	P	63	63	75	C + (F + A) + FF↓
	VNSP181E	97.5 ± 0.2	2.22 ± 0.18	<0.05	α	P	119	119	120	C + (F + A) + FF
	VNSP182E	94.1 ± 0.2	5.66 ± 0.21	<0.05	α	–	90	96	75	C + (F + A)
	VNSP183E	95.8 ± 0.2	3.89 ± 0.08	<0.05	α, As-rich	–	54	55	53	C + (F + A) + FF
	VNSP188E	97.9 ± 0.4	1.79 ± 0.39	<0.05	α, As-rich	P	77	80	78	C + (F + A)
	VNSP189E	95.2 ± 0.4	4.53 ± 0.33	<0.05	α, As-rich	P	155	204	119	C + (F + A) + FF

Table 8
Miscellaneous (B + G + H) (P: Present; C: Casting; A: Annealing; F: Forging; FF: Final forging; ↓: Low amount; ↑: High amount).

Miscellaneous (B + G + H)	Artefacts	Cu (wt%)	As (wt%)	Fe (wt%)	Phases	Inclusions Cu–O	HV0.2			Operational sequence
							Centre	Blade	Fract.	
B – Wires	VNSP123B	99.5 ± 0.1	0.21 ± 0.01	<0.05	α	P ↑	84	–	–	C + (F + A)
	VNSP124B	99.6 ± 0.1	0.19 ± 0.01	<0.05	α	P ↑	91	–	–	C + (F + A)
G – Socket	VNSP190G	98.2 ± 0.4	1.57 ± 0.31	<0.05	α	P	48	–	–	C + (F + A)
H – Indeterm.	VNSP025H	96.4 ± 0.3	3.37 ± 0.24	<0.05	α, As-rich	P	157	–	–	C + (F + A) + FF
Indeterminate	VNSP184H	96.1 ± 0.1	3.85 ± 0.04	<0.05	α, As-rich	P	51	–	–	C + (F + A)
	VNSP191H	94.3 ± 0.2	5.49 ± 0.19	<0.05	α, As-rich	P	61	–	–	C + (F + A) + FF↓
	VNSP192H	96.6 ± 0.4	3.13 ± 0.32	<0.05	α	P	48	–	–	C + (F + A)
	VNSP193H	97.4 ± 0.1	2.32 ± 0.18	<0.05	α, As-rich	P	50	–	–	C + (F + A)
	VNSP194H	99.2 ± 0.1	0.51 ± 0.12	<0.05	α	P	90	–	–	C + F?
	VNSP196H	99.0 ± 0.3	0.86 ± 0.28	<0.05	α	P	–[a]	–	–	C

[a] Vickers microhardness testing was made only in mounted cross-sections (HV0.2, 10 s).

weapons (Fisher exact test $p = 0.0003$). The application of a final forging operation on the manufacturing of artefacts presenting higher arsenic contents, and therefore with a different colouration from pure copper, could be justified in order to obtain a harder alloy. Another hypothesis would be to just apply a finishing operation with the intention of improving the surface aspect after annealing. Examples of analysed artefacts that could support the latter hypothesis are the awls VNSP001A (4.36% As), VNSP040A (3.39% As) and VNSP097A (6.04% As) that were sampled in the opposite end of the pointed tip and present a final cold hammering. Also, the chisels VNSP140C (3.43% As) and VNSP141C (2.61% As), longitudinally sampled, present a final forging treatment while VNSP139C (1.71% As), with lower arsenic content, also longitudinally sampled, did not present any indication of a final cold treatment. These results suggest that arsenic rich alloys would have been recognized and selected for the application of a final forging treatment.

For copper or lower arsenic content artefacts, a common observed feature was the presence of red inclusions (under DF and Pol illumination in OM). These inclusions, identified by SEM-EDS (Fig. 8) as being a Cu–O compound and assigned as cuprous oxide (Cu_2O), are formed due to a eutectic decomposition in Cu–O systems.

This Cu–O eutectic appears as an interdendritic network of oxide inclusions in the α-Cu matrix. The finer and elongated shapes of the above mentioned oxides observed in some of the microstructures are usually a consequence of the thermomechanical treatments.

A common consequence of non-equilibrium solidification in copper-arsenic alloys is the coring of primary α-phase grains. Intense mechanical work elongates these features resulting in what is normally designated as segregation bands, clearly visible after etching (Fig. 9A). In some samples, a blue-grey phase, identified by SEM-EDS (Fig. 10) as the arsenic rich γ phase, was observed along the α-copper grain boundaries (Fig. 9B). As expected, the presence of cuprous oxide inclusions in copper-arsenic alloys is much reduced due to the deoxidising properties of the arsenic (Hook et al., 1991).

These arsenic-rich formations are attributed to an inverse segregation phenomenon (resultant from shrinkage-driven flow of solute enriched liquid towards the outer direction) that occurs during solidification. A concentration of low melting constituents, such as arsenic in copper based alloys, occurs in those regions in which solidification first occurs (Craddock, 1995).

Accordingly to the Cu–As phase diagram (Subramanian and Laughlin, 1988 the α-Cu phase can dissolve up to approximately 8% of arsenic), in equilibrium conditions, before the formation of the arsenic rich phase (As-rich (γ) phase – Cu_3As), but due the relatively fast cooling rates of common casting, this γ phase has been observed in alloys with only 2% As (Northover, 1989) suggesting that there was no concern in homogenizing the alloy.

Earlier studies concerning ancient arsenical coppers also suggest that the annealing was conducted within temperatures of about 300–400 °C (Northover, 1989). This range of temperatures is noticeably lower than the temperature necessary to homogenize this type of alloys (approximately 600–700 °C) in a reasonable time. Moreover, the already segregated microstructures could require an even higher temperature to be homogenized (Budd, 1991).

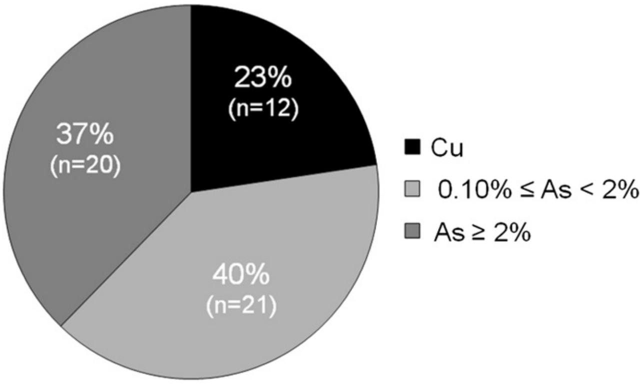

Fig. 3. Distribution of arsenic content in the studied collection of VNSP ($n = 53$).

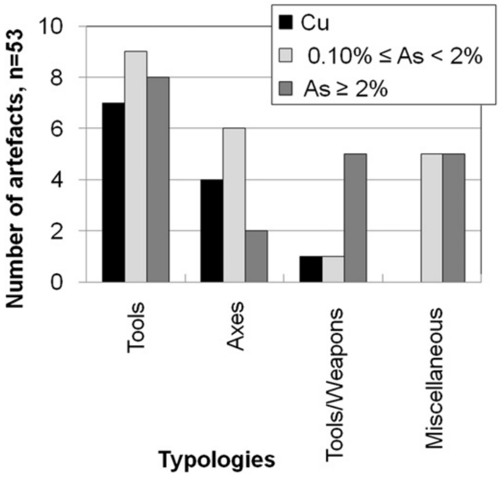

Fig. 4. Distribution of arsenic contents by groups of typologies ($n = 53$).

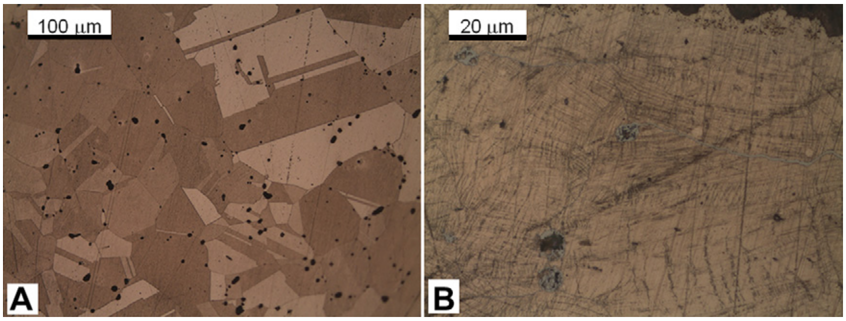

Fig. 5. OM images of VNSP133C (As < 0.10%) revealing annealing twins (A) and VNSP025I (As = 3.37%) revealing slip bands (B), (all BF illumination, etched).

4.3. Vickers micro-hardness measurements

The hardness of metallic objects is mainly determined by the composition of the alloy and the degree of thermomechanical processing. From a microstructural point of view, the observed increase in hardness with increasing arsenic content in the alloy may mainly be due to precipitation of a higher volume fraction of the intermetallic γ (As-rich phase) and the establishment of strain fields in the matrix (Budd and Ottaway, 1995; Northover, 1989). Also, some authors point to an improvement of the mechanical properties of arsenical coppers with a final cold hammering operation after forging plus annealing cycles (Mohen, 1990; Northover, 1989; Rovira, 2004).

When compared to pure copper, arsenical copper (As > 2%) is more ductile and can be more extensively shaped by cold working. If the presence of arsenic in the alloy is lower than 1.5–2%, this concentration is not sufficient to significantly increase the hardness of the metal (Budd and Ottaway, 1995; Northover, 1989). The level of ductility is almost constant until the solid solubility limit of arsenic in copper is reached (~8% As) (Lechtmann, 1996). Above 8% As, the metal could become brittle, although some authors state that brittleness is totally absent until the arsenic level exceeds 10–13% (Budd and Ottaway, 1995).

If subjected to forging and annealing cycles, arsenical copper alloys rapidly increase hardness, especially in the 0–50% reduction in thickness range. When approaching the solid solution solubility limit of arsenic in copper (5–7% As), the alloy continues to allow further work hardening, at least up to 87.5% reduction in thickness (Budd and Ottaway, 1995; Lechtmann, 1996).

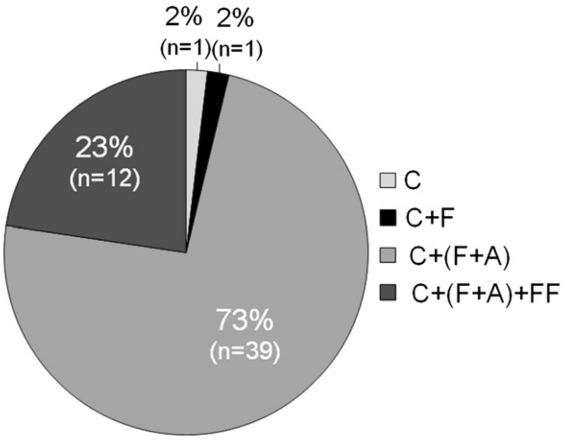

Fig. 6. Distribution of manufactured procedures in the studied collection of VNSP ($n = 53$).

In order to study the effect of the thermomechanical processing on the work hardening condition, microhardness measurements were made in the centre of the 51 mounted cross-sections and when applicable, also near the borders (fracture surfaces and cutting edge). See Fig. 2 and the description concerning the location of sampling in artefacts in the Methodology section. A more complete procedure was made in the chisel VNSP262C, since it was the only large fragment available to obtain microhardness cross-section profiles. Transversal and longitudinal cross-section profiles will be presented ahead.

The results for the microhardness values in the centre of mounted cross-sections are presented in Fig. 11, subdivided by attributed operational chain. A linear regression was performed ($y = 0.83x + 67.9$) and the 95% confidence interval (CI) for the line slope was determined (slope $= 0.83 \pm 4.73$). Although the measures have an apparent trend towards a positive slope, since the 95% confidence intervals included values less than zero, we cannot exclude the hypothesis of no positive correlation using a linear model.

Therefore, even though it should be expected that the increase of the arsenic content could confer hardness to the alloy we did not found any statistically significant association between the arsenic content and the measured hardness. Similar results were obtained when subdividing the analysis by operational sequence, C + (F + A) and C + (F + A) + FF. Also, groups of typologies analysed separately do not indicate any tendencies of the measured hardness even if only considering values above 2% As, where a more significant increase in the hardness of the material is expected (Budd and Ottaway, 1995; Northover, 1989). It must be taken into consideration that some samples were extracted from the respective artefacts in the shaft or in the opposite end of the tip or blade, as previously indicated in the Methodology section. Therefore, it is expected that in some areas (tips and blades) would be applied a more intense mechanical work and a harder final cold hammering

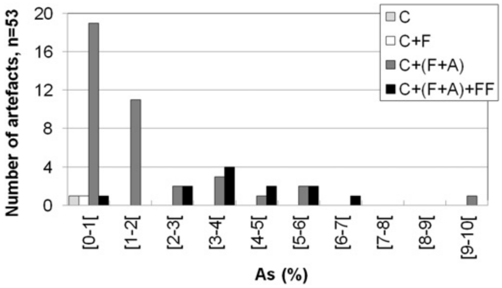

Fig. 7. Distribution of manufacture operation cycles by arsenic contents ($n = 53$).

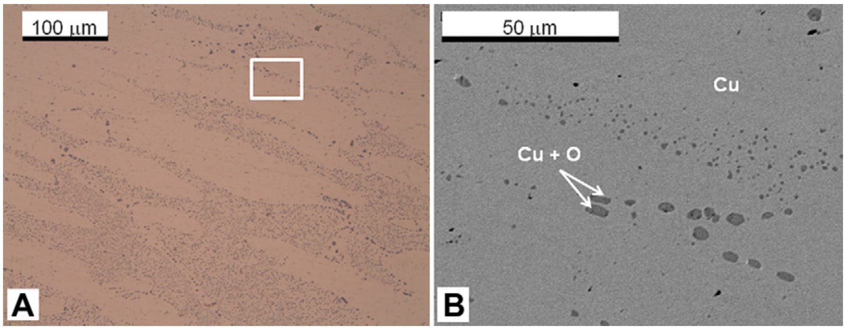

Fig. 8. A: OM image of VNSP268D (As < 0.10%) (BF illumination); B: SEM-BSE image with the region marked on the OM image showing the EDS identification of the α–Cu phase and Cu_2O inclusions (Cu + O).

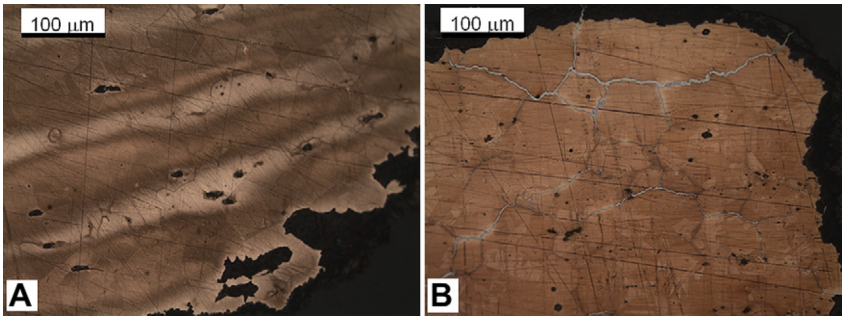

Fig. 9. OM images of VNSP146D (As = 2.04%) revealing the elongation of the segregation bands (A) and VNSP180E revealing the As-rich γ phase following the grain boundaries (B), (all BF illumination, etched).

than in others and, consequently, a higher increase in hardness would be obtained in the final shape. As a result, the different locations of sampling can contribute to the dispersion of observed hardness results.

There are other variables that would affect the material hardness and outweigh the influence of the arsenic content in the alloy. The different thermomechanical processing conditions applied to the artefacts (intensity and number of cycles) will result in microstructural differences among them. The great variability found in structural features, as grain size, inclusion distribution and morphologies, annealing twins and slip bands densities should contribute for the hardness dispersion observed. Also, the presence of intermetallic phases (in this case, arsenic-rich phase (γ) resulting from inverse segregation phenomenon) is an additional factor that could cause embrittlement and difficult the thermomechanical cycles of operation by slowing down the recrystallization rate and the formation of straight grain boundaries (Kienlin et al., 2006).

In order to compare the hardness near the cutting edge, near the opposite border of the cutting edge (named fracture) and the central region for 24 selected artefacts (Fig. 12), a paired *t*-test was performed. The artefacts VNSP186F, VNSP177E and VNSP189E were included in this test, although their sampling corresponded to the shaft area of the blade. However, the exterior edge is thinner than the centre, indicating that some mechanical work was applied in the shaping of this section.

The only statistically significant difference at 5% significance level is in the comparison of hardness between the cutting edge and the centre ($p = 0.037$), which reinforces the conclusion that the cutting edge is harder than the centre. The hardness

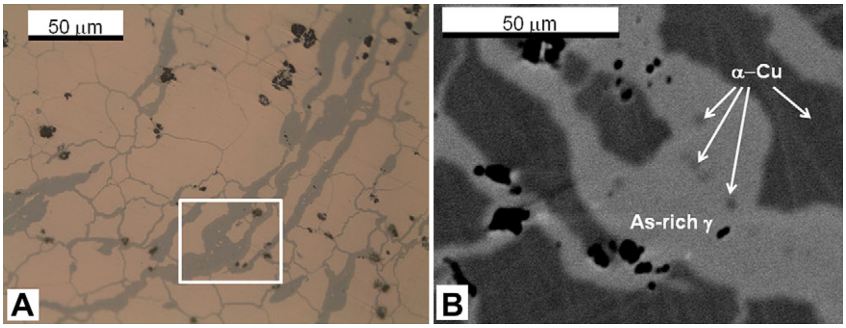

Fig. 10. A: OM image of VNSP148D (As = 9.13%) (BF illumination); B: SEM-BSE image with the region marked on the OM image showing the EDS identification of: As-rich γ phase, α–Cu phase and α–Cu islands.

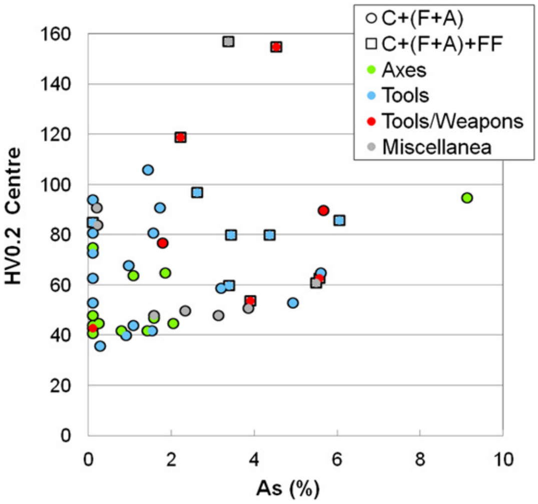

Fig. 11. Micro-HV measurements (HV0.2, 10 s) in function of arsenic content of the artefacts and operational sequence: C + (F + A) and C + (F + A) + FF, subdivided by groups of typologies ($n = 51$).

differences between the fracture and the centre are not statistically significant ($p = 0.457$). In this set of artefacts, it was also observed that 6 of the 9 artefacts that present high arsenic content (As > 2%), also present harder cutting edges. From these 6 artefacts, 4 present a final forging treatment. However it was not possible to have statistical evidence that the increase of hardness due to intensive thermomechanical processing would be more significant in copper-arsenic alloys then in pure copper metal.

These observations suggest that, in the case of copper alloyed with arsenic, the ancient metallurgists may not have been aware of the additional advantage of the hardening effect of these alloys (Kienlin et al., 2006). Although the presence of arsenic should present a visible positive influence in the pouring of the alloy, the cold forging operations seem to have been applied in order to give form to the object, rather than to intentionally make the alloy harder (Budd, 1991). Nevertheless, it is expected that the cutting edges of the artefacts would be harder since more thermomechanical operations were applied in order to shape them, i.e. an increase of hardness in localized areas was achieved. Therefore, the thermomechanical processes applied in the manufacture of an artefact could be intentional in order to increase the hardness in a specific section of an artefact (blade or tip) and obtain a better performance.

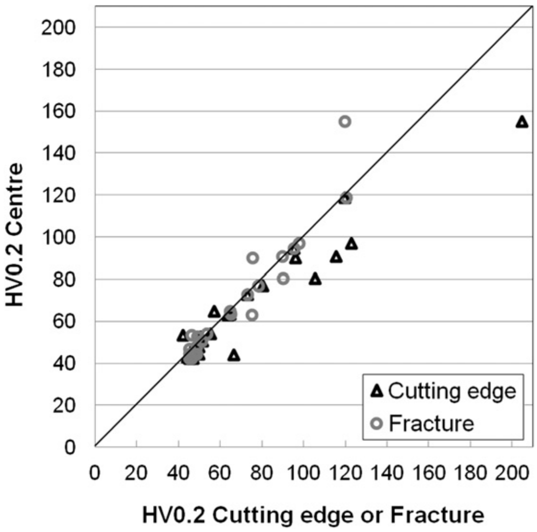

Fig. 12. Comparison of micro-HV measurements (HV0.2, 10 s) between cutting edge and fracture area ($n = 24$).

In the analysed collection, the artefacts VNSP180E (5.57% As; 63 HV0.2) and VNSP183E (3.89% As; 54 HV0.2) are examples of blades that would easily achieved higher hardness values (above 150 HV0.5) with only 25% of thickness reduction (Lechtmann, 1996). Nevertheless, the additional hardness was only 63 and 54 HV0.2, respectively. However it has been previously mentioned that the presence of arsenic-rich phase (γ) could be responsible for an additional difficulty and need of adjustments in the thermomechanical procedures (Kienlin et al., 2006). Despite the possible visual identification of arsenical copper alloys, evidence suggests that the potential hardness was not exploited.

The tendency for a harder cutting edge was also observed in the chisel VNSP262C. As referred above, the artefact VNSP262C was longitudinally cut and transversal and longitudinal microhardness profiles were measured along the cross section: 45 measurements in the longitudinal direction and 15 measurements in the transversal direction (Fig. 13). This chisel is constituted by nearly pure copper (As < 0.10%) and the manufacture procedure consisted of one or more cycles of forging and annealing. The microstructure also present elongated grains near the cutting edge of the chisel and near the borders, compared with the centre of the artefact, indicating the application of more intense thermomechanical processing in these regions.

The measurement data and the profile obtained for each case is presented in Fig. 14.

To evaluate if the longitudinal decrease in hardness observed in Fig. 14 was statistically significant, a linear regression model was calculated, assuming that all the measurements were evenly spaced. It yielded the following coefficients: slope $= -0.322 \pm 0.106$ for 95% confidence interval and y-axis intercept $= 93.637$. Since the 95% confidence interval for the slope does not include the value zero, the observed decrease of hardness from the blade to the interior of the artefact was statistically significant at 95% confidence. This means that the thermomechanical operations applied in the cutting edge of the chisel imprinted more hardness. The transversal profile also seems to indicate increasing hardness close to borders (see Fig. 14) but the low number of measures does not allow a statistical analysis to confirm this tendency.

Consequently, the microhardness measurements show that the application of more intensive thermomechanical processing on the cutting edge, most likely intentional and also as consequence of

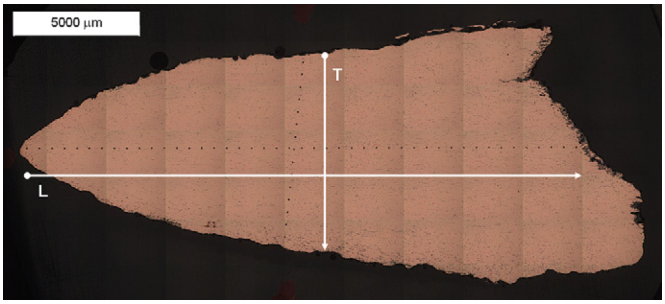

Fig. 13. View of the orientation of the cut made in the chisel VNSP262C. Micro-HV (HV0.2, 10 s) applied in two directions (arrows).

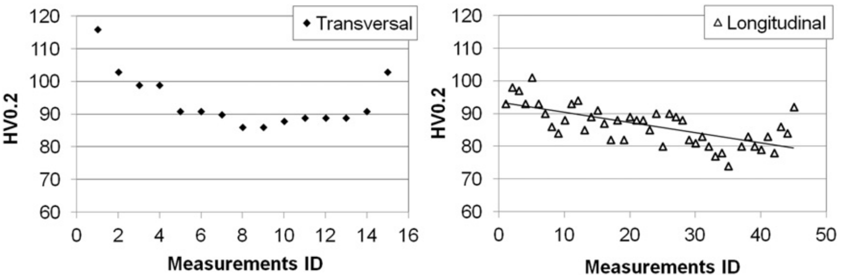

Fig. 14. Micro-HV measurements (HV0.2, 10 s) in longitudinal and transversal profile of VNSP262C.

shaping it, led to a greater hardness in this region of the artefact, in spite of the arsenic content.

5. Conclusions

The analysed collection of artefacts from VNSP is consistent with the overall picture of Chalcolithic Central Portuguese production of copper and arsenical copper. The large quantity of artefact fragments recovered in this settlement (some with signs of sectioning) suggests the existence of remelting and recycling operations and could be a cause for the variable concentrations on this element in the studied collection. Another cause, as referred before, can be the metallurgical processes used to obtain arsenical copper alloys, which could also have an important role in the variability of the arsenic content.

On the other hand, it must be taken into consideration that functional artefacts would be more frequently recycled resulting in a reduction of arsenic content since, at each melting of an arsenical copper alloy, there are losses by oxidation of the arsenic and evaporation of As_2O_3 (Mckerrell and Tylecote, 1972). More prestigious and less used artefacts would present higher arsenic contents since they would suffer less or none recycling operations (cf. Rovira, 2005).

The statistically significant association found between copper alloys with arsenic content over 2% and artefacts classified as tools/weapons point out for a deliberate selection of the alloy to the manufacture of certain typologies. In case artefacts included in the group of tools/weapons were considered prestigious items that could have influenced the choice of a different colour for these artefacts.

Although the majority of the analysed artefacts have been classified as tools, this does not mean that they would be all functional. Some could have a ceremonial function or to be also considered as prestige items explaining why some tools present high arsenic content (and would be less recycled).

The manufacture procedure more frequently used consisted of one or more cycles of forging plus annealing of the cast alloy (73% of the cases). The operational sequence of annealing followed by final forging procedure was applied in 23% of the cases. It was also observed an association between the presence of final forging treatment and artefacts presenting higher arsenic contents.

Although it could be expected that the presence of higher levels of arsenic could confer hardness to the alloy, it was not found any statistically significant association between the arsenic content and the measured hardness. Also, artefacts submitted to a final forging step were not consistently harder with increase of arsenic content. The variable number and intensity of thermomechanical cycles applied, grain size or presence of arsenic intermetallics are factors that influence the hardness of the material.

Therefore, the selection of arsenical copper alloys was possibly based in the observation of a different colouration from pure copper, considered more suitable for prestige or ceremonial artefacts since it was observed that potential hardness increase of arsenical copper alloys was not fully exploited and possibly not acknowledged. The final forging operation could be aimed just to obtain a more appellative surface finishing after the annealing heat treatment in those prestigious objects.

The presence of red inclusions (under DF and Pol illumination), when the alloy has a lower or inexistent arsenic content, was recognized by SEM-EDS as being the eutectic cuprous oxide (Cu_2O). It was also observed in Cu–As alloys a reduction of this cuprous oxide formation (due to the high oxygen affinity of the arsenic), and in some cases, a presence of a grey blue phase, As-rich γ phase, in the intergranular regions. These arsenic rich phase is due to inverse segregation and show no evidence of achieving chemical homogeneity during the artefact manufacturing which means that the casting operation and the subsequent cycles of thermomechanical treatments were not sufficient for the dissolution of this arsenic rich phase.

In spite of the indication of some degree of control over the identification and selection of the alloys used in VNSP it was observed that the ancient metallurgists were not completely aware of the hardening ability of alloys richer in arsenic. The thermomechanical operations applied with the intention of shaping and perhaps also producing harder cutting edges, during the manufacture of the artefact, were most likely independent of the arsenic content.

Therefore, the results of this study suggest that colour was probably the principal property determining the selection of the arsenical alloys by prehistoric metallurgists rather than their mechanical properties.

Acknowledgements

This research work has been financed by the Portuguese Science Foundation (FCT) through the EarlyMetal project (PTDC/HIS-ARQ/110442/2008) and the PhD Grant SFRH/BD/78107/2011 (FP). The financial support of CENIMAT/I3N through the Strategic Project-LA25-2011-2012 (PEst-C/CTM/LA0025/2011) is also acknowledged. Authors acknowledged the Museu Arqueológico do Carmo/Associação dos Arqueólogos Portugueses for providing the materials for study and to João Carriço for the contribution in the statistical analysis. We would like to thank the editor, Prof. Dr. Thilo Rehren and all the reviewers for their valuable comments in the earlier version of this paper.

References

Arnaud, J.M., Fernandes, C.V. (Eds.), 2005. Construindo a Memória: As Colecções do Museu Arqueológico do Carmo. Associação dos Arqueólogos Portugueses, Lisboa.

Budd, P., 1991. Eneolithic arsenical copper: heat treatment and the metallographic interpretation of manufacturing processes. In: Pernika, E., Wagner, G.A. (Eds.), Proceedings of Archaeometry, vol. 90. Birkhäuser, Basel, pp. 35–44.

Budd, P., Ottaway, B.S., 1995. Eneolithic arsenical copper: chance or choice? In: Jovanovic, B. (Ed.), International Symposium, Ancient Mining and Metallurgy in Southeast Europe. Archaeological Institute, Belgrade, pp. 95–102.

Cardoso, J.L., Guerra, M.F., 1997/1998. Análises químicas não destrutivas do espólio metálico do povoado pré-histórico de Leceia. Estudos Arqueológicos de Oeiras 7, 61–87.

Cardoso, J.L., Soares, A.M.M., 1996. Contribution d'une Série de Datations 14C, provenant du Site de Leceia (Oeiras, Portugal), à le Chronologie Absolue du Néolithique et du Chalcolithique de l'Estremadura Portugaise. Actes du Colloque de Périgeux 1995, Supplément à la Revue d'Archéométrie, 45–50.

Carmé, Costa, Manuel, E., Bonilla, Marta D.Z., García Sanjuan, Leonardo, Wheatly, David W., 2010. The Copper Age settlement of Valencina de la Concepción (Seville, Spain): demography, metallurgy and spatial organization. Trabajos de Prehistoria 67 (1), 85–117.

Craddock, P.T., 1995. Early Metal Mining and Production. The University Press, Cambridge. 284–292.

Delibes, G., Montero, I. (Eds.), 1999. Las primeras etapas metalúrgicas en la Peninsula Iberica II. Estudios regionales. Instituto Ortega y Gasset, Madrid.

Ferreira, O. da Veiga, 1961. Acerca da presença de arsénio em instrumentos encontrados em Portugal. Boletim de Minas 12, 1–5.

Harrison, R.J., Craddock, P.T., 1981. A study of the Bronze Age metalwork from the Iberian Peninsula in the British Museum. Ampurias 43, 113–179.

Hauptmann, A., Rehren, Th., Schmitt-Strecker, S., 2003. Early Bronze Age copper metallurgy at Shahr-i Sokhta (Iran). In: Stoellner, T., Koerlin, G., Steffens, G., Cierny, J. (Eds.), Man and Mining. Mensch und Bergau. Studies in Honour of Gerd Weisgerber, vol. 16. Der Anchnitt Beith, Bochum, pp. 197–213.

Hook, D.R., Freestone, I.C., Meeks, N.D., Craddock, P.T., Onorato, A.M., 1991. The early production of copper-alloys in south-east Spain. In: Pernicka, E., Wagner, G.A. (Eds.), Proceedings of Archaeometry, vol. 90. Birkhäuser, Basel, pp. 65–76.

IUPAC, 1978. Spectrochimica Acta B 33, 242.

Junghans, S., Sangmeister, E., Schröder, M., 1960. Metallanalysen kupferzeitlicher und frühbronzezeitlicher Bondenfunde aus Europa. Studien zu den Anfängen der Metallurgie 1. Gebrüder Mann Verlag, Berlin.

Junghans, S., Sangmeister, E., Schröder, M., 1968. Kupfer und Bronze in der frühen Metallzeit Europas. Studien zu den Anfängen der Metallurgie 2(1–3). Gebrüder Mann Verlag, Berlin.

Junghans, S., Sangmeister, E., Schröder, M., 1974. Kupfer und Bronze in der frühen Metallzeit Europas. Studien zu den Anfängen der Metallurgie 2(4). Gebrüder Mann Verlag, Berlin.

Kienlin, T.L., Bischoff, E., Opielka, H., 2006. Copper and bronze during the Eneolithic and early Bronze Age: a metallographic examination of axes from the Northalpine region. Archaeometry 48, 453–468.

Lechtmann, H., 1996. Arsenic bronze: dirty copper or chosen alloy? A view from the Americas. Journal of Field Archaeology 23, 477–514.

Lechtmann, H., Klein, S., 1999. The production of copper-arsenic alloys (Arsenic bronze) by cosmelting: modern experiment, ancient practice. Journal of Archaeological Science 26, 497–526.

Mckerrell, H., Tylecote, R.F., 1972. The working of copper-arsenic alloys in the Early Bronze Age and the effect of the determination of provenance. Proceedings of the Prehistoric Society 38, 209–218.

Mohen, J.P., 1990. Métallurgie préhistorique. Masson, Paris. 97–101.

Müller, R., Cardoso, J.L., 2008. The origin and use of copper at the Chalcolithic fortification of Leceia, Portugal. Madrider Mitteilungen 49, 64–93.

Müller, R., Pernicka, E., 2009. Chemical analyses in archaeometallurgy: a view on the Iberian Peninsula. In: Kienlin, T.L., Roberts, B. (Eds.), Metals and Society - Studies in Honour of Barbara S. Ottaway. Universitätsforschungen zur prähistorischen Archäologie, vol. 169. Verlag Dr. Rudolf Habelt GMBH, Bonn, pp. 296–306.

Müller, R., Soares, A.M., 2008. Traces of early copper prodution at the Chalcolithic fortification of Vila Nova de São Pedro (Azambuja, Portugal). Madrider Mitteilungen 49, 94–114.

Müller, R., Rehren, Th., Rovira, S., 2004. Almizaraque and the early copper metallurgy of Southeast Spain. New data. Madrider Mitteilungen 45, 33–56.

Müller, R., Goldenberg, G., Kunst, M., Bartelheim, M., Pernicka, E., 2007. Zambujal and the beginnings of metallurgy in southern Portugal. In: La Niece, S., Hook, D., Craddock, P.T. (Eds.), In Metals and Mines. Studies in Archaeometallurgy. Archetype, London, p. 15.

Northover, J.P., 1989. Properties and use of arsenic-copper alloys. In: Hauptmann, A., Pernicka, E., Wagner, G.A. (Eds.), Old World Archaeometallurgy. Der Anschnitt, Beiheft 7. Deutsches Bergbaumuseum, Bochum, pp. 111–118.

Paço, Afonso do, 1955. Castro de Vila Nova de S. Pedro, VII – Considerações sobre o problema da Metalurgia. In: Zephyrus. VI, Salamanca, pp. 27–40.

Paço, Afonso do, 1964. Castro de Vila Nova de S. Pedro, XVI – Metalurgia e Análises Espectrográficas. In: Anais da Academia Portuguesa de História. II Série, vol. 14, Lisboa, pp. 159–165.

Paço, Afonso do, Arthur, M.L.C., 1952. Castro de Vila Nova de S. Pedro, II – Alguns Objectos Metálicos. In: Zephyrus. III, Salamanca, pp. 31–39.

Rovira, S., 2004. Tecnología metalúrgica y cambio cultural en la Prehistoria de la Península Ibérica. Norba. Revista de Historia 17, 9–40.

Rovira, S., 2005. Tecnología metalúrgica Campaniforme en la Península Ibérica. Coladas, moldeado y tratamientos postfundición. In: Rojo-Guerra, M.A., Garrido-Pena, R., García-Martínez de Lagrán, I. (Eds.), El Campaniforme en la Península Ibérica y su Contexto Europeo. Junta de Castilla y León, Valladolid, pp. 495–521.

Rovira, S., Gómez, P., 2003. Estudios Metalográficos. Las primeras etapas metalúrgicas en la Península Ibérica. Instituto Ortega y Gasset, Madrid.

Rovira, S., Montero-Ruiz, I., Consuerga, S., 1997. Las primeras etapas metalúrgicas en la Península Ibérica, I. Análisis de materiales. Instituto Ortega y Gasset, Madrid.

Ruíz Taboada, Arturo, Montero-Ruíz, I., 1999. The oldest metallurgy in western Europe. Antiquity 73 (282), 897–902.

Sangmeister, E., 1995. Zambujal. Kupferfunde aus den Grabungen 1964 bis 1973. In: Sangmeister, E., Jiménez Gómes, M. (Eds.), Los Amuleto de las Campaños 1964 hasta 1973. Madrider Beiträge 5. Zabern, Mainz, pp. 1–153.

Soares, A.M.M., 2005. A metalurgia de Vila Nova de São Pedro. Algumas reflexões. In: Arnaud, J.M., Fernandes, C.V. (Eds.), Construindo a memória. As colecções do Museu Arqueológico do Carmo. Associação dos Arqueólogos Portugueses, Lisboa, pp. 179–188.

Soares, A.M.M., Cabral, J.M.P., 1993. Cronologia absoluta para o Calcolítico da Estremadura e do Sul de Portugal. In: 1° Congresso de Arqueologia Peninsular, Actas dos Trabalhos de Antropologia e Etnologia, XXXIII (3–4), Porto, pp. 217-235.

Soares, A.M.M., Araújo, M.F., Alves, L., Ferraz, M.T., 1996. Vestígios metalúrgicos em contextos Calcolíticos e da Idade do Bronze no Sul de Portugal. In: Miscellanea em Homenagem ao Professor Bairrão Oleiro. Edições Colibri, Lisboa, pp. 553–579.

Subramanian, P.R., Laughlin, D.E., 1988. The As-Cu (arsenic-copper) system. Bulletin of Alloy Phase Diagrams 9 (5), 605–617.