Materials and Manufacturing Processes

ISSN: 1042-6914 (Print) 1532-2475 (Online) Journal homepage: http://www.tandfonline.com/loi/lmmp20

Manufacture of copper weapons and tools from the chalcolithic settlement of São Pedro (Portugal)

P. Valério, R. Orestes Vidigal, M. F. Araújo, A. M. M. Soares, R. J. C. Silva & R. Mataloto

To cite this article: P. Valério, R. Orestes Vidigal, M. F. Araújo, A. M. M. Soares, R. J. C. Silva & R. Mataloto (2017) Manufacture of copper weapons and tools from the chalcolithic settlement of São Pedro (Portugal), Materials and Manufacturing Processes, 32:7-8, 775-780, DOI: 10.1080/10426914.2016.1198030

To link to this article: http://dx.doi.org/10.1080/10426914.2016.1198030

Accepted author version posted online: 22 Jun 2016.
Published online: 22 Jun 2016.

MATERIALS AND MANUFACTURING PROCESSES
2017, VOL. 32, NOS. 7–8, 775–780
http://dx.doi.org/10.1080/10426914.2016.1198030

Manufacture of copper weapons and tools from the chalcolithic settlement of São Pedro (Portugal)

P. Valério[a], R. Orestes Vidigal[a], M. F. Araújo[a], A. M. M. Soares[a], R. J. C. Silva[b], and R. Mataloto[c]

[a]Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, Bobadela LRS, Portugal; [b]Department of Materials Science, Faculty of Science and Technology, Universidade NOVA de Lisboa, Caparica, Portugal; [c]Município de Redondo, Praça da República, Redondo, Portugal

ABSTRACT

A collection of 30 copper-based artefacts recovered during archeological excavations at the São Pedro settlement (Redondo, Portugal) was characterized by optical microscopy and Vickers microhardness testing. The radiocarbon dating of bone samples and the existence of Bell Beaker ceramics establish a chronology of c. 2700–2000 BC for tools and weapons made of copper with varying arsenic contents. The manufacture included one or more cycles of forging and annealing, while final work hardening was uncommon. The collection shows a wide range of hardness (52–142 HV0.2) without any correlation with typology or arsenic content, suggesting unawareness of the hardening potential of this alloying element. Technological features of São Pedro artefacts were compared with those of coeval metallurgies from neighboring regions (Portuguese Estremadura and Southern Andalusia) revealing common and distinctive characteristics that help to understand the use of arsenical copper alloys among communities of the third millennium BC.

ARTICLE HISTORY
Received 25 February 2016
Accepted 26 May 2016

KEYWORDS
Alloys; archaeology; arsenic; chalcolithic; copper; hardness; microstructure; Portugal

Introduction

The knowledge of early metallurgical development in the Iberian Peninsula has many open issues because of the lack of reliable archaeological contexts and archeometallurgical research. The artefacts made of copper with varying arsenic contents and with simple typologies found in the Chalcolithic settlements of São Pedro [1], San Blas [2], and La Pijotilla [3], in the Ossa Morena Zone (OMZ, Fig. 1), represent an exception. It is generally accepted that Chalcolithic arsenical copper (i.e., copper with more than 2 wt% arsenic) is the natural result of smelting mixed copper ores [4]. Nevertheless, certain typologies, such as arrowheads, daggers, knives, and long awls from settlements in the OMZ (São Pedro) and Portuguese Estremadura (Zambujal [5], Leceia [6], and Vila Nova de São Pedro [7]), show higher arsenic contents. This fact suggests the selection of raw materials during the third millennium BC.

A higher amount of arsenic produces a superior hardness, especially in strain hardened metal [8]. Consequently, the comparison of composition, manufacture, and hardness of different typologies can provide important answers about the significance of arsenical copper alloys in prehistoric societies. Chalcolithic arsenical coppers from Southern Andalusia and Portuguese Estremadura do not show an improved hardness, suggesting that ancient communities were unaware of the mechanical superiority of high-arsenical copper and, in some cases, that the feature pursued by the metalworkers was the silvery color of the alloy [7, 9]. In Portuguese Estremadura, the Pb isotopic composition of artefacts [5, 6] and the petrographic analysis of amphibolite tools [10] indicate that raw materials came from the OMZ. In Southern Andalusia, the Pb isotope ratios of copper-based metals from Cabezo Juré suggest the smelting of ores from the Iberian Pyrite Belt [11]. Moreover, the Pb isotope ratios of metals from settlements such as La Pijotilla, located in the OMZ, point to local sources and the Iberian Pyrite Belt [3]. Hence, those neighboring regions clearly had close contacts, and probably share not only raw materials but also metallurgical knowledge.

This study presents the microstructural characterization of copper-based artefacts from the settlement of São Pedro (Redondo, Southern Portugal), located in the OMZ copper-rich district. It was recently established that nearly half of the collection is composed by arsenical copper alloys [1], but the post-casting operations of local artefacts are mostly unknown. Optical microscopy observations establish the distinctive features of processing operations (casting, forging, annealing, etc.), while Vickers hardness testing identifies any attempts to harden weapons and tools. The results are compared with the Chalcolithic metallurgical technology in Portuguese Estremadura and Southern Andalusia to appraise the true role of arsenical copper alloy in the southwestern end of the Iberian Peninsula during the third millennium BC.

Materials and Methods

Archeological excavations carried out in 2004–2009 at the settlement of São Pedro recovered metallic artefacts from four occupation phases from the second quarter of the third

CONTACT P. Valério, pvalerio@ctn.tecnico.ulisboa.pt Centro de Ciências e Tecnologias Nucleares (C2TN), Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear, Estrada Nacional 10 (km 139.7), Bobadela LRS 2695-066, Portugal.
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lmmp.

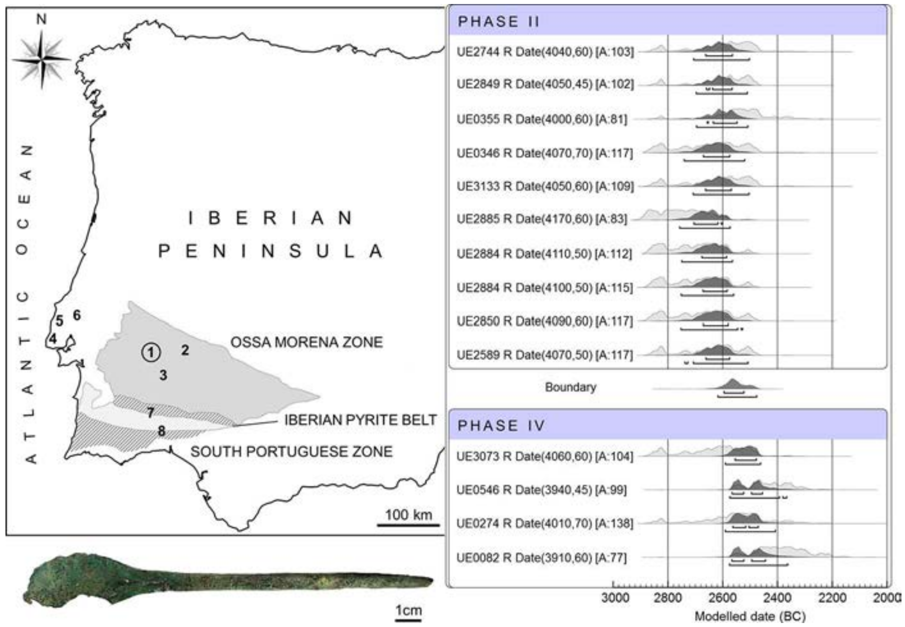

Figure 1. The location of relevant archaeological sites and geologic units in Iberian Peninsula (1 – São Pedro; 2 – La Pijotilla; 3 – San Blas; 4 - Leceia; 5 – Zambujal; 6 – Vila Nova de São Pedro; 7 – La Junta and 8 – Cabezo Juré), a photo of the spatula (SP58) with uncommon shape and calibrated radiocarbon dates of stratigraphic units at São Pedro settlement (A is the agreement index, A_{model} = 103; IntCal13 calibration curve [13] and OxCal program [14, 15]).

millennium BC (Phase II) to the Beaker Period (Phase V) [12]. Phase I contexts did not show traces of metallurgy. Radiocarbon dating of bone samples (Phases II and IV) attempted to discriminate the settlement chronology. Phase III occurred in a short period of time between the destruction of Phase II structures and the building of Phase IV structures. The calibration of radiocarbon dates was made with the IntCal13 calibration curve [13] and an Oxcal Bayesian modeling [14, 15]. The radiocarbon dataset established a long occupation in the second (Phase II) and third quarter (Phase IV) of the third millennium BC (Fig. 1). The final occupation of the settlement (Phase V) could not be radiocarbon dated, but the existing stratigraphy and the presence of Bell Beaker ceramics ascribes it to the last centuries of the third millennium BC.

Metallic artefacts include mostly tools and weapons, in addition to some fragments of unknown function. Weapons comprise arrowheads and daggers. One of the daggers has a rivet hole that ascribes it to the end of the third millennium BC (earlier daggers commonly have a tanged hilt). Tools include awls, chisels, spatulas, a needle, and a saw. The uncommon shape of the spatula SP58 (Fig. 1) has a possible parallel in the Chalcolithic settlement of Zambujal [16]. The scarcity or absence of copper ornaments in Chalcolithic contexts, such as São Pedro, suggests that this material did not possess a prestige value, and ornamental artefacts in those communities were made of gold or non-metallic materials [17].

The preparation for analytical processes involved the cleaning and polishing of a small area with about 3–5 mm diameter. In the case of some incomplete artefacts, a small cross-section (~1–3 mm long) was cut and mounted in epoxy resin. The metallic surface was polished with silicon carbide abrasive papers (1000, 2500, and 4000 grit sizes) and finished with diamond pastes (3 and 1 μm). Microstructural observations were made with a Leica DMI 5000 M optical microscope having bright field, dark field, and polarized light illumination modes. An aqueous ferric chloride solution was used for etching. Vickers microhardness testing of mounted samples involved a Zwick-Roell Indentec equipment with 0.20 kgf load during 10 s. The average hardness comprises at least three indentations with a relative standard deviation lower than 10%.

Results and Discussion

As a preliminary note, it should be mentioned that Phase II artefacts tend to have lower arsenic contents than later ones: Phase II has 1 arsenical copper out of 6 (~17% frequency), while Phases III to V have 8 out of 14 (54%). However, the observation of a tendency to an increased occurrence of arsenical copper alloys in the last stage of the third millennium BC is based on a limited number of examples. Moreover, no significant differences were observed in the microstructural features of artefacts from different phases, and hence the collection is considered as a whole in the following discussion on the evidence of casting conditions and post-casting operations of Chalcolithic artefacts from São Pedro (Table 1).

It was established that most artefacts have copper oxide inclusions dispersed in the α-Cu matrix (Fig. 2). Cuprous oxide inclusions occur by reaction of molten copper with oxygen, appearing by eutectic decomposition during solidification. Higher oxygen contents dissolved in the molten bath form an interdendritic network around the primary solid phase, while minor amounts occur as more or less rounded globules. SEM-EDS analyses of prehistoric arsenical coppers have shown that these inclusions are Cu-As oxides of variable composition [18]. In our collection, the few artefacts without oxide inclusions are of arsenical copper (SP61, SP68, SP55, SP67, SP57, and SP58 showing 2.46–4.92 wt% As). Arsenic commonly acts as deoxidizer by retaining dissolved oxygen, which is then removed as As_2O_3 fumes. However, even in artefacts

Table 1. Microstructural features of São Pedro artefacts.

Type	Artefact	Reference	Phase	As	Inclusions	Segregation	Phases	Grain size (μm)	Post-casting	HV0.2
Weapons	Arrowhead	SP61	–	3.65	–	P	α	20–60	(F + A) + FF	–
	Arrowhead	SP68	–	4.92	–	E	α and γ	60–100	(F + A)↑	142
	Dagger	SP05	V	<0.10	Oxides	–	α	20–60	(F + A)	105
	Dagger	SP09	III	2.89	Oxides	P	α	20–60	(F + A)	104
	Dagger	SP15	–	1.22	Oxides↑	E	α	<20	(F + A)↑	140
	Dagger	SP55	IV	3.15	–	P	α	60–100	(F + A) + FF↑	–
	Dagger	SP56	IV	3.86	Oxides	E	α and γ	60–100	(F + A)↑	98
	Dagger	SP67	–	3.45	–	–	α and γ	60–100	(F + A)	–
Tools	Awl	SP17	IV/V	3.54	Oxides↑	–	α	60–100	(F + A)	86
	Awl	SP22	II	<0.10	Oxides↑	–	α	60–100	(F + A)	–
	Awl	SP23	–	4.41	Oxides	E	α	20–60	(F + A)↑	–
	Awl	SP57	IV	2.46	–	P	α	<20	(F + A)	59
	Awl	SP62	–	3.62	Oxides	E	α	20–60	(F + A)↑	–
	Awl	SP64	III/IV	1.27	Oxides↑	–	α	60–100	(F + A)	97
	Awl	SP66	IV	1.40	Oxides↑	–	α	60–100	(F + A)	85
	Awl	SP69	–	2.23	Oxides	E	α	<20	(F + A)↑	–
	Awl	SP71	IV	0.62	Oxides	P	α	<20	(F + A)	126
	Awl	SP72	IV	5.08	Oxides	P	α and γ	<20	(F + A)	120
	Chisel	SP06	–	1.48	Oxides↑	P	α	<20	(F + A)	107
	Chisel	SP20	II	3.84	Oxides↑	P	α	60–100	(F + A)	52
	Chisel	SP60	V	<0.10	Oxides↑	–	α	20–60	(F + A)	–
	Chisel	SP70	II	0.84	Oxides↑	P	α	20–60	(F + A)	97
	Needle	SP07	II	0.96	Oxides↑	–	α	20–60	(F + A)	99
	Saw	SP59	–	2.89	Oxides	P	α and γ	20–60	(F + A)	–
	Spatula	SP58	III	4.38	–	–	α	60–100	(F + A) + FF	–
	Spatula	SP63	V	2.37	Oxides	E	α	20–60	(F + A)↑	–
Other	Plaque	SP14	–	<0.10	Oxides	–	α	60–100	(F + A)	82
	Fragment	SP02	II	1.87	Oxides	P	α	20–60	(F + A)	126
	Fragment	SP13	II	1.54	Oxides	P	α	20–60	(F + A)	86
	Rod	SP74	III/IV	<0.10	Oxides↑	–	α	60–100	(F + A)	86

Note: Arsenic in wt% [1]; ↑, high amount; P, present; E, elongated; F + A, forging plus annealing; FF, final forging; oxides correspond to Cu_2O for "pure" copper and Cu–As–O for remaining artefacts.

with significant arsenic contents, such as the chisel SP20 (3.84 wt% As), a high amount of oxide inclusions were found, indicating the use of open mold casting and/or impure copper with higher oxygen content. This was also observed in other primitive metallurgical traditions, and was interpreted as proof of limited control over gas absorption during melting and casting processes [19]. For instance, covering the crucible with a charcoal layer would promote a less oxidizing atmosphere and minimize the oxygen uptake. The use of closed molds has the same effect, and initially it was even suggested that the presence of oxide inclusions was an indication of casting in open molds [20].

When considering the primitive casting conditions of these arsenical coppers, it is not surprising to find that most artefacts show segregation bands (Table 1). The copper–arsenic system is prone to segregation by uncontrolled cooling conditions (see the high negative slope of solidus line [21]), so relics of dendritic segregation can be observed in copper with very low arsenic contents (0.62–0.84 wt%, Table 1). Furthermore, sometimes the segregation bands are heavily elongated, indicating a high post-casting deformation (Fig. 3).

A further feature is the existence of an As-rich (blue-gray) phase in artefacts with arsenic contents well below the solubility limit (in equilibrium conditions the α-Cu phase can dissolve around 8 wt% As [21]). In our set, the As-rich phase was observed in copper with 2.89 wt% As (SP59, Table 1), which attests fast cooling rates in open molds made of clay or stone (e.g., sandstone and steatite). The As-rich phase was found in intergranular regions of some artefacts, as in other prehistoric examples, where it was identified as γ phase (Cu_3As) [7, 18]. Recently, it was shown that part of the intergranular Cu_3As phase in prehistoric arsenical copper alloys occurs from long-term solid solution precipitation at ambient temperatures in the course of several millennia [22].

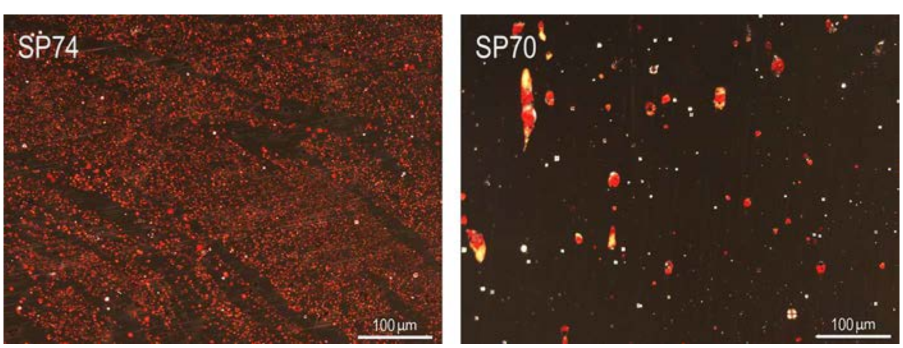

Figure 2. Optical microscopy images of copper rod SP74 and arsenical copper chisel SP70 (non-etched samples; polarised light; reddish inclusions are oxides).

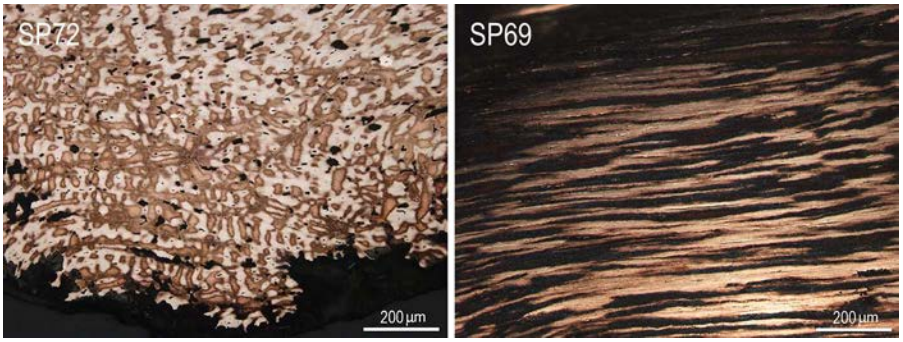

Figure 3. Optical microscopy images of arsenical copper awls SP72 and SP69 (etched samples; bright field illumination; lighter areas have higher arsenic content).

Concerning the microstructural features related with the post-casting manufacture, São Pedro artefacts show deformed equiaxial grains with annealing twins, indicating forging followed by annealing (Fig. 4). Studies of Chalcolithic artefacts from the Iberian Peninsula showed different post-casting setups, namely cold forging (F), annealing (A), cold forging followed by annealing (F+A), annealing followed by forging (A+F), and cold forging followed by annealing and a final forging (F+A+FF) [23]. Artefacts from São Pedro have different grain sizes indicating distinct processing conditions, that is, the number of thermomechanical cycles, amount of deformation, and annealing temperature and time. Several thermomechanical cycles might be used to achieve the required shape because annealing softens the metal avoiding fracture by additional plastic deformation. This is the case of artefacts with heavily elongated segregation bands. According to Northover [24], the recrystallization can be achieved in 30 min at 300–400°C. This setup is not sufficient to fully homogenize the alloy (homogenization requires 600–700°C for the same period of time) and this explains the common presence of segregation bands in prehistoric arsenical copper.

Annealing was applied to all artefacts from São Pedro, and this compares well with the high frequency of heat treatment on the manufacture of artefacts from Vila Nova de São Pedro (96% [7]) and, to a lesser extent, on those from La Junta and Cabezo Juré (66% [9]). The recurrent use of heat treatments in these sites differs from what we know on early findings of Chalcolithic metallurgy from other regions in the Iberian Peninsula, mostly from the southeastern region, where annealing seems less important (frequency of about 20%) in the third millennium BC [25].

Some of the artefacts show a significant incidence of slip bands (arrowhead SP61, dagger SP55, and spatula SP58, Table 1) indicating a final forging operation that could be used to smooth the surface or to sharpen specific areas, such as the cutting edge of a blade (Fig. 4). A considerable strain increases the hardness, but the São Pedro artefacts with slip bands were non-mounted samples and could not be tested. The minimal use of final forging seems to be a distinctive feature of Chalcolithic metallurgy since local Middle Bronze Age artefacts usually present slip bands [18, 26].

The hardness measurements of mounted samples show variable values ranging from approximately the value of pure copper (chisel SP20: 52 HV0.2) to almost a threefold increase (arrowhead SP68: 142 HV0.2) (Table 1). Besides, artefacts with similar typologies have distinct hardnesses, such as daggers (98-140 HV0.2), awls (59-126 HV0.2), and chisels (52-107 HV0.2). The higher hardness of some artefacts (e.g., arrowhead SP68 and awl SP72) is partially due to the establishment of strain fields from γ phase precipitation. A smaller grain size also confers a higher hardness (e.g., dagger SP15, awl SP71, and awl SP72), resulting from a higher deformation and/or weaker annealing. Moreover, the solid solution hardening of arsenic in copper is negligible [8].

Overall, the arsenic content of these artefacts does not show any significant correlation with hardness or function (Fig. 5). Despite some examples with a very high hardness (155 − 204 HV0.2) the arsenic content does not seem to be related to the hardness of artefacts from Vila Nova de São Pedro, La Junta, and Cabezo Juré (Fig. 5). The comparison with the hardness achievable through thickness reduction by cold hammering [8] suggests low hardness increase of most weapons and tools.

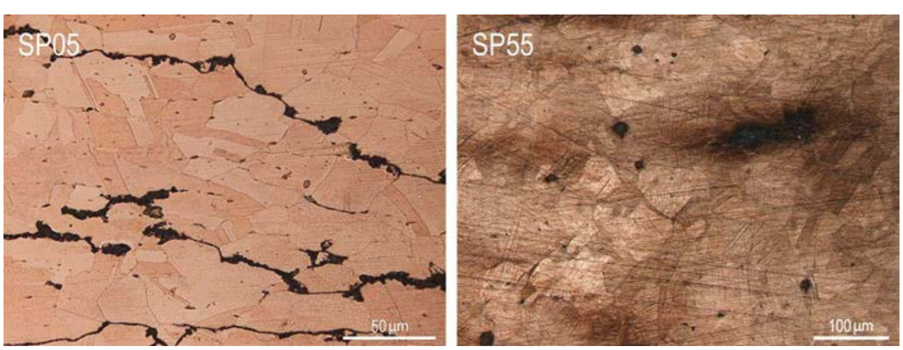

Figure 4. Optical microscopy images of copper dagger SP05 and arsenical copper dagger SP55 (etched samples; bright field illumination; deformed grains with annealing twins and, in the second example, slip bands).

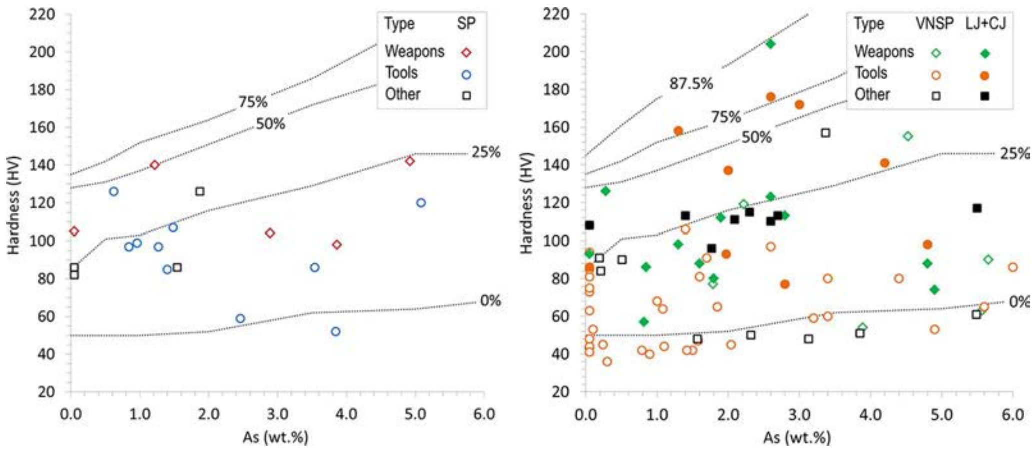

Figure 5. Arsenic content versus hardness of weapons, tools and other types of São Pedro (SP), Vila Nova de São Pedro (VNSP) [7], La Junta (LJ) [9] and Cabezo Juré (CJ) [9] (the dotted lines indicate the reduction in thickness by forging, adapted from [8]).

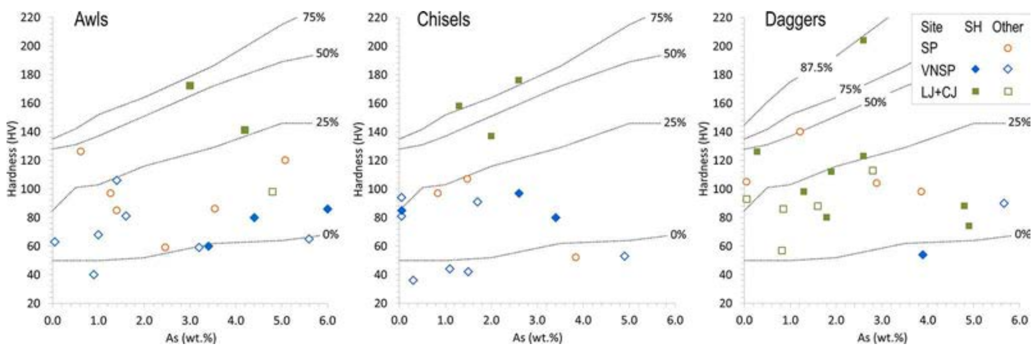

Figure 6. Arsenic content versus hardness of awls, chisels and daggers of São Pedro (SP), Vila Nova de São Pedro (VNSP) [7], La Junta (LJ) [9] and Cabezo Juré (CJ) [9] (SH – strain hardened artefacts; the dotted lines indicate the reduction in thickness by forging, adapted from [8]).

The comparison of arsenic content, hardness, and manufacture of awls, chisels, and daggers from São Pedro, Vila Nova de São Pedro, La Junta, and Cabezo Juré indicates that most examples have a hardness corresponding to a low thickness reduction, up to 25% (Fig. 6). Higher hardness is observed in strain-hardened artefacts with mid-range arsenic content, although the arsenical copper alloy remains ductile at compositions closely approaching the solid solubility limit of ~6 wt% As [8]. Therefore, it is clear that the strain-hardening advantage of arsenical copper was not exploited. In certain settlements, such as São Pedro and Vila Nova de São Pedro, final forging was barely used and usually was not intense enough to increase the hardness, while in sites like La Junta and Cabezo Juré, work hardening was not applied to copper with high arsenic content. Consequently, the Chalcolithic post-casting operations seem to be mostly directed to shaping the artefact and not to increasing the hardness.

Conclusions

The composition and manufacture of copper-based artefacts from the settlement of São Pedro indicate a primitive metallurgy, characterized by a limited control of casting conditions, in addition to a possible trend to a higher frequency of arsenical copper alloys during the second half of the third millennium BC. Post-casting operations of weapons and tools commonly included cycles of forging and annealing, while the use of work hardening was minimal, and similar to what is known from the Chalcolithic Portuguese Estremadura.

On the contrary, in Southern Andalusia the regular use of work hardening occasionally produced artefacts with significantly higher hardness, but these mechanically improved weapons and tools do not correspond to artefacts with higher amounts of arsenic. Apparently, unawareness of the potential arsenic hardening was a common feature of the metallurgical knowledge in the southwestern end of the Iberian Peninsula during the third millennium BC.

Funding

This work is funded by FEDER funds through the COMPETE 2020 Programme and National Funds through FCT − Portuguese Foundation for Science and Technology under the project numbers UID/Multi/04349/2013 (C2TN) and POCI-01-0145-FEDER-007688, Reference UID/CTM/50025 (i3N/CENIMAT).

References

[1] Vidigal, R.O.; Valério, P.; Araújo, M.F.; Soares, A.M.M.; Mataloto, R. Micro-EDXRF study of Chalcolithic copper-based artefacts from Southern Portugal. *X-Ray Spectrometry* **2016**, *45* (1), 63–68. doi:10.1002/xrs.2658

[2] Hunt-Ortiz, M.A.; Hurtado-Pérez, V.; Montero-Ruiz, I.; Rovira-Llorens, S.; Zalduegui, J.F. Chalcolithic metal production and provenance in the site of San Blas (Cheles, Badajoz, Spain); In 2nd International Conference Archaeometallurgy in Europe; AIM: Aquileia, Italy, 2007, 81–92.

[3] Hunt-Ortiz, M.A. Prehistoric mining and metallurgy in south west Iberian Peninsula. *British Archaeological Reports International Series* **2003**, *1188*, 418.

[4] Rovira, S.; Montero-Ruiz, I. Iberia: Technological development of prehistoric metallurgy; In *Metal Matters. Innovative Technologies and Social Change in Prehistory and Antiquity*, Burmeister, S. Hansen, S. Kunst, M. Müller-Scheessel, N. Eds.; Verlag Marie Leidorf: Rahden/Westfalen, Germany, 2013, 231–239.

[5] Müller, R.; Goldenberg, G.; Bartelheim, M.; Kunst, M.; Pernicka, E. Zambujal and the beginnings of metallurgy in southern Portugal; In *Metals and Mines. Studies in Archaeometallurgy*; Niece, S. Hook, D. Craddock, P.T. Eds.; Archetype: London, UK, 2007, 15–26.

[6] Müller, R.; Cardoso, J.L. The origin and use of copper at the Chalcolithic fortification of Leceia (Oeiras, Portugal). *Madrider Mitteilungen* **2008**, *49*, 64–93.

[7] Pereira, F.; Silva, R.J.C.; Soares, A.M.M.; Araújo, M.F. The role of arsenic in Chalcolithic copper artefacts - insights from Vila Nova de São Pedro (Portugal). *Journal of Archaeological Science* **2013**, *40* (4), 2045–2056. doi:10.1016/j.jas.2012.12.015

[8] Lechtman, H. Arsenic bronze: Dirty copper or chosen alloy? A view from the Americas. *Journal of Field Archaeology* **1996**, *23* (4), 477–514. doi:10.2307/530550

[9] Bayona, M.R. La investigación de la actividad metalúrgica durante el III milenio A.N.E. en al Suroeste de la Península Ibérica. *British Archaeological Reports International Series* **2008**, *1769*, 283.

[10] Lillios, K.T. Amphibolite tools of the Portuguese Copper Age (3000–2000 B.C.): A geoarchaeological approach to prehistoric economics and symbolism. *Geoarchaeology* **1997**, *12* (2), 137–163.

[11] Nocete, F.; Sáez, R.; Nieto, J.M. La producción de cobre en Cabezo Juré: Estudio químico, mineralógico y contextual de escorias; In *Odiel. Proyecto de Investigación Arqueológica para el Análisis del Origen de la Desigualdad Social en el Suroeste de la Península Ibérica*, Nocete, F. Coord.; Junta de Andalucía: Sevilla, Spain, 2004, 273–295.

[12] Mataloto, R.; Estrela, S.; Alves, C. As fortificações calcolíticas de São Pedro (Redondo, Alentejo Central, Portugal); In *Los Primeros Campesinos de La Raya. Aportaciones Recientes al Conocimiento del Neolítico y Calcolítico en Extremadura y Alentejo*, Cuenca, E.C.; Sierra, J.M.V. Eds.; Museu de Cáceres: Cáceres, Spain, 2007, 113–141.

[13] Reimer, P.J.; Bard, E.; Bayliss, A.; Beck, J.W.; Blackwell, P.G.; Ramsey, C.B.; Buck, C.E.; Cheng, H.; Edwards, R.L.; Friedrich, M.; Grootes, P.M.; Guilderson, T.P.; Haflidason, H.; Hajdas, I.; Hatté, C.; Heaton, T.J.; Hoffmann, D.L.; Hogg, A.G.; Hughen, K.A.; Kaiser, K.F.; Kromer, B.; Manning, S.W.; Niu, M.; Reimer, R.W.; Richards, D.A.; Scott, E.M.; Southon, J.R.; Staff, R.A.; Turney, C.S. M.; van der Plicht, J. IntCal13 and Marine13 radiocarbon age calibration curves, 0–50,000 years cal BP. *Radiocarbon*, **2013**, *55* (4), 1869–1887. doi:10.2458/azu_js_rc.55.16947

[14] Ramsey, C.B. Bayesian analysis of radiocarbon dates. *Radiocarbon* **2009**, *51* (1), 337–360.

[15] Ramsey, C.B. Oxcal 4.2 Manual; Web interface build number: 86; Last Updated: 5/9/2014; https://c14.arch.ox.ac.uk/oxcalhelp/hlp_contents.html.

[16] Sangmeister, E.; Jiménez-Gómez, M.C. *Zambujal. Kupferfunde aus den Grabungen 1964 bis 1973*; Philipp von Zabern: Mainz am Rhein, Germany, 1995, 236pp.

[17] Murillo-Barroso, M.; Montero-Ruiz, I. Copper ornaments in the Iberian Chalcolithic: Technology versus social demand. *Journal of Mediterranean Archaeology* **2012**, *25* (1), 53–73. doi:10.1558/jmea.v25i1.53

[18] Valério, P.; Soares, A.M.M.; Araújo, M.F.; Silva, R.J.C.; Porfírio, E.; Serra, M. Arsenical copper and bronze in Middle Bronze Age burial sites of southern Portugal: the first bronzes in Southwestern Iberia. *Journal of Archaeological Science* **2014**, *42*, 68–80. doi:10.1016/j.jas.2013.10.039

[19] Kienlin, T.L.; Bischoff, E.; Opielka, H. Copper and bronze during the Eneolithic and Early Bronze Age: a metallographic examination of axes from the Northalpine region. *Archaeometry* **2006**, *48* (3), 453–468. doi:10.1111/j.1475-4754.2006.00266.x

[20] Budd, P. A metallographic investigation of Eneolithic arsenical copper artefacts from Mondsee, Austria. *Journal of the Historical Metallurgy Society*, **1991**, *25* (2), 99–108.

[21] Subramanian, P.R.; Laughlin, D.E. The As-Cu (arsenic-copper) system. *Bulletin of Alloy Phase Diagrams* **1988**, *9* (5), 605–617. doi:10.1007/BF02881964

[22] Pereira, F.; Silva, R.J.C.; Soares, A.M.M.; Araújo, M.F.; Oliveira, M.J.; Martins, R.M.S.; Schell, N. Effects of long term aging in arsenical copper alloys. *Microscopy and Microanalysis* **2015**, *21* (6), 1413–1419. doi:10.1017/S1431927615015263

[23] Rovira, S.; Gómez Ramos, P. *Las Primeras Etapas Metalúrgicas en la Península Ibérica. III. Estudios metalográficos*; Taravilla: Madrid, Spain, 2003, 208 pp.

[24] Northover, J.P. Properties and use of arsenic-copper alloys; In *Old World Archaeometallurgy*, Hauptmann, A., Pernicka, E., Wagner, G.A., Eds.; Deutsches Bergbaumuseum: Bochum, Germany, 1989, 111–118.

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

[26] Valério, P.; Soares, A.M.M.; Araújo, M.F.; Silva, R.J.C.; Baptista, L. Middle bronze age arsenical copper alloys in Southern Portugal. *Archaeometry*. doi:10.1111/arcm.12212