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Technological continuity in Early Iron Age bronze metallurgy at the South-Western Iberian Peninsula – a sight from Castro dos Ratinhos

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ABSTRACT

A collection of 54 bronze artefacts recovered from the inland settlement of Castro dos Ratinhos (Portugal) and belonging mainly to the 9th–8th centuries BC, was studied by the use of non-invasive and micro analytical techniques. EDXRF, Micro-EDXRF, SEM-EDS and Optical Microscopy were used to determine the alloy composition and to identify the different thermo mechanical operations applied in the production of the artefacts. Results show that the collection is entirely composed of good quality binary bronzes (with an average tin content of $10.1 \pm 2.5\%$). Alloys with higher tin contents were kept in as-cast condition and used in the making of ornaments, while tools were often finished with forging and annealing operations. Despite the existence of some Orientalising features in the Castro dos Ratinhos, e.g. rectangular habitat structures, wheel-turned ware and amphorae, the exclusive use of binary alloys with a narrow range of tin content seems to be associated with an indigenous metallurgical tradition inherited from the Late Bronze Age. This may indicate that the Phoenician interaction within the inland indigenous communities was a slow and selective process, probably dependant on the social-economic and cultural development of local communities.

1. Introduction

Archaeological record shows that during the turn of the 2nd–1st millennium BC, Western European copper based metallurgical technology relied upon bronze alloys. Late Bronze Age (LBA) metallic artefacts from Atlantic Europe, such as the British Isles, Western France and North-Western Iberia, were made mainly of leaded bronzes ($Pb > 2\%$) (Rovira and Gómez-Ramos, 1998). On the other hand, European regions around the Mediterranean Sea, such as the major part of the Iberian Peninsula, Sardinia, Sicily, Italy and Greece, were using a technology of binary bronze (Hook, 2003; Kayafa, 2003).

The metallic collection composed of nearly four hundred artefacts from Ria de Huelva (South-Western Spain) is a characteristic example of the LBA Iberian metallurgical tradition of binary bronze with "suitable" tin contents (~8–14%) (Rovira, 1995b). It must be noted however, that during both prehistoric and proto-historic times, extensive sources of tin could be found in the Iberian Peninsula (Penhallurick, 1986). Contrary to this, Mediterranean regions imported this raw material from neighbouring areas. LBA low tin bronze alloys from the North-Eastern Italy, which were produced during a crisis in the trade of tin (Giumlia-Mair, 2005), are an excellent example of the importance of tin supply within the Mediterranean region. In general, Iberian bronze alloys present higher tin contents than artefacts from nearby Mediterranean regions. Therefore, the differences between these LBA metallurgical traditions are probably related to the abundance and supply of tin.

The rising influence of the Mediterranean World during the initial stages of the 1st millennium BC, introduced important transformations in the Iberian Peninsula. This influence culminated with the foundation of the first Phoenician Emporia and colonies in the littoral areas during the 10th and 9th centuries BC (Barros and Soares, 2004; González de Canales et al., 2006; Nijboer and Van der Plicht, 2006; Torres Ortiz, 1998).

Iberian bronze collections belonging to the Early Iron Age (EIA) present characteristic artefacts related to Mediterranean traditions, e.g. tweezers for body treatment or some specific types of fibula for vestment tighten. New metallurgical practices (e.g. *cire perdue* and silver cupellation) were introduced and the use of leaded bronze increased. Lead enhances the fluidity of the molten bronze alloy and increases the temperature solidification range, thus being very

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valuable for casting large or complex artefacts. During the EIA, leaded alloys were mainly used for ornaments, contrasting with its indiscriminate use at the LBA Atlantic world (Montero et al., 2003).

Studies regarding EIA bronze metallurgy in the Iberian Peninsula are still insufficient. In the South-Western region, collections from the Orientalising settlements of Quinta do Almaraz (Araújo et al., 2004), Medellin and El Palomar (Rovira et al., 2005) reveal a significant usage of leaded bronze. A similar situation has been recorded in the South-Eastern Iberian region (Montero Ruiz, 2008). The trend of an increased use of this alloy seems to be in constant widespread to areas with strong Orientalising influence.

The variability of the tin content in EIA binary alloys also increased due to several causes, such as alloy hardness, colour, recycling, etc. Furthermore, latter metallic assemblages exhibit lower average tin contents, which are more comparable with the Mediterranean metallurgical tradition (Rovira, 1995a).

Recent archaeological works which were carried out at Castro dos Ratinhos, Moura (Berrocal-Rangel and Silva, 2007) – a settlement with a complex fortified system implanted on top of an elevated ridge in the left bank of the Guadiana River (Fig. 1) – have allowed for the collection of 54 bronze artefacts, which study is presented here. At Castro dos Ratinhos two main occupation phases were recorded, which can be ascribed to the LBA and to the EIA. Radiocarbon dating established that the first phase belongs to the 12th–9th centuries BC, while the second phase is dated from the end of the 9th century, but lasting until the 8th century BC (Soares and Martins, in press). The latter is contemporary of the first Phoenician colonies in the Iberian coastal areas. Some Orientalising traces are already present, such as habitat structures with a rectangular plan, including one which could in fact be the remains of an altar related to the cult of *Asherah*, some imported wheel-turned pottery, namely red slip ware and amphorae, and iron and ivory artefacts (Berrocal-Rangel and Silva, 2007, in press).

The bronze collection recovered at Castro dos Ratinhos, belongs mainly to the EIA phase (9th–8th centuries BC), consequently coeval of the foundation of the first Phoenician colonies in the South of Iberia. Their chemical and metallographic analysis allows for the identification of alloy composition and metallurgical practices. The results can provide a new insight in the understanding of the Phoenician colonisation and the cultural exchange in the Iberian Peninsula during the first steps of the so-called Orientalising Period.

2. Metallic collection

The significant collection of the 54 bronze artefacts recovered from archaeological excavations at Castro dos Ratinhos, can be in fact be grouped, with the exception of a lot of 23 artefacts of unknown functionality, in ornaments, tools and weapons (Table 1).

The fibulae are among the most interesting ornaments recovered, including a serpentine (*ad occhio*), two double spring and, possibly, a Bencarrón type fibula (Fig. 2). The first two types are frequent in the LBA Portuguese archaeological contexts, whereas the double-spring fibulae present an extensive period of utilization that continues up to the Iron Age (Arruda, 2008). The Bencarrón type seems to be related to the Acebuchal fibulae, quite common in the Iberian Peninsula during the EIA (Melo et al., 2009). There are also two small conical heads that might have served as decorative rivets which belong to more complex artefacts or are part of pins for the fastening of clothes.

The tool set includes needles, chisels, knives, nails and a weight (Fig. 2). The latter is worthy of a special note – it weights 7.0 g and exhibits a bitroncoconic shape common in the Portuguese territory during the 12th–9th centuries BC (Vilaça, 2003). Weights belonging to the subsequent period are generally made of lead instead of bronze and present an increased number of typologies, i.e. besides the above mentioned classic shape there are also cubic and zoomorphic forms. Latter bitroncoconic and discoid examples often possess a central opening to insert the *pondarium*, such as the lead weight from Quinta do Almaraz (Valério et al., 2003).

A small dagger presenting an advanced corrosion state is the only weapon recovered by the archaeological excavations.

Fig. 1. Map of the Iberian Peninsula with the location of Castro dos Ratinhos and other archaeological sites mentioned in the text.

Table 1
Bronze artefacts from Castro dos Ratinhos.

Ornaments		Tools		Weapons	
Bead	1	Chisels	3	Dagger	1
Belt-locks	2	Fish-hook	1		
Decorative rivet/pin	2	Knives	2	Rings	11
Fibulae		Punch	1		
Bencarrón	1	Nails	2	Fragments	12
Double-spring	2	Needles	5		
Serpentine	1	Tweezers	1		
Spring fragments	3	Weight	1		
Necklace-lock	1				
Pendant	1				

Table 2
Results of micro-EDXRF analyses of ornaments from Castro dos Ratinhos (values in %; n.d. – not detected).

Phase	Artefact	Reference	Cu	Sn	Pb	As	Fe
EIA	Belt-lock	CRAT04/A1/Ib/M1	89.6	10.3	n.d.	0.18	<0.05
EIA	Belt-lock	CRAT04/A1/IIa/M4	88.8	11.1	n.d.	<0.10	0.06
EIA	Bencarrón fibula	CRAT07/M3/IIb/M1	89.9	9.8	0.16	0.13	<0.05
EIA	Decorative rivet/pin	CRAT05/D1/Ib/M3	84.1	15.9	n.d.	n.d.	<0.05
EIA	Double-spring fibula	CRAT05/C1/Ib/M3	93.3	6.3	n.d.	0.43	<0.05
EIA	Nail	CRAT04/B1/IIa/M1	90.3	9.4	n.d.	0.10	0.11
EIA	Nail	CRAT04/A2/IIa/M1	90.1	9.6	n.d.	<0.10	0.16
EIA	Necklace-lock	CRAT05/D1/Ib/M1	90.0	9.4	0.30	0.12	0.14
EIA	Pendant	CRAT05/D1/IIa/M2	91.4	8.3	0.17	<0.10	<0.05
LBA	Serpentine fibula	CRAT05/B1/IIc/M2	87.3	12.8	n.d.	n.d.	<0.05

As mentioned above, a considerable number of objects present an unknown functionality, namely 11 rings and 12 artefacts recovered in a very fragmented state. Rings can be divided into closed and open pieces – since it is generally accepted that bronze sections cannot be joined through heating and forging (Sarabia-Herrero et al., 1996). Closed rings were certainly cast in circular moulds, while the open pieces can be made with a straight rod that was bent after casting. A preliminary study concerning these rings (Valério et al., 2010) indicates the use of different operational sequences in their manufacture, which seems to prove their multipurpose functionality. Furthermore, it seems that the evidence of mechanical operations present in some of the rings could be due to a bending operation.

Finally, it should be mentioned that a major part of these metallic materials from Castro dos Ratinhos were recovered in EIA contexts, with only two knives, a tweezers, a serpentine fibula, two possible fibulae spring fragments and a ring from the LBA archaeological contexts. Beyond the metallic collection, a sandstone mould for the "carp-tongue" swords was also recovered, which is, up until now, the only evidence of the possible existence of a metallurgical workshop in the settlement.

3. Methodology

The entire collection was firstly analysed by energy-dispersive X-ray fluorescence spectrometry (EDXRF), used to identify the main constituents of the alloy. Subsequently, artefacts were studied by the use of different methodologies, which were selected according to their archaeological significance and conservation state. In a first group of 18 artefacts, it was possible to remove a small fragment that was mounted in epoxy resin and prepared for micro-EDXRF and optical microscopy (OM) analyses. Some of these mounted cross-sections were also analysed by scanning electron microscopy with X-ray micro analysis (SEM-EDS). Another set of 19 artefacts was cleaned from the superficial corrosion layer in a small elliptical area (~2–3 mm diameter), which was analysed by micro-EDXRF. Two artefacts were analysed by micro-EDXRF using these two procedures, establishing that both sampling methods provided comparable results. Some of the small cleaned areas were also observed by OM. The latter was more difficult to prepare and micrographs often presented imperfections, but with this method a satisfactory microstructural interpretation could be obtained with minimum damage to the artefact. The remaining 17 artefacts present an exceptional archaeological significance and/or an advanced corrosion process, which make it impossible to perform any type of micro analytical study.

3.1. EDXRF

Analyses were done with a Kevex 771 spectrometer, equipped with a 200 W Rh X-ray tube, secondary excitation targets, radiation filters and a Si(Li) detector with a resolution of 165 eV (Mo-Kα). Each artefact was analysed using two excitation conditions – Ag secondary target and Gd secondary target. Details regarding the equipment, analytical conditions and quantification procedures have been previously published (Araújo et al., 1993).

3.2. Micro-EDXRF

Small cleaned surface areas and mounted cross-sections were analysed with an ArtTAX Pro spectrometer 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). Poly capillary lenses collimate the primary X-ray beam enabling a sample spatial resolution of around 70 μm. Quantitative analyses performed in 3 different spots of each artefact use experimental calibration factors calculated through the analysis of a standard reference material.

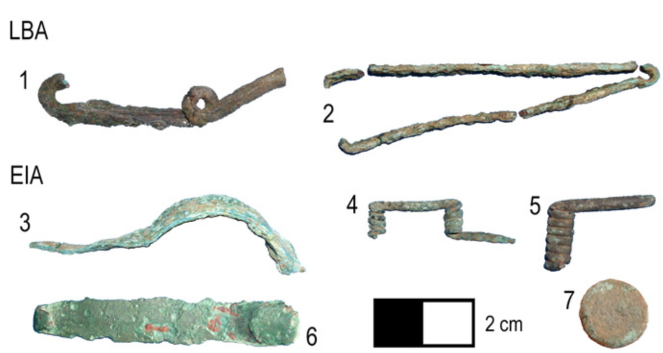

Fig. 2. Bronze artefacts from Castro dos Ratinhos belonging to the LBA: (1) serpentine fibula; (2) tweezers; and to the EIA: (3) Bencarrón fibula; (4–5) double-spring fibulae; (6) belt-lock and (7) weight.

Table 3
Results of micro-EDXRF analyses of tools from Castro dos Ratinhos (values in %; n.d. – not detected).

Phase	Artefact	Reference	Cu	Sn	Pb	As	Fe
EIA	Chisel	CRAT04/A1/IIa/M3	90.3	9.5	0.18	<0.10	<0.05
EIA	Chisel	CRAT06/C1/Ic/M1	88.3	11.4	0.19	0.15	<0.05
EIA	Chisel	CRAT05/D1/IIa/M3	89.5	10.2	n.d.	0.23	<0.05
EIA	Fish-hook	CRAT05/D2/Ic/M1	90.6	9.2	0.10	<0.10	<0.05
EIA	Needle	CRAT04/A1/IIa/M1	91.4	8.3	0.10	0.11	<0.05
EIA	Needle	CRAT05/C1/Ib/M2	89.2	10.3	0.18	0.29	<0.05
EIA	Needle	CRAT05/C1/IIa/M1	91.4	8.5	n.d.	n.d.	<0.05
EIA	Needle	CRAT05/D1/Ib/M2	92.3	7.2	0.30	0.19	<0.05
EIA	Needle	CRAT07/R1/IIc/M1	93.0	6.9	n.d.	n.d.	<0.05
EIA	Punch	CRAT05/C1/Ib/M4	93.6	6.3	n.d.	0.10	<0.05
EIA	Weight	CRAT06/C1/Sup/M1	84.2	15.5	0.18	<0.10	<0.05
LBA	Knife	CRAT04/A2/IIc/M1	95.1	4.9	n.d.	n.d.	<0.05
LBA	Tweezers	CRAT05/D1/IIc/M2	90.3	9.6	n.d.	<0.10	<0.05

Table 4
Results of micro-EDXRF analyses of unknown functionality artefacts from Castro dos Ratinhos (values in %; n.d. – not detected).

Phase	Artefact	Reference	Cu	Sn	Pb	As	Fe
EIA	Ring (closed)	CRAT04/A4/Ia/M1	85.7	14.3	n.d.	<0.10	<0.05
EIA	Ring (closed)	CRAT04/B1/IIa/M2	85.7	13.7	n.d.	0.51	<0.05
EIA	Ring (closed)	CRAT05/B1/Ic/M1	92.2	7.8	n.d.	<0.10	<0.05
EIA	Ring (closed)	CRAT06/C2/Ic/M1	88.4	10.5	0.97	0.16	<0.05
EIA	Ring (coiled)	CRAT07/Q1/Ib/M1	88.8	10.8	0.16	0.18	<0.05
EIA	Ring (open)	CRAT04/D1/IIa/M4	86.9	12.7	0.18	0.14	<0.05
EIA	Ring (open)	CRAT05/D2/IIa/M2	86.8	13.1	n.d.	0.12	<0.05
EIA	Ring (open)	CRAT06/N3/IId/M1	89.1	10.3	0.15	0.16	<0.05
EIA	Fragment (flat)	CRAT05/D2/IIa/M3	89.4	9.3	1.3	<0.10	<0.05
EIA	Fragment (flat)	CRAT06/S1/Ia/M1	91.6	8.3	n.d.	<0.10	<0.05
EIA	Fragment (non-flat)	CRAT04/A1/IIa/M2	90.1	9.7	0.14	0.10	<0.05
EIA	Fragment (non-flat)	CRAT05/D2/IIa/M1	86.5	13.5	n.d.	n.d.	<0.05
EIA	Fragment (non-flat)	CRAT05/D2/IIa/M4	90.7	8.5	0.80	<0.10	<0.05
LBA	Ring (open)	CRAT05/D1/IIc/M1	89.3	10.7	n.d.	n.d.	<0.05

Quantification limits (0.10% for Pb and As; 0.05% for Fe) were obtained with the analysis of two spectroscopic bronze standards (SS551 and SS552 from British Chemical Standards). Additional experimental details are described elsewhere (Valério et al., 2007).

3.3. OM

Mounted cross-sections were polished with SiC papers (P1000, P2500 and P4000 grit size) and diamond pastes (1 μm and ¼ μm). Small surface areas were cleaned and polished with 15 μm, 8 μm and 1 μm diamond pastes. Cross-sections and longitudinal samples were observed with a Leica DMI 5000 M, an optical microscope under bright field (BF), dark field (DF) and polarised light (Pol) illumination. Samples were observed unetched and after etching with an aqueous ferric chloride solution.

3.4. SEM-EDS

Mounted cross-sections were observed in a Zeiss DSM 962 scanning electron microscope equipped with a secondary electrons detector (SE) and a backscattered electrons detector (BSE). The equipment also includes an Oxford Instruments INCAx-sight EDS spectrometer with an ultrathin window used for semi-quantitative elemental analyses.

4. Results

4.1. Alloy type

EDXRF analyses indicate that the collection of the 54 artefacts is entirely composed of copper–tin alloys, with lead, arsenic and iron being the major metallic impurities. Some high lead concentrations measured on non-cleaned artefact surfaces revealed to be the result of a surface enrichment effect due to corrosion processes (i.e. subsequent micro-EDXRF analyses carried out in cleaned artefact areas revealed lead concentrations bellow 2%).

4.2. Alloy composition

Micro-EDXRF results of metallic artefacts from Castro dos Ratinhos (Tables 2–4) indicate without exception binary bronze alloys with an average tin content of $10.1 \pm 2.5\%$. In general there are no major differences between ornaments, tools and rings, but it should be noted that the few artefacts with higher tin contents (~13–15%) are usually ornaments or non-functional tools. Furthermore, only one exemplar exhibits a very low tin content (4.9%). Arsenic and lead being the main impurities, and exhibiting average concentrations of $0.2 \pm 0.1\%$ and $0.3 \pm 0.3\%$, respectively. Iron is almost always present in remarkably low concentrations ($<0.05\%$).

4.3. Microstructures

OM and SEM-EDS analyses identified different phases, common inclusions and casting defects (Table 5). In addition, the operational sequences were established with the characteristic signatures of the annealing and hammering operations, namely annealing twins, inclusion morphologies and slip bands density.

As-cast microstructures present columnar dendrites (conical head CRAT05/D1/Ib/M3, Fig. 3) or a more coarse morphology with coring (weight CRAT06/C1/Sup/M1, Fig. 3). The $(\alpha + \delta)$ eutectoid is present (with the characteristic α islands in a δ matrix – silver coloured matrix in BF illumination) due to the high tin content of these as-cast alloys (15.9% and 15.5%, respectively). Copper

Table 5
Microstructural characterization of bronze artefacts from Castro dos Ratinhos (C – Casting; A – Annealing; F – Forging; FF – Final forging; P – Present and D – Deformed).

Type	Artefact	Reference	Sn (%)	$\alpha + \delta$	Cu-S	Pores	Cracks	Operational sequence
Ornament	Decorative rivet/pin	CRAT05/D1/Ib/M3	15.9	P	P	–	–	C
Ornament	Decorative rivet/pin	CRAT07/N3/Ic/M1	–	–	–	–	–	C
Ornament	Double-spring fibulae	CRAT05/C1/Ib/M3	6.3	–	P	–	–	C + (F + A) + FF
Ornament	Necklace-lock	CRAT05/D1/Ib/M1	9.4	P	P	–	–	C + (F + A) + FF
Ornament	Pendant	CRAT05/D1/IIa/M2	8.3	–	P	–	–	C
Tool	Needle	CRAT04/A1/IIa/M1	8.3	–	P	–	–	C + (F + A) + FF
Tool	Needle	CRAT05/C1/Ib/M2	10.3	–	P	–	–	C + (F + A) + FF
Tool	Needle	CRAT05/C1/IIa/M1	8.5	–	P	–	–	C + (F + A)
Tool	Needle	CRAT05/D1/Ib/M2	7.2	–	P	–	–	C + (F + A) + FF
Tool	Needle	CRAT07/R1/IIc/M1	6.9	–	P	–	P	C + (F + A)
Tool	Punch	CRAT05/C1/Ib/M4	6.3	–	P	–	–	C + (F + A) + FF
Tool	Weight	CRAT06/C1/Sup/M1	15.5	P	P	–	–	C
Tool	Knife	CRAT04/A2/IIc/M1	4.9	–	D	–	–	C + (F + A) + FF
Unknown	Ring (closed)	CRAT04/A4/Ia/M1	14.3	P	P	–	–	C
Unknown	Ring (open)	CRAT04/D1/IIa/M4	12.7	P	P	P	–	C + (F + A) + FF
Unknown	Ring (open)	CRAT05/D2/IIa/M2	13.1	P	P	D	–	C + A + F
Unknown	Ring (open)	CRAT06/N3/IId/M1	10.3	–	P	–	–	C + A + F
Unknown	Fragment (flat)	CRAT06/S1/Ia/M1	8.3	–	P	–	P	C + (F + A) + FF
Unknown	Fragment (non-flat)	CRAT04/A1/IIa/M2	9.7	P	P	–	P	C + (F + A)
Unknown	Fragment (non-flat)	CRAT05/D2/IIa/M4	8.5	–	P	–	P	C + (F + A)
Unknown	Ring (open)	CRAT05/D1/IIc/M1	10.7	P	P	–	–	C + (F + A)

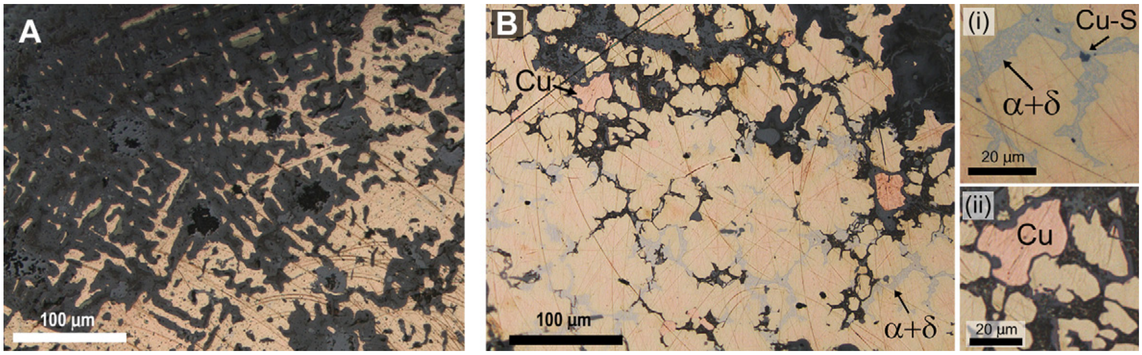

Fig. 3. Microstructures of (A) decorative rivet/pin CRAT05/D1/Ib/M3 and (B) weight CRAT06/C1/Sup/M2 with enlarged details on (i) $\alpha+\delta$ eutectoid and copper sulphide (Cu–S); and (ii) metallic copper (Cu), (BF-longitudinal, non-etched).

sulphide inclusions were segregated to the regions that take the longest to solidify due to their low miscibility in molten copper (Cu–S which appears as dark blue inclusions in BF illumination). The coarser microstructure also presents metallic copper redeposition due to tin oxidation (metallic copper appears as pink in BF illumination). The redeposition only occurs in regions where the oxidation potential is not enough (i.e. low oxygen content) in order to keep copper in an oxidized state.

A particular type of worked microstructure was observed in the ring CRAT06/N3/IId/M1 (Fig. 4). This appears to have been first homogenized and later finished by hammering since it presented a high density of slip bands but no discernible annealing twins. The slip bands appeared to be distorted, indicating that the final hammering of the ring was probably performed in order to bend the ring. Copper sulphide inclusions are more resistant to the alteration processes and some still remain in the corroded regions.

The majority of worked microstructures present equiaxial grains with annealing twins and slip bands (needle CRAT05/C1/Ib/M2, Fig. 5). This indicates the use of one or more cycles of forging and annealing and also that the operation sequence was finished with forging. In some artefacts this final forging procedure was not applied, which can be deduced from the absence of slip bands (needle CRAT07/R1/IIc/M1, Fig. 5).

A particular microstructure exhibits heavily deformed grains and very elongated copper sulphide inclusions (knife CRAT04/A2/IIc/M1, Fig. 6), clearly evidencing the high deformation applied to obtain the final artefact shape. This microstructure also displays tin oxide inclusions associated with some copper sulphides. Tin oxides are harder being neither easily nor highly deformed. Another noteworthy example (necklace lock CRAT05/D1/Ib/M1, Fig. 7) displays the $(\alpha+\delta)$ eutectoid despite a relatively low tin content (9.4%). This observation points out to that of an incomplete homogenization of the microstructure due to either a short time or low temperature of the annealing process. It should be noted that recrystallization starts to take place at around 500 °C, while homogenization of the tin microsegregation is only achieved at slightly higher temperatures, such as that of 650–700 °C (Northover, 2004). In this microstructure, iron appears associated with copper sulphide inclusions, whereas lead is dispersed in small globules due to its low miscibility in molten bronze.

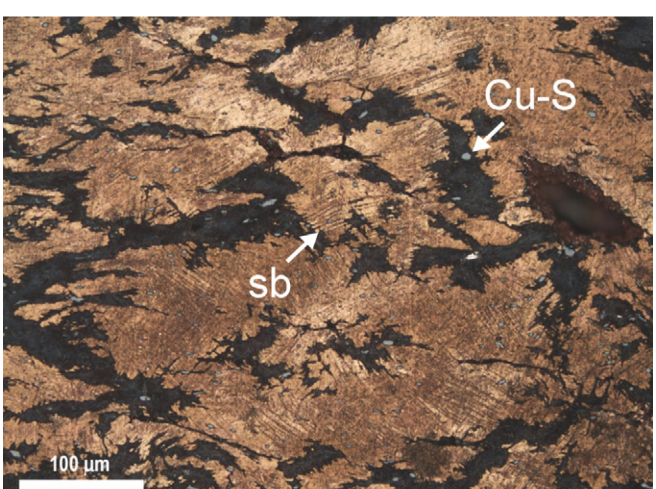

Fig. 4. Microstructure of the ring CRAT06/N3/IId/M1 showing slip bands (sb) and copper sulphide inclusions (Cu–S), (BF-cross-section, etched).

Intergranular and intragranular corrosion evidence the grain structure and the slip bands, respectively. Intragranular corrosion along crystallographic planes is a very useful indicator of corroded microstructures that were kept in a strain hardening condition.

Casting defects such as pores are not very common (with only some exceptions, Fig. 8) pointing out that there was a good control over the temperatures of the mould and molten metal during pouring. Cracks only appear in highly fragmented artefacts (Fig. 8), indicating that these could derive from prolonged corrosion processes rather than from excessive mechanical work.

5. Discussion

Alloys from the Castro dos Ratinhos, with an average tin content of 10.1 ± 2.5% seem to be strongly related to the LBA metallurgical tradition of binary bronze with tin contents of around 8–14%, which is present in the South-Western and Western areas of the Iberian Peninsula (Hunt Ortiz, 2003; Rovira, 1995b), e.g. Ria de Huelva (Rovira, 1995b), Baiões (Figueiredo et al., in press) and Canedotes (Valério et al., 2007) (Fig. 9).

Published values for binary EIA bronze from neighbouring regions with a chronology of the 7th–6th centuries BC, namely El Risco, Medellin (Montero Ruiz et al., 2003) and El Palomar (Rovira et al., 2005), present similar percentage averages of tin contents (Fig. 9). Conversely to that of Castro dos Ratinhos, these collections exhibit an extended variability within the tin content, which is in agreement with what is known within the South-Western EIA metallurgical tradition. Binary bronzes collected in more recent sites, such as Talavera la Vieja (Montero Ruiz and Rovira, 2006) and Cancho Roano (Montero Ruiz et al., 2003), present a reduced average tin content which is also in accordance with the usual values found in latter Orientalising bronze productions (Rovira, 1995a). Apart from the differences in the tin content, leaded bronzes and unalloyed coppers (i.e. where the main impurities,

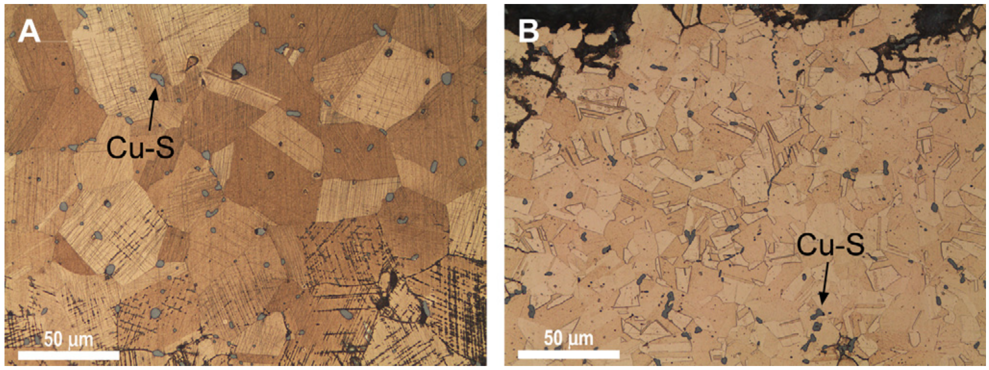

Fig. 5. Microstructures of (A) needle CRAT05/C1/Ib/M2 and (B) needle CRAT07/R1/IIc/M1 (BF-cross-section, etched).

usually Sn and Pb, have contents of less than 2%), are also common in those sites. The absence of leaded bronze and unalloyed copper in the metallurgical set at Castro dos Ratinhos, underlines its distinction from the above mentioned younger EIA collections.

The absence of low tin bronze and unalloyed copper indicates that scrap was not significantly used, since the preferential oxidation of tin during the recycling operation will necessarily produce bronze with a lower tin content or even copper with a small tin content (Sn < 2%) (Rovira and Montero, 2003). In the Castro dos Ratinhos metallurgical collection, the LBA knife is the only exception, presenting a low tin content (4.9%) and, interestingly, tin oxide inclusions. This could be considered to be non-reacted ore or could also result from partial tin oxidation during melting (Klein and Hauptmann, 1999). The oxide inclusions would normally be transferred to the slag, but a low casting temperature would prevent this occurring (Dungworth, 2000).

Alloys from Castro dos Ratinhos seem to have been selected according to the artefact functionality since all functional tools and ornaments present tin contents that can easily be thermally homogenized. Conversely, bronzes with higher tin content seem to be reserved for artefacts that did and do not require high mechanical strength (decorative rivets, weights, pendants and some rings: "finger-rings"?). Higher tin concentrations originate alloys which are far more brittle and difficult to work, since in tin concentrations of above ~14% the $(\alpha+\delta)$ eutectoid is always present. The high tin content of these artefacts could also be associated with their colouring, i.e. as-cast artefacts with increased tin concentrations present a more yellowish-brown tint that could be considered more suitable for prestige artefacts (Giumlia-Mair, 2005).

The iron content of bronze artefacts has been used as a technological indicator of the smelting process all over the Mediterranean region (Ingo et al., 2006). Craddock and Meeks (1987) identified an increase in this element when comparing LBA and Phoenician–Iberian bronzes from SE Spain (0.04 to 0.27%, respectively). The rise was understood to be the result of a more efficient copper smelting furnace, employed by the Phoenician–Iberian cultures. These metallurgical extractions run under high reducing conditions, enabling the reduction of iron impurities that are subsequently incorporated in the metallic bath. On the contrary, smelting operations conducted in crucible furnaces often operate under poor reducing conditions. Crucible furnaces were widely used in the Iberian Peninsula, sometimes until pre-Roman times (Delibes et al., 2001; Rovira and Montero, 2003). Potential evidence of their use was also found in the Phoenician settlement of La Fonteta (Renzi et al., 2007). Therefore, the low iron content found in bronze in Castro dos Ratinhos (<0.05%) is a possible indicator of the usage of these crucible furnaces. However, the low iron content could also be the result of an efficient copper refining or other metallurgical intervention. Consequently, only further research and the study of metallurgical debris (crucibles, slags and ores), materials not yet found in this site, could establish more definitive conclusions.

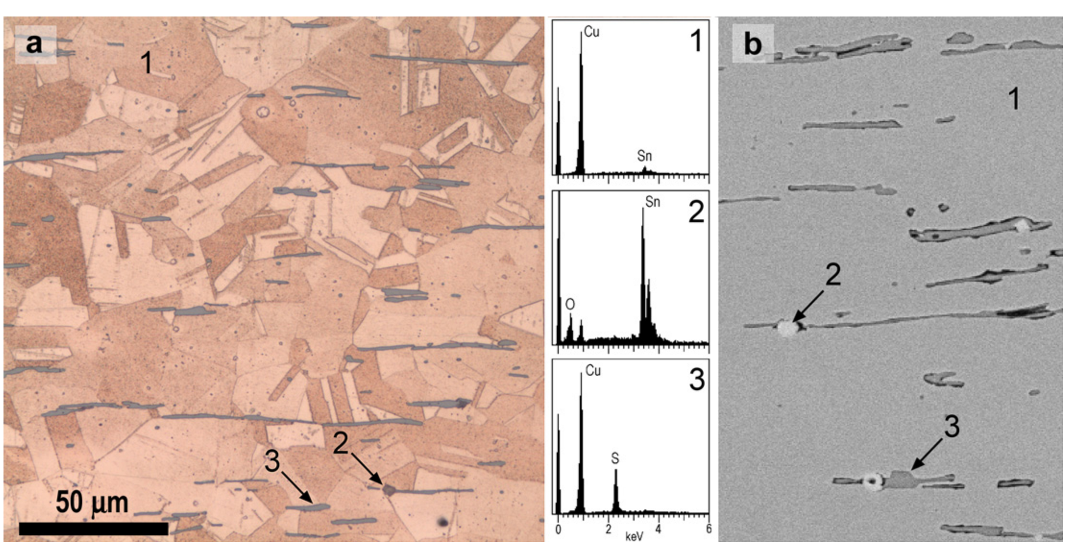

Fig. 6. Microstructure of the knife CRAT04/A2/IIc/M1 with EDS spectra of different areas indicated in (a) OM (BF-cross-section, etched); and (b) SEM image.

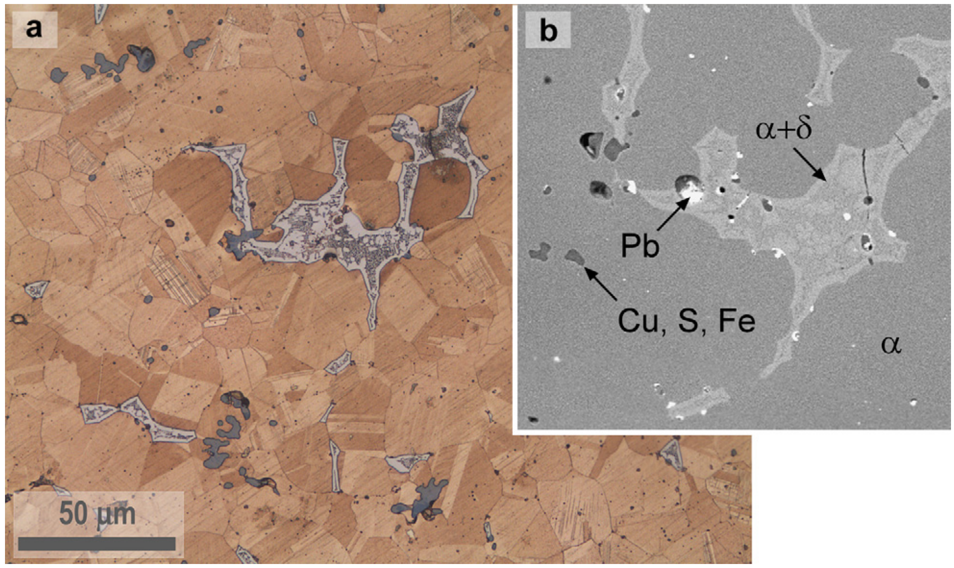

Fig. 7. Microstructure of the necklace lock CRAT05/D1/Ib/M1: (a) OM (BF-cross-section, etched); and (b) SEM image with different phases and inclusions identified by EDS.

Copper sulphide identified as being a common inclusion in our prehistoric bronze artefacts do not necessarily imply the smelting of sulphidic ores (e.g. chalcopyrite, bornite and covellite) often associated with more recent metallurgical processes. These inclusions could also arise from impurities present in oxidic copper ores (Chernykh et al., 1998).

The operational sequences identified in the manufacture of the artefacts collected from Castro dos Ratinhos, (Fig. 10) confirm the alloy sorting, since artefacts with higher tin contents, which are harder and more difficult to work, were kept in as-cast condition, while functional tools and ornaments were often mechanically and thermally worked. One of the most common operational sequences consists of one or more cycles of forging and annealing, which presents a relative frequency of 24%. Annealing restores the ductility lost during hammering, enabling yet further deformation by forging. Often, these cycles were ended with a final forging procedure in order to produce a harder alloy (with a relative frequency of 43%). The operational sequence of annealing of the cast alloy and followed by forging is only residual (with a relative

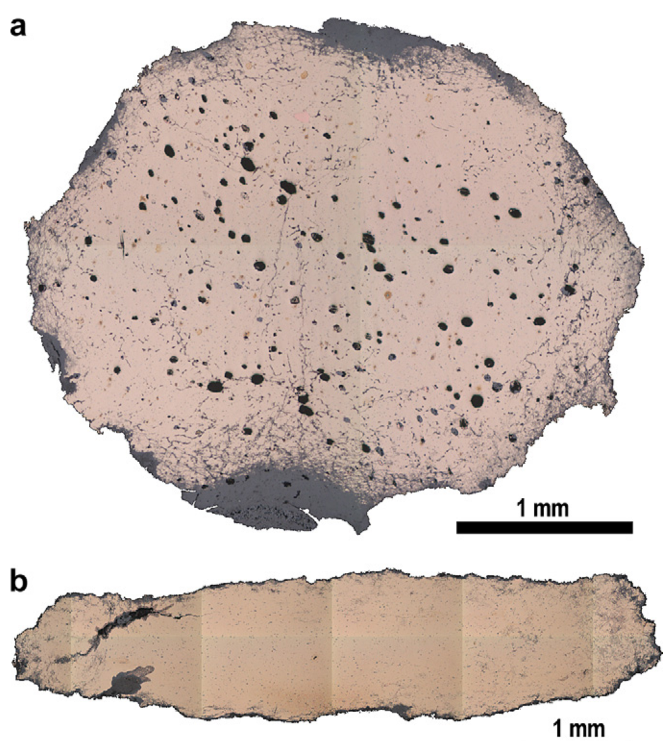

Fig. 8. (a) pores in ring CRAT06/D1/IIa/M1 and (b) cracks in flat fragment CRAT06/S1/Ia/M1.

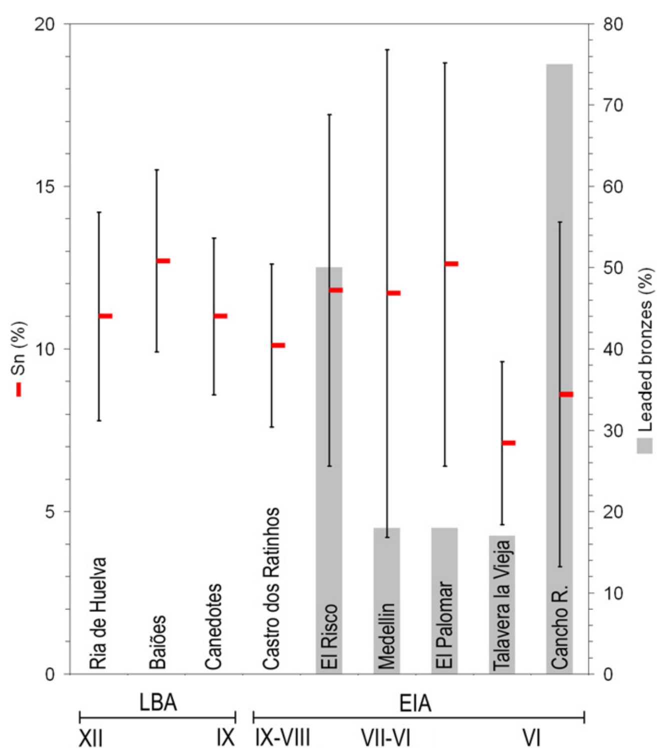

Fig. 9. Average ± standard deviation of tin contents and relative frequency of leaded bronzes in copper–tin alloys belonging to LBA and EIA sites from Portuguese territory and South-Western area of the peninsula.

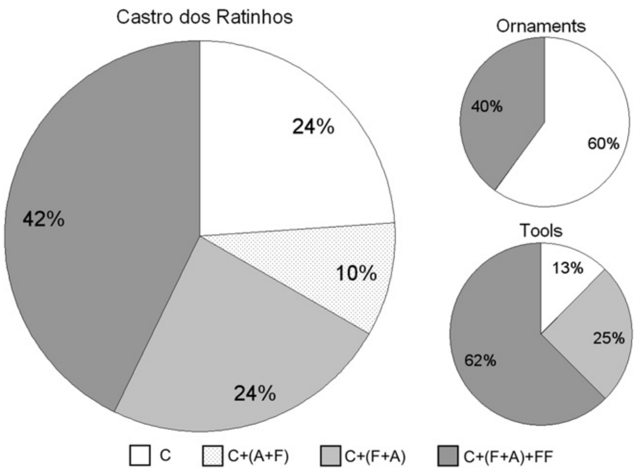

Fig. 10. Relative frequencies of operational sequences used in artefacts from Castro dos Ratinhos (C – Casting; A – Annealing; F – Forging; FF – Final forging).

frequency of 10%), as has been noted in other studies concerning the early metallurgy in the Iberian Peninsula (Rovira, 2004).

6. Conclusions

Copper based artefacts which were collected at Castro dos Ratinhos, namely those of EIA contexts, are without exception manufactured with binary alloys (Cu + Sn) with a suitable tin content (10.1 ± 2.5%). Recycling seems to be absent, whereas alloying was probably carefully controlled to obtain alloys with a narrow range of tin concentrations. Distinct operational sequences were applied according to the artefact functionality, i.e. ornaments were almost always kept in an as-cast condition, while tools were frequently produced by forging and annealing cycles. The low iron content found in bronzes from Castro dos Ratinhos (<0.05%) seems to indicate the use of crucible furnaces instead of the more efficient smelting furnaces employed by Phoenician–Iberian cultures. All these technological characteristics point towards a metallurgical practice inherited by the LBA indigenous tradition.

In fact, despite the presence of some Orientalising traces (e.g. rectangular habitat structures and wheel-turned ware) in the EIA contexts from Castro dos Ratinhos, the bronze metallurgy revealed no evidence whatsoever of any of the technological innovations in this field brought by the Phoenicians. These technological innovations in bronze metallurgy are noticeable in neighbouring South-Western EIA Iberian sites, such as Medellin, El Palomar or Cancho Roano. Nevertheless, it should be pointed out that these sites are dated back from the 6th century or at its most, from the end of the 7th century BC, such as is the case of few archaeological contexts from Medellin, while Castro dos Ratinhos is dated from the 8th century and to the end of the 9th century BC. These chronological differences may explain the distinct metallurgies recorded in the aforementioned EIA sites.

Cultural and technological improvements introduced by the Phoenicians were probably not immediately adopted by the indigenous communities, namely by those who inhabited the inland. If on the one hand some innovations arrived fast towards the inland, others seem to have had a slower dissemination, such as those related to the bronze metallurgy. Orientalising inland sites that present evidence of a more advanced bronze metallurgy are dated from the 7th to 6th centuries BC, i.e. one or two centuries after the foundation of the Phoenician colonies in the Iberian coasts. It seems that the Phoenician interaction with inland indigenous communities was not only a slow, but also a selective process, probably very dependent on the social-economic and cultural evolution of the local societies.

In conclusion, taking into account not only the chemical and metallographic results but also the interesting collection of bronze artefacts itself, together with the material culture recovered during the archaeological excavations at this important proto-historic settlement, Castro dos Ratinhos provides a new insight on the understanding of the Phoenician colonisation and cultural exchange in the Iberian Peninsula during the first steps of the so-called Orientalising Period.

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