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A multianalytical approach to study the Phoenician bronze technology in the Iberian Peninsula—A view from Quinta do Almaraz

P. Valério[a,*], R.J.C. Silva[b], M.F. Araújo[a], A.M.M. Soares[a], L. Barros[c]

[a]Instituto Tecnológico e Nuclear, Instituto Superior Técnico, Universidade Técnica de Lisboa, Estrada Nacional 10, 2686-953 Sacavém, Portugal
[b]CENIMAT/I3N, Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, FCT, Universidade Nova de Lisboa, 2829-516 Monte de Caparica, Portugal
[c]Museu Municipal de Almada, Olho de Boi, 2800-205 Almada, Portugal

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ABSTRACT

Phoenician settlers were responsible for very important changes on the metallurgical practices used in the Iberian Peninsula during the first half of the 1st millennium BC. The study of copper-based artefacts from the Phoenician settlement of Quinta do Almaraz (Portugal) was used to characterise exogenous influences on local metallurgy. Micro-EDXRF analyses on cleaned metal surfaces identified copper, low-tin bronze (2.2 to 8.1 wt.% Sn) and leaded bronze artefacts (4.6 to 5.9 wt.% Pb). Additionally, significant impurities of iron were found (0.15 to 1.3 wt.% Fe) suggesting the smelting of copper ores under a strong reducing atmosphere. SEM-EDS and optical microscopy identified polygonal and nearly equiaxial α-copper grains with annealing twins and slip bands, which indicate comprehensive manufacturing procedures involving hammering and annealing operations. Vickers microhardness testing was utilised to assess the mechanical performance attained by ancient metallurgists. The microstructural features and microhardness values showed that a common approach was to workharden the artefact with a strong final hammering (discernible by high density of slip bands), although some examples also benefited from a highly skilful usage of the forging plus annealing cycles (uniform and very small grain size). Comparison with coeval collections from the southwestern Iberian Peninsula has established that the metals in the settlement of Quinta do Almaraz were produced by a different technology from the indigenous metallurgy.

1. Introduction

An integrated approach has been developed in order to investigate the ancient metallurgy in the Portuguese territory. The metallic artefacts are characterised with microanalytical techniques to avoid a significant cleaning that could affect the chemical or physical integrity. Studies have involved the determination of the elemental composition of artefacts to establish the usage of different metals and alloys during a given period. Additionally, the microstructural features and hardness of the artefacts have been determined to establish the type and efficiency of manufacturing procedures. The combination of analytical data with typological and archaeological evidence has been providing new indications on the metallurgical processes used by early metallurgists.

* *Corresponding author.* Tel.: +351 219946207; fax: +351 219946185.
E-mail addresses: pvalerio@itn.pt (P. Valério), rjcs@fct.unl.pt (R.J.C. Silva), faraujo@itn.pt (M.F. Araújo), amsoares@itn.pt (A.M.M. Soares), barrosrat@gmail.com (L. Barros).

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Recent metallurgical research in the Iberian Peninsula has shown that one of the most interesting periods occurred during the first half of the 1st millennium BC. The copper-based metallurgy in this region during the Late Bronze Age (~1200–800 BC) was mostly characterised by copper–tin alloys [1], with the exception of northwestern area that was more associated with leaded bronzes. The establishment of Phoenician colonies in the southern and western coastal regions during the late 9th and early 8th century BC brought numerous innovations. The settlers came from a region where the bronze alloy was known for over a millennium, whilst weapons and tools were made with iron [2]. Consequently, the Iberian metallurgy during the Early Iron Age (~800–400 BC) has become more diversified. Several 8th–7th century BC inland settlements in the southwestern region, such as El Palomar (Spain) [3], Medellin (Spain) and El Risco (Spain) [4], exhibit a significant amount of leaded bronze and copper artefacts. On the contrary, only binary bronzes are present in the 9th–8th century BC settlement of Castro dos Ratinhos (Portugal), located about 150 km to inland in the southern Portuguese territory [5]. It seems that in spite of the modifications in the neighbouring region, the metallurgy of this western end of the Iberian Peninsula remained almost unchanged.

Due to scarcity of archaeometallurgical investigations in the Portuguese territory, new studies become absolutely essential to the understanding of the metallurgical evolution of this region, especially those concerning materials recovered in Phoenician colonies. The study of the metallic collection from the Phoenician site of Quinta do Almaraz, Portugal (Fig. 1) can give an excellent contribution on the subject. The archaeological excavations conducted at this coastal settlement revealed a diversified material culture, including copper-based, iron and gold artefacts, together with a significant amount of slags and crucibles [6]. A preliminary study based on EDXRF analyses in not cleaned surfaces of the artefacts has clearly indicated the importance of this collection, which is constituted by copper-based artefacts with rather variable amounts of tin and lead, iron artefacts and crucibles with evidences of the production of silver and gold [7]. The radiocarbon dating of stratigraphic layers from this archaeological site established that the artefacts can generally be ascribed to the 9th–7th centuries BC, even though a reduced percentage might belong to a wider period that continues up to the 5th century BC [8].

The collection of 23 copper-based artefacts selected for this study comprises simple typologies that were commonly used by ancient people, including bracelets and fibulae used to fasten clothing (Fig. 1). Several examples reveal further details about the everyday life at this seaboard settlement, as fishhooks for fishing, awls for working with leathers and arrowheads for hunting. Some artefacts present typologies that were common in the Iberian Peninsula during the Early Iron Age, such as the Acebuchal fibulae (e.g. MAH4414 and MAH9622) [9]. Nevertheless others, such as the tweezers (MAH4411) are relatively rare amongst the archaeological record of this region, clearly suggesting the foreign influences at the settlement.

The present work presents the micro-EDXRF analyses of cleaned surfaces of the artefacts to determine their elemental composition. EDXRF spectrometry has been widely used to study ancient artefacts, mostly due to its non-invasive, fast and multielemental nature [10]. Usually, the study of metallic artefacts involves also a microstructural characterisation with SEM-EDS and optical microscopy to determine the manufacturing procedure [11]. Additionally, this work discusses the effectiveness of the manufacturing procedures by measuring the microhardness of the metallic artefacts. The analytical data obtained from the copper-based artefacts from Quinta do Almaraz was compared with known patterns from coeval collections belonging to the southwestern Iberian Peninsula. The present study characterises for the first time the metallurgy introduced by Phoenician settlers in the Portuguese territory, adding considerable information to the knowledge on the metallurgical evolution occurred in the Iberian Peninsula during the Early Iron Age.

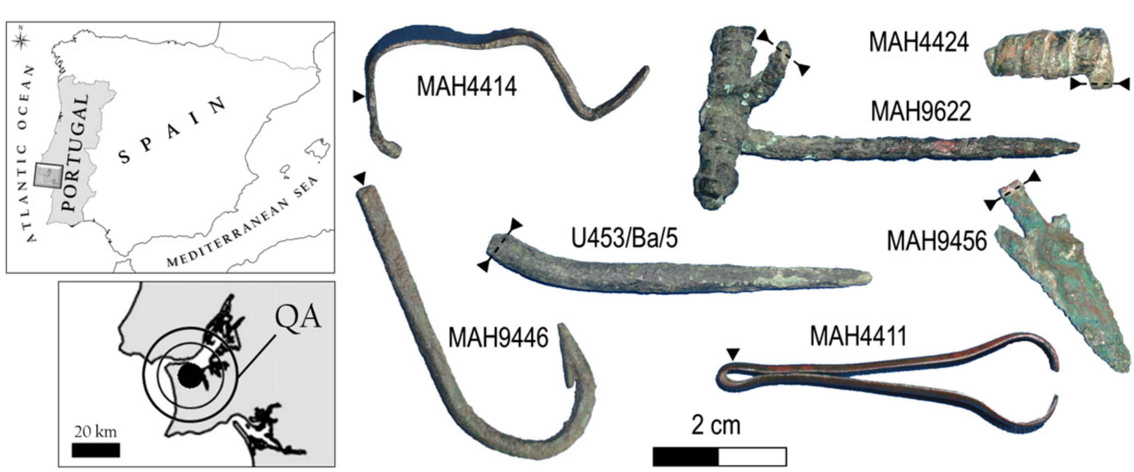

Fig. 1 – The location of Quinta do Almaraz in the western end of the Iberian Peninsula and some of the copper-based artefacts recovered during archaeological excavations (each artefact presents the area analysed).

2. Material and Methods

Artefacts were polished in a small area (∅ ~ 3–5 mm) using a manual drill and diamond pastes (up to 1 μm finishing). Optical microscopy observations ensured that the depth of polishing was enough to guarantee a cleaned metal surface for analysis. Specimens that were already fragmented were carefully sectioned using a manual jeweller's saw. The small section was mounted in an epoxide resin and polished using silicon carbide papers and diamond pastes (up to 1/4 μm finishing). After the analyses, the polished/sectioned areas were protected with corrosion inhibitor (benzotriazol dissolved in ethanol; 3% m/v) followed by an acrylic protection coating (Paraloid B-72 dissolved in acetone; 3% m/v). To replicate the coloration of the surrounding patina a mixture of pigments dissolved in the acrylic solution was applied followed by a final protection of microcrystalline wax.

Elemental compositions were given by micro-EDXRF analyses made with an ArtTAX Pro spectrometer equipped with a Mo X-ray tube, focusing polycapillary lens and silicon drift electro-thermally cooled detector (160 eV at 5.9 keV). The accurate positioning system and polycapillary optics enable a small area of primary radiation (∅ < 100 μm) at the sample [12]. Elemental compositions were obtained from the average of three independent spots, analysed with a tube voltage of 40 kV and a current intensity of 0.5 mA during 300 s. Quantifications were made with the WinAxil software. Experimental calibration factors were calculated with two reference materials—British Chemical Standards Phosphor Bronze 551 and BNF Metals Technology Centre Leaded Bronze C50.01. Accuracy was assessed with the Phosphor Bronze 552 reference material—the relative errors obtained were less than 2% for major elements and less than 10% for the minor ones. The quantification limits of minor elements present in the bronze alloys analysed are 0.10 wt.% Pb; 0.10 wt.% As and 0.05 wt.% Fe. Additional details concerning sampling and other experimental features have been previously published [13].

Microstructural characterisation involved the combined use of SEM-EDS analyses and optical microscopy observations. SEM analyses were made with a conventional tungsten filament scanning electron microscope (Zeiss DSM 962) with secondary electron (SE) and backscattered electron (BSE) imaging modes. The equipment also comprises an Oxford Instruments INCAx-sight EDS spectrometer with an ultra-thin window to detect elements with low atomic number (Z > 5). Typically, the analyses involved a working distance of 25 mm, 20 kV of accelerating voltage, approximately 3 A of filament current and 70 μA of emission current. The optical microscopy observations were made with a Leica DMI 5000M optical microscope. Samples were observed unetched and etched with aqueous ferric chloride solution, under bright field (BF), dark field (DF) and polarised light (Pol) illumination. Further experimental details including the preparation of the samples were previously described [5].

Vickers microhardness was determined in Zwick-Roell Indentec equipment using a low weight indentation of 0.2 kg and a dwell time of 10 s. The microhardness is given by the average value of at least three indentations, having a relative standard deviation lower than 5%. To ensure a good accuracy only the samples mounted in epoxide resin were tested.

3. Results and Discussion

Micro-EDXRF analyses of artefacts from Quinta do Almaraz have identified copper-based materials with highly variable amounts of tin and lead, together with impurities of iron and arsenic. These results allowed the classification of the

Table 1 – Results from micro-EDXRF analyses of artefacts from Quinta do Almaraz (values in wt.%; n.d.: not detected).

Artefact	Reference	Cu	Sn	Pb	As	Fe
Fibula	MAH4414	98.8 ± 0.2	n.d.	0.24 ± 0.08	0.66 ± 0.06	0.25 ± 0.01
Fragment	A12/4/19A	97.0 ± 0.3	1.4 ± 0.1	1.1 ± 0.3	n.d.	0.45 ± 0.01
Fragment	A12/8/31A	99.3 ± 0.1	n.d.	0.41 ± 0.04	n.d.	0.27 ± 0.02
Fragment	J282/4/12A	97.8 ± 0.1	1.6 ± 0.1	0.18 ± 0.02	n.d.	0.37 ± 0.02
Fragment	U453/11/117	98.1 ± 0.2	1.4 ± 0.2	0.10 ± 0.01	n.d.	0.31 ± 0.01
Rivet	A12/34B	99.7 ± 0.1	n.d.	< 0.10	< 0.10	0.21 ± 0.01
Rivet	J294/5/10	97.8 ± 0.2	1.2 ± 0.2	< 0.10	n.d.	0.91 ± 0.05
Cauldron handle	MAH4403	99.6 ± 0.1	n.d.	< 0.10	< 0.10	0.36 ± 0.01
Arrowhead (tang)	MAH9456	91.5 ± 0.2	8.1 ± 0.2	0.20 ± 0.02	n.d.	0.15 ± 0.01
Awl	C4/3/9	94.3 ± 0.1	5.3 ± 0.1	0.23 ± 0.01	n.d.	0.16 ± 0.01
Awl	U453/Ba/5	95.6 ± 0.2	3.2 ± 0.2	0.63 ± 0.16	n.d.	0.42 ± 0.01
Bracelet	MAH9600	93.8 ± 0.2	5.3 ± 0.2	0.19 ± 0.02	n.d.	0.68 ± 0.02
Bracelet	U453/11/81	93.8 ± 0.2	5.9 ± 0.2	n.d.	n.d.	0.27 ± 0.02
Fibula	MAH9622	92.9 ± 0.1	6.2 ± 0.2	0.66 ± 0.04	n.d.	0.24 ± 0.02
Fibula (pin)	A12/34A	90.9 ± 0.2	8.0 ± 0.1	0.19 ± 0.01	n.d.	0.80 ± 0.01
Fibula (spring)	MAH4424	94.1 ± 0.4	5.0 ± 0.4	0.58 ± 0.12	n.d.	0.29 ± 0.01
Fish-hook	J274/4/19	92.0 ± 0.1	7.2 ± 0.1	0.16 ± 0.01	n.d.	0.58 ± 0.01
Fragment	A12/4/19B	96.7 ± 0.2	2.2 ± 0.2	0.60 ± 0.07	0.10	0.36 ± 0.01
Fragment	A12/8/31B	90.8 ± 0.3	7.7 ± 0.2	0.16 ± 0.01	n.d.	1.3 ± 0.1
Fragment	J282/10/32A	94.1 ± 0.9	4.8 ± 0.9	0.55 ± 0.02	n.d.	0.50 ± 0.01
Fragment	J282/6/18A	96.1 ± 0.2	3.0 ± 0.2	0.28 ± 0.04	n.d.	0.64 ± 0.01
Fish-hook	MAH9446	91.5 ± 0.2	2.4 ± 0.1	5.9 ± 0.2	n.d.	0.16 ± 0.01
Tweezers	MAH4411	88.9 ± 0.8	6.2 ± 0.3	4.6 ± 0.6	n.d.	0.27 ± 0.03

collection in three different clusters, namely “unalloyed” copper, binary bronze and leaded bronze (Table 1).

The iron content of the artefacts is relatively high (0.43±0.28 wt.%) when compared with coeval bronzes from this region, which commonly have less than 0.05 wt.% Fe [5]. The increase in the amount of iron was first observed by Craddock and Meeks when comparing Late Bronze Age and Phoenician–Iberian bronzes from the southeastern Iberian Peninsula: the average iron content increased from 0.04 wt.% to 0.27 wt.% [14]. Other studies comprising Iron Age collections from the southwestern region endorse the higher iron contents of protohistoric bronzes across the Iberian Peninsula. Some examples can be found at Palhais, S Portugal (0.68±0.22 wt.% Fe [15]), El Palomar, SW Spain (0.38±0.15 wt.% Fe [3]), Talavera la Vieja, SW Spain (0.18±0.08 wt.% Fe [16]), Cancho Roano, SW Spain (0.29±0.20 wt.% Fe [4]) and Morro de Mezquitilla, SW Spain (0.36±0.33 wt.% Fe [17]). Actually, this increase has been used as a technological indicator of the bronze metallurgy all over the Mediterranean region [18]. The difference was understood to be the result of more efficient smelting operations carried out at these settlements. The copper ores were processed under higher reducing conditions, allowing for the iron impurity reduction that would be incorporated in the metallic bath [14]. The copper obtained could be purified down to iron contents of about 0.5 wt.%, but further reduction would be increasingly difficult and needless since it would not bring any noticeable improvement to the mechanical properties of the artefact [19]. Therefore, the high iron content of the artefacts from Quinta do Almaraz strongly suggests a foreign metallurgical technology, not previously acknowledged in the Portuguese archaeological record.

Similarly, the leaded bronzes (fish-hook MAH9446 and tweezers MAH4411) are a novelty amongst the coeval archaeological record from this region. However, the reduced number of leaded bronzes in this collection evidences the still low propensity to work with this alloy. SEM-EDS analyses of a binary bronze (fibula MAH9622, 0.66 wt.% Pb) plus a leaded bronze (fish-hook MAH9446, 5.9 wt.% Pb) clearly indicate the presence of lead inclusions with interdendritic and globular morphologies (Fig. 2). These low melting point inclusions are dispersed along α-Cu grain boundaries due to the low miscibility of lead in copper, being responsible by the higher castability of leaded bronzes over binary bronzes. The simple and small artefacts studied would hardly beneficiate from a high castability, whereas a high lead content might be disadvantageous for those artefacts that require higher strength due to the low hardness of lead-rich inclusions.

Most of the collection is composed of binary bronze alloys with lower tin contents (5.4±2.0 wt.%) than the indigenous alloys from the same period. For instance, the collection of Castro dos Ratinhos is composed of bronze alloys typical of the Late Bronze Age tradition, i.e. 10.1±2.5 wt.% Sn. Neighbouring collections from the Spanish territory are composed of similar alloys despite a somewhat higher range of the amount of tin. Some examples can be found in the sets from El Palomar (12.6±6.2 wt.% Sn), Medellin (11.7±7.5 wt.% Sn) and El Risco (11.8±5.4 wt.% Sn). On the contrary, other examples with reduced tin contents (Palhais: 4.4±2.4 wt.%, Talavera la Vieja: 7.2±2.5 wt.% and Cancho Roano: 7.2±3.2 wt.%) already belong to a late period (6th century BC). Thus the bronze metallurgy

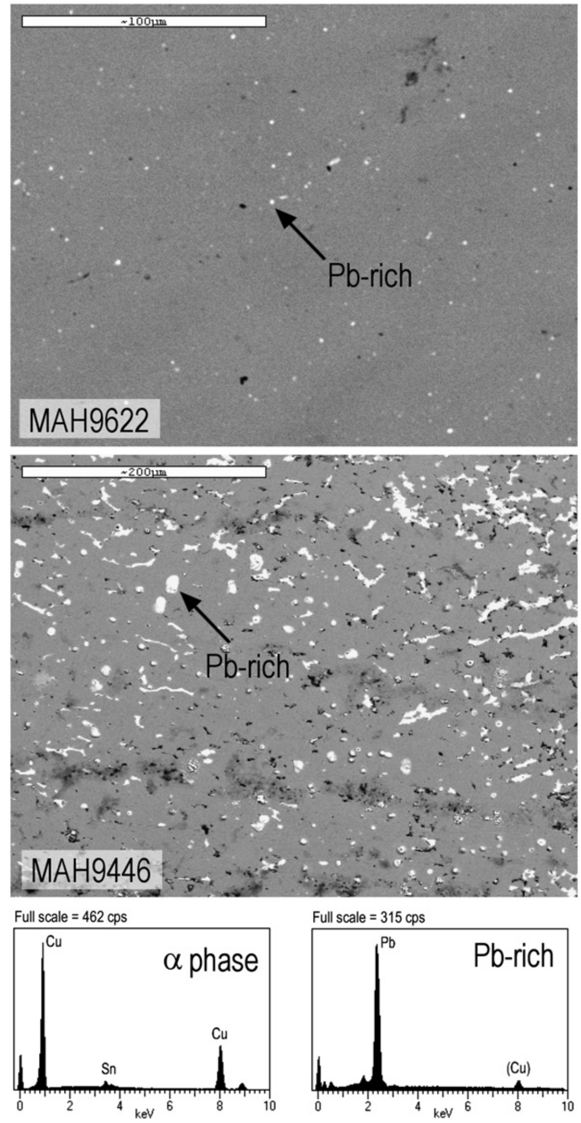

Fig. 2 – SEM-BSE images of fibula MAH9622, fish-hook MAH9446 and tweezers MAH4411 from Quinta do Almaraz (EDS spectra of α phase, Pb-rich inclusion, Cu–S inclusion and Cu–Fe–S inclusion).

at Quinta do Almaraz remains a unique example in this western end of the Iberian Peninsula. The presence of different metallurgical traditions in neighbouring regions is common throughout the Mediterranean Region. For instance, the comparison of Italian (~6 wt.% Sn) and Sardinian (~8–9 wt.% Sn) bronzes reveals the conservative metallurgical tradition of the island during this period [17].

A bronze metallurgy based in low tin contents is usually attributed to a significant use of bronze scrap since the preferential oxidation of tin during melting results in the depletion of this element in the alloy. Experimental trials proved that a bronze alloy with 10 wt.% Sn would be reduced to about 3 wt.% Sn after a few melting operations [20]. Nevertheless, additional factors must be considered when analysing the low-tin metallurgy of Phoenician settlements in the Iberian Peninsula. The few studies about the Late Bronze Age

Table 2 – Results from optical microscopy, SEM-EDS and Vickers microhardness testing of copper-based artefacts from Quinta do Almaraz (Sn in wt.% given by micro-EDXRF; C: Casting; A: Annealing; F: Forging; FF: Final Forging; ↑: high amount; ↓: low amount; hardness in HV).

Artefact	Reference	Sn	Phases	Inclusions	Manufacture	Hardness
Fibula	MAH4414	n.d.	α	Cu–S	C+(F+A)	–
Fragment	U453/11/117	1.4	α	Cu–S	C+(F↑+A)	–
Fragment	J282/4/12A	1.6	α	Cu–S	C+(F+A)	133±6
Fragment	A12/8/31A	n.d.	α	Cu–S↑	C+(F+A)	108±4
Fragment	A12/4/19A	1.4	α	Cu–S↑	C+(F↑+A)	150±5
Rivet	J294/5/10	1.2	α	Cu–S	C+(F+A)+FF	117±6
Rivet	A12/34B	n.d.	α	Cu–S	C+(F+A)+FF	140±3
Cauldron handle	MAH4403	n.d.	α	Cu–S	C+(F+A)	–
Arrowhead (tang)	MAH9456	8.1	α	Cu–S	C+(F+A)	97±1
Awl	C4/3/9	5.3	α	Cu–S	C+(F+A)+FF↑	142±7
Awl	U453/Ba/5	3.2	α	Cu–S↑	C+(F+A)+FF	113±7
Bracelet	MAH9600	5.3	α	–	C+(F+A)+FF↓	–
Bracelet	U453/11/81	5.9	α	Cu–S	C+(F+A)+FF↑	204±11
Fibula	MAH9622	6.2	α	Cu–S	C+(F+A)	103±2
Fibula (pin)	A12/34A	8.0	α	Cu–S	C+(F+A)+FF↓	–
Fibula (spring)	MAH4424	5.0	α	Cu–S	C+(F+A)+FF↑	221±4
Fish-hook	J274/4/19	7.2	α	Cu–S	C+(F+A)	–
Fragment	A12/4/19B	2.2	α	Cu–S	C+(F+A)	–
Fragment	A12/8/31B	7.7	α	Cu–S↑	C+(F+A)	158±5
Fragment	J282/10/32A	4.8	α	Cu–S	C+(F+A)+FF	237±1
Fragment	J282/6/18A	3.0	α	Cu–S	C+(F+A)+FF↑	158±2
Fish-hook	MAH9446	2.4	α	Cu–S	C+(F+A)+FF	–
Tweezers	MAH4411	6.2	α	Cu–S	C+(F+A)+FF	–

production of bronze in this region seem to point to the direct smelting of copper and tin ores [1,21]. At first glance, the somewhat variable metal content of ores and the changeable smelting conditions could hinder the production of bronzes with appropriate tin contents. However, the archaeological record has proven the other way—suitable bronzes could be produced by co-smelting, undoubtedly due to the knowledge accumulated over several centuries. A different method of bronze production was introduced during the Early Iron Age—the earliest evidence of melting of metallic copper and tin arises from the site of Carmona, SW Spain [22]. This method increased the compositional diversity of artefacts. Besides, the use of bronze scrap as a cheap source of tin would produce bronzes with much lower amounts of this element. The low-tin bronzes and few copper artefacts with impurities of tin (<2 wt.%) at the Phoenician settlement of Quinta do Almaraz most certainly resulted from this new metallurgy.

The copper artefacts from Quinta do Almaraz evidence the use of an inexpensive raw material to produce basic tools and ornaments. Copper artefacts are very scarce during the Late Bronze Age, but its use increases significantly during the following period, as evidenced, for instance by the study of about 200 artefacts from the southeastern Iberian Peninsula [23]. In some settlements copper was mainly used for specific typologies, for instance about 70% of the nails and rods from Morro de Mezquitilla are composed of copper, whilst the fibulae and pins are predominantly made with bronze (~6 wt.% Sn). However, the selection of alloys according to the type of artefact is not evident amongst the materials from Quinta do Almaraz. The fibulae are made either with copper (MAH4414) or bronze (MAH9622, A12/34A and MAH4424), whilst the fish-hooks are composed of binary bronze (J274/4/49) or leaded bronze (MAH9446). The copper rivets (A12/34B and J294/5/10) might be an exception because copper is known to be softer than bronze. The absence of a relation amongst the use of copper or bronze and functionality of the artefact might be due to the somewhat reduced number of studied artefacts. Regarding the remaining metallic impurities, the higher arsenic content of the fibula MAH4414 might be a result from the

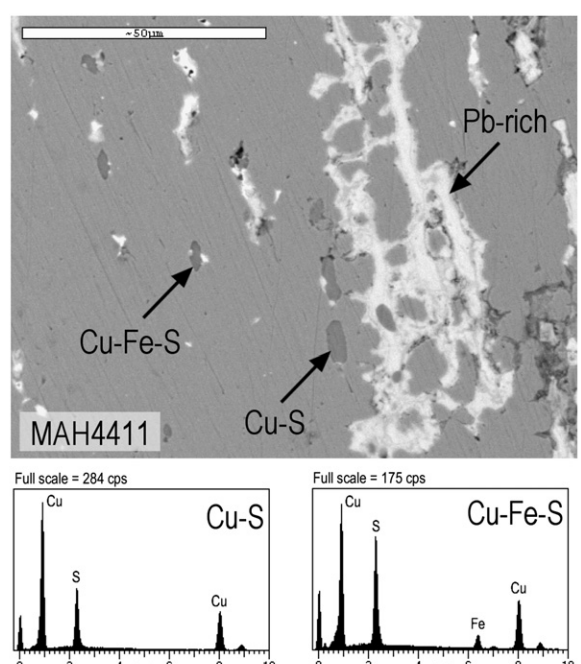

Fig. 3 – SEM-BSE image of tweezers MAH4411 from Quinta do Almaraz (EDS spectra of Cu–S and Cu–Fe–S inclusions).

exploration of a copper ore richer in arsenic or from the use of scrap richer in this element.

The optical microscopy observations evidenced many common microstructural features (Table 2). All artefacts present polygonal and near-equiaxial α grains without the α±δ eutectoid. The absence of the second phase is not only certainly related with the low Sn contents, but also reveals an efficient annealing because bronzes with similar composition often have remnants of the α±δ eutectoid. This is confirmed by the phase diagram of the Cu–Sn system, where the α±δ eutectoid is formed from ~4 wt.% Sn due to the relatively fast cooling rate of these small artefacts [24].

Optical microscopy observations have identified Cu–S inclusions in all metallic artefacts except in the bracelet MAH9600, whilst the SEM-EDS analyses have established that these inclusions are often associated to iron (Fig. 3). These sulphur-rich inclusions should result from different impurities present amongst the oxide/carbonate copper ores explored, such chalcocite, covellite, bornite or chalcopyrite.

The presence of annealing twins is an evidence of the use of forging and annealing (F+A) to manufacture these artefacts. The thermal treatment restores the ductility and softness to the workhardened material thus allowing for additional deformation. The cycle would be repeated until the artefact attains the desired shape. Excessively high temperatures lead to larger grain size and softer material (Fig. 4A), as shown by the arrowhead MAH9456 with 97 HV (note that the analysed area belongs to the tang and not to the sharp point). In the studied collection, the softened microstructures are often found in fragments with different sections (circular, quadrangular and flattened) that might belong to unfinished artefacts. Indeed the functionality of some artefacts would certainly require a higher hardness. Optical microscopy observations indicated that the common approach was to conclude the manufacturing procedure with a final hammering (FF) easily recognised by the presence of slip bands. More intense deformations are identified by a high density of slip bands leading to a harder alloy, e.g. awl C4/3/9—142 HV (Fig. 4B). Another method utilised to improve the artefact mechanical properties involves the skilled monitoring of forging and annealing cycles. Forging should produce the highest and more homogeneous deformation as possible, without rupture, whereas the conditions of the thermal treatment (temperature and time) should be the strictly necessary for a complete recrystallization. This sort of manufacturing produces a smaller grain size, which in conjunction with a final hammering results in an even harder alloy, as exemplified by the fragment J282/10/32A—237 HV (Fig. 4C). The extended range of hardnesses amongst bronze artefacts (97 to 237 HV) evidences variable manufacturing parameters (e.g.

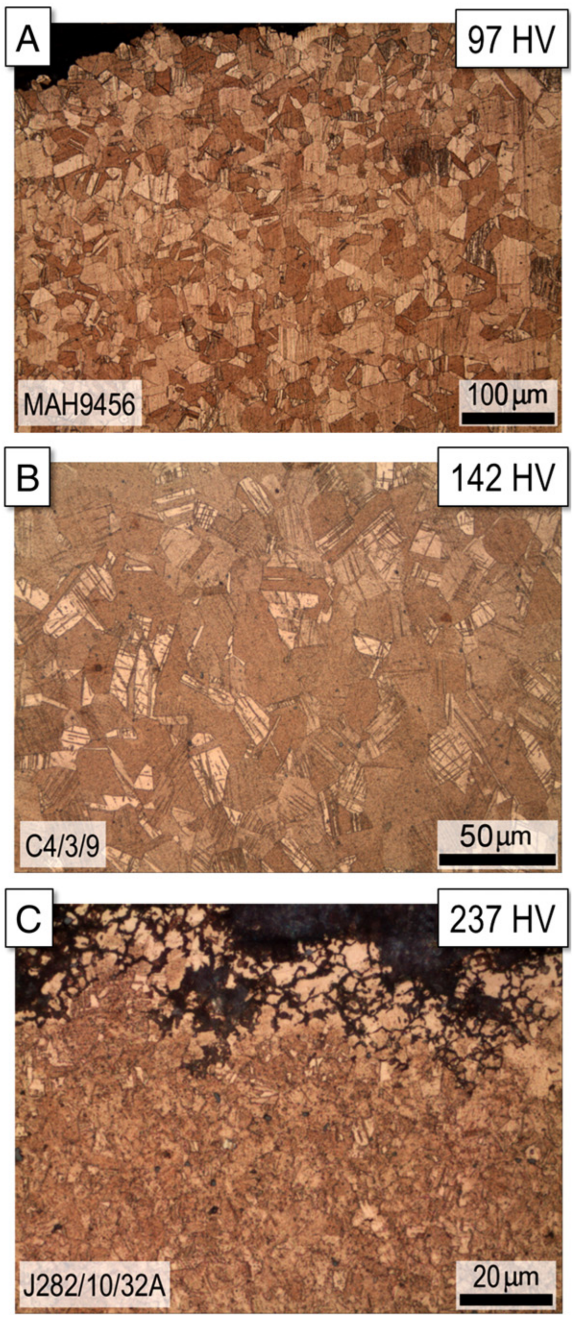

Fig. 4 – Optical microscopy images of arrowhead MAH9456, awl C4/3/9 and fragment J282/10/32A from Quinta do Almaraz (A: soften, B: workhardened and C: mechanically and "thermally" hardened; BF-etched).

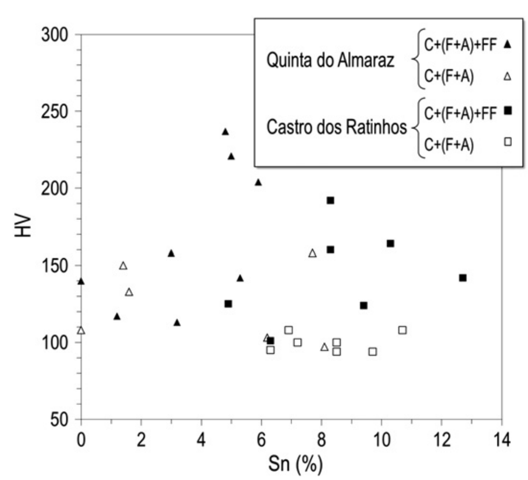

Fig. 5 – Vickers hardness of copper-based artefacts from Quinta do Almaraz and Castro dos Ratinhos.

total deformation, annealing efficiency, number of cycles and intensity of final hammering), as an outcome of the different skilfulness of metallurgists together with different artefact functionalities.

Generally, the bronzes from Quinta do Almaraz exhibit a higher hardness when compared to the artefacts of the indigenous settlement of Castro dos Ratinhos (Fig. 5). This is true for annealed (125±26 HV and 100±6 HV, respectively) and workhardened artefacts (167±48 HV and 144±30 HV, respectively). The microstructural observations indicate that this somewhat higher hardness was attained by increasing the efficiency of the hammering and annealing. In practice, this means that even low-tin bronzes could be worked to present suitable mechanical properties. It seems that the experienced Phoenician metallurgists, coming from a region with lack of tin sources, learned long ago how to improve the poorer tin alloys.

Finally, it was observed that certain metallic fragments (J294/5/10 and A12/34B) display morphological and microstructural features consistent with a rivet (Fig. 6). The head of the rivet J294/5/10 displays very elongated grains of much smaller size than in the rivet's body, probably induced by the riveting process. The extreme deformation of certain regions is also noticeable by the corrosion paths shaped by intergranular corrosion throughout these less pure areas (Fig. 6D).

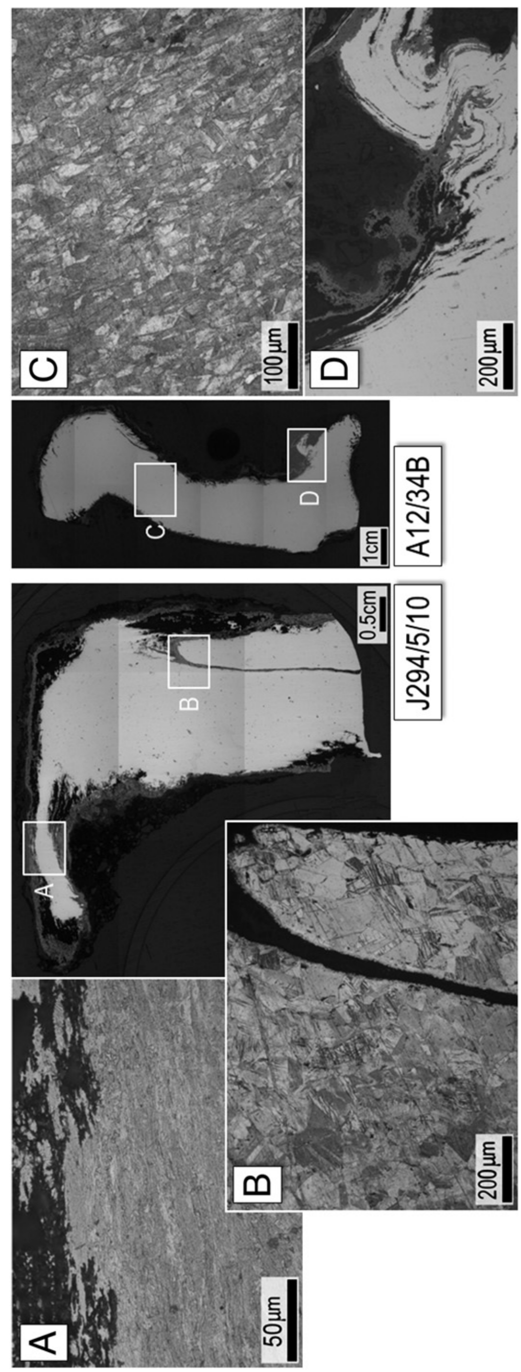

Fig. 6 – Optical microscopy images of rivets J294/5/10 and A12/34B from Quinta do Almaraz.

4. Conclusions

The artefacts of everyday usage at the Phoenician settlement of Quinta do Almaraz were composed of copper, bronze and leaded bronze alloys. The existence of a diversified metallurgy is a common characteristic of the Early Iron Age period in the southwestern Iberian region, but the coastal settlement of Quinta do Almaraz remains a unique example in the Portuguese territory. The relatively high iron content of the artefacts is typical of the Mediterranean region and resulted from an initial smelting of the raw materials under a strong reduction atmosphere. The low tin content of the bronzes is also remarkable and evidences a different method to obtain metallic artefacts. For instance, everyday tools and ornaments begin to be made with available raw materials. The mechanical drawback of low-tin bronzes was surpassed by skilful manufacturing processes, which were able to produce alloys with similar hardness to coeval bronzes richer in tin. The more common methodology was to workharden the material with a strong hammering operation. Additionally, some artefacts of even higher hardness benefited from a proficient usage of the forging plus annealing cycles.

The present study shows that the metallurgy at this Phoenician settlement was very different from the local technology inherited from the Late Bronze Age. However, the adoption of innovations by the indigenous cultures was a rather slow and unequal process. For instance, some inland settlements in the Iberian Peninsula persisted with some aspects of the indigenous metallurgy. On the other hand, the complexity of social interactions is quite evident in certain indigenous typologies that were apparently produced using Phoenician technology (e.g. Acebuchal or double-spring fibulae). These artefacts would be regional productions made by Phoenician or by local metallurgists that learned a new approach to produce metallic artefacts. Ultimately, this innovative metallurgy was the driving force behind the global evolution of the Iberian metallurgy over the Iron Age.

Finally, it must be emphasised that the multianalytical approach used in this work allowed for the characterisation of important cultural items whilst maintaining them unchanged for future studies and museological display. This is an evidence of the importance of non-invasive and micro analytical techniques to the characterisation of irreplaceable cultural artefacts.

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