Applied Radiation and Isotopes 69 (2011) 1205–1211

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Characterisation of Late Bronze Age large size shield nails by EDXRF, micro-EDXRF and X-ray digital radiography

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ARTICLE INFO

Article history:
Received 18 February 2011
Received in revised form
26 April 2011
Accepted 28 April 2011
Available online 6 May 2011

Keywords:
EDXRF
X-ray digital radiography
Non-destructive analyses
Archaeometallurgy
Late Bronze Age

ABSTRACT

In the present study six exceptional large size metallic nails, a dagger and a sickle from the Late Bronze Age archaeological site of Figueiredo das Donas (Central Portugal) have been analysed by EDXRF, micro-EDXRF and X-ray digital radiography for the study of material composition and technology of fabrication. The combination of these analytical and examination techniques showed that all artefacts are made of bronze with As, Sb and Pb impurities, and that the nails were most likely manufactured using the casting-on technique. These results reinforce the use of binary bronze by Late Bronze Age in the region, and the incorporation of new fabrication technologies that resulted from ancient spheres of interaction.

1. Introduction

Multidisciplinary studies involving chemical and physical analytical techniques applied to cultural objects, such as works of art and archaeological artefacts, are one of the most significant happenings in the last century that has contributed enormously to the understanding of past societies, ancient technologies, use of early materials and their degradation. Fields such as archaeometry and conservation science are products of such happening and are presently growing and developing.

Among these studies, various analytical techniques are being applied to very different materials (e.g. Creagh, 2005), and among them, non-destructive analyses, in the sense that most inorganic specimens are not altered by analytical procedure (Mantler and Schreiner, 2001) are frequently favoured (e.g. Adriens, 2005). In the study of ancient metals, elemental analysis such as energy dispersive X-ray fluorescence spectrometry (EDXRF) has been widely applied (e.g. Cesario et al., 2010; Guerra, 1995) due to its non-destructive character, relatively rapid and reliable results, besides being able to detect most of the constituents of ancient alloys. Also, the X-ray radiography examination method, of a non-destructive character, has been successfully applied to assist in the study of manufacturing techniques and state of conservation of diverse cultural materials (e.g. Calza et al., 2010; Scott and Maish, 2010). When artefacts cannot be subjected to any destructive or invasive procedure (such as sampling), the use of these two complementary techniques can produce relevant results for the study of ancient metallic artefact compositions and manufacturing techniques.

Late Bronze Age (LBA) (~1300–600 BC in many Western European areas) was a period that saw major interactions among distant populations and cultures (Kristiansen and Larsson, 2005), leading to the adoption of new materials and to the development of new technological skills. In the Iberian Peninsula, this period is characterised by the full adoption of bronze, as well as a diversification of the artefacts typologies, which can frequently be linked to Atlantic or Mediterranean influences (Coffyn, 1985).

Among the western Iberian Peninsula, the Central Portuguese Beiras region has been under the focus of recent archaeometallurgical studies due to the presence of interesting findings in many archaeological sites related to ancient metalwork. Among them, the Baiões/Santa Luzia cultural group (named after the largest sites) has provided a general picture of the metallurgy that was practiced in the region during LBA. Generally, the recent archaeometallurgical studies on metallic artefacts from that region have shown the prevalence of a binary bronze (Cu–Sn alloy) metallurgy with ~9–15% Sn and minor and variable

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doi:10.1016/j.apradiso.2011.04.027

amounts of Pb, As and Sb (Figueiredo et al., 2006, 2010a; Silva et al., 2008; Valério et al., 2006, 2007), and the sporadic use of copper to produce specific items when the properties of this metal were an advantage (e.g. Figueiredo et al., 2010b).

In that region, and during the first half of the XX century, six exceptional large size nails, a dagger and a sickle (Fig. 1) were found in the Figueiredo das Donas archaeological site (Vouzela) (Fig. 2). However, since their finding no archaeometallurgical study has been made on the collection.

The Figueiredo das Donas nails (Fig. 1, FD-01-06) are unique in the Iberian territory; their big size has no parallels among other nails and scarce parallels among similar items, as buttons, found in other Iberian sites (Coffyn, 1985). Detailed observations on the reverse side of the nails (Fig. 1, FD-01B to 06B) suggest that the nails are made of two independent pieces, the head and the pin, joined during the manufacture. Their large size indicates that they were used in heavy structures, and a suggestion has been made by one of the authors (J.C.S.M.) that they could have been shield nails, as those represented in warrior *stelae* attributed to a period of time that ranges from LBA to Early Iron Age and that have been found dispersed in south-western Iberian Peninsula. If this is the case, the metallic nails must have had a strong decorative function, since the shields were most likely made in an easy decaying material such as leather and/or wood, similar to others found in other European regions (Celestino Pérez, 2008).

Daggers as the one found in Figueiredo das Donas were widely used during LBA, and many have been found in Iberian contexts (Coffyn, 1985). The studied dagger (FD-07) is almost complete, and was joined to a hilt by the means of rivets (now missing), a frequent joining technique at the time. The sickle (FD-08) is complete and belongs to the Rocannes type, a typology found mainly in LBA contexts of the Portuguese territory (outside the Iberian territory only two have been found in Sardinia) (Giardino, 1995). This particular artefact appears to have been used in the past due to the worn condition of the cutting edge.

In this study the six large size nails, the dagger and the sickle, were subjected to an archaeometallurgical study performed with the aim of gathering information on the type of metallic material used in the production of the artefacts and to provide information on the technology of manufacture of the six nails. Due to the uniqueness of the collection, only non-destructive analyses were conducted. First, conventional EDXRF was performed on all the artefacts without surface preparation. This technique, when performed over patined surfaces, although not providing quantitative elemental information since the detected characteristic X-rays originate from a thin surface layer of the artefact, it allows the conclusive evaluation of the type of metal or alloy used, i.e. identification of major and minor elements. Besides, it can also provide information about special features such as the presence of composite artefacts (e.g. Cesario et al., 2010; Figueiredo et al., 2010b). After, micro-EDXRF analyses were performed in two small areas free of the superficial patina in one of the nails, in order to obtain quantitative information on the metallic composition. At last, X-ray digital radiography was performed on the six nails to investigate the union of the head and pin. This is achievable by searching for density inconsistencies that can be related to the manufacturing techniques. The combination of these analytical and examination techniques has the potential to provide a characterisation of the metallic materials and manufacturing techniques in a non-destructive way, very relevant

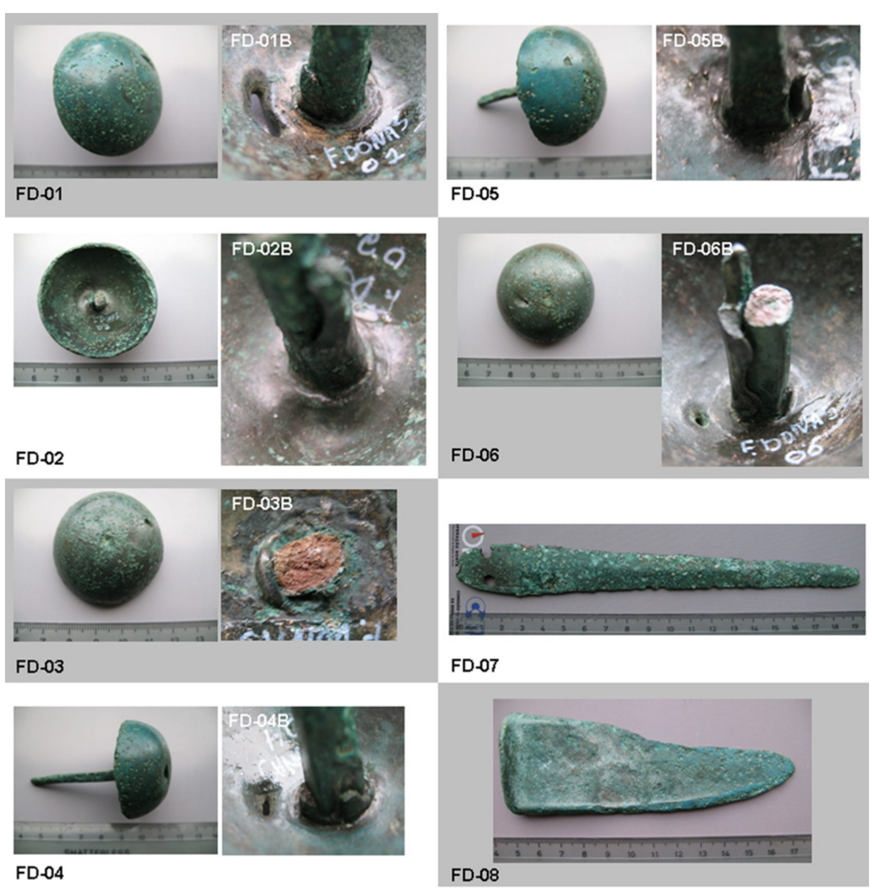

Fig. 1. Studied artefact collection from Figueiredo das Donas: nails (FD-01-06), dagger (FD-07) and sickle (FD-08). For each nail a detailed image of the head and pin junction area is shown (FD-01B-06B).

Fig. 2. Location of Figueiredo das Donas site among the Baiões/Santa Luzia LBA cultural group in the Iberian Peninsula. The emblematic site of Baiões is also depicted due to its proximity to Figueiredo das Donas.

to contextualise the artefact collection amongst the LBA metallurgical traditions.

2. Experimental

Conventional EDXRF analyses were performed on all the artefacts in two different areas, always as possible. Regarding the nails these analyses were made over the convex side of the head and over the pin, or, alternatively when the pin was missing, it was made over the concave side of the head. The analyses were conducted in a Kevex 771 spectrometer, equipped with a 200 W Rh X-ray tube with secondary targets and filters that allow the optimisation of the analytical conditions. The secondary target excitation mode was used in the present work. In this mode, the output of the X-ray tube strikes an adequate secondary target that emits X-rays with energies characteristic of the target material. The geometry of the source-detector system is a 45° incident angle and a 45° take-off angle. Characteristic X-rays are acquired by using a liquid nitrogen cooled Si(Li) detector with a resolution of 175 eV (Mn-Kα), after passing through a collimator (5 mm diameter) that allows only the X-rays that come directly from the sample into the detector. The sample spot area is close to 3 cm in diameter. Due to the contribution from the alteration patina in the results, the data was considered as semi-quantitative. The experimental setup involved two different excitation conditions: (1) silver secondary target, 35 kV, 0.5 mA and 300 s to detect Fe, Cu, As and Pb and (2) gadolinium target, 57 kV, 1.0 mA and 300 s, to detect Sn and Sb. Detailed description of the equipment, as well as the spectra processing and elemental analysis determinations have been done previously (Araújo et al., 1993, 2004).

One of the nails was analysed by micro-EDXRF on (1) a recent fracture on the pin and (2) over a small area free of corrosion products on the head to obtain the metallic composition. The micro-EDXRF analyses were performed with an ArtTAX Pro spectrometer, equipped with a low-power Mo X-ray tube (30 W), an electro-thermally cooled silicon drift detector with a resolution of 160 eV (Mn-Kα), and a set of polycapillary lens that generate a microspot of primary radiation of $\sim$70 μm in diameter (Bronk et al., 2001). The settings selected for the present analysis were 40 kV, 0.4 mA with counting times of 100 s for each analysed point. The quantification analysis involved the WinAxil software and calibration of the equipment using certified reference materials (Phosphor Bronze 551 from British Chemical Standards (BCS)). Further details on the quantification procedures have been described recently (Figueiredo et al., 2007; Valério et al., 2007).

A radiograph was obtained with the nails on different positions, to search for metal heterogeneities in order to assist the investigation on the manufacturing/joining technology. The radiographic investigation was conducted with a digital X-ray system, ArtXRay SEZ Series, manufactured by NTB GmbH (Dickel, Germany). The equipment consists of a high-power Y.MBS/160-F01 X-ray source (480 W), a digital camera radiation sensitive (10–160 kV) with a pixel size 83 μm and a resolution of 12 pixel/mm, and a manipulator that has a travelling distance of 1244 mm with a resolution of 4 μm/step. The parameters used were a maximum voltage of 130 kV and current intensity of 3.7 mA, and the focus-detector distance of 1.40 m, with the artefacts positioned within a distance of circa 20 cm from the detector. The image processing involved the iX-Pect software.

3. Results and discussion

3.1. EDXRF and micro-EDXRF analysis—artefacts metallic composition

The EDXRF analyses of the dagger (FD-07) and sickle (FD-08) showed that they were made of bronze (Cu–Sn alloy) with irregular impurities of As, Pb and Sb (Fig. 3). The low Fe contents, detected on some results, are probably due to soil incorporation on the patina (Robbiola et al., 1998).

The EDXRF analyses made on the nails, over the pins (when existent) and over the convex side of the heads, resulted in spectra with the same elements detected previously for the dagger and sickle – major Cu and Sn and minor As, Pb and Sb – with alike relative intensities (Fig. 4). These results show that both head and pin of the nails were made of bronze, probably of a

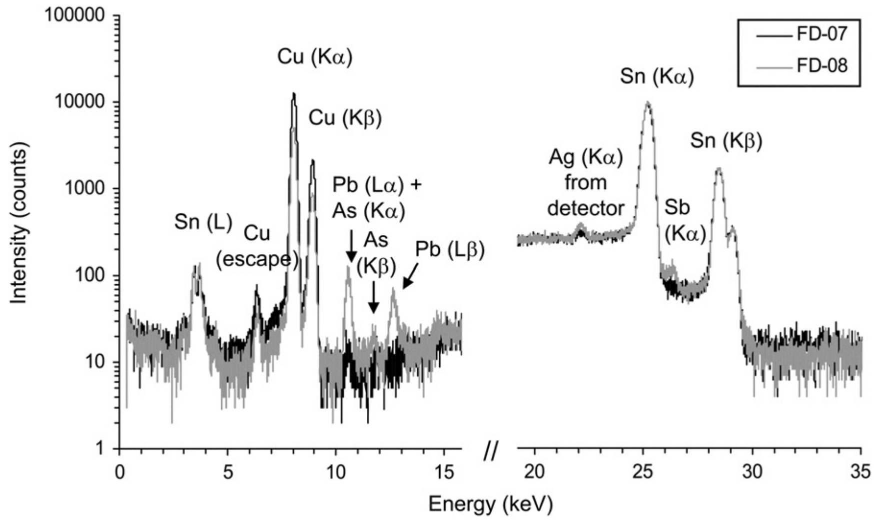

Fig. 3. EDXRF spectra of dagger (FD-07) and sickle (FD-08).

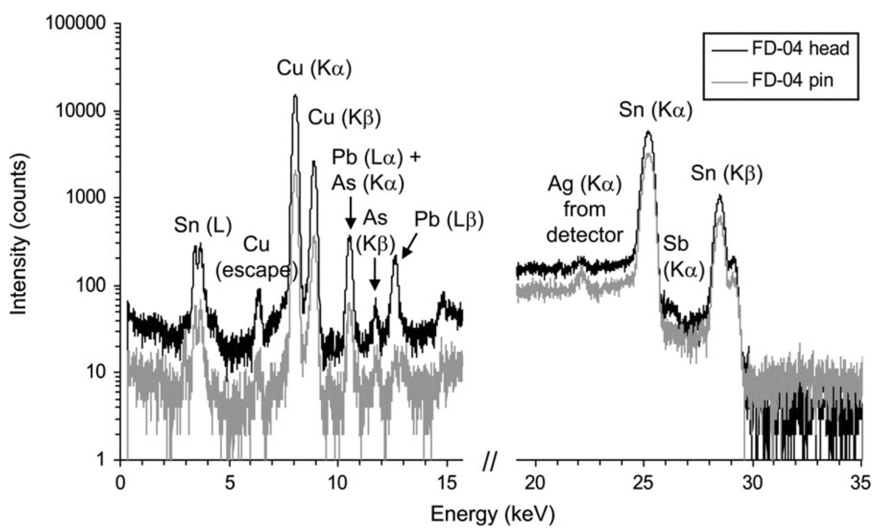

Fig. 4. EDXRF spectra of the nail FD-04 performed over the convex side of the head and over the pin (different intensities can be attributed to differences in the analysed areas that are due to the different sizes of the pieces).

similar composition. The analyses made on the convex and concave sides of the heads of those nails with broken pins, did also result in the same elements with alike relative intensities, giving no evidence of the use of a solder – a low melting temperature alloy, usually lead and/or tin rich (Coghlan, 1975) – for the joining of the pin to the head (Fig. 5).

The results of the micro-EDXRF analyses made on the nail FD-01 showed that both head and pin are made of bronze with a similar composition, with ~11 wt% Sn and impurities of Pb and As (Sb is under the detection limit <0.15 wt%) (Table 1).

This binary bronze composition relates to the metallurgical tradition of the Central Portuguese Beiras, namely to the Baiões/Santa Luzia cultural group. A bronze with ~11% Sn has optimal mechanical properties, being much harder than pure copper, and has a gold-like colour, that was probably also appreciated. The absence of a less valuable metal, such as copper, to manufacture the less visible pieces, such as the pin in the nails, may be related to the higher mechanical properties of bronze, very relevant to attach and sustain the nail in place, or to the general availability and use of bronze in relation to copper in the region during LBA.

3.2. X-ray digital radiography—manufacturing technique of the nails

The radiographic image obtained of the six nails is shown in Fig. 6. The image has been processed so that the darker areas refer to higher densities and the lighter areas to lower densities.

The radiograph shows no apparent fixing system joining the pin to the head. In those nails whose front view was examined, FD-01, 02, 03 and 06, a large bright region can be observed that in some cases is actually a hole (FD-01 and 06; FD-04 does also have a hole that is not visible in the radiographic image but can be observed in Fig. 1, FD-04B) and some small bright regions (dot-like light areas) can also be observed around the junction of pin and head.

Both the larger bright regions and the smaller dot-like bright areas in the radiograph can be related with the manufacturing process. In those nails where the larger bright region is not a hole (FD-02 and FD-03), visual observations clearly indicate that this region is constituted by a thinner metal than the surrounding regions. This is also true for FD-05 (not visible in the radiograph due to its positioning). These observations exclude the presence

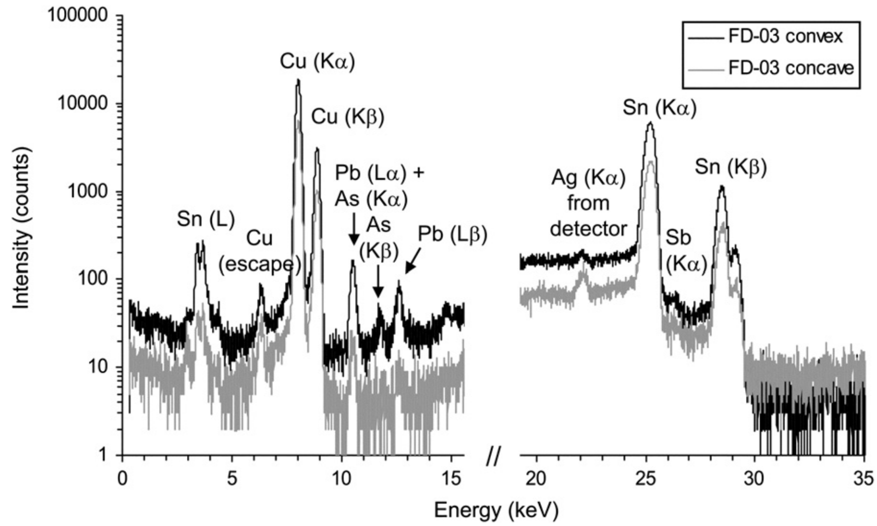

Fig. 5. EDXRF spectra of the head of the nail FD-03 performed over the convex and concave sides (different intensities are due to geometrical factors caused by the different surface shapes).

Table 1
Results of micro-EDXRF analyses performed on nail FD-01 (wt%, normalised).

	Cu	Sn	Pb	As
Head	88.5	10.9	0.11	< 0.1
Pin	88.4	11.4	0.14	< 0.1

of a closed void (e.g. large pore), and do not point out to metallic composition heterogeneities. The holes (in FD-01, 04 and 06) and the thinner metal regions (in FD-02, 03 and FD-05), all situated near the top of the heads, are probably a result of a large gas bubble entrapped in the mould, indicating difficulties in a proper escape of gas and in a free flow of metal to all parts of the work.

The small dot-like regions around the junction of pin and head suggest either the presence of gas bubbles entrapped in the contact zone of the two metallic parts, or the development of some corrosion along that contact zone, creating less dense regions. This supports the visual examination that suggested that the nails were manufactured by two independent pieces, joined during manufacturing, in contrast to one single piece, as would have resulted from a one-stage casting operation.

It is interesting to note that the heads of the nails are exactly of the same size and shape, and present quite smooth surfaces. If the lost-wax casting technique was employed in the manufacture of the heads, the use of a spinning wheel to shape each model in bees-wax could be one explanation to the homogeneity and control of the shapes. The use of these techniques (lost-wax casting and spinning wheel) during LBA in the Iberian Peninsula has been suggested by Perea and Armbruster (2008) for the manufacture of gold cylindrical shape items, such as the bracelets from Villena/Estremoz, with perfect symmetries. Otherwise, the heads of the six items could have been manufactured in the same mould resulting in identical shapes—a bivalve metal or stone mould could resist to multiple castings in comparison to the one-piece ceramic mould used in the lost-wax casting technique that was fragmented to recover the metallic object. The use of the same mould would probably better explain the recurrent region of metal lack next to the top of the heads of the nails (a hole in some cases). If different moulds were used to manufacture each nail (as would be necessary in the case of lost-wax casting technique) defects would most likely be avoided by improving the procedure each time.

The detailed visual observation of the contact surfaces of the pin and head shows that in all the nails a small portion of metal frequently in the form of a run-off (droplet) extending from the head along the pin surface is present. One of them, in the nail FD-06, was analysed by micro-EDXRF and the spectrum showed that it was of binary bronze, in agreement with the head and pin alloy (this analysis has not been presented in the previous section). In some of the nails these droplets have been broken. In those pins that have a near-quadrangular cross-section, the droplet follows the plain surfaces rather than the edges. These portions of metal appear to be a result of a leaking occurrence (see a good example in Fig. 1, FD-06B). A run of metal has also been observed in a radiograph made over a cast hilt of a Bronze Age dagger from Italy made of bronze (Cu–Sn alloy with traces of As and Pb), and has been explained as possibly resulting from an ancient repair (Sestieri et al., 2007).

Ancient repairs were frequently made by the casting-on technique, that consisted of casting a new piece of metal to a pre-existing one. This technique was known as Bronze Age (Coghlan, 1975) and was most certainly in use by the LBA metallurgists of the Central Portuguese Beiras (Armbruster, 2002–2003). Although it has been mostly associated to repairs, the casting-on technique seems to also have been used in the manufacture of artefacts, such as that evidenced by a composite artefact from the site of Baiões, a dagger with a blade made of iron and a handle made of bronze (one of the first iron items from the Iberian Peninsula and attributed to LBA) (Vilaça, 2006). The employment of this technique would explain the droplets in the nails, which would have formed during the pouring of the metal to make the head through a space between the mould and the pre-existing pin. Furthermore, the direction taken by the running droplets indicates that the pouring would have been performed with the mould of the head above the pin. This may relate to the lack of metal found near the top of the heads, as resulting from the last part to fill in the mould. Analysis of the shapes of several casting risers from Bronze Age artefacts have shown that the pouring was frequently performed with the mould in an angle that could reach 30° (Coghlan, 1975). In Fig. 7 a scheme illustrating the possible joining of the head to the pin by the casting-on technique is shown, and the pouring has been illustrated with the mould in an angle that can be related to the lack of metal next to the top of the nails head.

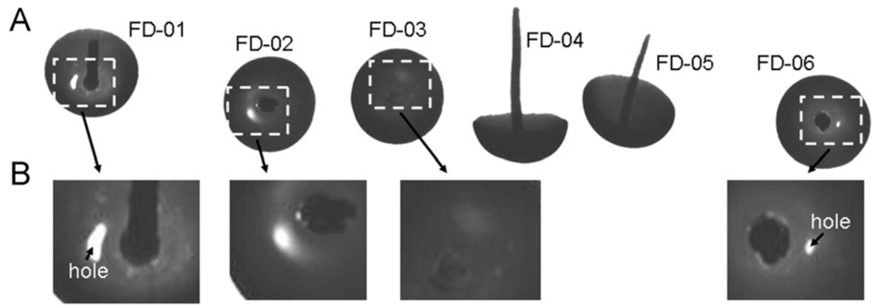

Fig. 6. X-ray radiograph of the six nails from Figueiredo das Donas. (A) General view and (B) detailed images of the regions around the junction of the pin and head of FD-01, FD-02, FD-03 and FD-06 nails.

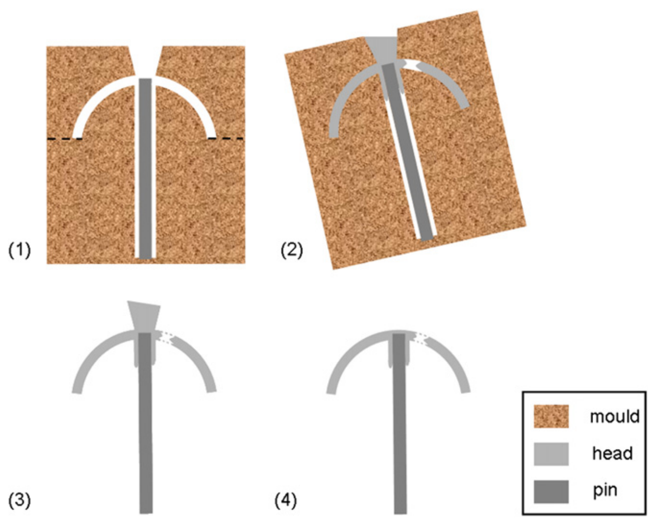

Fig. 7. Scheme illustrating the manufacture of the nails by the casting-on technique: (1) mould positioned above the metallic pin; the mould could be composed by one single piece if lost-wax technique was used, or it could be composed by two pieces, of stone or metal, with a possible union in the broken line; (2) pouring of the metal to make the head of the pin, with some leaking in the pin-mould junction and incomplete fill of the mould on the top-most area; (3) appearance of the nail after the mould has been taken off; (4) final appearance, subsequent to a final surface finishing.

4. Conclusions

The non-destructive analytical and examination procedures conducted for the study of the Figueiredo das Donas archaeological collection was adequate to characterise the type of metallic material used in the manufacture of the artefacts, as well as to evaluate the particular manufacturing technique employed in the joining of the head and pin to compose the exceptional large size nails.

The EDXRF and the micro-EDXRF investigations showed that all the studied artefacts were made of a binary bronze ($\sim$11% Sn on the FD-01 nail) with traces of Pb, As and Sb. This alloy composition is comparable to other bronzes from the region, suggesting that they were regional productions.

X-ray digital radiography investigation, associated to detailed visual observations, suggests that the manufacture of the nails involved joining the head to the pin by the casting-on technique. The employment of this technique can be understood as an evidence of the incorporation of innovative technological solutions by the local metallurgists, as a result of various spheres of interactions that were undergoing during LBA among the Mediterranean and Atlantic cultural axes.

Finally, the manufacture of the head and pin pieces of the nails in bronze with similar composition is probably related to (1) the generalisation of this alloy at the time in the region, (2) absence of leaded bronzes among the Baiões/Santa Luzia cultural group that, if existent, could have been preferred to manufacture the head due to its better casting properties (increased fluidity and lower liquidus/solidus temperature) probably avoiding the casting defect observed at the top of the heads and (3) the mechanical and aesthetical properties of this particular bronze composition when compared to others (as low tin bronzes) or to pure copper.

Acknowledgments

This research work has been funded by the Portuguese Science Foundation (FCT-MCTES) through the Grant SFRH/BPD/73245/2010 to EF and the EarlyMetal project PTDC/HIS-ARQ/110442/2008.

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