Non-invasive chemical and phase analysis of Roman bronze artefacts from Thamusida (Morocco)

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A B S T R A C T

A repertory of Roman military bronze equipment (1st–3rd century AD) found at the archaeological site of Thamusida (Rabat, Morocco) was analysed by non-destructive X-ray fluorescence and time of flight neutron diffraction (ToF-ND). Most objects are made of leaded alloys, where copper is combined with tin and/or zinc and, in six cases, to arsenic as well. A mixed technology was employed, making a limited use of “pure” semi-finished materials if compared with the large utilization of recycled materials (brass and bronze).

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1. Introduction

Copper-based artefacts are of primary importance in cultural heritage studies as they include objects linked to the daily life of medium–high social classes (e.g. lucernae), objects related to religious and/or honorary practices (e.g. statuary, ritual offers, etc.), most parts of army equipment, numerous categories of instruments used by doctors, architects, carpenters, etc. (e.g. scalpels, fistulae, etc.), as well as legal documents (e.g. military diplomas).

From an archaeometric standpoint, most research regards coinage, but many repertories including objects in daily use and military fittings have also been investigated (Jenkins, 1985; Unglik, 1991; Giulia-Mair, 1996; Dungworth, 1997; Ponting and Segal, 1998; Ponting, 1999, 2002). These studies provide a framework for interpreting the present results; however, it is worth underlining that available references are numerically limited compared with the variety of classes they examined (from silvered-bronze horse-trappings to nails) and with the ample diachronicity (from 1st century BC to 14th century AD). The few studies focused on the evolution of alloy compositions through time (Dungworth, 1997, 1996; Craddock, 1988; Jackson and Craddock, 1995), sometimes related to a specific class of objects (Bayley, 2001; Hook and Craddock, 1996), and are of outstanding importance and help for the present case.

The archaeometric investigation of copper-based objects is surely problematic when employing conventional analytical techniques. The destructiveness or the limited penetration power of most of them (unusual to pass through the alteration patina) represents major problems that cannot be simply overcome. The importance of the objects of the present study forbids any destructive sample manipulation, and furthermore, the alteration layers hamper an accurate and reliable estimate of the alloy compositions.

In this study, two non-invasive and non-destructive analytical techniques have been applied to the study of a repertory of Roman military equipment (1st–3rd century AD). A portable X-ray fluorescence spectrometer was first used in order to achieve spot chemical analyses directly from the surface. Time of flight-neutron diffraction was then applied for a quantitative phase analysis and, where possible, an estimate of the bulk alloy composition. Indeed, ToF-ND is able to overcome problems encountered in-situ techniques, such as PXRF, in the presence of degradation phenomena and inverse segregation.
The combination of these analytical techniques will characterise both the alloys and the alteration products in a non-destructive way. An element-sensitive instrument such as a portable XRF will probe the surface, while the high penetration power of neutrons will permit a truly non-destructive examination of the alloys. Moreover, neutron beam sizes are big enough to illuminate large parts of an object, thus overcoming a major disadvantage of many conventional archaeometric methods, where point sampling does not necessarily provide the characteristic material properties of the whole object. Moreover, the line widths of diffraction peaks, collected in backscattering on a time-of-flight instrument, are basically independent of sample thickness and sample shape.

The repertory was found at the archaeological site of Thamusida (Rabat, Morocco). At the boundaries of the Roman Empire, within a large alluvial plain of the Sebou river, Thamusida was founded by the Romans in the 1st century AD. The city included a military camp, temples, thermal baths and an industrial district with harbour stores and ovens for metal works (Papi and Akerraz, 2008). The archaeological excavations, performed by a team of Italian (The Siena University) and Moroccan (Institut National des Sciences de l’Archéologie et du Patrimoine) archaeologists from 1999 to 2005, brought to light numerous classes of ceramic material as well as different types of metal and glass objects (Gliozzo et al., 2009), which are currently under archaeological investigation.

2. Materials

Twenty-two copper-based objects, related to soldier and horse equipment (harness fittings, buckles, scabbard fittings, appliqué, phalera, etc.) and two military diplomas have been selected (Table 1; Fig. 1) according to a criterion of heterogeneity, including objects of different dimensions and functional destination. The distinction made between soldier and horse equipment is fairly simplistic (e.g. cymbals have been included as soldier equipment) but it has been adopted for convenience. The diplomas generally consisted of two bronze tablets joined by wires (as a book); they represented the certified copies – the original documents were affixed in Rome – testifying that the Emperor granted both Roman citizenship (civitas) and the right to marry (conubium) to discharged soldiers. The two diplomas found in Thamusida (THAM 96 and 99) can be surely dated back to 133/134 and 103/104 AD (Papi, 2003,2004); all other objects can be generally framed between the 1st and the 3rd century AD, based on findsite chronology.

3. Experimental

3.1. Portable X-ray fluorescence (PXRF)

A Bruker Tracer III–V portable X-ray fluorescence spectrometer was used to analyze metal artefacts. This technique provides an entirely non-destructive analysis. The flattest side of each artefact was subjected to an X-ray beam of 7 mm², which penetrates to a depth in the range of 10 μm. The instrument uses a thin Rh target in the X-ray tube, a Peltier cooled Ag-free SiPIN detector and a Ti–Al filter to minimize certain peak overlaps. The settings selected for the present analyses were 40 kV, 4 μA with counting times of 30 s for each analysed point. Instrument calibration was achieved using a series of certified alloys (BCR 691, see Ingelbrecht et al., 2001), available as a set of five polished discs (diameter 35 mm, thickness 2 mm), supplemented with a range of mixed alloy powder standards. Given that results provided by a spot analysis cannot be referred to the whole object and that the limited penetration implies that in some cases the alteration patina gives a large contribution to the final analysis, data were only qualitatively exploited. The XRF data for 21 objects were used as guidance for determining the alloy compositions from the ToF-ND data.

3.2. Time-of-flight neutron diffraction (ToF-ND)

The potential and peculiarities of ToF-ND analysis for copper-based materials have been demonstrated earlier (Siano et al., 2003, 2004, 2006; Rinaldi et al., 2005; Kockelmann et al., 2006; Arletti et al., 2007, 2008; Cartechini et al., 2008). The experiments have been performed on the Italian Neutron Experimental Station (INES), belonging to the Italian National Research Council (CNR), and situated at the ISIS spallation neutron source of the Rutherford Appleton Laboratory, UK. Nineteen objects were analysed and, where possible, two different points on an object were selected.

The INES diffractometer covers the d-spacing range between 0.2 and 12 Å and allows for the collection of high resolution patterns in backscattering geometry. INES is equipped with 144 squashed 3He detectors, grouped into 9 banks, covering 20 angles from 11° to 170° in the horizontal scattering plane. The samples were hosted in a large vacuum tank of 80 cm diameter.

Each sample was: (a) mounted in an individually prepared Al sheet holder, (b) a cadmium shield was placed inside hollow objects to prevent scattering from the back side, (c) placed in a 1 x 4 cm² or a 4 x 4 cm² size beam in order to cover, in most cases, the whole object and (d) measured in either a single or a double run for a total counting time of about 3 h. The data were normalized to the incident neutron flux distribution of the INES “white” incident neutron beam, which contains neutron wavelengths from 0.4 to 3.5 Å.

For every analysis point on an object, each of the nine detector sections provided a diffraction pattern, all of which are fitted simultaneously. A quantitative phase analysis was performed by the Rietveld method using the General Structure Analysis System (GSAS; Larson and Von Dreele, 2000). Reference structural models (symmetry, space group, lattice parameters and atom positions)
were taken from the Inorganic Crystal Structure Database (http://www.fiz-informationsdienste.de/en/DB/icsd/index.html). The Rietveld analysis yielded relative weight fractions of the crystallographic phases in the irradiated sample volume: the alpha-bronze, a Pb phase, and corrosion phases such as copper oxides and copper chlorides. The lattice parameter of alpha-bronze alloy was refined. The crystallographic space group for the alpha-phase is Fm-3m (fcc) with a lattice parameter in the range \( a = 3.6145 \) Å (pure copper)–3.6900 Å. The lattice constant expands with the addition of alloying elements such as Sn, Zn, As and Ag. A Pb-phase (space group Fm-3m, \( a = 4.9493 \) Å) was included. Pb does not dissolve into the copper lattice, and can therefore be observed as a separate phase with a characteristic Bragg peak at 2.86 Å.

The content of the alloying element in a binary alpha bronze phase can be obtained via determination of the lattice parameter and application of Vegard’s rule, however in practice using a calibration curve for the binary alloy (Siano et al., 2003, 2004). This procedure works well for Cu–Sn alloys since Sn provides considerable expansion of the copper-type crystal lattice, compared for instance with Fe and Zn. For ternary alloys, e.g. copper alloyed with Sn and Zn, extraction of element information from one lattice parameter is ambiguous. However, if the elemental concentrations of elements such as Zn and As can be shown to be small, for instance by XRF, then the measured lattice parameter can be corrected using Vegard-type relations, and good estimates of Sn contents can be obtained (Sidot et al., 2005). Considering that the neutron scattering lengths of Sn (6.20 fm), Zn (5.68 fm) and As (6.58 fm) are close, a reliable quantitative phase analysis – by scale factor refinement – can be obtained also without knowing the precise Cu–Sn–Zn–As proportions.
In conclusion, the adopted strategy implied the broad application of PXRF results in order to determine whether the alloy was binary or not. If for ternary alloys the XRF signal for Sn or Zn was found to be negligible, the “Sn equivalent” or “Zn equivalent” compositions, respectively, were calculated (Sidot et al., 2005) via Vegard’s rule. However, the quantitative phase analysis was performed by ToF–ND for the whole sample set whereas the separation of the alloy into elements was carried out for binary alloys only (19 samples).

4. Results

4.1. Portable X-ray fluorescence (PXRF)

The qualitative elemental composition served a definite purpose—to determine whether the alloy is binary, ternary, or quaternary. Results show that Zn and As are completely absent only in samples THAM 9 and THAM 16. Samples THAM 6 and THAM 16 show very low Zn and no As levels. Sn is absent in sample THAM 265, while Pb is absent in THAM 20, 192, 216, 219 and 265. Weak peaks of Fe are present in all objects with the sole exception of THAM 13, while traces of Ag have been detected in THAM 216 and 224. Lastly, As is clearly present in THAM 219 and 265, and weak peaks have also been detected in THAM 13, 20, 192, 216 and 224.

PXRF data show that the majority of objects are made of leaded alloys, where Cu is combined with both Sn and Zn. All samples studied can be grouped as follows:

(a) 3 leaded alloys made of Cu, Sn, Zn and As (THAM 219, 224 and 265);
(b) 3 unleaded alloys made of Cu, Sn, Zn and As (THAM 13, 20 and 192);
(c) 10 leaded alloys made of Cu, Sn and Zn (THAM 3, 6, 10, 15, 96, 99, 119, 133–134, 154, 195 and 208);
(d) 6 leaded alloys made of Cu, Sn and very low Zn (THAM 6, 119, 133–134, 154 and 195);
(e) 1 unleaded alloy made of Cu, Sn and Zn (THAM 216);
(f) 2 leaded tin bronzes (THAM 9 and 16).

4.2. Time of flight neutron diffraction (ToF-ND)

The phase analysis has been performed for the 19 samples listed above in groups c–f (Table 2), while the alloy composition has been determined for the 9 samples listed in groups d–f (Table 3).

4.2.1. Phase analysis

Small discrepancies between two measurements on the same object performed on THAM 6, 9, 10, 96 and 119 allow the conclusion that sample portions representative of the whole objects were probed (Table 2). For three samples (THAM 3, 96 and 99) diffraction profiles characterized by broad and structured reflections were observed as a result of a strong heterogeneity of the alloy composition. In these cases Rietveld refinement was carried out by assuming the presence of two alloy phases having...
compositions corresponding to the lower and the upper limit of the range of variation.

Most of the objects are macroskopically well preserved but weathering is testified by the ubiquitous presence of cuprite and, in five samples (THAM 134, 20, 216, 224 and 195), of nantokite as well.

Calcite and quartz signals derive from residues of the burial materials or ceramic core material, which were found in some samples.

The amount of copper alloy varies from 36.5 wt%, in a highly altered item, to 96.5 wt%. Weak peaks of metallic Cu – probably a residue of raw materials – were observed only in the pattern of sample THAM 16 (Fig. 2). Lead is present in very variable amounts in the analysed sample set: seven samples (THAM 154 in Fig. 2, THAM 208, 6, 10, 119, 96 and 99) contain more than 10 wt% of lead, four samples (THAM 15, 16, 3 and 133) between 5 and 10 wt%, five samples (THAM 9, 134, 13, 224 and 195) contain less than 5 wt% of metallic lead, while in four samples (THAM 20, 216 and 192) no Pb diffraction peaks were observed. It should be noted that the detection limit of Pb on INES is about 1 wt% for 3 h data collection.

4.2.2. Alloy composition

Whilst the determination of elemental composition of the copper alloy from ToF-ND is ambiguous, Pb concentration can be determined directly, and good estimates of Sn contents can be obtained taking into account the XRF data as a guide to the presence of various elements. Table 3 lists the obtained estimates of bulk Sn concentrations and Sn/Cu and Pb/Cu ratios for several objects. Systematic errors due to the presence of alloying elements are not taken into account but are assumed to be limited. For example, 2% Fe and 2% Zn in copper are responsible for lattice constant changes of 0.001 and 0.0045 Å, resulting – if ignored – in an overestimation of Sn-content by 0.2 and 0.8 wt%, respectively (Cu–Zn: CrystMet: the Metal Database; entry ID: 31649; W. Hume-Rothery, F. Lewin, P.W. Reynolds, Proc. R. Soc. Ser. A [PRLAAZ] 157A, 167–183 (1936); Cu–Fe: JCPDS powder diffraction database, entry 401294). In any case, the measured lattice parameter of the alpha phase poses an upper limit for the Sn fractions, which are dissolved in the copper lattice. The copper–tin alloys of THAM 9 and THAM 16 show tin fractions of 12 and 8 wt%, respectively. The copper–tin alloys, where small amounts of Zn have been further detected, show tin below the ToF-ND detection limit (THAM 216), intermediate (THAM 6, 134, 154, 195) or high tin (THAM 119, 133).

Samples THAM 219 and THAM 265, which contain significant amounts of As, were not considered for ToF-ND investigations since incorporation of either As or Sn yields similar large lattice expansions.

5. Discussion

Alloys vary independently from their social and functional destinations. For instance, a button for the soldier equipment (THAM 154) and a phalera for the horse equipment (THAM 119) show comparable compositions. Conversely, two objects functionally equivalent such as the two diplomas show different compositions.

Technological properties seem to influence the choice of materials only partially. Most as-cast objects show appropriate to slightly excessive amounts of lead (e.g. THAM 119), possibly as a deliberate addition to favour the casting process. On the other hand, sheet metal, requiring no or low lead to favour hammering, can show unnecessary and inappropriate amounts of lead. For instance, the high lead content of both diplomas is not easily explained, unless related to some expedient to facilitate the inscription.

Moreover, it is worth considering that the expected relationship linking object dimension and lead content is not respected: small objects like the button THAM 154 have a higher lead content than larger objects such as the phalera THAM 3. Lastly, the faint amounts of lead in THAM 13, 134 and 195 provide evidence for the involuntary addition of this component. The use of scraps as well as the residue of smelting ores can equally justify the negligible lead amounts in these objects.

PXRF and ToF–ND measurements performed on THAM 9 allowed different considerations on both the corrosion layer and the Cu–Sn alloy. In the corrosion layer, enrichment and depletion of Sn and Cu, respectively, are typical features of quaternary bronzes, tin bronzes and leaded tin bronzes (Constantinides et al., 2002). From a technological standpoint, high tin and low lead in THAM 9 provided a suitable alloy for casting. The alloy, very similar to that of “elbow” fibulae (Ponting and Segal, 1998), ensures strength and toughness to the object, although this characteristic is not required in making such studs. In THAM 16, lower tin and higher lead contents compared with THAM 9 greatly favoured casting, further decreasing production costs (Pb was cheaper than Sn). Analogous considerations can be drawn for samples THAM 6 and 154 and for sample THAM 133, respectively, similar to THAM 16 and to THAM 9.

Based on the conspicuous presence of As, THAM 219 and 265 stand out in the entire repertory. This result is remarkable considering that during Roman times As is infrequent in the alloys and, when present, its level is considerably lower than that found on average in Iron Age items (Dungworth, 1997). Lacking accurate
quantitative values, it is impossible to discuss technological issues (smelting, co-smelting, orpiment/realgar additions, etc.; Lechtman and Klein, 1999); however, in THAM 265, the significant amount of both As and Fe could indicate the exploitation of bornite and/or arsenopyrite ores. A deliberate addition, in order to confer a silvery effect, is to be kept in great consideration, based on two main reasons: (a) both objects are decorative buckles and (b) there is an aesthetical concern in the whole repertory, where silvered objects are also present. In fact, THAM 216 and 224 show appreciable amounts of Ag (detectable by surface sensitive PXRF but below the detection limit of ToF-ND), likely used in order to decorate the objects with a silver coating.

6. Conclusions

A relatively large number of Roman military fittings have been analysed in a non-destructive way by portable X-ray fluorescence and ToF neutron diffraction. Results allowed the reconstruction of a mixed technology, making a limited use of “pure” semi-finished materials but largely privileging recycled materials. The frequency of mixed leaded and unleaded alloys with two or three components, together with their wide compositional variability and the lack of a strict link between object destination and composition, indicates that scraps of both bronze and brass were frequently melted together. This reconstruction should be in line with studies available for other Roman finds, where low zinc brasses are rare, suggesting therefore that brass was rarely recycled on its own (Dungworth, 1997).

In this repertory of twenty-one objects, it is thus interesting to note that only two of them are made of a leaded tin bronze. The availability of raw and scrap materials seemed to orient the technological choice adopted, although remaining in a suitable functional field.

Lastly, it is worth noting that a general aesthetical concern is made evident by the deliberate addition of both As and Ag.

References


