IL NUOVO CIMENTO Vol. 30 C, N. 1 Gennaio-Febbraio 2007
DOI 10.1393/ncc/i2006-10048-4

Neutron diffraction study of Bronze Age tools from second millennium BC dwellings in Italy(*)

R. Arletti(1), L. Cartechini(2), S. Giovannini(1), R. Rinaldi(3)(**), W. Kockelmann(4) and A. Cardarelli(1)

(1) *Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia Modena, Italy*

(2) *ISTM-CNR, Perugia e Centro di Eccellenza SMAArt, Università di Perugia Perugia, Italy*

(3) *Dipartimento di Scienze della Terra e Centro di Eccellenza SMAArt Università di Perugia - Perugia, Italy*

(4) *Rutherford Appleton Laboratory, ISIS Facility - Chilton, Didcot, UK*

(ricevuto il 31 Ottobre 2006; pubblicato online il 16 Febbraio 2007)

Summary. — Neutron diffraction was utilized to characterise XX to XIII century BC bronze axes (Ancient to Late Bronze Age) from "Terramare" and other Bronze Age settlements near Modena, Italy. Archaeometric metallurgy issues have been addressed by means of phase and texture analysis from measurements carried out at the ROTAX and GEM beam lines of the neutron spallation source ISIS of the Rutherford Appleton Laboratory (UK). Neutron data provide accurate composition and structural information from the bulk of the alloy, with good grain statistics, without limitations due to surface alterations and with few limitations as to sample size. Bronze composition results are in good agreement with data obtained by micro-sampling and traditional analytical techniques thus confirming the validity of the method used for a totally non-destructive determination of the alloy composition from precise lattice parameter measurements. Phase analysis from diffraction profiles provides identification and quantification of surface alteration and corrosion products, free of interference with the analysis of the bulk alloy. Furthermore, texture analysis techniques may yield information on the ancient production methods of the artefacts.

PACS 61.12.Ld – Neutron diffraction.
PACS 81.05.Bx – Metals, semimetals, and alloys.

(*) Paper presented at the Workshop "RICH—Research Infrastructures for Cultural Heritage", Trieste, December 12-13, 2005.

(**) E-mail: rrinaldi@unipg.it

1. – Introduction

In the panorama of the new advanced physical methods recently applied in the field of cultural-heritage material science, neutron diffraction represents a powerful non-destructive diagnostic tool to address fundamental issues regarding archaeological metal artefacts such as: ore provenance, composition and structural characterization of crystalline phases, description of metallurgic and manufacturing techniques and evaluation of the state of preservation [1-4].

The diagnostic capability obtained from the combination of high penetration power, resulting from the weak interaction of neutrons with matter, with precise analytical information provided by the Rietveld refinement of diffraction profiles [5], was exploited to non-destructively study some bronze artefacts belonging to the most important Bronze Age settlements in Northern Italy: the "Terramare" from the plains near Modena and other earlier settlements in the same area. The term "Terramare" applies to artificially fortified villages which, between the 17th and the 12th century BC, were densely occupying the central part of the river Po plains [6, 7]. The success of the economic, social and cultural model of these settlements determined a strong demographic growth associated with a large specialised artisan production. In particular, the metallurgic production of bronze seems to have been most prominent and varied. Such an articulated production implies a remarkable workmanship and the knowledge of many different working procedures depending on the use and type of object being produced.

Neutron diffraction was utilized to obtain composition and structural information on three XX to XIII century BC bronze axes (Ancient to Late Bronze Age) by means of phase and texture analysis at the ROTAX and GEM beam lines of the neutron spallation source ISIS of the Rutherford Appleton Laboratory (UK). The analytical investigations are part of a research project aimed at studying the ancient metal technology and its development through the Bronze Age on the Italian territory, with general implications for studies of similar materials throughout Europe. The analysed axes belong to a wider sampling of Bronze Age artefacts, previously studied [8] by conventional techniques (Optical Microscopy, Scanning Electron Microscopy, Electron Probe Micro Analysis), in order to understand the provenance of the raw materials. A further aim of this work is to probe the consistency of the results obtained by a totally non-destructive technique (neutron diffraction) as compared with invasive conventional techniques, in order to consider the widespread use of the method for bronze finds which should not undergo any kind of sampling or preparation procedure.

Neutrons are particularly suited to non-destructively investigate ancient metal artefacts for the following reasons:

i) They provide a signal from the bulk of the alloy, hence independent of alteration or corrosion surface layers. These are actually detected as distinct signals. Binary alloy compositions, such as in the present study, can be derived by the accurate determination, by Rietveld refinement, of the unit cell expansion due to the incorporation of Sn into the copper fcc lattice [9, 10].

ii) They are insensitive to the geometry and shape of the objects under examination, hence no sample preparation is required. The object is left undisturbed and the analysis is totally non-destructive and non-invasive. Activation decay is relatively fast (36–72 h, depending on thickness, for about 7 h of exposure) allowing the pieces to be safely handled after a couple of days on average [2].

iii) The relatively large beam dimensions (typically $10 \times 10\,\mathrm{mm}^2$) offer the advantage of probing large sample volumes representative of the overall composition and with high

3D grain statistics. This latter aspect is especially advantageous for texture analysis.

iv) Minor phases within the alloy can be detected in the bulk of the object as well as in the alteration surface layers at the level of a few tenths of a wt% (down to 0.2 wt% at ROTAX and GEM [4]), a remarkable level for a method exploiting elastic interactions.

v) The composition and textural information neutrons provide is useful in distinguishing various levels of sophistication of the manufacturing techniques and their development through the time span represented by the samples under investigation [4, 11, 12].

2. – Experimental

The neutron spallation source ISIS delivers a pulsed polychromatic beam (in the domain of thermal energies, with wavelengths typically from 0.5 to 5.0 Å) allowing high-resolution diffraction measurements and exploiting the time structure of the pulses by the Time-of-Flight (ToF) technique. The method rests on the double dispersion, in energy and Bragg angle. The former is resolved by detecting the neutron velocity typically from 8000 to 800 meters per second. The latter is resolved by the position-sensitive detectors. Combining de Broglie's equation: $\lambda = ht/m_n L$ (where h = Planck's constant; m_n = neutron mass; L = flight distance; t = time of flight) with Bragg's law ($\lambda = 2d_{hkl}\sin\theta$) one obtains the following expression as a function of the crystallographic d-spacing:

$$d = \frac{h}{2m_n} \cdot \frac{t}{L\sin\theta}\,,$$

where the first factor is a constant and the second one contains the measurements.

ROTAX and GEM beam-lines have a multi-detector set-up yielding the acquisition of complete diffraction patterns free of detector and/or sample movements [13,14]. More in detail, ROTAX, with a flight path of 15 m, is equipped with 3 in-plane detector banks, each one consisting of 256 channels and collectively spanning from the backward to the forward scattering directions in the 2θ-range from 10 to 150 degrees. GEM, with a flight path of 17 m, is characterized by a 3D large coverage detector assembly consisting of 6500 elements arranged in 6 banks in the 2θ-range from 1.2 to 171.4 degrees. For texture analysis these 6500 detector segments are typically partitioned into 160 detector groups representing the same number of orientations. This leads to the main advantage of obtaining composition and texture measurements (namely the collection of diffraction data exploring different sample/detector/beam orientations) in a completely stationary experiment and in much shorter acquisition times than with ROTAX. Due to a more limited detector coverage, texture analysis from ROTAX requires the use of a goniometer for the sequential data collection from many sample orientations.

Although diffraction data have been collected on the three bronze axes for both composition and texture analysis on GEM and ROTAX, here we only present results of the phase analysis, alloy composition, and line broadening as obtained from Rietveld refinement of the diffraction profiles. Texture analysis will be the subject of a further study to be accounted for elsewhere.

Time-of flight diffraction patterns are normalized to the incident number of neutrons per neutron wavelength. This is needed to discriminate between different neutron velocities (wavelengths) but the normalization also allows the direct comparison of data sets with different measuring times. The diffraction patterns therefore show "normalized neutron counts" on the y-axis which may be considered arbitrary units (see fig. 1).

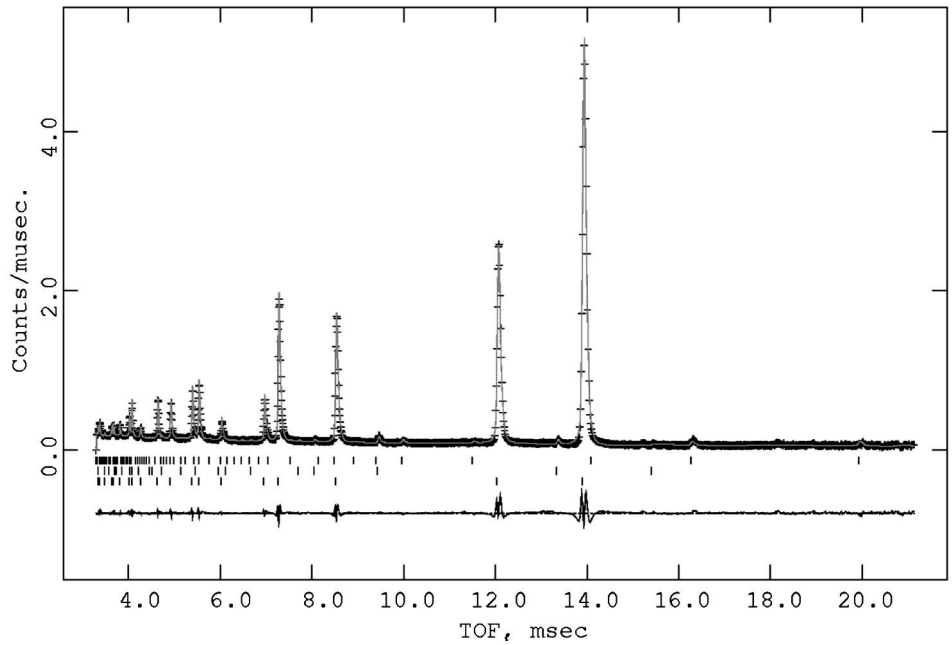

Fig. 1. – Neutron diffraction ToF profile and Rietveld analysis from Rotax (bank 3) data of sample Montale 1 collected 40 mm from the edge (see table I). The fitted profile (line) is shown with the experimental data (crosses). The three sets of bars under the profile mark the theoretical diffraction positions of bronze (bottom), aluminium (middle) and cuprite (top), respectively. The bottom graph represents the difference between observed and calculated profiles.

Diffraction data have been collected at several points along the length of the axes according to sample dimensions (the largest sample is about 15 cm × 5 cm and has 0.5 cm thickness) and beam size ($10 \times 10\,\mathrm{mm}^2$ for both ROTAX and GEM). Acquisition times were about 5 h on ROTAX, and a mere 15′ on GEM for each analysis point. Aluminium foil wrapping the samples was used as an internal standard for powder pattern calibration based on Al lattice parameter measurements. Reference structure models (symmetry, space group, lattice parameters, atom positions) were taken from the ICSD and CrystMet databases [15, 16]. Experimental data were treated by Rietveld refinement by means of the GSAS package [17] with the EXPGUI [18] interface. Phase analysis (expressed as weight fraction percentage, wt%) was obtained by refining one overall Debye-Waller parameter and one common absorption parameter for all patterns of the same analysis spot. Determination of alloy composition was carried out exploiting the linear correlation between Rietveld refined lattice parameter of bronze and the Sn wt% content (Vegard-type Cu cell expansion); the experimental calibration curve based on bronze standards (Sn wt% 1–14) was obtained from similar studies at ROTAX by Siano *et al.* [10, 12]. The accuracy in the determination of bronze composition has been checked on several certified bronze reference materials (results not shown) and the corresponding error was estimated to be ±0.5 Sn wt%.

Linewidth analysis was performed on the diffraction profiles recorded in the backward scattering direction alone, *i.e.* bank 3 and bank 6, for ROTAX and GEM, respectively,

which are exempt from line broadening caused by sample thickness. Line broadening analysis on ROTAX and GEM also profits from the low intrinsic instrumental linewidth broadening as obtained from measurements on non-strained certified standard reference materials. The measured line broadening on the sample can therefore be ascribed to:

i) Crystal deformations from micro-strain effects;

ii) Alloy composition heterogeneity;

iii) Particle size broadening.

Of course, a combination of these factors can also be present. The γ_1 parameter obtained from Rietveld analysis has been used to estimate peak broadening assuming a Lorentzian function and ignoring grain size effects. The so-called micro-strain parameter is then calculated from $\varepsilon_\gamma = \gamma_1/C \cdot 100\%$, where C is a diffractometer constant ($C = 6606.55$ for ROTAX-bank 3; $C = 9072.33$ for GEM-bank 6) [17]. It is worth noting that, in spite of the name, ε_γ may represent broadening from both strain and alloy composition variation.

3. – Results and discussion

Tables I and II report the results obtained from Rietveld refinements of ROTAX and GEM data, respectively. ROTAX measurements have been mainly dedicated to alloy and phase composition analysis probing a large number of data points, whereas the GEM beam-line has been primarily exploited for texture measurements. However GEM measurements can also be used for alloy and phase composition analysis in order to corroborate ROTAX results.

In spite of the limited number of samples, the results obtained allowed us to assess the capability of our analytical approach to provide significant information for the study of the evolution of manufacturing materials and techniques. Having chosen materials covering a large time span (from the XX to the XIII century BC), the results obtained can be correlated with different metallurgical technologies. In tables I and II, results from ROTAX and GEM data analysis, respectively, are in good agreement and show different tin contents (low concentration) for the early Bronze Age axe (Savignano 994) with respect to the most recent ones. Various explanations can be inferred from this, *i.e.* limited tin availability during the first period of the Bronze Age or an incomplete control of bronze production, as well as a limited knowledge of alloy composition effects on bronze mechanical properties. Even if these data are related to only 3 samples, the trend observed for the tin content (lower levels in the ancient bronze, higher in the medium bronze and intermediate in the recent bronze) is consistent with data obtained on a large number of bronze axes of the same period [8]. Moreover, the tin content along the length of the axes shows a slight increase from the edge to the body. Although the observed variation is almost at the limit of our experimental error the slight trend observed suggests the possible occurrence of a temperature gradient in cooling the cast. Considering the mass of the objects, the gradient is expected to stem from migration of the high temperature from the edge to the core; thus the Cu-Sn components having a lower melting point (*i.e.* Cu-Sn with higher Sn contents) would tend to be more concentrated in the body of the artefacts. The only data point at variance with this observation is that obtained from GEM on the edge of sample Savignano 994.

TABLE I. – *Bronze lattice parameter* (a_{Cu})*, broadening analysis* (ε_γ)*, alloy composition (*Sn *and* Cu *wt%) and phase analysis (wt%) from ROTAX data.*

Axe	Rietveld refinement		Bronze composition (estimated error ±0.5 wt%)		Phase analysis (estimated error ±0.2 wt%)			
Formigine 2452 (XIII c. BC)	a_{Cu} (Å)	ε_γ	wt% Cu	wt% Sn	wt% Bronze	wt% Cu_2O	wt% Nantokite	wt% Pb
body	3.6404(2)	0.09	95.3	4.7	94.5	3.1	0.3	2.1
middle	3.6381(1)	0.26	95.7	4.3	91.7	6.1	0.3	1.8
edge	3.6377(1)	0.34	95.8	4.2	91.7	6.1	0.2	1.9
Montale 1 (XVI-XV c. BC)	a_{Cu} (Å)	ε_γ	wt% Cu	wt% Sn	wt% Bronze	wt% Cu_2O	wt% Chalcocite	wt% Pb
body (50 mm)	3.6535(2)	0.17	93.1	6.9	99.6	0.4	-	-
40 mm	3.6535(2)	0.19	93.1	6.9	99.2	0.8	-	-
30 mm	3.6537(2)	0.23	93.1	6.9	99.2	0.8	-	-
20 mm	3.6527(1)	0.27	93.3	6.7	97.2	1.8	1.0	-
10 mm	3.6524(2)	0.32	93.3	6.7	98.4	0.8	0.8	-
edge	3.6514(2)	0.43	93.5	6.5	96.5	3.5	-	-
Savignano 994 (XX c. BC)	a_{Cu} (Å)	ε_γ	wt% Cu	wt% Sn	wt% Bronze	wt% Cu_2O	wt% Malachite	wt% Pb
body	3.6234(2)	0.06	98.2	1.8	95.8	2.7	1.5	-
edge	3.6219(1)	0.11	98.5	1.5	97.3	1.2	1.5	-

In addition to the bronze phase, diffraction data evidenced the presence of lead inclusions in variable amounts in two of the axes. The ancient axe (Savignano 994) does not contain lead. In the axe from the middle Bronze Age (Montale 1) lead is present in small amounts, close to the detection limit whereas the most recent axe (Formigine 2452) shows significant Pb contents at about 2 wt%. This may indicate the unintentional presence of lead from ore inclusions in the middle Bronze Age axe, while it could be intentional in the most recent one in order to modify the mechanical properties or to lower the melting point of the alloy [19].

The different response in the determination of lead concentrations obtained by GEM and ROTAX measurements is ascribable to two main observations: first, lead inclusions have a random distribution and the measurements at ROTAX and GEM have been collected from different spots on the axes; second, there are different detection limits for different phases and the case of lead is less favourable, its detection limit being closer to 1.0 wt% rather than to the quoted value of 0.2 wt% for the most favourable cases. This fact partially depends on counting statistics (counting time and sample volume) where GEM has a considerable advantage over ROTAX.

Cuprite (a red cuprous oxide, Cu_2O) is the main copper oxidation product typically found in ancient bronzes [20] occurring over a wide range of corrosion conditions. Mala-

TABLE II. – *Bronze lattice parameter* (a_{Cu})*, broadening analysis* (ε_γ)*, alloy composition (*Sn *and* Cu *wt%) and phase analysis (wt%) from GEM data.*

Axe	Rietveld refinement		Bronze composition (estimated error ±0.5 wt%)		Phase analysis (estimated error ±0.2 wt%)			
Formigine 2452 (XIII c. BC)	a_{Cu} (Å)	ε_γ	wt% Cu	wt% Sn	wt% Bronze	wt% Cu_2O	wt% Nantokite	wt% Pb
body	3.6431(2)	0.15	94.9	5.1	95.9	2.1	0.1	2.0
edge	3.6402(1)	0.30	95.4	4.6	92.8	4.8	0.3	2.1
Montale 1 (XVI-XV c. BC)	a_{Cu} (Å)	ε_γ	wt% Cu	wt% Sn	wt% Bronze	wt% Cu_2O	wt% Chalcocite	wt% Pb
body	3.6531(1)	0.29	93.2	6.8	96.8	1.5	0.5	1.0
edge	3.6513(1)	0.40	93.5	6.5	96.7	1.3	0.7	1.3
Savignano 994 (XX c. BC)	a_{Cu} (Å)	ε_γ	wt% Cu	wt% Sn	wt% Bronze	wt% Cu_2O	wt% Malachite	wt% Pb
body	3.6220(1)	0.10	98.4	1.6	97.3	1.2	1.2	-
edge	3.6243(2)	0.15	98.1	1.9	95.4	0.8	1.5	-

chite and nantokite have also been found in the axes. Malachite is known to form in significant amounts in the patina developing during corrosion of bronze buried in soil; it usually forms next to cuprite and the growth of a uniform layer accounts for the appreciated green patina of bronze antiquities [20]. Nantokite has been observed on the axe showing the poorer state of preservation (Formigine 2452); this compound is part of the class of minerals (copper chlorides) which can give complications for long-term conservation of bronzes. In fact, the so-called "bronze disease" is usually ascribable to the presence of copper chlorides, among which nantokite is one of the most important.

The observation of some chalcocite (a sulphide) in the axe from the middle Bronze Age may be explained in terms of the presence of inclusions from the original ore or may come from residues of sulphide minerals that, in this period, started to be used instead of native copper and carbonates for bronze production, thus indicating the development of more sophisticated metallurgical techniques. All these points need further investigation.

Finally, from line broadening analysis in terms of ε_γ values, a coherent dependence of the strain parameter has been observed as a function of the position of the points probed along the axes. Particularly, as reported in tables I and II and shown in fig. 2, the broadening effect increases from the body to the cutting edge. Of the possible factors to be involved in peak broadening, the increased linewidth at the edge of the axes can be explained in terms of both, a higher heterogeneity in alloy composition due to faster cooling and stronger crystal deformations and dislocations leading to micro-strain, due to cold working. This could explain the higher values of the strain parameter in the blade which underwent more intense treatments. Interestingly, a lesser degree of broadening was observed in the case of the most ancient axe where tin is present in the smallest

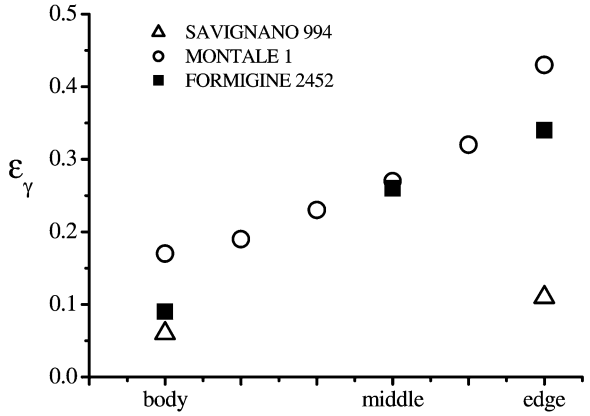

Fig. 2. – Plot of the strain parameter, ε_γ, against the probed point positions along the length of the axes; body, middle and edge. For sample Montale 1 intermediate positions have also been analysed (see table I).

amount and the broadening effect due to Sn concentration variation becomes negligible.

Texture results will provide further information on this point by comparing the texture of the body with that of the cutting edge. In the case of a manufacturing technique based on cold treatments of the blade a typical texture fingerprint should be observed.

4. – Conclusions

The present work reports on the use of neutron diffraction as a non-invasive tool to provide detailed compositional and structural information on ancient bronze alloys, capable of discerning between the effects due to differences in materials and ancient metallurgic and manufacturing techniques. Significant variations in alloy composition have been observed in the bronze axes examined which are representative of a large time span. An evolution in the production technique could also be identified based on bronze inclusions (lead and chalcocite) in agreement with earlier work carried out with traditional invasive techniques on a larger number of samples. Diffraction peak broadening analysis provided a useful tool to study effects from forging and working treatments. Additional information has been obtained on the state of preservation of the axes from the characterization of patina and corrosion components. Results on the composition of the alloys are in good agreement with those obtained with traditional invasive techniques on samples of the same provenance [8].

Based on these findings neutron diffraction investigations could be extended to other materials from the "Terramare" and other Bronze Age settlements in order to explore the time evolution of the metal production techniques and the changes occurred as a function of the different use of the artefacts in a totally non-destructive, non-invasive mode.

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The Italian Ministry of Education (MIUR) is acknowledged for grant PRIN-2004041033 to the Universities of Modena and Perugia. We thank CNR for access to the ISIS Facility through the mutual Agreement (No. 01/9001) between CNR and CCLRC.

The "Centre of Excellence for Scientific Methodologies Applied to Archaeology and Art" (SMAArt) of Perugia University is also acknowledged for support.

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