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ASPECTS OF METALLURGICAL ACTIVITY IN LIGURIA (ITALY) IN THE MIDDLE AND LATE BRONZE AGE

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Abstract

Prehistoric metal findings from Liguria are numerous, however, even though there were many metalliferous mines, the metal-working sites have not yet been ascertained.

This work discusses results on some metal objects from different archaeological sites in Liguria.

The objects examined were:

1) two melting drops 2) an axe, and 3) a knife.

The physico-chemical investigation techniques employed were:

- X-ray diffraction,
- radiography,
- microdrawing method, followed by optical and electron scanning microscopy observations,
- differential thermal and thermogravimetric analyses to characterize the clay core found inside a socketed knife.

Keywords: archaeometallurgy, thermal analysis, thermogravimetry

Introduction

Besides problems relating to the technology of manufacturing metals, archaeometallurgy involves the provenance of raw materials, the commercial exchanges and investigations of metal-working sites.

The present study involved some Ligurian findings, which illustrate the metal-working in this region. The techniques used were TG, DTA, X-ray diffractometry, metallographic and SEM analyses. The objects examined were

1) two bronze drops from Bric Tana (Millesimo),
2) a socketed knife from Grotta del Sanguineto, and
3) a terminal-winged axe from Grotta del Sanguineto.

The bronze fusion drops from Bric Tana (Millesimo) are the most ancient evidence of metallurgical activity in Liguria. The drops were found in a Middle Bronze Age settlement (16th–14th century B.C.), recently excavated (excavations of

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the Soprintendenza Archaeologica della Liguria, 1987–1992). The settlement is sited in a terraced dolina.

The socketed knife and the terminal-winged axe, now in the Civico Museo di Archaeologia Ligure of Genoa, belong in the collection of G. B. Rossi, a Ligurian collector who dug in many caves of Finale Ligure after 1885, and particularly in the Sanguineto or Matta cave. From the excavation reports [1], we see that Rossi found the axe at a shallow depth, and the knife at the depth of 1.20 m under the surface, but we do not know the exact location and the stratigraphic situation of the findings. As the archaeological deposit has been widely disturbed today, we have to date the artefacts back to a wider period from the Ancient Neolithic to the Iron Age.

The socketed knife shows the presence of casting flash, and is clearly unfinished and probably never used. It is of Nazari type, mainly found in Veneto in the 8th century B.C. [2]. The therminal-winged axe is devoid of a shoulder and according to Carancini [3], it is a unique specimen. In this case, too, the artefact was unfinished after casting; in fact, the flashes are still placed and the wings are not folded for hafting. On the basis of these characters, and by comparison with a multiple stone mould [4] conserved at the Musée Calvet of Avignon (France), this axe can be attributed to the type defined as *hache rectangulaire à ailerons terminaux de longueur moyenne*, datable to the Final Bronze IIIb and the ancient Hallstatt, between the 8th and 7th century B.C. and largely present in southern France. The presence, on this stone mould, of a knife matrix very similar to our object is very remarkable, so we can suppose that the axe and the knife of the Sanguineto cave belonged in the same group of artefacts.

Experimental

In order to investigate the morphology and composition of the different artefacts, we employed non-destructive techniques. In contrast, in the case of the drops, a micro-core was obtained by using a special milling machine [5].

The techniques used were:

1) Thermogravimetry and differential thermal analysis with a Netzsch STA 409 apparatus in static air, at a heating rate of 5°C min^{-1} up to 1000°C, with Al_2O_3 as reference;

2) X-ray diffraction with a Philips PW 1729 powder diffractometer, with ASPO [6] data acquisition and evaluation software;

3) optical and electron microscopy;

4) electron probe microanalysis (EDS).

Results and discussion

Fusion drops

The fusion drops are shown in Fig. 1.

A micro-core was drawn from the bottom of one drop (Fig. 2).

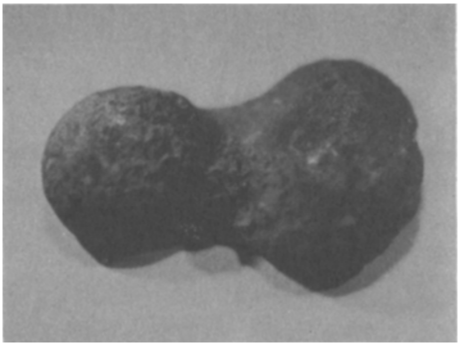

Fig. 1 The fusion drops

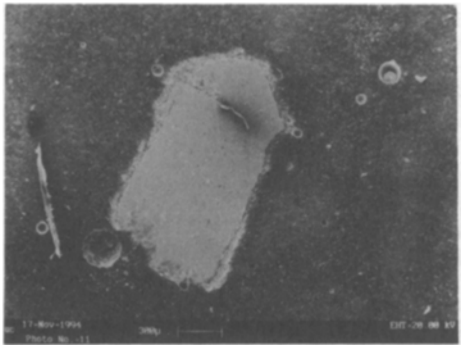

Fig. 2 The microsample taken from the bottom of a fusion drop

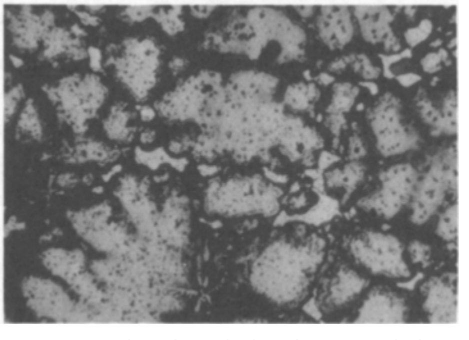

Fig. 3 Optical metallography of the fusion drop morphology (320 times)

After polishing and etching with a solution of NH_4OH and H_2O_2 in water, it was observed under an optical microscope. The micrograph in Fig. 3 shows the dendritic structure, typical of an as-cast alloy, and numerous inclusions, apparently differing in composition. The morphology was also investigated by means of SEM analysis [7], as shown in Figs 4 and 5. EDS microanalysis provided the average composition of the alloy; 90.5% at. Cu and 9.5% Sn.

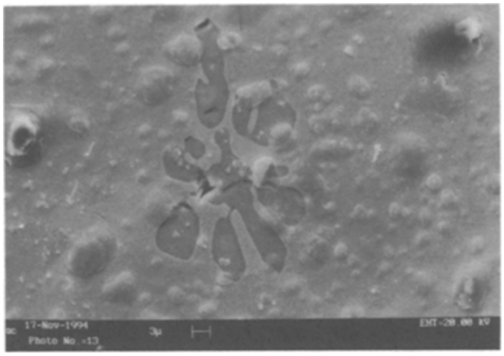

Fig. 4 S.E.M. metallography (1330 times) of the fusion drop structure

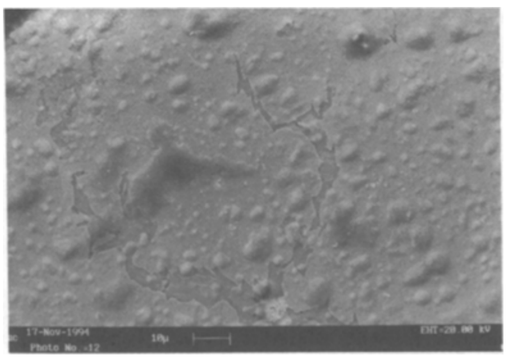

Fig. 5 S.E.M. metallography (800 times) of the fusion drop structure

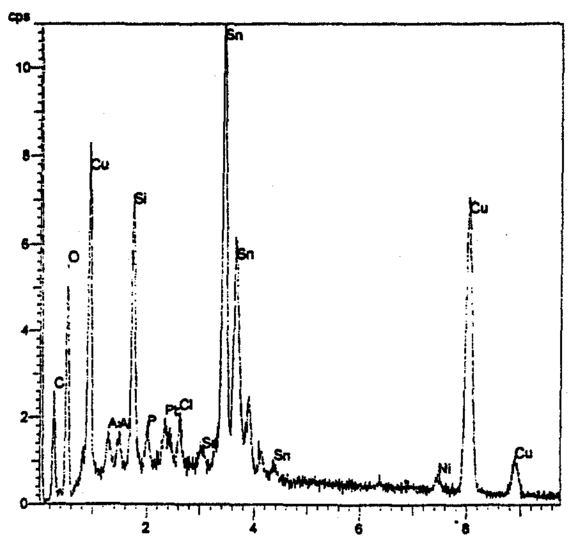

Fig. 6 Terminal-winged axe: EDS microanalysis results

An investigation in different areas revealed spots characterized by a high percentage of Sn, and spots where Cu, S and a very little Sn were present. From the heterogeneous composition and from the presence of numerous copper sulfide inclusions (probably residues of the raw mineral), it was possible to conclude that the drops consist of bronze in the first phase of the melting process; the drops may therefore be regarded as proof of prehistoric metallurgical activity in Liguria.

Terminal-winged axe

The SEM and EDS analyses were carried out directly on the axe. The entire surface was examined, and at different points the internal composition of the alloy was analysed. The results of the analyses are reported in Fig. 6. It is possible to observe the enrichment in Sn on the surface; in constrast, the analysis of the internal part gives the average composition of the bronze.

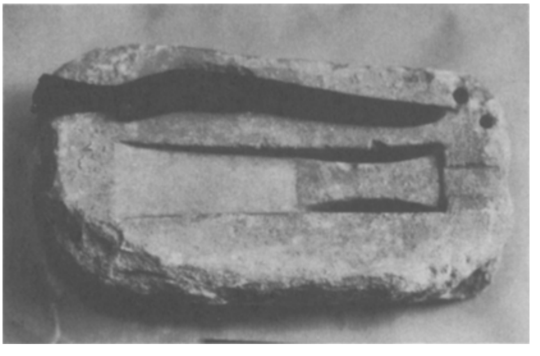

Fig. 7 The knife from the Grotta del Sanguineto in the mould of the Calvet Museum

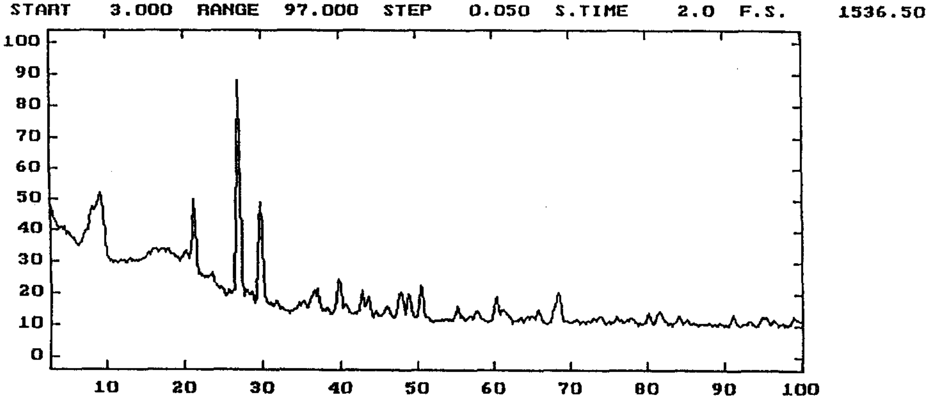

Fig. 8 X-ray diffractogram of the earth found within the socket of the knife from the Grotta del Sanguineto

Socketed knife

This knife, like the axe found in the same cave, was unfinished and unused. The interest in these two objects is principally due to their peculiarity of being unfinished artefacts and to their adaptability to the mould form (conserved in the Calvet Museum in Avignon, Fig. 7), which points to the great similarity in their fabrica-

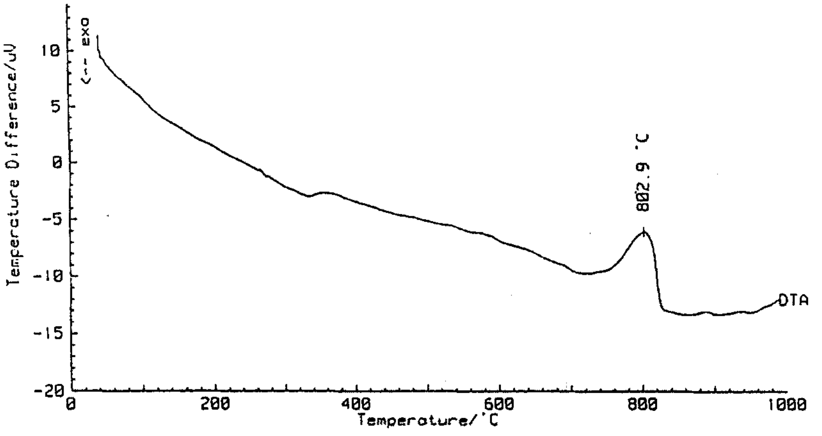

Fig. 9 DTA curve of the earth found within the socket of the knife from the Grotta del Sanguineto

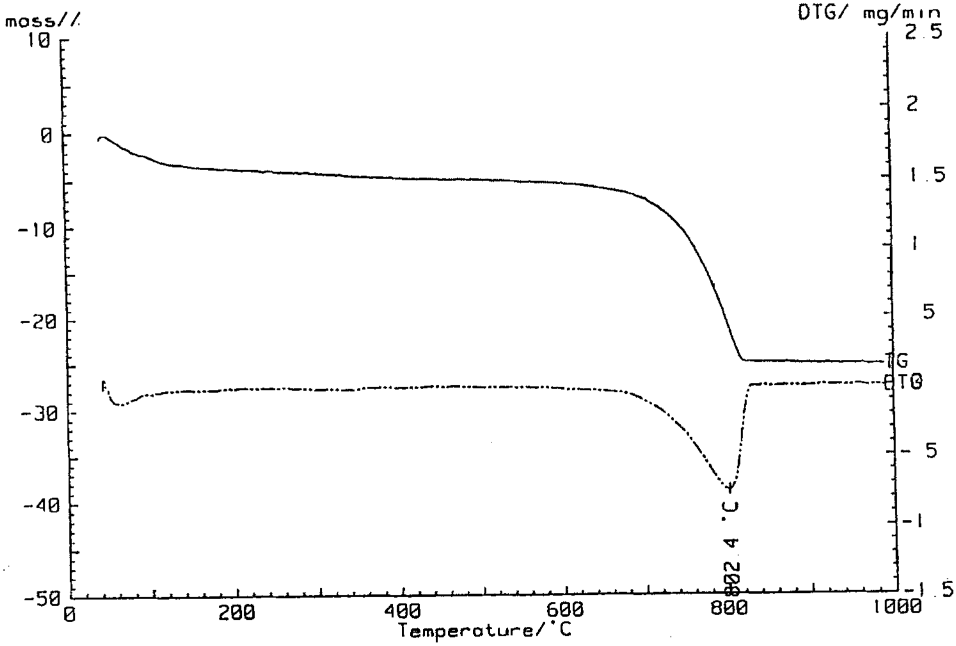

Fig. 10 TG and DTG curves of the earth found within the socket of the knife from the Grotta del Sanguineto

tion. In particular, for the knife some earth was contained inside the socket; a series of investigations were carried out on it, ranging from XRD, through optical and SEM observations, to DTA and thermogravimetry.

Figure 8 reports the XRD pattern obtained, Fig. 9 the DTA curve, and Fig. 10 TG and DTG results.

The DTA curve depicts an endothermal peak at 803°C; corresponding to this thermal effect, the TG curve reveals a mass loss of about 20%; these data demonstrate the whole reaction occurring.

The shapes of the DTA and TG curves up to 700°C provide evidence of an almost regular mass loss (probably due to dehydroxylation of the clay minerals); between 700 and 840°C, calcite undergoes decomposition. From these data, the amount of $CaCO_3$ in the starting mixture was evaluated as approximately 40% by mass.

From a comparison of the earth found inside the knife socket with the calcareous stone forming the mould, it will be possible to establish if the two materials may have the same provenance.

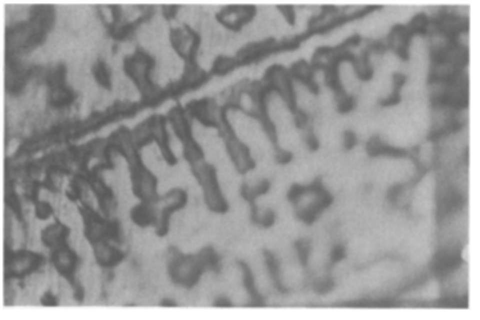

Fig. 11 The dendritic structure of the socket ot the knife from the Grotta del Sanguineto (320 times)

Information on the working process was yielded by the micrograph corresponding to the socket of the knife (Fig. 11). This reveals the typical morphology of an as-cast alloy, without any trace of deformation due to mechanical work or heat treatment. This confirms the hypothesis that the knife has never been used.

* * *

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