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Non-invasive characterization of Nuragic bronzes through neutron based techniques

M.Cataldo[1], F. Grazzi[2], A. Scherillo[3], A. Fedrigo[3], A. Depalmas[4], A. Canu[5], A. Brunetti[1]

[1]*Dipartimento di Chimica e Farmacia, Università degli Studi di Sassari*
[2]*CNR, Istituto di Fisica Applicata "Nello Carrara", Sesto Fiorentino*
[3]*Science and Technology Facility Council, ISIS Neutron Source, Didcot, UK*
[4]*Dipartimento di Scienze Umanistiche e Sociali, Università degli Studi di Sassari*
[5]*Soprintendenza Archeologia, Belle Arti e Paesaggio per le province di Sassari e Nuoro*

Abstract **– As part of a research project on Sardinian bronze metallurgy, neutron diffraction and neutron imaging experiments were performed on a set of Nuragic bronzes at the ISIS Neutron and Muon Source (Didcot, UK). Neutron based techniques are a very effective tool for the study of archaeological samples: neutron diffraction provides important information regarding the composition, the microstructure and the conservation status of metallic materials; while neutron imaging provides information about the structure and the morphology of the given samples. These data are of great value and, when compared with archaeological information, they can add new and different insights about the investigated artefacts. Furthermore, from data analysis, it is possible to answer some unresolved questions about the artefacts, such as their effective use and their manufacturing procedure. In this work, we present the results of the analysis of a bronze dagger.**

Keywords: Neutron imaging, Neutron diffraction, Nuragic bronze casting, Non-destructive analysis

I. INTRODUCTION

The production of Nuragic Bronze artefacts represents a rich historical archive that provides key information about the metal production and casting techniques relative to the development of the metallurgy in the Mediterranean area. For the understanding of the Sardinian bronze metallurgy, it is important to determine, through non-invasive methods, which construction techniques were employed for the manufacturing of bronze artefacts. Neutron imaging and neutron diffraction are very interesting non-invasive methods for materials characterization. Neutrons are a very effective probe for the study of metallic materials: compared to traditional physical investigation techniques (such as PIXE or XRF) they can penetrate deeper into the matter, giving the possibilities of bulk studies. [1]. The choice to work with these particular techniques resides in the possibility of obtaining a considerable number of information aimed at characterizing the samples in their entirety in a non-invasive way: the multiphase analysis of the diffraction data allows to quantify the different phases present in the artefacts and the peak shape analysis leads to information regarding the production techniques; neutron imaging, instead, gives information about the morphology and the structure of the samples.

Figure 1 - The INES station. The diffractometer is composed by a table (centre), 9 detector banks that cover a 165° angle range. The neutron beam enters from a window on the left side and is collimated by boron-enriched jaws.

The research project is mainly focused on the characterization of Nuragic artefacts from the Early Bronze Age to the Early Iron Age [2,3]. The sample object of this work is a bronze dagger and its two rivets found in the archaeological site of Abini, in the centre of Sardinia. The site was discovered in the late XIX century and it belongs to the village-sanctuary category since common buildings were built alongside votive ones [4]. The dagger has a triangular blade characterized by a prominent spine and a simple back end (see figure 2); the two little rivets served as a connection for the handle. The artefact is in a quite good conservation status: alteration phases are visible in the point and near the single hole side, while evidence of use are present all over the blade. These types of artefacts are a very common finding in Sardinian archaeological sites, testifying a great diffusion among the Nuragic. Such type of object is of great interest, considering that the production of weapons was always performed using the best materials and the most advanced technologies available in terms of casting, thermal and mechanical treatments available at the time. Furthermore, one recurring question about Nuragic weapons is about their effective use: since findings occur both in common sites and in votive ones, it is always unclear their destination. Weapons, objects for daily usage or offers to the shrine? By the means of neutron diffraction, one can try to answer these questions.

II. MATERIALS AND METHODS

The sample was previously analyzed at the IMAT imaging station and then carried to the INES station, to obtain a complete characterization and phase mapping of the entire structure.

A. The IMAT neutron imaging station

IMAT (Imaging and MATerials science and engineering) is a cold neutron imaging instrument for attenuation-based transmission measurements (neutron radiography and tomography) and energy-selective and energy-dispersive neutron imaging located at the ISIS target station 2 [5, 6]. Neutron imaging allows obtaining information about the morphology of the sample and its microstructure, making it possible to understand how the parts are connected or how the distribution of materials varies in the samples (the contrast between different elements is enhanced by cold neutrons). The instrument is equipped with an x-y-z-ω rotation stage for samples up to 1.5 t. For this measurement, the IMAT natural neutron bandwidth (1–6 Å) was used as well as a 2048×2048 pixels ANDOR Zyla sCMOS 4.2 PLUS camera coupled with a scintillator screen for the acquisition of transmission images. Neutrons that are transmitted or scattered by the sample, are registered by the neutron camera and then stored as images or events. To perform tomography reconstruction, the dagger was wrapped in aluminium foil (a material almost transparent to neutrons) and put into an aluminium cylinder mounted on the rotating stage. Image filtering for gamma white spot removal was performed using ImageJ [7] and normalization was done using the Octopus Reconstruction software [8].

B. The INES Diffractometer

INES is a time of flight diffractometer located at the ISIS target station 1 (Fig.1) [9]. Together with 144 squashed Helium 3 neutron detectors (divided into 9 banks), the instrument is equipped with an x-y-z-ω table that allows moving and orienting the sample respect to the neutron beam. This system allows measuring objects of different size, even when dealing with challenging sample shape. For the experiment, the samples were mounted on the INES table and measured in six different points.

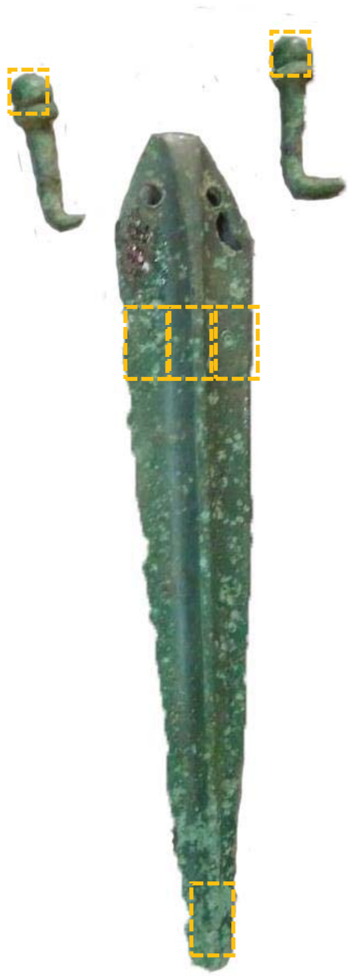

Figure 2 - The dagger (14 cm long). Highlighted in yellow, the measured areas.

Each measurement area was decided previously, based on the morphology of the sample (see fig. 2): the irradiated areas range from 10 mm^2 to 120 mm^2. The measuring time was decided accordingly to the thickness and the size of the selected area and it took from 2 to 7 hour for every measurement. After that, the sample activation was measured using a Geiger counter: one drawback of neutron analysis, indeed, is that, after the irradiation, samples stay active for a period which can vary from a few hours to several days depending on the composition and the irradiation time.

The collected data were normalized with the Mantid code [10] and the Rietveld analysis [11] was performed by the means of GSAS I software through the EXPGUI interface [12]. The Rietveld analysis allowed to quantify the different phases present in the artefacts and the diffraction peak shape analysis was performed to obtain information regarding the production techniques [13].

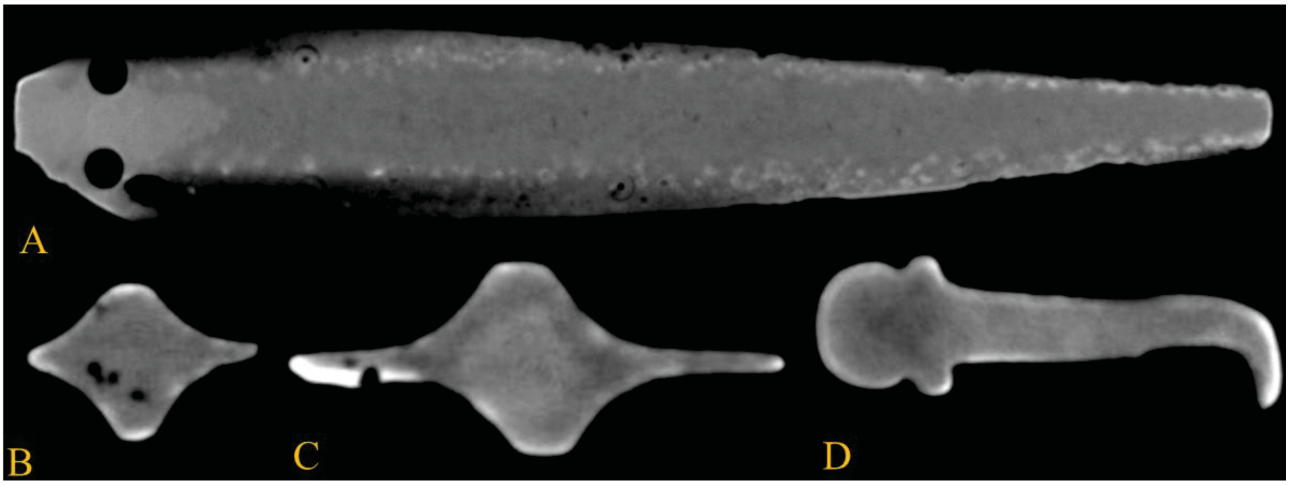

Figure 3 - Neutron tomographies of the dagger (greyscale). A - the slice is taken XZ plane showing the presence of 3 sets of punchings; B: the slice is taken in the XY plane showing pores; C: plane slice showing an area of corrosion that is affecting the metal; D: rivet slice taken in the XZ plane. A layer of corrosion is visible in the outer part of the metal

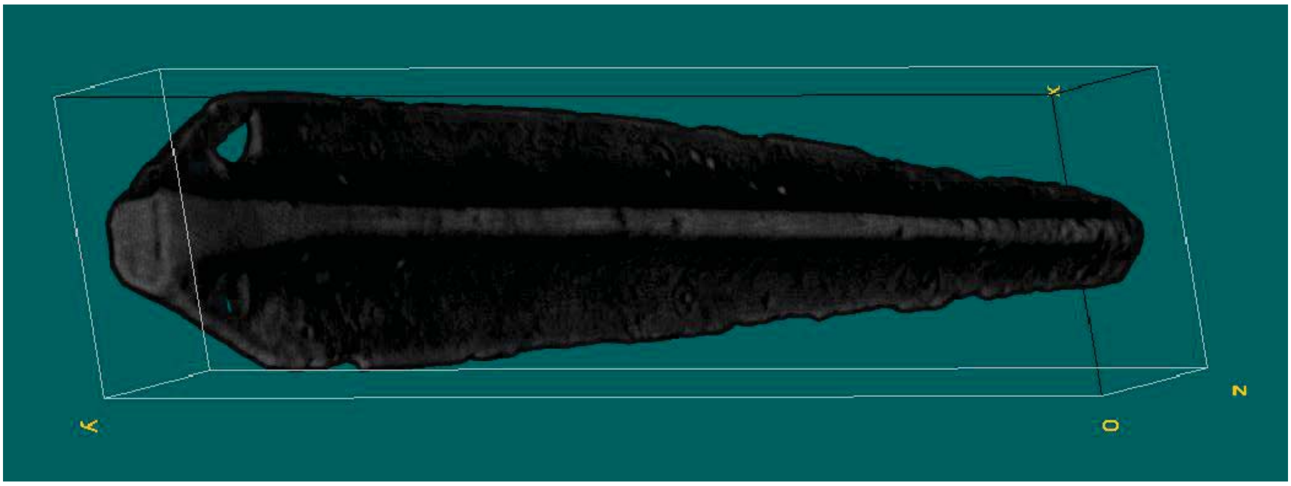

Figure 4 - 3D rendering of the dagger recreated by using the 3D viewer plugin of ImageJ [7]. Along the blade, the 3 pairs of punching are visible as well as traces of use

III. RESULTS

A. Neutron imaging

Throughout the study of neutron tomographies is possible to see beneath the surface of the investigated material: what is possible to see are all the slice images (in three different orthogonal view) that constitute the entire sample. This gives the possibility to study different parts of the material and their characteristics. It is also possible to discriminate the alteration phases from the metal, since the beam is more attenuated by the firsts, so they result brighter in the tomography. As it is possible to see in figure 3C, near the one-hole side edge, a brighter part with a hole is visible: this is an area strongly affected by alteration, and the hole has almost gone through all thickness. Another brighter part is at the point of the blade (not shown), which is more altered than the rest of the blade, as it is possible to see also in figure 2. Figure 3B shows an interesting slice of the dagger: the darker circles within the sample are small pores. Porosities are small air pockets that are formed at the moment of casting, due to the presence of gasses trapped into the molten metal or as a consequence of the cooling of the metal in the mould. The presence of pore is negative for the mechanical properties of the metal since they are defects within the structure, that is less resistant to external stresses. An interesting characteristic of the sample is the presence of a series of punching along the thinner sides of the blade, as it is possible to see from figure 3A and 4. These pair of punchings are meant to be a decoration and from the tomographies is possible to see the deformation of the metal, that was pressed by the instrument used for the punchings. Figure 3D, instead, reports a slice of the short rivet. Finally, from a tomography it is possible to assess if an artefact is made by a single casting or is the sum of different parts: in this case, is quite clear that the dagger was made as a single casting.

Table 1 - Metallic and mineralization phases characterization in wt %.

Position	αCu-Sn		Pb	Cu_2O	CuCl	Cu_2S
	I	II				
One hole side edge	65.1 ± 1.8	33.4 ± 1.6	0.8 ± 0.2	0.4 ± 0.1	0.3 ± 0.1	-
Centre	70.2 ± 0.1	28.3 ± 0.1	1.1 ± 0.2	0.2 ± 0.1	-	-
Two hole side edge	73.7 ± 1.6	24.5 ± 1.6	0.8 ± 0.3	0.8 ± 0.1	0.3 ± 0.1	-
Point	97.58	-	0.6 ± 0.2	0.7 ± 0.1	0.7 ± 0.1	0.4 ± 0.3
Short rivet (pin)	39.47 ± 0.8	59.1 ± 0.8	-	1.1 ± 0.1	0.5 ± 0.1	-
Long rivet (pin)	32.4 ± 2.3	63.8 ± 2.3	0.7 ± 0.3	0.9 ± 0.1	0.5 ± 0.1	1.5 ± 0.6

Table 2 - Lattice parameter of the two alpha phases in Angstrom and tin concentration in wt %.

Position	αCu-Sn		Sn wt % dendrite I	Sn wt % dendrite II	Sn average weight concentration
	I	II			
One hole side edge	3.66887	3.68832	9.3 ± 0.3	12.6 ± 0.2	10.5 ± 0.3
Centre	3.66516	3.68899	8.6 ± 0.3	12.7 ± 0.2	9.8 ± 0.2
Two hole side edge	3.67714	3.68959	10.7 ± 0.2	12.8 ± 0.2	11.2 ± 0.2
Point	3.68460	-	-	-	11.9 ± 0.2
Short rivet (pin)	3.64648	3.66998	5.4 ± 0.2	9.5 ± 0.2	7.8 ± 0.2
Long rivet (pin)	3.64583	3.67031	5.3 ± 0.3	9.5 ± 0.2	8.1 ± 0.2

B. Neutron diffraction

The multiphase analysis revealed the presence of two α-phases in every measured area except from the point. The good conservation state is confirmed by the low amount of mineralization phases, generally lower than 1% in weight as reported in table 1. The blade centre shows dendritic segregation with tin equivalent weight concentration of about 9.5 % and 12.5% for the two alpha phases; while for the two rivets the tin equivalent weight concentration is about 5.4 % and 9.5 % (see table 2). This evidence suggests that the cast was poured in a cold mould and then let cool down; also, we can assume that the high content in the tin is a needed characteristic for the artefact since with more tin the alloy is harder and more resistant. Along the structure, the average concentration of tin is similar except from the point, which has a slightly more elevate average concentration, as shown in figure 5. This could be due to a different viscosity of the molten metal or to a gravity effect: in the first case, the less viscous part of the molten metal, richer in tin, could have filled firstly the thinner parts of the mould, such ad the point; in the second case, the mould was placed vertically, with the point towards the ground: in this case, the higher concentration could be due to the different weight of the two elements forming the alloy. Then, the point, underwent a more rapid cooling down than the rest of the cast, since no dendritic segregation is present in this area. The two rivets, instead, show a lower concentration of tin, around 8% in weight. Rivets needed to be more ductile than the rest of the artefact, since they were supposed to be plastically deformed: inserted in the hole of the dagger, they then created the connection with the handle. Moreover, in this case, it is noticeable that these are not two simple rivets, but two upper parts of simple globular headpins used for this purpose. Finally, lead was detected but with a concentration always lower than 1.1 %: the presence of this element can be due to the mineralization used for the casting rather than an intentional addiction. For what regards the microstructure characterization, two parameters used for the refinement of the diffraction data, can describe the peak shape. Gaussian s400 and the Lorentzian broadening γ2 are related to the broadening of the peaks and can assess special features within the structure, giving important information. However, due to the presence of dendritic segregation, is not possible to give a significant description of these two parameters. A parameter that, instead, can be interpreted is the texture index J: if the crystallographic domains show preferred orientations the sample is textured and $J>1$, while when $J = 1$, no texture is present. In the measured point of the dagger, J is bigger than one: since no evidence of annealing was found, this value suggests that the blade was cold worked, to shape and give more strength to the material.

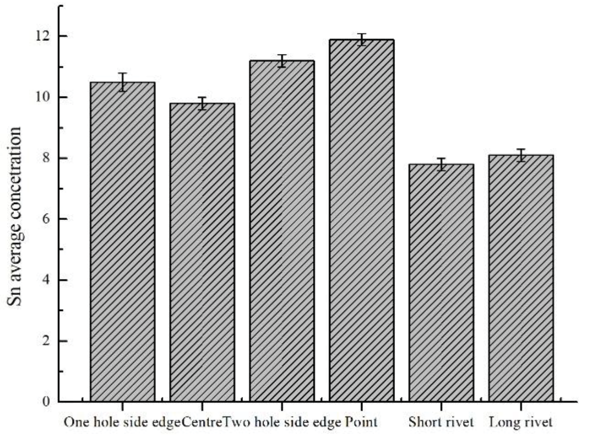

Figure 5 - Sn average concentration in the measured areas (wt %). The difference between the rivets and the dagger is visible

IV. CONCLUSIONS

The results of the data analysis are very interesting and offer the possibility to make some assumptions regarding the investigated samples. We found differences between the dagger and the two rivets, due to their separate use and we highlighted the presence defects in the structure (pores) as well as elements of decorations (punchings) thanks to the study of neutron tomographies. Furthermore, from neutron diffraction analysis it was possible to characterize the mineralization phases and the alloy. The artefact has high tin content, resulting in a quite hard alloy: this suggests that the artefact is not votive; the high tin concentration could be a requested characteristic since the dagger should have resisted to external stresses and be able to cut or shape other materials. Furthermore, the result of the analysis allows us to assess that two different castings were made for the dagger and the two rivets. It should be mentioned that the rivets can be worked in place, like the ones analyzed in the already published work of Brunetti & Al [2]. Finally, no evidence of annealing was found, even in the rivets: this could suggest that the rivets were not heated up to be inserted in the holes. The two experimental techniques used in this work are not a very common application in the study of an archaeological artefact, but as it is possible to see, their use and their combination can give very interesting insights about the investigated material.

V. ACKNOWLEDGEMENTS

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