

BRONZE ARCHAEOLOGICAL FINDS FROM THE VILLANOVAN NECROPOLIS OF ORTO GRANARA (BO): STUDY OF MANUFACTURING TECHNOLOGIES AND EVALUATION OF THE CONSERVATION STATE

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The following study focuses on a number of Villanovan bronze artefacts of different typologies, coming from a necropolis discovered in 1998 on the site of Orto Granara (Castel S. Pietro Terme – Bologna – Italy). The period of use of the necropolis spanned from the end of the 8th to the first half of the 7th century B. C. Among the metallic finds retrieved during the excavation, a set of samples has been chosen in order to conduct a set of archaeometallurgical analyses aimed at defining their nature (both in the sense of their chemical composition and their microstructure) and evaluating their state of conservation.

Samples have been analysed through optical microscopy (OM), stereomicroscopy (SM) and Extended Pressure Scanning Electron Microscope (EP-SEM) in VP-mode with EDS microprobe for the localised evaluation of the composition. The corrosion products were studied by infrared spectroscopy (FTIR) and the alloy composition by Flame Atomic Absorption Spectroscopy (FAAS).

The results thoroughly confirmed the knowledge of Villanovan and Etruscan metal technology that has been defined by analyses conducted in recent years.

PAROLE CHIAVE: High Nitrogen Stainless Steel, Microsegregation, Modelling, PESR, gas nucleation

INTRODUCTION

In spring 1998, during the digging of a gravel pit at Orto Granara (a site in the municipality of Castel S. Pietro Terme, some 30 kilometres south-east of Bologna – Italy), the excavator brought to light a wooden case burial datable to the early 7th century B. C. and referable to the Villanovan culture. In consequence of this discovery, an archaeological investigation of the

site was planned and carried out, leading to the identification of the remnants of an Early Iron Age settlement, including a small reclamation ditch, and a small necropolis.

After two archaeological seasons, a total of thirteen tombs have been recovered, and a better knowledge of the settlement has been achieved. The excavations show the presence of a small quadrangular furnace and some house structures [1]. The number of large scale tombs is remarkable, evidence that immediately indicates the probable funerary ritual wealth exhibition of an aristocratic group.

The small settlement discovered at Orto Granara was likely part of the program of territorial rearrangement started during the 8th century B. C. by the prominent Villanovan centre of Felsina (modern Bologna): the earlier network of small villages, characterized by a subsistence economy system, was gradually replaced by a strongly hierarchical economic organization meant to allow Felsina to control the surrounding area. This reorganization of the territory led to the establishment of a great

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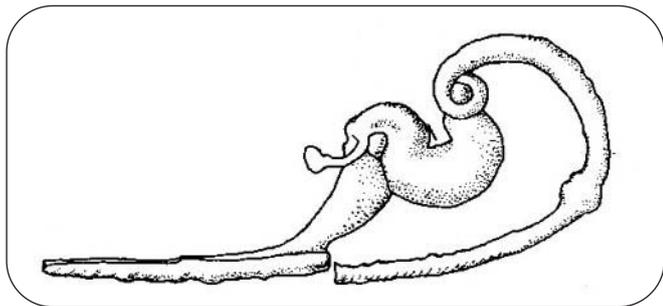
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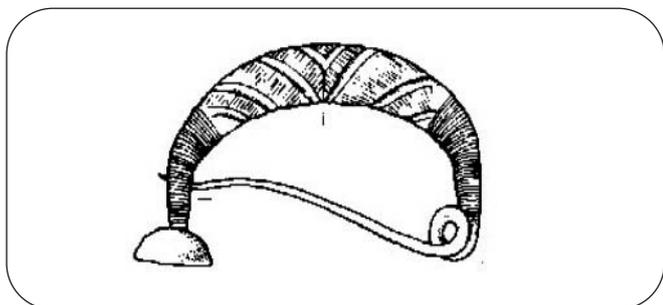
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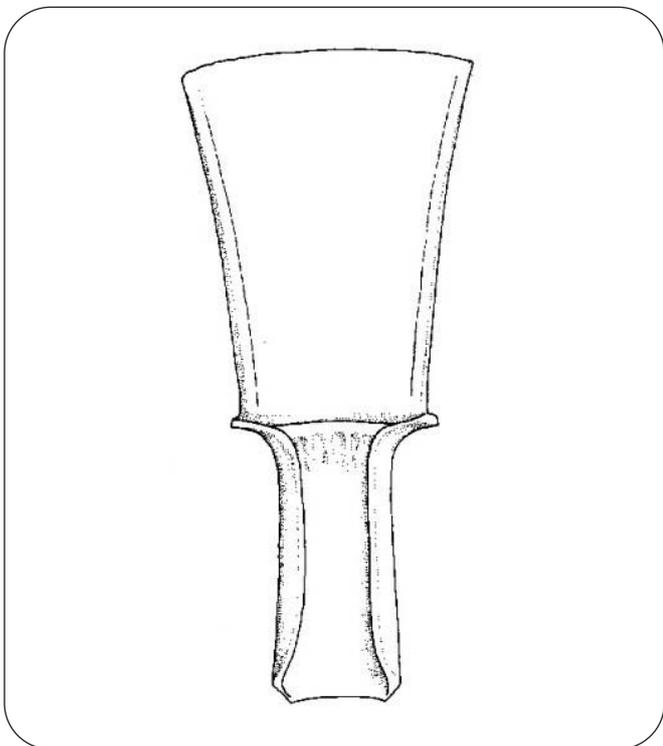
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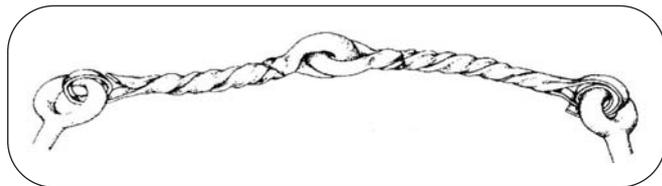
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Fig. 1
"a drago" type fibula.
esempio di fibula a drago.



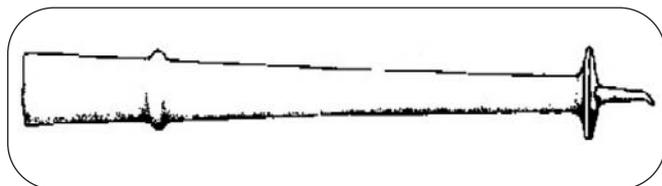
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Fig. 2
Lowered thickened arc fibula (decorations not matching those of the studied specimen).
Esempio di fibula ad arco ingrossato ribassato, con decorazioni differenti rispetto all'esemplare studiato.



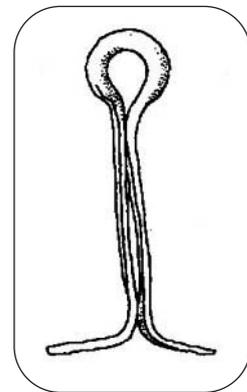
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Fig. 3
"ad alette" type axe.
Ascia ad alette.



▲
Fig. 4
horse bit made with two convoluted bronze bars.
Filetto di morso a verga ritorta.



▲
Fig. 5
Goad.
Stimolo.



▲
Fig. 6
Eyelet.
Eyele.

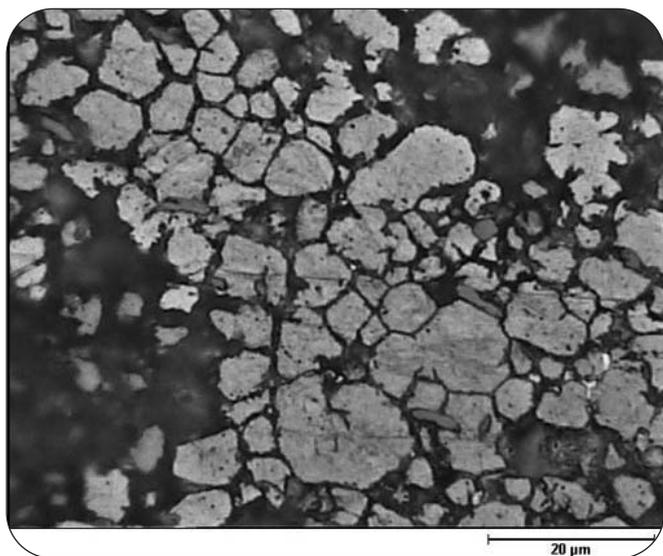
number of settlements, scattered through the part of the Po plain bounded on the west by the Panaro river and on the east by the Santerno river, a portion of land made suitable for extensive cereal farming by massive canalization and reclamation works.

This network of medium and small size sites (brought to light in recent years, even if only partially in some cases) was essential to the agricultural exploitation of the plain surrounding Bologna; prominent among these sites is Orto Granara. It is evident that, the settling typology was based on "piccoli nuclei sparsi definibili come 'fattorie', dipendenti in questo caso dal grande centro di Felsina" [2], possibly for the first time in such an exhaustive way for periods so ancient.

The intervention on the finds from Orto Granara's tombs has been limited till now to the first activities carried out at the time of the discovery, which only aimed at avoiding loss of fragments. Thus, the project regarded a group of bronze objects coming from some of the burials discovered, especially from tombs 5, 6 and 11. It was aimed at the restoration of the objects through several analyses, which were meant to gather information on the technology involved in the making of the artefacts, on their chemical composition and on their state of preservation.

A list of the finds analysed in the project is given below:

- Three pins of different typologies (trident-shaped with globular heads – find n° 5.31; with globular metallic head – n° 5.47; with composite head – n° 11.13),
- Four fibulae (three "a drago" (see Fig. 1) – finds n° 5.27, 5.30 and 5.44; one with lowered thickened arc (see Fig. 2) – n° 11.25),
- Two axes (see Fig. 3 – finds n° 6.6 and 6.7)
- two horse-bit (see Fig. 4; finds n° 11.15a-b)
- one ring (horse fitting - find n° 11.26)
- one goad (see Fig. 5 – find n° 11.23)

▲
Fig. 7

OM image of the trident shaped-pin 5.31.

Microstruttura dello spillone trifido 5.31 al microscopio ottico (dopo attacco).

- two bronze “eyelets” (carpentry elements (see Fig. 6) – finds n° 11.33 and 11.36)
- four copper ingots (finds n° 6.26a-d)

Depending on the different conditions of preservation of the finds and on the relevant kind of sampling possible on each of them, always keeping in mind restoration necessities, not the same set of analysis has been carried out on every object.

Given that the analysed objects are still being studied and thus are unpublished, in order to make the general morphology clear some drawings of objects of the same typology are here reproduced.

MATERIALS AND METHODS

Samples have been observed through optical microscopy (OM), stereomicroscopy (SM) and Extended Pressure Scanning Electron Microscope (EP-SEM) in VP-mode with X-ray Energy-Dispersive Spectroscopy (EDS) probe for localised for the localised compositional analysis. In order to characterise the microstructure, samples have been embedded in epoxy resin and prepared for metallographic observation following the procedure described by Scott [3]. When possible, metal composition has been evaluated by Flame Atomic Absorption Spectroscopy (FAAS), following the procedure for ancient bronzes described by Hughes et al. [4]. Corrosion products were scraped and analysed by FTIR spectroscopy.

RESULTS AND DISCUSSION

The results of the microstructural characterisation indicate that most of the objects have undergone extensive plastic deformation alternated with annealing cycles. Most samples are still in a strain-hardened state, with some exceptions. For example, among the three pins studied, only the trident shaped one (5.31, Fig. 7) has been completely annealed in the final step of the working cycle, while the other two pins (5.47 and 11.13, Fig. 8) show a microstructure with distorted twins and strain lines inside the grains. The difference is also visible in the corrosion

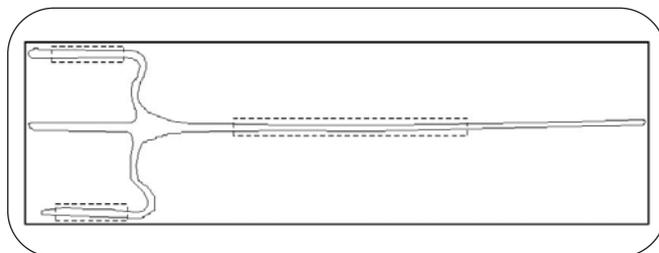
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Fig. 8

OM image of the pin 11.13; distorted twins and strain lines are visible in the grains.

Microstruttura dello spillone 11.13 al microscopio ottico dopo attacco; sono evidenti i geminati distorti e le linee di scorrimento.

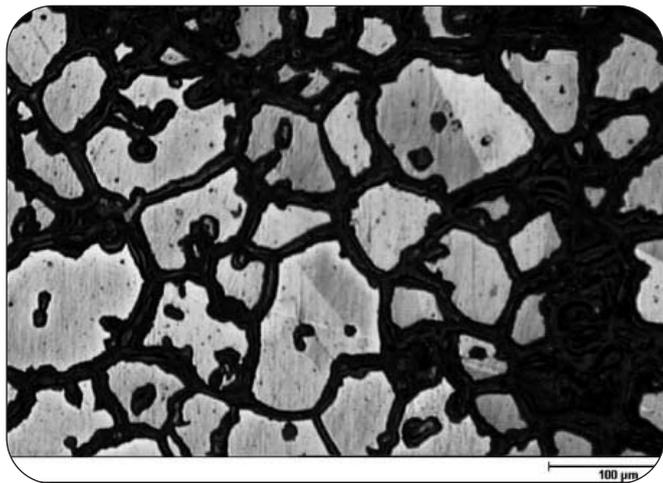
behaviour of the pins: the patina of cuprite grown on the surface of pin 5.31 is continuous and in good conditions with few small spots of other corrosion products, while the surface of the pins 5.47 e 11.13, being more reactive, appears completely covered by copper carbonates like azurite and malachite. An explanation of this difference could be found in the particular and quite unusual shape of the trident shaped pin: it could have been produced by a different workshop, more experienced with hot working cycles, or by the same workshop using special working conditions for valuable objects of important commitments. In fact, the trident shaped pin is the only one showing traces of an engraved decoration in the area of the sample under examination. The pin may have been heated during engraving in order to make the decoration step easier, thus producing a recrystallised microstructure in decorated areas.

The good state of conservation of the pin could therefore be explained with the fact that the decoration was located not only on the two lateral arms but also on a wide area of the central stem. The point of conjunction of the 3 arms (Fig. 9) and the end

▲
Fig. 9

Schematic drawing of the pin 5.31, the dashed lines indicate the position of the decorations. The three globules, one located on the top of each arm, are not drawn.

Disegno schematico della forma dello spillone 5.31, con indicate a tratteggio le zone dove è presente la decorazione. Non sono rappresentati i tre globuli alla sommità dei rebbi.



▲
Fig. 10

OM image of the eyelet 11.33; recrystallized grains with straight twins.

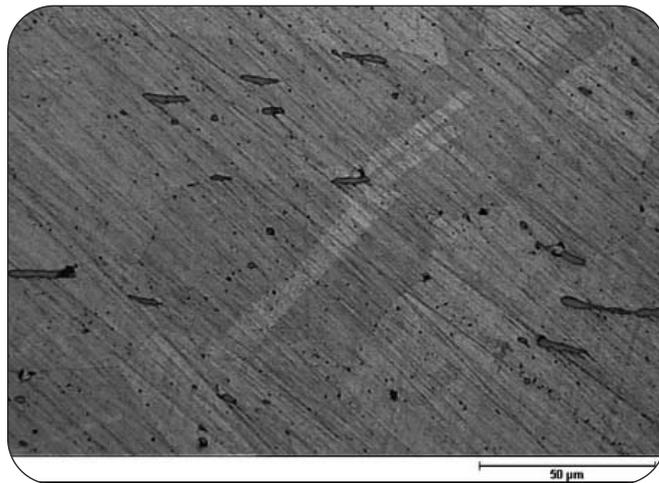
Immagine al microscopio ottico dell'occhiello 11.33 dopo attacco. Si notano i grani ricristallizzati con geminati rettilinei.

of the central arm, where no traces of decoration are present, are more heavily corroded, even if it should also be taken into account that the thinner part of the stem is also more heavily worked.

These hypotheses could be confirmed by the comparison of metallographic observations both in correspondence of the engraving and at the end of the stem. It is generally believed that these decorations were directly obtained on pins by casting the metal into a mould obtained from an already decorated wax model [5, 6]. Unfortunately, conservation requirements do not allow further analyses on these objects.

Furthermore, also the two eyelets (11.33, 11.36) show a completely annealed microstructure (Figs. 10, 11), with equiaxed twinned grains free from strain lines. The composition of the alloy, estimated by SEM-EDS corresponds to a monophasic Cu-7%wt Sn alloy, with very low amounts of lead dispersed in the -Cu matrix. Since the eyelets were probably used to link together leather parts of horse fittings, their final shape was obtained on site after manufacturing the straight eyelet with arms closed and unbent. Subsequently, the arms of the eyelets were heavily bent (nearly 90°) and therefore heated before/during bending, thus producing a recrystallised microstructure also in the bent area (Fig. 10).

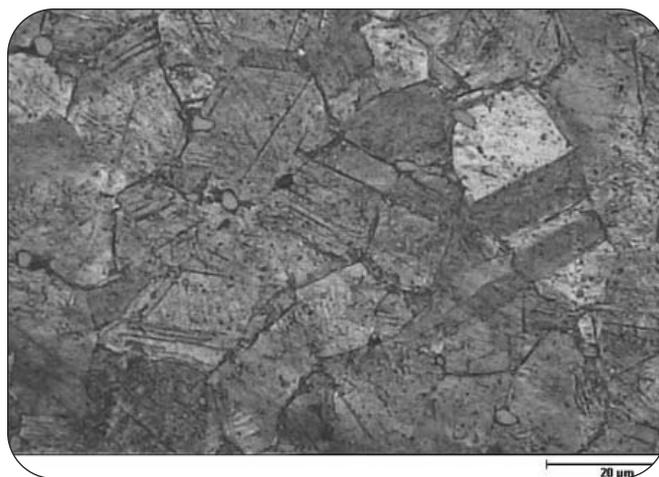
Annealed microstructures are therefore the consequence of special finishing procedures which required heating in the final step of the manufacturing process, as confirmed also by investigations on two parts of fibula, the apophysis (head), sampled from 5.27, and the needle from 5.44. These samples are taken from two different fibulae, but very similar in shape, so that it could be assumed a similar manufacturing technique. The microstructure of the needle of fibula 5.44 shows recrystallized grains with strain lines and distorted twins, indicative of cold working (Fig. 12); on the contrary, the microstructure of the apophysis 5.27 is the consequence of final annealing or hot working (Fig. 13). The manufacturing process probably required more extensive deformation in the case of the apophysis and therefore annealing was necessary in order to retrieve enough ductility. The production of "a drago" fibulae, obtained directly by a casting process (with the two apophyses already included) followed by some cold work-



▲
Fig. 11

OM image of the eyelet 11.36; the microstructure is similar to the one of the eyelet 11.33, but less corroded.

Immagine al microscopio ottico dell'occhiello 11.36, con le stesse caratteristiche del reperto 11.33 ma molto meno interessato da processi corrosivi (dopo attacco).



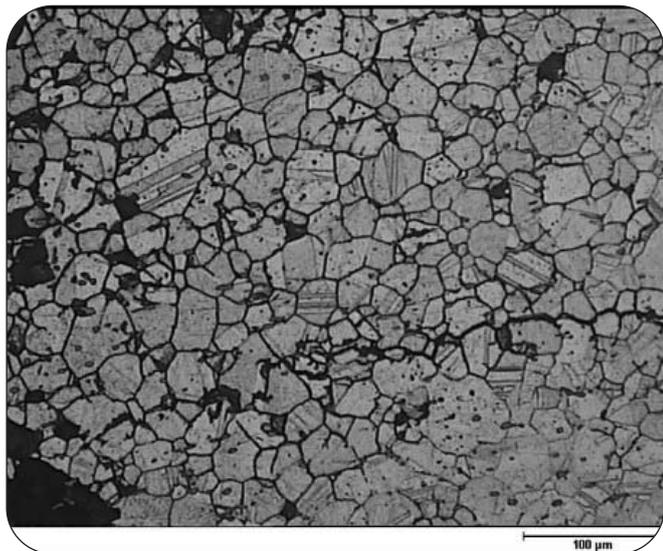
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Fig. 12

OM image of the fibula 5.44; distorted twinned grains and strain lines are visible in the grains.

Microstruttura dell'ago della fibula 5.44 dopo attacco, con evidenti grani geminati ed estesi sistemi di linee di scorrimento.

ing to finish the object or by the addition of further apophyses, has been already reported (5). Cold working of the apophysis 5.27 can be revealed also by the corrosion morphology, observed in the cross section of a metallographic sample: corrosion products still reproduce the stratifications induced by plastic flow. (Fig. 14).

The microstructure of the axe 6.7 can be interpreted in two different ways. On one hand, the high frequency of strain lines evidenced by corrosion, without any etching of the sample, indicates the absence of final annealing (Fig. 15). Moreover, the fact that the blade is strain-hardened, would suggest a functional use of the axe. On the other hand, also a ritual-funerary function would be coherent with the small thickness of this axe: in this case the common practice for the production of functional axes has been followed also for the ritual one.



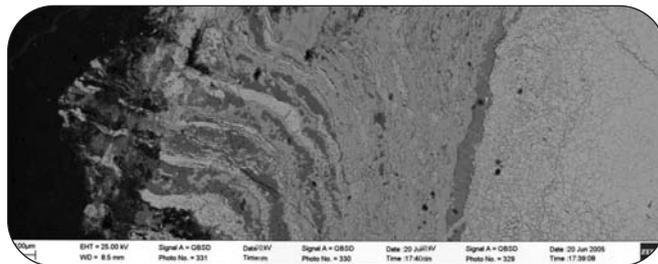
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Fig. 13

OM image of the needle of the fibula 5.27; recrystallized grains are visible.

Microstruttura dell'antenna della fibula 5.27 dopo attacco; si notano i grani ricristallizzati privi di linee di scorrimento.

The empirical knowledge of the properties of the different alloys, chosen according to the different manufacturing requirements, is evident also from the results of elemental analysis in Tab. 1.

Apart from ingots, which will be discussed later, the only object with a lead content high enough to be considered as an intentional addition, is the fibula 5.30. Its composition, in particular lead and tin contents, is functional to the production by casting of an object with complex shape, and at the same time the lead content is low enough to allow some cold working. The values reported in Table 1 are fully coherent with previous studies reported from other authors on Etruscan fibulae dated back to VII–VI cent. BC [7], and also on “a drago” fibulae of different production obtained by the same production sequence [5]. A fibula found in



▲
Fig. 14

SEM image (back scattered electrons) of the head of the fibula 5.27: uncorroded core (right hand side) covered with stratified layers of corrosion products.

Micrografia SEM in elettroni retrodiffusi della capocchia della fibula 5.27. Si nota il cuore di metallo integro (a destra) e la stratificazione dei prodotti di corrosione (a sinistra).

the tomb 89 from Verrucchio [8] has a much lower lead content, but a tin content which is coherent with data from other studies and with the composition of fibula 5.30. Also in the horse bits, in the goad, in the axe and in the fibula with lowered thickened arc, the same attention to the choice of the amount of the main components (lead and tin) in the alloy has been noticed, as a function of the subsequent cold working and of the geometry of the object. The shape of the horse bits and goad do not require a high fluidity of the alloy. Furthermore, for the horse bits, plastic deformation of the primary rod with rectangular section, obtained by casting, should have been very intense.

Similar values has been found also in some parts of the horse-bits from the necropolis of Lippi in Verrucchio [8], even if these objects have been obtained by casting, with very low plastic deformation involved. In particular the tin content found in eight samples taken from bits, lateral parts of the head stall (“tiranti”) and decorative elements of it (“montanti”), ranges from 6.94%wt and 8.54%wt; lead content varies from 0.34%wt to 1.64%wt, but only for bits and “tiranti” from 0.34%wt and 0.49%wt. Also from the tomb 47 in Verrucchio, two parts of an horse-bit has been analysed: one (a “montante”) shows similar

	Weight (mg)	Sn	Pb	Fe	Ni	As	Zn	Bi	Ag	Sb
Fibula “a drago” (5.30)	8,6*	13,0	2,50	0,27	0,20	0,80	-	-	0,28	-
Axe (6.6)	13,1	9,6	0,61	0,17	0,11	0,75	0,01	-	0,16	0,35
Horse-bit (15.a1)	10,2	7,7	0,32	0,09	0,17	0,19	0,01	-	0,14	-
Horse-bit (15.a2)	12,6*	7,2	0,34	0,20	0,18	0,24	0,01	-	0,14	0,14
Horse-bit (15.b1)	11,8*	8,3	0,32	0,15	0,22	0,46	0,01	-	0,17	n.d
Horse-bit (15.b2)	21,6	7,4	0,30	0,09	0,22	0,40	0,01	-	0,15	0,16
Goad (11.23)	9,7*	6,8	0,25	0,30	0,25	0,44	0,01	-	0,13	0,16
Fibula with lowered thickened arc (11.25)	18,5*	6,2	0,77	0,20	0,09	0,44	0,05	-	0,10	0,17

* : samples with dissolution problems, (semi-quantitative data)

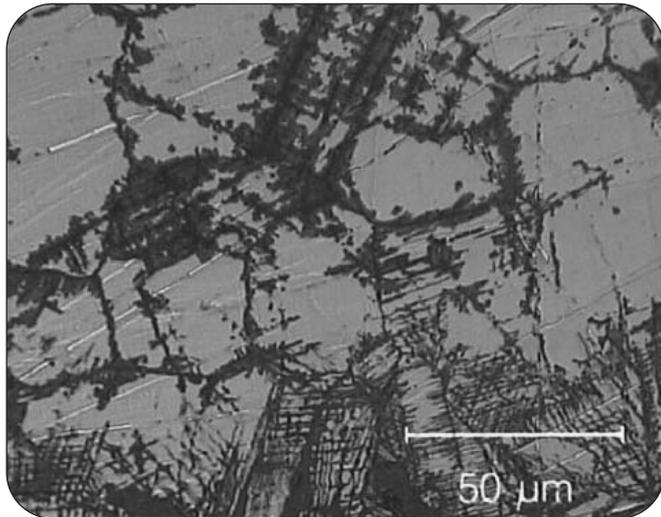
- : element not detected

n.d : element not analysed

▲
Tab. 1

Results of the elemental analysis by FAAS (wt%).

Risultati delle analisi tramite FAAS per gli oggetti finiti (% in peso).



▲
Fig. 15

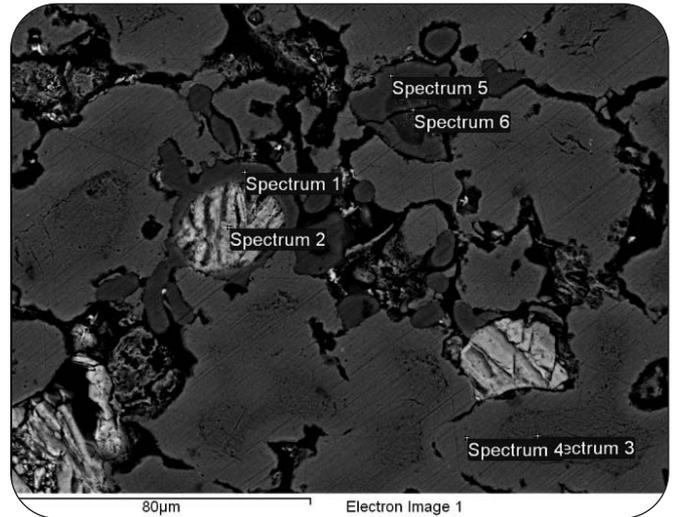
OM image of the blade of the axe 6.7: grains and strain lines are visible because of corrosion.

Piccolo frammento della lama dell'ascia 6.7 osservato al microscopio ottico; la corrosione evidenzia i grani ricristallizzati e le linee di scorrimento anche in assenza di attacco metallografici.

composition to the already described object, but the other has a different composition [9]. Due to the higher standardization of the typology of the bits than of the decorative elements, on the basis of these results it has been assumed a different origin for the two objects, with the possibility of a different workshop or of a different ore. A second hypothesis takes into account the high amount of arsenic as an intentional addition in order to obtain a higher tensile strength [9]. The comparison with the data of the objects from Orto Granara, seems to indicate that the practice of intentional use of alloys with high arsenic content wasn't very common. It seems hence confirmed the hypothesis that for the production of the objects from Verrucchio a less refined alloy has been used. The comparison of axe 6.6 with other axes from Verrucchio show a good homogeneity of the metallurgical background, even if the objects from Verucchio show slightly higher lead contents and slightly lower tin contents.

The fibula with lowered thickened arc 11.25, shows a lower tin content if compared with the arc of the fibula from the tomb 89 of Verucchio, and also the lead content results are low for a cast that, even if simply shaped, is supposed to reproduce the incisions made on the wax model.

The explanation can then be found in the need of deeply working the cast to produce the spring and the stirrup (the U-shaped sup-



▲
Fig. 16

SEM image (back scattered electrons) of ingot 6.26a, with indicated the points of EDS analysis (results in Table 3). The coring of the dendrites is visible.

Fig. 18: micrografia SEM del lingotto 6.26a (elettroni retrodiffusi), con indicati i punti di analisi localizzata i cui risultati sono riportati nella tabella 3. Si nota la microsegregazione dendritica.

port for the needle point), excluding the possibility that the arc could have been cast-on after the production of the needle.

The coherence among the data of this fibula, the horse bits and the goad allows to assume that the alloy has been produced in the same way: the same workshop could have hence used the same optimised alloy to produce many different objects, that required plastic deformation after casting.

Among the object studied, only the big ring 11.26 (probably connected with horse fittings) has not been deformed, as demonstrated by its dendritic microstructure. A high number of lead inclusions has also been detected. SEM-EDS analysis showed the presence of copper sulphide inclusions at the interface between the lead rich phase and the copper rich matrix. The latter shows a micro-segregated structure, typical of a non-equilibrium solidification. Also in this case lead has been intentionally added in order to increase the casting properties of an alloy that was not to be plastically deformed.

Typical copper sulphide inclusions were detected in this object, but also in the fibula 5.27, in the horse bit 11.15, in the eyelet 11.36 and in the ingots (see Tab. 2).

All the ingots are copper-based with low tin and lead content, in particular ingots 6.26a, b, and c. Also some minor elements like iron, nickel, arsenic and antimony were detected (Tab. 2). The optical

	Peso (mg)	Sn	Pb	Fe	Ni	As	Zn	Bi	Ag
Ingot (6.26a)	23,1	0,1	0,08	0,93	0,98	1,55	0,02	-	1,84
Ingot (6.26b)	23,7	0,1	0,02	1,47	3,89	6,12	0,02	-	n.d.
Ingot (6.26c)	23,5	0,0	0,03	1,25	4,98	2,69	0,08	-	1,69
Ingot (6.26d)	25,7	2,4	1,13	0,89	3,12	2,79	0,06	-	1,26

▲
Tab. 2

Results of the elemental analysis by FAAS on the ingots (wt%).

Risultati delle analisi tramite FAAS per i lingotti (% in peso).

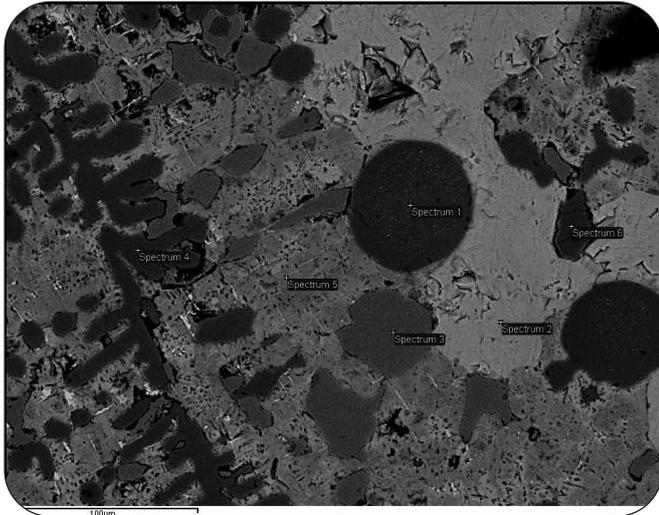


Fig. 17
SEM image (back scattered electrons) of ingot 6.26b.
*micrografia SEM del lingotto 6.26b (elettroni retrodiffusi).
 E' evidente la complessità della struttura, caratterizzata
 dalla compresenza di numerose fasi differenti.*

micrographs of ingots 6.26 a and b, show an as-cast dendritic microstructure with a high amount of inclusions, segregated into the interdendritic spaces. The morphology of inclusions (globular, dendritic, acicular and of other irregular shapes) as well as their variety (Figs. 16, 17) are quite similar to those found in slags from a fairly primitive smelting process [10] or in ingots for metal trading purposes [11]. These data suggest that these ingots were the results of an intermediate step in the production of metal objects.

Also in the case of ingots, like for the ring 11.26 (that as an as-cast object is the most comparable to the ingots), coring of the dendrites can be observed (Fig. 16). The composition of the ingot 6.26d is unique, with amounts (>1% wt) of many elements such as silver, arsenic, lead, nickel, antimony (4,7% wt) and tin, whose presence is not likely to be due to intentional addition. Furthermore, because of the high content of some secondary elements, in particular the highly volatile arsenic and antimony, metal recycling can be excluded. It can be hence assumed that ingot 6.26d has been produced from a different ore. The relatively high amounts of arsenic and antimony, even if the latter is also present as a solute in the dendritic matrix, can be explained by the presence in the ingots of stable compounds of these elements, like copper antimoniate and arseniate [12], coherently with the data from the EDS elemental analysis (Figs. 16, 17 and Tab. 3).

Sb-enriched inclusions surrounded by a crown of copper sulphides can be observed in the ingots 6.26a (see the bright areas in Fig.16). Elements like Fe, Co, Ni, As and Sb are generally present in the Cu-based matrix (Table 3). The darker inclusions in ingot 6.26b (Fig.17), with a round or dendritic morphology (spectra 1,4,6), consist of copper sulphides. The brightest phase in matrix (spectrum 2) is mainly composed by Sb, whereas in other areas of the matrix a white acicular phase rich in Ag can be observed. Grey inclusions (spectrum 3) correspond to a copper-enriched phase with relevant quantities of As, Sb, Ni. Volatile elements such as arsenic and antimony remained included in the ingots due to the formation of stable compounds [12].

Assuming that these ingots are representative of the metal supplied to the workshops of production of the other examined objects, it seems clear that a further refinement had to be done in these workshops before starting the casting procedure. This refinement should have been performed in a standardised way, considering the concentrations of the minor elements found in the final objects. Among these, it is worth noting that the concentrations of residual iron are all superior to the 0.05% value indicated by Craddock and Meeks [13] as the statistical limit between the copper refinement carried out through primitive slagging (so decreasing iron concentration in copper) and another using faster and more lucrative procedures. These data are consistent with the advanced metallurgical technique appearing from Orto Granara finds, even if this is not an incontrovertible marker [5].

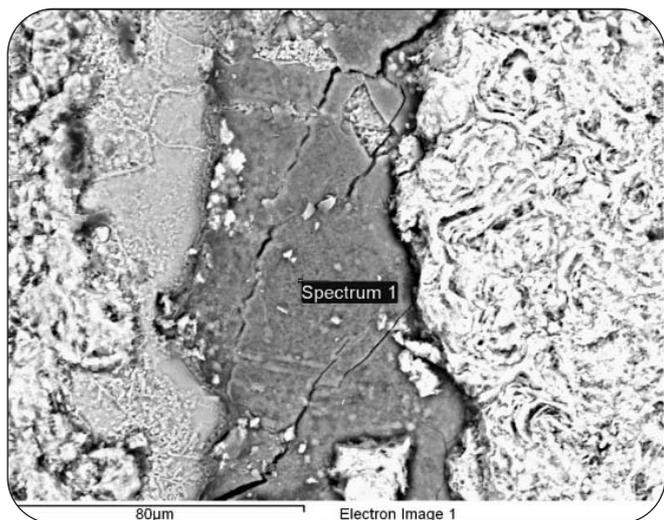
Concerning the tin content in the objects and in the ingots 6.2a-c, it appears evident that this element was usually alloyed in a second time to ingots of different composition and source.

On the contrary, lead is scarcely present in the analysed objects, with the exception of the fibula 5.30 where the addition is obviously intentional. Actually, these low quantities suggest that lead comes from the residual impurities of the intermediate products (ingots) supplied to the metal workshop. In the cases where addition was intentional, it can be supposed that lead was separately available to the metal workshops (for a similar case study see reference 14).

The study of the inclusions inside these ingots allows some considerations on the ore and on the mining procedures [11]. In this case, it is relevant to notice the presence of copper sulphides. The presence of iron in some of these inclusions suggests the use of the mixed sulphide chalcopyrite (CuFeS₂) as copper ore, which has not been completely roasted and therefore remained in the microstructure [15]. The hypothesis that these ingots are effectively the intermediate products for the final objects under examination is suggested by the common presence of copper sulphides, silver (see sample 11.33) as well as the same impurities (As, Sb), in lower percentage in the objects as a consequence of melting and casting that lead to a

Spectrum	O	S	Fe	Co	Ni	Cu	As	Ag	Sb
Spectrum 1	0	16.27	0.13	0	0	83.25	0	0	0.34
Spectrum 2	18.50	0	0	0	0	3.58	1.92	0	75.73
Spectrum 3	1.94	0	1.63	1.16	1.56	92.06	0.62	0.21	0.80
Spectrum 4	1.24	0	0.49	0.44	1.15	89.84	2.13	0.45	4.17
Spectrum 5	0.89	15.45	0.20	0.19	0.15	80.94	0.33	0.47	1.34
Spectrum 6	4.64	13.01	0.23	0.14	0.14	80.57	0	0	1.16

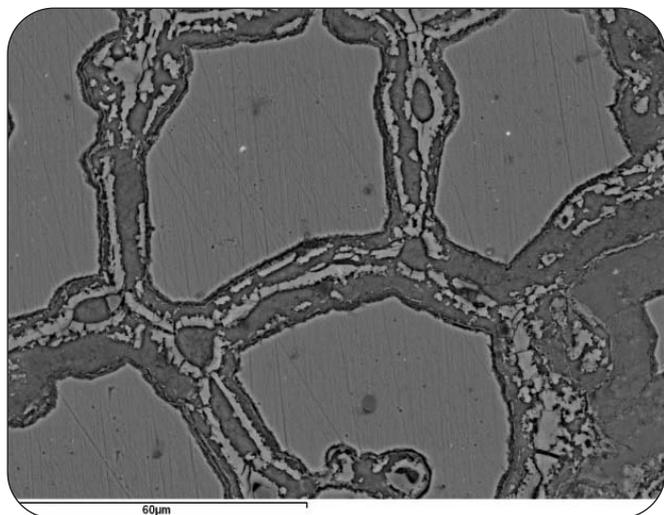
Tab. 3
EDS elemental analysis of the points in ingot 6.26a, indicated in Fig. 16.
 ??????????????????????



▲
Fig. 18

Backscattered SEM image of the head of fibula 5.27 at the metal (right) / patina (left) interface; EDS analysis of the copper chlorides layer in the point indicated by label "spectrum1" : 24.9% Cu, 16.8% Cl, 26.8% C, 31.8% O (atomic %).

Immagine SEM in elettroni retrodiffusi della capocchia della fibula 5.27, nella zona di passaggio tra il metallo e gli strati di corrosione (a sinistra); nel mezzo si nota uno strato probabilmente di nantokite (sp. 1). L'analisi EDS nel punto indicato restituisce valori (at %) di 24.9% per il Cu, 16.8% per Cl, 26.8% per C, 31.8% per O.



▲
Fig. 19

BSE image of the metal core in eyelet 11.33 : intergranular corrosion.

Occhiello 11.33 osservato al SEM (elettroni retrodiffusi) nella zona a cuore del manufatto: si osservano segni evidenti di corrosione intergranulare.

decrease in the concentration of volatile elements.

Usually, the ingots with an "early" currency function such as the well known ramo secco bars [16,17] contain adulterant elements such as iron [13,16,18,19], to lower the cost of production and increase weight. Similarly, also lead is known to be used as an adulterant in Roman aes [17]. On the contrary, the copper ingots from

Orto Granara are ready to undergo further refining before casting. This indicates that these ingots did not have a value of accumulation nor ostentation, which is instead attributed to the ingots during the deposition inside the grave, thus testifying the high status of the deceased.

Finally, some considerations can be done on the morphologies of corrosion and composition of the patina observed on the analysed artefacts.

The interaction with the burial soil is evident in the EDS spectra, which show abundance of Ca, Si, Al in the external layers of the patina (see fibulae 5.27, 5.30) whereas these elements are absent in the internal layers, as typically reported for archaeological bronzes [20,21]. IR analyses reveal that the patina on most samples is rich in malachite and azurite, whereas only cuprite is detected on the majority of the restored objects. Moreover, tin compounds with an amorphous nature, which are very likely to be present in these corrosion patinas, are the objects of ongoing research.

In Fig.18, SEM image of the cross section of the head of the fibula 5.27 is reported. It is interesting to notice the presence of a layer of chlorine and copper-based compound, probably nantokite, at the interface between the residual metal and the more internal layer of the patina mainly consisting of cuprite: this type of patina often originates the so-called bronze cancer [22].

Inside the copper chloride layer some unalloyed copper inclusions are also present, similarly to those described in [23-24]. As a whole, the patina has grown following the original morphology of the apophysis, alternating layers of copper oxides, tin based compounds and unalloyed copper with acicular morphology. The metal near the interface underwent a strong decuprification process, the copper percentage decreasing from the not corroded bulk to the corroded surface [20]. Typically, corrosion has followed the preferential path along grain boundaries and intergranular cracks.

In the case of eyelets (11.33, 11.36), intergranular corrosion down to the bulk has left visible the "ghost" structures of the original metal (see Fig.19-22). In each grain the corrosion proceeds from grain boundary to the core with stratified morphology (Fig. 20). Fig. 24 shows a silver-rich layer around the grain: this makes a connection with the high content of silver in the composition of the ingots (6.26a,c-d), as previously mentioned.

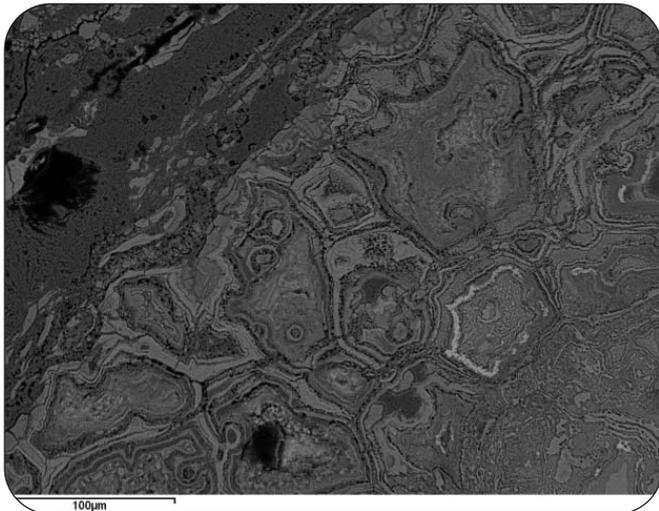
Finally, the extent of corrosion does not allow to comprehend if the higher concentration of tin at grain boundaries is due to the presence of δ phase or if it is the final step of a decuprification process. Also metallurgical factors such as work-hardening or the exposure to heat sources (i.e. funeral pyre) have found to be influencing the corrosion behaviour of these objects. As an example of the first, among the observed pins, the best state of conservation is ascribable to 5.31, with an annealed microstructure in opposition to the other pins 5.47 and 11.13.

As regards other factors such as the exposure to the funeral pyre, it is interesting the case of hooks 11.33 and 11.36 with the same microstructure: the first one, with traces of earth from the pyre, is more fragile and corroded than the second one which has no signs of proximity with fire.

CONCLUSIONS

The bronze artefacts found among the funeral gifts in the graves of Orto Granara, even if representative of a small statistical sample, present a metallurgical situation in full agreement with that described in other works concerning the Villanovan and Etruscan metallurgy [7-9, 25-27].

The microstructural characterisation has shown a full mastery of the working technique based on work-hardening and annealing cycles. The final annealing step does not seem to be a usual practice;

▲
Fig. 20

BSE image of eyelet 11.33 in a corroded area near the surface. Corrosion preserved the original grain microstructure (ghost structure), proceeding from the grain boundary to the very centre of the grain with a stratified morphology.

Occhiello 11.33 osservato al SEM (elettroni retrodiffusi) in una zona vicina all'interfaccia completamente corrosa. La corrosione ha preservato l'aspetto della microstruttura a grani del metallo, procedendo dai bordi verso il centro dei grani con una morfologia stratificata.

probably it has been performed only in objects where surface finishing required further plastic deformation.

Elemental analyses confirm the deep knowledge of the ancient craftsmen, clearly indicating how the alloys were prepared in order to obtain the best properties according to the expected function of the object and to the complexity of the shape. In particular, strong differences are evidenced, especially in the lead content, between the objects cast nearly in a definitive shape and those requiring subsequent plastic deformation.

Raw materials should have reached the metal workshops in an intermediate form between ore and refined metal, with copper, tin and lead available in different ingots. Further refining was carried out before/during the casting procedure, as demonstrated by the lower level of impurities found in the final objects compared to the ingots.

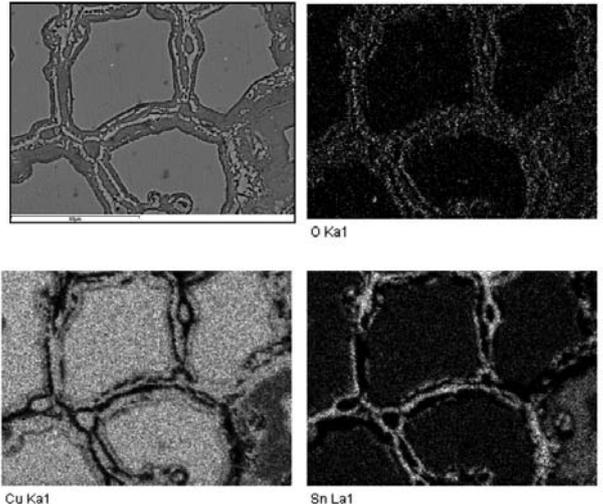
The corrosion processes originated a stratified patina covering the surface of all objects, with evidence of an intergranular attack down to the bulk of the metal. A layer of copper chlorides is often found in the interface between metal and patina, thus alerting about the bronze cancer usually caused by this type of patina. Strain hardening of the object also favoured the corrosion attack.

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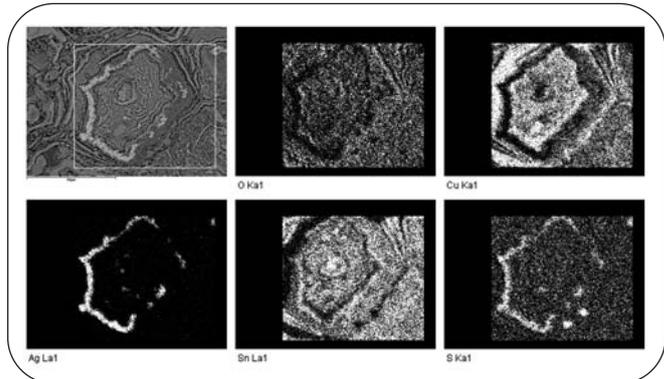
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▲
Fig. 21

Eyelet 11.33: BSE image and elemental maps for O, Cu and Sn showing the layers of corrosion along grain boundary.

Occhiello 11.33 osservato al SEM e mappe elementali per O, Cu e Sn che mostrano chiaramente la stratificazione della corrosione lungo i bordi di grano.

▲
Fig. 22

Detail of a completely mineralised grain in eyelet 11.33, near the surface. Elemental maps for O, Cu, Ag, Sn, S show the heterogeneity of the layers of corrosion products.

Particolare di uno dei grani completamente corrosi dell'occhiello 11.33, nella zona esterna del campione. Le mappe elementali relative alla distribuzione di O, Cu, Ag, Sn, S mostrano la stratificazione di prodotti differenti causata dal processo corrosivo.

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ABSTRACT

REPERTI ARCHEOLOGICI IN BRONZO DALLA NECROPOLI VILLANOVIANA DI ORTO GRANARA (BO): STUDIO DELLE TECNOLOGIE PRODUTTIVE E VALUTAZIONE DELLO STATO DI CONSERVAZIONE

Keywords: rame e leghe, metallografia, storia della metallurgia

Oggetto dello studio sono alcuni manufatti villanoviani in bronzo di diversa forma e tipologia provenienti da una necropoli scoperta vicino a Castel S. Pietro Terme (BO) in località Orto Granara, il cui periodo di uso si colloca tra la fine dell' VIII e la prima metà del VII secolo a.C. Su un nucleo di oggetti in bronzo proveniente da alcune delle sepolture è stata impostata una serie di indagini volte a raccogliere informazioni sia sulla natura dei materiali (in senso compositivo e microstrutturale) sia sullo stato di conservazione dei reperti.

I microcampioni prelevati sono stati analizzati mediante microscopia stereoscopica, ottica ed elettronica a scansione a pressione variabile (VP-SEM), con sonda EDS. Alcuni prodotti di corrosione sono stati inoltre sottoposti ad analisi mediate spettroscopia FTIR. La composizione delle leghe è stata valutata mediante spettrometria di assorbimento atomico (AAS).

I risultati delle indagini condotte si inseriscono pienamente nel quadro metallurgico che, alla luce di precedenti studi, si è potuto delineare per le produzioni villanoviane ed etrusche.

Per i manufatti rinvenuti nei corredi tombali di Orto Granara, benché quello analizzato sia un campione statisticamente ridotto, i risultati delle indagini indicano un quadro metallurgico pienamente in linea con quello già delineato in altri lavori concernenti la metallurgia villanoviana ed etrusca [7,8,10,22,23,24].

La caratterizzazione microstrutturale condotta in microscopia ottica ha mostrato la piena padronanza della tecnica di lavorazione basata su cicli di lavorazione e ricottura, funzionali ad apportare al grezzo di colata le modifiche volute tenendo sotto controllo il progressivo incrudimento, così da non dare luogo a fratture. La fase di ricottura finale non risulta essere una pratica diffusa, bensì l'esito di un riscaldamento mirato a facilitare particolari rifiniture solo su alcuni oggetti (decorazioni ad

incisione, messa in opera con ulteriore deformazione).

L'analisi elementale ha confermato il buon livello di consapevolezza dei metallurghi, fornendo per la composizione delle leghe utilizzate nei vari oggetti dei valori che indicano chiaramente come le materie prime fossero miscelate in modo da ottenere le caratteristiche migliori, in base alla futura funzione dell'oggetto ma soprattutto alla complessità della forma. Nette sono le differenze, specialmente nel contenuto in piombo, tra gli oggetti che venivano fusi in una forma anche complessa ma praticamente definitiva e quelli invece che avrebbero necessitato di una forte deformazione plastica.

Le materie prime dovevano giungere alle officine di produzione dei manufatti in uno stadio intermedio tra il minerale ed il metallo raffinato, in lingotti differenti per rame, stagno e probabilmente anche per il piombo. Una ulteriore raffinazione veniva condotta prima di procedere alla fusione degli oggetti, come dimostra il livello di impurità notevolmente più basso rispetto ai lingotti che si ritrova negli oggetti finiti.

La microstruttura dei lingotti è particolarmente complessa, ma assolutamente in linea col loro stato di prodotti intermedi della lavorazione; le impurità sono varie ed anche in percentuali non trascurabili, con quantità elevate di elementi volatili (arsenico ed antimonio) dovute alla formazione di particolari composti stabili rimasti inclusi nei lingotti.

Le morfologie di corrosione finora esaminate mostrano alcuni esiti interessanti. Nel caso in cui si è riscontrata la presenza di cloruri, questa ha comportato l'instaurarsi del processo comunemente definito "cancro del bronzo", con un deposito di cloruro di rame a contatto con il metallo, quindi al di sotto degli strati di corrosione, che porta ad una ciclicità delle reazioni corrosive.

Dove la deformazione plastica dell'oggetto ha determinato una particolare reattività del metallo e piccole differenze composizionali da zona a zona, il processo corrosivo si dimostra sensibile a queste variazioni e può presentare una morfologia stratificata. In altri casi la stratificazione ha avuto uno sviluppo intragranulare, portando ad una separazione di strati a diversa composizione all'interno dei singoli grani, mettendo in certi casi in evidenza particolari concentrazioni di impurità eterogeneamente distribuite nella struttura.