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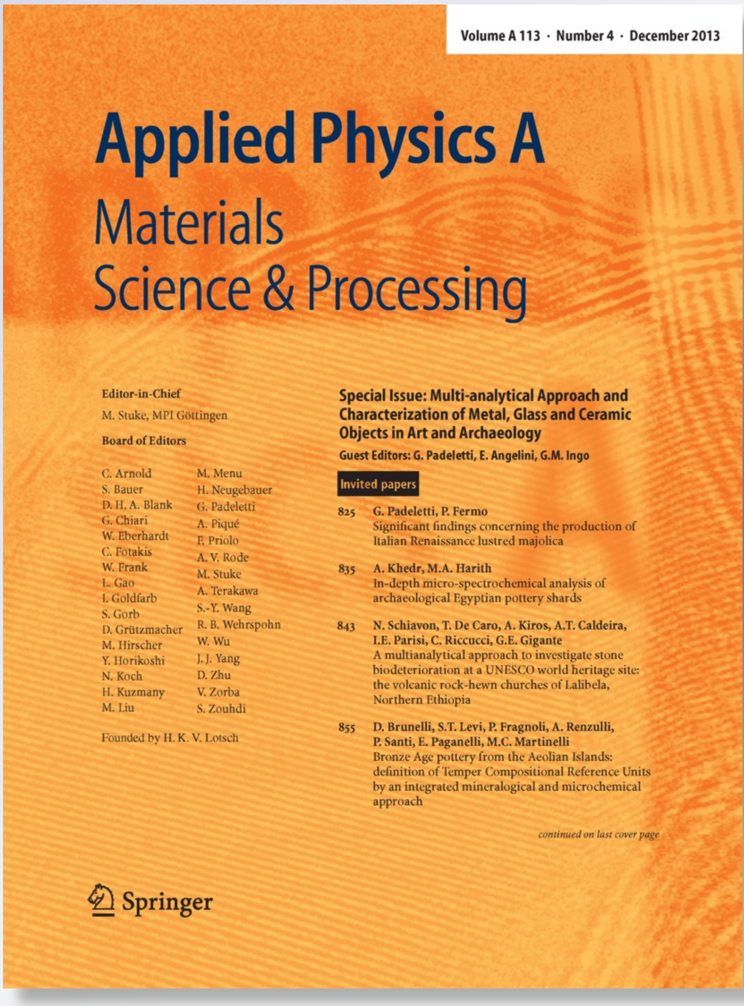
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Abstract This study concerns the archaeometric characterization of two artefacts from the medieval site of San Rocco (Castelfranco Veneto, Italy). Both of them belong to a larger set of metallic objects, some being part of tomb ornaments belonging to two very well distinct periods of frequentation of the site. Both items are buckles and they have been selected as representative of two very well-known and established typologies. The older one, at the end of the sixth—beginning of the seventh century AD, is made of silver, although relicts of gold have been found. A number of relevant counterparts of this item have been found in different sites of the Longobard Italy. The main body of the second artefact (second half of the fourteenth century AD) consists of a bent strip of a copper rich alloy, coated on one side with a nearly continuous, decorated, gold layer. This is a so-called lyre-buckle, with a widespread diffusion not only in Italian, but also North European contexts. From the results of the analyses carried out using low-vacuum scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray diffractometry, information on manufacturing, gilding technology and materials have been obtained that will be an useful benchmark for the archaeometric characterization of similar items from selected collections. In this way, the already established typological affinity of these two classes of items will be extended to technological and materials aspects, also.

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1 Introduction

The artefacts considered in this study all come from the North Eastern Italian site of San Rocco (Vittorio Veneto, Treviso, Italy). This site is located on the top of a small hill, after which it has been named. From historical local information [1], it turns out that the site had been used during the thirteenth–fourteenth centuries as a fortification, better known as *castrum Sancti Elisei* (Camp of Saint Eliseo). There are indications of an earlier occupation of the site, starting at the beginning of the Romanization period, dating back to the second–first century BC. Since then, the site was inhabited nearly uninterruptedly until the present times. The first archaeological survey was conducted in 2003 [2], after an occasional find in 1983 of a late Roman *amphora*, dating to the fifth–sixth centuries. The site is interesting in several respects, concerning the remains of building structures, walls, and several metallic and ceramic objects that were found in the area over the years. Particularly important is the burial place, featuring tombs of different kinds: ground and digger in the rock sepultures, most of which have been disrupted over the years, so that it is now difficult a reliable dating. More reliably, this can be made for *amphora* tombs of young babies, as this sort of sepulture was adopted until later, in a period that can be located between the second half of the fifth and the first half of the sixth century AD.

In the nearby area also, animal bones have been found. As to these latters, no conclusive hypotheses have been made on their origins, for the lack of a reliable archaeological context consequent to the already mentioned, uncontrolled disruptions of the site.

In association with the undamaged tombs, several objects from funeral ornaments have been found. The interest of the present study is concentrated on two of them, featuring as a common aspect, the use of gilding to decorate part of their surfaces with a gold layer. These items turned out to be made of a copper and silver alloy, respectively. Of the different gilding procedures [3], *fire gilding* [4] seems to be the one used for the selected items. A common aspect of such approach is the usage of a gold amalgam, a paste made of Au and Hg, whose consistency can be varied by suitable additions or subtractions of mercury. In all cases, the final step of the manufacturing is a thermal treatment of a few minutes, conducted at an estimated temperature of 250–300 °C, thus below the boiling point of mercury, equal to 357 °C.

The main reason why these finds have been selected is that, from an archaeological point of view, they belong to well established types, both having a broad distribution in Italian and European contexts [5], as concerns the respective relevant periods. The investigation presented herewith, regarding technological and materials aspects, is thus meant to set the basis for the application of a similar approach to a broader number of specimens available in several European collections that have not been analyzed from this point of view as yet.

2 Sample description

One of the finds that has been investigated is a buckle, codenamed *n. 86*, dating to the late Medieval time (second half of the fourteenth century) and diplayed in Figs. 1a and 1b. The main body of the *n. 86* artefact is made of a metal sheet, bent onto itself to hold the shaft of the tongue that is missing. Two holes, with a diameter of 3 mm approximately, are visible and can be interpreted as the sites of two small studs, which were there to join the belt, possibly made of tissue or leather, to the buckle, squeezed between the two edges of the bent sheet. For its shape and aestethical features, the item can be associated to the class of the so-called lyre-buckle, with a widespread diffusion not only in Italian but also North European contexts of the period [5].

The other item considered in the present study (Figs. 1c and 1d) is a buckle, also completely different from the previous one, even because much older. This buckle has been dated to the end of the sixth—beginning of the seventh century and codenamed as *n. 85*. Similar items, that were probably used as footware accessories, have been found in several coeval sites of the Longobard Italy [5]. In this case, the tongue is still present and held in place by the bent sheet of metal. The two studs, as in the case of *n. 86*, are probably there for connecting the buckle to the shoe string or belt. On the back side (Fig. 1d), ring-shaped pieces are present. Actually, just one of the two is complete, being the other one partially broken. However, this latter too was recovered dur-

Fig. 1 (**a**) Micrographs of the two samples that have been investigated in the present study (side of the squares = 10 mm): Copper buckle of the fourteenth century: front-gilded side. Codename: find n. 86. (**b**) back side. (**c**) Silver buckle of the seventh century: front side. Codename: find *n. 85*. (**d**) Back side from which comes the analyzed sample displaying residual traces of gilding. Arrowed the ring-piece similar to the detached one that analyzed and that is shown by Fig. 10 (see below)

ing the excavation and was analyzed, together with the rest of the item.

Following the procedure adopted for all metal artefacts coming from this site, even the two analyzed specimens have been thoroughly cleaned so that no significant traces of the burial ground were retained. The items have been consolidated, if required, and protected by a layer of Paraloid, that was not removed during the analyses.

3 Experimental methods

Scanning electron microscopy (SEM) observations were carried out with an instrument equipped with an energy dispersive X-ray spectrometer (EDXS) with a Si(Li) detector sensitive to elements from carbon to uranium. SEM observations have been particularly important in the characterization of the microstructural aspects of the two objects, that, being covered with an insulating layer of Paraloid, were observed in a low-vacuum mode (LV SEM). This prevented any charging effect and, most importantly, the use of conductive metalization that apart from the obvious interference with the spectral lines, would have introduced unacceptable irreversible modifications in the two items.

X-ray diffraction (XRD) analyses were conducted on one of the two specimens (*sample n. 86*) in order to identify the phases that resulted from the manufacturing procedure, including the gilding process. Crystallographic texture analyses were conducted, using a 4-circle X-ray diffractometer equipped with a curved position sensitive detector. The orientation distribution functions (ODFs) for each of the detected phases were determined using a Rietveld diffraction pattern fitting approach [6–9], implemented using the MAUD software [10–12] that was even used for the evaluation of the concentrations and relevant microstructural parameters of the detected majority phases.

4 Results and comments

A feature that immediately appears evident on eye inspection of the *n. 86* sample is that its front and back sides are quite different one from the other. The front side is coated with a yellowish layer with strips of decoration, featuring a repeated pattern, most probably carved onto the metal surface (Fig. 1a). The back side is brownish and, as confirmed by the spectroscopy data, it is made of a copper-rich alloy. Copper was also detected when analyzing the front side of the item in association with a significant concentration of gold that turns out to be the main element in the top layer.

The situation is clearly depicted by the EDXS spectrum in Fig. 2a, that refers to the region of the sample shown by Fig. 2b. The occurrence of copper characteristic lines in the

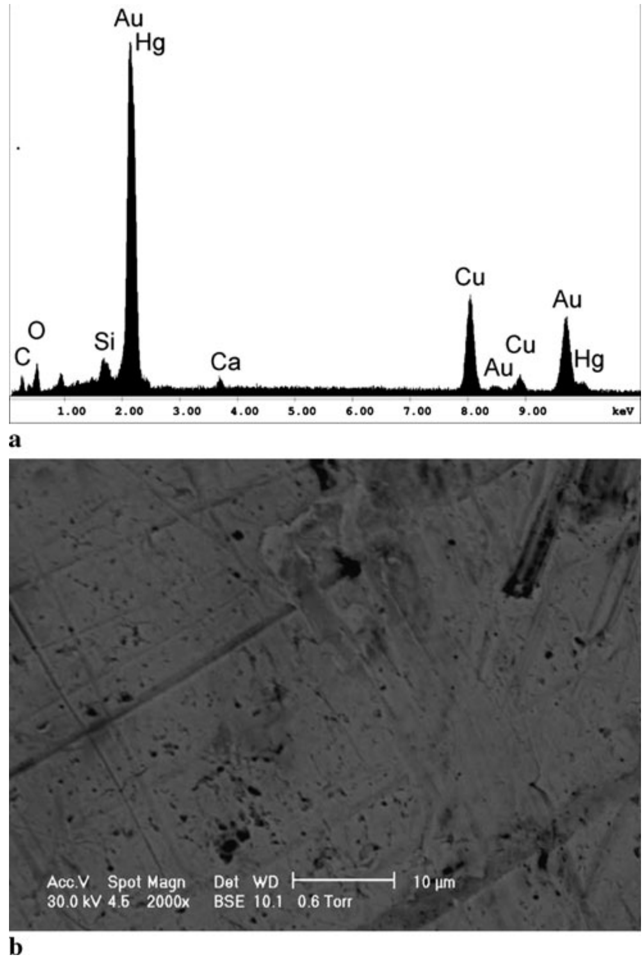


Fig. 2 (**a**) EDXS spectrum coming from the front side of *n. 86* find. The presence of gold, in association with copper, is compatible with the structure of the object, consisting of a copper sheet, on which a thin layer of gold has been applied. In the application of gold, a role is played by mercury, whose X-ray lines are also visible (see text for details). (**b**) BSE (backscattered electrons)–SEM micrograph of the surface region of the front side of *n. 86* sample from which the X-ray spectrum (a) has been acquired

EDXS pattern in Fig. 2a, demonstrates a limited thickness of the gold layer that allows the primary electron beam to sample and to excite even X-rays from the underlaying copper alloy. The surface morphology appearing in Fig. 2b is substantially the same as all over the rest of the front face of the sample, with scratches and dark spots uniformly distributed. Scratches can be due to a combination of several factors: original manufacture process, usage, damage in the burial environment, polishing procedures. As to the dark spots, they might be ascribed to impurities and inclusions already present in the gold material. To complete the picture, it can be noticed that the EDXS pattern in Fig. 2a displays even the characteristic lines of mercury. In view of the discussion that will follow, it is worth quoting the Au/Hg relative concentrations, as estimated from the analytical data, equal to 83/17 (wt%).

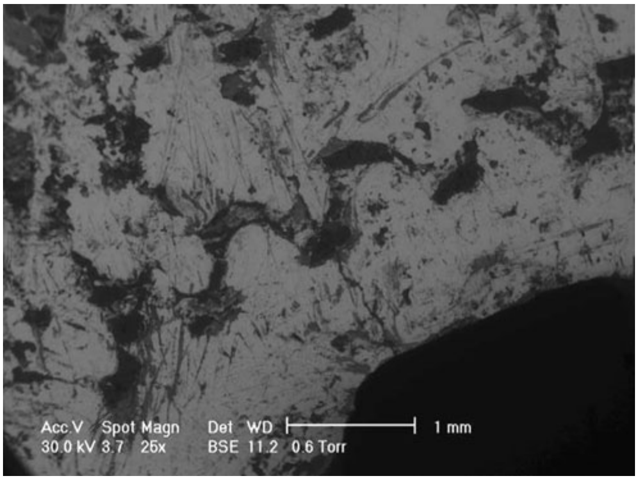


Fig. 3 BSE–SEM micrograph displaying the microstructural details of the surface of the sample *n. 86*, decorated with a carved pattern (see Fig. 1a)

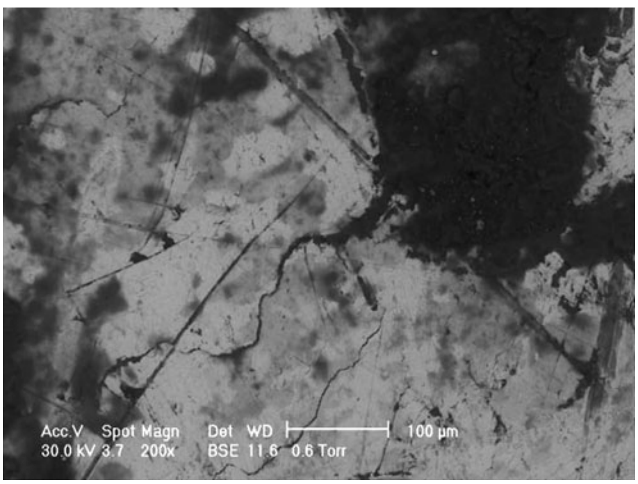


Fig. 4 BSE–SEM micrograph displaying the interrupted Au layer along the line of the carved decoration and some cracks departing from it

A further clue on the microstructural aspects of this sample comes from the details of the carved decoration, visible on the gold layer (Fig. 1a) and imaged at higher magnification in the SEM micrograph in Fig. 3. Two aspects are worth to be mentioned. The gold layer results to be largely broken and interrupted, not just deformed, along the decoration pattern. Moreover, cracks in the gold layer, departing from the edge of the decoration, are visible.

In Fig. 4, these two microstructural features are better visible. In particular, it is possible to evaluate the approximate thickness of the gold layer, a few micrometers, i.e., 2–3 μm. This thickness would be in the right range for gold lamina obtained with the conventional beating technique [4]. By beating either gold *foils* or gold *leaves* can be obtained, according to the thickness actually achieved, depending on the purity of the metal: the purer the thinner, as discussed in [3, 13]. The use of a cold-working technique, like beating, should have induced in the gold layer some crystallographic texture. For this reason, a thorough structural investigation was conducted.

The main phases detected in the diffraction pattern acquired from the gold coated surface of the buckle were copper and gold with lower concentrations of Cu_2O (cuprite) and two intermetallics of the Au–Cu sistema: Au_3Cu and AuCu (Fig. 5). The orientation distribution functions displayed by the pole figures of some representative reflections (Fig. 6) for the two phases indicate that quite a complex cold working procedure, not just beating [14], was adopted for the fabrication of the sheet used as the main body of the buckle. Indeed, copper has a clearly textured structure with significant {100} fiber component (Fig. 6a). Normally an hammered or cold worked copper sheet displays a {110} texture in the direction of the applied load as reported for several artefacts [15, 16] and consistently with a Taylor plastic deformation model [17]. Therefore, the {100} texture cannot be induced by a plain process and may arise from a more complex procedure, for instance involving a series of different steps of deformation and recovery thermal treatments. Gold displays the presence of a slightly inclined fiber component along the {111} planes (Fig. 6b) instead. Such a texture is not even compatible with any kind of cold-working that might have been used to produce a metal *foil* or *leaf*. Indeed, as unambiguously shown by an experimental work in which the conditions of traditional pack and hammering technique to manufacture *gold foil* and *leaf* were reproduced, depending on the thickness range, gold initially displays a {110} texture, replaced, at lower thickness, by {100} [18]. This second texture starts to prevail for gold thickness in the micrometric range and becomes the typical texture in submicrometric layers. Incidentally, this situation has been actually found in a genuine gold foil used for the decoration of medieval Islamic glassed ceramics [19]. A {111} texture in gold, like the one observed in the investigated *n. 86* specimen, has been actually reported for electroless plated gold layers [20], as well as for other electrochemical depositions, obtained with a process not involving any mechanical working. The lack of any cold-working related texture and the detected mercury remains would suggest a decoration procedure for obtaining the gold layer based on the exclusive use of a Au–Hg amalgam, spread onto the surface of copper and then consolidated with a suitable thermal treatment, as described in the *Introduction*.

As noticed with reference to Fig. 4, the decoration pattern present on the gold surface displays a diffuse breakage that provides an useful access path to analyze the underlaying copper alloy and the joining region at the interface between the two metals: copper and gold.

In this region, patches of granular gold, like those displayed in Figs. 7a and 7b, low and high magnification image,

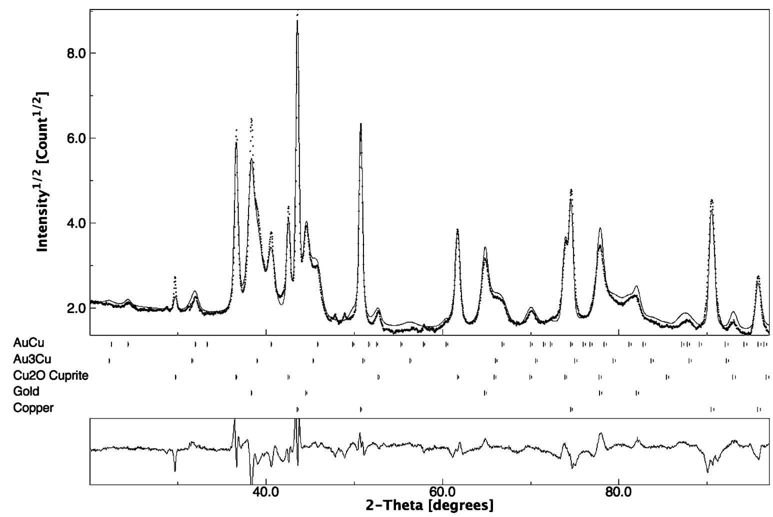


Fig. 5 XRD pattern acquired from the gold covered side of the buckle. *Dots*: experimental data points. *Continuous lines*: modeled pattern obtained from the full pattern fitting procedure based on the Rietveld method implemented in the software MAUD [8–10]. The identified phases, as indicated in the figure, are: Cu, Au, CuO_2, Au_3Cu, AuCu. These two intermetallic phases are both ordered

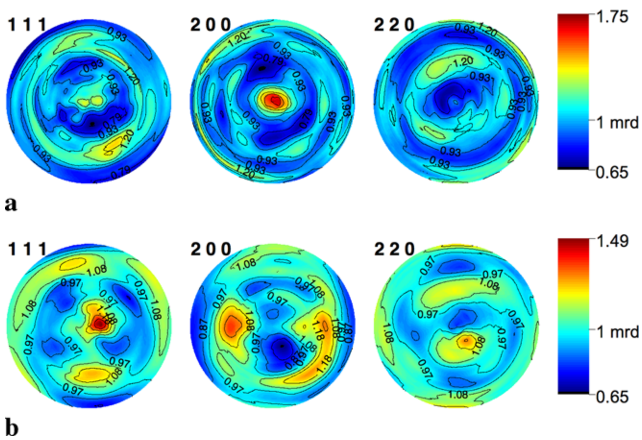
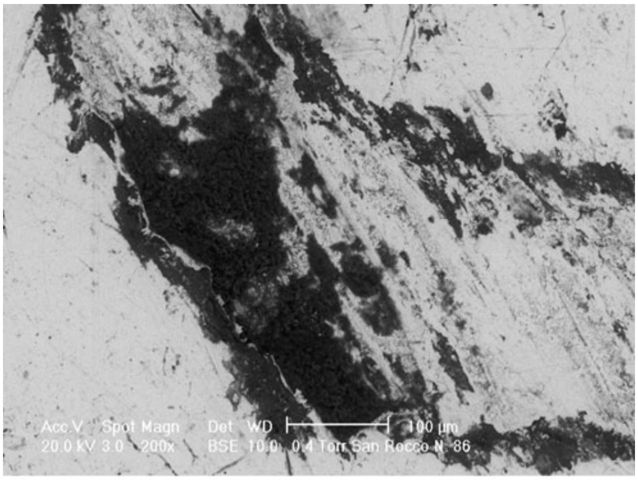


Fig. 6 Reconstructed pole figures from the orientation distribution function for the main XRD reflections of copper (**a**) and gold (**b**) as evaluated from texture analysis of the specimen

respectively, have been observed. This kind of microstructure has been reported for mercury fire gilded artefacts and results from the relief of gaseous mercury from the gilding Au–Hg amalgam, leaving behind submicrometric gold grains [21]. A similar microstructure has been actually observed even in systems not strictly related to archaeological samples, in which the evaporation of mercury from an Au–Hg amalgam has been induced by treatments conducted under controlled conditions to tailor the microstructural features of the resulting gold particles [22]. Indeed, the size of gold grains is the result of two concurrent factors: the kinetics of gaseous mercury relief and the mass transport that would be required to fill the gaps, vacancies and pores, left behind by mercury itself. Both phenomena are of course occurring at the same time at the cited comparatively low temperatures, as are those typically employed in *fire gilding* [23].

On the basis of these observations, the following manufacture procedure for the fourteenth century gilded buckle (*n. 86* specimen) is proposed. After the copper sheet has been produced, then cut and bent to obtain the wanted geometry and shape of the buckle, a layer of Au–Hg amalgam was applied onto the front face of the buckle. Subsequently, a heating step at the comparatively low temperatures quoted above, probably achieved just putting the whole piece in a workshop furnace, was performed to eliminate mercury and to consolidate the copper-gold interface. The observed thickness of the gold layer is definitely compatible with the reported ones for gilded [4, 21, 24, 25] and silvered layers [21, 25, 26], observed on a number of items, though belonging to quite different contexts. To complete the picture of the proposed manufacturing process for the fourteenth century gilded buckle, it has to be said that also the detected presence of two intermetallic phases, Au_3Cu and AuCu (Fig. 5), is compatible with a *fire gilding* based technology. Notwithstanding the comparatively low temperatures involved in the process, mercury has favored the reciprocal solutioning of gold and copper through liquid phase diffusion. Au_3Cu that has a FCC like structure, shows a similar {111} texture as gold. This can be explained well in terms of the faster growing plane of FCC structures during deposition processes, confirming the in situ formation of the intermetallics, whose grains could nucleate and grow without substantial constraints from the surrounding amalgam matrix. The bonding between the two metals, copper and gold, may also benefit to some extent from the cold welding produced by the decoration cladding procedure, realistically carried out once the gold layer was fully consolidated. In this respect, the breakage of the gold layer has to be considered as a fault of the manufacturing process, determined by an excessive pressure applied during cladding.

The Au–Hg amalgam has been probably used even to decorate the copper head of the buckle, where residual traces of a gold coating are clearly visible (see Fig. 1a and Fig. 8a) and confirmed by EDXS analyses. In this case, too, the



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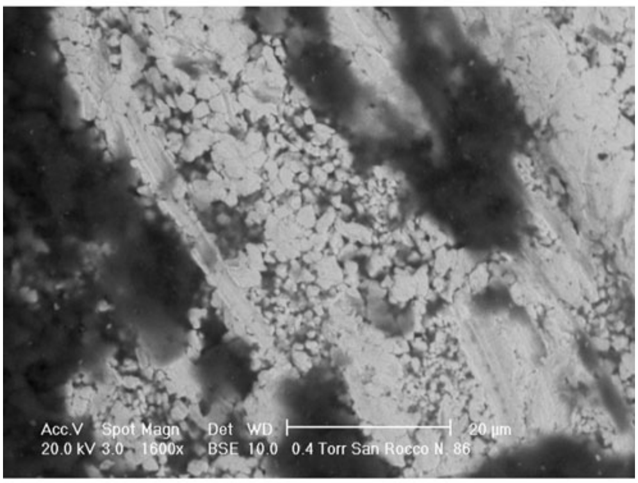
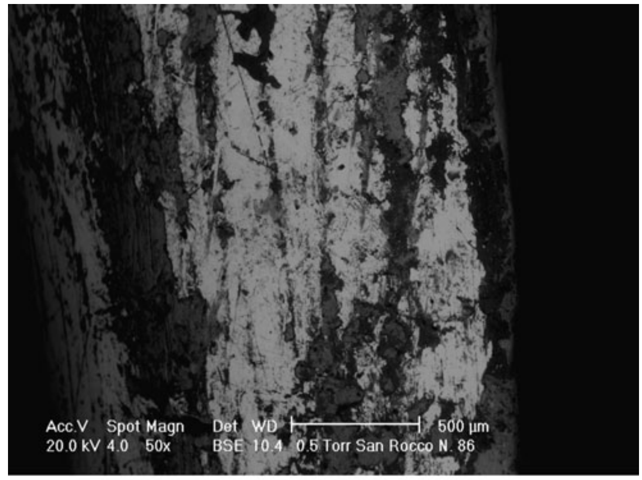


b

Fig. 7 BSE–SEM micrograph displaying the granular structure at the copper–gold interface, resulting from the evaporation of mercury from amalgam: general view of the area (**a**) and detail with micrometric gold grains (**b**)



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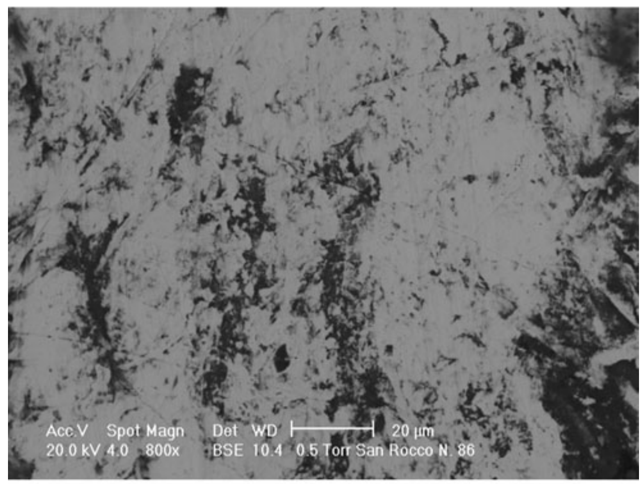

b

Fig. 8 Two BSE–SEM images, at different magnifications of the gold residuals on the head of the buckle *n. 86*. See text for comments on the application procedure of the gold layer

amalgam was directly applied onto the copper surface, possibly with a tiny brush. After mercury evaporation, the remaining gold layer was the only decorative element of this part of the buckle. This layer displays both the damage and disruption due to its usage and subsequent burial, but even the porosity that was probably there from the beginning, as deriving from the manufacturing process. A further aspect that would confirm an amalgam based technology for the decoration of this part of the buckle, is the presence of scratches of submicrometric width that were apparently intentionally made to homogenize the granular regions and to render them smoother. They are visible both in the SEM micrographs in Figs. 5b and 8b. Some of them are certainly occasional, whereas other are most likely there as a result of mechanical polishing and surface finishing. Using a suitable turnishing tool, made of bone, ivory, wood, etc., gilder artisans used to remove the opaque aspect that the gilded surface had acquired after firing, owing to the granulated surface morphology and to contamination from the combustion residuals [27]. After this polishing treatment, the gilded surface would recover a brighter and shiny appearance.

From the above picture, the level of the gilding technique and procedure used for the manufacturing of the *n. 86* artefact can be inferred. Certainly, mercury gilded objects were known and used by the people living in the place all over the medieval time, as proved by other finds coming from the site and dating back to the Early Middle Age. This is the case of the *n. 85* item (Figs. 1c and 1d). In Fig. 9a, the surface morphology of this sample is displayed. The different shades of gray of the backscattered electron (BSE) SEM micrograph would correspond to different local compositions. The object resulted to be made of silver, that was actually the main detected element in the EDXS patterns (Figs. 9b and 9c). Silver is accompanied by copper and iron, impurities typically reported for silver alloys and originating from

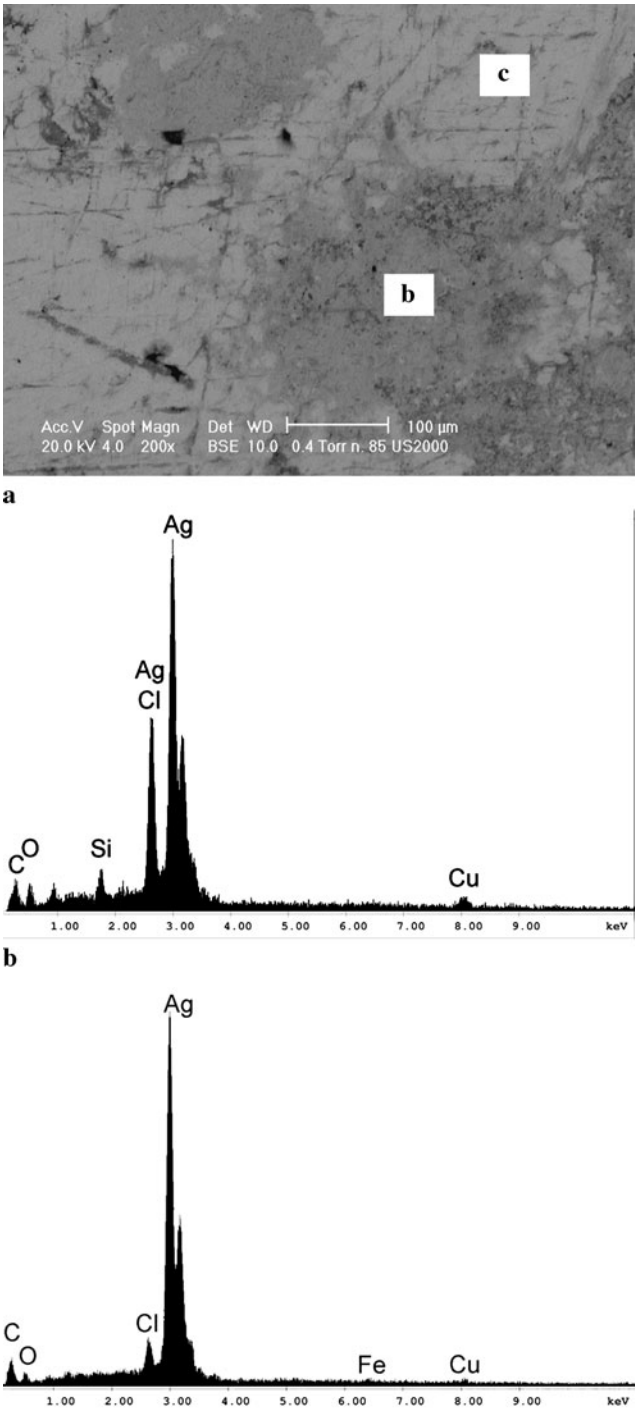

Fig. 9 (**a**) BSE–SEM image of the surface of the buckle n. 85. The EDXS patterns corresponding to the *dark gray regions* and to the brighter ones are displayed in the (**b**) and (**c**) *insets* respectively, as indicated by the corresponding letters in the micrograph

the extraction stage [27, 28]. Still with reference to Fig. 9a, from the dark gray region, EDXS pattern with a sensitive concentration of chlorine is obtained (Fig. 9b), a proof of the, after all expected, presence of a surface chloride layer, deriving from the corrosion processes silver alloys are usually prone to under different conditions, burial ground included. Chlorides are also present on the brighter zones, although a weaker intensity of chlorine characteristic line seems to indicate that a thinner layer of these compounds on this part of the alloy surface is present (Fig. 9c). Other ubiquitous elements, like magnesiun, silicon, aluminum, etc., are clearly traces of the burial ground, that were not completely removed by the cleaning procedures.

An interesting aspect emerged from the analysis of a fragment of the *n. 85* buckle that was found already detached in the neighborhood of the main body of the item. This fragment is companion to the ring-shaped detail still attached to the buckle, indicated by the arrow in Fig. 1d), probably used to connect the buckle to the shoe-belt. The fragment is displayed by the BSE-SEM image in Fig. 10a, in which a diffused corrosion, with crevices that have clearly weakened its structure. The brighter arrowed region turned out to contain gold and mercury in comparable concentration (see EDXS spectrum in Fig. 10b and can be taken as a trace of amalgam. It was argued that similar features might have been present in other parts of the item, as residuals of a complete or partial decorative coating, possibly applied to enhance the preciousness and aesthetics of the buckle. However, no similar observations were made elsewhere on the surface of the buckle that was thoroughly analyzed, even on the basis of chromatic indications obtained from low magnification optical microscopy. This lead to the conclusion that probably the observed amalgam traces (arrowed in Fig. 10a) were not residuals of some decoration but rather a sort of repair made on the jewel during its manufacturing or after some time of usage. A mercury richer composition, giving a Au/Hg ratio equal to 45/55 (wt%), as compared to typical percentages of retained mercury in gilded layers (8–25 %, [4]), would suggest an alternative usage of amalgam, for instance as a repairing material. This interpretation, disregarding aesthetical reasons, would also made plausible an otherwise too hidden positioning for a decorative golden motif.

5 Final comments and further perspectives

In the present study, two medieval items coming from the cemetery context of the same Medieval site (San Rocco, Vittorio Veneto, Italy) but belonging to two quite different periods (Early Middle Age: sixth–seventh century, Late Middle Age: fourteenth century) have been investigated to shed light on some aspects of their manufacturing technology and materials.

Item *n. 85* turned out to be made of silver and contains typical impurities for these alloys. Traces of Au–Hg amalgam were found. It is proposed it was used in this case for a repair intervention.

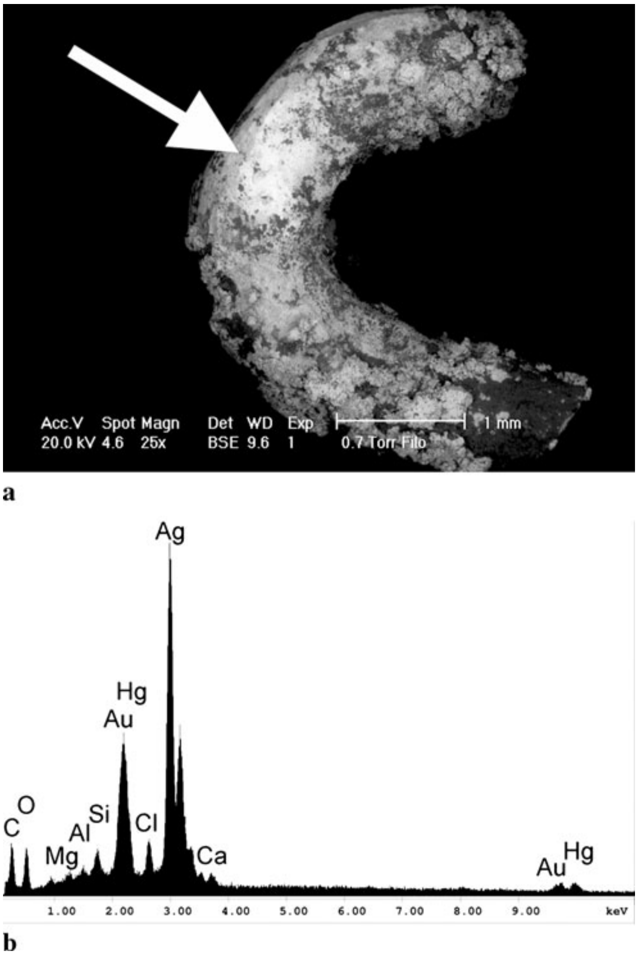

Fig. 10 (**a**) BSE–SEM micrograph of a fragment from the *n. 85* sample. The *arrowed region* turns out to be rich in gold and mercury, as shown by the relevant EDXS spectrum (**b**). This grain is probably an amalgam residual that had not been treated to remove mercury, still present to a significant extent. The proposed hypothesis is that the amalgam in this case was used for a repair

In item *n. 86*, a proper decorative fire gilding procedure was inferred from the analyses, using Au–Hg amalgam to produce a complete coverage of one side of the buckle.

The multianalytical approach used, in analogy with other studies [26, 29, 30], to characterize better the two items, has been particularly effective in the study of the *n. 86* sample, as lead to the original result regarding the formation of the two Cu–Au intermetallic phases, promoted by the Hg-assisted interdiffusion of copper and gold.

The results presented in this paper, obtained in a fully nondestructive mode as concerns the archaeometric approach, can be taken as an excellent starting point to extend the research to a wider number of similar artefacts that as stated in the *Introduction*, were quite common in different parts of Europe in the relevant periods, but that have never been systematically investigated as concerns their materials and technological aspects.

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