A silvered shield grip from the Roman Period: a technological study of its silver coating

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Abstract

A unique shield grip decorated with openwork rivet plates was found in a Roman Period cemetery of the Przeworsk culture in Czersk, Central Poland. The artefact underwent specialist analyses with the use of various techniques in order to reveal its silvering technology. Several silvering techniques were considered as the most probable: foil silvering, mercury silvering and silver plating. A number of complementary analytical methods such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), scanning electron microscopy with energy-dispersive X-ray (SEM-EDX), X-ray diffraction and neutron techniques were used in the examinations. Two silvering technologies were identified: foil silvering and mechanical treatment of silver pieces. On the basis of the specific correlation of maximum contents of silver (Ag), copper (Cu) and tin (Sn) in external layers of the artefact, it was found out that the surface of the openwork plates had been first covered with alloy with a high content of tin and copper as a solder. Then, a thin silver foil was applied onto it. On the other hand, combs of the shield grip were ornamented using non-soldering technology, i.e. hammering and punching.

Keywords Przeworsk culture · Barbaricum · Roman Period · Ancient metallurgy · Silvering techniques · SEM-EDX · Neutron techniques · LA-ICP-MS · XRD

Introduction

Ornamentation of plates with the use of silvering processes was a difficult task to perform, which can be a reason for the absence of such artefacts in the territory of present-day Poland. Shield grips which bear some visual similarity have been found in Radved in Jutland (Kjaer 1900: p.114ff, Fig. 3; Watt 2003, Fig. 9b), Brodstrup in Öland Island, Sweden (Rasch 1991: p.109) and Hamfelde, Kreis Herzogtum Lauenburg, Germany (Bantelman 1971: p.124). A study of these artefacts can provide us with some indications

concerning possible ornamentation analogies outside the territory of the Przeworsk culture. Furthermore, it informs us about trade directions in the Roman Period. Until now, no results of physico-chemical analyses of such artefacts have been published.

Although visual features of all the mentioned grips are similar, almost no silvered layers survived to our times, apart from the ornamentation on the artefact from Czersk. La Niece isolates the following methods of silvering:

- (a) *Foil silvering*, i.e. covering an artefact with silver foil, which was attached by means of hammering onto a grooved surface. Sometimes, adhesives were used, e.g. calcite (CaCO₃). More popular techniques made use of various types of solders. These could be silver–copper, as in the case of Greek and Roman coins, or silver–copper–tin, as identified in some finds of Viking Age jewellery. In other cases, it was possible to use tin or tin–lead solders. This solution is known, e.g. from Roman artefacts (La Niece 1993, 202–204; see also Meeks 1993; Giumlia-Mair 2005; Miazga 2014; Miśta and Gójska 2016). There is also some evidence that this technology

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was known in the Barbaricum in the Late Roman Period (Hammer 1998: p.196).

- (b) *'Sheffield' plating*, whose name comes from mid-eighteenth c. Sheffield plate industry. In this technique, silver and copper are heated in close contact. It comes to a limited diffusion, and a low melting-point alloy forms at their interface. This method is considered to be more reliable than foil silvering. It has been suggested for Minoan artefacts dated to the mid-second c. BC, as well as for a number of Greek and Roman finds. On the other hand, similar microstructures could be produced by silver–copper solder. It has been therefore suggested that the use of this method cannot be excluded for ancient times, but it cannot be unambiguously confirmed, either (La Niece 1993, 204–205).
- (c) *French plating*—the name of this technique comes from the eighteenth c., but it was certainly in use much earlier and was described by Theophilus Presbyter. In this method, the artefact's surface is first grooved and then a silver foil is attached to it by means of heating and rubbing (La Niece 1993, 205; see also Šmit et al. 2008; Ingo et al. 2017; Miazga 2014).
- (d) *Application of a silver coating while molten*—in this case, powdered silver–copper alloy is heated until it flows and plates the artefact's surface with hard solder. Artefacts covered with this kind of silver–copper plating are known from Macedonian, Celtic and Roman contexts (La Niece 1993, 205–206).
- (e) *Depletion silvering*, that is, removing of copper from the surface of a silver–copper alloy artefact. The removal of copper can be done either chemically or by means of heating the surface in order to oxidise the copper, which is then removed using chemical methods. This technique is known from Pre-Columbian America but also from the Roman Empire (La Niece 1993, 206).
- (f) *Mercury silvering*—in this technique, an amalgam of silver and mercury is applied to the surface of a copper or copper alloy artefact. Then, it is gently heated until mercury evaporates. This method perhaps originated in ancient China. It may have been known in early medieval Europe, but in this continent it became more widespread in the High Middle Ages (La Niece 1993, 207–209; see also Blair and Ramsey 2001; Theophilus 1979: p 113; Ingo et al. 2013; Weiszbürg et al. 2017). On the other hand, Vlachou et al. suggest that this method may have been used in Late Roman Empire for silvering of mass minted coins, which were composed of Cu–Sn–Pb–Ag alloys. The surface of such coins was covered with a very thin layer of silver. On the basis of experimental research, these authors propose that the successfulness of this method depended on many factors, such as proportions of Ag and Hg in the amalgam, its additional processing or

the composition of alloys in artefacts which were silvered (Vlachou et al. 2002, II.9.2.3–II.9.2.7). The mercury amalgam could be obtained from geological ores of native mercury which occurs in amalgam systems with silver, gold, lead and palladium (Rytuba 2003). Taking into account European trade routes in Antiquity, the amalgamation silvering could also be used in the territory of the Przeworsk culture. There is some evidence (Hammer: p.196) that this technology was known in the Barbaricum in the Late Roman Period, but no metallurgical studies have been done on this issue until now.

- (g) *Silvering pastes and solutions*—in this case, a solution of silver (modern pastes are usually composed of silver in solution with nitrate or ammonium salt) is rubbed onto a metal surface. This method produces an extremely thin layer (less than 0.005 mm) of fine-grained silver. As such layers are extremely fragile and hardly survive, it is difficult to say when and where this method was first used. Such thin layers are known from artefacts found in Pre-Columbian Peru and in the Mediterranean (third c. BC). The use of this method has been suggested for Late Imperial Roman coinage, but it became more widespread from the sixteenth c. onward (La Niece 1993, p.209; see also Vlachou et al. 2002, II.9.2.3).

An irregular shape and traits of silvered layers in the shield grip from Czersk did not provide definite clues concerning the applied technology. Some other processes may have influenced the final state of preservation of the find. Corrosive degradation of both the upper layer and base alloy (Sandu 2006) should be taken into account. Galvanic corrosion is also possible. This type of process occurs when different metals are next to each other and the less noble metal is deeply attacked. In effect, oxides were formed in the interphases of Ag–Cu-rich layers. These oxides could cause an uplift of internal silver layers (Flament and Marchetti 2004).

Archaeological background

The village (former town) of Czersk, Góra Kalwaria Commune, is located in the central part of Poland, on the left bank of the Vistula river (see Fig. 1).

Settlement traditions of this locality date back to Antiquity. A cremation cemetery of the Przeworsk culture has recently been discovered there. It has a broad chronology from the Pre-Roman to the Late Roman Period, i.e. approximately between 220/250 BC and AD 450. The cemetery is situated on a small elevation on the upper flood plain of the Vistula River. The elevation is composed of

Fig. 1 Location of Czersk in the map of Europe and Poland

sandy mud, while typical locations of cemeteries in the Przeworsk culture were mainly related to the presence of elevated sandy dunes. The location of the cemetery influenced the preservation conditions of the artefact. Due to the vicinity of flood plains and centuries-long cultivation of this area, an extremely unfavourable environment for preservation of metal artefacts was formed. As a consequence, most metal artefacts from this site were marked with very advanced corrosion.

During the archaeological research carried out in 2008, archaeologists from the State Archaeological Museum in Warsaw discovered a richly furnished cremation urn burial (Grave 93), which contained several finds of weaponry (Czarnecka 2014; Czarnecka 2012) (Fig. 2).

Fig. 2 Grave 93, where the discussed shield grip was found. A burial urn can be seen in the upper centre of the photo. The grip is located next to it (photo K. Watemborska-Rakowska)

A significant part of the cemetery contains graves with weaponry. This is not surprising, bearing in mind that the Przeworsk culture was a warrior culture. The equipment found in Grave 93 indicates this type of burial. Two artefacts from this grave deserve a special attention because of their unique rich ornamentation. These are parts of a wooden shield—a shield boss (see Fig. 3) and a shield grip (see Fig. 4). The latter artefact was the subject of our research.

These artefacts have silvered parts; however, the main metal component of the shield boss is iron alloy and that of the shield grip is copper-based alloy.

Characteristics of this grave suggest that the buried person belonged to a higher social class. Therefore, silver and silvered artefacts can originate from the shield of the deceased individual. *The main goal of this project was to examine the ancient metallurgical technique which was used for silvering the surfaces of symmetrical rectangular plates of the shield grip.*

The plates of the shield grip are covered with a thin silver layer. The silver layer on the external side of the plate (that is, the side which was visible when the plate was attached to the shield) is significantly thicker than that on the internal side (Fig. 5). The silvered plates are separated by combs from the central part (the handle). This part of the grip is of triangular cross section. The comb tops are decorated with filigree pigtails whereas their sides are covered by silver sheets (cf. Fig. 5). The dimensions of the artefact are the following: the silvered plates—6.5 cm long and 2.6 cm wide, the handle—10.2 cm long. The entire artefact is 16.7 cm long. Two rivet holes can be seen in each plate. Between the rivet holes, there are conical studs made in silver filigree technique. Openwork rosette ornaments are cut out around the studs. The shield grip survived in three parts: the comb together with the silvered plate, the central part (handle) and the other silvered plate with the other comb.

Fig. 3 Shield boss from Czersk made of iron alloy and its silver rivets. Optical photos of the artefact: **a** side view, **b** bottom view. Photos **c–f** are a views from X-ray computed tomography scans of the shield boss with visible fragments of the shield fittings and burnt bone remnants (indicated with arrows) trapped in a large iron corrosion lump presented in **a** and **b**

Fig. 4 Drawing of the shield grip (T. Miśta-Jakubowski)

Fig. 5 Shield grip from Czersk after conservation. Top, the entire artefact. Bottom left, one of the silvered rectangular plates with the comb. Bottom right, side view of the comb with a visible cross section of the plate. Copper corrosion products can be seen in the bottom part of the plate (photo K. Watemborska-Rakowska)

Experiment

The sampling areas

Examinations were carried out in the following parts of the find (Fig. 6): the surface of the plate with the comb (Fig. 6a, a', and a'') and the cross section of the plate where samples were taken (Fig. 6b). A sample of the cross section of the base alloy from the handle shown in Fig. 6a'') was also obtained in an unintentional way, i.e. as a splitter from the artefact. As it can be seen that the base alloy in the cross section of the grip's handle is strongly affected by corrosion (see Fig. 6a''). Therefore, the area corresponding to Fig. 6a'' was sampled and studied in two ways:

- 1) The surface of the grip handle (without preparation) was examined by microinvasive LA-ICP-MS and X-ray diffraction (XRD).

- 2) The cross section of the grip handle (obtained as a splitter sample) was analysed by XRD and optical microscopy (OM).

In order to identify the chemical composition of the metal, a LA-ICP-MS analysis was carried out on the surface of the artefact (Fig. 6a, a', and a''). It was found out that the structure identified in Fig. 6a'' (called the subsurface region) was similar to that of the base alloy in the silvered plate (see below in Table 1).

Examination techniques

Details of analytical techniques which were used in our examinations are well known and have been thoroughly discussed in archaeometallurgical research (see, e.g. Miazga 2014; Ashkenazi et al. 2015; Gójska and Mišta 2016; Mišta et al. 2015, 2016; Mišta et al. 2017; Matthew and Young 2016). In this case, the research procedure commenced with elemental and structural composition analyses of representative technological parts of the shield grip. The examination of the cross section of the artefact was made by optical microscopy (OM) in order to determine the distribution of alloy layers. The arrangement of the technological layers of the artefact was examined by neutron imaging (NI) (Anderson et al. 2009; Mišta et al. 2015, 2016; Sołtysiak et al. 2018). A microinvasive LA-ICP-MS (Fig. 6a, a', and a'') as well as a non-invasive SEM-EDX were used to determine the elemental composition of the representative technological parts of the artefact (see Fig. 6b). The LA-ICP-MS study of the surface provided information about the depth of element distribution (Gutierrez-Gonzalez et al. 2015). Furthermore, X-ray diffraction was used to determine the structure of the selected parts of the shield grip. The main goal of these examinations was to reveal the silvering technique or techniques used to produce the coating of the grip's plate.

Fig. 6 Shield grip from Czersk—zones of examinations: a'' cross section of the grip's handle. Corrosion products can be seen (mag × 6). **b** Fragments (I–III) of the sample which represent the cross section of the silvered plate

Table 1 Results of the LA-ICP-MS quantitative (rel. wt%) elemental composition analysis of the artefact parts and the SEM-EDX results obtained for the fragments of the cross-section cut (below LLD = 0.1 wt%; *nd* not determined). The samples' designation is described in Fig. 6

Technique	Sample	Ag	Cu	Zn	Sn	Pb	Fe	Au	Hg	As	Sb	Bi
LA-ICP-MS	For the entire artefact without preparation											
	(a)/surface	17.6	62.5	2.2	12.0	1.8	2.7	0.2	nd	0.6	0.3	nd
	(a')/comb	92.4	5.0	0.6	nd	1.6	nd	0.4	nd	nd	nd	nd
	(a'')/subsurface = base alloy	4.7	79.8	2.4	9.4	1.0	1.5	0.1	nd	0.4	0.6	nd
SEM-EDX	For the cross-section cuts (b), the centre of the samples											
	I	13.5	73.3	0.8	9.7	1.0	0.6	0.4	0.1	0.1	nd	0.4
	II	4.1	81.9	1.0	9.3	1.0	0.8	0.5	0.1	nd	nd	1.2
	III	14.3	70.8	3.1	9.3	0.7	0.7	0.1	0.4	0.1	nd	0.3
	Average	13.5	73.3	1.0	9.3	1.0	0.7	0.4	0.1	0.1	nd	0.4

Structural studies

Microscope observations were carried out using a Nikon SMZ800 stereoscopic microscope. What was studied was the cross section of the handle called sample a'' in Fig. 6 (sample without preparation). A Nikon Epiphot 200 Inverted Metallographic Microscope with mag. $\times 50$ –500 was used to study sample b in Fig. 6. The surface of these samples was polished and then etched with a 1 HClO₄/2 C₄H₆O₃ solution for 10 s. Next, electron scanning microscopy (SEM) observations were made using a Carl Zeiss EVO MA10 scanning electron microscope.

In neutron imaging (NI) study (Pranzas 2008; Anderson et al. 2009; Mišta et al. 2015, 2016; Sołtysiak et al. 2018), the Maria research reactor located in the National Centre for Nuclear Research in Otwock, Poland (www.ncbj.gov.pl) was used as a neutron source. NI experiments were carried out with the NGRS station, which is a standard Dynamic Neutron Radiography facility. The NGRS comprises neutron beam collimators, a fluorescent screen (250 mm $\times$ 250 mm), a mirror, optical zoom lenses and a CCD camera. The detector is a 0.1-mm-thick fluorescent medium containing Li6. The neutron beam flux at the sample was about 107 cm⁻² s⁻¹. The high-sensitivity Hamamatsu ORCA-ER CCD camera (1280 $\times$ 1024 pixels, 12-bit dynamic range) is used in the system. The collimating L/D ratio was 165, and the exposure time was 1.6 s. The projection ratio provided by the optical system was 0.154 mm/pixel. The sample was placed at the distance of 5 mm from the converter's screen. The image analysis was performed with the HiPic and ImageJ software packages. Before image analysis, preprocessing procedures were applied. They included a correction of pixel brightness for the black current, normalisation for neutron beam flux fluctuations and median filtering.

The XRD method was used for phase identification. Powder X-ray diffraction measurements were carried out with Cu-K α radiation ($\lambda = 1.5418$ Å) using a Siemens D5000 diffractometer equipped with a semiconductor Si:Li

detector cooled with liquid nitrogen and a ICDD PDF4 2014 database. The powder diffraction pattern was measured in $\theta/2\theta$ scanning mode with a step of 0.02 and integration time of 10 s/step.

Elemental composition studies

The alloy of the artefact in reference points described in Fig. 6 was studied with regard to case concentrations of copper (Cu), tin (Sn), lead (Pb), iron (Fe), zinc (Zn), silver (Ag), gold (Au), mercury (Hg), arsenic (As), bismuth (Bi) and antimony (Sb).

LA-ICP-MS was applied to study surface and subsurface layers (up to 10 μ m) of the artefact (without surface preparation). The areas of sampling are described in Fig. 6 as a, a' and a''. An ELAN 9000 inductively coupled plasma mass spectrometer (Perkin Elmer SCIEX, Canada: www.perkinelmer.com) equipped with an LSX-200⁺ laser ablation system (CETAX, USA: www.cetax.com) was used. The SLX-200⁺ system combines a stable environmentally selected 266 nm UV laser (Nd-YAG, solid-state, Q-switches) with a high sampling efficiency, a variable pulse repetition rate (1 to 20 Hz) and a maximum energy up to 6 mJ/pulse. The NIST610 standard reference material has been used for quantitative determination of the elemental composition. The measurement error was < 10%, and the low limit detection was 0.1 wt%.

The SEM analysis (Goldstein 2003; Barbacki 2007) was carried out with a Carl Zeiss EVO MA10 scanning electron microscope equipped with an EDAX XFlash Detector 5010 with 123 eV spectra resolution (Zeiss Poland; www.zeiss.com) and with a Bruker Quantax 200 Esprit 1.9 system to analyse the EDX spectra. The SEM images were recorded using a secondary electron detector (SE) with a resolution up to 2.0 nm. An accelerating voltage of 20.0 kV was applied, and other characteristics of the current, the field magnification and the type of surface sampling were in each case adapted to the type of the analysed sample. The spectra were registered by an energy-dispersive spectrometer which collects the entire spectrum of X-ray from 0 to 20 keV. Then, the average

Fig. 7 Neutron images of individual parts of the shield grip in false colour: **a** side view of the silvered plates with the silvered comb; **b** shield grip handle. The colour change shows differences in neutron absorption due to a different thickness and alloy composition. The images were false coloured using a SigmaScan™ software with a three-folded blue spiral. Scale: 0.154 mm/pixel

concentration of elements was obtained. The measurement time was set to 120 s for a multi-point analysis and to 5 min for mapping. Three EDX measurements were done for each sample. The quantitative analyses were done using the non-pattern method. The measurement error is < 10% for main elements (above 1 wt%) and < 30% for trace elements (below 1 wt%), whereas the low limit detection is 0.1 wt%.

Fig. 8 Microscopic images (scale 500 μ m) of the cut fragments sampled from the cross section of the silvered plate shown in Fig. 6b. External layers of the cuts correspond to the silvering area

Results

A preliminary structural study of the artefact revealed a heterogeneous and irregular structure of the find. This is mainly due to the poor state of preservation of the artefact, which is strongly corroded (see Fig. 6a"). Furthermore, the neutron radiography study provided images which indicate a different thickness of the metal in the same technological parts, as it can be seen in Fig. 7.

The microscale material heterogeneity of the structure (different layers of corrosion) is visible in OM images (see Figs. 6a" and 8). This certainly influences the current appearance of the artefact's surface.

As indicated by the LA-ICP-MS elemental analyses, the base alloy is that of copper (Cu 79.8 ± 8.0 wt%) and tin (Sn $9.4 \pm .9$ wt%) with an addition of lead (Pb 1.0 ± 0.1 wt%) and zinc (Zn $2.4 \pm .2$ wt%). This is also confirmed by the EDX method (see Table 1). Such an alloy can be termed as brass or "leaded gunmetal". Furthermore, such a chemical composition may imply that recycled alloy was used in this case, which was a common practice in ancient Rome (see, e.g. Craddock 1978, 1–14). The presence of iron (Fe) is probably a result of soil contamination and impurities of the raw base alloy.

Figure 9 offers results of the XRD analyses for the cut fragments (see Fig. 6b): I Cu_2O (cuprite), alloyed Ag, $\text{Cu}_{41}\text{Sn}_{11}$ (copper tin); II Cu_2O_3 , Sn; III Cu_2O , copper zinc, silver and Ag_4Sn (tin silver) were detected, respectively. Similar structural analyses were made also for the silver coating of the combs and for the surface of silvered plate. In the case of the combs, the presence of alloyed silver was detected. XRD analyses for the plates demonstrated the presence of

alloyed silver (a silver-based solid solution), Cu–Sn conglomerate, tin and copper oxides and covellite (CuS). All crystallographic data provided information that the Ag–Sn–Cu system with relevant corrosion products was present in the structure. This corrosion may have influenced the present shape of the silver surface of the plates.

Alloyed tin and silver were detected as part of the crystal structure of the cuts, which are the cross section of the plate (Fig. 9). LA-ICP-MS results show that silver alloy in the comb has the following elemental composition (wt%): Ag 92.4 ± 9.2 , Cu 5.0 ± 0.5 , Pb 1.6 ± 0.2 and an addition of zinc and gold (see Table 1, a'). Therefore, it is not the same type of raw material as that in the silvered layer of the openwork plate (see Table 1, a). The silvered surface of the plate is enriched in copper (Cu) 62.5 ± 6.2 , zinc (Zn) 2.2 ± 0.2 , iron (Fe) 2.7 ± 0.3 and—which is significant—tin (Sn) 12.0 ± 1.2 (see Fig. 5a).

Figures 10, 11, and 12 below demonstrate the correlation of the main elements which were determined in the surface and subsurface area.

Correlations in the form of a laser ablation depth profile (Gutierrez-Gonzalez et al. 2015) can be observed concerning the contents of silver (Ag), tin (Sn) and copper (Cu) in the silvered surface of the plate in relation to the signal intensity of these elements in the silver comb's alloy. Figure 10 shows an Ag–Sn–Cu intensity correlation measured by 166 s using the LA-ICP-MS method. There is no explicit correlation with regard to the analysis time and the thickness of the examined material. The measurement time corresponds to the increasing depth of sampling. The signal intensity of a specific element correlates with its concentration in base alloy. Therefore, the obtained data is only relative. As regards the plate (Fig. 10a), all we know is that in the measurement time of 36–40 s, layers with increased contents of copper (Cu) and tin (Sn) were

Fig. 9 XRD results for parts of the cut (b) in Fig. 4: parts I, II and III, respectively

* Cu₂O, # Ag, + CCuO₃, o Cu₄O₃, & (Cu,Sn), @ Ag₄Sn

Fig. 10 LA-ICP-MS results as a signal intensity in time for concentrations of silver (Ag), copper (Cu) and tin (Sn) in **a** the silvered surface of the plate (Fig. 6a) and **b** the silver comb (Fig. 6a')

detected, while in the time of 36–37 s silver (Ag) enrichment was also found. After 42 s of the measurement, there are no significant anomalies in concentrations. SEM-EDX analyses also reveal this type of Ag–Sn correlation, as it can be seen in Figs. 11 and 12. For the comb, there is no visible signal from tin—what is mainly registered is a signal from silver and addition of copper to this alloy (see Table 1, a').

A SEM-EDX map of copper (Cu), silver (Ag) and tin (Sn) concentrations (Fig. 11) demonstrates an enrichment in Ag and Sn in the area located ca. 500 μm from the surface of the cut. Below this zone, a Cu-enriched layer can be seen. The EDX maps inform us that below the Ag–Sn layer there is a Sn–Cu zone.

In order to get a better insight into the ancient silvering technology, EDX linescans were carried out (Fig. 12). The maximum yields for Ag and Sn are located in the vicinity of the sample's border (the μm range from 307.67 to 1362.53). This gives the length of 1054.86 μm that can be identified as a silver coating on the shield grip's plate.

Furthermore, attention was paid to the ornamental combs of the grip. The neutron images of the combs' structure are presented in Fig. 13c, d. Figure 13c (right) offers a view of the

top of the comb with damaged top ornament with filigree pigtales (as it is seen in Fig. 5—the right comb). In NI, no empty space between individual parts of the comb can be seen. For the combs with the damaged top ornament (the right comb), the base alloy between the comb sheets is visible, whereas in the case of the comb with surviving ornament, the NI shows the thickness of the surface ornament. It seems that the interiors of the studs are filled with rivets, around which the filigree wire is wrapped (see Fig. 13). Furthermore, in one stud (that on the right), there is a gemstone (see Fig. 13a, b—images on the right).

Discussion

The results of the analyses strongly imply that the amalgam technique was not used for silvering of the discussed artefact. Traces of mercury are up to 0.4 wt%, as determined by the SEM-EDX analyses (see Table 1). The mercury probably came from geological ores which were enriched in amalgam compounds (Bode 1997). Furthermore, mercury can evaporate in the course of a peculiar fire-silvering process, as

Fig. 11 SEM -EDX map results for cut fragment I (Fig. 6b) with a surface distribution of silver (Ag), tin (Sn) and copper (Cu) in the cross section of the silvered plate. Bottom image depicts the superimposed maps for all elements

described by Theophilus (1979: p. 113). However, on the basis of a clear correlation between silver and tin as shown in Figs. 10, 11 and 12, we can conclude that mercury-silvering was not the case here. Instead, silvering techniques based on the application of tin-based solder were used.

The base alloy for silvering is “lead gunmetal” (Craddock 1978). Typical tin bronze has the following elemental composition (%wt): Cu 86–89%, Sn 1–9% and Zn

3–5%. Due to a similar composition to tin bronze, such metal is classified as casting alloy with good mechanical properties and corrosion resistance (Domke 1982: p.209, Wesołowski 1972: p.396). As compared with typical tin bronze, the base alloy of the shield grip is depleted in copper (Cu) and zinc (Zn). Furthermore, it contains traces of iron (Fe: up to 1.5 wt%) and lead (Pb: up to 1.0 wt%) (see Table 1). Considering the Ag–Cu–Sn system shown in Figs. 9, 10, 11,

Fig. 12 SEM-EDX linescan distribution of silver (Ag), tin (Sn) and copper (Cu) in fragment I (Fig. 6b) of the cut's cross section

Fig. 13 Neutron images with false colours of the silver studs (**a**, **b**) and the silver comb (**c**, **d**) in a side and top view. Scale: 0.154 mm/pixel

12, and 13 with regard to the use of soldering, it should be remembered that in a higher temperature of metallurgical treatment, the structure of alloy allows for an easy diffusion process of silver into the internal layer of the base alloy and of elements from the base alloy to the silver surface. However, the tin enrichment in the subsurface (see Figs. 10, 11, and 12) suggests that a tin mixture (which has a low melting point) was applied as solder to the base alloy in the silvering process. Copper content in subsurface layers could be an effect of diffusion from the Cu-based core of the silvered plates or could be an intentional addition to Sn-based solder. Furthermore, according to La Niece (1993), the Ag–Cu–Sn mixture could be used for soldering of silver foil onto the surface. The maximum amount of Ag–Cu–Sn mixture is visible in Fig. 10 (36–37 s of LA measurement) and in Fig. 12 (up to 1056 μm from the surface of cut).

A study of the Ag–Cu–Sn phase diagram (Roshanghias et al. 2015: Fig. 4) for a particle radius from 3.5 to 3.9 (as shown by the neutron scattering study which was additionally carried out for the grip) demonstrates that the Ag–Sn–Cu system with a higher Sn content caused a slight lowering of the melting temperature for Cu-based solid solution. With regard to that, the tin-based solder which was applied to the base copper-based alloy lowers the melting point of the surface. Therefore, it facilitated the application and final adhesion of the silver foil sheet at a lower temperature than for gunmetal bronze and silver separately. Then, hot hammering was used for a betted adhesion of the silver foil to the bronze covered by tin-based solder.

Moreover, due to the corrosion of the subsurface and the internal structure (see Fig. 6a'') of the metal layers (Scott 1991:

p. 45; Piccardo 2007; Masi et al. 2016; Ingo et al. 2015), it is possible that corrosive irregularities may have influenced the surface shape of the silvered layer (Sandu et al. 2006). The surface of the internal layer of the openwork plate is smoother than that of the external layer. It may have been caused by the fact that the external layer was more exposed to corrosion processes.

Conclusions

The extensive physico-chemical analysis of the unique shield grip from Czersk provided an insight into its structure and allowed for the identification of two silvering technologies which were used for the ornamentation of the artefact. Concerning the mould-cast openwork plates, the Sn–Ag–Cu correlation which was observed in the silvered surface and the subsurface layers can be explained by the intentional process of using tin-based soldering. This process was fairly widespread in the Roman Period and is known as foil silvering (La Niece 1993). The silver sheet was applied to the copper base alloy (cast gunmetal) by tin-based (tin–copper or tin–copper–silver) soldering after heating the solder to a temperature close to its melting point. Moreover, the influence of the corrosion structures of the external copper alloy should be taken into account. A different technology, that is, hammering of silver-rich sheets to alloy base, was used for the combs of the grip. Furthermore, the high content of silver in the combs' alloy may additionally confirm the aforementioned observation that the comb was silvered by means of covering it with a metal sheet without high-temperature treatment. Due to the

lack of any traces of solder in the silver comb alloy (see Table 1, Fig. 10), the silver sheets of the comb were hammered together (as there is no empty space between them) until a contact with the base alloy and massive piece of silver on their top occurred. This massive piece of silver is ornamented with punched filigree pigtails.

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