Research on a laddered chape from a Late La Tène scabbard with an openwork fitment from the River Ljubljanica

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Izvleček

Članek podaja izsledke raziskav lestvičastega okova nožnice z okovom okrašenim v predrti tehniki, ki je bil najden v reki Ljubljanici. Preiskovanje je vključevalo revizijo restavratorskega postopka in sondažne posege v lestvičasti okov, določanje zlitin z metodo protonsko vzbujenih rentgenskih žarkov (PIXE; glej Šmit, Istenič, Perovšek 2010), opazovanje dveh odlomkov prečk lestvičastega okova v vrstičnem elektronskem mikroskopu (SEM), semikvantitativne kemijske analize izredno majhnih površin v elektronskem mikroskopu (SEM/EDS) ter metalografske raziskave.

Izsledki so pokazali, da je bil lestvičast okov iz kovanega jekla in da so zelo tanke plasti brona v sprednjih prečkah delovale kot spajke, kar tudi nakazuje, kako je bil lestvičasti okov narejen.

Ključne besede: Ljubljanica, Bevke, lestvičasta nožnica, tehnologija, druga polovica 1. stoletja pr. Kr., metalografske raziskave, SEM

Abstract

The paper gives the results of our research into the technique of manufacture of the laddered chape from the sword scabbard with openwork fitment from the River Ljubljanica. In addition to characterisation of the alloys by proton-induced X-ray emission spectrometry (PIXE; cf. Šmit, Istenič, Perovšek 2010) the study included observation of fragments of bridges from the laddered chape using scanning electron microscopy (SEM), semi-quantitative chemical analysis of minute areas under an electron microscope (SEM/EDS) and metallographic research.

Results of the study indicate that the laddered chape was made of forged steel and that the very thin layers (lamellae) of bronze in the front bridges acted as solders, thus giving an idea of how the laddered chape was constructed.

Keywords: Ljubljanica River, Bevke, laddered chape, technology, second half of the 1st century BC, metallographic examination, SEM

1. INTRODUCTION

When analysing Late La Tène scabbards with openwork copper alloy or silver plates (cf. *fig. 1*), we also broached the subject of the technique that was used in the manufacture of their steel[1] laddered chapes, as well as the copper alloy fitments with openwork decoration, typical of this type of scabbard. In previous publications varied and sometimes conflicting opinions regarding their manufacture were expressed (Istenič 2010, 137–138).

In our opinion the openwork plates were not made by casting; the thin sheet metal was modelled by hammering and the decoration was then shaped with various chisels, used to remove the excess metal and also for chasing (Istenič 2010, 127–138). The subject of manufacturing laddered chapes was only briefly touched upon in our previous publication (Istenič 2010, 137–138), because the study was not yet complete at the time. It is the aim of the present paper to give the results of our research into the techniques of manufacture of laddered chapes.

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[1] In the archaeological literature the term "iron" is widely accepted to denote an alloy of iron and a small part (up to 2 %) of carbon, rather than chemically pure iron. In the metallurgical literature, such an alloy is called steel (Rekar 1972, 481). To standardize the terminology of the article, we use the term "steel" (cf. Kmetič, Horvat, Vodopivec 2004, 291–292 fn. 1).

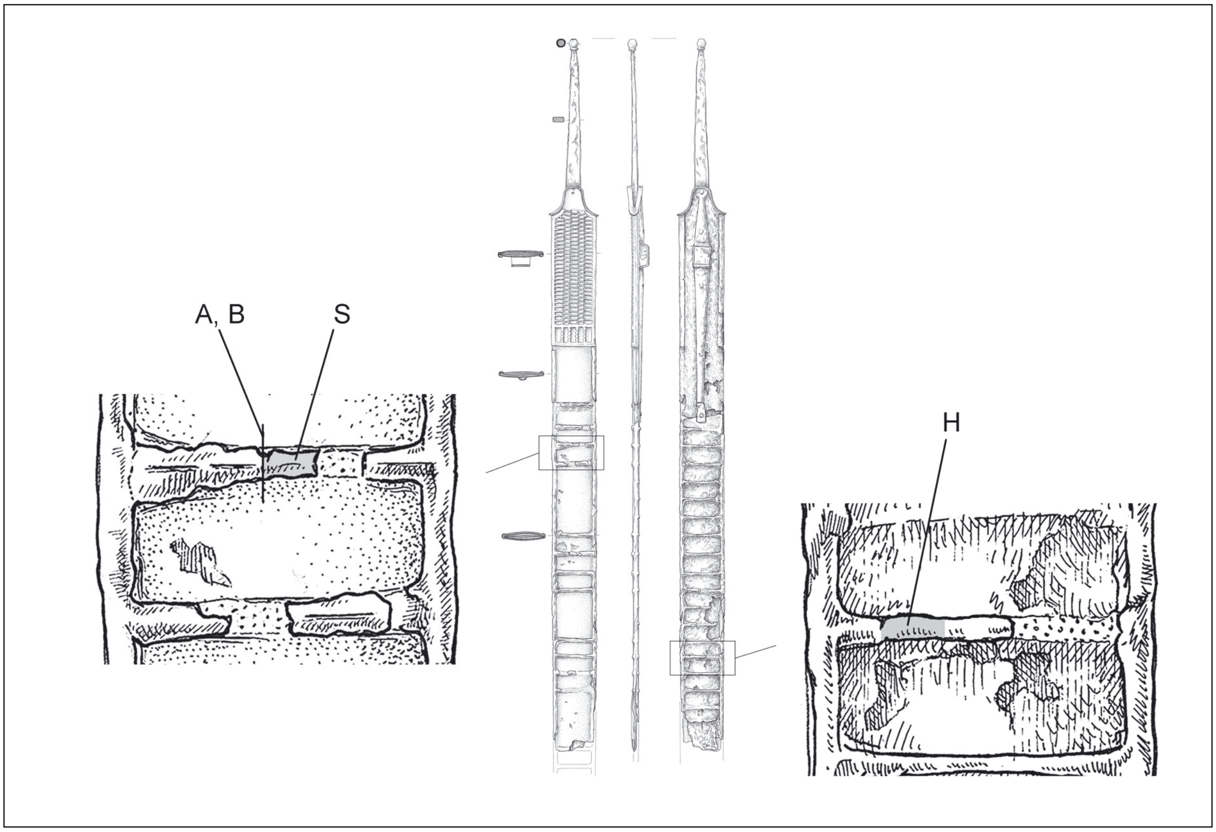

Fig. 1: The River Lubljanica near Bevke. Front and back of the scabbard, indicating the position and details of the 3rd front bridge and its transverse fractures (**A**, **B**), as well as the position of the samples taken for metallographic analysis. **S** – sample of the 3rd front bridge; **H** – sample of the 14th back bridge. Scale 1:8, details 1:1.*
Sl. 1: Ljubljanica pri Bevkah. Sprednja in hrbtna stran nožnice z označeno lego prelomov 3. sprednje prečke (**A**, **B**) in vzorcev, ki smo jih metalografsko preiskali. **S** – vzorec 3. sprednje prečke; **H** – vzorec 14. hrbtne prečke. M. = 1:8, detajli 1:1.*

* Unless otherwise indicated, the scabbard is oriented in the photographs with its tip down.
* Če ni navedeno drugače, je nožnica na fotografijah orientirana tako, da je njena konica spodaj.

2. PREVIOUS RESEARCH

The question of how the laddered chapes of the Late La Tène scabbards with an openwork fitment were made was first addressed by Westphal (1998, 250–252), when he studied the construction of a scabbard from the Badenheim Late La Tène grave (Böhme-Schönberger 1998).

Westphal's findings about the construction of the scabbard from Badenheim were the result of a careful examination of the already conserved scabbard, which had been ritually bent in the middle and damaged on the funeral pyre (Westphal 1998; 248; Böhme-Schönberger 1998, fig. 13). A ca 1 mm thick steel plate at the back and a slightly thinner copper alloy plate at the front (traces on its rear suggest it was made by hammering) are joined together by a steel laddered chape. He suggested that the scabbard was constructed by pushing the plates into a ready-made laddered chape and then secured by (slightly) pressing together the sides of the chape. Westphal (1998, 250–252), however, could not answer the question of how the laddered chape was made, despite giving it a lot of attention. He could not find any traces of soldering, welding or riveting (... "waren weder Lötnähte, noch Schweißstellen, noch Nietungen festzustellen").

Haffner (1995, 140) believed that the laddered chape of the scabbard from the Büchel grave, partially melted in a secondary fire and heavily distorted because bent several times, was made by forge welding[2] ("Schweißverbundtechnik"). He claimed the X-ray image revealed tiny bronze

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[2] In forge welding the previously heated metal parts are joined by hammering.

rivets, connecting the chape-end to the two plates. Unfortunately, the image was not published.

3. INVESTIGATION OF THE SCABBARD FROM THE LJUBLJANICA: OBJECTIVES AND METHODS

In our opinion the construction of the laddered chapes in question by forge welding seems unlikely. Namely, the fitment is very narrow on the inside and it would have been very difficult to use the appropriate anvil needed for forge welding. This problem could have been largely avoided by forging a pipe-like fitment and then flattening it. However, it is hard to imagine how this technique could have been used to make the spur-like chape-end.

Laddered chapes were also not cast, because steel forging, rather than casting was in use in Europe during the Late Iron Age and Roman period; also, cast steel would be too brittle for such a chape (Manning 1976, 143; Tylecote 1992, 48; Craddock 1995, 235, 239).

On examining the laddered chapes from three scabbards from Slovenian sites (one from the River Ljubljanica and two from Verdun; Istenič 2010, fig. 9, 11) by naked eye, as well as by magnifying glass and an optical microscope, we could not find any traces of either welding, soldering[3] or rivetting. X-rays – including images of the sword from the Ljubljanica made with an X-ray generator, capable of micro focusing with a magnification factor of 50[4] – also did not show traces of these techniques (Istenič 2010, fig. 3). It is worth mentioning that all three scabbards are relatively well preserved; none of them was damaged by fire or deliberately bent, as was the case with the scabbards from Badenheim and Büchel.

The three scabbards we have examined had previously been conserved and restored in the Römisch-Germanisches Zentralmuseum in Mainz (Istenič 2010, 125, 131, 134). We opted for a partial revision of conservation and restoration of one of them. It was carried out on the scabbard from the Ljubljanica, in agreement with the curator Bernarda Županek and the Head of the Conservation Department, Katarina Toman Kracina, both from the Museum and Galleries of Ljubljana (Muzej in galerija mesta Ljubljana), where the object is kept. The revision yielded interesting results, which called for further study. This included the following methods (in the order in which they were applied): characterisation of the alloys by proton-induced X-ray emission spectrometry (PIXE; Šmit, Istenič, Perovšek 2010, 166–169, table 1); observation of fragments of bridges from the laddered chape using scanning electron microscopy (SEM); semi-quantitative chemical analysis (energy-dispersive X-ray spectroscopy) of minute areas under an electron microscope (SEM/EDS); and metallographic research.

The terms up, down, left and right, above and below are used in reference to the orientation of the scabbard with its mouth facing upwards and its front facing the viewer.

4. A PARTIAL REVISION OF THE SCABBARD FROM THE LJUBLJANICA

The scabbard found in the River Ljubljanica at Bevke is one of only a few examples of its kind that were not damaged in the secondary (funeral) fire or deliberately bent. It is also one of two found in water (cf. Istenič 2010, 148, list: No. 23). It is very well preserved, as is the case with most finds from the Ljubljanica (Milić et al 2009a). Save for the missing tip, it seems to be the most perfectly preserved example of this type of scabbard.

All of the described procedures on the scabbard from the Ljubljanica were performed by Sonja Perovšek in 2010. From several areas of the scabbard she removed the added (reconstructed) parts of the laddered chape made of epoxy resin (Araldite) and a residue of firmly ingrained silicone rubber (presumably from making a mould in the workshop of the Römisch-Germanisches Zentralmuseum in Mainz); she also used precise microsanding[5] on carefully selected areas to remove various plaques formed in the river, and on a small scale also thin layers of corrosive products Examination of all of the front bridges of the scabbard (i.e. 1–4, 6, 8 and 9) revealed a reddish alloy in the steel (*fig. 2*). PIXE analysis of four such areas (on the 2nd, 3rd, 4th and 9th bridges) identified bronze with ca 4–7 mass percent of tin (Šmit, Istenič, Perovšek 2010, table and fig. 1: 11,12a,13,15).

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[3] In soldering, metal parts are joined by a fusible metal or alloy (a solder).

[4] Radiography was performed at ETA CERKNO d.o.o. company on an YXLON 160kV/4mA generator with a HAMAMATSU tube. The X-rays can penetrate iron samples up to 32 mm thick.

[5] In microsanding, the surface is cleaned by accelerated fine jets of sand or glass particles.

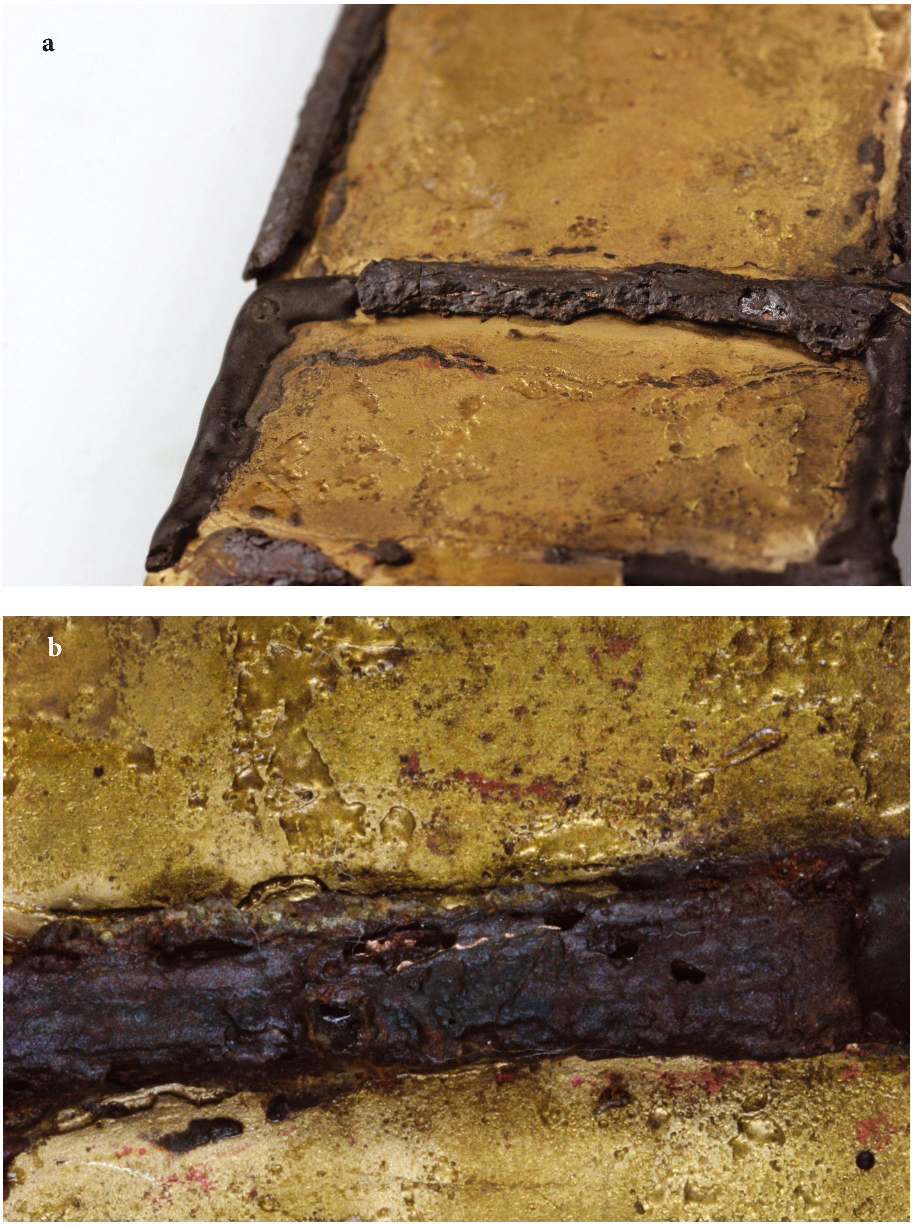


Fig. 2a–b: Bronze in iron front bridges of the scabbard. **a:** in the 1st bridge; **b**: in the 2nd bridge (remains of epoxy resin on the left). Not to scale (photo: S. Perovšek).
Sl. 2a–b: Bron v železu sprednjih prečk okova. **a**: v 1. prečki; **b**: v 2. prečki (na levi strani ostanki epoksidne smole). Brez merila (foto: S. Perovšek).

Upon removing the added resin parts, two fragments of the 2nd and 3rd bridges were released. Their undersides revealed a layer of copper alloy, which became prominent after precise microsanding (*fig. 3c; fig. 4b*). The left edge of the fragment, broken off from the 3rd bridge, as well as the edge of the bridge still attached to the scabbard (*fig. 1:* A,B) were more or less vertical and therefore suitable for observation of their cross-section. On the fracture of the broken-off fragment, three thin bronze layers were discerned under the optical microscope; they run horizontally with regard to the cross-section of the bridges and more or less parallel to the scabbard plates (*fig. 5*). They vary in thickness around less than 0.1 mm. The other fracture surface revealed only one copper-alloy layer, similarly oriented (*fig. 6*).

Just above the 9th front bridge, on the inner side of the U-shaped part of the back of the chape, a copper alloy layer was revealed; it was identified as bronze with ca 6 mass percent of tin (Šmit, Istenič, Perovšek 2010, table and fig. 1: 14). Its visible part is ca 4 mm long (*fig. 7*). Judging by the shape of its

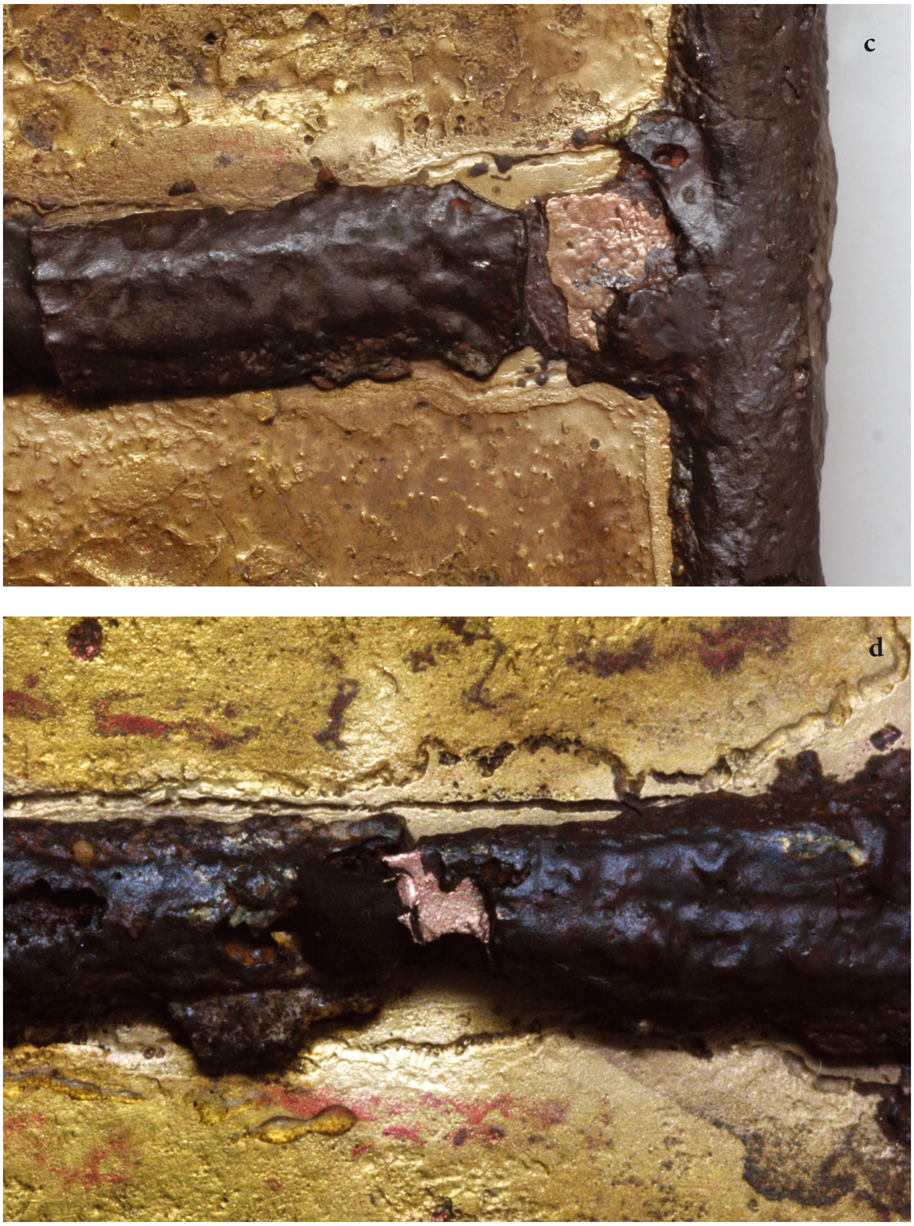


Fig. 2c–d: Bronze in iron front bridges of the scabbard. **c**: in the 4th bridge; **d**: in the 9th bridge. Not to scale (photo: S. Perovšek).
Sl. 2c–d: Bron v železu sprednjih prečk okova. **c**: v 4. prečki; **d**: v 9. prečki. Brez merila (foto: S. Perovšek).

upper end, the layer actually ends there, whereas on the other side, towards the 10th front bridge, it most likely continues under the U-shaped part of the chape. The relation between the bronze layer and the brass plate could only be observed on a small portion of the scabbard: there seems to be no steel between them – the bronze plate seems to lie directly on the brass plate and stretches beyond it by at least 2 mm. Originally, however, there could have been a thin layer of steel between the bronze and the brass layers (which would indicate that the bronze layer was in the steel, similarly to the front bridges), but is not discernible due to corrosion.

Roughly symmetrically, i.e. at the 9th front bridge and from the 11th back bridge to ca 1 cm below the 13th back bridge, a less than one millimetre thick non-ferrous layer was discovered (*fig. 8*). It can be followed for ca 3.7 cm. Mostly it is seen in cross-section as a very thin layer in the steel corrosion products; its surface is discernible only over a small area. PIXE analysis showed that the layer is a copper alloy with ca 5 mass percent of

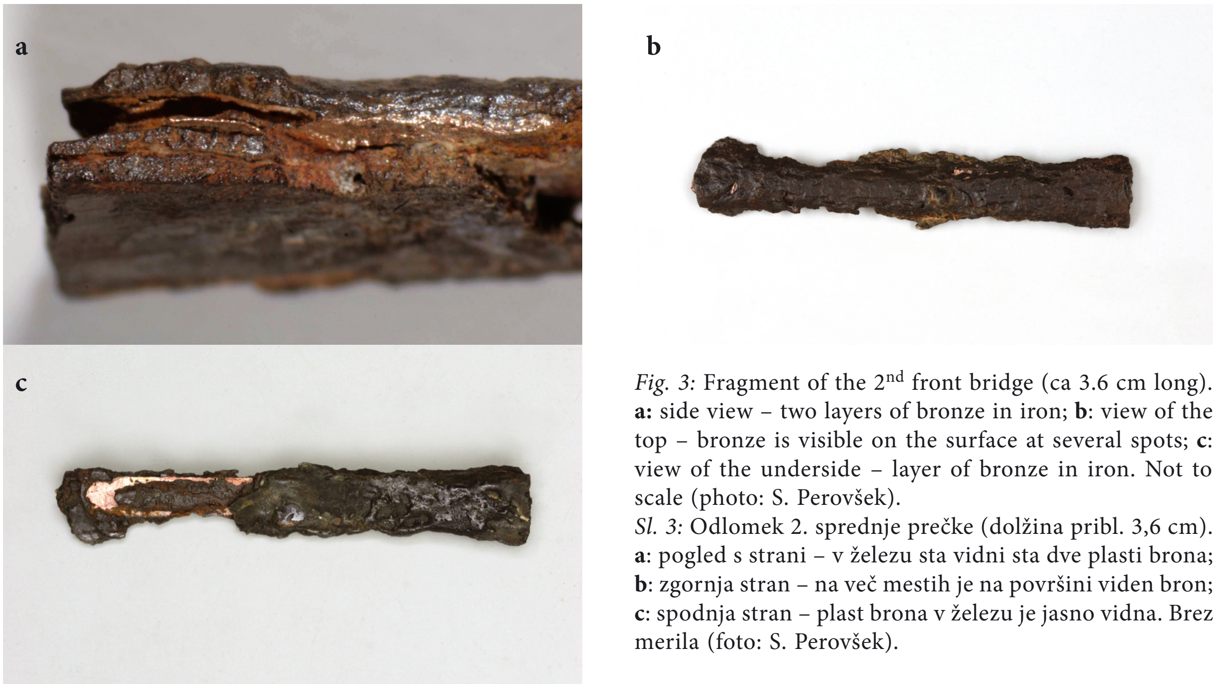


Fig. 3: Fragment of the 2nd front bridge (ca 3.6 cm long). **a:** side view – two layers of bronze in iron; **b**: view of the top – bronze is visible on the surface at several spots; **c**: view of the underside – layer of bronze in iron. Not to scale (photo: S. Perovšek).
Sl. 3: Odlomek 2. sprednje prečke (dolžina pribl. 3,6 cm). **a**: pogled s strani – v železu sta vidni sta dve plasti brona; **b**: zgornja stran – na več mestih je na površini viden bron; **c**: spodnja stran – plast brona v železu je jasno vidna. Brez merila (foto: S. Perovšek).

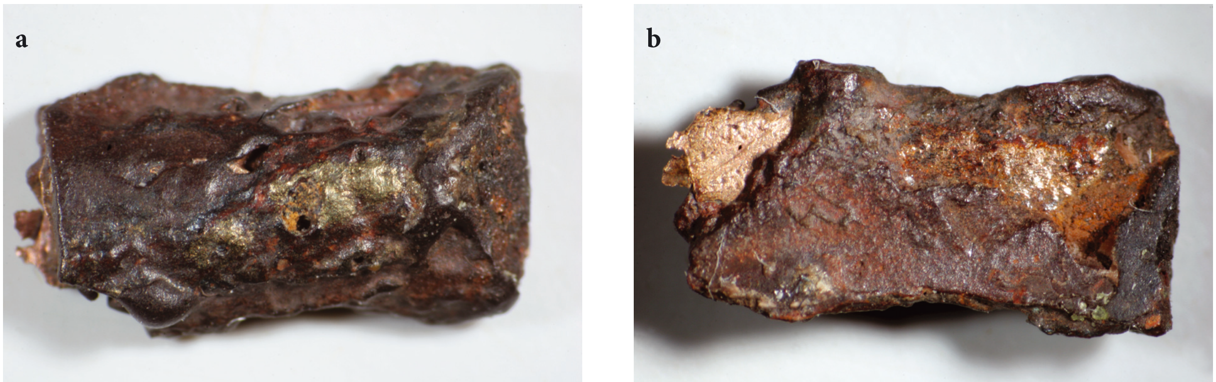


Fig. 4: Fragment of the 3rd front bridge (0.9 cm long). **a**: top – chalcopyrite on the surface of the fragment and a layer of bronze on the left; **b**: underside – two layers of bronze. Not to scale (photo: S. Perovšek).
Sl. 4: Odlomljeni del 3. sprednje prečke (dolžina 0,9 cm). **a:** zgornja stran – na levi strani je vidna plast brona, na površini zgornje strani odlomka pa zlato svetleča plast halkopirita; **b:** spodnja stran – vidni sta dve plasti brona. Brez merila (foto: S. Perovšek).

zinc, rather than bronze (Šmit, Istenič, Perovšek 2010, table and fig. 1: 9).

Upon examination of the back bridges of the scabbard, a copper alloy was identified in only one of them, i. e. the 10th bridge, and only in its left half (*fig. 9*). The right half of the bridge, separated from the left one by a reconstructed part of epoxy resin, contains no copper alloy. We believe that this part of the bridge was displaced from the front (possibly from the 11th or 12th bridge) to the back of the scabbard during the conservation and restoration process. This is also indicated by a shallow groove along the middle of the left side of the 10th bridge; this is common on the front bridges of the scabbard (cf. *fig. 2*), but, with the exception of one half of the 10th bridge, cannot be found anywhere on the back bridges. The type of copper alloy was not analysed, because it is discernible on only very small areas. In analogy with the analyses of copper alloys in the front bridges, we presume it is bronze.

A very thin layer with a golden shine is visible in several areas on the front side of the laddered chape, as well as on other steel surfaces (*fig. 4a*).

Fig. 5: Fragment of the 3rd front bridge, transverse fracture (cf. *fig. 1:* A); width ca 3.5 mm, height ca 1.5 mm. Three layers of bronze are visible in the iron. Not to scale (photo: S. Perovšek).
Sl. 5: Odlomljeni del 3. prečke, prelom (prim. *sl. 1:* A); širina okoli 3,5 mm, višina okoli 1,5 mm. Vidne so tri plasti brona. Brez merila (foto: S. Perovšek).

Fig. 6: Fracture of the fragment of the 3rd front bridge still attached to the scabbard (cf. *fig. 1:* B); width of the fracture ca 3.6 mm, height 1.4 mm. A layer of bronze is visible in the iron. Not to scale (photo: S. Perovšek).
Sl. 6: Prelom 3. prečke na delu, ki je ostal na nožnici (prim. *sl. 1:* B); širina opazovanega preloma 3,6 mm, višina 1,4 mm. Vidna je ena plast brona. Brez merila (foto: S. Perovšek).

Fig. 7: Guttering (lateral part of the laddered chape) at the 9th bridge. A layer of bronze in/beneath? the iron. Orientation of the scabbard: its tip is pointing towards the right upper corner of the photograph. Not to scale (photo: S. Perovšek).
Sl. 7: Robni del lestvičastega okova pri 9. sprednji prečki. Plast brona v železu ali pod njim. Nožnica je orientirana tako, da je konica usmerjena proti desnemu zgornjemu vogalu fotografije. Brez merila (foto: S. Perovšek).

Fig. 8: The back of the scabbard between the 9th and the 14th bridge (**a**), and between the 11th and the 13th bridge, detail (**b**). Not to scale (photo: S. Perovšek).

1 – remains of the 13th bridge or its imprint in the corrosion layer. **2** – underside of the brass plate, which covers the front of the scabbard; its surface is covered by corrosion and patina except on its edge (**2'**), where metal (golden yellow) is exposed. **3** – a thin reddish layer of copper alloy containing ca 4.6 % zinc: it is discernible as a thin line in the iron guttering (**3'**), and in small part also as a layer that follows the U-shaped guttering (**3**). **4** – the blade of the sword. **5** – the back plate of the scabbard, iron. **6** – guttering (lateral part of the laddered chape); **7** – reconstruction of the laddered chape, resin.

Sl. 8: Hrbtna stran nožnice med 9. in 14. prečko (**a**). Detajl hrbtne strani nožnice med 11. in 13. prečko (**b**). Brez merila (foto: S. Perovšek).

1 – ostanki 13. prečke oz. njen odtis. **2** – spodnja stran medeninaste platice, ki prekriva sprednjo stran nožnice; njen stranski rob (**2'**) je zlatorumene barve, sicer pa je njena površina prekrita z ostanki korozije in patino. **3** – tanka plast rdečkaste zlitine bakra z okoli 4,6 % cinka, ki v manjšem delu sledi obliki robnega dela železnega okova, sicer pa je vidna le kot tanka črta v železu (**3'**). **4** – jekleno rezilo meča. **5** – jeklena hrbtna platica nožnice. **6** – robni del jeklenega lestvičastega okova. **7** – rekonstrukcija lestvičastega okova iz epoksidne smole.

5. STUDY BY SEM/EDS

During revision of the conservation of the scabbard, 3.6 and 0.9 cm long fragments were loosened from the 2nd and 3rd front bridges of the scabbard. The two pieces were found suitable for observation by scanning electron microscope coupled with an energy dispersive spectrometry (SEM/EDS). The aims of this examination were as follows:

– characterisation of copper-alloy (verification of the results given by the PIXE method);

– answering to the question of the composition of the thin, bright, golden yellow shiny layer on the surface of the rung;

– identification of the metal found under, above and between the layers of copper alloy (is it steel?);

– finding possible other materials beside copper alloy and steel. Of particular interest were the

Fig. 9: Area (**a**) between the 8th and the 12th bridge at the back of the scabbard. Detail (**b**) of the 10th bridge, where bronze is discernable in the iron. Not to scale (photo: S. Perovšek).
Sl. 9: 8.–12. prečka na hrbtni strani nožnice (**a**). Leva polovica 10. prečke, detajl (**b**) – vidni so ostanki bakrove zlitine v železu. Brez merila (foto: S. Perovšek).

lower surfaces of the rungs, which were in contact with brass plates on the front site of the scabbard.

Microanalyses were carried out at the Geological Survey of Slovenia using a JEOL JSM 6490LV scanning electron microscope coupled with an Oxford INCA energy dispersive spectrometer at 20 kV accelerating voltage and 10 mm working distance. The samples were observed in high vacuum using the backscattered electron mode (BSE). Due to the good conductivity of the sample material it was not necessary to coat it with gold, thus enabling the material to remain completely unchanged after the electron microscope microanalysis.

The results of microanalysis showed that the bright golden shiny surface on the steel base consists of iron, sulphur and copper in proportions corresponding to a $CuFeS_2$ compound, i.e. chalcopyrite (iron-copper sulphide). We assume this coating was formed since the scabbard was immersed in the Ljubljanica. It developed in the reducing conditions of the river bottom mud in a complex chemical reaction between the iron in steel, copper in brass plates and sulphur in river bottom mud.

Detailed observation of the breakage on the third rung clearly showed three layers of bronze of different thicknesses (about 0.02, 0.03 and 0.05 mm). The layers were approximately parallel to the flat rung surface with which it was in contact with the scabbard (*figs. 10–13*). A trace of a fourth, extremely thin (about one thousandth of a mm) layer was also indicated on the upper part of the plate (*figs. 10, 14*). SEM/EDS analyses showed that between the layers, as well as above the upper and below the lower layer, there is iron oxide or iron oxihydroxide.

SEM/EDS analyses of the copper alloy in several places confirmed that it was bronze. The ratio of copper (Cu) and tin (Sn) in the first three layers is about 9: 1. In the top (fourth) layer, which is extremely thin, tin strongly dominates, with a Cu : Sn ratio of about 1: 5.

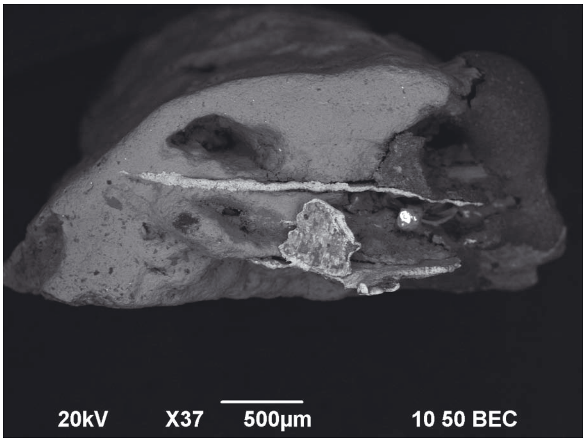


Fig. 10: Transverse fracture of the fragment of the 3rd front bridge (cf. Fig. 1: A and Fig. 5). Three layers of bronze are clearly visible. Above them a barely discernible layer in which tin clearly predominates (ratio Cu : Sn is ca 1 : 5). The bright spot on the right is most likely the result of electrons hitting the surface of a poorly conductive particle. The sample was not coated with a conductive layer. SEM, BSE.
Sl. 10: Prelom odlomljenega dela 3. sprednje prečke. Jasno so vidne tri plasti brona, nad njimi pa je komajda opazna plast, v kateri močno prevladuje kositer (razmerje Cu : Sn je pribl. 1 : 5). Svetla pika na desni strani je verjetno posledica udarjanja elektronov na površino slabo prevodnega delca – vzorca namreč nismo naparili s prevodno plastjo. SEM, povratno sipani elektroni (BSE).

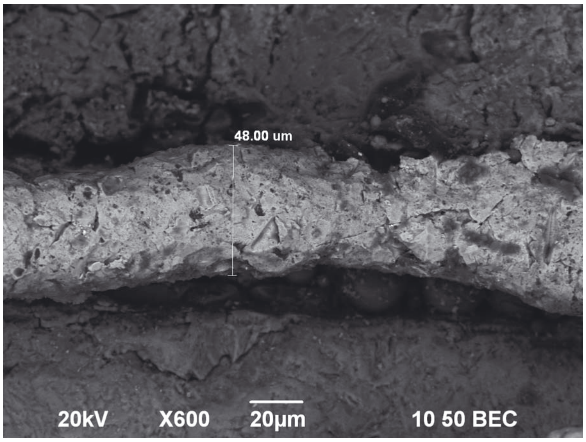


Fig. 11: The upper bronze layer, ca 0.05 mm thick, in the transverse fracture of the fragment of the 3rd front bridge. SEM, BSE.
Sl. 11: Okoli 0,05 mm debela zgornja bronasta plast v prelomu odlomka 3. sprednje prečke: SEM, povratno sipani elektroni (BSE).

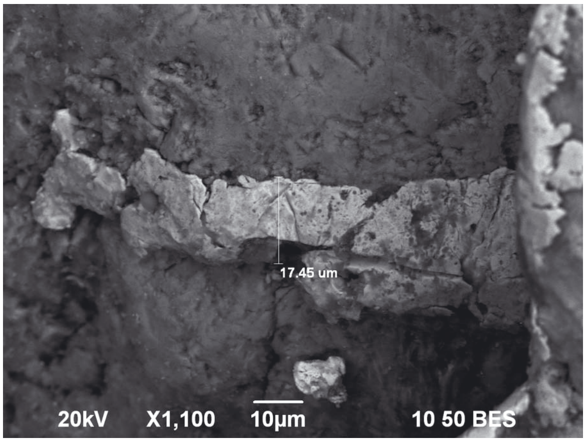


Fig. 13: The third (lowest) bronze layer, ca 0.03 mm thick, in transverse fracture of the fragment of the 3rd front bridge. SEM, BSE.
Sl. 13: Okoli 0,03 mm debela tretja (spodnja) bronasta plast v prelomu odlomka 3. sprednje prečke. SEM, povratno sipani elektroni (BSE).

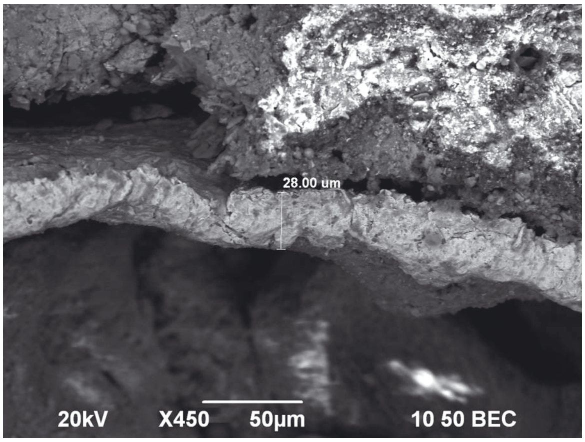


Fig. 12: The second bronze layer, ca 0.02 mm thick, in transverse fracture of the fragment of the 3rd front bridge. SEM, BSE.
Sl. 12: Okoli 0,02 mm debela druga bronasta plast v prelomu odlomka 3. sprednje prečke. SEM, povratno sipani elektroni (BSE).

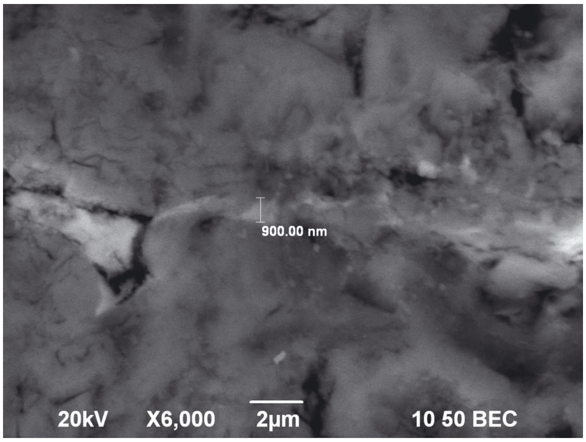


Fig. 14: The barely visible layer of tin-copper alloy (ratio ca 5 : 1), ca 0.009 mm thick. SEM, BSE.
Sl. 14: Komaj vidna plast kositra in bakra (razmerje pribl. 5 : 1) debeline okoli 0,009 mm. SEM, povratno sipani elektroni (BSE).

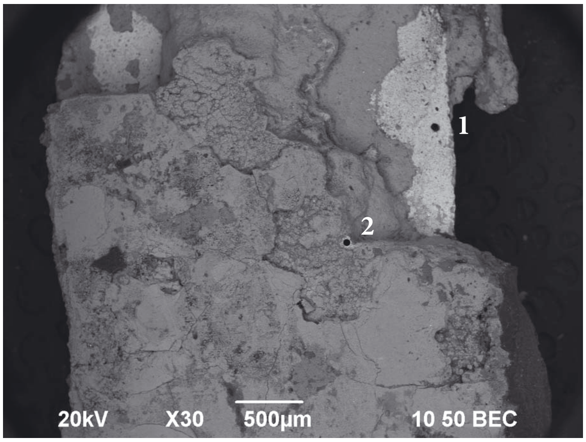


Fig. 15: Underside of the fragment of the 2nd front bridge: two layers of bronze (**1**, **2**) and several iron corrosion layers are visible. SEM, BSE.
Sl. 15: Spodnja stran odlomka 2. prečke: vidni sta dve plasti brona (**1**, **2**) in razne plasti preperelega železa. SEM, povratno sipani elektroni (BSE).

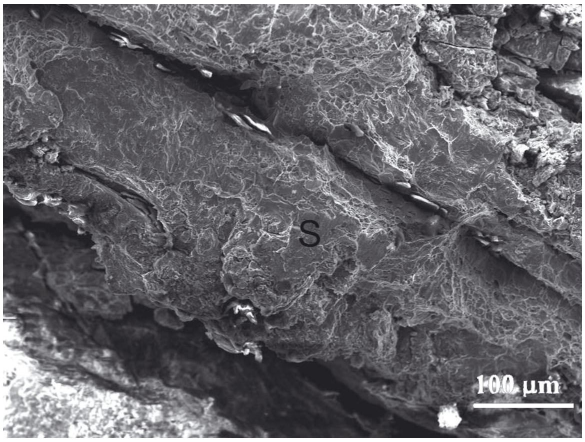


Fig. 16: The back bridge, transverse fracture: metal core (S). SEM, SEI.
Sl. 16: Hrbtna prečka, prečni prelom: kovinska sredica (S). SEM, slika sekundarnih elektronov (SEI).

Electron microscopy and SEM/ EDS analysis of the bottom of the breakage on the 2nd rung showed that there were two visible layers of bronze and various layers of steel corrosion products (*fig. 15*)

6. MICROSTRUCTURAL EXAMINATION

One part of bridge 3 from the front side and one part of bridge 14 from the rear side were devoted to the microstructural examination. The main purpose of this investigation of the front bridges was to determine if the bronze layers embedded in steel had been melted down. Hence, we could conclude that the bronze layers were solder. However, investigation of the back bridge was intended to determine how the bridge was made (forging?) and of what type of steel it was made.

6.1 Back bridge

The sample of the back bridge (with a length of 0.9 cm) was strongly corroded. During rupture in the transversal direction the sample showed considerable resistance in the ambient condition. In the middle of the fracture surface of the bridge a metal core was observed (*fig. 16*). The dimple fracture shows high ductility (plasticity) of the metal core (*fig. 17*). From one half of the sample a metallographic specimen for further analyses was prepared. It was ground with SiC paper to reveal the non-corroded metal core. Then the specimen was polished and etched with 2 % nital. EDS microanalysis of the transversal fracture confirmed that the sample is mostly iron (98.9 wt. %).

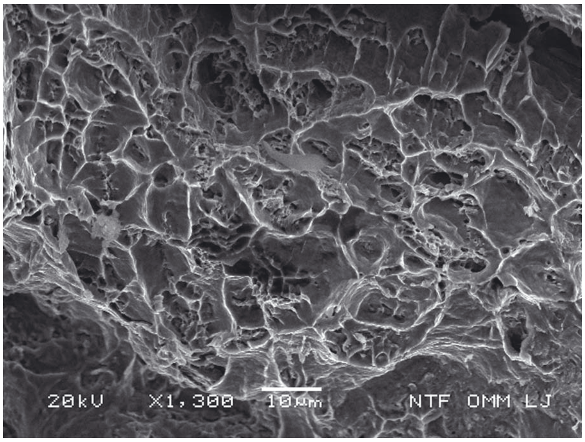
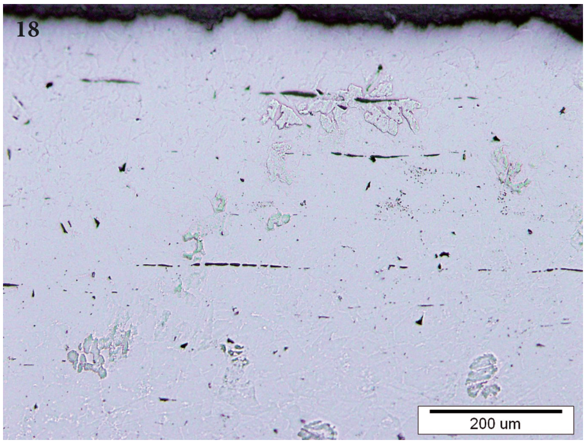


Fig. 17: The back bridge, transverse fracture: ductile dimple fracture of the metal core. SEM, SEI.
Sl. 17: Hrbtna prečka, prečni prelom: jamičast (duktilni) prelom kovinske sredice. SEM, slika sekundarnih elektronov (SEI).

In the longitudinal section of the metal many non-metallic inclusions (*figs. 18, 19*), as well as other slag inclusions (*fig. 19*) were observed. The shape and distribution of the non-metallic inclusions indicates that the material was forged in a direction perpendicular to these inclusions.

In section of the corroded part of the bridge there is an area which is microstructurally different. There are many angular particles of different sizes; they are mainly of flint sand (SiO_2) with a small addition of iron; some also contain aluminium, potassium, 18



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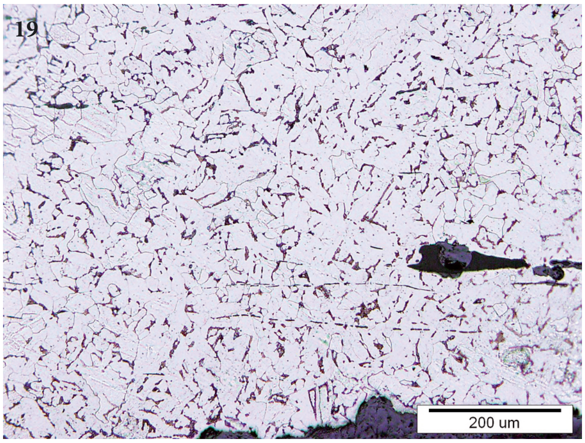

Fig. 18: The back bridge, longitudinal section (slightly etched with 2 % nital): non-metallic inclusions (dark and thin horizontal lines) in the steel. Optical microscope.
Sl. 18: Hrbtna prečka, vzdolžni prerez (rahlo jedkano z 2-odstotnim nitalom): nekovinski vključki (temne in tanke vodoravne linije) v jeklu. Optični mikroskop.

Fig. 19: The back bridge, longitudinal section (etched with 2 % nital): microstructure of steel – ferrite (light crystal grains), perlite (dark crystal grains), non-metallic inclusions (dark thin horizontal lines in the bottom part of the image) and bigger slag inclusions. Optical microscope.
Sl. 19: Hrbtna prečka, vzdolžni prerez (jedkano z 2-odstotnim nitalom): mikrostruktura jekla – ferit (svetla kristalna zrna), perlit (temna kristalna zrna), nekovinski vključki (tanki temni vodoravni liniji v spodnji polovici slike) in veliki vključki žlindre. Optični mikroskop.

calcium and sodium. These particles do not show any effects of forging, i.e. they are not changed in form or crushed. Flint sand (SiO_2) was presumably added to the steel in order to remove iron oxide (FeO). The melting point of FeO is 1377 °C, i.e. higher than the temperature of forging. By reaction between SiO_2 and FeO, fayalite ($2FeO{\cdot}SiO_2$ or $FeSiO_4$) is formed. Above 1200°C fayalite is liquid and will be squeezed from the free surfaces of the steel during forging, leaving a pure iron surface to be forge welded (cf. Buchwald 2005, 65). *Fig. 20* shows particles of flint sand which remained in the corrosion products of the back bridge.

The ferritic-perlitic microstructure of the steel (*fig. 21*) indicates that iron carburised in the hearth during production of the bridge. According to the proportion of perlite in the microstructure it can be estimated that the steel contains less than 0.1 wt. % of carbon. Perlite is finely lamellar; however, some particles of cementite were also observed in the microstructure of the steel (*fig. 21*). The steel hardness was 112–118 HV.

6.2 Front bridge

A section of the front bridge (of a length of 0.7 cm) was badly damaged by corrosion. This sample was cut off in two pieces using a special saw. Thus two separate metallographic specimens were prepared; namely, one in the longitudinal direction according to the bridge and the other in the transversal. The metallographic specimens were examined in the optical and scanning electron microscopes.

After initial grinding only one lamella (layer) was seen in the corroded steel in the scanning electron microscope (SEM); however, after a second grinding another lamella showed up (*fig. 22*). EDS analysis confirmed that these lamellae are of Cu-Sn alloy (tin bronze), in general with less than 10 wt. % Sn.

After chemical etching with a solution of ferric chloride, hydrochloric acid and ethyl alcohol it was shown that the chemical composition and the microstructure of the bronze in the lamellae are not homogeneous (*figs. 23, 24*). The dendritic microstructure which usually forms during the solidification of metals indicates that the bronze lamellae are solders. Under non-equilibrium solidification conditions, tin segregations in the bronze occurred to such an extent that also the peritectic[6] (a phase with 28 wt. % Sn) could be seen. The maximum measured concentration

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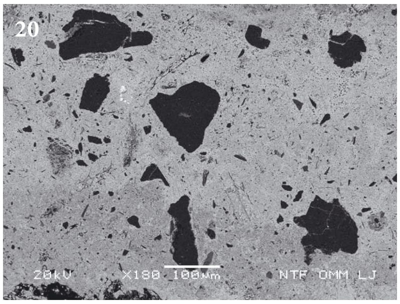
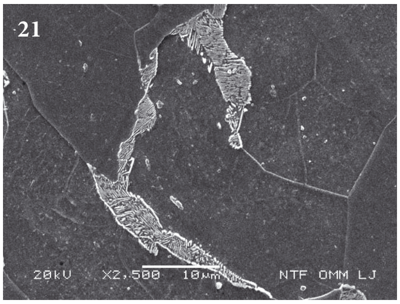
[6] The peritectic is a solid phase that forms by a reaction between the primary crystallised solid phase and the rest of the melt.





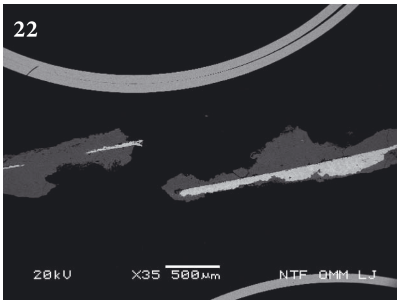


Fig. 20: The back bridge, transverse section (non-etched): the grains of flint sand (SiO_2; dark) in corrosion products of steel (light grey). SEM, BEI.
Sl. 20: Hrbtna prečka, prečni prerez (brez jedkanja): zrnca kremena (SiO_2; temno) v korozijskih produktih jekla (svetlo sivo). SEM, slika povratno sipanih elektronov (PSE).

Fig. 21: The back bridge, longitudinal section (etched with 2 % nital): the microstructure of steel – fine-lamellar perlite (white to light grey), ferrite (dark grey) and small particles of cementite in ferrite. SEM, SEI.
Sl. 21: Hrbtna prečka, vzdolžen prerez (jedkano z 2-odstotnim nitalom): mikrostruktura jekla. Drobnolamelarni perlit (svetel), ferit (temen) in drobna zrnca cementita v feritu. SEM, slika sekundarnih elektronov (SEI).

Fig. 22: The front bridge, longitudinal section; orientation: the lower part of the bridge is below (non-etched); two lamellae of bronze (light grey) surrounded by corrosion products of steel (grey); SEM, BEI.
Sl. 22: Sprednja prečka, vzdolžen prerez, spodnji del prečke je na sliki spodaj (brez jedkanja): lameli brona (svetlo), obdani s produkti korozije jekla (svetlo siva). SEM, slika povratno sipanih elektronov (PSE).

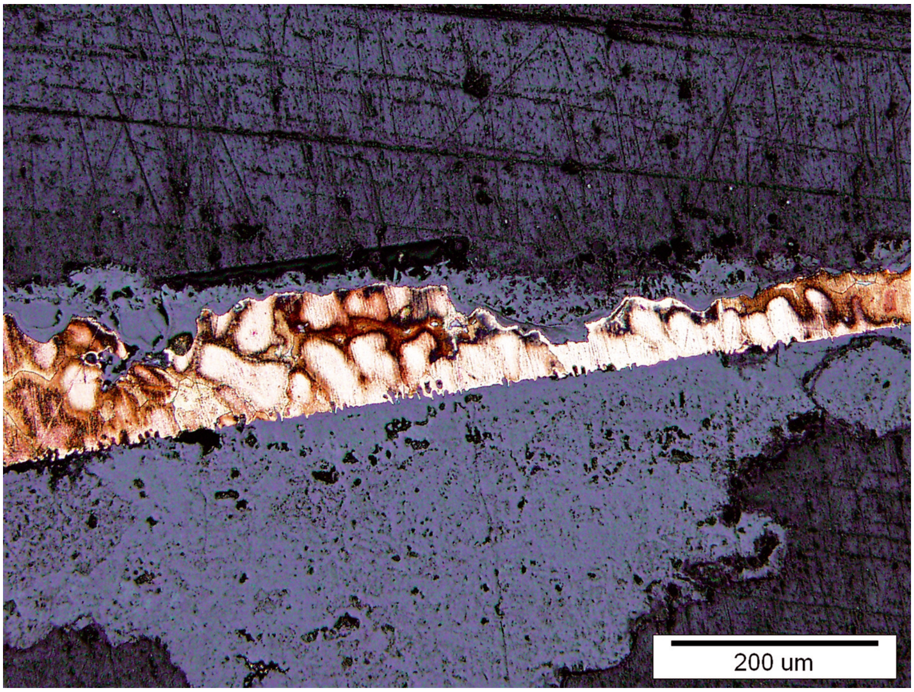


Fig. 23: The front bridge, longitudinal section (etched with a solution of ferric chloride and hydrochloric acid in ethanol): the microstructure of the bronze lamella. The beige to light brown parts contain more tin than the dark brown ones. During non-equilibrium solidification dendrites (beige to light brown) and dendritic segregations (brown, dark brown) were formed. The lower interface of the bronze lamella clearly shows grain boundary diffusion of copper and tin into iron. Optical microscope.
Slika 23: Sprednja prečka, vzdolžen prerez (jedkano z raztopino feriklorida in klorovodikove kisline v etilnem alkoholu): mikrostruktura lamele brona. Obarvanost odseva izcejanje kositra: svetlejša območja vsebujejo več kositra kot temnejša. Vidni so dendriti (svetlo) in dendritne izceje (temno), ki nastanejo pri neravnotežnem strjevanju. Spodnja površina lamele brona jasno kaže na interkristalno difuzijo bakra in kositra v železo. Optični mikroskop.

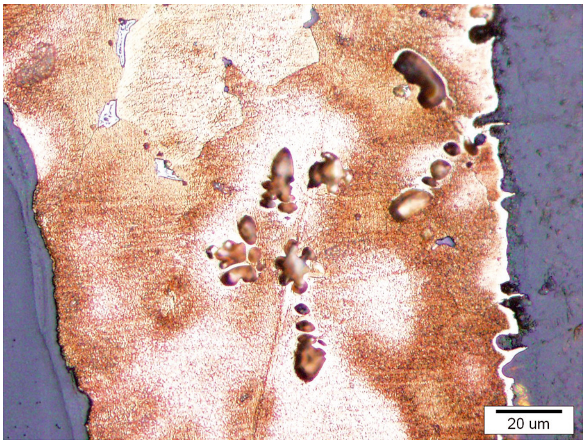


Fig. 24: The front bridge, longitudinal section (etched with a solution of ferric chloride and hydrochloric acid in ethanol) – the microstructure of the bronze lamella. The crystal grains of solid solution of tin in copper and small iron-rich dendrites (~90 wt. % Fe, ~10 wt. % Cu, ~0.4 wt. % Ni) are shown. The colour contrast reflects the intensity of tin segregation: the beige to light brown parts contain more tin than the dark brown ones. The lower interface of the bronze lamella (positioned vertically at the right side of the image) clearly shows grain boundary diffusion of copper and tin into iron. Optical microscope.

Sl. 24: Sprednja prečka, vzdolžen prerez (jedkano z raztopino feriklorida in klorovodikove kisline v etilnem alkoholu) – mikrostruktura brona lamele. Vidna so kristalna zrna trdne raztopine kositra v bakru in drobni dendriti faze, bogate z železom (~90 m. % Fe, ~10 m. % Cu, ~0,4 m. % Ni). Obarvanost odseva izcejanje kositra: svetlejša področja vsebujejo več kositra, temnejša pa manj; modrikasti delci so peritektik δ, ki se je ob ohlajanju evtektoidno transformiral. Spodnja površina lamele brona (na posnetku leži navpično na desni strani fotografije) jasno kaže na interkristalno difuzijo bakra in kositra v železo. Optični mikroskop.

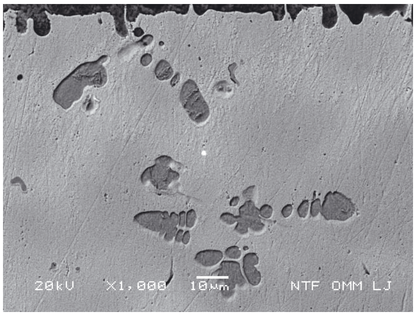


Fig. 25: The front bridge, longitudinal section (etched with a solution of ferric chloride and hydrochloric acid in ethanol): iron-rich dendrites (cf. *fig. 26*) in the bronze lamella. SEM, BEI.

Sl. 25: Sprednja prečka, vzdolžen prerez (jedkano z raztopino feriklorida in klorovodikove kisline v etilnem alkoholu): dendriti faze z velikim deležem železa (prim. *sl. 26*) v lameli iz brona. SEM, slika povratno sipanih elektronov (PSE).

of tin in copper solid solution (α_{Cu}) was around 8 wt. %, while the minimum was around 3.1 wt. %.

Some iron-rich dendrites were also observed in the bronze lamellae (*figs. 24, 25*). EDS analysis shows that the iron dendrites contain almost 90 wt. % of iron, while the rest (around 10 wt. %) is copper with a small addition of nickel (around 0.4 wt. %). It could be assumed that the iron entered the bronze when hot liquid bronze melted the steel base. The iron-rich phase crystallised from bronze during solidification of bronze when the bronze was still liquid.

The boundary between the bronze and the corroded steel layer is not even but rather branched (*figs. 23, 24*). This also indicates that molten bronze and the steel base reacted during solidification of the bronze. In the bronze some rare inclusions of copper sulphide (Cu_2S) were also found (*fig. 24*). Their formation is probably the result of the reaction between copper and an atmosphere which contained sulphur. The measured hardness of the bronze was around 96 HV.

In transverse section a steel core was observed in the corrosion products of steel between the bronze lamellae (*fig. 26*). The microstructure of the steel consists of ferrite and fine lamellar perlite (*fig. 27*). According to the ferritic-perlitic microstructure the steel contains between 0.3–0.4 wt. % of carbon. The hardness of the steel core is 130–135 HV.

In the sample of the front bridge, besides the steel core, three nearly undamaged lamellae of tin bronze were also seen. The microstructure of the bronze indicates that the bronze was melted. It can also be seen that molten bronze reacted with the surrounding steel. All together, this proves that the bronze lamellae are solders.

In comparison to the back bridge, the higher content of carbon in the front bridge shows that this steel was carburised. We assume that this happened due to heating of the steel during soldering of the socket at the front bridge.

7. CONCLUSIONS

Metallographic examination indicates that the laddered chape was made of forged steel and confirmed that in the front bridges there are very thin layers (lamellae) of bronze. This also showed that these lamellae acted as solders. Presumably the bronze lamellae were not detected in the X-ray images because they are extremely thin.

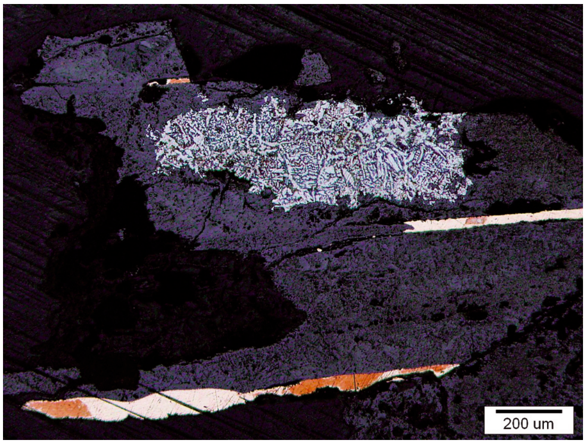


Fig. 26: The front bridge, transverse section. The lower part of the bridge is at the bottom of the image. (Etched with a solution of ferric chloride and hydrochloric acid in ethanol). In the corrosion products of steel (dark grey) three bronze lamellae (brown and light brown) are visible, as well as the metal core (light grey) between the upper two bronze lamellae. Optical microscope.
Sl. 26: Sprednja prečka, prečni prerez, orientirano tako, da je spodnji del prečke spodaj (jedkano z raztopino feriklorida in klorovodikove kisline v etilnem alkoholu): v korozijskih produktih (temno siva) so vidne tri lamele brona (rjava in svetlo rjava) ter jeklena sredica (svetlo sivo) med dvema lamelama brona. Optični mikroskop.

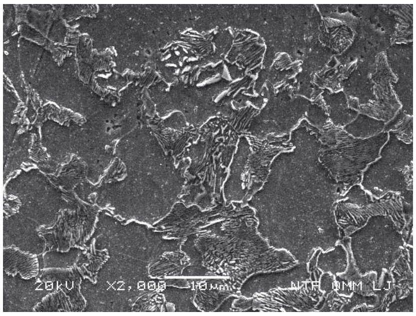


Fig. 27: The microstructure of the steel in the core of the front bridge (etched with 2 % nital): ferrite (dark grey) and fine-lamellar perlite (light grey). SEM, SEI.
Sl. 27: Mikrostruktura sredice jekla v sprednji prečki (jedkano z 2-odstotnim nitalom): ferit (temen) in drobnolamelarni perlit (svetel). SEM, slika sekundarnih elektronov (SEI).

In the sample of the front bridge examined, one side of a bronze lamella (i.e. on the underside; the underside of the bridge lay on the front plate of the scabbard) is flat and shows a strong indentation of bronze in steel (*figs. 23, 24*), indicating that here the interface/linkage between bronze and steel is stronger than on the other side.

On the left as well as on the right side of the laddered chape, roughly at the beginning of its lower half, two layers of copper alloy were discovered. The brass layer in the steel of the U-shaped part on the left side of the chape is probably a solder. Presumably the same applies for the bronze layer observed in the steel of the U-shaped part on the right side of the chape, although it cannot be excluded that in this case the thin bronze layer is a lining which was placed between the two plates and the U-shaped part of the laddered chape (the guttering).

The metallographic investigation of samples of the front and the back bridge of the laddered chape showed that the steel parts were severely corroded; however, in both samples a non-oxidized metal core was preserved (in the back bridge somewhat better). The steel of the back bridge contains less carbon (around 0.1 wt. %) than the steel of the front bridge (around 0.4 wt. %) which most probably carburised on heating during manufacture of the chape.

We presume that the laddered chape was made so as to form a flat netlike fitment, which was then twice folded lengthwise and closed by soldering the front bridges. We would expect soldering of two layers of steel, which would produce one layer of solder; in the investigated sample, however, there are three layers of solder. This could suggest soldering three layers of very thin steel sheets (thickness of about half a millimetre). Investigation of only one sample of the front bridge was made, so it is not clear whether the three layers of brass in the bridge are the rule or perhaps an exception.

We assume that soldering was done by heating very thin steel and bronze strips to the melting point of bronze. The dissimilarities in the part where the bronze and the steel connect would suggest that during the procedure the laddered chape was facing front-side down.

The soldering at the guttering, which is roughly symmetrical on the left and right sides of the scabbard, would suggest that the netlike fitment was made from at least two parts that were then joined by soldering.

In addition, the study showed that during restoration a part of the scabbard's front bridge was erroneously used to replace a part of the tenth back bridge.

This study of a laddered chape has advanced our knowledge of its construction and manufacturing process, but the details remain unexplained. We would like this publication to prompt further research into scabbards with copper-alloy or silver openwork plates (cf. Istenič 2010, list) in order to prove or disprove the validity of our findings for other such fitments, and possibly throw light on the questions to which we could not find answers.

BÖHME-SCHÖNBERGER, A. 1998, Das Grab eines vornehmen Kriegers der Spätlatènezeit aus Badenheim. – *Germania* 76, 217–256.

BUCHWALD, V. F. 2005, *Iron and steel in ancient times.* – Copenhagen.

CRADDOCK, P. T. 1995, *Early Metal Mining and Production*. – Edinburgh.

HAFFNER, A. 1995, Spätkeltische Prunkschwerter aus dem Treverergebiet. – In: H.-H. Wegner (ed.), *Berichte zur Archäologie an Mittelrhein und Mosel* 4, Triererer Zeitschrift, Beiheft 20, 137–151, Trier.

ISTENIČ, J. 2000, A Roman late-republican *gladius* from the River Ljubljanica (Slovenia) / Rimski poznorepublikanski gladij iz Ljubljanice. – *Arheološki vestnik*, 51, 171–182.

ISTENIČ, J. 2005, Brooches of the Alesia group in Slovenia / Fibule skupine Alesia v Sloveniji. – *Arheološki vestnik* 56, 187–212.

ISTENIČ, J. 2010, Late La Tène scabbards with non-ferrous openwork plates / Poznolatenske nožnice s predrtim okrasnim okovom iz bakrove zlitine ali srebra. – *Arheološki vestnik* 61, 121–164.

KMETIČ, D., J. HORVAT and F. VODOPIVEC 2004, Metallographic examinations of the Roman Republican weapons from the hoard from Grad near Šmihel / Metalografske preiskave rimskega republikanskega orožja iz zaklada z Gradu pri Šmihelu. – *Arheološki vestnik* 55, 291–312.

MANNING, W. H. 1976, Blacksmithing. – In: D. Strong, D. Brown (eds.), *Roman Crafts,* 143–154, London.

MILIĆ, Z., G. LEMAJIČ, S. PEROVŠEK and J. ISTENIČ 2009a, The conservation and restoration of finds from Ljubljanica. – In: P. Turk et al. (eds.), *The Ljubljanica, a River and its Past,* 32–37, Ljubljana.

MILIĆ, Z., G. LEMAJIČ, S. PEROVŠEK and J. ISTENIČ 2009b, Konserviranje in restavriranje najdb iz Ljubljanice. – In: P. Turk et al. (eds.), *Ljubljanica, kulturna dediščina reke,* 30–35, Ljubljana.

PAULIN, P. 1997, Mala slovenska enciklopedija metalurgije. – *Rudarsko-metalurški zbornik* 44/1–2, 1–139.

REKAR, C. 1972, Železo in grodelj. – In: A. Kveder (ed.), *Metalurški priročnik,* 479–562, Ljubljana.

ŠMIT, Ž., ISTENIČ, J., PEROVŠEK, S. 2010, PIXE analysis of Late La Tène scabbards with non-ferrous openwork plates (and associated swords) from Slovenia /Analize PIXE poznolatenskih nožnic s predrtimi okovi (in pripadajočih mečev) iz Slovenije. – *Arheološki vestnik* 61, 165–173.

TYLECOTE, R. F. 1992, *A history of metallurgy.* – London, Brookfield.

WESTPHAL, H. H. 1998, Die Untersuchung des Schwertes aus Badenheim. – In: Böhme-Schönberger 1998, 248–255.

Raziskave lestvičastega okova poznolatenske nožnice s predrtim okrasom iz Ljubljanice pri Bevkah

1. UVOD

Pri proučevanju poznolatenskih nožnic s predrtim okrasnim okovom (prim. *sl. 1*) iz bakrove zlitine ali srebra smo se med drugim poglobili v vprašanje načina izdelave njihovih železnih/jeklenih[1] lestvičastih okovov in za te nožnice značilnih okovov iz bakrove zlitine s predrtim okrasom. V dotedanjih objavah smo namreč zasledili različna in nasprotujoča si mnenja o tem, kako so bili izdelani (Istenič 2010, 156–157).

Po našem mnenju ni dvoma o tem, da okrasni okovi s predrtim okrasom niso bili narejeni z ulivanjem, temveč, da so pločevino okrasnih okovov oblikovali s tolčenjem, okras pa naredili s pomočjo dlet z različno oblikovanimi delovnimi površinami, s katerimi so odstranili odvečno pločevino in tudi puncirali. Vprašanje načina izdelave lestvičastih okovov pa smo v navedeni objavi obravnavali le kratko in deloma, saj naše raziskave takrat še niso bile zaključene (Istenič 2010, 156–157). Izsledke zato podajamo v tem članku.

2. PREDHODNE RAZISKAVE

Vprašanje, kako so izdelovali lestvičaste okove poznolatenskih nožnic s predrtim okrasnim okovom, je prvi izpostavil Herbert Westphal (1998, 250–252) ob proučevanju konstrukcije nožnice, ki je bila najdena v poznolatenskem grobu iz Badenheima (Böhme-Schönberger 1998).

Westphalove ugotovitve o zgradbi nožnice iz Badenheima izhajajo iz pozornega opazovanja (predhodno) že konservirane nožnice, ki je bila delno poškodovana v sekundarnem ognju (ob sežigu pokojnika na grmadi) in je bila v sredini

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[1] V arheološki literaturi je izraz "železo" splošno uveljavljen za oznako materiala, ki kemijsko ni čisto železo, temveč zlitina železa in majhnega dela (do 2 %) ogljika. V metalurški literaturi tako zlitino imenujejo jeklo (Rekar 1972, 481). V nadaljevanju članka zaradi enotnosti uporabljamo izraz jeklo (prim. Kmetič, Horvat, Vodopivec 2004, 307 op. 1).

obredno prepognjena (Westphal 1998, 248; Böhme-Schönberger 1998, sl. 13). Okoli 1 mm debelo jekleno hrbtno platico in malo tanjšo sprednjo platico iz bakrove zlitine (sledovi na hrbtni strani kažejo, da je bila izdelana s tanjenjem) spaja jeklen lestvičasti okov. Po njegovem mnenju so nožnico sestavili tako, da so platici potisnili v prej izdelan lestvičasti okov in fiksirali tako, da so (malo) stisnili njegov robni del. Westphal (1998, 250–252) pa ni našel odgovora na vprašanje, kako je bil narejen lestvičasti okov, čeprav mu je posvetil precej pozornosti. Na njem namreč ni odkril sledov spajkanja, varjenja ali kovičenja (“waren weder Lötnähte, noch Schweißstellen, noch Nietungen festzustellen”).

Haffner (1995, 140) je za lestvičasti okov nožnice, ki je bila najdena v grobu iz Büchla in je bila deloma staljena v sekundarnem ognju ter močno zvita, menil, da je bil izdelan v tehniki kovaškega varjenja (“Schweißverbundtechnik”).[2] Na rentgenskem posnetku pa je opazil drobne bronaste zakovice, ki zaključek lestvičastega okova povezujejo z obema pločevinastima platicama. Rentgenskega posnetka žal ni objavil.

3. RAZISKAVE OKOVA NOŽNICE IZ LJUBLJANICE: IZHODIŠČA IN UPORABLJENE METODE

Izdelava obravnavanih lestvičastih okovov s pomočjo tehnike kovaškega varjenja se nam zdi malo verjetna. Notranja širina okova je namreč zelo majhna, zato bi težko uporabili za tako varjenje potrebno nakovalo. V večjem delu okova bi to težavo lahko zaobšli tako, da bi skovali cevast okov in ga nato sploščili. Vendar pa si ne znamo predstavljati, kako bi na tak način in v enem kosu oblikovali ostrogast zaključek okova.

Obravnavanih okovov prav tako niso ulili, saj jekla v Evropi v mlajši železni in rimski dobi še niso ulivali, temveč so ga kovali; poleg tega bi bilo ulito jeklo zaradi svoje krhkosti za tak okov neprimerno (Manning 1976, 143; Tylecote 1992, 48; Craddock 1995, 235, 239).

Pri pregledu lestvičastih okovov treh nožnic iz slovenskih najdišč, tj. primerka iz reke Ljubljanice in dveh primerkov iz Verduna (Istenič 2010, sl. 9, 11), tako makroskopsko kot s pomočjo lupe in optičnega mikroskopa, nikjer na površini nismo opazili sledov varjenja, spajkanja[3] ali kovičenja. Rentgenski posnetki, ki smo jih pri meču iz reke Ljubljanice naredili tudi z rentgenom, ki omogoča mikrofokusiranje s 50-kratno povečavo,[4] prav tako niso pokazali sledov navedenih tehnik (Istenič 2010, sl. 3). Omeniti velja, da so vse tri nožnice razmeroma dobro ohranjene, saj nobena od njih ni bila poškodovana v ognju niti namenoma zvita, kot je bil to primer pri nožnicah iz Badenheima in Büchla.

Vse tri nožnice, ki smo jih proučevali, so bile pred tem že konservirane in restavrirane v delavnici Rimsko-germanskega muzeja v Mainzu (Istenič 2010, 153, 155). Odločili smo se za delno revizijo konservacije lestvičastega okova enega primerka. Ob soglasju pristojne kustosinje Bernarde Županek in vodje konservatroske delavnice Katarine Toman Kracina (obe Muzej in galerije mesta Ljubljana) smo jo izvedli na nožnici iz Ljubljanice. Revizija je dala zelo zanimive rezultate, ki so narekovali nadaljnje raziskave. Te so vključevale določanje zlitin z metodo protonsko vzbujenih rentgenskih žarkov (PIXE; Šmit, Istenič, Perovšek 2010, 173, tab. 1), opazovanje odlomkov prečk lestvičastega okova v vrstičnem elektronskem mikroskopu (SEM), semikvantitativne kemijske analize (energijska disperzijska spektroskopija z rentgenskimi žarki) izredno majhnih površin v elektronskem mikroskopu (SEM/EDS) ter metalografske raziskave (navedeni vrstni red ustreza časovnemu zaporedju raziskav).

V objavi izraze zgoraj, spodaj, levo in desno uporabljamo glede na tako lego nožnice, pri kateri je njeno ustje zgoraj, lice pa gleda proti gledalcu.

4. DELNA REVIZIJA NOŽNICE IZ LJUBLJANICE

Nožnica, ki je bila najdena v reki Ljubljanici pri Bevkah, sodi med redke primerke svoje vrste, ki niso utrpeli poškodb v sekundarnem ognju in niso bili namenoma zviti. Poleg tega je eden od dveh primerkov, ki sta bila najdena v vodi (prim. Istenič 2010, 164, seznam: št. 23). Je odlično ohranjena, kar velja za večino predmetov iz reke Ljubljanice (Milić et al. 2009b). Zdi se, da (izvzemši

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[2] Pri kovaškem varjenju z udarci (tj. kovanjem) spajamo do zmehčanja segrete dele.

[3] Pri spajkanju spaja kovinske dele temu namenjena kovina ali zlitina (spajka).

[4] Za rentgeniziranje, ki smo ga izvedli v podjetju ETA CERKNO, d. o. o., smo uporabili aparat YXLON 160kV/4mA z rentgensko glavo HAMAMATSU. Aparat omogoča presevanje vzorcev iz železa debeline največ 32 mm.

manjkajočo konico) predstavlja najbolje ohranjen primerek obravnavanih nožnic.

Vse tu opisane posege na nožnici iz Ljubljanice je izvedla Sonja Perovšek v letu 2010. Z več mest je odstranila z epoksidno smolo (Araldit) rekonstruirane dele lestvičastega okova nožnice in ostanke v predmet močno zažrtega silikonskega kavčuka (ti so posledica izdelave kalupa predmeta, ki je bil narejen v delavnici Rimsko-germanskega muzeja v Mainzu) ter s skrbno izbranih mest s preciznim mikropeskanjem[5] tudi razne obloge, ki so se na predmetu odložile v reki, in v majhni meri včasih tudi tanek sloj korozijskih produktov.

V vseh tako raziskanih prečkah sprednje strani nožnice, tj. v 1.–4., 6., 8. in 9., se je v jeklu pokazala rdečkasta zlitina (*sl. 2*). Analize štirih takih mest (na 2.–4. in na 9. prečki) z metodo PIXE kažejo, da gre za bron z okoli 4–7 masnih % kositra (Šmit, Istenič, Perovšek 2010, pregl. in sl. 1: 11,12a,13,15).

V 2. in 3. prečki sta se ob odstranitvi plastičnega rekonstruiranega dela sprostila odlomka. Na njuni spodnji strani se je pokazala plast bakrove zlitine, ki je postala izrazita po preciznem mikropeskanju (*sl. 3c; 4b*). Levi rob odlomljenega dela 3. prečke in rob te prečke, ki je ostal na nožnici (*sl. 1:* A,B), sta bila približno navpična in zato primerna za opazovanje prečnega prereza. Pod optičnim mikroskopom so bile na prelomu odlomljenega dela vidne tri take bronaste plasti, ki ležijo vodoravno glede na prerez prečk oziroma približno vzporedno z lego platic nožnice (*sl. 5*). Njihove debeline so različne in so manjše od 0,1 mm. Na drugem prelomu pa je vidna le ena, enako ležeča plast (*sl. 6*).

Tik nad 9. sprednjo prečko (v smeri proti ustju nožnice) se je na notranji strani robnega dela okova pokazala plast bakrove zlitine, vidna v dolžini okoli 4 mm (*sl. 7*), za katero smo ugotovili, da je bron z okoli 6 masnimi % kositra (Šmit, Istenič, Perovšek 2010, pregl. in sl. 1: 14). Oblika njenega zgornjega zaključka nakazuje, da se je ta plast tu zaključila; na drugi strani, proti 10. sprednji prečki, pa se verjetno nadaljuje pod robnim okovom. Odnos med bronasto plastjo in medeninasto[6] platico smo lahko opazovali le na majhnem delu: zdi se, da med njima ni jekla ter da bronasta plast leži neposredno na medeninasti platici in jo presega najmanj 2 mm. Vendar pa bi med bronasto in medeninasto plastjo prvotno lahko bila tanka plast jekla (kar bi pomenilo, da je bronasta plast bila v jeklu, podobno kot v sprednjih prečkah), ki pa je na opazovanem mestu zaradi korozije ni videti.

Približno simetrično, tj. ob 9. prečki na sprednji strani, oziroma od 11. prečke do pribl. centimeter pod 13. hrbtno prečko, smo v robnem delu jeklenega okova odkrili manj kot milimeter debelo plast neželezne kovine (*sl. 8*). Zasledovali smo jo lahko v dolžini okoli 3,7 cm. V večjem delu je vidna v profilu kot zelo tanka plast v korozijskih produktih jekla, v manjšem delu pa se je pokazala površina te plasti. Meritve z metodo PIXE so pokazale, da raziskovana plast ni bron, temveč zlitina bakra z okoli 5 masnih % cinka (Šmit, Istenič, Perovšek 2010, pregl. in sl. 1: 9).

Ob pregledu prečk na hrbtni strani nožnice smo ugotovili bakrovo zlitino le v eni, tj. deseti prečki, natančneje v njeni levi polovici (*sl. 9*). V desni polovici prečke, ki jo od leve loči rekonstruirani del iz epoksidne smole, bakrove zlitine ni. Domnevamo, da so med konserviranjem in restavriranjem ta del prečke pomotoma premestili s sprednje strani (morda z 11. ali 12. prečke) na hrbtno stran nožnice. To poleg bakrove zline v prečki nakazuje tudi plitev žleb vzdolž sredine prečke, ki je običajen na prečkah prednje strani nožnice (prim. *sl. 2*), na prečkah hrbtne strani pa ga, razen na polovici 10. prečke, ni opaziti. Vrste bakrove zlitine nismo določali, saj je ta vidna le na zelo majhnih površinah. Glede na opravljene analize na drugih prečkah domnevamo, da gre za bron.

Na sprednji strani nožnice smo na prečkah okova, pa tudi drugih jeklenih površinah, na več mestih opazili zelo tanko zlato sijočo plast (*sl. 4a*).

5. RAZISKAVE S POMOČJO SEM/EDS

Pri 2. in 3. prečki sprednje strani nožice sta se ob odstranitvi rekonstruiranega dela sprostila 3,6 oziroma 0,9 cm dolga odlomka prečke (*sl. 1; 3; 4*), ki sta se zdela primerna za opazovanje v elektronskem mikroskopu (SEM). Pri tem nas je predvsem zanimalo:

– kakšna je sestava bakrove zlitine (preverjanje rezultatov, ki jih je dala metoda PIXE);

– kakšna je sestava tanke, svetle, zlato rumene sijoče površine na površini prečke;

– ali je pod, nad in med plastmi bakrove zlitine jeklo;

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[5] Pri mikropeskanju s pospešenimi tankimi curki peščenih ali steklenih zrn čistimo površino.

[6] V metalurgiji za zlitino bakra in cinka uporabljajo izraz med (méd, médi; cf. Paulin 1997, 58), vendar v članku ohranjamo doslej v arheološki literaturi uporabljano poimenovanje medenina (cf. Istenič 2000; 2005).

– ali so poleg bakrove zlitine in jekla prisotne tudi druge snovi. Pri tem nas je posebej zanimala spodnja površina prečk, ki je nalegla na medeninasto platico na sprednji strani nožnice.

Mikroanalize smo izvedli v Geološkem zavodu Slovenije z *vrstičnim elektronskim mikroskopom JEOL JSM 6490LV* v kombinaciji z *energijsko disperzijskim spektrometrom (SEM/EDS) Oxford INCA*. Vzorca smo opazovali s tehniko razpršenih odbitih elektronov (BSE) pri pospeševalni napetosti 20 kV in delovni razdalji 10 mm. Zaradi dobre prevodnosti opazovanega materiala vzorca nismo naprašili z zlatom in smo ga opazovali nenaprašenega. Tako je vzorec tudi po opazovanju v elektronskem mikroskopu ostal popolnoma nespremenjen.

Iz mikroanalize sledi, da je svetla zlato svetleča površina na jeklu sestavljena iz železa, žvepla in bakra, in sicer v razmerju, ki ustreza spojini $CuFeS_2$, tj. halkopiritu (železo-bakrov sulfid). Domnevamo, da je na nožnici nastal po tem, ko je ta prišla v Ljubljanico. V redukcijskih razmerah, kakršnim ustreza lega v blatu, je nastal po kompleksni kemijski reakciji med železom v jeklu, bakrom v medeninasti platici in žveplom v blatu na rečnem dnu.

Pregled preloma 3. prečke je jasno pokazal tri različno debele (okoli 0,02, 0,03 in 0,05 mm) plasti brona, ki ležijo pribl. vzporedno z ravno ploskvijo prečke, s katero je ta nalegala na nožnico (*sl. 10–13*), nakazuje pa se še sled četrte, izredno tanke (okoli tisočinke mm) plasti, ki glede na lego prečke na medeninasti platici leži najvišje (*sl. 10; 14*). Analize SEM/EDS so pokazale, da je med njimi in nad zgornjo ter pod spodnjo plastjo železov oksid ali železov oksidhidroksid.

SEM/EDS analize bakrove zlitine na več mestih so potrdile, da je to bron. Razmerje med bakrom (Cu) in kositrom (Sn) se v prvih treh prečkah giblje okrog 9 : 1. V zgornji, četrti prečki, ki je izredno tanka, pa močno prevladuje kositer, ki ga je približno petkrat več kot bakra (razmerje Cu : Sn ~ 1 : 5).

Na spodnji strani odlomka 2. sprednje prečke so opazovanje v elektronskem mikroskopu in SEM/EDS analize pokazali, da sta tu vidni dve bronasti plasti in različne plasti korozijskih produktov jekla (*sl. 15*).

6. METALOGRAFSKE (MIKROSTRUKTURNE) RAZISKAVE

Za metalografske raziskave smo žrtvovali po en del 3. prečke s sprednje in 14. s hrbtne strani lestvičastega okova (*sl. 1:* S,H). Osnovni namen raziskav sprednje prečke je bil ugotoviti, ali so bile bronaste plasti, ki ležijo v jeklu, staljene. V tem primeru bi namreč sklepali, da predstavljajo spajko. Pri raziskavah hrbtne prečke pa nas je zanimalo, kako je bila izdelana (s kovanjem?) in iz kakšnega jekla.

6.1 Hrbtna prečka

Vzorec hrbtne prečke (dolžina 0,8 cm) je bil močno korodiran. Prelomili smo ga prečno glede na njegovo dolžino, pri čemer je nudil precejšen odpor. V prelomu smo v sredini prečke opazili svetlo kovinsko jedro (*sl. 16*). Jamičasti prelom kaže, da je kovina zelo duktilna (*sl. 17*). Polovico vzorca smo zalili v polimerno maso tako, da je bil pripravljen za analizo vzdolžnega prereza. Odbrusili smo ga toliko, da se je odkrilo nekorodirano kovinsko jedro (nekorodirana kovinska sredica). Površino prereza smo opazovali v poliranem in jedkanem stanju (nital, 2 %).

Z mikroanalizo prečnega preloma v elektronskem mikroskopu (SEM/EDS) smo ugotovili, da v kovini močno prevladuje železo (98,9 masnih % Fe).

V vzdolžnem prerezu kovinske sredice so številni nekovinski vključki (*sl. 18; 19*) in vključki žlindre (*sl. 19*). Oblika in enotna lega vključkov kažeta na kovanje, in sicer v smeri od zgoraj in spodaj (glede na smer prereza prečke).

Na korodiranem delu prereza prečke je področje, ki se mikrostrukturno precej razlikuje od ostalega. Tu je veliko ostrorobih delcev različnih velikosti, ki so po sestavi pretežno iz kremena (SiO_2) z majhnim deležem železa, nekateri delci pa vsebujejo še aluminij, kalij, kalcij in natrij. Na teh delcih (vključkih) ni opaziti učinkov kovanja, saj niso plastično deformirani ali zdrobljeni. Domnevamo, da so kremenov pesek (SiO_2) jeklu dodali zaradi odstranjevanja železovega oksida (FeO). Ta ima tališče pri 1377 °C, kar je višje od temperature kovanja. Z reakcijo med SiO_2 in FeO nastane fajalit ($2FeO{\cdot}SiO_2$ oz. Fe_2SiO_4), ki je pri temperaturi nad 1200 °C staljen, zato se pri kovanju na tej temperaturi iztisne iz prostih površin jekla. Ostane čista jeklena površina, ki je primerna za kovaško varjenje (cf. Buchwald 2005, 65). *Slika 20* prikazuje zrnca kremenovega peska, ki so ostala v korozijskih produktih hrbtne prečke.

Mikrostruktura jekla je iz ferita in perlita, kar kaže, da se je železo med izdelavo predmeta naogljičilo, verjetno med segrevanjem v ognjišču. Po deležu perlita ocenjujemo, da je v jeklu manj kot 0,1 % ogljika. Perlit je drobnolamelast. Jeklo vsebuje tudi zrnca cementita (*sl. 21*). Trdota jekla je 112–118 HV.

6.2 Sprednja prečka

Vzorec sprednje prečke (dolžina 0,7 cm), močno poškodovan zaradi korozije, smo prerezali z rezilno ploščo na polovici, ki smo ju ločeno vložili v polimerno maso: eno vzdolžno, drugo prečno na potek prečke. Vzorca smo postopoma brusili ter opazovali v optičnem in vrstičnem elektronskem mikroskopu.

Na vzdolžnem prerezu smo po prvem brušenju s pregledom v vrstičnem elektronskem mikroskopu v korozijskih produktih vzorca opazili eno lamelo (plast), po drugem brušenju pa dve (*sl. 22*). Analize SEM/EDS so pokazale, da sta lameli iz bakrove zlitine s kositrom (kositrov bron), v povprečju z manj kot 10 % Sn.

Po kemičnem jedkanju z raztopino feriklorida, klorovodikove kisline (HCl) v etilnem alkoholu, se je pokazalo, da sta kemična sestava in mikrostruktura brona v lamelah nehomogeni (*sl. 23; 24*). Dendritna mikrostruktura, ki praviloma nastane pri strjevanju kovin, kaže, da te lamele predstavljajo spajke. Zaradi neravnotežnih pogojev pri strjevanju so nastale izceje (segregacije) kositra, ki so tolikšne, da se je pojavil celo peritektik (faza z 28 % Sn), tj. trdna faza, ki nastane pri reakciji med primarno izločeno fazo in preostalo talino. Največja v vzorcu izmerjena koncentracija kositra v trdni raztopini bakra (α_{Cu}) je okoli 8 masnih %, najmanjša pa okoli 3,1 masnega %.

V lamelah brona smo opazili tudi dendrite z velikim deležem železa: v njih je blizu 90 masnih % železa, ostalo pa je baker (približno 10 masnih %) s primesjo niklja (približno 0,4 masnih %; *sl. 24; 25*). Železo je prišlo v bron, ko je staljeni bron raztapljal jekleno podlago. Faza, bogata z železom, se je izločila iz brona med strjevanjem, ko je bil bron še tekoč.

Na reakcijo med staljenim bronom in jekleno podlago kaže tudi razvejana meja med bronom in korodirano plastjo jekla (*sl. 23; 24*). V bronu smo opazili tudi redke vključke bakrovega sulfida (Cu_2S), ki so verjetno posledica reakcije bakra z atmosfero, ki je vsebovala žveplo (*sl. 24*). Trdota brona je okoli 96 HV.

Na prečnem prerezu smo v korozijskih produktih jekla in med lamelama brona opazili jekleno sredico (*sl. 26*). Vsebuje 0,3 do 0,4 masnih % ogljika (C), njeno mikrostrukturo pa sestavljata ferit in drobnolamelasti perlit (*sl. 27*). Trdota jekla sredice je 130–135 HV.

V vzorcu sprednje prečke so poleg jeklene sredice še tri praktično nekorodirane lamele iz kositrovega brona, ki je bil glede na mikrostrukturo staljen. Iz njegove mikrostrukture tudi lahko sklepamo, da je intenzivno (učinkovito) reagiral z jeklom v okolici. Oboje jasno kaže, da so te bronaste lamele spajke.

V primerjavi s hrbtno prečko večji delež ogljika v jeklu sprednje prečke kaže, da se je jeklo te prečke naogljičilo – domnevamo, da med segrevanjem jekla pri spajkanju okova na sprednjih prečkah.

7. SKLEP

Metalografske raziskave so pokazale, da je bil lestvičasti okov iz kovanega jekla, in potrdile, da so v sprednjih prečkah zelo tanke plasti (lamele) brona. Obenem so tudi pokazale, da so imele te plasti vlogo spajke. Domnevamo, da take spajke na rentgenskih posnetkih niso vidne, ker so izredno tanke.

V preiskanem vzorcu so lamele brona na spodnji površini (pri čemer je spodnja površina prečk lestvičastega okova ležala na nožnici) ravne in se izrazito zajedajo v jeklo (*sl. 23; 24*), kar nakazuje, da je na tej površini nastal močnejši spoj med jeklom in spajko kot na drugi površini.

Na levem in desnem robu lestvičastega okova nožnice, približno na začetku njegove spodnje polovice, smo odkrili podlogo ali spajko iz dveh različnih bakrovih zlitin. Medenina v jeklu levega robnega dela lestvičastega okova je najverjetneje spajka. Domnevamo, da enako velja za bron v jeklu desne strani robnega dela lestvičastega okova, vendar pa ne moremo izključiti, da je v tem primeru tanka plast brona podloga, ki je bila nameščena med obe platici in robni del lestvičastega okova.

Metalografski pregled vzorcev sprednje in hrbtne prečke nožnice kaže, da so jekleni deli prečk v veliki meri propadli zaradi korozije. Kljub temu sta se v obeh vzorcih ohranili jekleni sredici, v hrbtni bolje kot v sprednji. Jeklo hrbtne prečke vsebuje manj ogljika (okoli 0,1 masnega %) kot jeklo sprednje prečke (okoli 0,4 masnega %), ki se je verjetno naogljičilo s segrevanjem v ognju med izdelovanjem okova.

Sklepamo, da so lestvičasti okov izdelali tako, da so skovali ploščato "mrežo", ki so jo nato po dolžini dvakrat zapognili in sklenili s spajkanjem sprednjih prečk. Pričakovali bi spajkanje dveh plasti jekla, in torej eno plast spajke, v preiskanem vzorcu pa so tri plasti spajke. Ali to nakazuje spajkanje treh plasti izredno tanke jeklene pločevine (debeline okoli pol milimetra)? Podrobno smo preiskali le en vzorec sprednje prečke, zato ne vemo, ali so tri plasti brona v njih pravilo ali morda izjema.

Domnevamo, da je spakanje potekalo tako, da so zelo tanke jeklene in bronaste trakove v ognju segreli do tališča brona. Razlike v stiku brona in jekla nakazujejo, da je bil pri tem postopku lestvičasti okov obrnjen s sprednjo stranjo navzdol.

Spajkanje v robnem delu okova, približno simetrično na levi in desni strani nožnice, nakazuje, da so mrežasti okov naredili najmanj v dveh delih in nato sestavili s spajkanjem.

Stranski izsledek naših raziskav je ugotovitev, da so med restavriranjem nožnice po pomoti del sprednje prečke prestavili na mesto 10. hrbtne prečke.

Opisane raziskave lestvičastega okova so izboljšale uvid v njegovo zgradbo in način izdelave, vendar pa so podrobnosti ostale nepojasnjene. Želimo si, da bi ta objava spodbudila raziskave drugih primerkov lestvičastih okovov nožnic s predrtim okovom iz bakrove zlitine ali srebra (prim. Istenič 2010, seznam). Take raziskave bi namreč pokazale, ali izsledki naših raziskav veljajo tudi za druge take okove, in bi morda tudi pojasnile vprašanja, na katera nismo našli odgovora.

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