Complex metallographic study on Gepid bronze and silver buckles from the Great Hungarian Plain (5–6th cent.)

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A newly developed non-destructive X-ray diffraction method was applied on the artefacts for the first time, as a novel approach, for sampling-free residual stress measurements. Other techniques such as optical microscopy and scanning electron microscopy combined with energy dispersive spectrometry have also been used. In addition to residual stress, crystallographic texture and properties of the reflections were analysed as well. The combined application of these methods was found to be an effective tool to deduce the production technologies of the examined artefacts. In addition to defining the characteristics of the material structures and compositions on the surfaces of the artefacts, the typical traces of several technological methods as casting, forming, coating were detected which are used for making various types of artefacts.

ABSTRACT

This work presents a complex metallographic examination of bronze, silver and golden artefacts from early medieval German (Gepid) cemeteries of the Hungarian Plain, focusing on the finds from Tiszapüspöki. A newly developed non-destructive X-ray diffraction method was applied on the artefacts for the first time, as a novel approach, for sampling-free residual stress measurements. Other techniques such as optical microscopy and scanning electron microscopy combined with energy dispersive spectrometry have also been used. In addition to residual stress, crystallographic texture and properties of the reflections were analysed as well. The combined application of these methods was found to be an effective tool to deduce the production technologies of the examined artefacts. In addition to defining the characteristics of the material structures and compositions on the surfaces of the artefacts, the typical traces of several technological methods as casting, forming, coating were detected which are used for making various types of artefacts.

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Introduction – Archaeological background

The Gepids from the Eastern Germanic group came from the region of the estuary of the river Vistula and reached the Carpathian Basin in the upper region of the river Tisza in 269 (Fóthi, 2000: 88). As the Sarmatians were pushed out, they gradually moved their living preserves southwards. The Gepids expanded their territory to both sides of the Tisza (Tisia) and to the area of the Körös (Crisia) rivers as well, when the Huns arrived. After Attila’s death (453) the Gepids took over the primary tribal territories of the Huns. The Kingdom of the Gepids, existing between 454 and 567, included the regions of both coasts of the river Tisza in the Hungarian Plain, the interfluve of Körös and Maros (Marisia) rivers, Dacia and later the former Roman provinces Pannonia Secunda, Moesia Prima and Dacia Ripensis (Bóna, 1974: 25-26; Bóna, et al., 1993: 54-55; Nagy, 1999: 31-33). The Kingdom of the Gepids was abolished by an Avar-Longobard alliance in 567 (Bóna, 1974: 83). However, archaeological evidence and a few sources demonstrate that some Gepid communities continued to exist in the Avar Empire (Kiss, 2010).

A total number of ninety-five graves dated to the late 5th – early 6th century were unearthed in the vicinity of Tiszapüspöki (Jász-Nagykun-Szolnok County, Hungary) in 2015. As other Gepid cemeteries in the Great Hungarian Plain, the Tiszapüspöki–Fehértópart site also lies in the close vicinity of the river Tisza.

In spite of the extensive plunder, the cemetery can be regarded as considerably rich in metal finds: bronze belt buckles, one with a loop made of crystal, sword belt buckles, one with blue inlay, a golden ornament inlaid with garnets, a silver and a gold ring, a bronze needle case, an oversized bronze ring with rounded knobs and bronze rivets were discovered. A minimum of 45 iron, bronze and silver buckles was found in the greaves.

The examined artefacts of this study were unearthed at the Tiszapüspöki-Fehértópart and Szolnok-Szanda (Jász-Nagykun-Szolnok County, Hungary) sites. The distance between the two sites is no more than 15 kms. In Szolnok-Szanda, one of the biggest Gepid cemeteries of the Hungarian Plain with 222 graves was excavated in the 1950s (Bóna, et al., 1993: 97). Despite extensive graverobbing, an all-round assemblage was unearthed, including a number of bronze and silver buckles and exclusive fibulas, among others. These artefacts broadly represent the quality of the Gepid metalworking in the 5th and 6th centuries.

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Nine buckles made of bronze and silver from Tiszapüspökő and Szolnok-Szanda were examined by the experts of the Archaeometallurgical Research Group of the University of Miskolc (ARGUM) in the laboratories of the Institute of Physical Metallurgy, Metal-forming and Nanotechnology of the University of Miskolc. The examination included optical microscopy (OM), scanning electron microscopy with energy-dispersive spectroscopy (SEM–EDS) in order to reveal the composition, microstructure, the mechanical properties (e.g. ductility) of the finds and manufacturing processes. In the case of a silver buckle from Szolnok-Szanda (Bóna and Nagy, 2002: 217, 318), a newly developed non-destructive X-ray diffraction (XRD) method was used.

Moreover, this study focuses on the methodology, usefulness and complexity of the applied (newly developed and commonly used) surface-examining techniques from an archaeometrical point of view. The combined application of these methods was found to be an effective tool to deduce the production technologies of the examined artefacts. In addition to defining the characteristics of the material structures and compositions on the surfaces of the artefacts, the typical traces of several technological methods such as casting, forming, coating were detected, which are typically used for making various types of artefacts.

**Examination methods**

**Microscopy**

Metallographic investigation is the only effective way in studying the manufacturing techniques in the case of metallic artefacts. However, it is a destructive method of materials testing. For the investigation, a polished and chemically etched flat surface is required. This flat surface must be perpendicular to the main optical axis in optical microscopic observations. Sampling and sample preparations easily ensure these circumstances. In the case of the examined buckles, sample taking was not allowed. Another important task is the preservation and restoration of the artefacts for exhibitions. A method was allowed for metallographic investigation which did not injure the artefacts in a manner which would disturb or change its nature and aesthetic in exhibitions.

The main task was to choose the examination surface during the planning of the experiments. It was necessary to choose an area which was not visible on the exhibited buckles, typical in the analysis of processing techniques, and which can easily be positioned during the microscopic observation. The end of the tongue was chosen for investigation (Figure 1). It was a nearly plain area in all cases. It is not visible in an exhibition. The positioning was a challenge during the preparation and the observation. It was not possible to mount the artefacts in resin due to the same reason as sampling was prohibited. Instead, a careful free hand preparation was used. Therefore, mainly in the case of small sized objects, it was not possible to make a perfect preparation. But in all cases a surface could be found where the microstructure was successfully studied. A special sample holder was developed and used for positioning the prepared surface element during the optical microscopic observation. But it was also hard to set the optimal position of the sample on the microscope.

During the metallographic preparation mechanical grinding was used. After all processing steps, the removal of the corrosion products was controlled. The chosen ground surface was polished mechanically with diamond particles (3 μm). Immersion etching and K₂CrO₄ reagent was used. Etching was performed carefully so that the reagent only reached the preparation surface. After etching the object was washed in flowing distilled water. The K₂CrO₄ reagent is a strong oxidizing agent, therefore to prevent the tongues and laboratory EHS reason it must be removed from the objects. After washing the examined surface area was cleaned with pure alcohol. Micrographs were taken with a Zeiss Axiolmager M1 m optical microscope. The SEM-EDS analysis was performed with a Zeiss Evo-Ma10 electron microscope, equipped with an EDAX microprobe. After the examination the surface was not treated with additional methods in the laboratory.

**X-ray diffraction**

Obtaining the X-ray diffraction (XRD) pattern is a commonly used method to acquire information about the characteristics of the crystal lattice of the examined volume (Pearson, 1958). Conventional X-ray diffraction, however, requires a sample with well-defined size and geometry limitations. In archaeological applications, where sample cutting is often prohibited, the availability of conventional X-ray diffraction is strongly limited. Centreless X-ray diffractometers were developed to measure the residual stress within automotive and other industrial components without the need of sample cutting (Fitzpatrick, et al., 2005). Using such equipment, the measurement is performed directly on the complete component, which remains unharmed after the examination. This feature makes centreless X-ray diffractometers suitable to be used on archaeological objects. X-ray diffraction examinations were carried out using a Stresstech Xstress 3000 G3R type centreless diffractometer, shown in Figure 2. The equipment was specifically designed to measure residual stresses in machine components without the need of sample cutting. Centreless X-ray diffractometer applied on archaeological artefacts was applied here for the first time.
Usually, with centreless diffractometers, only a section of the full XRD spectrum can be recorded. Actually, the examination of one single reflection is sufficient to provide many properties (e.g. residual stresses, dislocation density) of the crystal lattice. The distortion (strain) of the crystal lattice caused by the actual residual stress state of the object can be measured based on the shift of the peak position of the examined reflection in different tilting positions (Krawitz, 2001, Fitzpatrick, et al., 2005, Schajer, 2013). Lattice strain was calculated from the shift of the reflection of Ag {222} lattice plains recorded in 5/5 tilting positions in the $\chi = -45^\circ ... +45^\circ$ tilting range in so called modified $\psi$ mode of the measurement set-up. Residual stress was calculated with the so called $\sin^2 \psi$ method using Young’s modulus of 83000 MPa and a Poisson’s ratio of 0.37, which are generally used values in the case of bulk silver. As a result, the residual stress component parallel with the tilting plane of the equipment was obtained.

The degree of deformation of the examined object is proportional to the width of the reflection described with “full width at half maximum” (FWHM). The full width of half maximum value is directly provided by the software of the equipment. The angle of diffraction, that is, the Bragg-angle depends on the lattice plane distance of the examined peak series, which is determined by the lattice parameter. The Bragg-angle actually is the angle between the X-rays and it’s projection in the chosen lattice plane. Bragg’s law describe that X-rays interfere which were reflected by the different parallel crystallographic plane when the path difference between the rays equal to the wavelength of the rays. The lattice, the lattice parameter and the reflection means a geometrically fixed system, where the interference can be described by the Bragg-angle (Fitzpatrick, et al., 2005). The lattice parameter is affected by the composition of the examined phase. Finally, measuring the Bragg-angle at different locations provides information about compositional differences of the examined phase. FWHM and Bragg-angle data were obtained from the Ag {222} reflections measured for residual stress calculations.

Pole figures provide intensity distribution maps of the examined reflections. To see the Bragg-angle there are two independent rotation angle which means a free rotation of the sample. It is possible to measure the diffraction pattern of the chosen crystallographic plane as a function of these angles. Pole figures is a descriptive and useful plot of the results, where clearly can be seen that directions where the normal of the planes are thickened. They represent the crystallographic texture, which describes the orientation distribution of grains. Isotropic (texture-free) pole figures refer to randomly oriented grains, while anisotropic (textured) pole figures indicate that most of the grains are oriented in preferred direction(s). The preferred orientation of grains can be induced by casting, or severe plastic deformation. From the type (shape, sharpness) of pole figures, the manufacturing type, and the degree of deformation can be yielded (Kocks, et al., 1998, Engler and Randle, 2010, Suwas and Ray, 2010).
The crystallographic texture of the buckle was characterised using incomplete pole figures. Pole figure measurements were carried out according to the Hungarian patent P1600500 and are the first instances of incomplete pole figure measurements without sample cutting, using macroscopic spot sizes applied on archaeologic artefacts (Benke, et al.) without any preparation of the surface of the artefacts.

X-ray diffraction data was collected at two locations (marked as 1 and 2) on the flat upper surface of the silver buckle, shown in Figure 3. The examined points are free of decorations. A 3 mm spot size was chosen for the X-ray diffraction examinations. Residual stress measurements were carried out in two directions (x and y) perpendicular to each other at both locations. The Ag {222} and {311} pole figures were measured at one location (marked as 2) shown in Figure 3, also using a 3 mm spot size.

**Results and discussion**

**Microscopy**

Six buckles were examined from Tiszapüsköki, including five copper based finds and a silver buckle, as well as three copper based buckles from Szolnok-Szanda. The buckles can be grouped into three different groups based on the raw material. Two groups are copper-based, of which one is tin-bronze, the other is brass. Based on the composition the original color of the buckles was nearly gold. The long time general corrosion affects different materials to different extents. Therefore a significant difference can now be seen between the buckles. The third group consists of silver buckles.

Figures 4-8 show the microstructure of the brass buckles (Fig. 4: buckle 32 from Tiszapüspökő, and buckle 59 from Szolnok-Szanda). Buckles 51 and 59 were made from a homogenous brass alloy. The Zinc content is nearly 26 wt%. Buckle 32 contains more Zn, small areas of the β phase can be discovered between the dendrite arms. The dendritic structure shows that the buckles were made by casting. The macroscopic shape of the buckles and tongues also confirm the manufacturing method. Buckles 32 and 51 exhibit a build-up of large dendritic grains. This suggests a low cooling rate during the solidification. Buckle 59 has a similar size as the other two, but it contains much smaller dendrites. This structure forms under faster cooling. The origin of this difference could be related to the material of the molds.

Figure 5 shows a SEM micrograph taken from buckle 59. The copper materials contain a small amount of lead (≈1 wt%) in general. White dots can be discovered in a uniform distribution in Figure 5,a which are the lead phases. Figure 5,b shows the dots in higher magnification. Point 1 indicates the brass matrix which contains the mentioned 26wt% zinc only. In area number 2 the EDS analysis shows a high amount of lead. The copper does not dissolve the lead, therefore the lead forms small droplets in the copper, or in this case, in the homogeneous brass matrix. This amount of lead is generally found in copper based metallic artefacts. The lead could be accompanying the copper or the zinc ore, too. This fine disperse structure also confirms the faster cooling of buckle 59.

The majority of the buckles is made from a bronze alloy. Figures 6, 7 show the microstructure of three example buckles. At first glance, the dendritic structures show that these buckles were also produced by casting. In contrast to the brass buckles, the microstructures are inhomogeneous. The buckles contain a high amount of tin (≈20 wt%). In all cases, the microstructure consists of α dendrites and eutectoid between the dendrites. During the solidification δ phase forms from the molten metal, but phase transformation products of the decomposition of δ can be seen between the dendrites. One interesting difference between samples from Tiszapüspökő and Szolnok-Szanda is that the buckles from Tiszapüspökő contain a higher amount of Sn (22-25w%), whereas buckles form...
Szolnok-Szanda contain 17-19wt% of tin. However, all buckles produced from bronze contain ∼10wt% of zinc. This high amount of tin and the additional zinc made the casting easier because the alloying decreases the melting temperature so a better fluidity of the melt is achieved at the same casting temperature. This is related to the observation that the generally smaller buckles are made from bronze and the larger buckles are casted from brass. It was easier to imitate the color of gold with brass than tin-bronze.

An interesting microstructure can be seen in the case of buckle 71 from Tiszapüspöki. A strong segregation was found in the center of the tongue, additionally, nearly pure copper particles were discovered. This could be caused by two effects: insufficient alloying or corrosion. The area fraction of the segregated area and the difference in the microstructure suggests that this segregation cannot form during solidification. This segregated area was situated on the center of the cross section, and the appearance of the phases suggests that this segregation is caused by corrosion. It is necessary to take into consideration that only the surface area could be examined without sample taking. Probably the corrosion layer was not removed deeply enough in this case during the grinding. This was confirmed by the micrographs taken from the other samples too. This case strengthens the fact that the surfaces of the artefacts were handled carefully during examination. But it can be examined in the other area, and with the SEM investigation the phases of the non-segregated area were studied.
Figure 7 shows the typical phases in the microstructure. Point 1 indicates the $\alpha$ phase in the copper-tin alloy system, which is a substitution solid solution. The tin content is 12wt%, which is nearly the maximal solubility of the tin in copper. The fine microstructure also shows the forced cooling of the casting during the solidification. The precipitation processes are slow processes in a copper-tin system, so during the forced cooling the excess amount of tin remains in the solid solution. This phase, as well as the others, contains nearly 10wt% of zinc. Phases which are signed with 2 contain only 2 wt% of tin and zinc. This also proves that this phase forms during the corrosion of the tongue. Therefore we cannot take this phase into consideration during the analysis of the results. Point 3 shows a heterogeneous area with two different phases. The concentration of the area is 35wt% tin and 10wt% zinc. The tin content shows that is an eutectoid from the decomposition of the $\delta$ phase.

Metallographic analysis of two silver buckles using an optical microscope was also carried out. Figure 8,a shows the microstructure of silver buckle 128 from Tiszapüspöki. A typical eutectic of silver and copper can be observed between the primary silver dendrites. This means a relatively high copper content (intended alloying), but this alloy has extremely good casting properties due to its low melting point. This alloy is good for casting small and/or ornamented buckles. Buckle 131 from Szolnok-Szanda contains a lower fraction of eutectic than buckle 128 but it can be found in the microstructure between the silver dendrites (Figure 8,b). The microstructures of these buckles also show that the silver buckles were made by casting.

X-ray diffraction

Results of the residual stress measurements and additional X-ray diffraction data obtained during the residual stress measurements are summarized in Table 1.

At both locations 1 and 2 weak compressive stresses of around -53 MPa and -71 MPa were measured in both x and y directions. The presence of weak compressive stresses suggest that the buckle is in a mildly compressed state. The small deviation between the measured stress values in the two directions and the two locations mean that the stress field of the buckle is uniform at locations 1 and 2 of the buckle. The width of the examined Ag $\{222\}$ reflection (FWHM) was found to be between 4.43° and 4.59°, which is...
characteristic to metallic objects being in a plastically deformed state, therefore containing a relatively large amount of dislocations. The value of the Bragg-angle varies between 154.28° and 154.39°, which means that no major difference is present between the lattice plane distances of the Ag solid solution at the examined areas of the silver buckle. Accordingly, no notable composition difference is present between examination points 1 and 2. The measured Ag {222} and {311} pole figures obtained at location 2 are shown in Figure 3.

It can be seen in Figure 9 that no local intensity maxima are present on the Ag {222} and {311} pole figures, that is, the pole figures are texture-free. The uniformly smooth pole figures revealed that the examined silver buckle has a texture-free, semi-isotropic crystal structure. The texture-free crystal structure suggests that the silver buckle is not in a severely deformed state.

Conclusions

Microscopy

The end of the tongues of buckles were examined which were chosen as relevant surfaces related to the production technology. All buckles were produced by casting either from Tiszapüspöki or Szolnok-Szanda. This is verified by the macroscopic shape and the dendritic microstructure. Three different types of buckles were identified based on the raw materials: homogeneous brass buckles, bronze buckles and silver buckles. Brass buckles contain nearly 26wt% zinc. The bronze buckles from Szolnok-Szanda consist of 17-19wt% of tin, buckles from Tiszapüspöki consists of 22-25 w% of tin. All bronze buckles contain an additional 10wt% of zinc. The bronze buckles have an inhomogeneous microstructure which consists of α solid solution dendrites, and eutectoid from the decomposition of δ intermetallic phase. The difference between the bronze buckles from Tiszapüspöki and Szolnok-Szanda is the higher tin content of the buckles from Tiszapüspöki. The microstructure of silver buckles contain eutectic structure of Ag-Cu alloys. Brass buckles from Tiszapüspöki have coarser dendritic structure due to the moderate cooling during solidification. All bronze and brass buckles contain nearly 1wt% lead as an impurity.

X-ray diffraction

The measured Bragg-angle values are close to each other, which means that there is no notable difference between the solute and/or impurity content of the Ag solid solution of the silver buckle at the examined areas. According to the residual stress measurements the silver buckle is in a mildly compressed state. This is confirmed by the measured width of the Ag {222} reflection which was found to be relatively large, being similar to plastically deformed metallic objects. The measured incomplete pole figures revealed that the silver buckle is free of crystallographic texture which is usually introduced by severe plastic deformation or casting. During the interpretation of the measured X-ray diffraction data obtained from archaeological artefacts, it must be kept in mind that the measured data are characteristic to the actual state of the artefact. If the production of the artefact is not followed by any thermal and/or mechanical history influencing the lattice, the obtained data hold the characteristics of the manufacturing conditions. If that case can be assumed, the final manufacturing step of the examined silver buckle (before the surface decoration) was a mild plastic deformation which was not followed by annealing heat treatment.

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