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ORIGINAL RESEARCH PAPER

Non-destructive characterization of bronze objects from Ráksi and the Pusztasárkánytó depot find

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ABSTRACT

Eight ornaments and a dagger were analyzed using completely non-destructive techniques to determine their alloy compositions and to draw conclusions about the production technology. Prompt-gamma activation analysis and time-of-flight neutron diffraction proved that the studied objects are tin-bronzes. Difference was observed in the amounts of ore-related minor components (arsenic, silver, nickel) of the objects belonging to the two distinct archaeological sites. Based on the diffraction analysis of the microstructure, the objects are casts that were exposed to different degrees of manufacturing to reach their final forms.

KEYWORDS

PGAA, TOF-ND, XRF, non-destructive, alloy composition, texture analysis

INTRODUCTION

Metallography proved to be a powerful tool in the analysis of archaeological alloys, although destructive sampling raises ethical issues.[1] For this reason, we involved completely non-invasive and non-destructive techniques in this study. Nine copper-alloys from the Middle Bronze Age were selected for analysis. Four objects belong to the Ráksi grave find that can be dated to the Koszider horizon at the end of the Middle Bronze Age. Five objects are part of the Pusztasárkánytó (Mosdós-Sárkánytó-puszta) depot find which is older than the Ráksi grave find. The Pusztasárkánytó assemblage is characteristic to the Bronze Age Encrusted Pottery culture. The objectives of the study were 1) to determine the alloy compositions and 2) to conclude on the production technologies of the objects.

METHODS

X-ray fluorescence analysis (XRF) was applied for pre-screening the bronzes and to identify the main components, using an InnovX Delta Premium handheld XRF spectrometer. This equipment weighs only 1.5 kg, therefore it is excellent for on-site measurements, and provides concentration data on the measured spot within a minute. These parameters make this technique very attractive, but the results need to be handled with care, or co-interpreted with the results of a bulk method.[2] XRF technique provides chemical composition of the

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[1] Szabó 2010.
[2] Szabó *et al.*, 2019.

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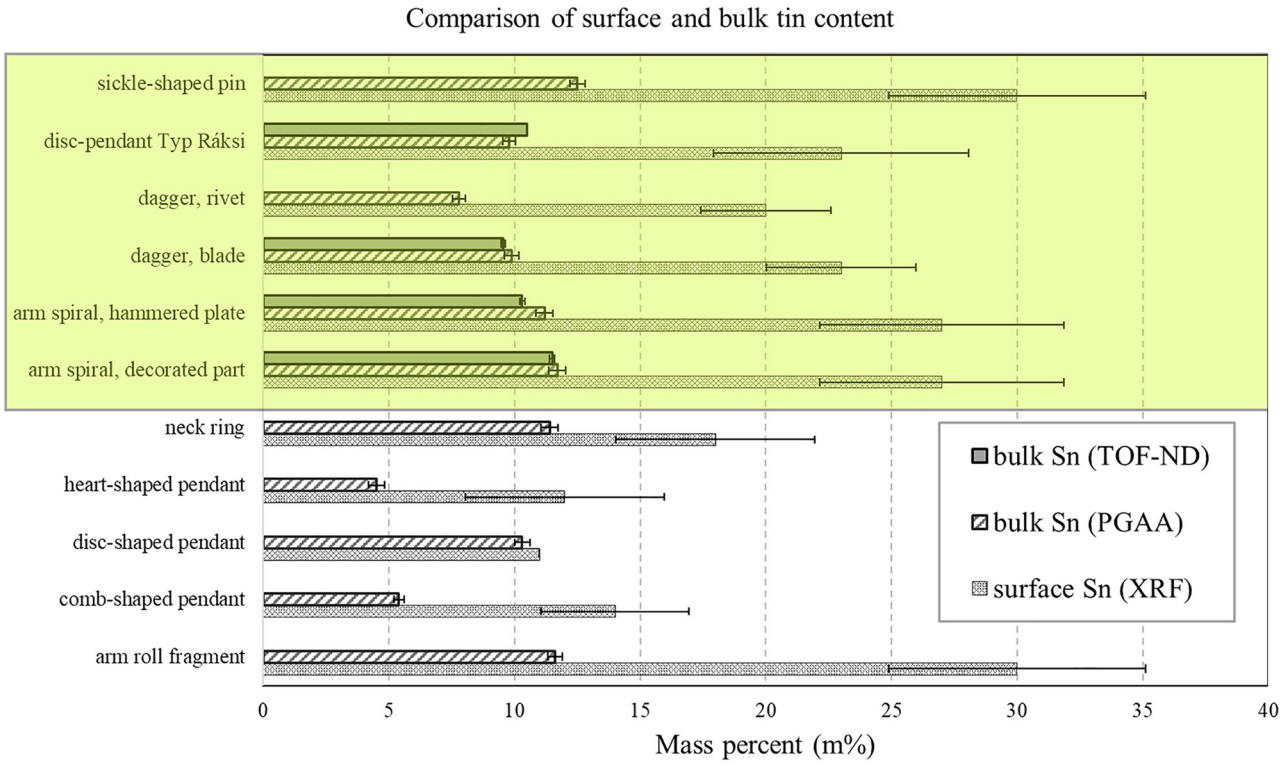

Fig. 1. Surface and bulk tin contents of the objects from Ráksi and Pusztasárkánytó-Mosdós depot find expressed in mass percents (m %) together with their uncertainties. Please note that the XRF results are the average of several individual measurements on various parts of the object. The highlighted objects are part of the Ráksi grave find

near-surface layers, thus, these data are not representative of the whole volume of the bronzes, especially for these archaeological objects that are covered with patina and corrosion products.[3] Since sampling and sample preparation were prohibited in this study, prompt-gamma activation analysis (PGAA) technique[4] and Time-of-Flight Neutron Diffraction (TOF-ND)[5] were used to determine the composition, and for the phase and texture analysis of the bulk, respectively.

Both the PGAA and TOF-ND measurements took place in the Centre for Energy Research at the Budapest Research Reactor. Two element analysis facilities are installed at the end of a guided cold neutron beam, PGAA is for the analysis of samples with dimensions $4 \times 4 \times 10\ cm^3$, while NIPS can accommodate larger objects,[6,7] PGAA method is based on the radiative neutron capture, where neutrons are absorbed by the nuclei of the sample and gamma photons are emitted. The gamma photons are detected with a high-purity germanium detector. The energies of the photons are nuclide specific, while their intensities are proportional to their quantities, that is the basis of the quantitative analysis. The element identification was performed with the prompt gamma-ray spectrum catalog,[8] while the concentration calculation was done with the ProSpeRo software.[9]

TOF-ND is installed in a separate building on a radial thermal channel. The thermal neutrons are highly penetrating, and the available beam cross-section is 10×2.5 cm, therefore the method can analyze large objects in-depth. The neutron diffraction on crystalline materials allows to investigate the microstructure of the examined object. The diffracted neutrons are detected with a large-surface back-scattering detector bank built from 88 pieces of squashed ^{3}He tubes. TOF-ND is a well-established method in the detailed structural characterization of binary alloys with qualitative known compositions.

For the more comprehensive characterization of the objects in this study, the results of the three different methods are discussed jointly.

RESULTS AND DISCUSSION

XRF pre-screening indicated that all objects are tin bronzes with various amounts of nickel, antimony, and silver. Even though arsenic was not reported by the factory calibrated software, K_α and K_β peaks of arsenic were identified in all spectra.

[3] Robbiola *et al.* 1998.
[4] Révay and Belgya, 2004.
[5] Káli *et al.* 2007.
[6] Szentmiklósi *et al.* 2010.
[7] Szentmiklósi *et al.* 2013.
[8] Révay *et al.* 2004.
[9] Révay 2009.

Altogether eleven PGAA measurements were done on the objects since the dagger and the decorated arm spiral were analyzed at two different parts. Three out of the nine objects were subjected to numerous TOF-ND analyses to conclude on the potential differences in their crystalline structure and consequently, in their production technologies.

Figure 1 depicts the differences in the tin concentrations determined on the surface and in the bulk of the objects. Except for the disc-shaped pendant from Pusztasárkánytó-Mosdós (Inv. Nr. 2013.11.09.), the surfaces of the objects are highly enriched in tin, as 2–3 times more tin was detected with XRF than with PGAA or TOF-ND. TOF-ND results are in good agreement with the PGAA data.

Ráksi grave find

Dagger. Two different parts – the blade and a rivet – of the dagger (Inv. Nr. 2013.10.03.) were measured with PGAA (Table 1). Besides Cu and Sn, the dagger contains minor amounts of As and Ni. Hydrogen and chlorine, which are possibly present in various corrosion products, were detected as well. 0.121 m% (±0.003 m%) and 0.042 m% (±0.002 m%) hydrogen contents were determined in the rivet and the blade parts, respectively. Higher chlorine content was measured at the rivet part (0.279 ± 0.006 m%) than in the blade (0.030 ± 0.001 m%). These results imply that the object is covered with corrosion products, especially the rivets and their vicinity.

TOF-ND measurements were done on the blade of the dagger, rotating it around both the longitudinal and lateral axis. The cast is well-homogenized; only weak crystallographic preferred orientation was observed which may indicate hot working. Phase analysis verified that the dagger is an α-bronze without pure copper or higher bronze phases. The tin concentration is 9.55 ± 0.10 m%, in good agreement with the PGAA result. Based on these results it can be assumed that the dagger blade (edge) was manufactured by forging after the casting.

Arm spiral. The arm spiral (Inv. Nr. 2013.10.04.) was also analyzed at two different parts. The tin-bronze contains minor amounts of Sb, As and Ni. The decorated part and the hammered plate were irradiated to determine the bulk composition with PGAA (Table 2). Only a slight difference was observed in the alloy composition. Here, the hammered plate seems to be more corroded (0.144 ± 0.003 m% hydrogen and 0.116 ± 0.002 m% chlorine), than the rolled-up spiral end-part (0.063 ± 0.003 m% hydrogen and 0.058 ± 0.002 m% chlorine).

TOF-ND analyses identified the alloy as α-bronze. The tin-equivalent concentrations (assumed as a binary alloy) calculated from the Vegard's law are 11.55 ± 0.10 m% in case of the spiral end-part and 10.30 ± 0.10 m% in the hammered plate. Weak, but systematic anisotropy was observed in case of the plate, which refer to repeated hammering and annealing processes during its production/elaboration. The difference in the tin concentrations in the α-bronze of the spiral end-part and the hammered plate raises the possibility of tin segregation. Since there is no significant difference in the bulk tin concentrations based on the PGAA results, the presence of tin-rich phases is presumed (surface tin-enrichment) in case of the hammered plate, that are

Table 1. PGAA results of the dagger (Inv. Nr. 2013.10.03.) from Ráksi find in mass percent (m%) unit. Sb (detection limit: 0.2 m%) and Ag (0.01 m%) were not detected. Weak peaks of Co were identified (detection limit: 0.02 m%), but the quantification of cobalt was not possible due to the high uncertainty

Measured part	Cu	±	Sn	±	As	±	Ni	±
dagger, nail	**91**	*0.3*	**7.8**	*0.2*	**0.25**	*0.02*	**0.56**	*0.02*
dagger, blade	**89**	*0.3*	**9.9**	*0.3*	**0.32**	*0.05*	**0.58**	*0.01*

Table 2. PGAA results of the arm spiral (Inv. Nr. 2013.10.03.) from Ráksi find in mass percent (m%) unit. Ag (0.01 m%) was not detected. Weak peaks of Co were identified (detection limit: 0.02 m%), but the quantification of cobalt was not possible due to the high uncertainty

Measured part	Cu	±	Sn	±	Sb	±	As	±	Ni	±
spiral end-part	**86**	*0.3*	**11.7**	*0.3*	**0.8**	*0.2*	**0.38**	*0.03*	**0.66**	*0.03*
hammered plate	**87**	*0.3*	**11.2**	*0.3*	**0.5**	*0.1*	**0.42**	*0.04*	**0.61**	*0.01*

Table 3. PGAA results of the disc pendant (Inv. Nr. 2013.10.01.) from Ráksi find in mass percent (m%) unit

Measured part	Cu	±	Sn	±	Sb	±	Ag	±	As	±	Ni	±	Co	±
Disc-pendant Typ Ráksi	**86**	*0.3*	**9.8**	*0.3*	**2.5**	*0.1*	**0.029**	*0.002*	**0.69**	*0.02*	**0.99**	*0.0*	**0.038**	*0.002*

difficult to identify with TOF-ND. In case of the spiral end-part, only a low-degree of manufacturing could be observed. The identified diffraction peak-profiles can be explained by a lower degree of homogeneity, and/or the micro-tension caused by the bending of the spiral.

Disc-pendant Typ Ráksi. The pendant decorated with concentric circles (Inv. Nr. 2013.10.01.) contains higher amounts of antimony, nickel and arsenic, than the arm spiral, and silver content was also detected (Table 3). Relatively high hydrogen (0.129 ± 0.003 m%) and chlorine (0.200 ± 0.005 m%) contents were determined that are possibly present in the corrosion products.

The structural and peak profile analyses of the TOF diffraction patterns indicate that the whole object is a cast. It has cooled slowly or/and was reheated to about 400–500 °C to manufacture the hanger of the pendant. The average tin-equivalent concentration in the α-phase is 10.5 m%. The concentration profile shows saturation at 13 m% in tin equivalent. The total concentration based on the PGAA data of Sn and Sb should be 13 m%. Some residual tin and antimony must be present in the δ or ε-phase, although these phases were not possible to detect due to the small volume of the object. Similar tin concentration was determined in the hanger, but it has been significantly homogenized by the effect of the local heating and hot working.

Sickle-shaped pin. The average bulk PGAA results of the pin (Inv. Nr. 2013.10.06.) are listed in Table 4. Among the objects in this study, the pin has the highest tin concentration. Corrosion-products–related elements, such as hydrogen and chlorine were determined, both in the range of 0.1 m%.

Pusztasárkánytó (Mosdós-Sárkánytó-puszta) depot find

The objects from the second find were characterized with PGAA. There is significant difference in the silver contents of the artefacts. The pendants have 0.8–1.0 m% silver content, and these contain 0.5–1.7 m% antimony as well. The spiral bracelet and the neckring have 9–24 times less silver content, and contrary to the pendants, antimony was not identified in their bulk (Table 5). In the disc-shaped pendant, a low-intensity lead peak was identified, close to the detection limit of PGAA (2 m%). The chlorine content (0.01–0.02 m%, or below 0.01 m%) of these bronzes is lower than the finds from Ráksi, which may refer to better state of preservation.

Table 4. PGAA results of the sickle-shaped pin (Inv. Nr. 2013.10.06.) from Ráksi find in mass percent (m%) unit. Sb (detection limit: 0.2 m%), Ag (detection limit: 0.01 m%) and Co (detection limit: 0.02 m%) were not detected. Low amount of iron (0.4 m%) was identified, but it is not listed in the table due to its high uncertainty

Measured part	Cu	±	Sn	±	As	±	Ni	±
sickle-shaped pin	**86**	0.3	**12.5**	0.3	**0.39**	0.01	**0.60**	0.01

Table 5. PGAA results of the objects from Pusztasárkánytó depot find in mass percent (m%) unit. Co (detection limit: 0.02 m%) was not detected. <.D.L. – under detection limit

Inv. Nr.	Object	Cu	±	Sn	±	Sb	±	Ag	±	As	±	Ni	±
2013.11.06.	heart-shaped pendant	**91**	*0.5*	**4.5**	*0.3*	**1.7**	*0.2*	**1.00**	*0.04*	**0.6**	*0.06*	<D.L. (0.04 m%)	
2013.11.09.	disc-shaped pendant	**86**	*0.3*	**10.3**	*0.3*	**1.2**	*0.1*	**1.02**	*0.04*	**1.1**	*0.2*	<D.L. (0.04 m%)	
2013.11.17.	spiral bracelet fragment	**88**	*0.3*	**11.6**	*0.3*	<D.L. (0.1 m%)		**0.043**	*0.004*	**0.09**	*0.01*	**0.140**	*0.004*
2013.11.13.	neckring	**88**	*0.4*	**11.4**	*0.3*	<D.L. (0.1 m%)		**0.094**	*0.004*	**0.18**	*0.03*	**0.053**	*0.001*
2013.11.14.	comb-shaped pendant	**93**	*0.4*	**5.2**	*0.4*	**0.50**	*0.03*	**0.81**	*0.03*	**0.32**	*0.02*	**0.068**	*0.005*

SUMMARY

All objects in the present study are tin bronzes with 4.5–12.5% tin contents and minor amounts of arsenic. The objects of Ráksi find contains higher amounts of nickel than the artefacts from Pusztasárkánytó depot. The ornaments from the latter site contains more silver, in the range of few tenths to 1 m%. The TOF-ND results showed that the objects underwent different degrees of manufacturing. After casting, the disc-pendant Typ Ráksi was only reheated to form its hanger, while the dagger was manufactured by forging (hot working). The plate of the arm-band reached its final form via multiple, repeated hammering and annealing processes.

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