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ARTICLE

Non-destructive Analyses of Bronze Artefacts from Bronze Age Hungary using Neutron-based Methods

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In this paper we present the application of various neutron-based methods carried out at the Budapest Neutron Centre. Non-destructive and non-invasive neutron radiography (NR), Prompt Gamma Activation Analysis (PGAA) and time-of-flight Neutron Diffraction (TOF-ND) analysis was applied to reveal more information on raw material and production techniques of bronze artefacts that can be dated to the Central European Bronze Age (2000–1200 BC).

1. Introduction

Various neutron-based methods (neutron radiography, prompt gamma activation analysis and time-of-flight neutron diffraction; Szentmiklósi 2013) were applied at the Budapest Neutron Centre, Hungary, thanks to our EU FP7 NMI3 pilot project *(Studies on local metal production of the Carpathian Basin from the late Copper Age until the Middle Bronze Age 3500–1500 BC)* in order to explore the compositions and the manufacturing techniques of copper and bronze artefacts. Most of the studied finds are unique in their form and function, that is why, considering aspects of heritage protection, we decided to use non-destructive methods to provide more information on raw material and production techniques. In this paper we present the investigations of three bronze objects from the Middle and Late Bronze Age in Hungary (2000-1200 BC) (Fig. 1).

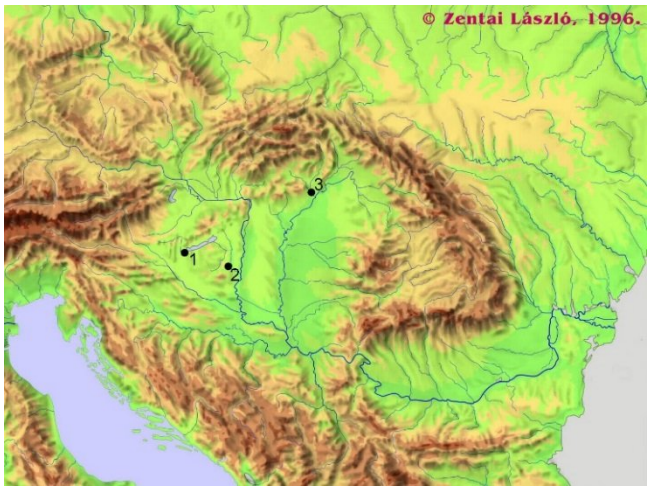

Fig. 1. Location of the studied artefacts in Hungary: 1. Zalaszabar, 2. Bonyhád, 3. Abaújdevecser

2. Analytical methods

Various non-destructive and non-invasive neutron-based instruments of the Budapest Neutron Centre (with the cooperation of the Wigner Research Centre for Physics, and the Centre for Energy Research, Hungarian Academy of Sciences) have been applied on the three archaeological bronze objects.

2.1. Neutron Radiography (NR)

The guided neutron beams coupled to a research reactor can effectively be exploited for the radiographic (NR, 2D) and tomographic (NT, 3D) imaging of objects. Due to the different neutron attenuation coefficient of the sample's inner parts different contrast levels (so called grey values) can be visualized in the projected images. These images show then some structural information of the object in a non-destructive way.

The NIPS-NORMA station, a combined element analysis and imaging facility, is situated at the end of the neutron guide No. 1 of the Budapest Neutron Centre. The thermal equivalent neutron flux was measured to be 2.7×10^7 n/cm^2/sec. The NIPS (Neutron Induced Prompt gamma-ray Spectrometry) facility (see later) is used to provide the element composition of the object, in some cases even as a spatially resolved information. The NORMA (Neutron Optics and Radiography for Material Analysis) facility is used for transmission based neutron radiography and tomography. The components of the station (Fig. 2) could be operated either independently or in a combined mode. This latter serves the experiments yielding both composition and inner structural information.

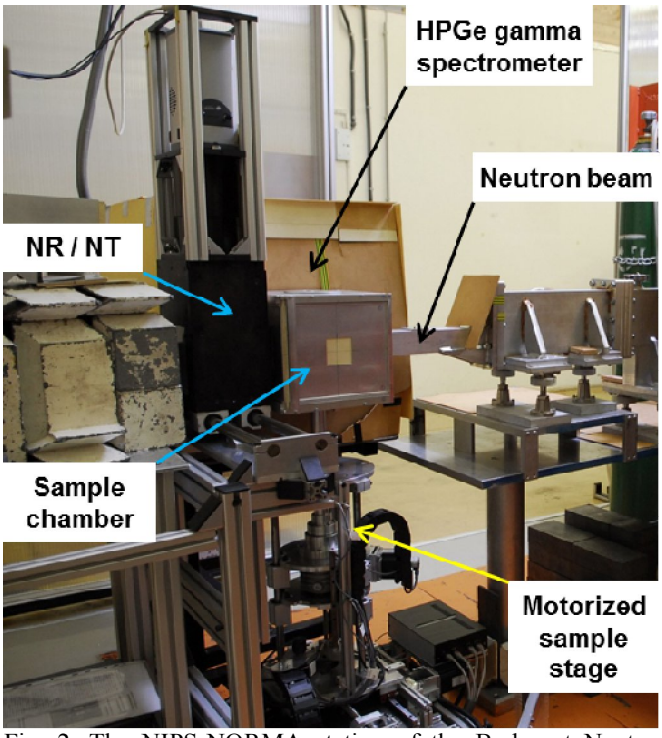

Fig. 2. The NIPS-NORMA station of the Budapest Neutron Centre

The detailed description of the imaging part (NORMA) of the station: The beam arrives through a 5×5 cm^2 flight tube into the sample chamber, which has the dimensions of 20×20×20 cm^3. It is made of AlMgSi alloy, and lined from inside with a neutron absorbing ^{6}Li-enriched polymer. By removing one or more side panels, larger objects up to 5 kg weight could be analyzed (such as a sword, vase, stones, etc.). Samples could be positioned to the measurement position in the chamber either manually from the top side, or automatically by the use of a XYZ-ω sample stage. The stage has a travel distance of 200 mm with a guaranteed precision of 15 μm.

The NORMA imaging system comprises its main elements in a light-tight house. These are a 100 μm thick, green-light-emitting ^{6}Li/ZnS scintillator, a quartz mirror with a surface covered by a thin Al layer, and a cooled, black-and-white, back illuminated Andor iKon M CCD camera with 16-bit gray value depth and 1024×1024 pixel resolution. The customized optics projects a 48.6×48.6 mm^2 area (in which the beam spot is 40×40 mm^2) onto the 13.3×13.3 mm^2 sensitive surface of the CCD chip. The measured resolution of the imaging system is about 230-660 μm depending linearly on the object-screen distance.

The exposure time for a projection is the function of the neutron's energy, and it is 1.8 sec for cold neutrons. The acquired images are then corrected for both the inhomogeneity of the beam (flat-field) and the dark current of the camera chip.

Although the neutrons have large penetration power its attenuation is heavily dependent on both their energy and the material they are traveling. In the case of bronzes the cold neutrons can be transmitted through a thickness of some tens of a millimetre. It has a consequence that objects to be subject to a tomography should not be larger than these sizes along the path of the neutron beam.

2.2. Prompt Gamma Activation Analysis (PGAA)

PGAA is a non-destructive and non-invasive nuclear analytical method applicable to determine the elemental composition of the samples.[1] The samples are irradiated with an external cold neutron beam, and the gamma photons emitted in (n,γ) reaction are detected. PGAA is a panoramic method, in principle all the chemical elements – except helium – can be quantified, without any prior knowledge about the sample.[2] Energies and intensities of the gamma lines in the spectra are characteristic for the elemental composition of the samples, but independent of their chemical forms. Since both the incoming neutrons and the emitted photons are highly penetrating, the provided results are volumetric average values characteristic for the whole irradiated volume.

The PGAA experiments have been performed at the NIPS facility.[3] In case of the flanged axe and the axe, a beam of 20 mm^2 was used. The acquisition times have been chosen to be between 7000 s and 11500 s, in order to collect statistically sufficient counts in the spectra.

Detection of gamma photons originated in (n,γ) reaction is performed in Compton-suppressed mode using HPGe detector surrounded by BGO scintillators. Signals from the detector system are collected by a 64k multichannel analyser. Detailed description of the NIPS-NORMA experimental station can be found as described earlier.[4] Spectrum fitting has been done with Hypermet PC software.[5] The element identification was done using the ProSpeRo code, which is based on our prompt-gamma library.[6] The results were corrected for the spectral background measured at open beam without the sample.

As a result of the irradiation with cold neutrons, short lived radioactivity is induced which decayed within a few hours, thus the objects were allowed to transport back to the owners.

The composition of the objects, as measured on the indicated parts on Figs 6 and 7, are given in Table 1. The concentration data, their uncertainties, as well as detection limits are given in weight%.

2.3. Time-of-flight Neutron Diffraction (TOF-ND)

The TOF-ND instrument of BNC is installed at a radial thermal channel of the reactor. It consists of a 20m long 25×100mm cross-section neutron guide, a chopper system and detectors. The beam passes through a tunnel from the reactor to the measuring hall (Fig. 3).

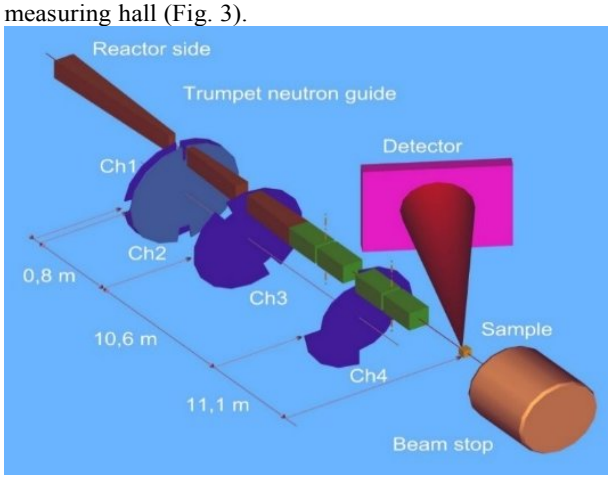

Fig. 3. The time-of-flight neutron diffractometer of the Budapest Neutron Centre

The short neutron-pulses are produced by a fast double-disc parallel our counter rotating high speed (12000 rpm) double chopper. The shortest pulse length is 10 microseconds, the total flight path of the neutrons to the detectors is 25 m. In the highest resolution mode, at backscattering geometry (detector position fixed at 175º) diffraction spectra with peak widths of 1.5×10^{-3}Å can be measured. The available wavelength range is 0.7-4.5 Å, but it can be covered in one step at lower resolution only. According to the high penetration depth of the neutrons in copper at the applied wavelength and the large beam cross-section (10×2.5 cm), bulk average results can be gained. In the present study the aim of the diffraction experiment was the phase analysis of the bronze and the revealing of the presence of texture.

2.3.1. Phase analysis

In the investigated objects no other alloying elements were observed by PGAA, so the analyses were confined to determine the amounts and concentration of normal tin-bronze phases, such as α-phase and γ- (probably γ-) bronzes. Since no other than the solid solution (α-phase) was found, to avoid the effect of any anisotropy, the tin concentration was determined directly from the shape of diffraction peaks. The solute atoms of a solid solution change the lattice constants of the host lattice and shifts the position of the diffraction peaks. In the case of α-bronze this change is proportional to the concentration (Vegard's low). In casts the concentration distribution is not homogenous: the chemical concentration within the grains can changes from zero to the maximal solubility at the temperature of the solidification. This inhomogeneity results a peak broadening, and the shapes of the diffraction peaks reflects the chemical distribution. The method was tested on reference samples, and the concentration for them was determined by 0.25% precision.[7-8] Unless the alloy is not completely homogenized, the peak is broad, so other properties such as stress, grain sizes, etc., has no perceptible effect on the peak shape.

2.3.2. Texture

By the effect of the cold or low temperature plastic deformation, the originally random orientation of crystallites becomes more regular, reflecting the type and the degree of the deformation. Preferred orientation or texture is formed, what can fully be described by the orientation distribution function (ODF). The ODF can be determined from a set of diffraction spectra covering sufficiently large number of peaks and recorded from sufficiently many directions. In the practice the texture generally is characterized by the pole figures of several representative diffraction peaks. Since our diffractometer is not equipped with automatic sample rotating mechanism, and the detector solid angle is too small, the texture was analysed by measuring a few spectra at some given angles of rotation around two perpendicular axes of the objects.

2.3.3. Experimental conditions

The instrument was set up to take neutron-diffraction patterns suitable to determine the composition and the texture as well. The wavelength range was chosen from 1.2 to 2.9 Å to cover 8 sufficiently intense diffraction peaks from (022) to (115). As a compromise between the bandwidth, resolution and intensity, moderate resolution (d_{FWHM}=0.03Å) double band mode was chosen with 10000rpm parallel rotating pulse choppers. The textures are characterised with the relative integrated peak intensities. The intensities are normalised to powder-like (fully random orientation) spectrum. Since the effective scattering volume cannot be determined (because of the irregular shape of the objects, the back-scattering geometry and the absorption), the relative intensities in one spectrum are determined for a common factor near to one.

3. Investigated artefacts

We investigated three bronze objects from the Middle and Late Bronze Age in Hungary (2000-1200 BC; Fig. 1): a flanged axe, a special type axe, and an oversized, 12 kg arm/ancle ring with spiral ends.

3.1. Flanged axe

The flanged axe (L.: 12.4 cm) was discovered in a Middle Bronze Age 2000-1500 BC) hoard in Zalaszabar (western Hungary), containing mainly dress ornaments and some tools weighing 1.5 kg of bronze (Fig. 4.1).[9-10] Large numbers of similar flanged axes[11] are often found in depositions near to the copper mines of western Central Europe, that is why they are usually defined as ingots of copper raw material or special purpose 'pre-money'.[12-14] However, several scholars consider them as tools based on post-casting elaboration of their edge.[15-16]

The aim of our investigations was to provide data regarding raw material composition and manufacturing techniques, in order to complete the long discussion about the function of the flanged axes, without destruction of the artefacts.

Fig. 4. 1: Flanged axe of the hoard from Zalaszabar, 2: special type bronze axe from Bonyhád

3.2. Special type bronze axe

The special Bonyhád type axe (L.: 18 cm; Fig. 4. 2) was excavated from a Middle BronzeAge cremation grave in Bonyhád (western Hungary).[17-18] Our investigations targeted the function and use value of the special Bonyhád type axe, whether it was as a prestige weapon or a tool.

3.3. Unique, oversized bronze spiral

The 43 cm large (W.: 12 kg) bronze spiral (Fig. 5), dated to the Central European Middle or Late Bronze Age; 1600-1200 BC), was found in Abaújdevecser-Ortásföldek (Békás lake; northeastern Hungary) as a single find.[19-23] Based on its size and weight it can be considered as an oversized ritual single find depot.[24] The aim of our investigations was to analyse the

production technique and to provide data regarding the raw material.

Fig. 5. Unique, oversized bronze spiral from Abaújdevecser

4. Results

Using the non-destructive PGAA method, the bulk chemical composition of the tested volumes can be determined. The results are shown in Table 1. The exact positions of the measured volumes within the objects are shown in the figures of the individual subsections (Figures 6 and 8).

4.1. Flanged axe

4.1.1. Elemental and phase analysis

Based on the results of the PGAA method, the determined elemental composition of the alloy of the flanged axe is 90.2±0.7 wt% copper, 9.6±0.7 wt% tin, 0.18±0.01 wt% silver and 0.056±0.004 wt% hydrogen. By TOF-ND (A1), the obtained tin content is 7.5±0.5 wt%. The results of the PGAA and TOF-ND method related to tin deviate more than one sigma confidence interval. A third dataset from a previous, destructive sampling for energy-dispersive X-ray fluorescence (EDXRF) measurement (Table 2) was considered.[25] From Table 2 the 8 wt% tin content is consistent with the TOF-ND within the margin of the uncertainty. For the copper and silver content of the flanged axe, PGAA and EDXRF results are in good agreement, while some important impurities (Fe, Co, Ni, Zn, As, Se, Sb, Te, Au, Pb and Bi) were below the detection limits of the of the PGAA.

4.1.2. Production techniques

The radiographic imaging of the bronze flanged axe was carrying out by acquiring 8 overlapping 2D projections in a tiled manner to be able to cover the whole object. By the use of the MosaicJ plugin of the FIJI image processing software the tiles can be stitched together to obtain a transmission image of the whole axe (Fig. 6.1). The change in gray values corresponds generally to the different thicknesses of a homogeneous material. Macroscopic structural deviation can only be found at two distinct areas. The first is a fissure at the edge of the axe, which can be seen as a magnified area in Fig. 6.2. The small circle with a diameter of 5 mm indicates the irradiated area for the purpose of PGAA element analysis, and its center is 12 mm far from the edge of the axe. The second area contains several lighter small spots in the middle part of the axe (Fig. 6.3-4), which might correspond to either former samplings, or defects due to shrink holes or corrosion. Therefore the lighter spots in the radiographic images only indicate presumable surface deviations apart from the deviations from former sampling for EDXRF measurements. The differences in the gray values of the radiographic image are well recognizable in the 3D surface plot of the projection (Fig. 6.4). The peaks indicate the lighter spots, and a higher peak means less neutron attenuation. It is of less probability that the spots are due to bubbles created during a casting in a lying position.[26] Available projections, however, do not allow for a precise determination of their nature: whether these are sites of corrosion or inhomogeneities caused by casting defects. 3D tomography investigation is suggested in the future to explore the spatial (surface or bulk) position of the mentioned porosity spots.

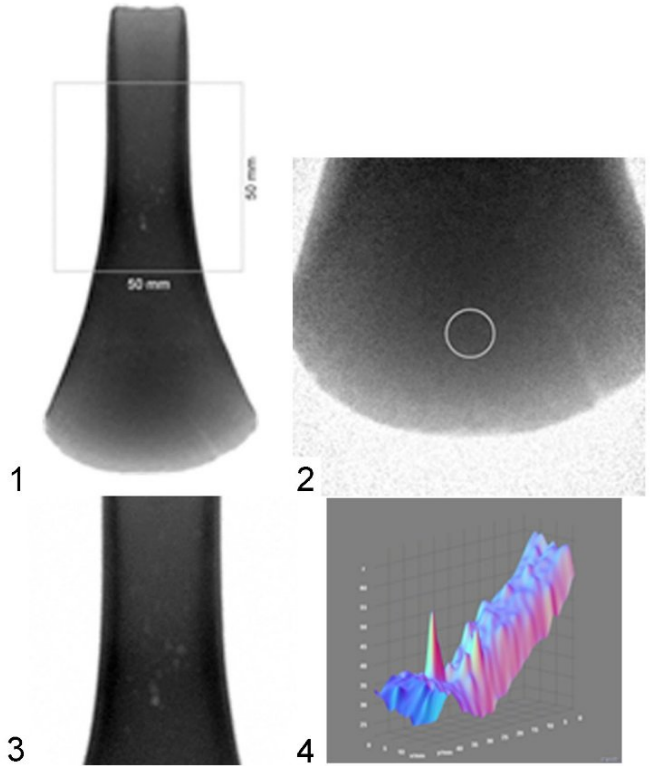

Fig. 6. 1: The neutron radiography of the flanged axe from Zalaszabar, 2: PGAA measurement area, 3: area of former destructive sampling (50×50 mm^2 shown in panel 1), and the lighter spots around it, 4: the 3D surface plot of panel 3

TOF-ND texture analysis was carried out in two parts of the axe (Fig. 7):

1. At the neck part ("*ny*"), placing it vertically to the beam – i.e. rotation about the horizontal axis of the object. The angle of the scattering vector is measured from the normal direction of the flat surface. A small part of the head was illuminated as well.
2. At a 20mm width band of the edge *(„e20"*). The axe placed horizontally – the edge vertically – in the beam, i.e. rotation around the edge. The angle is measured from the normal direction of the plane in which the edge lies. Two set of spectrum was taken from this part.

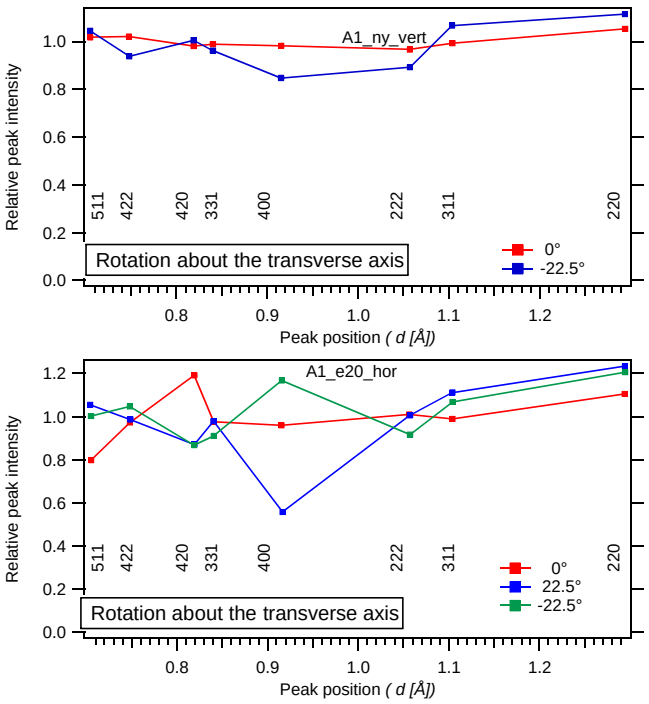

Fig. 7. Texture results of the TOF-ND analysis a: at the neck, b: at the edge of the Zalaszabar axe (errors are ±0.05-0.01 from the smallest to the largest *d-spacing* values)

The spectrum, measured from the perpendicular direction to the flat plane of the neck indicates isotropic oriental distribution. This suggests that the object is a cast. At higher angles a weak, but significant anisotropy appears. Since, at this positions the shoulder and the side of the neck turned more into the beam, the anisotropy can belong to this parts. In this case, the upper layer of the side has to be strongly anisotropic. The type of this texture (decreasing intensities in the directions of 100 and 111) could be formed by forging of the sides.

The edge is definitely oriented. Turning to the direction of the edge, the intensity of the 100 peak strongly decreases, although the texture can be more complex. It make it obvious, that the edge had been manufactured at least for hardening.

4.2. Special type axe

3.2.1. Elemental and phase analysis

The PGAA results of the special type axe are shown in Table 1. The exact irradiated volume is marked in Figure 9 (round-shape neutron collimator). The centre of the measured area is 18 mm from the edge of the axe, and the diameter is 5 mm. The bulk composition of the irradiated volume is 88.0±0.6 wt% copper, 12.0±0.6 wt% tin, and 0.025±0.003 wt% hydrogen. The TOF-ND (A2) result for tin content is 11.07±0.5 wt%.

4.2.2. Production techniques

Due to the difficulties of positioning only one NR projection was acquired for the axe object (code: J37; Fig. 8). The grey scale values could correspond to portions with different thicknesses of a homogeneous material. Macroscopic casting defects (shrink holes), or other structural differences are not visible.

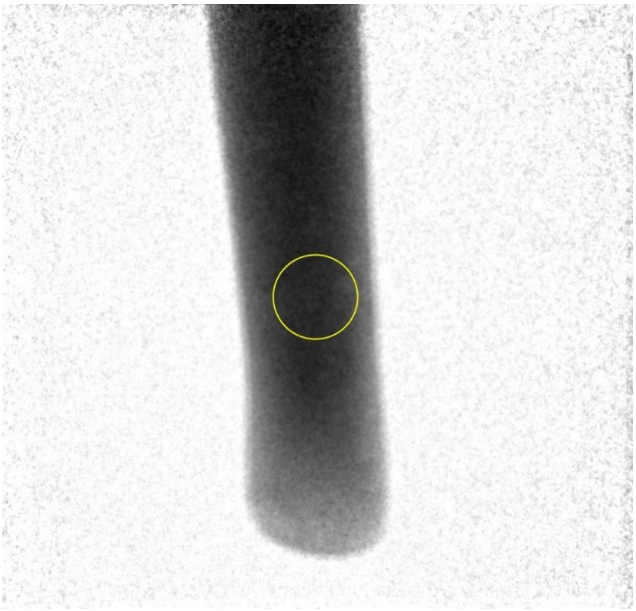

Fig. 8. Special type bronze axe (code: J37) from Bonyhád

TOF-ND texture analysis was carried out in three parts of the axe:
1. At the central part („*back*"), opposite to the protrusions vertically („*vert*"),
2. At the edge of the axe („*nail*"),
3. At the protrusions parts, at two different setup („*but*").

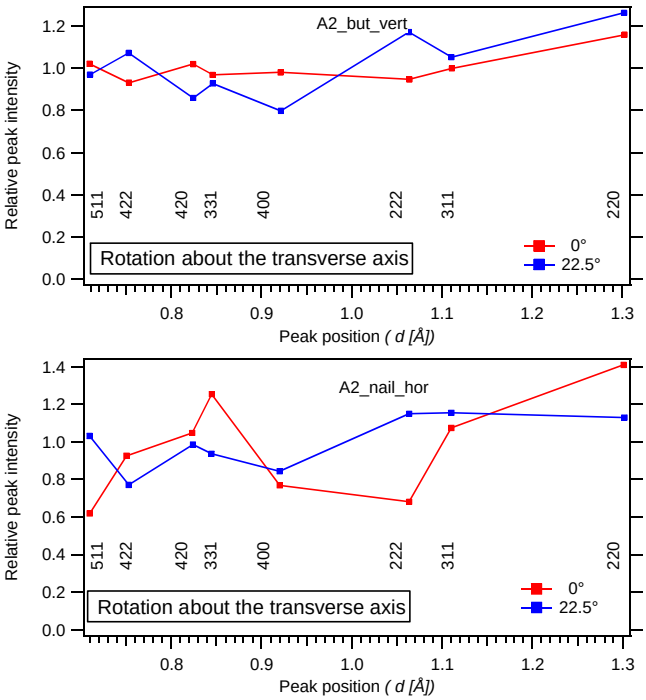

Fig. 9. Texture results of the TOF-ND analysis a: at the neck, b: at the edge of the Bonyhád axe (errors: ±0.07-0.015)

The bulk shows isotropic orientation distribution indicating, that the object was made by casting. Because of the small volume of the edge, the spectra taken from here are rather noisy. Even so, the presence of the texture is demonstrable, although its magnitude is uncertain. The most difficult was the investigation of the protrusions. Measuring from the direction

perpendicular to its surface, the scattering from the much larger volume barrel oppresses the signal from the surface layer and seems to be texture less. To separate the upper layer, spectra were taken from the direction nearly parallel to the surfaces, covering the barrels with absorber. The measured peak intensities indicate texture, but the angle dependence is rather weak. In summary, we concluded that the shoulders were formed after casting by hammering.

4.3. Oversized bronze spiral

Due to the its great size radiography and PGAA analyses were not acquired for the bronze spiral.

4.3.1. Elemental and phase analysis

By TOF-ND, the obtained tin content of the bronze spiral (code: S) is 10,38±0,5 wt%.

4.3.2. Production techniques

TOF-ND texture analysis were carried out in four parts of the spiral (Fig. 11):

1. In middle region of one of the coiled up spiral ends („*1a*"), from the opposite,
2. In middle region of the same coiled up spiral ends („*1b*"), from the back,
3. The octagonal cross-section part of the spiral rod („*2o*"),
4. The round cross-section part of the spiral rod („*3o*").

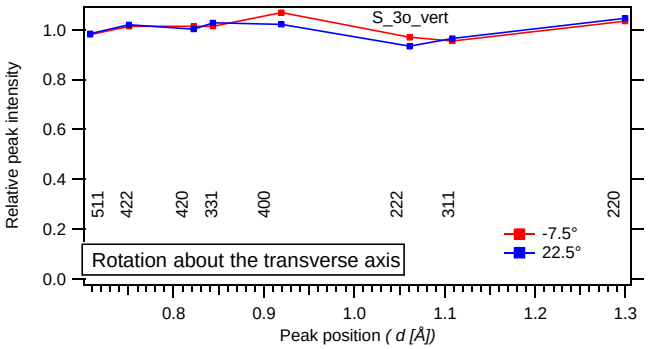

Fig. 10. Texture results of the TOF-ND analysis at the round cross-section central part of the Abaújdevecser bronze spiral (errors: ±0.02-0.004)

Since all the spectra – apart from one – show isotropic orientation distribution, indicating that the object is cast, the description of every single experiment would be meaningless. The only exception is the first one, where at 40 degree a weak anisotropy (hardly beyond the error) can be observed. It could come to existence during casting or finishing the surface, or some larger crystallites are present at this part.

5. Conclusions

5.1. Elemental and phase analysis

In case of the flanged axe from Zalaszabar, it was also possible to compare different analytical methods. Non-destructive TOF-ND analysis yielded results similar to the EDXRF method (Table 2), while the PGAA analysis provided somewhat discordant results regarding tin concentrations (Tables 1-2), that can be explained by non-homogenous composition of the prehistoric bronze objects. The PGAA and TOF-ND tin results of the special Bonyhád type axe agreed within uncertainty limits.

EDXRF analysis of the flanged axe from Zalaszabar showed an elevated arsenic, silver and antimony content, suggesting that the artefact was produced of ore from a deposite dominated by fahlores and chalcopyrite.[27] Silver content could be well measured by PGAA, but arsenic and antimony were below the detection limit.

5.2. Production techniques

The examined flanged axe (Fig. 4.1) was worked after casting at least at the edges. Metallographic studies of numerous flanged axes are in concordance with these results: at the neck the metal structure suggests nothing else, but as-cast microstructure. Near the edge, however, an ultrastructure, typical for working, could be observed.[28] Significant advantage of TOF-ND analysis was that we could reproduce the same results with a non-destructive method.

The neutron radiographic image showed light areas at different locations, that can be interpreted as presumable surface deviations, probably sites of corrosion, apart from the deviations from former sampling for EDXRF measurements. A casting in a standing position would be supported by the presence of bubbles at the upper end of the axe, but such bubbles could not be found in the case of this axe from Zalaszabar. Based on other technical details of production, the position of the fracture surface of the broken casting sprue, the axe was cast in a standing position. The homogeneity of the upper end of the axe (Fig. 6.1), supported by the lack of bubbles, show a good quality casting procedure. However, more exact localization of porosity spots would be possible by 3D tomography with higher energy, thermal neutrons.

The special Bonyhád type axe (Fig. 4.2) was cast and then worked at the edge (hardened and sharpened by hammering) that also suggests that it was used as a tool. The two small protrusions that also helped to fix the axe to the handle, were originally casting gates and their surface was later smoothened by hammering. This hammering resulted in the formation of flanges on them. The hammered surface was then decorated by punctuation (Fig. 4.2). Macroscopic casting defects (shrink holes), or other structural differences are not visible neutron radiographic image (Fig. 8).

Analysis of the bronze spiral from Abaújdevecser (Fig. 5) confirm that the lost-wax casting method was used during its production. First, a long wax rod was made, with an octagonal cross-section of its middle region. The thinner end parts were coiled up, mimicking the typical design of smaller, hammered arm/ancle rings with spiral ends. This resulted in mildly conical disks that were smoothened on the upper surface, keeping the streamline of cast metal also in mind. This process can be well reconstructed from the traces of coiling, differing on the two surfaces and the fine, crack-like lines created by the surface of the wax. After shaping the mass of the artefact, small pieces of wax were attached to the model at the centers of the disks, in order to place casting gates. This can be very well observed on one of the disks (Fig. 5), where the dimensions of the removed sprue can also be measured on the imperfectly hammered, otherwise typically granular surface. Before placing it into the casting mold, smaller corrections were also made on the artefact, one end was cut away, for example and a slant surface was established. During the casting process, the mold was placed horizontally, with the conical disks facing upwards (Fig. 5).

6. Summary

Regarding the elemental composition, it is important to compare the results of multiple methods (non-destructive PGAA and TOF-ND as well as EDXRF) when analyzing historical artefacts of non-homogenous compositions. EDXRF, is better suited for analysis of the surface layers, containing higher quantities of tin;[29] while mainly bulk raw material composition data could be obtained from PGAA and TOF-ND analysis.

NR and TOF-ND study of the three artefacts has served new information regarding the different phases of production and shed light on the function of the artefacts. Forging, as suggested by TOF-ND results, provides important information on the function of the special type axe from Bonyhád that could otherwise, based on its extraordinary shape, could be interpreted as a symbolic sign of prestige. Additionally, in case of the flanged axe from Zalaszabar, these results also help in the decision whether this artefact should be regarded as an ingot or a tool.[30-31] Forged edges of both axes provide strong evidence supporting that these artefacts were indeed used as tools. Our analyses show anisotropic structure proving post-casting elaboration (recrystallization), due to forging and annealing carried out following the casting procedure, on edges of the axe and the flanged axe. It is important to note that while post casting elaboration was formerly identified by destructive microstructure analysis of flanged axes,[32] we could detect the same without sampling or any destruction of the artefacts. Neutron radiographic images showed some sign of inhomogeneity, indicating signs of corrosion rather than imperfect casting.

The completely isotropic structure of the arm/ankle ring from Abaújdevecser, according to TOF-ND results, support the technological observations that the object was made by the lost-wax casting technique without any other post-casting procedures.

Based on the above we provide data completing the long discussion about the function of Early Bronze Age raw material ingots with the analysis of a flanged axe, without destruction of the artefacts. Forging suggests that the axes were used as tools, and not as prestige weapons or ingots, however flanged axes could also serve as ingots.[33] Significant advantage of our analysis was that we could produce results on production techniques with non-destructive methods, that is very important for the investigation of unique prehistoric metal artefacts considering aspects of heritage protection.

Acknowledgements

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Notes

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