

Available online at www.sciencedirect.com

SciVerse ScienceDirect

www.elsevier.com/locate/matchar

Archaeometallurgical characterization of the earliest European metal helmets

Marianne Mödlinger^{a,*}, Paolo Piccardo^a, Zsolt Kasztovszky^b, Imre Kovács^c,
Zoltán Szőkefalvi-Nagy^c, György Káli^d, Veronika Szilágyi^b

^aDipartimento di Chimica e Chimica Industriale (DCCI), Università degli Studi di Genova, Via Dodecaneso 31, I-16146 Genova, Italy

^bCentre for Energy Research, Hungarian Academy of Sciences, Konkoly Thege Miklós út 29-33, H-1121 Budapest, Hungary

^cWigner Research Centre for Physics, Hungarian Academy of Sciences, Konkoly Thege Str. 29-33, H-1121 Budapest, Hungary

^dWigner Research Centre for Physics, Hungarian Academy of Sciences, Konkoly Thege u., 29-33, H-1121 Budapest, Hungary

ARTICLE DATA

Article history:

Received 11 January 2013

Received in revised form

4 February 2013

Accepted 7 February 2013

Keywords:

Bronze Age

Helmets

Tin-bronze

Manufacturing techniques

Metallography

SEM-EDXS

PIXE

PGAA

TOF-ND

ABSTRACT

Archaeometric analyses on conical and decorated cap helmets from the Bronze Age are presented. The helmets are dated to the 14–12th century BC according to associated finds in hoards. Alloy composition, material structure and manufacturing processes are determined and shed light on the earliest development of weaponry production in Central and Eastern Europe. Analyses were carried out using light and dark field microscopy, SEM-EDXS, PIXE, TOF-ND and PGAA. The results allowed reconstructing the manufacturing process, the differences between the cap of the helmets and their knobs (i.e. alloy composition) and the joining technique of the two parts.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Bronze Age European metal defensive armour, as opposed to weapons, is scarce. With a few exceptions such as the armour from Biecz, Dendra or Knossos, the first armour appears in Central and Eastern Europe in the beginning of the Urnfield culture (ca. 1300 BC). Today, we know of approximately 120 helmets, 95 shields, 55 greaves and 30 cuirasses from the European Bronze Age. The distribution area of each type of

armour is different; only in the Carpathian basin and a bit further to the north we find all types of armour. Indeed, we do not know any finds of shields in France or the Iberian Peninsula, though depictions are known. In the United Kingdom, finds of metal helmets or greaves are unknown, while shield finds are common [25, pl. 166–167].

European Bronze Age helmets are distinguished in two main groups: in Western Europe, the conical cap is usually made of two halves, resulting in a central crest where the halves are joined

* Corresponding author. Tel.: +39 010 353 6145 (lab.), +39 340 1388 506.

E-mail addresses: Marianne.moedlinger@univie.ac.at (M. Mödlinger), paolo.piccardo@unige.it (P. Piccardo), kasztovszky.zsolt@energia.mta.hu (Z. Kasztovszky), kovacs.imre@wigner.mta.hu (I. Kovács), szokefalvi-nagy.zoltan@wigner.mta.hu (Z. Szőkefalvi-Nagy), kali.gyorgy@wigner.mta.hu (G. Káli), szilagyi.vera@gmail.com (V. Szilágyi).

together. In Austria, three cap helmets with different crests are known. Their chronological classification is still a matter of discussion (most recent: LIPPERT 2011). In Central and Eastern Europe, conical helmets, cap helmets and bell helmets dominate: all three types consist of a cap made of one single metal sheet. In most cases, the cap bears a central knob or socket. In the following, we focus on the manufacture of conical helmets, the oldest European helmets, and their successor, the decorated cap helmet. Of the conical helmets and decorated cap helmets (including fragments) discussed, two thirds could be studied in detail, since some are in private collections or simply could not be found in the museums concerned (Table 1).

Two conical helmets are under analyses at other facilities. The Hungarian helmets could be studied non-invasively only, without being brought outside the country. The European CHARISMA-project enabled analyses with Prompt-gamma activation analysis (PGAA), particle induced X-ray emission spectroscopy (PIXE) and Time of Flight-Neutron Diffraction (TOF-ND) at the Budapest Neutron Centre. The effectiveness of neutron-based methods in provenance, authenticity and conservation studies has been demonstrated earlier [2,7,14]. The micro-fragments of the helmets that museums allowed to be sampled were analysed with bright and dark field light microscopy and SEM-EDXS at the metallurgical lab of the DCCI, Università degli Studi di Genova.

2. The Helmets

So far, ten conical helmets are known; another close related find with boar tusk decoration is noted as well [5]. They are distributed from Knossos, Crete in the southeast of Europe to Biecz, Poland, in the northwest. The distribution centre, with the highest number of finds, is the Carpathian basin (Fig. 1). The helmets are dated to the 14–13th century BC; only the helmet from Knossos derives from the middle of the 15th century BC. Chronological aspects as well as development and distribution were recently discussed in detail [16]. Four helmets are complete or missing only small parts: Biecz, Dunaföldvár, Lúčky and Oranienburg. From the two Slovakian finds from Spišská Belá and Žaškov only the sockets are preserved. The helmet from Keresztéte consists today of one fragment only; however, an older photograph still shows an almost complete helmet [27, pl. 150:9]. The knobs are missing on the unfortunately not completely preserved helmets from Dunaföldvár and Keresztéte. The caps from the helmets from Knossos, Nadap and Síg are not completely preserved either; however, typological and chronological classification as well as sampling in two cases was possible. All conical helmets (Fig. 2) have a very thin cap, which is also indicated by their light weight, ranging from 353 g (Biecz) to 638 g (Oranienburg) and almost 700 g (Knossos) for complete pieces with a total height of 17 cm (Biecz) to 21 cm (Oranienburg). On top of the conical cap, a small, spool-shaped socket with hole in the centre was applied (Fig. 3). Only the helmet from Knossos has a riveted-on knob. The closely related helmet with the boar tusk decoration instead bears a knob, which was made out of the same bronze sheet as the cap and thus is a direct part of the cap. The socket or knob served to support an organic plume. According to the rivet holes all along the edge of the

helmets, usually an inner organic padding was riveted to the helmets.

Decorated cap helmets are more numerous than conical helmets. So far, seven complete helmets and nine fragments most likely belonging to decorated cap helmets are known (Fig. 4). The helmets are dated to the 12th century BC, maybe even up to the early 11th century BC [15]. The main distribution area of complete decorated cap helmets, though poorly provenanced, is the Carpathian basin. So far, the helmet from Paks represents the only known complete helmet with a firm provenance and more detailed find circumstances. Fragments of the same type of helmets are all part of large Late Bronze Age hoards and show a much wider distribution than the complete helmets (Fig. 1). The distribution area spreads from Elsterwerda, Germany, in the north to Poljanci, Croatia, in the south and from Strassengel, Austria in the west to Gușterița, Romania in the east. The completely preserved cap helmets from Žiar nad Hronom, Paks and four other examples from Hungary with uncertain findspot are richly decorated caps with tubular sockets on top. On the side of the helmets, two or three bundles of several embossed, parallel ribs are visible. On top of the cap of some helmets, the so-called star decoration is visible [15]. The helmets from Žiar nad Hronom as well as one from the former Guttmann collection are the only ones with cheek plates being preserved. This made it possible to connect the cheek plates from Gușterița, Hočko Pohorje, Mezőnyárad, Stetten and Uiora de Sus to this type of helmet as well. The cheek plates all have a rather round, kidney-shaped form with a central ridge. Unfortunately, three of the complete decorated cap helmets could not be studied in detail at all, since their actual repository is unknown. However, the alloy composition of the two helmets from the former Guttmann collection was previously published by Born and Hansen [3, p. 270].

The helmets were not worn on the bare head. An inner organic padding or a separate organic cap beneath was used. In addition, an organic plume – possibly feathers, horsehair or something similar – was attached to the knob or socket. Both types of helmets show regularly distributed rivet holes parallel to the rim of the helmet. Only the conical helmet from Biecz has three rivet holes each only in the centre of its broader sides – most likely to attach cheek plates. For chin straps, two rivet holes would be sufficient and they would not be so far from each other, as it is known from other bronze cap helmets (Thonberg, Wonsheim Szikszó). For the helmet from Biecz, we therefore have to assume a separately worn organic cap or padding under the helmet and not directly fixed to it. The other helmets instead show regularly distributed rivet holes all around the rim to attach the organic padding.

3. Protocol of Investigations: Invasive Methods

3.1. EDXS Compositional Analysis

The EDXS composition analyses were performed on drilling samples as well as cross-sections of microfragments mechanically sampled from the helmets or the cheek plates. In order to perform the metallographical analyses, the microfragments were mounted in epoxy resin and polished with diamond paste up to 0.25 μm of diameter. The alloy composition was characterized by

Table 1 – Conical helmets and decorated cap helmets. Overview on all helmets allocated to the two types. Already carried out analyses are mentioned as well.

Type	Findspot	Find circumst.	Condition	Museum	Inv. no.	Analyses
Conical	Biecz, Poland	Hoard (bog)	Complete	British Museum, London, United Kingdom	1868-1228.248	British Museum (in preparation)
Conical	Dunaföldvár, Hungary	Single find	Almost complete	Wosinsky Mór Megyei Múzeum, Szekszárd, Hungary	O.93.33.1	PGAA, PIXE
Conical	Keresztéte, Hungary	Hoard	Fragment	Magyar Nemzeti Múzeum, Budapest, Hungary	31/1941/1-25	PGAA, PIXE
Conical	Knossos, Greece	Grave	Almost complete	Heraklion Archaeological Museum, Heraklion, Greece	–	–
Conical	Lúčky, Slovakia	Hoard	Complete	Archeologické múzeum SNM, Bratislava, Slovakia	4518	–
Conical	Nadap, Hungary	Hoard	Half preserved	Szent István Király Múzeum, Székesfehérvár, Hungary	–	–
Conical	Oranienburg, Germany	River	Complete	Heimathmuseum, Oranienburg, Germany	–	H. Born in preparation (pers. comment)
Conical	Sig, Romania	Hoard	Fragments	Muzeul Județean de Istorie și Arlă-Zalău, Zalău, Romania	–	SEM, metallography
Conical	Spišská Belá, Slovakia	Hoard	Knob	Podtatranské Múzeum, Poprad, Slovakia	882	SEM, metallography
Conical	Žaškov, Slovakia	Hoard	Knob	Slovenské národné múzeum, Martin, Slovakia	3504	–
Conical	Unknown (related to conical helmets)	Unknown	Complete	Private collection	–	–
Dec. cap	Hungary	Unknown	Complete	Magyar Nemzeti Múzeum Budapest	62.1.213	PGAA, PIXE
Dec. cap	Northern Hungary?	Unknown	Complete	Magyar Nemzeti Múzeum Budapest	77.4.1	PGAA, PIXE
Dec. cap	Paks, Hungary	River (Danube)	Complete	Városi Múzeum Paks	2002.11	PGAA, PIXE
Dec. cap	Žiar nad Hronom, Slovakia	Unknown	Complete	Archeologické múzeum SNM Bratislava	AP 75.990	–
Dec. cap	Hungary (?) A	Unknown	Complete	Private collection	–	–
Dec. cap	Hungary (?) B	Unknown	Complete	Former Guttman collection; now unknown private collection	AG 246	AAS [26]
Dec. cap	Hungary (?) C	Unknown	Complete	Former Guttman collection; now unknown private collection	AG 1126	AAS [26]
Dec. cap	Veliko Nabrđe, Croatia	Hoard	Fragment cap	Arheološki muzej u Zagrebu	10.237	SEM, metallography
Dec. cap	Poljanci I, Croatia	Hoard	Fragment cap	Brodsko Posavlje Muzej Slavonski Brod	A 1805	SEM, metallography
Dec. cap	Elsterwerda, Germany	Hoard	Fragment cap	Landesmuseum Sachsen-Anhalt, Halle	10.727	–
Dec. cap	Strassengel, Austria	Hoard	Socket	Archäologiemuseum Schloss Eggenberg, Joanneum	7219	SEM, metallography
Dec. cap	Gușterița, Romania	Hoard	Socket	Muzeul Național Brukenthal Sibiu	546	–
Dec. cap	Stetten/Wöllersdorf, Austria	Hoard	Cheek plate	Naturhistorisches Museum Wien	37404	SEM, metallography
Dec. cap	Hočko Pohorje, Slovenia	Hoard	Cheek plate	Pokrajinski muzej Maribor	2146	SEM, metallography
Dec. cap	Uiora de Sus, Romania	Hoard	Cheek plate	Muzeul Național de Istorie a Transilvaniei Cluj	III 6005; III 5319	No; museum is under construction
Dec. cap	Mezőnyárád, Hungary	Hoard	Cheek plate	Herman Ottó Múzeum Miskolc, Hungary	74.38.1	No; lost?



Fig. 1 – Distribution map of conical helmets (●) and decorated cap helmets (○).

Energy Dispersive X-Ray Spectroscopy (using a PENTAFET® EDXS detector sensitive to light elements, $Z > 5$) connected to a Scanning Electron Microscope (SEM) Evo40 Zeiss. The operating conditions were: acquisition time of 60 s with 2000 channels of 5 eV each and accelerating voltage of 20 kV, $P < 10^{-5}$ bar. The cobalt calibration was applied with ZAF 5 correction and real standards for the quantitative analyses. Element concentrations lower than 0.3 wt.% were considered as semi-quantitative and taken into account only when the identification peaks were clearly visible in the spectrum acquired. The compositions as reported in the tables in this paper are normalized and in weight percent. They correspond to the mathematical average of 4 to 20 spectra with suitable fit index per each sample.

4. Protocol of Investigations: Non-invasive Methods

4.1. PGAA

Prompt-gamma activation analysis (PGAA) is a non-destructive bulk analytical method for quantitative determination of major and some trace elements. PGAA is based on the detection of characteristic gamma photons, emitted in (n,γ) reactions [21]. For the analysis, a selected part of an object is irradiated with a collimated beam of cold neutrons, and the emitted characteristic gamma photons are detected simultaneously. Since neutrons can penetrate deep into the sample material, the method provides an average bulk composition for the illuminated volume of a few cm^3 . Following the analysis no significant induced radioactivity is produced.

The PGAA analysis was carried out at the $10^8 \text{ cm}^{-2}\text{s}^{-1}$ intensity horizontal cold neutron beam of the Budapest Research

Reactor (for the recent developments of the Budapest PGAA system, see [24]). The prompt gamma spectra were collected by a Compton-suppressed HPGe detector, which has been precisely calibrated. The gamma-ray spectra were evaluated using the Hypermet-PC program [22]. The quantitative analysis is based on the k_0 principle, using the spectroscopic data libraries developed at the Budapest PGAA laboratory [8]. The composition was determined using the methods described by Révay [23]. In principle, PGAA enables quantitative measurement of all the chemical elements, but the detection limits depend strongly on the neutron absorption cross-sections of the given nuclei. With PGAA, we were able to quantify Cu and Sn content, as well as traces of Fe, Co, Ni, As, Ag and Cd in most cases. Unfortunately, Pb is one of the most difficult elements to detect; it can be quantified with acceptable precision only above 1.5 wt.%. The actual detection limits, however, depend on the matrix composition, as well as the acquisition time. Background corrections for the contribution of construction material (lead shielding against γ -radiation) were taken into account. The advantage of PGAA for archaeological objects is that it does not require sampling or any object preparation.

4.2. PIXE Analyses

External milli-beam particle induced X-ray emission spectroscopy (PIXE) is one of the most popular methods for non-destructive elemental analysis of archaeological objects. Illustrative applications can be found in the special publication of the EU COST Action “Ion beam study of art and archaeological objects” [9]. Some recent works on metal objects including bronzes should also be cited [4,11,12]. Energetic protons bombard selected spots on an object of practically any size and shape, and the characteristic X-rays produced are used for quantitative

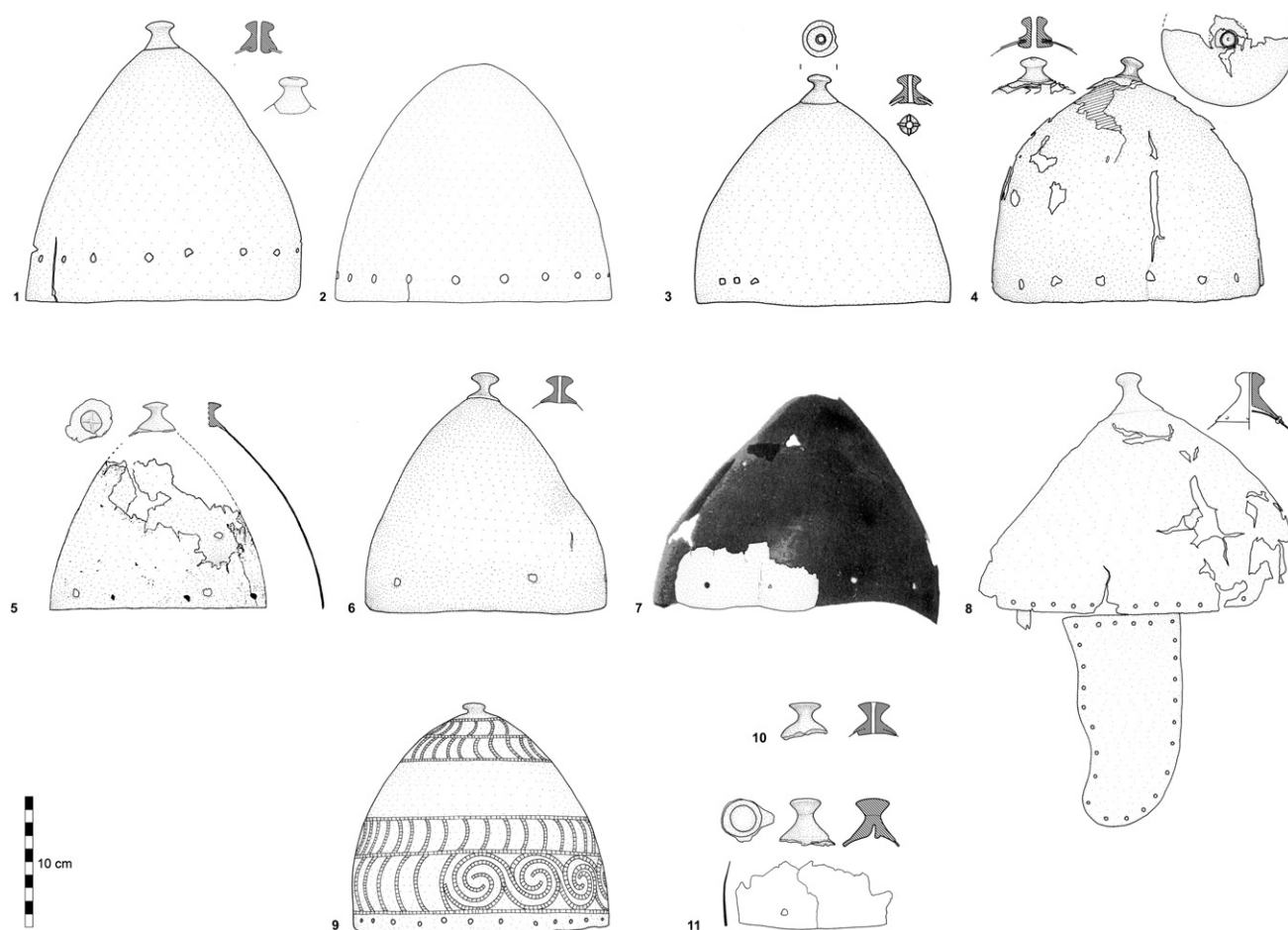


Fig. 2 – Conical helmets (scale: 1:4): 1 — Oranienburg. 2 — Dunaföldvár. 3 — Biecz. 4 Nadap. 5 — Sîg. 6 Lúčky. 7 — Keresztéte. 8 — Knossos. 9 — Unknown (Greece); related to conical helmets. 10 — Žaškov. 11 — Spišská Belá.

analysis of the irradiated volume. Taking into account both the slowing down of the bombarding protons in the sample and the absorption of the exiting X-rays, the method is inherently sensitive for the surface region of thicknesses up to some tens of a micrometer, depending on the composition of the sample and the proton energy. Among standard detection conditions, elements from Al to U can simultaneously be detected to ppm sensitivities under favourable conditions [13].

The PIXE measurements were performed at the 5MV Van de Graaff accelerator of the Institute of Particle and Nuclear Physics, Wigner Research Centre, Hungarian Academy of Sciences. The properly collimated proton beam of 2.5 MeV energy was extracted from the evacuated beam pipe to air through a 7.5 μm thick Kapton foil. Target-window distance of 10 mm was chosen for the measurements at which distance of the beam diameter was found to be about 1.5 mm. The objects to be analysed were fixed to a micro-manipulator, enabling accurate three-dimensional positioning. External beam currents in the range of 1–10 nA were generally used depending on the target objects. The characteristic X-rays were detected by a DSG Si(Li) detector of horizontal geometry positioned at 135° with respect to the beam direction. The energy resolution was 150 eV for the Mn Ka line. Conventional Canberra NIM electronics

and a Canberra 35+ MCA were used for signal processing and storing. The net X-ray peak intensities and the concentration calculations were made by the off-line GUPIX program package [6].

4.3. TOF-ND

The neutron diffraction technique is applicable for quantitative non-invasive bulk characterization of phase composition and the structural properties of the constituents of materials averaged in a macroscopic volume. In the present study, the helmets were investigated by the high-resolution time-of-flight diffractometer (TOF-ND) at the BNC. In this instrument the neutron pulses (as short as 10 μs) are produced by a fast double disc chopper, and the total flight path of neutrons to the detectors is 25 m. In the highest resolution mode and back scattering geometry – here detector position fixed at 175° – diffraction spectra with peak widths of $1.5 \times 10^{-3} \text{ \AA}$ can be collected. Since the penetration depth of neutrons in copper at the applied wavelength range is in the order of 1 cm, and the maximum beam size is $10 \times 2.5 \text{ cm}$, real bulk average results could be gained.

In the case of substitutionally disordered solid solutions (such as the alpha phase of tin bronze), the shape of the



Fig. 3 – The socket from the helmet from Žaškov. Note the line in the slimmer area of the knob, indicating the cast-on reparation on the socket base. On the inside of the helmet, a metal drop from the cast-on reparation is still visible.

diffraction peaks is mainly determined by the concentration distribution (within grains and/or spatial) of the solute atoms. Unless it is completely homogenised, other properties – such as stress, grain sizes, etc. — are difficult to determine from the peak broadening, the measurement was optimized to gain information about the phase composition in reasonable measuring time. The system was set up to cover three Bragg peaks due to non-coplanar reciprocal vectors of copper – (220), (311), and (222) – to let us take into account the preferred orientation.

The data analysis method was also chosen to precisely determine the alloying degree. Instead of any least square refinement methods, after the standard corrections (background, incoherent scattering, wavelength distribution and instrumental effects), three distribution functions were gained versus the relative peak shifts. This distribution functions were further corrected to individual shifts relative to each other and a common function was created versus the weight fraction of tin, using Vegard's law and taking into account the incoherent loss and crystallographic parameters. Finally, the central moments of the distributions were determined — here the average and the standard deviations are presented. This method allows treating any kind of concentration distribution, but it is assumed here that the alpha phase contains only tin. The method was

checked by as-cast and annealed 11% and 13% tin content reference samples (Fig. 5). The TOF-ND results were checked with reference bronzes with 11 and 13 wt.% of tin, giving an error of 1.5%.

The intensity per mass fraction of the delta phase was determined from higher concentration reference. The TOF and PGAA results show acceptable agreement (Fig. 6). Other phases, as alpha-delta, or inclusions as lead might also be detected if present in the appropriate volume concentration. The anisotropic peak shifts mentioned above – small elongation in the (111) direction – can indicate macroscopic residual stress. It was observed only on the knobs, although its magnitude was one order less than the peak width.

5. Results

5.1. SEM-EDXS

The results of the compositional analyses of all currently known and analysed conical helmets and decorated cap helmets are reported in Table 2. We consider not only the SEM-EDXS results by the main author, but also the previously published results from the AAS [3, 270] and the XRF analyses from the helmet connected to the conical helmets [5, 146], in order to provide an optimal overview on all the analyses carried out so far. The British Museum is currently analysing the helmet from Biecz, and H. Born (Berlin) is analysing the helmet from Oranienburg (H. Born, pers. comment). The elements detected with the SEM-EDXS can be distinguished in alloying elements (>2%), minor elements (0.1–2%) and trace elements (<0.1). Other elements eventually present are below the detection limit. All helmets as well as their knobs and rivets were made of tin-bronze with a wide range from 5.2 to 14.4% tin.

Elements including P, S, Ca, Si, Fe, Al and Cl were observed by SEM-EDXS analysis at the corrosion layer of the artefacts. These elements are commonly found in the corrosion of archaeological bronzes [10] that were deposited in soil, thus also giving indications about the soil context, a useful aid when the find context of the object is not known. Unfortunately, no samples could be taken from the helmets with unknown find context (all cap helmets; one from Žiar nad Hronom; the two complete cap helmets from the Magyar Nemzeti Múzeum, two from the former Guttmann collection and six from a private collection). Other important elements that might be found in the internal corrosion layers are As, Sb and Ag. Such elements show a lower ionic diffusivity in the copper based oxide matrix as is the case of tin. Therefore, whenever these elements are present as minor or trace elements in the alloy, they concentrate in the oxidised patina. Elements such as As, Sb and Ag present in the corrosion are usually not derived from the soil and they therefore contribute to the discussion about the (qualitative) amount of minor elements in the alloy — as also visible in the PIXE results of the helmet from most likely Northern Hungary or Keresztéte, Hungary. Sulphur, which is usually present as sulphide in copper alloys, does not react at room temperature during the corrosion process and is found untouched in composition and shape within the different corrosion layers. The intensive mechanical cold working with annealing treatments enabled extensive intergranular corrosion phenomena,

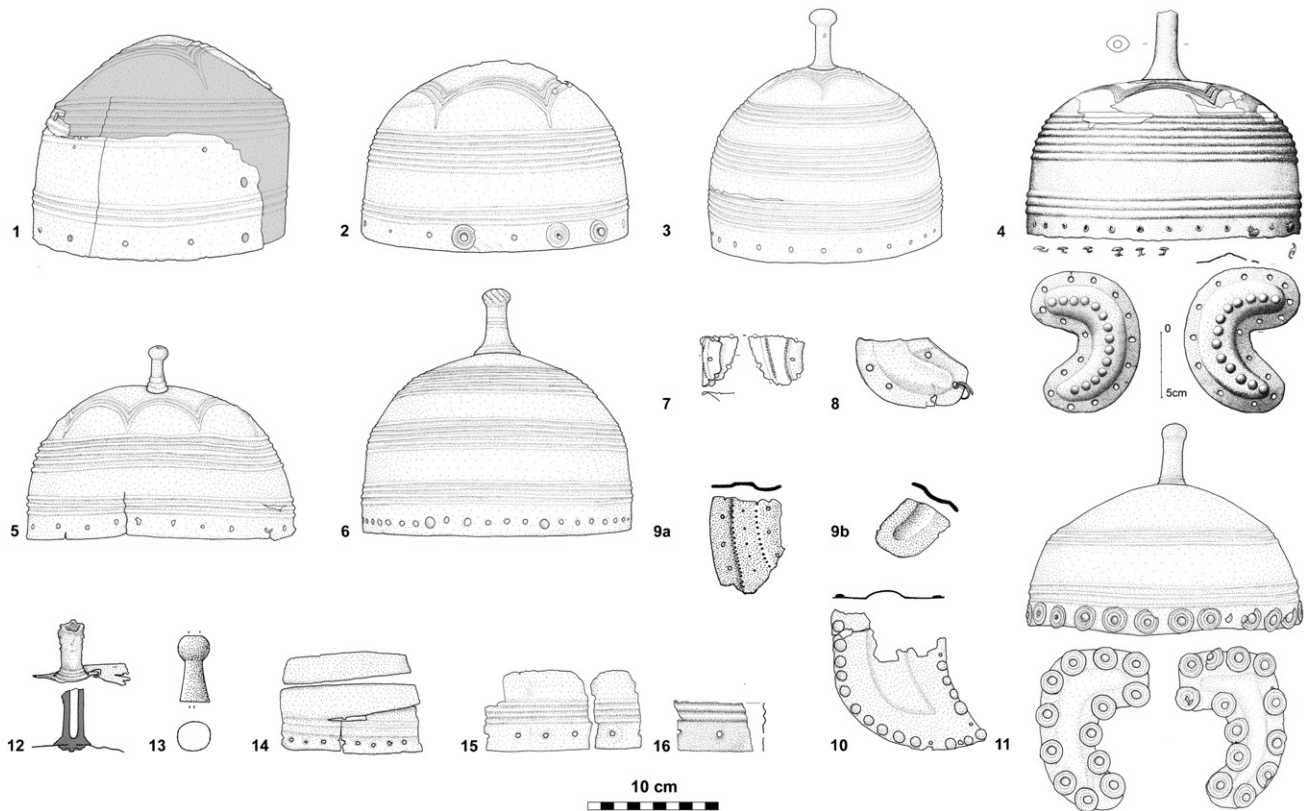


Fig. 4 – Decorated cap helmets (scale: 1:4): 1 — Hungary (recent reconstruction of the helmet marked grey). 2 — most likely Northern Hungary. 3 — most likely Hungary A. 4 — Žiar nad Hronom. 5 — Paks. 6 — most likely Hungary B. 7 — Hočko Pohorje. 8 — Wöllersdorf. 9 — Uiora de Sus. 10 — Mezőnyárad. 11 — most likely Hungary C. 12 — Strassengel. 13 — Gușterița. 14 — Poljanci I. 15 — Veliko Nabrdie. 16 — Elsterwerda.

since the grain size decreases while the amount of grain boundaries and distortions increases [18]. The intensive corrosion on some of the micro-samples made etching unnecessary, since the microstructure was already completely visible in the corrosion (Fig. 6).

5.2. PGAA, PIXE and TOF-ND

Since the study focuses on manufacturing techniques applied on the object, the apparent uncertainties for trace elements arising from the different natures of the methods do not severely

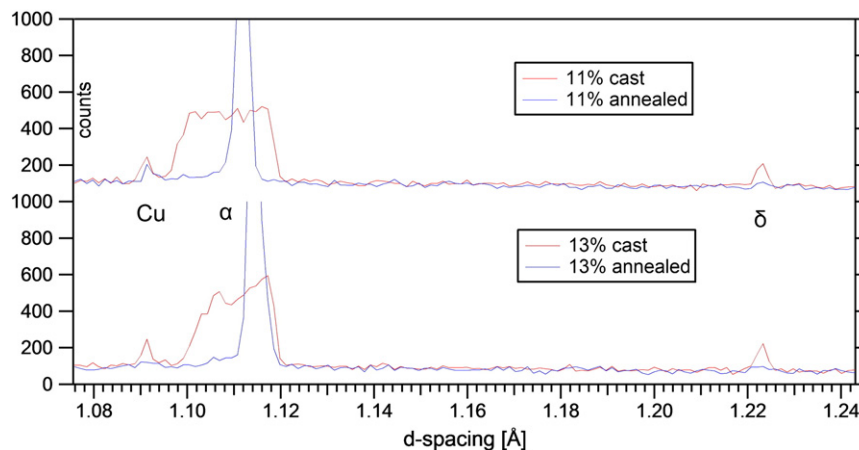


Fig. 5 – An extended part of diffraction spectra from reference samples. For homogenised 11% sample the analysis gives $10.973 \pm 0.15\%$, while for the 13% it gives 12.85% . There is a significant amount of low concentration and even pure Cu in the first. The missing amount can be present in the δ -phase below the observation limit. For the as cast samples (9.8% and 11.4% in α and 15.2% max.), the total mass fraction (including δ) is also within $\pm 0.25\%$.

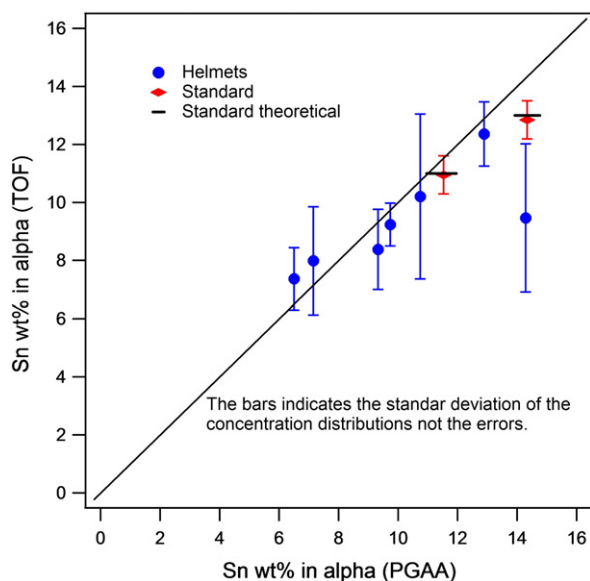


Fig. 6 – Comparison of PGAA and TOF data — errors are not indicated. For reference samples a scale factor slightly different from the unit can be estimated. The significantly underestimated point is discussed in the text (helmet from Keresztéte).

influence the conclusions of the study and are not considered in the following discussion. We consider the amounts of Cu, Sn, Pb and As (also as indicator for the corrosion level as discussed

afterwards) for the following discussion. For the main alloying elements (Cu, Sn), the PIXE analysis indicates a point-to-point variation of Cu and Sn concentration in the near surface layer and in the case of the helmet caps from Northern Hungary and Paks it deviates from that detected by PGAA and ToF in the bulk, which might be explained by corrosion and environmental effects on the surface. As already mentioned before, the quantification limit of Pb is around 1.5 wt.%, therefore we will apply (*) mark in the following tables to indicate that the Pb concentration measured by PGAA can only be considered qualitatively. The Sn in the bulk could be analysed by both PGAA and TOF-ND, and the results are in good agreement (Table 3).

In the following, the results of every helmet will be discussed separately. In accordance with the emphasis of this paper, alloying elements such as Cu and Sn as well as minor elements such as As and Pb, which can influence the manufacture of the objects, are considered.

5.2.1. Northern Hungary

The cap helmet from (presumably) Northern Hungary is made of a bronze sheet that is very thin, with an average thickness of 0.4 mm, and very light at 292 g. The helmet is completely covered with smooth, dark green corrosion products. Only in the area around the rivet holes is the cap less corroded. Here, carbonates are almost absent and mainly copper oxides remained. The PGAA was carried out in the green, copper carbonate rich corroded area of the cap, while the PIXE was carried out in less corroded areas next to the rivet holes. However, the high As amounts measured with PIXE is not detected by PGAA (since below detection limit).

Table 2 – Alloy composition of the helmets studied. According to the different methods used and cited, different sensitivities have to be noted.

Findspot	Point of analyses	Method	Cu	Sn	Pb	As	Ag	S	Ni	Fe	Co	Zn	Sb	Cd	Bi	Au	No. spectra
Sîg, Romania	Cap	SEM-EDXS	89.2	10.3	0.2	0.1	tr.	0.3	0.1	tr.			0.1				4
Sîg, Romania	Knob	SEM-EDXS	84.5	14.4	0.2	0.2	0.1	0.4	0.2	tr.			0.3				20
Spišská Belá, Slovakia	Knob	SEM-EDXS	85.1	13.5	0.2	0.5	0.2	0.3	0.1	0.2							5
Spišská Belá, Slovakia	Cap	SEM-EDXS	89.0	8.6	0.4	0.2	0.1	0.9	0.1	0.8			0.2				4
Stetten/Wöllersdorf, Austria	Cheek plate	SEM-EDXS	91.2	7.1	0.2	0.4	tr.	0.4	0.5	0.3							11
Strassengel, Austria	Cap	SEM-EDXS	89.0	8.5	0.1	0.5	tr.	0.4	1.0	tr.		tr.	0.3				5
Strassengel, Austria	Knob	SEM-EDXS	87.2	8.1	0.8	1.0	0.1	0.6	1.4	0.3	0.1		0.5				7
Veliko Nabrđe, Croatia	Cap	SEM-EDXS	87.9	10.8	0.3	0.2	0.1	0.5	0.2	0.1	tr.		0.2			0.3	7
Poljanci I, Croatia	Cap	SEM-EDXS	87.1	10.9		0.2	0.3	0.5	0.3	0.3	tr.	0.1	0.2	0.5		0.3	5
Hočko Pohorje, Slovenia	Cheek plate	SEM-EDXS	86.9	12.2	0.3	tr.	tr.	0.7	tr.	tr.	tr.						9
Hungary (?) B	Cap	AAS ^a	87.5	12.2	>0.025	<0.1	0.0		0.1	0.1	<0.005	0.0	0.1	<0.001	<0.025	<0.01	
Hungary (?) B	Knob	AAS ^a	86.9	12.9	0.0	<0.1	0.0		0.1	0.1	<0.005	0.0	0.1	<0.001	<0.025	<0.01	
Hungary (?) B	Rivet	AAS ^a	87.3	12.5	<0.025	<0.1	0.0		0.1	0.1	<0.005	0.0	0.0	<0.001	<0.025	<0.01	
Hungary (?) C	Cap	AAS ^a	87.6	12.1	0.2	<0.1	0.1		0.0	0.0	0.0	0.0	0.0	<0.001	<0.026	<0.01	
Hungary (?) C	Knob	AAS ^a	90.0	5.9	1.2	0.1	0.1		0.4	0.7	0.1	0.0	0.6	<0.001	<0.025	<0.01	
Hungary (?) C	Rivet	AAS ^a	90.7	5.2	1.0	1.0	0.1		0.4	0.9	0.1	0.0	0.6	<0.001	<0.025	<0.01	
Unknown (close to conical helmets)	Cap/knob	XRF ^b	90.0	10.0		tr.					tr.						

^a Analyses published by Born and Hansen (1991, p. 270). The sensitivities or the protocol of the AAS-analyses are not mentioned.

^b Analyses published by [5, 146].

Table 3 – Non-invasive alloy characterization of Hungarian helmets by PGAA, PIXE and TOF-ND. For better comparison of the results, TOF data are corrected for the mass fraction of Cu and Sn measured by PGAA. The measured values are marked in brackets.

Object		PGAA	Abs. unc ±	PIXE	Abs. unc ±	TOF	±	Sdv
Northern Hungary (cap)	Cu	90.6	1.0	83.1				
	Sn	6.3	0.3	8.7	0.59	7.1 (7.4)	0	1.1
	Pb*	2.3	1.0	1.8				
	As	<D.L.		3.6				
Northern Hungary (rivet)	Cu			84.3				
	Sn			10.0	0.9			
	Pb			1.6				
	As			2.90				
Dunaföldvár (cap)	Cu	83.8	1.0	85.5				
	Sn	12.4	0.5	11.6	0.61	11.9 (12.4)	0	1.1
	Pb*	3.7	0.9	0.2				
	As	<D.L.		0.1				
Paks (cap)	Cu	88.1	0.4	91.5				
	Sn	9.5	0.4	6.9	0.36	9.0 (9.2)	0	2.8
	Pb*	1.7	4	0.6				
	As*	0.1	0.01	0.3				
Paks (knob)	Cu	88.9	0.6	89.3				
	Sn	10.7	0.6	10.1	0.38	10.1 (10.2)	1	0.7
	Pb	<D.L.		0.2				
	As	<D.L.		0.1				
Keresztéte (cap)	Cu	81.6	1.6	82.5				
	Sn	13.6	0.7	14.1	1.10	9.0 (9.5)	1	2.6
	Pb*	4.0	1.7	2.0				
	As	<D.L.		0.5				

Therefore, we consider the analysed area as corroded with the corresponding enrichment of As. The Pb amount ranges in the cap of the helmet from 1.8 (PIXE) to 2.3% (PGAA) with an absolute uncertainty of $\pm 1\%$. Therefore, we consider Pb as minor element and not as alloying elements and the PGAA Pb value as quantitative. The range of Sn from $6.3\% \pm 0.3\%$ (PGAA) to $8.7\% \pm 0.6\%$ (PIXE) is most likely due to the different level of corrosion in the areas measured. Due to the thin metal sheet, the bulk analyses of PGAA and TOF as well as the PIXE analyses are considered semi-quantitative. In addition, the PIXE analyses of the one measured rivet of the helmet, which show an unusually high amount of As at 2.9%, indicate severe influence of corrosion on the analytical result and are therefore considered qualitative. The good statistical diffraction peaks from the TOF-ND are significantly broadened, but its shapes rather indicate the presence of microscopic strain than incomplete homogenisation. There are no traces of other phases, and the alpha phase contains $7.4 \pm 0.3\%$ tin.

5.2.2. Dunaföldvár

The surface of the helmet from Dunaföldvár was cleaned and copper carbonate corrosion products were eliminated. Today, mainly oxides remain as corrosion products on the surface. Three PIXE analyses were carried out on the corroded surface, giving an average of 11.6 wt.% that is in good agreement with the results obtained by PGAA and TOF. Lead is present as minor element (PIXE). The concentration distribution of tin as demonstrated with the TOF-ND reaches the maximum solubility, indicating that intermetallics should be present (e.g. alpha-delta eutectoid mixture). The separate delta phase peaks are not observable, but the alpha peak probably has weak satellites. However, the TOF data are representative for the alpha phase only.

5.2.3. Paks

Similarly to the helmet from Dunaföldvár, the main corrosion layers were removed mechanically from the helmet from Paks. Nevertheless, the surface is covered with (recent) oxides. Concerning the knob of the helmet, all three analytical methods show a similar amount of Sn, while the low amount of Pb measured with PIXE was below the detection limit of the PGAA. The results of the cap of the helmet, on the other hand, differ widely. TOF results for Sn are within the absolute uncertainty of the PGAA result. The PIXE results are much lower, most likely due to the impact of corrosion. Also, the amounts of As do not differ widely considering different levels of corrosion. The TOF-ND analysed demonstrated that the knob is a slightly homogenised pure alpha bronze with a wide continuous concentration distribution from zero to the maximum solubility. There is no trace of pure copper or intermetallics, and the knob most likely was cast in hot form. The cap is very well homogenised with a little bit lower mass fraction of tin, but internal stress can be present.

5.2.4. Keresztéte

The fragment of the helmet from Keresztéte is the most corroded, without any area of uncorroded metal surface visible. Concerning the amount of Sn, PGAA and PIXE results are similar, but the TOF results instead indicate much lower amounts of Sn. A possible explanation might be that PGAA and PIXE were influenced by the (Sn–Pb) soldering: two fragments of the helmet were soldered together during restoration. The amount of As measured with PIXE is reasonable and was below detection limit for the PGAA. PGAA measured $4\% \pm 1.7\%$ of Pb, while PIXE results show only 2%. The PGAA is considered as qualitative. Since the diffraction pattern of the TOF-ND measured on this specimen is very noisy,

the presence of other phases than the alpha cannot be ruled out. The Bragg peaks are very broad but symmetric. It is not clear whether this is caused by the concentration distribution (up to the maximum solubility) or internal stresses; both probably play a role. Nevertheless, the 9.5% tin content is representative for the alpha phase.

6. Discussion

6.1. Alloy Characterization

Unfortunately, it was not possible to measure each of the objects studied with all techniques available. The Hungarian finds could be studied non-invasively in Budapest only, while the other helmets could be sampled.

While TOF-ND and PGAA analyses – using neutrons of similar energies with similar penetration power – involve the whole volume of an object, PIXE is only applied to a restricted area. PIXE is sensitive for selected surface areas. Since all objects are affected by surface corrosion, we have to consider corrosion effects in the determination of the metal alloy composition. Considering the average thickness of the helmet's caps of 0.5 mm, where the corrosion covers usually more than 100 µm on both inside and outside as shown on reference micrographs of helmets of the same type as measured with PGAA and PIXE, certain elements such as As can be overestimated. These alteration layers can severely influence the average composition because they represent normally more than 40% of the sample. However, on samples with less corrosion, the results of TOF-ND, PGAA and PIXE are supposed to be in better agreement (i.e. Dunaföldvár) than on other, more severely corroded examples (i.e. Keresztéte). At the same time, it is important to remember that TOF-ND calculation method could be affected by the presence of other elements (As, Ni, Ag, Sb, ...) in the solid solution. Vegard's law should be recalculated in case of additional alloying elements other than tin.

The detected minor elements such as Ni, Ag, As, and Sb as well as Fe, S and Pb are common in prehistoric bronzes, and are directly connected to the smelting and melting processes of the copper ore and metal. Elements such as As or Sb also vary in quantity during remelting and recycling copper or bronze. Elements such as Ag, As and Sb usually concentrate as impurities on the grain boundaries, while Fe, Pb (up to 1 wt.%) and S are minor or trace elements mainly concentrated as inclusions (i.e. as iron rich copper sulphides or lead nodules). Normally, S and Fe form with Cu $\text{Cu}_2\text{-}_x\text{Fe}_x\text{S}$ -inclusions in the tin-bronze matrix. According to the main topic discussed in this article, we focus on the following alloying elements of the bronze used for the manufacture of the helmets. Detailed studies on trace elements or origin of the metal are not our primary interest here, and might be discussed elsewhere. Nevertheless, the rather high amounts of As (1 wt.%) and Ni (1.4 wt.%) on the socket of the helmet from Strassengel should be noted (SEM-EDXS on the cross-section). Obviously rather 'fresh' copper ore with rather high impurity amounts, such as Fahlore, was used for the production of the socket.

The amount of tin in the caps of the helmets ranges from 6 to 14 wt.%. A closer look at the distribution of tin quantity according to the type of helmet reveals that like the distribution of trace

elements, it is not dependant on date or type of the helmet. Half of the knobs or sockets show a tin values above 12 wt.% within a total range of 5.9–14.4 wt.%. Moreover (and keeping in mind the small number of analyses) we cannot detect a clear connection between date and type of the helmets; though it is worth noting that both knobs from conical helmets have the highest amount of tin. The knob and the cap of the helmet from most likely Hungary B and the cap and the knob from the helmet from Strassengel as well as (most likely) the knob and the cap from the helmet from Paks are each made of the same alloy, while the knob of the helmet from most likely Hungary C has only 6 wt.% Sn and the cap 12 wt.% Sn. The alloy used for cap and socket of the helmet of Strassengel is, concerning the Sn-amount, the same; only Pb, As and Ni amounts differ. All four helmets are decorated cap helmets. In contrast to this type of helmet, the conical helmets from Sîg and Spişská Belá have a different composition: the caps have 10 wt.% and 8.6 wt.% Sn, while the knobs show significantly higher amounts of Sn with 14.4 wt.% and 13.5 wt.%. Considering the production techniques, this makes perfect sense: the helmet's caps underwent extensive mechanical deformation while the knobs and sockets are as-casts. Additionally, differences in the metal colour were visible, once the helmet was freshly polished.

Having a closer look at the amount of tin according to the part of the helmet sampled, we notice that the two rivets have the highest variety from 5.2 to 12.5% Sn. Both rivets belong to the same type of helmet, so we can exclude a tin-amount depending on date or type of object. However, the tin-rich rivet of the helmet from the former Guttmann collection (Inv. no. AG 246) has the same composition as the associated cap and knob (see above), thus the high amount of tin in the rivet might be connected to the practicability of using the same alloy for all parts of the helmet. In general, however, rivets show much lower amounts of tin than the bronze parts they connect because of the demands placed on the material.

The two cheek plates analysed differ widely in their composition; the one from Hočko Pohorje, Slovenia, has up to 12.2% Sn

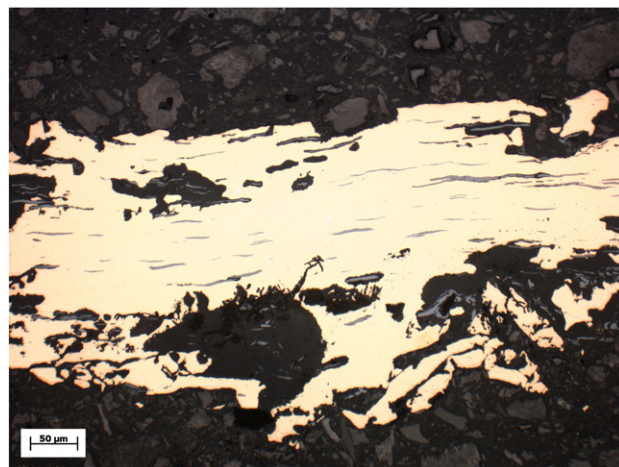


Fig. 7 – Helmet from Sîg, Romania. The micro-sample was taken close to the knob. Note the high deformation visible on the unetched sample. The $\text{Cu}_2\text{-}_x\text{Fe}_x\text{S}$ -inclusions are highly elongated but in the corroded area deformed and torn apart due to the heavy corrosion.

Table 4 – Average total deformation and thickness of the as-cast plates used for the production of the helmets.

Cat no.	Findspot	Sampled area	Thickness cap (mm)	Average total deformation %	Min. thickness of as-cast (mm)	Sn wt.% in alloy
C 9	Sîg, Romania	Cap close to knob	0.4	88	2.9	10.3
C 10	Spišská Belá, Slovakia	Cap close to knob	0.2	79	1.4	8.6
DC 8	Veliko Nabrđe, Croatia	Cap close to rim	1.0	78	4.6	10.8
DC 9	Poljanci I, Croatia	Cap close to rim	0.5	85	2.9	10.9
DC 11	Strassengel, Austria	Cap close to socket	0.5	94	7.8	8.5
DC 13	Stetten/Wöllersdorf, Austria	Cheek plate	0.7	77	2.9	7.1
DC 14	Hočko Pohorje, Slovenia	Cheek plate	0.4	83	2.2	12.2

and less minor elements, while the second one from Stetten/Wöllersdorf, Austria, only 7.1% Sn with slightly higher amounts of trace elements.

6.2. Manufacturing Process — Microstructural Observations

The first step of production was the cast of a circular, thin plate from which the caps and cheek plates were made. Since $\text{Cu}_2-x\text{Fe}_x\text{S}$ -inclusions deform in a manner similar to the metallic matrix and, moreover, are not influenced by the common annealing temperatures, their shape factor (SF) gives clear information about the total amount of deformation as well as the direction of the mechanical deformation applied during the manufacturing process [17,19]. It is important to use only inclusions from the intact metallic matrix, since aggressive corrosion can result in breakage and distortion of the inclusions as well (Fig. 7). The average SF (shape factor) and the corresponding percentage of reduction of the as-cast plate were calculated for every helmet cap fragment analysed (Table 4), indicating a minimum thickness of the as-cast raw plate of 1.7 mm. However, this value cannot take into account all material losses occurring during shaping, such as flaking off of oxygen, polishing and grinding and usage. The biaxial deformation is itself an approximation of the real movement of matter during the shaping process, the so-called die-forging. All helmets were manufactured following the same process, but with a slightly different intensity of total deformation (ranging between 78 and 94% and on the cheek plates from 77 to 83% of thickness reduction) according to the initial thickness of the as-cast. Slightly higher average total deformation was noticed near the socket/knob in comparison to the samples taken close to the rim of the helmets. Macroscopic analyses show a much thinner cap on top compared to the rim. Furthermore – as we can assume from the small number of sampled helmets – the average total deformation depends less on the tin-amount measured in our helmets, but more on the thickness of the as-cast plate. The value of the initial thickness of the as-cast plate should be considered as the minimum possible thickness obtained by casting because finishing and working losses decrease the value. The thickness of the as-cast plate depends furthermore on several factors such as casting temperature, composition, thermal properties and shape of the mould, speed of pouring and, of course, the composition of the alloy [20]. Sulphide inclusions as well as hammering traces (also clearly visible on the inside of the helmets, see Fig. 8) suggest biaxial deformation that produced a thinner and larger cap on which decorations were applied as the last phase of metalwork before the finishing of the surface.

To pass from the as-cast raw bronze disc to the final shape of the helmet's cap several steps of cold deformation by hammering followed by recrystallization annealing treatments were applied – most likely with die forging. The total deformation with these working steps reached up to 94% and on the cheek plates up to 83%. On some samples, the corrosion was developed to such a degree that etching was not necessary, since the corrosion followed the microstructure. Fig. 9 shows intergranular corrosion with recrystallized grains with slipping bands and mechanical twins crossing each other. Additionally, not etching enables further studies on corrosion products. The microstructural and compositional features of the cross sections generally show a still slightly inhomogeneous solid solution with deformed, polygonal recrystallized crystals with slip lines (Figs. 10–12 right). According to the Sn-amount in the alloy composition of the caps, the recrystallization annealing took place between 550 and 630 °C. Within this temperature range, the solubility of tin achieves its maximum with 15.8 wt.% in copper. The recrystallisation process – usually between 300 and 400 °C – therefore is fast, effective and with a certain grain growth [1]. For the alloys used, we can exclude hot deformation according to the high thermal conductivities of the alloys. During the deformation process it is normal that cracks appear on the rim of the deformed object. These cracks had to be chiselled off to avoid further growing, flaking off or the breakage of the future



Fig. 8 – Helmet most likely from Northern Hungary. On the inside of the helmet hammering traces are visible. Also, the left rivet hole was not completely punched through. Note also the manufacturing traces of the application of the embossed ribs.

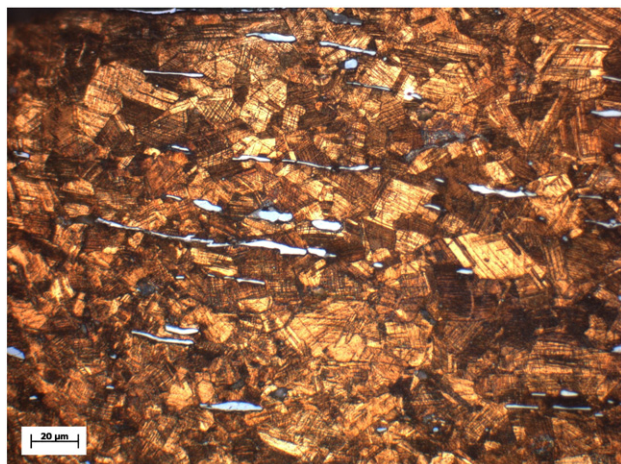


Fig. 9 – Microstructure from the cap of the helmets from Poljanci I. Both samples were taken close to the rim of the helmet and etched with FeCl_3 .

cap. Only one micro-fragment was taken from knobs and sockets, since the macroscopic studies already clearly demonstrate cast-on sockets for both types of helmets (see below). The knob from the helmet from Spišská Belá is as-cast, as is clearly visible from macroscopic investigation on all knobs and socket. Globular $\text{Cu}_{2-x}\text{Fe}_x\text{S}$ inclusions, α - δ eutectoid and dendritic structure are clearly visible (Fig. 12, left).

6.3. Manufacturing Process — Macroscopic Observations

Macroscopic studies reveal the same processes of manufacture for both types of helmets: the production of the cap with several cycles of hammering and annealing out of a circular, as-cast plate with a minimum starting thickness of 1.4 mm and a total deformation of 77–94%. After application of embossed decoration, rivet holes were punched through followed by the final grinding, polishing and smoothing of the surface. However, though it did not leave traces as β -phase due to the last annealing and hammering processes, we might also consider water quenching as part of the manufacturing process, as this

prevents the growth of brittle phases as delta-phase at the grain boundaries, thus facilitating the working process.

At the end, the knob or socket was cast on the top of the cap around a small, central hole, and also smoothed and polished. The as-cast surface of the cast-on is still visible on the inside of the helmets. As a final step, the cheek plates, the plume and the inner organic padding, possibly with a neck guard, were attached to the helmet. The only differences within the manufacturing process of the two types of helmets are the application of embossed decorative ribs on the cap helmets and the thicker rim or edge of the conical helmets, while the cap helmets show a rather thin rim. The rivet holes were made the same way on all helmets: after the cap was finished, the rivet holes were punched through from the outside to the inside with a chisel (when wider) or a pin/punch (when smaller). For conical helmets we can only assume cheek plates; aside from the helmet from Knossos, no further conical helmet with cheek plates is known. For decorated cap helmets we instead can assume the regular combination of helmet and cheek plates; two helmets (Žiar nad Hronom and most likely Hungary B) both have cheek plates and several single finds of similar cheek plates are known (Stetten, Hočko Pohorje, Uiora de Sus and Mezőnyárad). The cheek plates were attached to the helmets with bronze wire or directly with the inner organic padding. They were not attached directly with rivets to the helmet, since that would decrease the mobility of the plates. The rivets on helmet and cheek plates instead served mainly for the fixation of the inner organic padding, which might have consisted of linen, wool, fur, leather, rushes or similar materials or a combination of these.

Cast-on sockets appear first on the helmet from Biecz and are commonly found through the Late Bronze Age, i.e. on the decorated cap helmets discussed here or the later bell helmets. The two older Aegean helmets show a different application or design of the spool-shaped knob. The knob of the helmet from Knossos is riveted on with seven rivets, and the knob from the helmet related to the conical helmets is formed out of the same bronze sheet as the cap, but with double thickness [5]. The different methods of joining knob and cap might indicate different production centres for the helmet from Knossos and the helmet related to the conical helmets, and for the other

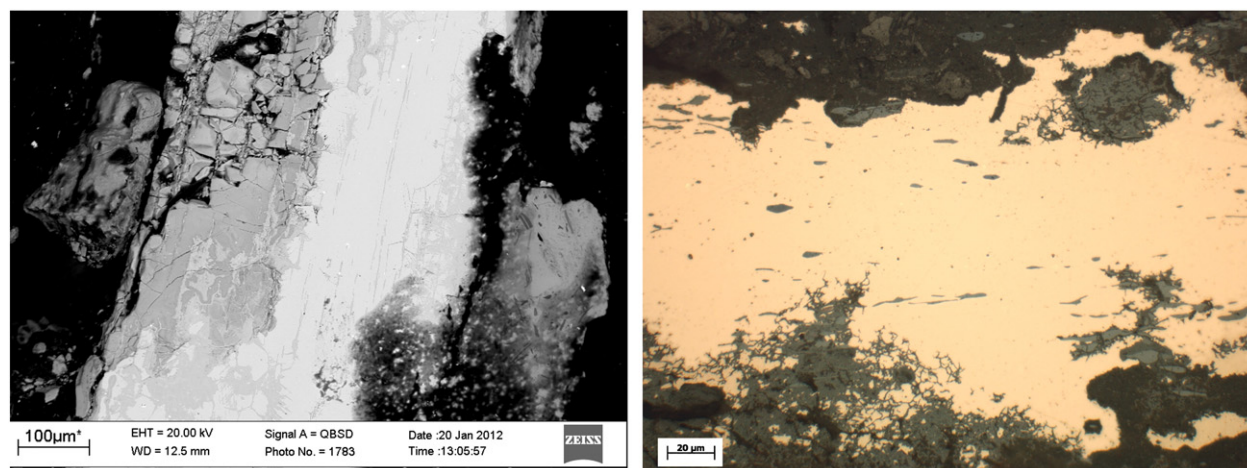


Fig. 10 – Intergranular corrosion shows recrystallized grains with slipping bands and mechanical twins crossing each other. Unetched helmets from Strassengel (left) and Spišská Belá (right). Both samples were taken close to the socket/knob.

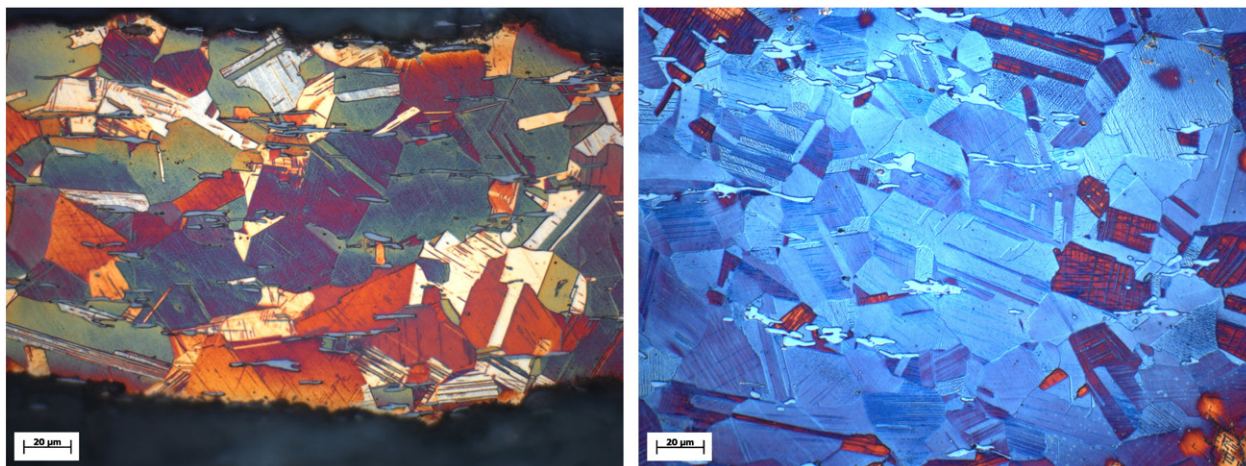


Fig. 11 – Microstructure from the cheek plate from Hočko Pohorje (left) and from the helmet from Veliko Nabrđe (right). The sample from the helmet was taken close to the rim of the helmet. Both samples were etched with Klemm II.

European helmets, and might also mark a development of manufacture. The socket from the helmet from Žaškov was repaired and the upper part cast on the lower part, thus resulting in a closed spool-like cross section that now only remains in the lower part (Fig. 3). A drop of metal from the upper part of the socket is still visible inside the central hole, which formerly passed all the way through the spool-shaped knob. The socket from the helmet from Sîg has a shallow, 3 mm diameter hole, which could not have been of much practical use.

The rim of the helmets from Biecz, Keresztéte and Lúčky was not completely plain; a small aperture or cut-out, meaning a shallow semicircular slice taken out of the rim or upward curve in the rim, is visible on one of the smaller sides of the helmets. It guaranteed most likely additional free moving space for the neck or it gave space to a possible organic neck guard, which could have been an extension of the internal organic padding.

After the smoothing of the outer surface to eliminate all traces of hammering, the decoration of the decorated cap helmets – circular ribs and the star-like decoration on top of the

helmet – was embossed using a chisel, as it is visible by the cross section of the embossed decoration and the smooth backside of the ribs. The application of the decoration also served practical purposes, since the decorative elements led to an enhanced stiffness of the thin cap. The final polishing of the surface was carried out with materials such as grinding stones, ceramics, sand, and clay with the support of leather or other organic or inorganic substances to obtain an optimum smooth and shiny surface.

7. Conclusions

Out of the total number of 12 conical helmets (including one related helmet with unknown repository) dated to the 15–13th century BC and with origins from Knossos, Greece to Biecz, Poland, detailed observations on manufacture traces could be carried out on eight helmets. Five helmets were studied even more detailed with SEM-EDXS and PGAA. To compare the helmets with the local successor type of helmet, the decorated

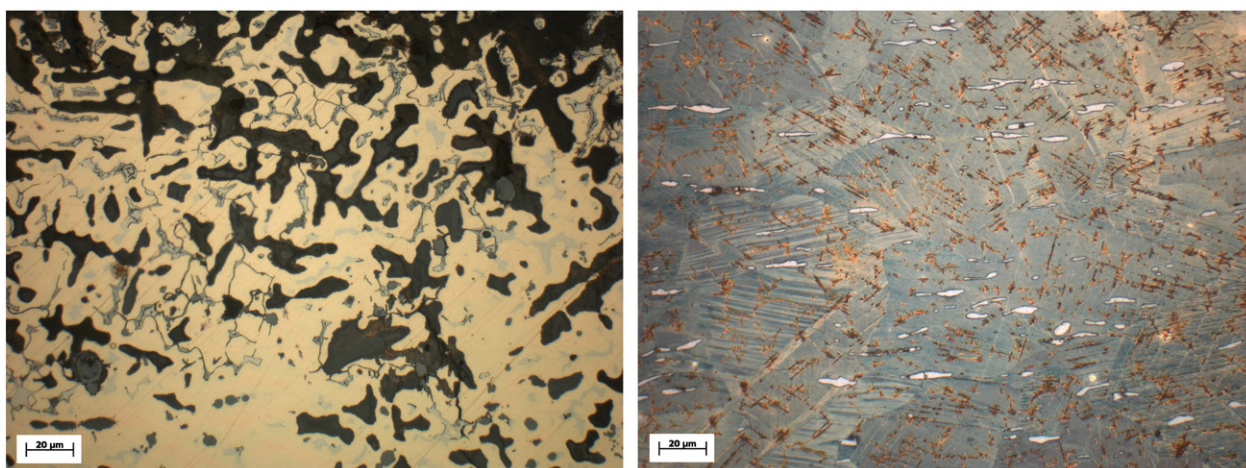


Fig. 12 – Unetched microstructure of the cast-on helmet knob from Spišská Belá (left). On the right, the microstructure of the cheek plate from Wöllersdorf, etched with Klemm II.

cap helmets, these helmets were studied as well. This type of helmet dates to the 12th century BC and has the distribution centre in the Carpathian Basin. From decorated cap helmets, seven complete helmets (of which three are in private collection and not accessible), three cap fragments, two single sockets and four cheek plates (two not accessible) are known. Out of the 12 accessible artefacts, all were studied in detail concerning manufacture traces. Eight of them were additionally studied in detail with SEM-EDXS and PGAA.

All helmets as well as their rivets, cheek plates and knobs were made of tin-bronzes within a range of 5–14 wt.% tin. For the helmet's cap, the tin-amount is between 6 and 14%, which indicates that advanced knowledge in the production of thin bronze sheet objects, even with higher tin amount up to 14 wt.%, was already present in the Middle Bronze Age. The other elements found in the alloys are considered minor or trace elements, resulting from impurities from the copper ores used as well as iron rich copper sulphides, representing the only typology of inclusions common to all findings. On six helmets (Síg, Spišská Belá, Paks, most likely Hungary B and C, Strassengel) the alloy composition of both cap and knob/socket was detected. The two conical helmets have knobs with 4–5% Sn than the cap; the knob of the decorated cap helmet most likely Hungary C instead shows a cap with 6% more tin than the socket. On the other three helmets, all decorated cap helmets, similar if not the same alloys were used for both cap and knob. There might be a connection with the desire, to have a brighter knob on conical helmets, and the same colour on both cap and knob a darker knob on the later decorated cap helmets.

The metallurgical features observed on cross sections of the caps of both types of helmets are coherent, suggesting the following manufacturing process: casting of the raw plate with at least 1.7 mm of thickness, mechanical shaping by several steps of cold hammering and recrystallisation annealing, mechanical production of decorations and final polishing. Combined with the macroscopic observations and the microstructure of the micro-sample from the helmet from Spišská Belá, we can reconstruct the following cast-on of the sockets or knobs with lost-wax-casting. After removing the casting relicts, grinding and polishing of the surface, the organic parts of the helmets were added: plum and inner padding, the latter fixed with rivets all around the edge of the helmets. Furthermore, we have to assume the combination of the helmet's cap with cheek plates.

The metallurgical analyses showed the same *modus operandi* for the two cheek plates studied as for the cap: casting of a small, raw disc with at least 2.8 mm of thickness in a closed mould, mechanical shaping by several steps of cold hammering and recrystallisation annealing with potential water quenching in order to avoid brittle phases, mechanical production of decorations and final polishing.

Acknowledgements

The authors would like to thank the Austrian Science Fund (FWF) and the FP7/Marie Curie actions who were supporting the research of Marianne Mödler with the Schrödinger-fellowship no. J 3109-G21. This research project has also been supported by the European Commission under the 7th Framework Programme through the Key Action: Cultural Heritage Advanced Research

Infrastructures: Synergy for a Multidisciplinary Approach to Conservation/Restoration, Grant Agreement Nr. 228330-CHARIS-MA. The PGAA experiments have been done with the support of NAP VENEUS05 Contract No. OMFB 00184/2006. Special thanks to the curators of the museums concerned who permitted the analyses and the sampling of the helmets: Jacqueline Balen (Arheološki muzej u Zagrebu, Croatia), Ioan Bejinariu (Muzeul Judeean de Istorie și Arlă-Zalău, Zalău, Romania); Katalin Biró and Ildikó Szathmári (Magyar Nemzeti Múzeum, Budapest, Hungary); Anton Kern and Hans Reschreiter (Naturhistorisches Museum Wien, Austria); Vesna Koprivnik (Pokrajinski muzej Maribor); Marta Kučerová and Magdaléna Bekessová (Podtatranské Múzeum, Poprad, Slovakia); Marko Mele (Archäologiemuseum Schloss Eggenberg, Joanneum); Lidia Miklik-Lozok (Muzej Slavonski Brod, Croatia); Péterfi Váradyné (Városi Múzeum Paks) and Márta Vizi (Wosinsky Mór Megyei Múzeum, Szekszárd, Hungary).

REFERENCES

- [1] Ammannati N, Ienco MG, Martellucci E, Piccardo P. L'energia di attivazione nel processo di ricristallizzazione del bronzo: influenza del tenore di stagno. *Metall Ital* 2006;1:31–8.
- [2] Arletti R, Cartechini L, Rinaldi R, Giovannini S, Kockelmann W, Cardarelli A. Texture analysis of bronze age axes by neutron diffraction. *Appl Phys* 2008;90:9–14, doi:10.1007/s00339-007-4225-0.
- [3] Born H, Hansen S. *Helme und Waffen Alteuropas. Sammlung Axel Guttman*, vol. 9. Mainz: Philipp von Zabern; 2001.
- [4] Bourgarit D, Thomas N. Late medieval copper alloying practices: a view from a Parisian workshop of the 14th century AD. *J Archaeol Sci* October 2012;39(10):3052–70.
- [5] Buchholz H-G, Matthäus H, Wiener M. Helmentwicklung und ein unbekannter altägäischer Bronzehelm. In: Buchholz H-G, editor. *Archaeologia Homerica 1, Kapitel E, Teil 3. Kriegswesen, Ergänzungen und Zusammenfassung*, Göttingen: Vandenhoeck & Ruprecht; 2010, p. 135–208.
- [6] Campbell JL, Hopman TL, Maxwell JA, Nejedly Z. The Guelph PIXE software package III: alternative proton database. *Nucl Instrum Methods B* 2000;170:193–204.
- [7] Cartechini L, Rinaldi R, Kockelmann W, Bonamore S, Manconi D, Borgia I, et al. Non-destructive characterization of compositional and textural properties of Etruscan bronzes: a multi-method approach. *Appl Phys A* 2006;83(4):631–6.
- [8] Choi HD, Firestone RB, Lindstrom RM, Molnár GL, Mughabghab SF, Paviotti-Corcuera R, et al. Database of prompt gamma rays from slow neutron capture for elemental analysis. Vienna: International Atomic Energy Agency; 2007.
- [9] Demortier G, Adriaens A, editors. *Ion beam study of art and archaeological objects*. European Commission; 2000 [EUR 19218].
- [10] Dillmann P, Beranger G, Piccardo P, Matthiesen H, editors. *Corrosion of metallic heritage artefacts — investigation, conservation and prediction of long-term behaviour*. Woodhead Publishing; 2007.
- [11] Gutiérrez Neira PC, Zucchiatti A, Montero-Ruiz I, Vilaça R, Bottaini C, Gener M, et al. Late Bronze Age hoard studied by PIXE. *Nucl Instrum Methods Phys Res, Sect B* 2011;269(24):3082–6.
- [12] Gyódi I, Demeter I, Hollós-Nagy K, Kovács I, Szőkefalvi-Nagy Z. External-beam PIXE analysis of small sculptures. *Nucl Instrum Methods Phys Res, Sect B* April 2 1999;150(1–4):605–10.
- [13] Johansson SAE, Campbell JL, Malmqvist KG. *Particle-induced X-ray emission spectrometry (PIXE)*. New York: John Wiley & Sons; 1995.

- [14] Kasztovsky Z, Rosta L. How can neutrons contribute to cultural heritage research? *Neutron News* 2012;23(1):25–8.
- [15] Mödlinger M. Star ornamentation on Late Bronze Age helmets, cups and decorated discs in central and south-eastern Europe. *Arheološki Vestnik* in press;64.
- [16] Mödlinger M. From Greek boar tusk helmets to the first European metal helmets: new approaches on development and chronology. *Oxf J Archaeol* in press;32(4).
- [17] Mödlinger M, Piccardo P. Manufacture of Eastern European decorative discs from the 12th century BC. *J Archaeol Anthropol Sci* 2012, doi:10.1007/s12520-012-0111-6 [online: 15.12.2012].
- [18] Pernot M. Forming bronze by plastic deformation around the 1st millennium BC in Western Europe. In: Yue S, Essadiqi E, editors. *Thermomechanical processing of steel*. J. J. Jonas Symposium. Met. Soc, Canada; 2000. p. 615–26.
- [19] Piccardo P, Pernot M. Studio analitico e strutturale di alcuni vasi celtici in bronzo. *Metall Ital* 1997;11:43–52.
- [20] Piccardo P, Amendola R, Adobati A, Faletti C. Studio della fluidità di leghe a base rame. *Metall Ital* 2009;5:31–8.
- [21] Révay Z, Belgia T. Principles of PGAA method. In: Molnár GL, editor. *Handbook of prompt gamma activation analysis with neutron beams*. Dordrecht/Boston/New York: Kluwer Academic Publishers; 2004. p. 1–30.
- [22] Révay Z, Belgia T, Molnár GL. Application of Hypermet-PC in PGAA. *J Radioanal Nucl Chem* 2005;265:261–5.
- [23] Révay Z. Determining elemental composition using prompt gamma activation analysis. *Anal Chem* 2009;81:6851–9.
- [24] Szentmiklósi B, Révay Z, Kis Z. Upgrade of the prompt gamma activation analysis and the neutron-induced prompt gamma spectroscopy facilities at the Budapest research reactor. *J Radioanal Nucl Chem* 2010;286:501–5.
- [25] Uckelmann M. Die Schilde der Bronzezeit in Nord-, West- und Zentraleuropa. *Prähistorische Bronzefunde* III, 4; 2013 [Stuttgart].
- [26] Born H, Hansen S. Ein bronzener Prunkhelm der Hallstattzeit. *Sammlung Axel Guttman* 1. Berlin: Verlag Sammlung Guttman; 1991.
- [27] Mozsolics A. Bronzefunde aus Ungarn. *Depotfundhorizonte von Aranyos, Kurd und Gyermely*. Budapest: Akadémiai Kiadó; 1985.