Interdisciplinary Study of a Bronze Hoard from Gorj County, Romania

Ana DROB¹, Petre COLȚEANU², Viorica VASILACHE³

Abstract. This paper presents the study of bronze artefacts resulting from an accidental discovery in the Preajba neighbourhood of Târgu Jiu municipality, Gorj County, Romania. In addition to the presentation of the field assessment and artefact analogies, the objects were analysed using optical microscopy (OM) and scanning electron microscopy (SEM) coupled with Energy-Dispersive X-Ray (EDX), in order to highlight the morphology of the corrosion crust and to determine the elemental composition of corrosion and soil contamination products. Thus, it was possible to establish the nature of the materials used and the manufacturing technology.

Rezumat. În lucrare se prezintă studiul artefactelor de bronz rezultate în urma unei descoperiri întâmplătoare în cartierul Preajba, municipiul Târgu Jiu, jud. Gorj, România. Pe lângă prezentarea evaluării de teren și a analogiilor artefactelor, acestea au fost analizate prin microscopie optică (OM) și microscopie electronică de scanare (SEM) cuplată cu energia dispersivă de raze X (EDX) pentru evidențierea morfologiei crustei de coroziune și stabilirea compoziției elementale a produșilor de coroziune și a celor din contaminare din sol. Astfel s-a putut identifica natura materialelor folosite și tehnologia de manufacturare.

Keywords: Bronze, corrosion, OM, SEM-EDX.

Introduction

Systematic research, as well as accidental discoveries, reveals a rich archaeological material that leads to a better understanding of the prehistoric communities. Study of whole or fragmentary artefacts, from different historical periods, by involving non-destructive (preserving the integrity of the artefact) or micro-invasive (the need for sampling or cleaning a very small surface due to the formation of corrosion layer on the artefact) analyses methods, aims to determine the composition of alloys, the mechanism of chemical,
electrochemical, microbiological corrosion, as well as the compounds formed by the alteration processes.

On the territory of Preajba locality, Gorj County, was discovered a bronze hoard and two atypical ceramic fragments, which are the object of another investigation. In this study were analysed only the metal fragments consisting of: three fragmentary bracelets, three fragments of a sword blade, a pendant and a celt fragment. The artefacts were analysed using OM and SEM-EDX methods in order to establish the raw materials and the production technology.

1. Archaeological context

After the accidental discovery of a bronze hoard made with a metal detector, in Preajba locality, Gorj County, a request was made by the Gorj County Department for Culture to conduct a field assessment to determine the archaeological potential of the region. The area under investigation is located in the Getic Subcarpathians, in the Târgu Jiu Depression. From an administrative point of view, the area is located in the north of Gorj County and belongs to the city of Târgu Jiu. The site where the hoard was discovered is approximately 2 km west of DC2 Preajba, in the forest, between two streams, the Holdun River to the east and the Gornac creek to the west (45° 04' 55.00643"; 23° 22' 36.96681") (Figure 1).

Initially, the research focused on the perimeter where the bronze hoard was discovered. To determine the archaeological context of the discovery, was drawn an archaeological trench (T1), oriented NW–SE, with dimensions of 5.30×1 m and with the depth of -0.60 m (Figure 2). In the trench profile were identified the remains of a pit, noted Context no. 1 (Cx. 1), with a depth of -0.30 m and an oval shape (0.60×0.40 m). This complex represents the hoard pit, largely destroyed in the moment of the discovery.

Following the field evaluation, it we decided to expand the research area because there were some clues that nearby were located a previously unidentified archaeological site, as well as a tumular necropolis. Both hypotheses have been confirmed. In the point called "La Fântâni" was discovered a settlement whose level of habitation begins during the

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5 From this deposit, two other celts were handed over by the management of the County Museum "Alexandru Ștefulescu" Gorj for analysis to another institution. The information according to which all the objects were in the same deposit is based only on the statements of the discoverer and on the report signed between him and the Gorj County Department of Culture.

6 The research team included Gheorghe Calotoiu ("Alexandru Ștefulescu" Gorj County Museum), Petre Colțeanu, Ana Drob and Sebastian Drob. We would like to thank Mr. Gh. Calotoiu for the kindness in giving us the materials for publication.

7 The field evaluation report was submitted to the Gorj County Department of Culture.
transition period to the Bronze Age (Coțofeni Culture), continues in the Bronze Age, and the latest archaeological materials identified belong to Hallstatt A (Vârtop Group). Site number 2, "In Pădure" is a tumular necropolis from which 16 mounds have been identified, without the possibility of cultural classification, these probably belonged to the first period of the Iron Age and the beginning of the second.

Figure 1. The discovery place of the bronze hoard

Figure 2. Archaeological context of the discovery: a-Archaeological drawing of trench 1 (Cx. 1 Pit containing bronze hoard, P1 Pit dug by the metal detectorist); b-photos during the survey
2. Materials and methods

2.1. Archaeological description of artefacts

*Bracelet fragment (Armringe) – B1* — The fragment (Figure 3) comes from a round bracelet with analogies in Transylvania at Moigrad \(^{10}\), belonging to the Moigrad-Tăuteu series (Ha B1- B2). The bracelet is broken from antiquity, the diameter of the section is 0.7 cm and the weight is 13.414 g, being decorated with rows of incised lines twisted around the bracelet.

*Bracelet fragment (Armschutzspiralen) – B2* — The second bracelet fragment (Figure 4) comes from an arm bracelet found in Transylvania, in Stâna \(^{11}\), being included in the Uriu-Domânești series (Bz D-Ha A1), as well as in Tăut \(^{12}\) and Aiud \(^{13}\), Cincu-Suseni series (Ha A1). The piece is torn from antiquity, but was also affected by the discoverer. It is round, the diameter of the section is 0.5 cm and has a total weight of 18.160 g, being decorated with a series of short incised lines twisted around the bracelet. The piece consists of three fragments, marked B2a, B2b, B2c that also correspond to the sampling areas.

*Bracelet fragment (Armschutzspiralen) – B3* — The third item is also an arm bracelet (Figure 5), having the same analogies as B2. This piece was also broken from antiquity and damaged at the time of discovery. The bracelet is circular with 0.4 cm diameter of the section and a total weight of 21.137 g, being decorated with a series of short incised lines on either side of the bar.

*Sword blade fragments (Schwerter) – S* — (Figure 6) have the best parallels in Caransebeș \(^{14}\), being part of the Cincu-Suseni series (Ha A1). The blade is broken from antiquity and, only three pieces were discovered (Sa, Sb, Sc). They have a width of about 3 cm, and a total length of 12.8 cm, with three nervures on each side. The total weight is 95.172 g.

*Pendant fragment (Anhänger) – P* — (Figure 7) it belongs to a pendant \(^{15}\), that has similarities in Transylvania, at Caransebeș \(^{16}\) (Bz D-Ha A1), Pecica I \(^{17}\) and Răbăgani \(^{18}\), Cincu-Suseni series (Ha A1). The pendant has five arms, four of which are broken from antiquity. The piece is not decorated and weighs 2.84 g.


\(^{11}\) PETRESCU-DÎMBOVIȚA 1977, 203, pl. 64/15; 1978, tafel 47/5.

\(^{12}\) PETRESCU-DÎMBOVIȚA 1977, 279, pl. 213/16; 1978, tafel 159/6; 1998, Tafel 20/156.


\(^{15}\) The terminology that defines this piece includes the variants: pendant, lunula, needle guard „Nadelhalter/Nadelschütz” — CHIDIOȘAN & EMÖDI 1981, 165.

\(^{16}\) GUMĂ 1992, 53–58/56.

\(^{17}\) PETRESCU-DÎMBOVIȚA 1977, 260, pl. 176/20.

Socketed axe fragment (Tüllenbeil) – C — (Figure 8) this piece weighs 22.535 g and the lack of specific elements makes it impossible to identify chronological and cultural similarities.

Figure 3. Images of B1: left – drawing; right – photo; a, b – sampling area

Figure 4. Images of B2: left - drawing; right - photo; a, b, c - sampling area

Figure 5. Images of B3: left – drawing; right – photo; a, b, c – sampling area
Figure 6. Images of S: left – drawing; right – photo; a, b, c – sampling area

Figure 7. Images of P: left – drawing; right – photo; a, b – sampling area

Figure 8. Images of C: left – drawing; right – photo; a, b, c – sampling area
2.2. Sampling areas

Samples for analysis were taken from areas with cracks or detachments, thus not affecting the integrity of the artefacts. These were noted with the letter P, followed by numbers from 1 to 6 in the order of the description of the pieces and the letters corresponding to the sampling areas illustrated in the figures of the objects (Figures 3–8).

2.3. Analysis methods

Microscopic analysis — The microscopic analysis was performed, at 50× magnification, with a Zeiss Stemi-2000C stereomicroscope that has a Canon G9 camera attached, from the Bioarchaeology Laboratory of the Arheoinvest Center from the “Alexandru Ioan Cuza” University of Iași.

SEM-EDX analysis — The analysis used a scanning electron microscope, SEM, model VEGA II LSH by TESCAN coupled with a third generation, X-flash type EDX detector, type QUANTAX QX2 made by Bruker/Roentec. The microscope, fully controlled by computer, has an electron gun with tungsten filament, which can achieve a resolution of 3nm at 30kV, with magnification power between 30× and 1,000,000× in "resolution" operating mode, acceleration voltage between 200 V at 30 kV, scan speed between 200 ns and 10 ms per pixel. The working pressure is less than 1×10-2 Pa. The images obtained for the analysed samples consisted of secondary electrons (SE) or backscattered electrons (BSE) at magnifications between 200× and 1000×. Quantax QX2 is an EDX detector used for qualitative and quantitative micro-analyses.

3. Results and discussions

The bracelet fragment – B1 was analysed OM on two areas (Figure 9/a). On the first one, the uniform patina without corrosion products is highlighted, and on the other, we can see traces of soil from the burial environment.

The SEM-EDX analysis was performed on a micro-sample of corrosion crust both at the interface with the metal (P1a) and on the external face (P1b), corresponding to the SEM images in Figure 9. The elements of the basic alloy were identified - Cu and Sn, the impurities in the ore (As and Fe), those in the corrosion products (C and O) and Si, Al and S that come from the soil contamination (Table 1). The higher concentration of Sn from the outside is due to the process of segregation to the surface, where it forms corrosion products. Due to its
amphoteric character and the tendency to agglomeration in the form of micro-lenticels, it controls both segregation and corrosion processes.\textsuperscript{19}

The bracelet fragment - B2, presents areas with detachments of the corrosion crust, and by the OM and SEM analysis (Figure 10/a, b) corrosion products of the basic copper carbonates type are highlighted.

Elemental analysis (EDX) was performed on two areas with corrosion products (P2a and P2b) and on one with the core (P2c). Thus, the elements of the basic alloy were highlighted: Cu and Sn, along with those of the ore Ni, Fe and As. The elements of corrosion and contamination products are the same as in B1, with the exception of S, which comes from the period of installation and use, having as source cysteine and cystine present on the human skin with which it has been in contact. The presence of Ag in high concentration (18.85%, 11.35% and 6.04%) only in corrosion products means that the artefact was coated with Ag, a process known since the late Bronze Age and illustrated by modern methods of analysis.\textsuperscript{20} The mapping performed on the analysed micro-samples highlights the arrangement of Ag (Figure 11/a–b), which confirms its presence in the silvering process.

The OM analysis (Figure 12/a) highlights the uneven arrangement of corrosion products, as well as areas of soil contamination. The EDX analysis was performed on the SEM images (Figure 12/b) corresponding to the core (P3a), the corrosion zone (P3b) and patina (P3c). Thus, the basic alloy consists of Cu and Sn, along with the ore microelements (Ni, Fe and As). In addition to corrosion products, higher concentrations of soil contaminants have been identified in the P3c area, in addition to Mg and K (Table 1). In addition, as in the case of fragment B2, Ag was identified in high concentrations (7.01%) arranged in the form of fine wires that indicate the use of the silvering process (Figure 12/a–b).

The sword blade (S) presents a uniform corrosion layer with detachments (Figure 14/b), and by the OM analysis (Figure 14/a), were identified deposits of basic carbonates and copper oxides randomly arranged. EDX analysis was performed on a surface area of each fragment (P4a, P4b and P4c) corresponding to the SEM images in Figure 14/b. Thus, the composition of the alloy was identified as Cu, Sn and Pb, along with the ore microelements - Fe and As (Table 1). The high concentration of lead indicates that it is part of the alloying elements, because bronzes with an appreciable Pb content are used to make objects that must withstand the action of prolonged slip.\textsuperscript{21} There are also elements from corrosion products (C and O) and those from soil contamination (Si and P).

OM and SEM analyses of the pendant fragment (P) highlight the uneven distribution of corrosion products (Figure 15/a, b).

\textsuperscript{19} SANDU et al., 2014, 918–927; VASILACHE, APARASCHIVEI, SANDU 2011, 117–126; VASILACHE et al., 2015, 633–642.
\textsuperscript{20} FIGUEIREDO et al., 2010, 287–289.
\textsuperscript{21} CURA D’ARS DE FIGUEIREDO JUNIOR, FREITAS CUNHA LINS, BELLIS, 2007, 7104.
The elemental analysis was performed on two areas (P5a and P5b), identifying the elements of the alloy (Cu, Sn and Pb), the elements in the ore (Fe, Ni and As), as well as the elements of the corrosion products and soil contaminations. The presence of lead in appreciable concentrations (7-8%), in the case of small objects, can be explained by its properties of increasing the fluidity and allowing the precise casting of parts that require details\textsuperscript{22}. 

<table>
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<th>Ag</th>
<th>As</th>
<th>Fe</th>
<th>S</th>
<th>Si</th>
<th>Al</th>
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\textsuperscript{22} GOFFER 1980, 170.
The OM and SEM-EDX analyses (Figure 16/a, b) on the socketed axe (C) were performed on a small sample taken from the area with active corrosion products, as follows: on the outside (P6a), the metal interface (P6c) and an area with a metal core (P6b). The elements of the basic alloy were identified: Cu and Sn and the ore microelements (Fe, Ni and As). Corrosion elements (C and O) and those of soil contamination (Si and Al) were also identified as can be seen from Table 1.

Figure 11. Images with Ag arrangement on the sample on the bracelet fragment - B2; a - SEM and b - Mapping of SEM surfaces

Figure 12. Images of the analysed area on the bracelet fragment – B3; a - OM and b - SEM

Figure 13. Images with Ag arrangement on the P3c sample; a - SEM and b - Mapping of the SEM surface
Figure 14. Images of the analysed area on the sword blade – S; a - OM and b - SEM

Figure 15. Images of the analysed area on pendant fragment – P; a - OM and b – SEM

Figure 16. Images of the analysed area on socketed axe fragment – C; a - OM and b - SEM
Conclusions

From a typological point of view, the hoard pieces have analogies in central and southwestern Transylvania and they can be assigned to Early Hallstatt, Cincu-Suseni (Ha A1) and Moigrad-Tăuteu (Ha B1–B2) series.

Based on the results obtained by combining the OM and SEM-EDX analyses, it can be said that the analysed fragments are made of Cu and Sn based alloys. Samples S and P also contains a high concentration of lead, which helps to increase the malleability for casting and the resistance to use of objects. Thus, we can assume that there is an important link between technological processes and the content of the alloy needed to make certain pieces, which indicates a good knowledge of the properties of these metals. Fragments B2 and B3 were silvered, a process known in the late Bronze Age in south-western Europe.

The presence of As even in very small quantities indicates that the objects were not obtained by melting metal scrap23. Traces of arsenic below 1% are the result of the use of polymetallic ores and not the result of an intentional production of arsenical bronze24.

During the burial period, the pieces underwent strong processes of segregation of active metals towards the surface and a series of degradations and damages, developed from the surface to the interior due to redox, acid-base and complexation processes, assisted by monoliths by including contamination elements from the ground. Thus, some chemical compounds such as oxides (CuO, Cu₂O, Fe₂O₃, Fe₃O₄, SiO₂, etc.) and basic carbonates (CuCO₃, Cu(OH)₂, CuSO₄.3Cu(OH)₆, etc.) have been identified in the corrosion of bronze.

Typologically, the pieces from the analysed hoard seem to come, most likely, from the Transylvanian metallurgical centre. Besides the analogies of the bronze objects, the place of their discovery represents another argument, the river Jiu's valley being probably a way of transporting the goods inside the Carpathian arch to the south, towards the Getic Plateau. A future objective is represented by performing other types of analyses in order to identify the source of raw material, which will lead to the identification of local productions or imports.

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23 BUGOI et al., 2013, 1242.
24 ZORI, TROPPER, SCOTT 2013, 1173.
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