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## Conservation and technological-chemical analyses of metal artefacts from the bronze hoard from Jabłonka

**Abstract:** The artefacts from Jabłonka were subjected to conservation treatment, including the application of a cutting-edge method of chlorine reduction in plasma chamber. In addition, technological-chemical analyses were carried out to determine the chemical composition of particular artefacts and identify the methods of their manufacture.

**Keywords:** conservation, copper alloy artefacts, corrosion, lost-wax casting, bivalve mould casting, tin bronze

### 1. Conservation and analysis of chemical composition

The artefacts from Jabłonka, Opolskie Province, submitted for conservation were made from copper alloy. Despite hundreds of years buried underground, the state of their preservation should be described as very good. They include the following objects: a cup with a riveted, band-like handle decorated with stamped and incised motifs; a decorated band bracelet; 4 decorated band armlets or ankle-rings (2 of them partly deformed by ploughing); 2 armlets or ankle-rings from an oval-sectioned bar, one of them twisted; 1 disc with a loop (phalera); and 1 socketed axe with a small loop. Apart from dirt resulting from the time spent in the soil, most of the artefacts were covered with a noble patina which, as the analysis has demonstrated, is comprised of compounds similar to malachite, i.e. basic copper carbonate ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ), with admixtures of other elements, for example Ca and Si. It should be mentioned, however, that destructive chloride compounds were also visible in places on the patina, in the dihydrate form ( $\text{CuCl}_2$ ). In order to protect them against corrosion all the artefacts were subjected to conservation, as well as to technological and chemical examination.

After washing all the artefacts with distilled water and removing the layers of dirt resulting from their deposition in the ground, the first stage of the works included observation with an optical microscope, aimed at preliminary assessment of the state of preservation and identification of the patina layer. The next stage was the analysis of chemical composition. After removing the patina in spots chosen for examination, the analysis was carried out with an energy dispersive X-ray fluorescence spectrometer of the Spectro-MIDEX type. The results were analysed using the TURBO QUANT programme from the SPECTRO X-LAB package.

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The primary goal of the analysis was the identification of the raw material from which the artefacts in question were made and an evaluation of its quality, which would help reconstruct the processes of manufacture.

The analysis showed that all the artefacts were made from bronze, i.e. alloys of copper with differing contents of tin and other alloying elements (Table 1). Next, all the artefacts were placed for one hour in a plasma chamber, in low-pressure hydrogen plasma which reduces chlorine compounds. The process was repeated four times. The verification with an EDS analysis using a scanning microscope showed a distinct drop in chlorine compounds in the patina, reaching 80%. In order to protect as much of the noble patina as possible and eliminate any potentially remaining deleterious chloride compounds, the artefacts were submerged in a 3% solution of benzotriazole in methyl alcohol. After drying in a heating chamber the surfaces of the artefacts were hot covered with a protective layer of microcrystalline wax and then polished.

**Table 1.** Chemical composition of artefacts from the Bronze Age hoard from Jablonka

ARTEFACT	Cu	Sn	Pb	As	Sb	Ni	Ag	Fe	Co	Ti	Zn
ARMLET 1	86.55	8.21	2.33	1.21	0.24	0.22	0.38	0.28	0.05	0.04	0.16
ARMLET 2	87.53	7.90	1.81	0.89	0.34	0.32	0.15	0.40	0.04	0.09	0.24
ARMLET 3	93.91	3.95	0.41	0.49	0.35	0.41	0.06	0.08	0.04	0.03	-
ARMLET 4	93.60	4.52	0.42	0.49	0.23	0.38	0.08	0.07	0.04	0.01	-
BRACELET 5	88.43	6.24	1.15	0.99	0.37	0.29	0.15	0.14	0.07	0.05	-
ARMLET 6	90.54	7.15	0.35	0.92	0.25	0.40	0.06	0.07	0.11	0.02	-
ARMLET 7	92.10	6.11	0.28	0.63	0.22	0.32	0.04	0.08	0.08	0.02	-
CUP 8	93.86	4.17	0.40	0.48	0.36	0.42	0.06	0.06	0.03	0.02	-
DISC 9	88.95	9.35	0.27	0.25	0.33	0.45	0.09	0.02	0.03	0.01	-
AXE 10	86.98	11.36	0.27	0.56	0.18	0.31	0.06	0.07	0.06	0.02	-

## 2. Analysis of the material

The analysis of chemical composition of the discussed artefacts has produced interesting results. Each of the 3 pairs of armlets or ankle-rings (nos. 1–2, 3–4, and 6–7) was cast from a slightly different raw material. The first pair (nos. 1–2, Fig. 3: 1–2<sup>2</sup>) was cast using the lost wax technique (Table 2), from tin-lead bronze (Cu-Sn-Pb), most likely from exactly the same raw material and in the same workshop. This is suggested by similar contents of basic alloying components used, namely copper (86.55%, 87.53%), tin (8.21%, 7.90%) and lead (2.33%, 1.81%). Such composition results in a multi-element alloy highly resistant to corrosion and makes it well suitable for casting and plastic treatment.

The second pair of armlets (nos. 3 and 4, Fig. 6: 1–2) was probably also cast in the lost wax technique (Table 2), from tin bronze (Cu-Sn) distinguished by a significantly higher content of

<sup>2</sup> Figure numbers refer to the illustrations in W. Blajer's paper in this volume.

copper (93.91%, 93.60%) at the expense of tin (3.95%, 4.52%) and lead (0.41%, 0.42%). Also in this case, the similar composition of the alloy suggests the same raw material and the same workshop.

The third pair of armlets – although representing different types (nos. 6 and 7, Fig. 6: 3–4) – was undoubtedly manufactured in the same manner as the previous two pairs, i.e. by the lost wax technique (Table 2). They were cast from tin bronze (Cu-Sn), and the contents of the basic alloying elements show a certain similarity to both the first and second pairs. The content of copper was 90.54% and 92.10%, tin 7.15% and 6.11%, and lead 0.35% and 0.28%, which allows us to assume that both armlets were made from similar material, probably originating from the same workshop.

Bracelet no 5 (Fig. 3: 3), in which the percentage values of the basic elements of the tin-lead bronze (Cu-Sn-Pb) are somewhat similar to the first pair of armlets (nos. 1 and 2), deserves particular attention. The copper content is 88.43%, with tin at 6.24% and lead at 1.15%. Thus, not only the similar ornamentation but also the raw material used for casting this artefact (in the lost wax technique – Table 2) suggests that the bracelet was manufactured in the same workshop and may have originally formed a set with armlets 1 and 2.

It is also worth noticing a certain resemblance in terms of raw material between the decorated phalera and the axe (Fig. 9: 1–2). Both artefacts were made from tin bronze (Cu-Sn), with copper contents of 88.95% and 86.98% respectively, and with much greater contents of tin than in the objects discussed above, amounting to 9.35% and as much as 11.36%. Such high tin content considerably increases the hardness of the alloy which, in the case of the axe, is quite understandable and surely intentional. Also in the Roman Period, when making brooches the alloys used for pins were richer in tin than those from which bows were made (cf. Biborski *et al.* 2016, 263, table 2). Both objects were cast, but using different methods: the phalera was cast in the lost wax technique and the axe in a bivalve mould (Table 2). The axe has a large fracture near the cutting edge. This is a manufacturing defect, resulting from stress created by the segregation of metal crystals, probably due to too rapid cooling. The segregation in bronzes can be removed by long annealing, which apparently was not applied in this case.

In terms of artistic qualities and technology the cup (Fig. 7–8) stands out from the other artefacts. It was made from sheet metal, probably formed from a lump of tin bronze (Cu-Sn) using the repoussage technique, in which sheet metal is shaped with special hammers and punches, allowing for the manufacture of objects lavishly decorated with complex relief motifs (cf. Blajer, in this volume). In the places where it has been hammered, not only does the sheet metal become thinner, but its crystalline structure partially modifies and thus weakens, which results in accelerated corrosion. In the case of the discussed cup this phenomenon can be observed in a few places in the form of perforation of the sheet metal.

Finally, it is worth mentioning the other alloying components identified in the Jablonka bronzes, which were recorded as trace elements, such as As, Fe, Ni, Sb, Co,

**Table 2.** Technology of manufacture of artefacts from the Bronze Age hoard from Jablonka

ARTEFACT	ALLOY TYPE	TECHNOLOGY
ARMLET 1	Cu-Sn-Pb	Lost-wax cast, chased
ARMLET 2	Cu-Sn-Pb	Lost-wax cast, chased
ARMLET 3	Cu-Sn	Lost-wax cast, chased
ARMLET 4	Cu-Sn	Lost-wax cast, chased
BRACELET 5	Cu-Sn-Pb	Lost-wax cast, chased
ARMLET 6	Cu-Sn	Lost-wax cast, chased
ARMLET 7	Cu-Sn	Lost-wax cast, chased
CUP 8	Cu-Sn	Repoussé
DISC 9	Cu-Sn	Lost-wax cast, chased
AXE 10	Cu-Sn	Bivalve mould, chased

Ag, and Ti. They usually accompany the ores of copper and tin and are believed to have no significant impact on the quality of the produced raw material. On the other hand, small admixtures of lead (from 0.27% to 2.33%), as well as zinc, which was identified in the first two armlets (nos. 1–2, between 0.16% and 0.24%), were probably components added intentionally. Even the slightest addition of such metals, and an increase in their contents up to a few percent, improves the casting properties, increases workability, and results in better plasticity of bronzes (Wesołowski 1981, 420–423; Dobrzański 1999, 505–508). One should also notice the considerable similarity of percentage values of the above-mentioned trace elements in all of the analysed artefacts. This allows us to suppose that all the objects were most likely made from copper ores originating from one geographic region and manufactured in one workshop. One can suggest here the exploitation of deposits of chalcocite ( $\text{Cu}_2\text{S}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), or other minerals, which can be found, among other places, in the ores from Sudetic sediment deposits.

### Konserwacja i technologiczno-chemiczne analizy metalowych wyrobów ze skarbu brązowego z Jabłonki

Na większości zabytków z Jabłonki zachowała się patyna szlachetna, którą tworzą związki zbliżone do malachitu, z domieszkami m.in. Ca i Si. Stwierdzono też, że miejscami występują szkodliwe związki chlorkowe ( $\text{CuCl}_2$ ). W celu zabezpieczenia przed dalszym działaniem korozji wszystkie zabytki poddano zabiegom konserwatorskim oraz badaniom technologiczno-chemicznym.

Po umyciu wodą destylowaną i odczyszczeniu zabytków z warstw zabrudzeń, w pierwszym etapie prac przeprowadzono obserwacje pod mikroskopem optycznym, mające na celu wstępną ocenę stanu zachowania oraz identyfikację materiału i warstwy patyny.

Analiza wykazała, że wszystkie zabytki wykonano z brązu, ze stopów miedzi o różnej zawartości cyny i innych pierwiastków stopowych (Tabela 1). Do prac konserwatorskich wykorzystano komorę plazmową, z plazmą wodorową, o działaniu redukującym związki chloru. Proces ten prowadzono czterokrotnie w czasie 1 godziny. Następnie w celu zablokowania ewentualnych pozostałych szkodliwych związków chlorkowych zabytki poddano kąpielom w 3% roztworze benzotriazolu, w alkoholu metylowym i zabezpieczono je warstwą wosku mikrokrystalicznego.

Z przeprowadzonych badań wynika, że każda z 3 par naramienników lub też nagolenników została wykonana z innego materiału. Pierwsza para odlana została na wosk tracony z brązu cynowo-ołowiowego (Cu-Sn-Pb), najpewniej z tego samego surowca i w tym samym warsztacie. Kolejna para naramienników odlana została także prawdopodobnie na wosk tracony z brązu cynowego (Cu-Sn), z tego samego materiału i w tym samym warsztacie. Trzecia para naramienników (nr 6 i 7) niewątpliwie także została wykonana w ten sam sposób co dwie poprzednie (Tabela 2), z brązu cynowego (Cu-Sn), pochodzącego zapewne z tego samego warsztatu.

Na uwagę zasługuje bransoleta, u której skład podstawowych pierwiastków stopu brązu cynowo-ołowiowego (Cu-Sn-Pb) pod pewnymi względami zbliżony jest do pierwszej pary naramienników (1 i 2). Możemy przyjąć, że ornamentyka i materiał użyty do odlewu zabytku w technice na wosk tracony (tabela 2) pozwala łączyć ową bransoletę z tym samym warsztatem i być może stanowiła ona komplet z parą naramienników 1 i 2. Pewne podobieństwo pod względem materiałowym występuje pomiędzy ozdobną tarczką z uszkiem i siekierką. Oba zabytki wykonano z brązu cynowego (Cu-Sn) o wysokim udziale cyny. Oba wykonano metodą odlewu, jednak z tą różnicą, że tarczkę na wosk tracony, a siekierkę w formie odlewniczej (Tabela 2).

Całkiem odmiennie pod względem artystycznym i technicznym przedstawia się czarka. Wykonana została z blachy wykutej zapewne z placka brązu cynowego (Cu-Sn), przy użyciu techniki trybowania.

Reasumując należy wspomnieć też o pozostałych składnikach stopów brązów z Jabłonki, występujących w ilościach śladowych, takich jak As, Fe, Ni, Sb, Co, Ag i Ti. Znaczne podobieństwo wartości procentowych pierwiastków śladowych wśród badanych zabytków pozwala sądzić, że wszystkie zostały wykonane z rud miedzi pochodzących zapewne z jednego regionu geograficznego i w tym samym warsztacie.

## References

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