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The Analysis of Foundry Engineering of Copper Alloys Based on the Research of a Metallurgist Settlement in Szczepidło

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Abstract

The article presents chosen aspects of foundry engineering of the settlement dwellers, including the archaeometric characteristics and metal science analysis of the artefacts, as well as an attempted reconstruction of the production organization. Discovered in Szczepidło (Greater Poland), the foundry workshop is unique in Central European Bronze Age.

This workshop foundry operated roughly XIV-XII Century BC. Its production is evidenced by the presence of markers of the whole production cycle: semi-finished and finished products, production waste, fragments of crucibles and casting ladles with traces of usage, and tools. On this basis, the alloys and foundry technologies used have been described.

The analysis of foundry technology of copper alloys in the settlement area was carried out by observing the surface and structure of the products, semi-finished artefacts and fragments of crucibles by applying optical microscopy (OM), confocal microscopy (CLSM) and X-ray radiography (RT). The investigations of compositions were made by means of the energy dispersive X-ray fluorescence spectroscopy (ED-XRF) and scanning electron microscopy (SEM) coupled with an energy dispersive X-ray analysis system (EDS).

Keywords: Non-destructive testing, Archaeometallurgy, Bronze age workshop, Investment casting, Copper alloys, X-ray fluorescence spectroscopy

1. Introduction

The history of casting technology is documented in metalworking evidenced by castings, crucibles and casting moulds, found at archaeological sites [1-2].

One of the earliest settlement on which local foundry activity from the Early Bronze Age was identified is Bruszczewo, Greater Poland. [3-6].

During the ten-year-excavations in Szczepidło (Konin District, Greater Poland) conducted by Institute of Prehistory, Adam Mickiewicz University in Poznań, there were documented relicts of a Bronze Age settlement together with proofs of mastering the melting and casting technology for copper alloys as well as developing the production of bronze artefacts. The origin of this metallurgical workshop was dated to 1350-1150 BC [7]. In the settlement area, there were noted numerous traces of intensive and long-term foundry manufacturing: scrap of bronze

artefacts, semi-finished products and slags, pieces of raw materials as well as fragments of crucibles and ladles. The analysis of their spatial distribution revealed their concentration in one feature, defined as a metallurgical workshop. The evidence obtained testifies to the use of, among others, the lost-wax casting method in copper alloys casting.

The lost-wax casting was one of the oldest manufacturing methods, used in the production of weapons and ornaments. Today, the method is still refined in terms of materials used, and the castings produced in this way are used both in military and medical industries, as well as jewelry and many others [8-15].

2. Method and Materials

At the discussed site, there were documented 140 items of bronze, including completed products, but, what is especially important for recognizing the technology, also semi-finished products, production waste and lumps of raw material. The paper presents the study of fragments of ceramic crucibles, conducted with optical microscopy (OM), confocal microscopy (CLSM), X-ray radiography (RT) and X-ray fluorescence spectroscopy (XRF). Semi-finished products, finished products and production waste were tested using the energy dispersive X-ray fluorescence spectroscopy (ED-XRF) and scanning electron microscopy with X-ray microanalysis (SEM-EDS). The investigations were realized at AGH - University of Science and Technology in Kraków.

3. Results

The archaeometric characteristics of the effects of the casting process have been conducted by discussing successively the groups of finds. The results have been supplemented with regard to the data published earlier [7] and have been presented in the form of graphs.

3.1. Crucibles – industrial ceramics

In the group of artefacts linked to the foundry workshop, a set of ceramic objects was assembled. After conducting the observations and analyses, it was confirmed that they served as crucibles in the technological process of copper alloys. The crucibles were made from clay with a significant amount of sand, which allowed the removal of moisture and heat exchange, and it affected the required fire resistance of the ceramics. The following are the chosen results that demonstrate that the ceramics were in contact with the liquid metal. This contact resulted in penetration of metal into the porosity of the crucible walls, which is visible in microscopic photographs as drops of liquid alloy formed in the porosities (Fig. 1).

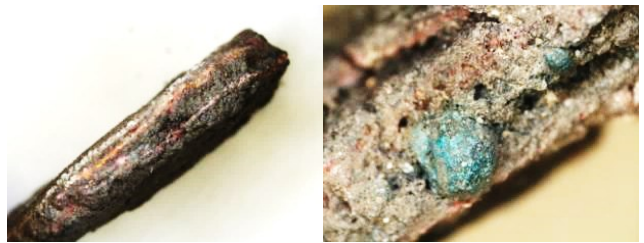


Fig. 1. Part of crucible wall No. Sz-656 with visible drops of alloy

The fractures of the crucible walls were investigated using confocal microscopy, which allows obtaining spatial picture where different topography layers of the artefact investigated can be seen (Fig.2). There are significant differences in levels visible in the place where the solidified drops of the alloy were expected.

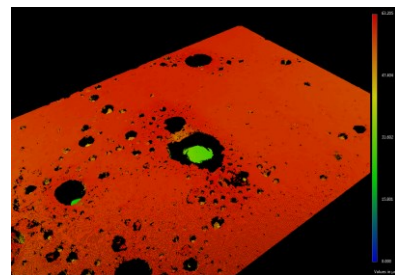


Fig. 2. Topography of the fracture of crucible No. Sz-657, magnification 200x, drops of alloy visible. The scale shows values in μm

The contact of ceramics with molten metal was also shown in radiographic volume tests (Fig. 3).

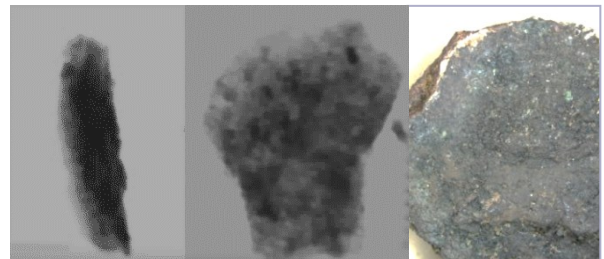


Fig. 3. The result of testing a part of crucible wall No. Sz-14467 by X-ray defectoscopy

The pictures of the material structure confirm that the thin crucible walls are saturated with metal. The inside layers of the crucible are shown in dark colour which means that a composite layer of ceramics-metal was created, because of temperature and contact of the ceramics with molten metal. The presence of metallic elements in the walls of the crucible was also confirmed based on X-ray fluorescence spectrometry (Fig. 4, Tab. 1).

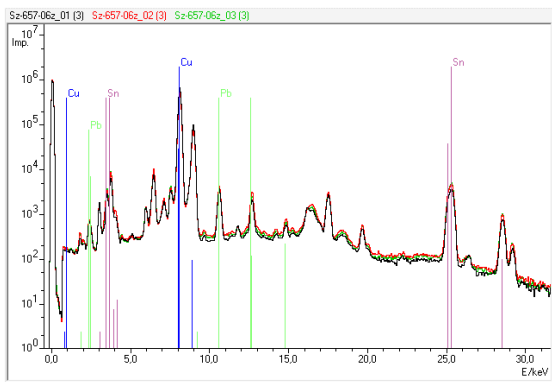


Fig. 4. Graph of fluorescence spectra for crucible No. 657 with marked characteristic elements: copper and alloying tin and lead

The dominant share of copper and the alloying elements of tin and lead was confirmed. Based on analyses, pottery fragments with visible traces of metals need to be regarded as industrial ceramics used for production of tin bronze (crucible No. 662) and tin-lead bronze (crucible No. 657).

3.2. Slags

Macro- and microscopic pictures were taken of the slags, as well as defectoscopic pictures (Fig. 6a) and chemical content analysis was performed. The slags contained trace amounts of metallic elements, apart from a few cases where small amounts of copper were observed. The pictures (Figs. 5-6) reveal inhomogeneous structure of the slag. Numerous porosities and voids visible inside point to air bubbles locked in the slag structure, testifying to a significant gassing of the alloy.

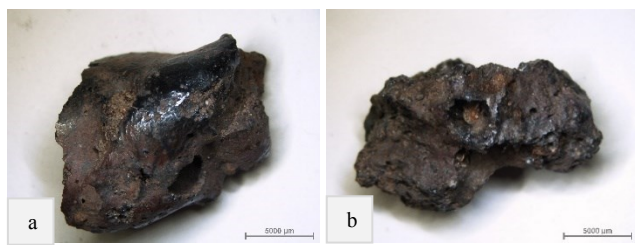


Fig. 5. Macroscopic pictures of slags No. 14060-13.5 (a) and 13.7 (b)

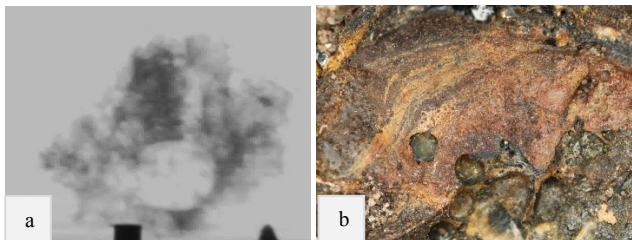


Fig. 6. The result of X-ray defectoscopic tests (a) and microscopic observations, 20x (b) of fragments of No. Sz-14044

The slags should be regarded as remains of a typical bronze melting process, they were collected from the metal surface together with non-metallic impurities present in the metal bath.

3.3. Production waste and semi-products

Within the group of production discards and semi-products, numerous artefacts (Fig. 7) were investigated pointing directly to the foundry activities conducted in the settlement area. Production waste as home scrap was probably used also as raw material in the process of bronze melting.

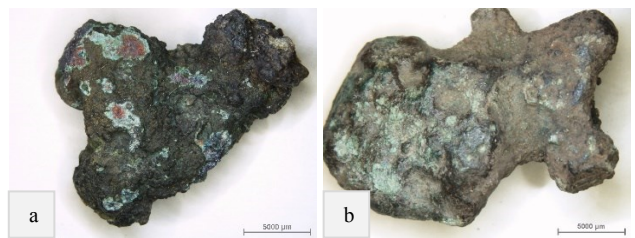


Fig. 7. Semi-products No. 512 (a) and 519 (b)

Three objects were added to this group (No 553, 579 and 533) based on their technological meaning, because they are pouring cups. There were mainly conducted microscopic investigations and chemical content analysis using ED-XRF and SEM-EDS methods. The tests confirmed that the dominant element in all investigated cases was copper, and its main alloying element was tin. There was also lead present as the second, intentionally added alloying element. The results of chemical content analysis are presented in Table 1.

The investigation revealed a few groups of alloys. One of them is two-component Cu-Sn bronze, characteristic of the samples No.634, 14061 and 14046 as well as pouring cup No. 533 and the alloy in crucible No. 662. The lead content in the alloy is insignificant (0,02-0,59%), which means that probably it is a tramp element, which also applies to arsenic, antimony, nickel and silver.

The second, dominant group of alloys (No. 506, 514, 519, 576, 658, 514) is described as Cu-Sn-Pb bronze with a high tin content and lead addition (over 1%), with other elements (arsenic, antimony, nickel, zinc, iron and silver) remaining from the original copper ore.

To this group belongs also the alloy from crucible No. 657 and pouring cups No. 553 and 581 separated from the casts.

The material usually shows high inhomogeneity. In this group of alloys, the greatest number of metallurgical impurities in the structure, connected to the increased nickel, antimony and arsenic content, was found in sample No 506.

A different alloy is represented by the material numbered as 1474 and, within the group of the materials tested, it is most untypical as an alloy of copper with lead with the addition of tin (Cu-Pb-Sn). The average content of significant alloying elements is as follows: 89.71% Cu, 7.35% Pb and 1.74% Sn. The degree of this material contamination with tramp elements is insignificant. In this group of presumed raw materials, an alloy of lead and tin (No. 551) was also found.

Table 1.
Chemical content of semi-products and raw materials (wt %)

Element	Alloy in crucible		pouring cups					semi-products and production waste							
	657	662	533	553	581	506	514	519	576	634	658	1474	14046	14061	551
Fe	1.13	0.57	0.00	0.42	0.04	1.43	0.12	2.16	3.72	0.12	0.54	0.04	0.2	0.33	1.47
Co	0.10	0.10	0.08	0.08	0.05	0.14	0.1	0.05	0.07	0.06	0.12	0.06	0.08	0.1	0.09
Ni	0.47	0.26	0.46	0.36	0.32	1.8	0.3	0.3	0.35	0.31	0.31	0.21	0.3	0.61	0.03
Cu	75.19	70.56	86.96	78.6	95.58	77.04	58.98	68.33	42.81	93.13	69.86	89.71	70.88	79.22	0.10
Zn	0.27	0.14	0.14	0.15	0.15	0.14	0.13	0.13	0.21	0.12	0.15	0.14	0.11	0.14	0.13
As	0.19	0.31	0.27	0.32	0.19	1.71	1.34	0.74	0.6	0.18	0.76	0.15	1.08	0.21	<0.00051
Ag	0.04	0.03	0.06	0.04	0.06	0.12	0.2	0.09	0.1	0.02	0.12	0.05	0.22	0.02	<0.020
Sn	20.65	27.66	11.04	18.19	0.65	15.33	36.38	25.29	49.87	5.88	25.84	1.74	25.94	18.9	5.88
Sb	0.31	0.14	0.23	0.2	0.13	1.09	0.36	0.42	0.39	0.10	0.66	0.15	0.44	0.06	<0.051
Pb	1.27	0.20	0.59	1.29	2.80	1.07	1.59	2.46	1.4	0.08	1.16	7.35	0.53	0.13	92.00
Bi	0.01	0.02	0.04	0.03	0.04	0.03	0.14	0.03	0.05	0.01	0.05	0.1	0.05	0.02	0.29

The microstructure image of the chosen samples (No. 506 and 634) showed the characteristic dendritic structure of the material. There are copper dendrites visible (α solid solution), while in the interdendritic spaces there are intermetallic phases of Cu-Sn-Pb-As. Also, the presence of copper sulfides Cu_2S was noticed. Near the porosity, oxide precipitates Cu_2O i SnO_2 were documented, as the products of copper and tin corrosion. The presence of big copper dendrites (of variable size) points to the slow solidification in a sand or clay mould (Fig.8). Below the pictures, the results of chemical analysis in microareas are compiled, expressed as weight percentage (Fig.9).

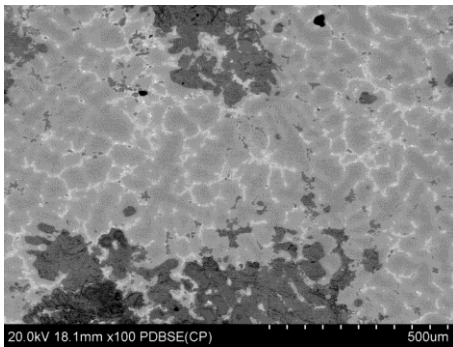
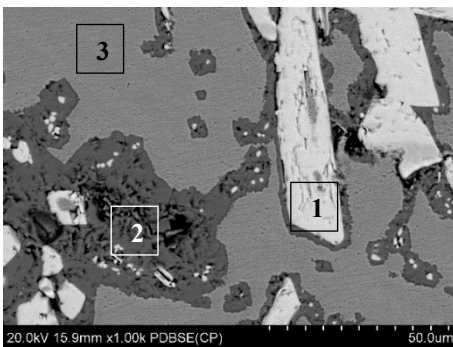


Fig. 8. SEM microstructure No. 506, 100x



Point/Element	O-K	Ni-K	Cu-K	Sn-L
634 pt1	23.18	0,00	2.36	74.46
634 pt2	10.21	0,00	89.79	0,00
634 pt3	0.50	0.39	99.11	0,00

Fig. 9. Microstructure image and SEM-EDS analysis No. 634

The connection of these artefacts with the foundry workshop is also confirmed by fragments of gating systems, especially the funnel-shaped gates, with the plane of free solidification clearly visible, which is characteristic of casts solidifying in open moulds. There are lines and directions of solidification clearly visible as well as a forming contraction cavity (Figs.10-12). Two of the pouring cups do not show any seams resulting from two-part moulds, so they can be treated because of precision casting by lost-wax method. The shape of the third cup (No 533) however, relates to a two-part mould, which signifies that both technologies were used in the discussed workshop.



Fig. 10. Pouring cup No. 553



Fig. 11. Pouring cup No. 581



Fig. 12. Pouring cup No. 533

3.4. Products

In the group of metal artefacts most items are faulty products, either because the casts were unsuccessful or because they were mechanically damaged. Because of that they were probably destined to be re-melted. To this group belong arrowheads with clear casting defects (the most common are so called short run castings), pins, bracelets, rods or other objects that could have been used e.g. as tools. Practically all of them are mechanically damaged; broken and preserved in fragments. These artefacts were made using casting technique, some of them were later wrought and others show traces of surface working.

The compilation of the results is presented in Table 2 and in the graph (Fig. 13).

In the compiled results, a similar chemical composition can be noticed in the little arrowhead group (No. 502, 510, 566), pins (No.557, 615, 638), bracelet (No. 527) wires (No.523, 568), and tool (No.542) described as tin bronze with a heightened tin content (17,79-34.91%), with a small share of lead (0,21-0,59%) and other additives. Within the artefacts, also a two-component bronze group Cu-Sn can be singled out, with a lower tin content (6,06-14,40%). The tin-lead bronzes are present in three cases only (No. 541, 642, 578). In the last case (No. 578) the lead content is very high and it is 20.13%, which comes close to the tin content in this sample. Other elements do not have such a great technological significance in alloys. In the researched metal artefacts, an increased content of arsenic (0,02-1,39%), nickel (0,11-0,62%), antimony (0,01-1,28%), and in some cases also silver (0,02-1,78%) is observed.

Principal components analysis of bronze objects: tin, antimony, arsenic, lead, bismuth, nickel, silver, iron and cobalt is presented in the graph (Fig. 13).

Probably the content of an alloying element relates to the object function and so, an increased amount of tin ensures higher hardness while its low content results in greater plasticity of the

alloy. An addition of lead increases castability and workability of the alloy.

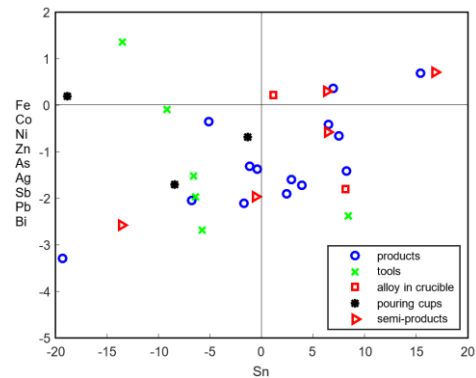


Fig. 13. Principal components analysis of bronze objects: tin, antimony, arsenic, lead, bismuth, nickel, silver, iron and cobalt.

Distance from the average content (wt%). Zero means the average concentration of Sn (x-axis) and the average value of the sum of the other components Fe, Co, Ni, Zn, As, Ag, Sb, Pb, Bi (y-axis). Marked groups: finished products (little arrowheads, pins, bracelets, wires), tools, alloy in crucible, pouring cups, semi-products and production waste. It needs to be acknowledged that the material tested is very inhomogeneous which shows in structure images and the values of chemical content. Because of the great inhomogeneity of chemical content and the presence of tramp elements such as arsenic, antimony, nickel and silver it is difficult to define the properties of the analyzed alloys. The analyses of strength and plastic properties cannot be carried out on the historic material because of the destructive character of these tests.

Table 2. Chemical content of metal artefacts (wt %)

Element	Little arrowheads			pins			bracelets			wires			tools							
	510	502	566	557	615	638	522	527	523	568	579	648	13772	541	542	550	613	642	578	608
Fe	0.99	0.01	0.08	0.05	0.02	0.29	0.18	0.31	0.55	0.05	0.03	0.72	0.06	0.00	0.40	0.12	0.04	0.05	0.03	0.05
Co	0.10	0.09	0.10	0.10	0.09	0.08	0.10	0.08	0.09	0.09	0.05	0.10	0.06	0.08	0.07	0.08	0.07	0.06	0.11	0.08
Ni	0.88	0.52	0.41	0.49	0.55	0.39	0.17	0.28	0.62	0.18	0.08	0.11	0.18	0.45	0.08	0.41	0.33	0.17	0.35	0.27
Cu	60.83	69.72	70.03	78.65	74.74	75.59	85.74	76.25	70.49	80.77	99.46	69.56	82.2	86.17	70.82	85.04	85.31	89.00	55.59	85.32
Zn	0.12	0.12	0.13	0.12	0.11	0.12	0.15	0.12	0.12	0.12	0.12	0.23	0.11	0.12	0.12	0.12	0.12	0.12	0.1	0.12
As	1.38	1.07	0.40	0.52	0.47	0.47	0.35	0.32	0.66	0.16	0.00	0.07	0.94	0.53	0.02	0.37	0.36	1.39	0.27	0.15
Ag	0.03	0.13	0.08	0.07	0.09	0.06	0.08	0.06	0.08	0.04	0.00	0.05	0.89	0.07	0.01	0.05	0.04	1.78	0.04	0.02
Sn	34.91	26.99	27.80	19.14	23.42	22.45	12.72	21.96	26.02	17.79	0.24	26.48	14.4	10.35	27.99	12.90	13.08	6.06	22.92	13.79
Sb	0.48	0.33	0.20	0.26	0.28	0.26	0.2	0.20	0.43	0.19	0.00	0.08	0.94	0.42	0.01	0.24	0.20	1.28	0.17	0.04
Pb	0.27	0.59	0.72	0.54	0.21	0.27	0.26	0.28	0.56	0.59	0.00	2.51	0.00	1.78	0.48	0.66	0.43	0.01	20.13	0.14
Bi	0.02	0.05	0.05	0.06	0.03	0.03	0.04	0.03	0.05	0.04	0.01	0.07	0.05	0.03	0.01	0.02	0.02	0.07	0.11	0.02

4. Conclusions

The tested evidence in the form of raw materials, crucible fragments and bronze scrap as well as ready, well developed products indicate clearly that in Szczepidło, in Greater Poland, an

advanced foundry workshop was discovered. All these elements occurring together testify to production processes carried out at this place. Because of their partial preservation and the lack of any workshop facilities (furnaces, ovens) it is impossible to determine exactly the production volume. However, numerous discovered artefacts can be treated as proof of an intense

workshop operation, which yielded rather small, precisely cast objects. The found products, damaged during the casting process or as the result of usage, were the effect of the workshop operation. The workshop used tin bronze or tin-lead bronze. Some of the studied artefacts have a high lead content, which may indicate an intentional addition of this element, changing some technological properties of the products, and thus it points to the modification of the alloys made there in the workshop. The found fragments of the gating systems, specifically the main gates (in the form of a funnel, shaped from the mould), broken off from the finished product, testify to the foundry production realized on site and directly to the composition of castings prepared here. In the absence of moulds from the site, the thesis can be accepted that clay and stone moulds were used at the workshop. Finished products show traces of working with them using various techniques. The casts show evidence of hammering, grinding and polishing aimed at technological treatment to eliminate product defects and aesthetic treatment to enhance their decorative value. The studied ceramics are industrial in character and they are connected with melting and casting processes implemented in the workshop production of bronze. The research revealed that the walls of the crucibles contain metal residues of copper and tin (approximately the content of tin is twice as high in the walls of the crucible; it is related to the metal density and is associated with the penetration of elements into the porosities of ceramics). The inner layer of the crucible, as the result of contact with the molten metal, received composite structure, which can be seen on the X-ray. In the crucibles drops of alloy were also found which fit within the previously studied bronze melts. Slags contain small amounts of metals. They probably come from the surface of the molten alloy, gathering non-metallic impurities and oxide phases with minimal share of alloy components. The analysis of the workshop finds is important especially in terms of production technology of bronze artefacts. It keeps track of the technological thought of old and its willingness to introduce modifications. From the point of view of copper alloys casting, these studies allow evaluation of the alloys used, and in subsequent steps restoring them and studying the properties of the materials.

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