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STUDY OF INVESTMENT CASTING TECHNOLOGY FROM BRONZE AGE. CASTING WORKSHOP IN GRZYBIANY (SOUTHWEST POLAND)

Investment casting technology that utilizes lost-wax casting is one of the most-important achievements of ancient society. In Lower Silesia, Poland (Grzybiany, Legnica county), a 7-6 BC casting workshop was discovered with numerous artifacts, confirming the existence of the manufacturing process of metal ornaments using ceramic molds.

The paper presents the research of molds and casts from the Bronze and Early Iron Ages. Microscopic analyses of the casting molds were performed, along with radiographic and chemical composition tests of the artifacts (the latter employing the use of the X-ray fluorescence spectroscopy method). The clustering method was used for alloy classification. The microstructure was analyzed by means of Scanning Electron Microscopy with Energy Dispersive Spectroscopy. Conclusions from the research were utilized in further experiments.

Keywords: archeometallurgy, copper alloys, investment casting technology, lost-wax casting, x-ray spectroscopy

1. Introduction

The method of precision casting by applying lost-wax casting is one of the most-revolutionary achievements in ancient technology; in fact, it has been successfully utilized through the present day. The lost-wax casting technique significantly influenced the development of civilizations and helped popularize metal artifacts.

Implementation of the lost-wax casting technique was an important step in the development of casting technology [1]. By using the lost-wax casting technique with ceramic molds, it became possible to make the molds small yet complex in shape. It enabled the casting of complicated decorative ornaments, more-massive bracelets, necklaces, and greaves (as well as tools). The process started with shaping the model in wax, which was then covered in clay and dried; the wax was then melted, and the mold was fired. The mold was filled with liquid metal and then broken to pieces. An improvement of this procedure was the lost-wax technique used for casts that were empty inside, with a clay core imitating the inside shape of the cast. This clay core was covered with a wax layer, whose outside shape (after firing and breaking the clay mold) mirrored the surface of the cast with its artistic three-dimensional reliefs and ornaments.

Loam molds were generally broken up after pouring. Hence, if the loam molds were well-prepared and used to prepare a casting, it is rare to find them intact at archeological sites.

The investment casting technology is still important nowadays. It is still used in the automotive, aviation, military and, medical industries as well as in jewelry and artistic casting [2-7].

One of the oldest archeological sites where typical lost-wax casting molds have been found is Tell edh-Dhiba'i, Iraq (located in the suburbs of Baghdad) dating to the first half of the second millennium BC [8-13]. However, the process of lost-wax casting had already been developed in Mesopotamia at about 2500 BC; that is, at least 900 years before the mold from Tell edh-Dhiba'i was created [12].

A clay mold indicating the application of the lost-wax method was found in Poliochni at the site connected to metal working, on Lemnos Island (in the Aegean Sea) [12,14-16]. The mold was prepared for the casting of an axe head; however, it was not used due to it being damaged. This mold is about 1000 years older than the Tell edh-Dhiba'i one; therefore, it seems to represent an earlier tradition of using the lost-wax method [12,17-18].

Older metal objects made with the lost-wax technique come from the collection discovered in the Nahal Mishmar cave in the Judah Desert near the Dead Sea. The dating of the copper artifacts places their manufacture at about 3700 BC [19-20]. The

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hoard contained 416 objects made of pure copper, antimony- and arsenic-rich copper, and nickel-arsenic copper. Some of the artifacts could have been cast by the precision casting method in expendable molds by lost-wax casting over a stone core [12,18,21] (analogous to the casts from Shiqmim in the northern part of the Negev Desert) [17].

Copper alloy amulets from Mehrgarh, a Neolithic settlement belonging to the civilization of the Indus valley in today's Balochistan in Pakistan, come from 5000 BC. Metallographic tests show that the ornaments were cast using the lost-wax method from a copper alloy with the addition of lead [12,22]. Therefore, Mehrgarh might be the place where the development of lost-wax technology started.

There have been archeological sites researched in Poland that include casting workshops where the lost-wax process was applied, coming from the second millennium BC [23].

Study of a workshop dating back to the Hallstatt C period (from the seventh to mid-sixth century BC) that was functioning in Lower Silesia, Poland, indicates a common knowledge of lost-wax casting [24-26]. The local casting manufacturing was comprised of mold technology, alloy melting, and casting sites characteristic of the manufacturing technology of that time. From this settlement in Grzybiany comes rich research material consisting of ceramic casting molds assessed to be the biggest collection of molds for the manufacture of bracelet and necklace in Poland. Alongside, there were also metal artifacts and other objects discovered in the workshop area that were connected to the foundry process; namely, ladles and tuyeres [24,27].

In the workshop vicinity, the main findings consist of fragments of ceramic molds used in the production of band or hoop ornaments. Apart from these, some metal antiques were discovered that were indirectly related to the local casting manufacturing and products directly related to it, like the casting spoon (Fig. 1).



Fig. 1. Casting spoon from Grzybiany workshop

Application of the wax-model casting technology for the local production of ornaments has also been confirmed by findings at other excavation sites in the Silesia, Greater Poland, Kuyawia, and Eastern Pomerania regions [28].

The mold-preparation technology for the lost-wax process was complex and consisted of many stages. The most-common

cause of mold damage was their cracking during the drying stage, wax melting, and especially during the mold firing. Manufacturing technology of the ceramic materials was analyzed based on their thermal characteristics. It was assessed that, after preliminary heating (which was aimed at removing the wax model), the mold was fired at 850°C [24].

These artifacts connected with the functioning of the casting workshop in Grzybiany have been researched by an interdisciplinary team at the Faculty of Foundry Engineering of AGH University of Science and Technology in Krakow, in cooperation with the Copper Museum in Legnica and Institute of Archeology at the University of Wroclaw [25-27].

The archeological site connected with the workshop in Grzybiany (Site 3, Kunice muni., Legnica county) is situated on the promontory of Lake Koskowickie in Lower Silesia (Fig. 2). Archeological excavations were conducted during the periods of 1959-1962, 1970-1973, 1977-1980, and 2010-2011. An analysis of the portable artifacts showed that the second level of the settlement should be dated to the Ha C period; that is, from the seventh to mid-sixth century BC. However, in the layer related to the metallurgical workshop, there were artifacts with both older and younger features than from Ha C.

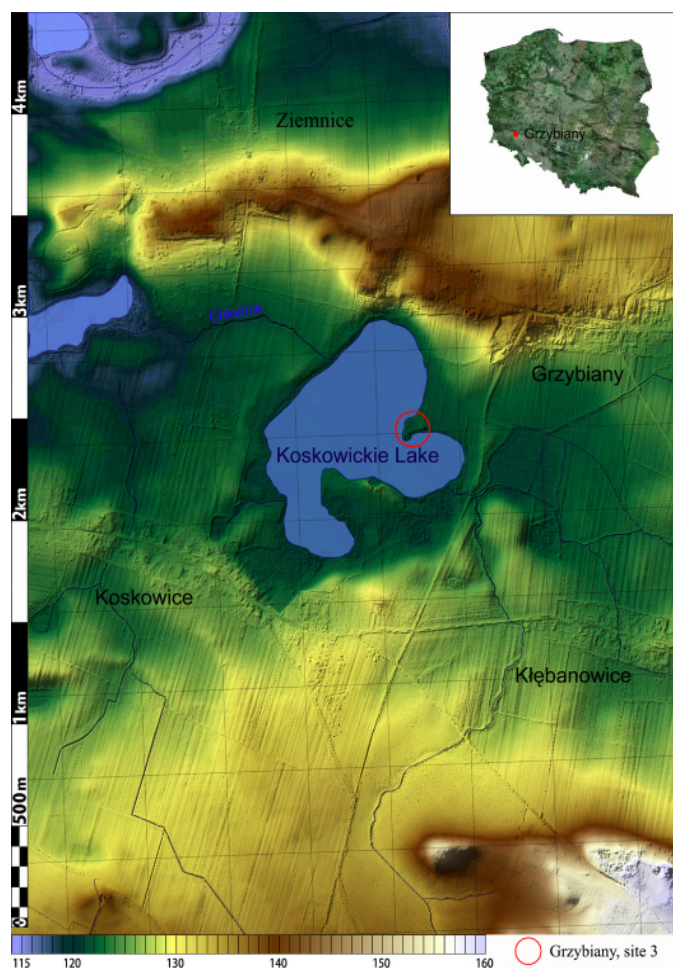


Fig. 2. Location of Grzybiany site in SW Poland and numerical terrain model of Grzybiany site and its vicinity. Source: ISOK project, CODGiK. Developed by P. Rajski, T. Stolarczyk

2. Research methodology

The collection of casting molds and metal artifacts from Grzybiany settlement was investigated. The material was submitted to the following non-destructive tests: macro- and micro-observations, assessment of the chemical composition, and defectoscopic tests. The clustering method was used for alloy classification.

The observations were conducted to document the structures and surfaces of the ceramic and metal artifacts. Phase content of the casting molds was confirmed by means of X-ray diffraction (XRD) analysis. The quantitative determination of the elemental composition of the artifacts was performed by X-ray fluorescence spectrometry with a Spectro Midex spectrometer with energy-dispersive X-ray fluorescence (ED-XRF). The spectrometer is equipped with a molybdenum X-ray lamp and Si Drift Detector (SDD). The analyses of the structural and chemical compositions were conducted in the micro-areas by applying scanning electron microscopy with X-ray microanalysis (SEM-EDS). The alloys were divided into groups by chemical composition with the clustering method, using Euclidean distance.

The tests were conducted by means of X-ray imaging (defectoscopic method [RT] with YXLON MU2000 systems for non-destructive material testing) in order to check the content of the molds and to recreate the cavity shape along with its gating system.

3. Results and discussion

The researched group of artifacts should be considered as the part of the workshop where the molds and casts were prepared by applying the lost-wax technology. The molds from Grzybi-

any belong to dispensable forms, destroyed after the mold was filled in order to pull out the ready artifact (Fig. 3). The molds were made of clay and sand with variable granularity. Organic materials were also likely used for mold making but were later burned-out in the process of drying and firing the molds, leaving porosities (which facilitated the release of gases from the mold). If this release of gases is obstructed, it causes casting defects in the artifacts such as pinholes visible on the surface or shrinkage porosities inside the casts. The lack of repeatability of most of the mold dimensions as well as their flat and even back sides indicate that the molds were shaped by hand on a flat surface. The sides of the different molds have variable thickness (from 3.5 to 16 mm), but their bottom sides (where the surface is flat) are noticeably similar to each other. This suggests that the mold-making started with the preparation of the bottom clay layer on which a wax model was placed and covered by another layer. This way of mold-preparing can explain the irregular placement of the model inside. It is worth noticing, however, that the inside of each mold is similar in shape and size, which proves that the molds must have been manufactured using models created in series; e.g., made by pouring wax into stone or clay molds. Another possibility is that the molds were created by imprinting clay models fired earlier in the moist clay of the mold. The sprue was likely started with a pouring cup, but it was not preserved in the molds. However, pouring cups were found separately among the fragments of the destroyed molds. A mold fired earlier was filled when placed vertically, which enabled the proper filling of the cavity with a liquid alloy.

Some of the clay casting molds are preserved whole or in larger fragments, likely comprising unsuccessful or unused molds [26], as well as small fragments of molds used for production. This group of largely intact molds is dominated by those used for the production of various ornaments (Fig. 4).



Fig. 3. Fragments of clay mold for bracelet or necklace casting

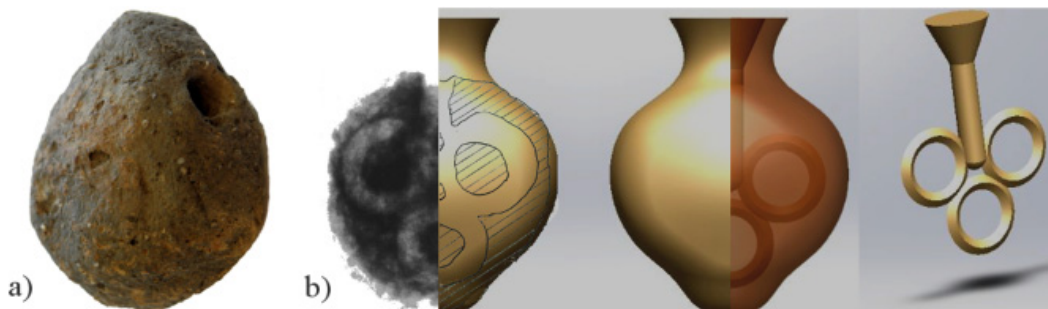


Fig. 4. Casting mold (a) [27]; graphic documentation based on radioscopic image: visualization of casts connected by gating system comparison with X-ray image and visualization of casting mold (b)

These include full bracelets with a circular cross-section, rings, ornaments consisting of three joined rings [26-27], bracelets in the shape of a double coil and rectangular cross-section, and the handles of pins or awls. Some of the molds have ornaments inside in the form of notches or cuts.

Two groups can be distinguished among the investigated molds. The first consists of molds that were not filled with a liquid alloy, which means that they were not used for making casts. The most-common damage here was fracturing while drying or wax melting, especially during a mold firing. Tests of the chemical compositions of these molds did not confirm the presence of any metallic elements in them, which would have to occur in case the mold cavity had had contact with a liquid alloy. Macroscopic analysis also did not confirm cavity contact with a liquid alloy.

In other, smaller mold fragments, microscopic observations and chemical content analysis showed a heightened concentration of metallic elements in the mold cavity area, which indicates that the mold had contact with liquid metal.

The X-ray and macroscopic images of the casting molds show preserved cavities and profiles of various shapes inside the molds (Fig. 5). Based on these, the following molds were identified: molds for necklaces, bracelets with circular cross-sections, double coil and C-shaped bracelets, bracelets adorned with notches, pins, and rings.

Lost-wax casting ceramic molds for two bracelet types and fragments of metal artifacts were chosen for our research.

Computer-modeling methods were used for visualization and cast reconstruction.

3.1. Macroscopic and microscopic observations of casting molds

The molds from the Grzybiany site belong to the group of expendable ones (those that are destroyed after being filled). Observations of the casting mold surfaces and their structures point to the fact that the molds consist of a mixture of clay, sands of different granularity, and organic elements; they were made by applying the drying and firing processes, leaving behind visible pores that facilitated the release of gases from the molds (Figs. 6-7).

The mold fragments were chosen based on their geometry and composition as well as our microscopic observations; it was assessed that these molds did not have any contact with any liquid alloy streams, which means that they were damaged before being filled (likely during drying or firing). These molds became the basis for reconstructing the metal artifacts. In some of the researched molds, sprues with a cross-section diameter of 6 mm are preserved. From the technological perspective, the sprues in the preserved molds is rather narrow, which suggests that there must have been an additional element with a broadened entry (called a pouring cup) facilitating the filling of the mold with a liquid alloy.



Fig. 5. Casting mold with damaged gating system (a); X-ray image of mold cavity – front view (b) and side view (c) [6]

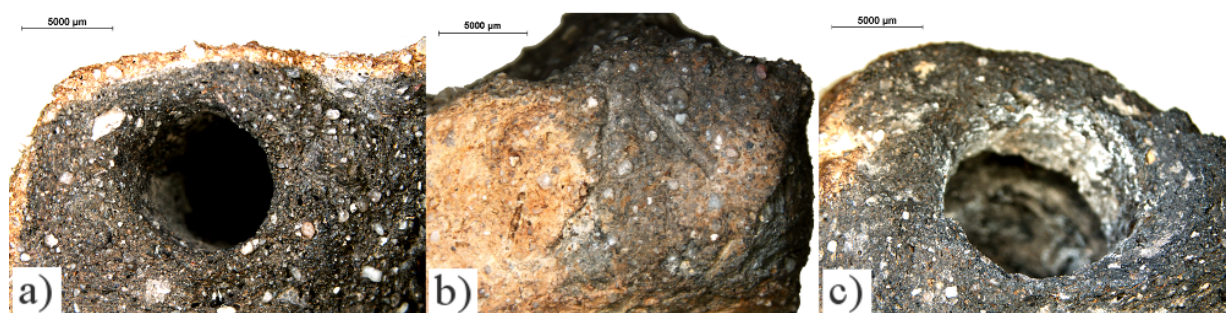


Fig. 6. Macroscopic picture of mold surface

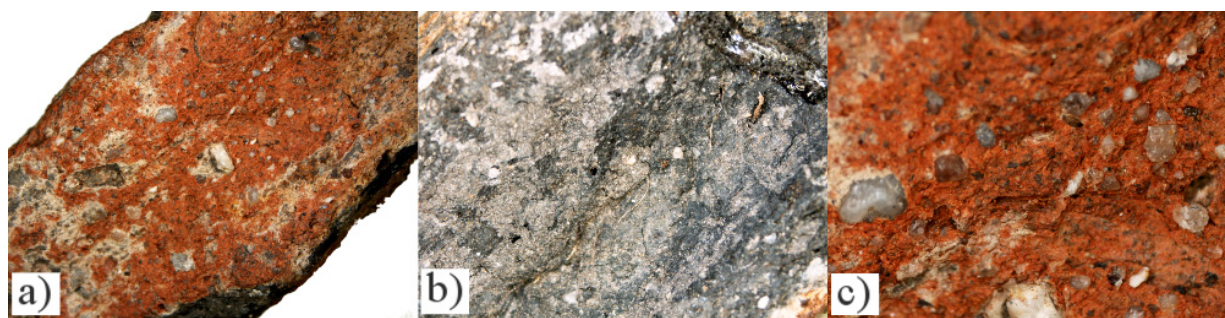


Fig. 7. Macroscopic picture of mold surface; 6,7× (a), 10× (b), 20× (c)

3.2. Content and structure analyses of metal artifacts

Analysis of the content and structure of the metal artifacts required us to apply a range of specialist research methods to enable their exact classification. Knowledge about the materials as well as the technologies necessary for making the artifacts has played an important role in the studies of the technological development throughout history [6,23]. A special significance of these studies can be seen in the conservation and protection of metal artifacts [29].

Studying the content and structure of historical artifacts demands the application of special procedures due to their antique character and the impossibility of applying standardized chemistry [30]. The historical artifacts from the settlement in Grzybiany were investigated using non-destructive or micro-destructive methods. In the research, light microscopy was used as well as scanning microscopy, with a chemical content analysis applying X-ray fluorescence in the macro- and micro-areas.

In our macroscopic and microscopic studies, the material was analyzed from the perspective of its content, structure, and technique of craftsmanship. Apart from a few exceptions, a macroscopic analysis of the surface of the metal artifacts shows a common application of the casting method as well as particular instances of mechanical working (beating) and chiseling (grinding, polishing).

Fifty-two metal artifacts were characterized based on the conducted research, allowing us to identify certain groups. Among the artifacts, the most-interesting ones were ornaments and half products or the production wastes. In many cases, distinct mechanical and corrosion damages were observed.

The chemical composition test results were sorted by the content of the metallic constituents, which is accepted as an important technological indicator. The analyses were conducted and presented in the form of macro- and micro-scopic photographs, a summary table, and diagrams. The main group among the described materials was comprised of copper alloys (mainly tin bronzes), two-component-type Cu-Sn, or multicomponent type Cu-Sn-Pb. A special case was comprised of Cu-Pb, lead bronzes, and bronzes with a predominant share of lead as the alloying element but with a lower tin content of the Cu-Pb-Sn type (Table 1).

Numerous metallic and non-metallic impurities were identified in the content and structure of the alloys. They are related

to the use of polymetallic ores and the technological limitations of the metallurgical processes that made it difficult to remove the unwanted elements. The following elements are regarded as traces connected to the ores' origin and casting technology: antimony, arsenic, nickel, iron, zinc, and silver [1,31]. Tin and lead are presumably intentional alloy additions that were introduced into the copper to improve the technological, utility, and aesthetic properties. The luster and color of the alloy were important, as well as its castability; that is, its ability to fill the cavity of the mold, lower the tendency for defects, and improve the material parameters as a result of heat treatments and plastic working [1,32]. The analyzed bronzes differed in their content of impurities, which can indirectly point to their different origins as well as to their different courses of the technological process influencing the material quality. The issue of the origin of the raw materials used in the foundry workshop in Grzybiany has yet to be settled.

Because of the fact that a complex study of technological properties of historical alloys is not possible in the case of historical metal artifacts due to its invasiveness, a decision was made to recreate the chosen alloys seen as model materials. In this way, the influence of the alloy additives, impurities, and casting technology on the properties of the copper alloys was studied. It needs to be kept in mind that the content of impurities and intentional additives significantly changes an alloy's properties (mainly by increasing its hardness). Based on the alloy's chemical composition and its conditions of melting, it will be possible to recreate the structure and technological properties of the alloys. The model alloys are to be used for the analysis of the macro- and micro-structures as well as the mechanical and technological properties of historical metals and alloys. During the research, the structural analysis was performed based on the experimental melts, microscopic studies, thermal analysis, and equilibrium systems of individual components of the alloys. The basis for the experiment was the research of the chemical content of historical metal artifacts [33].

3.3. Analysis of artifacts from Grzybiany in terms of chemical composition similarity

Testing the intentionality of alloying is meant to show whether certain types of objects were made of a particular alloy

Alloys groups from Grzybiany. Breakdown of Grzybiany alloys into groups by clustering method (Wt. %)

Group no.	Number of artefacts in the group	Artefacts inv. no. in the group	Cu %				Sn %				Pb %				Sum of dopants % (As,Sb,Ni,Ag, Zn,Fe,Bi)			
			min	max	mean	std	min	max	mean	std	min	max	mean	std	min	max	mean	std
1	1	'46a-2010'	78,13	78,13	0,00	3,57	3,57	0,00	4,11	4,11	0,00	13,62	13,62	0,00				
2	1	'22/2010'	60,28	60,28	0,00	10,01	10,01	0,00	27,70	27,70	0,00	1,73	1,73	0,00				
3	1	'47/2010'	54,05	54,05	0,00	0,00	0,00	0,00	31,95	31,95	0,00	13,74	13,74	0,00				
4	1	'CL6569'	83,06	83,06	0,00	0,23	0,23	0,00	7,02	7,02	0,00	9,57	9,57	0,00				
5	1	'23/2010'	84,45	84,45	0,00	2,92	2,92	0,00	6,42	6,42	0,00	6,21	6,21	0,00				
6	1	'CL6200'	74,92	74,92	0,00	1,24	1,24	0,00	15,57	15,57	0,00	8,28	8,28	0,00				
7	1	'2A-18'	63,54	63,54	0,00	11,00	11,00	0,00	21,79	21,79	0,00	3,14	3,14	0,00				
8	1	'38/79-01'	29,97	29,97	0,00	17,31	17,31	0,00	8,70	8,70	0,00	43,91	43,91	0,00				
9	1	'106/80'	67,91	67,91	0,00	14,25	14,25	0,00	5,13	5,13	0,00	12,71	12,71	0,00				
10	1	'121/79'	80,40	80,40	0,00	7,59	7,59	0,00	7,04	7,04	0,00	4,97	4,97	0,00				
11	2	'25/2010' '294/79'	90,84	91,80	91,32	0,68	4,69	4,79	4,74	0,07	0,51	1,10	0,81	0,42	2,80	3,27	3,04	0,33
12	2	'292/78' '128/79'	74,06	76,79	75,43	1,93	13,22	13,56	13,39	0,24	3,94	4,33	4,14	0,28	6,05	8,05	7,05	1,41
13	2	'312/79' '10/71'	94,31	97,21	95,76	2,05	0,00	0,00	0,00	0,00	0,00	0,09	0,05	0,06	0,28	2,57	1,43	1,62
14	4	'38/77' '434/77' 'CL6534' '170/79'	74,25	80,36	76,79	2,82	17,24	19,16	18,23	0,86	0,73	3,35	1,89	1,10	1,67	4,46	3,09	1,23
15	4	'19/79' '44/2010' 'CL6299' '45/2010'	87,57	92,16	89,69	2,23	0,00	2,49	0,95	1,08	0,41	0,46	0,43	0,02	5,97	11,40	8,31	2,46
16	7	'556/78' '253/79' '40/79' 'CL6568' '14/72' '61/80' '10/78'	78,73	84,77	81,34	1,85	11,99	15,02	13,54	1,01	0,43	3,44	1,90	1,21	1,23	4,70	3,22	1,16
17	15	'363/79' '107/80' '102011' '83/77' '279/79' '300/78' '44/80' '300/79' '244/79' '53/77' '30/72' '44/71' 'CL6201' '1/72' '24/2010'	83,40	88,43	86,10	1,66	7,76	11,10	9,43	1,12	0,09	2,80	1,14	0,77	1,02	5,71	3,09	1,39

(Fig. 8). Groups were formed as a result of clustering, in which the main elements (Sn, Pb) and all of the elements considered natural impurities (Ni, As, Ag, Sb, Bi, Fe, Zn, Co) were taken

into account. Seventeen groups were created, including ten single-element groups, three groups with two elements, two four-element groups, one group with seven elements, and the biggest group consisting of as many as fifteen elements (Fig. 9). The investigation results are presented in Table 1. Groups in the

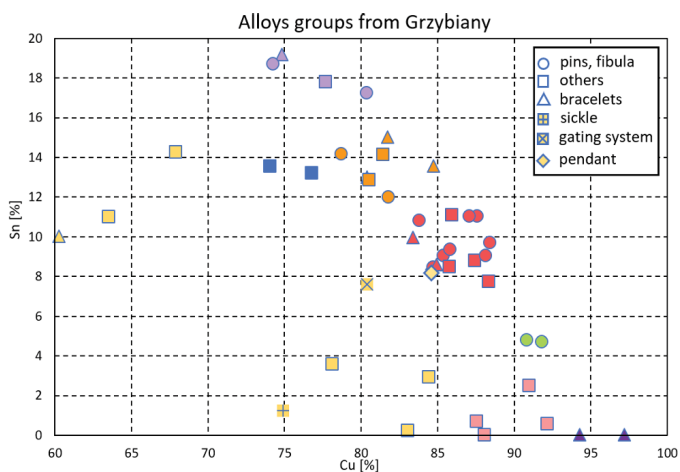


Fig. 8. Breakdown of Grzybiany alloys into groups by clustering method. Dependency of Sn content on Cu (Wt. %) marked on the graph. Alloy groups from Grzybiany. Colors indicate artifact's casting group affiliation as in Table 1. Symbols denote kind of artifacts: \diamond – zoomorphic pendant; + – sickle; \times – gating system; Δ – bracelets, \circ – pins and fibula, \square – others

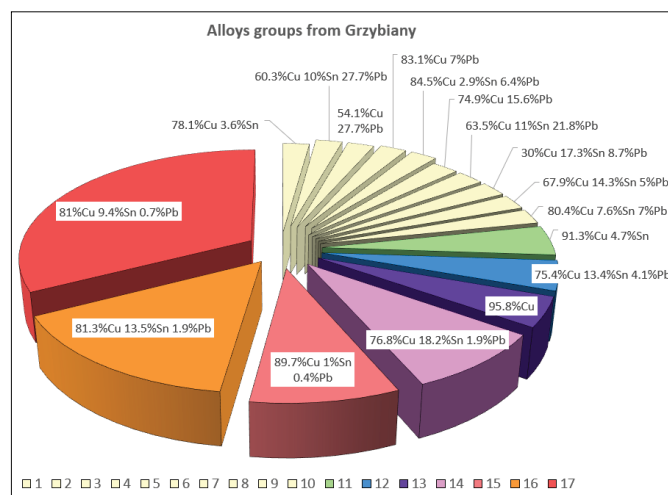


Fig. 9. Graphical presentation of groups of Grzybiany alloys. Group numbers correspond to presentation in Table 1

graphs and in the table were marked in color except for the one-element groups (which were marked in black).

The biggest group identified as Number 17 is comprised of 15 alloys, containing Cu 83.40 (88.43%), Sn 7.76 (11.10%), and Pb 0.09 (2.80%) and including natural admixtures with a maximum share of 5.71%. Clustering shows a large diversity in the examined alloys. It could be the result of using raw materials with an uncontrolled chemical composition and of the smelting of previously damaged products that accidentally combined alloy components.

What is interesting is the differences in the chemical compositions of different kinds of archeological objects. Different kinds of copper alloy objects are marked on the graph with different symbols. The following groups are denoted this way: bracelets, needles, utensils, tools, and production waste. The biggest group (No. 17) of tin alloys (9.4% Sn on average) with a low lead content (1.1% Pb on average) and relatively low proportion of admixtures (3.1% on average) contains mainly small items such as needles, wires, two bracelets, a zoomorphic pendant, (Fig. 10) and a bronze fibula. The second biggest group (No. 16) of tin alloys with a larger proportion of tin (13.5% on average) and slightly larger proportion of lead (1.9%) and admixtures (3.2%) contains three bracelets, two needles, and a button. Group No. 14 with a high proportion of tin (18.23% on average) consists of a bracelet, a button, and two needle fragments, while group No. 15 contains only two needle fragments.



Fig. 10. Bronze zoomorphic pendant from Grzybiany workshop



Fig. 11. Bronze miniature sickle with button from Grzybiany workshop

A bronze miniature sickle with a button (Fig. 11) belongs to a single-element group of an alloy with a low tin (1.2%) and high lead (15.7%) content. The runner system, which confirms the existence and functioning of a local foundry, also belongs to a single-element group of tin/lead alloy (7.6% Sn and 7.0% Pb).

3.4. Analysis of microstructure using Scanning Electron Microscopy with Energy Dispersive Spectroscopy

Among the investigated metal antiques, objects important from the point of view of their casting technology that represent the observed groups of alloys were singled out. These antiques were characterized by means of microstructure testing. The bronze zoomorphic pendant (inv. no. 300/78) represents one of such group.

The scanning microscope pictures (Figs. 12-13) present the pendant surface fragments. The chemical composition analysis performed in the micro-areas indicated large fractions of a dendritic grey phase, being a solid solution of tin, nickel, and iron in copper and bright interdendritic spaces. Copper, tin, antimony, and arsenic as well as an increased content of silver, nickel, and iron were identified in the interdendritic spaces. Clusters of dark, clearly shaped intermetallic phase dendrites of copper and iron sulfides are seen in the structure. The distribution of elements is shown as mapping (Fig. 14).

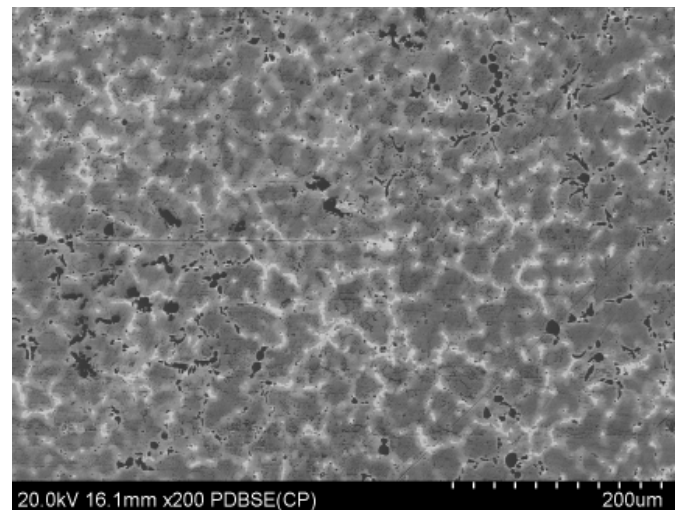
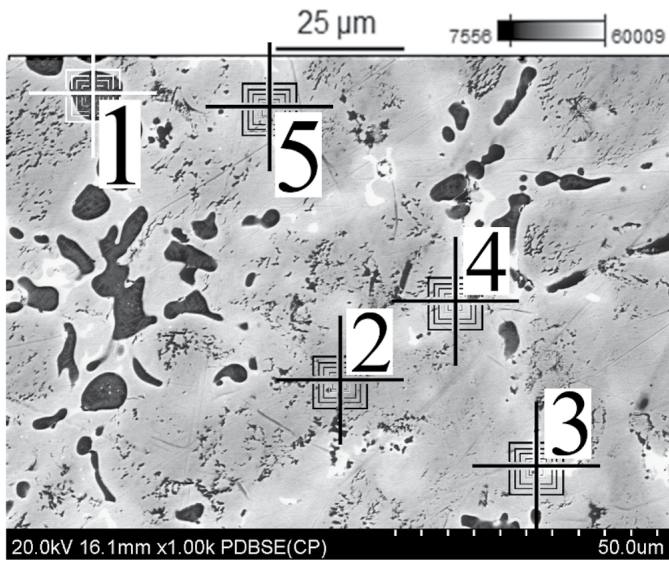


Fig. 12. Bronze zoomorphic pendant. SE picture, 200×

4. Conclusions

The mold set from Grzybiany proves the existence of the technology of precision casting into ceramic molds in the seventh to sixth centuries BC in southwest Poland. The numerous collection of clay molds from the Bronze and Early Iron Ages that was being studied suggested a close cooperation between mold-making and casting workshops. This cooperation can be



Point	Concentration (Wt. %)								
	S	Fe	Ni	Cu	As	Ag	Sn	Sb	Pb
300_pt1	25.21	10.90	-	63.8	-	-	-	-	-
300_pt2	-	3.10	1.06	91.72	-	-	4.12	-	-
300_pt3	-	0.27	1.79	65.06	1.19	0.90	23.82	6.98	0.00
300_pt4	-	1.00	1.75	65.56	0.87	0.97	23.65	6.19	
300_pt5	-	0.99	1.12	87.46	1.72	-	8.71	-	-

Fig. 13. Bronze zoomorphic pendant, SE picture with EDS analysis, 1000×

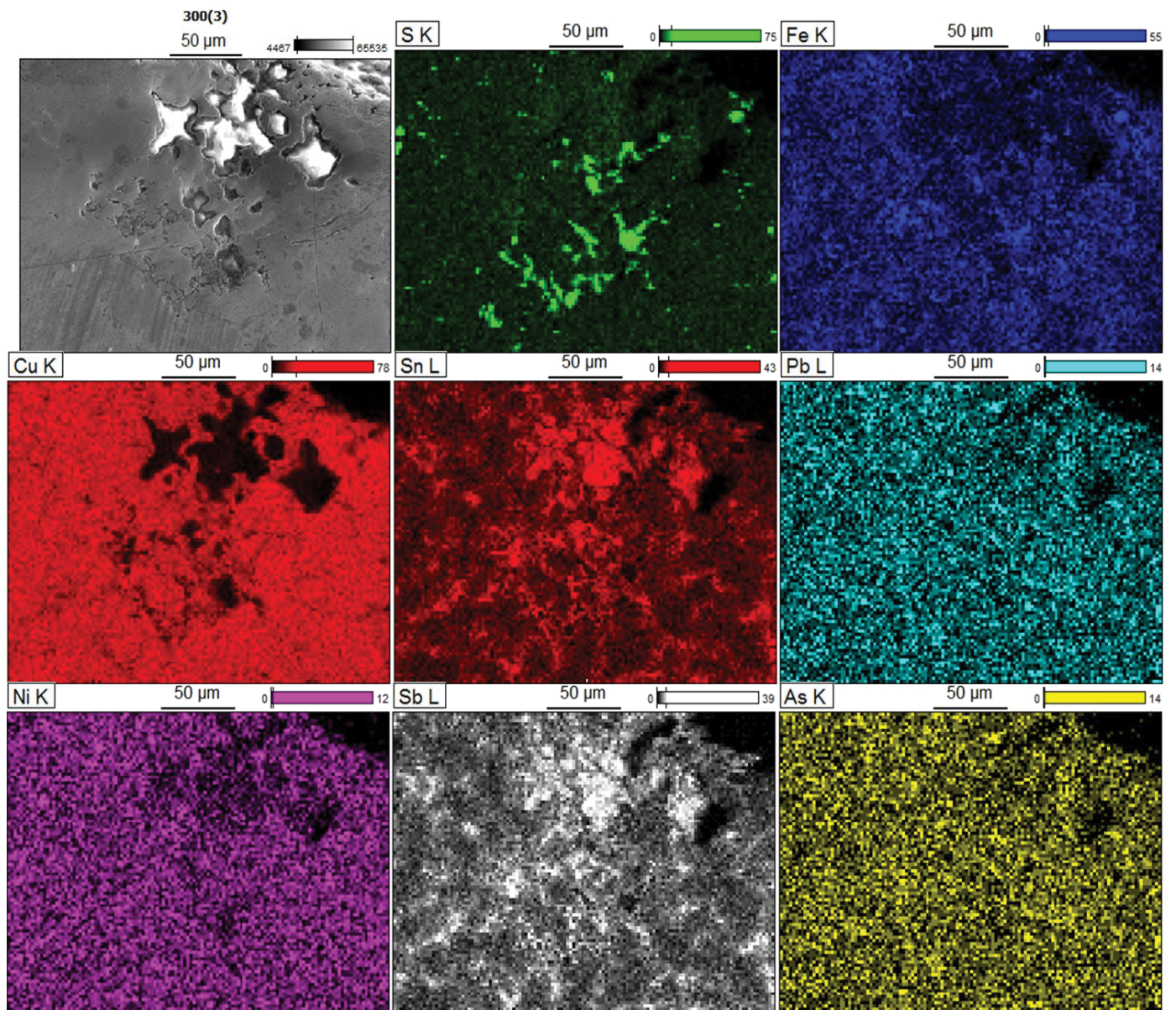


Fig. 14. Bronze zoomorphic pendant, SEM, mapping of sulfur, iron, copper, tin, lead, nickel, antimony and arsenic

proven by the correlation between the shape and dimensions of the molds and the tested metals. The craftsmanship of the researched artifacts points to a common application of casting, which justifies the operation of such complex casting workshops that consisted of the mold technology as well as the alloy melting and casting workplaces. This workshop must have functioned in an organized way, having a back-up of raw-material facilities, tools, hearths, and furnaces as well as competent workers lead by a master with specialist knowledge and experience. The research material comprised of ceramic molds and cast metal ornaments needs to be treated complementarily, as a source of knowledge about the ancient technology for manufacturing metal artifacts.

Macro- and micro-structure tests of the molds allowed for the material to be analyzed from the perspective of the mold structure and casting technology.

Defectosopic tests revealed the shape and layout of the gating system elements as well as the shape of the mold cavity. As far as the cavity shapes and sizes are concerned, it can be agreed that the models were repetitive in character.

The clustering procedure enabled the automation of product classification based on their chemical composition. It also showed a connection between the chemical composition and type of product. Therefore, the biggest group of tin bronzes contained mainly small ornaments.

Chemical composition tests show varied chemical profiles in the necklace and bracelet parts. In the investigated alloys, tin and lead can be treated as alloying elements that were introduced intentionally. The tin content in the alloys varies between 0.01 and 19.16%, while for lead, it is 0.09-31.95%. The remaining elements (Ag, Sb, Ni, Fe) are related to the copper origin and the technology of its smelting.

The research yielded significant technological information in the field of bronze casting, especially the alloys used and the artifacts made from them. The variety of chemical composition helps us group the alloys, but it still cannot explain the origin of the historical artifacts; it only separates them and points the direction for further research. The studies need to be acknowledged as an important step of the methodology development in the broad subject of the beginnings of metallurgy as well as copper and bronze casting.

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