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Microstructure of Archaeological 17th Century Cast Copper Alloys

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Abstract

In Poland, researchers have a very strong interest in archaeometallurgy, which, as presented in classical works, focuses on dating artefacts from the prehistoric and early medieval periods in the form of cast iron and copper castings. This study, extending the current knowledge, presents the results of a microstructure investigation into the findings from the Modern era dating back to the late Middle Ages. The investigated material was an object in the form of a heavy solid copper block weighing several kilograms that was excavated by a team of Polish archaeologists working under the direction of Ms Iwona Młodkowska-Przepiórowska during works on the marketplace in the city of Czestochowa during the summer of 2009. Pre-dating of the material indicates the period of the seventeenth century AD.

The solid copper block was delivered in the form of a part shaped like a bell, named later in this work as a "kettlebell". To determine the microstructure, the structural components, chemical composition, and homogeneity, as well as additives and impurities, investigations were carried out using light microscopy, scanning electron microscopy including analysis of the chemical composition performed in micro-areas, and qualitative X-ray phase analysis in order to investigate the phase composition.

Interpretation of the analytical results of the material's microstructure will also help modify and/or develop new methodological assumptions to investigate further archaeometallurgical exhibits, throwing new light on and expanding the area of knowledge of the use and processing of seventeenth-century metallic materials.

Keywords: Metallography, Archaeometallurgy, Microstructure, Excavations, Phase analysis

1. Introduction

In Poland, interest has been revived in archaeometallurgy [1, 2], which, as presented in classical works [3, 4], focuses on dating artefacts from the prehistoric and early medieval periods in the form of cast iron and copper castings.

This study, extending the previous area of research, presents the results of microstructural investigation of the findings from the late Middle Ages. The investigated material was an object in the form of a heavy solid copper block weighing several kilograms that was extracted from the ground by a team of archaeologists working under the direction of Ms Iwona Młodkowska-Przepiórowska during excavations of the marketplace in Czestochowa during the summer of 2009. Pre-dating of the material indicates the period of the seventeenth century AD.

The solid copper block was delivered in the form of a part shaped like a bell, named later in this work as a "kettlebell". To determine the microstructure, in particular the structural components, chemical composition, and homogeneity, as well as additives and impurities, numerous investigations were carried out. Another important part of the identification and description of the findings in this case is the appliance of multidisciplinary research with the participation of specialists from the areas of archaeology, materials science, and metallurgy [5].

The obtained research results provide relevant information for determining the original manufacturing process and technology and the use of the produced object. Interpretation of the analytical results of the material microstructure will also help modify and/or develop new methodological assumptions to investigate further archaeometallurgical exhibits, throwing new light on and expanding the area of knowledge of the use and processing of the seventeenth-century metallic materials.

2. Material and methodology

The study deals with investigations concerning artefacts excavated from the ground during archaeological excavations. In this paper, the remnants of foundations and buildings that were discovered below the ground level of the city market are studied.

Metallographic tests were performed using a Leica light microscope together with the analysis of images obtained with the help of Leica QWIN dedicated computer software designed to support and control the microscope. Examination of the structure and analysis of the chemical composition were performed on micro-areas using a Zeiss Supra 35 scanning electron microscope (SEM), with an accelerating voltage of 20 kV, also equipped with an Energy-dispersive X-ray spectroscopy detector (EDS).

The material for the metallographic examinations carried out on the optical microscope was mounted in thermoset polymer. Finally, the samples were etched with Nital (5% nitric acid, HNO_3, in 96% ethanol, C_2H_5OH, with a concentration of 96%).

Phase analysis was carried out using a PANalytical X-ray diffractometer with filtered radiation; a cobalt anode was chosen as the source. The measuring step was set as 0.05 degree and the pulse count time was 10 seconds.

3. Investigation results

The study involved an archaeological artefact in the shape of a lump. During preliminary studies, the outer layer burst, revealing the casting itself in a shape resembling, or similar to, a bell. It was named a "kettlebell" by the authors (Fig. 1). As a result of a break in the surface layer, several fragments were obtained (Fig. 2).

The base of the weight has a nearly circular shape with a diameter of 130 mm. In its geometric centre, there is a cavity with a diameter of 40 m and a depth of 10 mm. The cross-section is an ellipsoid shape with a clearly clipped, blunt tip at a height of 90 mm. In the middle, a small recess and character (like a number 4, probably a craft sign of ownership) are visible.

On the surface of the weight, the presence of a large number of small craters was revealed (Fig. 1). They are most likely a result of the release of air bubbles during casting. This is a casting defect that results from the inability of the foundrymen (craftsmen) to dispose of the gases from the molten metal.

Fig. 1. The kettlebell excavated on the market place in the city of Czestochowa in summer 2009

Fig. 2. Fragments derived from the mould surrounding the bell-like part

The sample cut from the weight was investigated in terms of structure, and qualitative phase analysis was performed by SEM with tests to determine the chemical composition in micro-regions.

A qualitative X-ray phase analysis was performed to determine the phases that had formed during the casting process (which may indirectly provide evidence about the techniques used by contemporary foundrymen). The results of X-ray analysis (Fig. 3) confirmed that copper is the main component of the test weight, crystallizing in the A1 lattice type. The study also confirmed the presence of arsenopyrite (FeAsS), which crystallizes in a monoclinic system ($a = 5.7412$ Å, $b = 5.6682$ Å, $c = 5.7704$ Å, and $\beta = 111.93°$).

Observations of metallographic specimens of the weight material revealed that the structure consists of a matrix (Fig. 4), which is probably the copper and three other phases. Moreover, numerous voids arising from the foundry process are present in the structure.

Large precipitates of spherical shape as well as numerous light coloured smaller precipitations and numerous voids can be found in the structure of the investigated material (Fig. 5). The presence of voids in the material has already been attributed to the imperfection of the casting process that was practised. During the casting process, artisans were unable to degas the copper in the liquid state. Currently, the sulphur (S) is removed from the metallurgical copper material and the obtained artefact comprises a metal containing only 0.5 to 1% impurities [6].

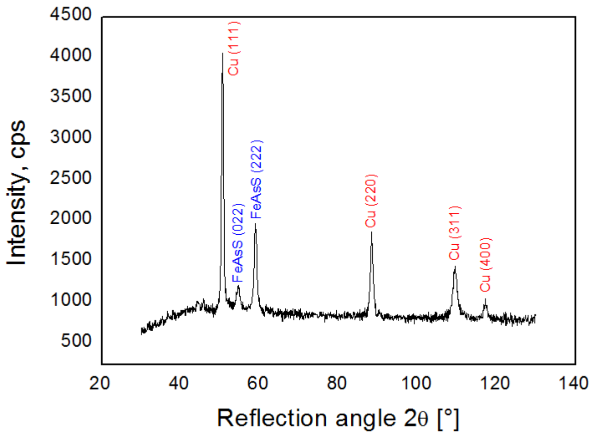

Fig. 3. X-Ray diffraction phase analysis of the investigated material

Subsequent analysis of the chemical composition, as shown in Fig. 5, indicates that the dominant element of the examined weight is copper (> 94%). The presence of arsenic at a concentration of 3.7 mass% was also found.

The main element in archaeological copper castings is arsenic, especially in the finds from the Bronze Age. The fact that copper ore occurred together with arsenic ore (mimetite) explains the presence of arsenic in the alloy. In archaeology, it is assumed that an As content of above 0.2% in an Cu-Sn casting classifies the casting as one made in the Bronze Age [7].

The most important ore of arsenic, arsenopyrite (FeAsS), only occurs in Poland in Lower Silesia in the area of the Zloty Stok . It is a common mineral from the copper ores and is similar to mimetite ($Pb_5(AsO_4)_3Cl$), a rare mineral occurring in Poland, also mainly in Lower Silesia. Due to its frequent occurrence, together with common copper, arsenic ore is indicated by the presence of As in the material weight. Furthermore, arsenic dopant may be derived from copper and arsenic sulphide – enargite (Cu_3AsS_4). This polymorphic ore of copper and arsenic is present in Poland, also in Lower Silesia, in the copper-bearing shales [8, 9].

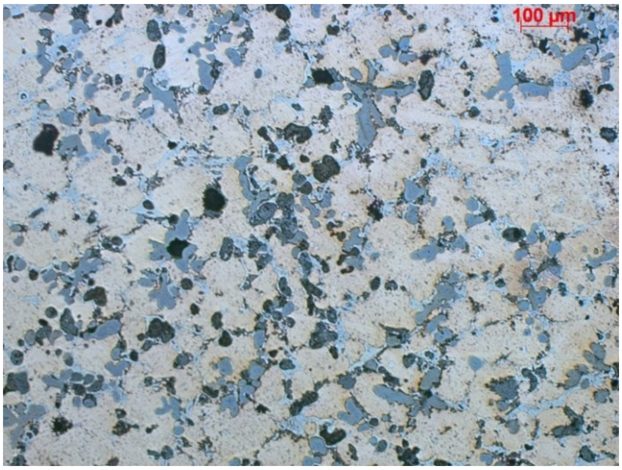

Fig. 4. Microstructure of the weight alloy, LM

In contrast, based on the analysis of the chemical composition of the spherical precipitates (2), it was found that copper is the most frequently determined element with the largest content in this phase (mass concentration of approx. 64.6%). The results of the investigations of the chemical composition confirmed the presence of sulphur (S), with a content of approximately 25%, iron (Fe), with a content of approximately 9%, and cobalt (Co), in a very low concentration of less than 1 mass% (Fig. 5).

On the other hand, the results of chemical analysis of a very fine longitudinal shaped precipitate or particle (3), which is surrounded by another precipitate of white spherical shape, are interesting. The analysis only showed the presence of antimony (Sb) at a concentration of 67.6 mass% and nickel (Ni) at a concentration of 32.4 mass%.

The presence of copper was also not found in area (4), but the element with the highest mass concentration (90%) is lead (Pb). Besides Pb, the presence of oxygen (O) at a concentration of 8% and about 2% aluminium (Al) was also confirmed.

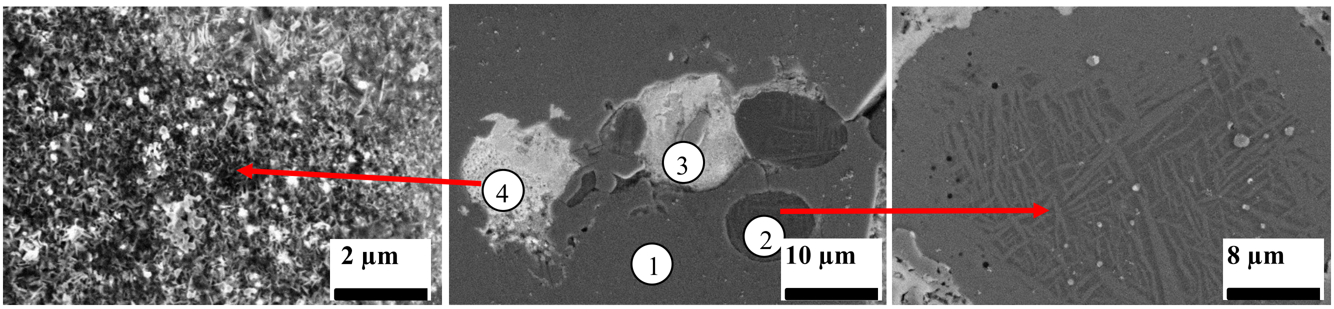

Fig. 5. Microstructure of the weight alloy, SEM

Many voids (Fig. 6) were found in numerous places in the investigated material. The voids are a consequence of failure to remove gases from the molten metal during the metallurgical casting process. EDS analysis of area (5) revealed the presence of lead (Pb) with a concentration of 56.7 mass%, antimony (Sb) at a concentration of 12.2%, oxygen (O) at a concentration of 9.3%, copper (Cu) at a concentration of 8.8%, chlorine (Cl) at a concentration of 5%, aluminium (Al) and arsenic (As) at concentrations of 3.4% each, and iron (Fe) at a concentration of 1.2%.

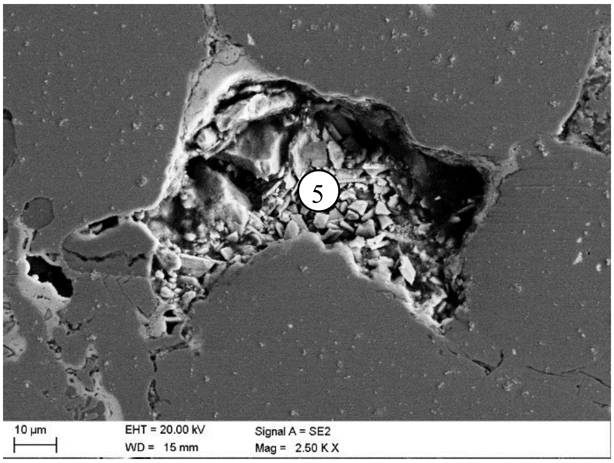

Fig. 6. Microstructure of the weight alloy, SEM

To determine the hardness, three sets of 10 measurements were carried out on the inner surfaces of the weight and the results are shown in Table 13. Based on the 30 measurements it was found that the smallest value was 159.6 HV and the highest was HV 227.3. The average value of all 30 measurements was 186 HV and the standard deviation was only 9.7% of the average, which shows that the hardness of the material is rather constant throughout the material.

Table 1.
Microhardness measurement results of the weight on different sections

1 series	2 series	3 series	together	
188	179	190	186	average [HV]
24.4	12.6	15.3	18.2	Standard deviation
13%	7%	8%	9.7%	

Three parts of the investigated weight shell, are presented in Fig. 2. The first of them, called "part No. 1" during the observations in order to distinguish triangle-shaped and elongated parts, is covered by a patina, which raises the hypothesis of a high copper content. Patina consists basic of copper carbonate and has a characteristic green colour. It is also the product of atmospheric copper corrosion in a sufficiently moist environment. In a clean atmosphere, the main component is the main hydroxy copper carbonate (II), $[Cu(OH)]_2CO_3$. This type of coating is very durable and is a result of the last stage of the corrosion process, which ensures its passivity. In an atmosphere that contains sulphur dioxide, the patina also includes sulphite (VI) of hydroxy copper (II), $[Cu(OH)]_2SO_4$, but the film has no protection against further corrosion. The covering of the surface of metal with patina lasts for decades, but the first symptoms of corrosion may begin to appear after few years.

Part No. 1 has a length of 90 mm, a width of 50 mm measured at the widest point, and a height of 45 mm. Part No. 2 reveals embedded ceramic fragments and charcoal residue as well as a small amount of patina. Its length is 75 mm, the width measured at the widest point is equal to 45 mm, and its height is 25 mm. Part No. 3 is in the form of a tetrahedral block and is of an elongated shape with visible areas affected by corrosion products derived from its iron impurities and compounds as well as small areas covered with patina.

The metallic nature of the material was confirmed in one cross-section of part No. 1. The qualitative X-ray phase analysis results presented in Fig. 7 confirm that copper (Cu) is the dominant element in the material of part No. 1, crystallizing in the face-centred cubic (FCC) crystallographic system. In addition to copper, the phase FeAsS (arsenopyrite), which crystallizes in the monoclinic system with d-spacing values of a = 5.741 Å, b = 5.668 Å, c = 5.770 Å, and β = 111.93, was also confirmed in the material. Other phases like copper sulphide (Cu_2S and CuS_2) and copper chloride (CuCl and $CuCl_2$) were also present. Both arsenopyrite (FeAsS) and copper sulphide are assumed to be the remains of the ore used for production of this alloy.

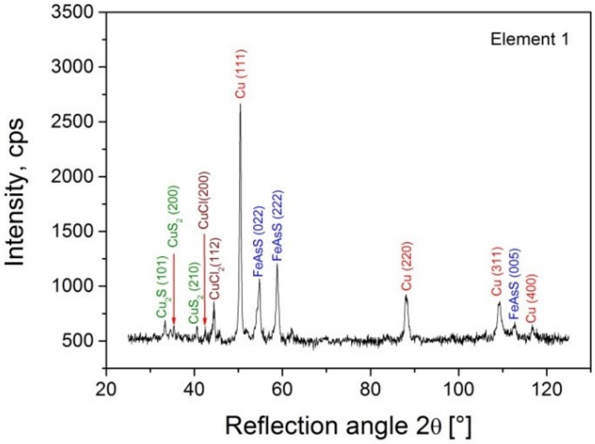

Fig. 7. X-Ray diffraction for phase analysis of the investigated material of part No. 1

Because of the microscopic observation, four phases are revealed in the structure of part No. 1. The amounts of the particular phases are very different (Fig. 8):

- Dark blue or black coloured phase is observed after etching and occurs in the form of oval dots on the phase boundary
- Light blue coloured phase observed after etching occurs most frequently in the form of blue coloured stripes. It creates integrated bands parallel to each other in certain areas. Between these phase areas, an angular system shift is observed.
- Cu_α phase is observed in the form of spots of irregular shape.
- Black coloured phase observed after etching occurs in the form of irregular shaped patches.

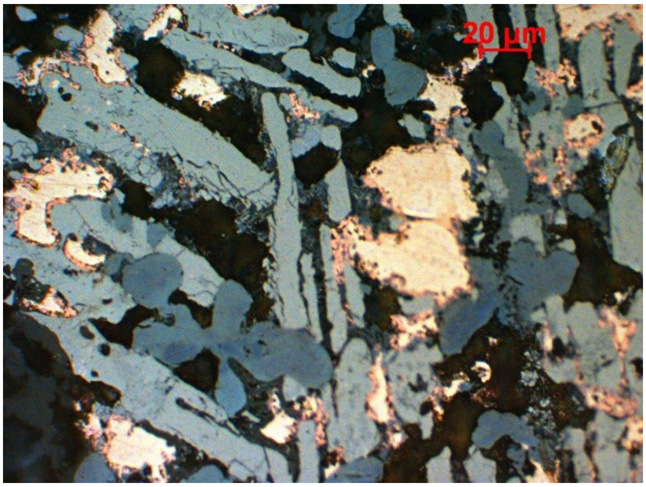

Fig. 8. Microstructure of part No. 1, four different phases are visible

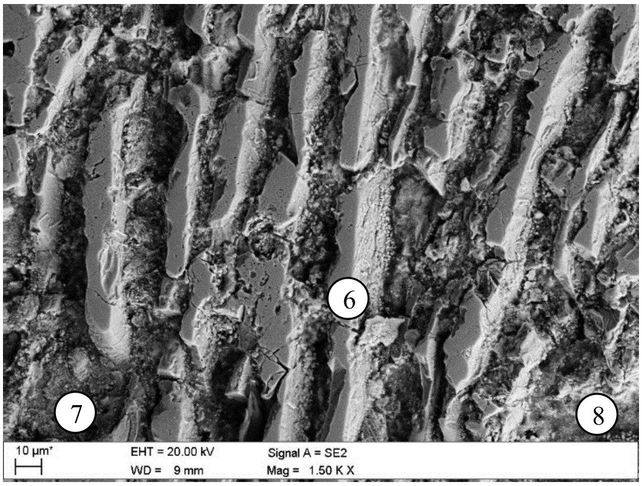

Fig. 9. Microstructure of part No. 1, bright field, SEM

Investigations carried out by SEM allowed the composition of the particular phases to be pre-determined. Due to its elongated shape and parallel arrangement of the belt, Region (6) presented in Fig. 9 has been identified as a pale blue phase (Fig. 8). In this micro-area (6), elements including mainly contaminants in copper ores were also confirmed: iron (Fe), arsenic (As), nickel (Ni), cobalt (Co), and the remains of the melting process, namely carbon (C) (Table 2). A characteristic feature of the copper ores present in the Polish territory, except for ores in the Tatra region, is a lower concentration of antimony than arsenic [10].

Analysis of the chemical composition of pale blue sections (Fig. 8) shows that this is a phase rich in iron (Fe). Three analyses showed that the concentration of this element in the investigated phase is 17–30%. Arsenic (As), with a relatively high concentration of 21–35%, and nickel (Ni), with a concentration of 8 to 16%, are also present in this phase, while the concentration of copper (Cu) is in the range of 5–33% (Table. 2). In addition, on analysing the chemical composition, carbon (C) also occurs at a concentration of 5.8–7.1% as well as cobalt (Co) at a concentration of about 6%.

However, the analysis of the chemical composition of the whole micro-area presented in Fig. 9 also reveals the presence of other elements such as oxygen (O), silicon (Si), sulphur (S), and chlorine (Cl). The presence of sulphur is most easily explained by the fact that, as a rule, sulphur occurs in Poland in copper ores called chalcocite, namely copper glance (Cu_2S), covellite (CuS), bornite (Cu_3FeS_2), and chalcopyrite ($CuFeS_2$), and minerals, namely malachite ($CuCO_3 \cdot Cu(OH)_2$), and azurite ($2CuCO_3 \cdot Cu(OH)_2$). Chalcocite ore occurs in Lower Silesia in Lubin, Polkowice, Sieroszowice, and Rudna, in New Church, in the foreland of Kaczawa in the Golden Mountains, and also in Rudawy Janowickie. It is an important source of copper because it contains up to 80% Cu [6, 11].

The occurrence of iron (Fe) in the investigated material can also be explained in the same way as oxygen (Tables 3 and 4), which is present in the copper ores as cuprite (Cu_2O)) [6, 11].

Table 2.
The results of quantitative EDS chemical analysis in microregions (6) of the Cu alloy

element	Wt.%	At.%
$\mathbf{O_K}$	9.0	24. 8
$\mathbf{F_K}$	5.4	12.4
$\mathbf{Si_K}$	2.3	3.6
$\mathbf{S_K}$	1.8	2.5
$\mathbf{Cl_K}$	1.3	1.6
$\mathbf{Fe_K}$	17.3	13.6
$\mathbf{Ni_K}$	8.0	6.0
$\mathbf{Cu_K}$	33.5	23.1
$\mathbf{As_K}$	21.4	12.5

Table 3.
The results of quantitative EDS chemical analysis in microregions (2) of the investigated Cu alloy

element	Wt. %	At. %
$\mathbf{O_K}$	3.6	12.2
$\mathbf{Pb_M}$	0.7	0.2
$\mathbf{Fe_K}$	12.3	12.9
$\mathbf{Cu_K}$	68.6	63.0
$\mathbf{As_K}$	14.8	11.7

Table 4.
The results of quantitative EDS chemical analysis in micro regions (3) of the investigated Cu alloy

element	Wt%	At%
$\mathbf{O_K}$	14.5	43.1
$\mathbf{Si_K}$	5.6	9.0
$\mathbf{Pb_M}$	21.0	4.8
$\mathbf{Fe_K}$	3.7	3.1
$\mathbf{Cu_K}$	42.8	32.0
$\mathbf{As_K}$	12.6	8.0

Other oxide ores, namely malachite $CuCo_3Cu(OH)$ forming a dense mixture of minerals with azurite: azurite malachite, chrysocolla, turquoise, pseudo-malachite (eltalite), which occurs in Poland in small quantities in the province of Świętokrzyskie (Miedzianka, Miedziana Góra) and Lower Silesia] and azurite, $2CuCo_3Cu(OH)_2$ (found in the Góry Świętokrzyskie and Lower Silesia, near Lubin and Głogów), contain cobalt in the chemical composition, explaining its presence in the material.

The dark coloured particles (9) were identified as inclusions (Fig. 10) having a composition fairly similar to the phases observed in bloomer furnace iron (Table 5) [1, 3, 12–15]. Cu rich places in the investigated area may come from the second phase (visible as bright spots). Because of the similarity of the chemical composition of the inclusions in bloomer furnace iron, they can be considered as a residual phase during the melting process.

Further study of the chemical composition in micro-regions allowed the identification of two phases, but it is very difficult to compare them with the phases exposed by light microscopy due to their similar geometries in the current state.

Phase rich in copper and chlorine (10) is visible as a smooth irregularly shaped stain (Fig. 15), wherein the mass ratio of $\frac{Cu}{Cl} \approx \frac{65}{35}$, as well as the atomic ratio of both elements, $\frac{Cu}{Cl} \approx 1$, Table 6) indicates that the phase is most likely the copper chloride phase (CuCl). Finally, determination of this issue requires further study.

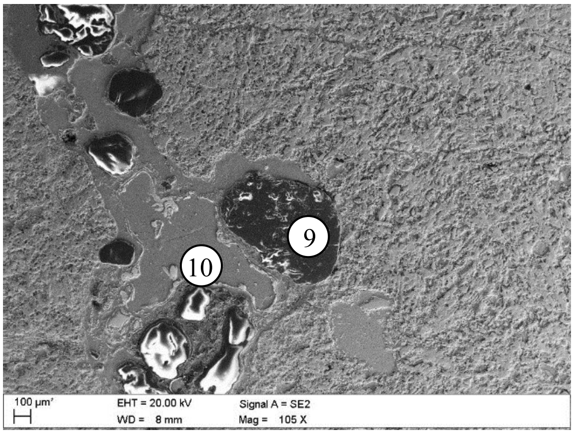

Fig. 10. Microstructure of part No. 1, bright field, SEM

Table 5.
The results of quantitative EDS chemical analysis in micro regions of the investigated Cu alloy

element	Wt%	At%
O$_K$	35.7	51.7
Cu$_K$	3.8	1.4
Al$_K$	11.1	9.5
Si$_K$	34.8	28.7
Cl$_K$	1.1	0.7
K$_K$	13.6	8.0

The presence of aluminium in the chemical composition can be explained by the use at that time of furnace lining constituted of clay from a sedimentary rock, whose main components are obtained by weathering of feldspar, in particular aluminosilicates, calcium, potassium, and sodium. Very rarely, clay can also be composed of pure kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). However, large grains (11 and 12) shown in Fig. 11 are mainly characterized by high contents of silicon (Si), with a content above 50%, and oxygen (O), with a content above 35%, and a small amount of copper (Cu), with a content of approximately 6–8% [16–18].

These results of the chemical composition analysis of the micro-regions conclusively indicate the presence of silica (SiO_2), also known as common sand, a compound that is very widespread in the Earth's crust, in a very clean form of mostly sand and sandstone, which makes up approximately 12% of the mass of the Earth's crust.

The presence of silica in such high concentrations can be explained by the presence of silicate ores: chrysocolla ($Cu_2SiO_2 \cdot 2H_2O$), a relatively common mineral of the silicate class, which is a mineral occurring in zones of copper oxidation and in dioptase ($CuSiO_2 \cdot 2H_2O$), which, like chrysocolla, is a secondary mineral, present in the ventilation zone of copper ores. In addition, it is worth mentioning that dioptase coincides with calcite, chrysocolla, malachite, azurite, limonite, and other ores containing copper.

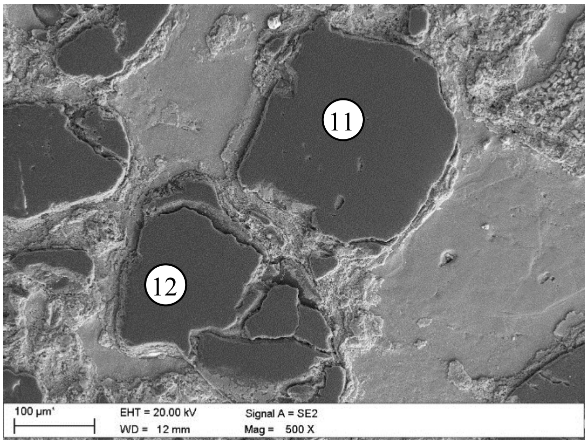

Fig. 11. Microstructure of part No. 1, bright field, SEM

There is no information in the literature on the presence of potassium (K) and fluorine (F) in such alloys. It is possible that they could be used to identify the type of ore, mining, and production or for the dating of a part [19–20].

4. Conclusions

After analysing the results of the investigation, the following conclusions were formulated:

1. The weight is made of copper-based alloy with additions of elements such as arsenic, lead, antimony, iron, and aluminium, contaminated with oxides and impurities such as residues left after the melting process: carbon and silicon.
2. Casting defects, namely voids, were observed in the weight structure.

3. Among the investigated materials, the highest hardness of the material is measured for the copper weight, and the lowest for part No. 1. In the case of the weight, this is probably due to the much higher metallurgical purity as well as the addition of antimony, which will strengthen the alloy.
4. In part No. 1, that is, the shell of the mould, copper is the main alloying additive, but part No. 1 also contains other elements, sometimes in very high amounts, which confirms the very low metallurgical purity of the material and thus shows that it is not the ordinary bronze alloy that was produced at that time and was often considered as a by-product of the production process (e.g. the casting).
5. High amounts of impurities in the microstructure of part No. 1 can also indicate that the item is produced of scrap-metal or may be considered as a preparation for continued production/melting.

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