

The investigation of microstructure and hardness of archaeological alloys

J. Konieczny ^{a,*}, Ł. Kondziółka ^a, I. Młodkowska-Przepiórowska ^b

^a Institute of Engineering Materials and Biomaterials,

Silesian University of Technology, ul. Konarskiego 18a, 44-100 Gliwice, Poland

^b Museum of Czestochowa, Al. NMP 45, 42-200 Czestochowa, Poland

* Corresponding author: E-mail address: jaroslaw.konieczny@polsl.pl

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Materials

ABSTRACT

Purpose: The aim of the work was to investigate the microstructure and hardness of archaeological metal.

Design/methodology/approach: The investigations of the microstructure were made on ZEISS SUPRA 25 with EDX method. Investigation of structure were made on PANalytical's X'Pert diffractometer.

Findings: Metallographic studies were carried out on archeological finds that have been extracted from the ground during excavations on the market in Czestochowa (Poland) during the summer of 2009. In addition to the remains of buildings discovered under the level of market research objects were excavated in the area. Preliminary dating of the material shows a broad interval.

Research limitations/implications: In the examined finds the main component is copper, but they also contain other elements, sometimes in large numbers, that indicates a very low-purity metallurgical material and thus proves that this is not a typical bronze how manufactured at that time. The metal nails are characterized by high purity metallurgical.

Practical implications: The presented results are an important contribution to the accurate characterization of found objects and also can help to determine more accurately determine their age and use in daily life of ancestors.

Originality/value: These factors indicate new areas of research in materials science that significantly enrich the knowledge of times past.

Keywords: Metallic alloys; Archaeological metal; Casting; Copper alloys

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1. Introduction

The origins of smelting, casting and forging of copper dates from the period around 5000 years BC whereas the smelting of copper mixed ore containing arsenic and lead in 1000 years later and receiving bronze by melting copper with tin ore and copper with tin for a period of about 2500-2200 BC. About 1000 years BC people have mastered the ability to receive the bronze by

melting copper with zinc ore in the presence of carbon. Because periods, such as the Bronze Age ore Iron are the only conventional it is known that copper alloy foundries did not stop with the mastery of iron technology receiving by people [1-5] and work on improving the structure and properties of copper alloys are still in progress [6-13].

After a long period of stagnation, on the Polish lands revives interest of archeometallurgy [14,15], which, like the classical

works [16,17] focuses on the origin of period dating from the prehistoric and early medieval iron, steel. The following study presents the results of tests carried out on modern discoveries, responding in this way in 1961, denounced prof. J. Piaskowski appeal: "Metallographic research of the old metal products do not end in the vicinity of the thirteenth century, but must reach the moment when our steel mills and foundries were introduced systematic laboratory studies "[18].

The aim of the work was to investigate the microstructure and hardness of archaeological metal.

2. Material and methods

Test investigated materials were the elements which have been extracted from the ground by a team of archaeologists working under the direction of Mrs. Iwona Młodkowska-Przepiórowska during excavations under the market in Czestochowa (Republic of Poland) during the summer of 2009. The buildings foundations and the remains were examined, which were discovered under the market level. Preliminary age determination material shows a broad interval.

Metallographic studies were carried out on light microscope LEICA cooperating with a PC equipped with software LECICA QWIN to handle microscope. Studying the structure and chemical composition analysis in micro-square was performed on scanning electron microscope (SEM) Zeiss Supra 35 at 20 kV accelerating voltage equipped with a snap-in to analyze the chemical composition of micro-square (EDS - Energy-dispersive X-ray spectroscopy).

At the outset in order to prepare materials for these studies was purified from the remaining land after which the metal artifacts were removed corrosion products in order to expose the metal free from damage slaughter corrosion process. In the next stage of preparation material for metallographic examination on light microscopy mount the test samples in thermosetting polymer at 180°C, and then polished on wet emery paper of decreasing grain size of 220, 500, 800 to 1200. Further preparation of metallographic specimen included wet polishing with Al₂O₃ powder about a diameter of 3 microns. Thus prepared metallographic specimen digested in NITAL (5% solution of nitric acid HNO₃ in ethanol at a concentration of C₂H₅OH 96%).

X-ray phase analysis of samples was performed on PANalytical's X'Pert diffractometer using the filtered radiation of cobalt anode lamp. Measuring time was 0.05 and counts the pulses was 10 s.

3. Results and discussion

3.1. Slug copper (weight)

A slug of copper was delivered in the form of two components: a bell-shaped form called later in the development work by the authors' "weight" (Fig. 1), which revealed a fracture through the surrounding shell and shell elements (Fig. 2).

Basis weight was in the shape of a circle with a diameter of

130 mm with coaxial cavity with a depth of about 10 mm and a diameter of about 40 mm. Ellipsoidal cross-section with a blunt apex clearly truncated at a height of 90 mm. In the middle of a small cavity and visible sign (resembling the Figure 4, the most likely craft a proprietary mark). Surface is covered with a large number of small craters (Fig. 1), which probably originated from the time of casting the solid (presumed defect in the casting - air bubbles).



Fig. 1. Investigated weight



Fig. 2. Excerpts from the mold surrounding the bell element

Three fragments from the mold (shell), which was made of weight is shown in Figure 2. The first one (named in the course of observation in order to distinguish elements) Element 1 oblong, triangle-shaped, covered with a patina (green rot), which suggests a high content of copper, because the patina is basic copper carbonate with a characteristic green color. Patina (rust) is a product of atmospheric corrosion of copper and its alloys in a sufficiently moist air. In a clean atmosphere, its main ingredient is the main carbonate hydroxy copper (II) - [Cu(OH)]₂CO₃. Patina is a coating which is durable effect of the last stage of the corrosion process, which ensures its passivity. In the atmosphere, which contains sulfur dioxide, the composition of the patina also includes sulfite (VI) hydroxy copper (II) - [Cu(OH)]₂SO₄, but this

is not a coating protecting it from further corrosion. The whole process of overlapping metal surface patina coating lasts several years, although the first symptoms may begin to appear after a few years.

Element 1 is the length of 90 mm, the width measured at the widest point: 50 mm and 45 mm height. Element 2 with flush piece of pottery, charcoal and a small amount of patina. Length: 75 mm, the width measured at the widest point: 45 mm, height: 25 mm. Element 3, tetrahedron of elongated shape places with visible effects of corrosion (rust), derived from compounds of iron and the small areas covered with patina.

After cutting element is a cross-section clearly visible metallic nature of the material (Fig. 3). Judging by the color, it is likely to alloy with the main alloying element is copper (Cu).



Fig. 3. Cross section of an Element 1

To confirm these suppositions, X-ray analysis of the qualitative phase composition of the material Element 1 were performed in order to identify the phases which occur in it. The results of X-ray qualitative phase analysis (Fig. 4) confirm that the dominant element in material Element 1 is a copper (Cu) crystallizes in the face-centred cubic lattice of regular system A1. In addition to the copper in the material phases also confirmed the presence of FeAsS (arsenic), which crystallizes in the monoclinic system ($a=5.7412$, $b=5.6682$, $c=5.7704$; $\beta=111.93$), copper sulfides Cu_2S and CuS_2 and copper chloride CuCl and CuCl_2 . The presence of both arsenic (FeAsS) and copper sulfide certainly is residue ore used in the manufacture of the alloy. It should be noted that this type of analysis can reveal the phase composition of the present phase if its volume exceeds 3% of the tested material. So they can occur in the material, other chemical compounds whose volume does not exceed 3% threshold of detection.

The microscopic observation revealed four phases occurring in the material from which the Element 1 was made. Participation phases is very unequal (Figs. 5 and 6):

- dark phase that occurs most often in the form of oval spots on the interface or in the dark phase (Fig. 8 and Fig. 9);
- light blue phase occurs most often in the form of blue color bands. Creates systems fringes parallel to each other in certain areas. Between areas the present angular offset of the observed systems (Fig. 7 and Fig. 10);
- copper phase - is observed in the form of spots of irregular shape (Figs. 5-10);
- black phase - visible in the form of spots of irregular shape.

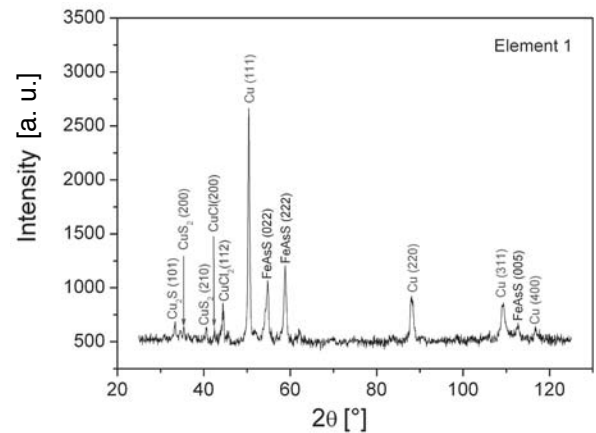


Fig. 4. X-ray diffraction of qualitative phase analysis material Element 1

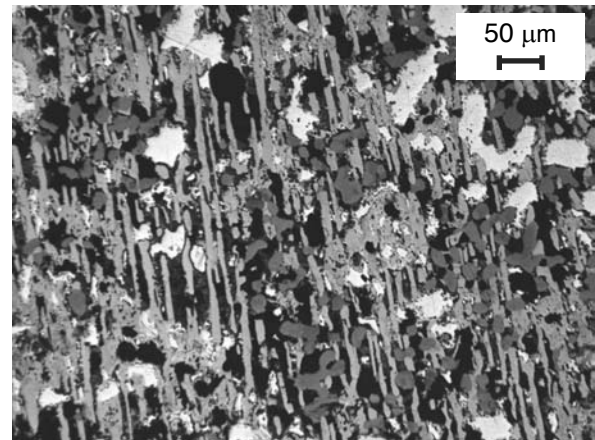


Fig. 5. Transverse metallographic specimen of copper shell elements. Visible 4 different phases

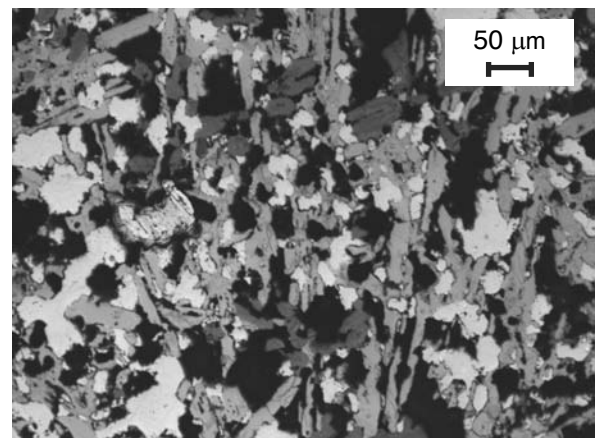


Fig. 6. Transverse metallographic specimen of copper shell elements. Sample taken from the same part of the shell as metallographic specimen observed in Fig. 5

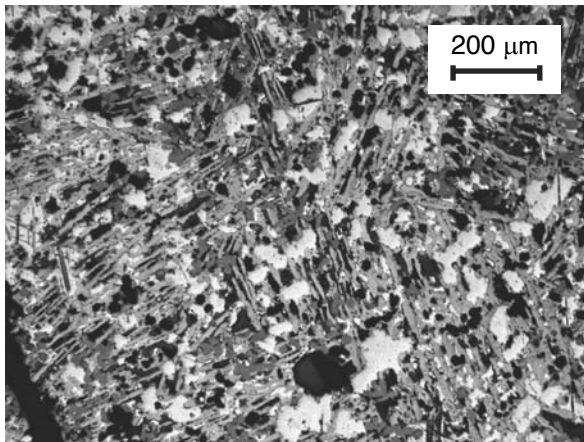


Fig. 7. Lateral metallographic specimen of shell element, see the blue phase belt systems angled relative to each other

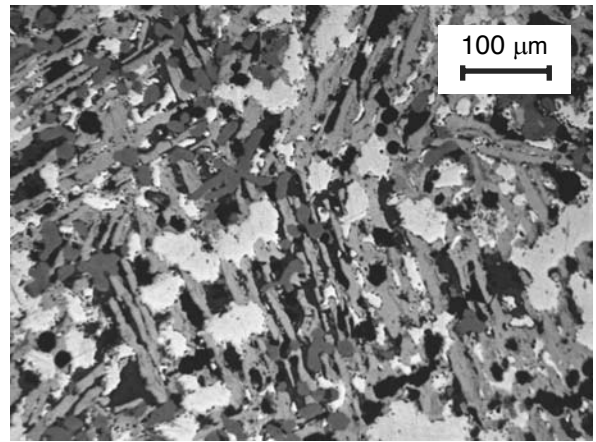


Fig. 10. Lateral metallographic specimen of shell element

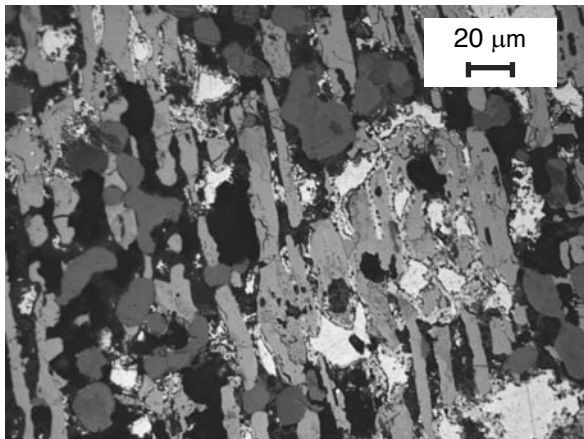


Fig. 8. Lateral metallographic specimen of shell element

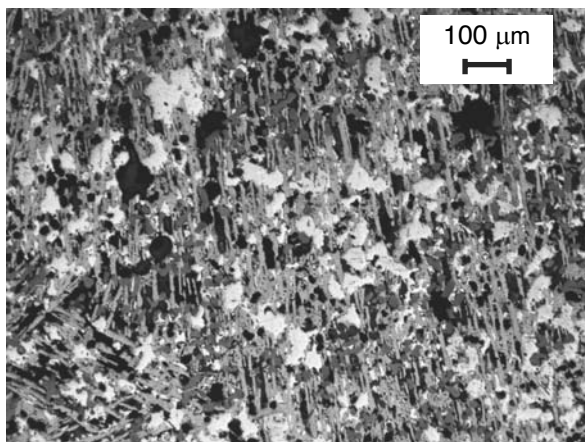


Fig. 9. Lateral metallographic specimen of shell element

A study of scanning electron microscope allowed us to determine the initial chemical composition of phases. Area (1) shown in Figure 11 due to the elongated shape and parallel arrangement of lanes has been identified as the phase of light blue (Figs. 5-10). In the micro-square (1) revealed the presence of elements which are primarily contamination of copper ores (Fig. 12): iron, arsenic, nickel, cobalt and the smelting process residues - carbon (Table 1). A characteristic feature of copper ore found on Polish soil, except for the Tatra ore, is concentration of antimony less than the arsenic in ores [19].

Analysis of the chemical composition of the light blue sections (Figs. 5-10) showed that it is a phase rich in iron (Fe). Three analysis conducted using scanning electron microscope and an integrated module of the EDS analysis showed that the concentration of this element in the test phase is 28.6 to 30%. Also, arsenic occurs in this phase in a relatively large share of 30.8 to 35.45 as well as nickel in the share of 15.4 to 16.7%. While the concentration of copper is several times smaller and ranges from 4.8-11.5 (Fig. 12, Table 2). In addition, the chemical composition of this phase is carbon at a concentration of 5.8-7.1%, and cobalt at a concentration of about 6%.

However, the analysis of chemical composition of the micro-region presented in Fig. 11 also revealed the presence of other elements such as oxygen (O), silicon (Si), sulfur (S) and chlorine (Cl). The easiest way to explain the presence of sulfur, since sulfur usually occurs in Poland in ores called chalcocite copper - copper glance (Cu_2S), covellite (CuS), bornite (Cu_3FeS_2) and chalcopyrite (CuFeS_2) and minerals: malachite ($\text{CuCO}_3 \cdot (\text{OH})_2$) and azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$). Chalcocite ores occur in Lower Silesia, in Lubin, Polkowice, Sieroszowicach, Rudna), in the Nowy Kościół, in the Foothills Kaczawa, Złote Góry, Rudawy Janowickie. It is an important source of obtaining the copper, it contains up to 80% Cu [20,21].

Also, the presence in the material of iron can be explained in the same manner and to oxygen (Fig. 13, Fig. 14, Tables 3 and 4), which occurs in the copper ore called cuprite (Cu_2O) [20,21].

Arsenic is an important element in dating the finds of metal. In some publications it was stated that the contents of more than 0.2% As in the alloy means that it comes from the bronze age [22]. However, such dating is regarded as an approximation due

to the lack of justifications for such categorical statements. Arsenic ore - mimetite $Pb_5(AsO_4)_3Cl$ (mineral arsenates of the cluster, which occurs in Poland in Lower Silesia in the Rudawy Janowickie, near the town of Czarnów and Rędziny) and arsenic $FeAsS$ (mineral salts of sulfuric clusters of common and widely occurring in Poland, among others in the Złoty Stok on Lower Silesia, operated from the Middle Ages to the 50s of the twentieth century, and also in Kowary and Przecznicza - cobalt carrying) very often occur together with copper ores.

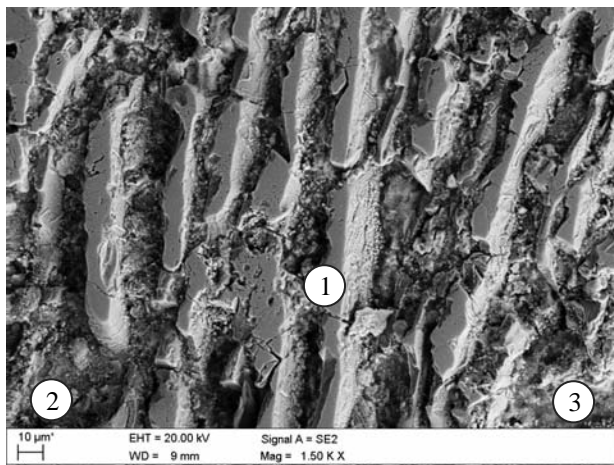


Fig. 11. Structure of the Element 1, SEM

Table 1.
The results of quantitative chemical analysis of copper alloy in micro-square on Fig. 11

Element	Wt%	At%
OK	09.04	24.78
FK	05.36	12.36
SiK	02.28	03.57
SK	01.84	02.52
ClK	01.27	01.57
FeK	17.26	13.55
NiK	08.05	06.01
CuK	33.49	23.11
AsK	21.42	12.53

Similarly, it explains the presence of this element in the tested material. In addition, the source of arsenic in the alloy may also be sulphide of arsenic and copper - enargite (Cu_3AsS_4), which is polymorphic ore Cu and As occurring in Poland in the copper-bearing shales in the Lower Silesia [23].

Dark phase (4) has been identified as inclusions (Fig. 15), with a composition similar to those observed in smelting iron (Table 5) [24-26]. Copper in the study area may come from the second phase (visible as bright spots). Due to the similarity of the chemical composition of inclusions in smelting iron phase can be regarded as the melting process residue.

Further studies on the chemical composition of micro-square areas even helped distinguish two phases, although the identification of phases discovered by light microscopy due to their similar geometries in the present state of research is impossible.

Phase rich in copper and chlorine (5), seen as smooth patches of irregular shape (Fig. 15), in which mass participation $\frac{Cu}{Cl} \approx \frac{65}{35}$ and the participation of the atomic of both elements $\frac{Cu}{Cl} \approx 1$ (Table 6) indicate that this phase is probably the copper chloride ($CuCl$). Ultimate decision on this question, however, requires further study.

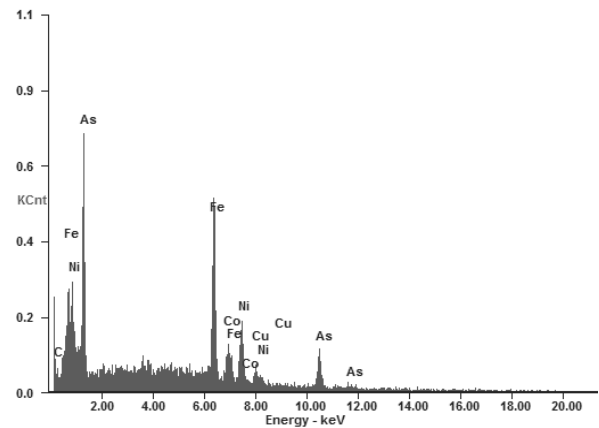


Fig. 12. EDX microanalysis performed on the marked places (1) on Fig. 11

Table 2.
The results of quantitative chemical analysis of copper alloy in micro-square (1) on Fig. 11

Element	Wt%	At%
CK	07.01	28.34
FeK	30.03	26.13
CoK	06.40	05.28
NiK	16.74	13.85
CuK	04.86	03.71
AsK	34.96	22.68

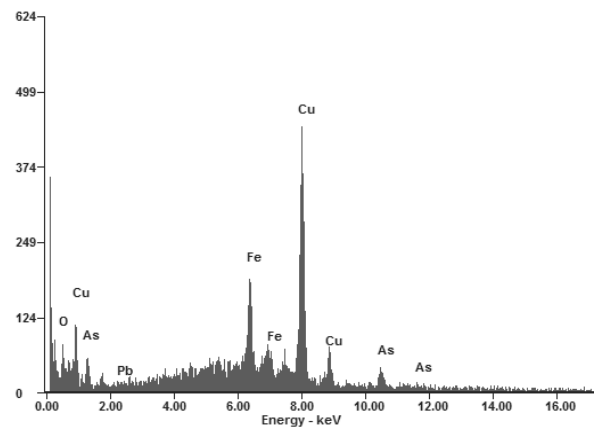


Fig. 13. EDX microanalysis performed on the marked places (2) on Fig. 11

Table 3.
The results of quantitative chemical analysis of copper alloy in micro-square (2) on Fig. 11

Element	Wt%	At%
OK	03.35	12.23
PbM	00.69	00.20
FeK	12.32	12.87
CuK	68.63	63.02
AsK	15.00	11.68

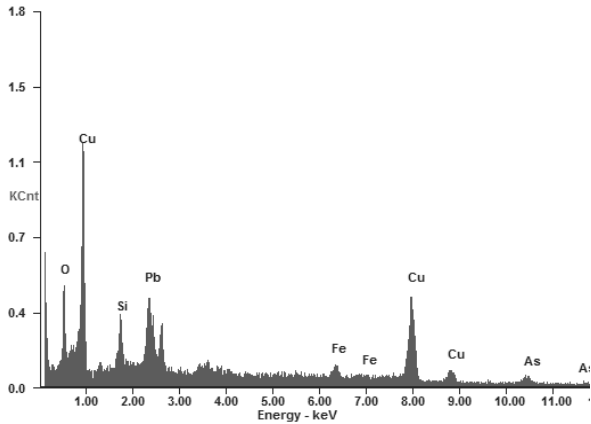


Fig. 14. EDX microanalysis performed on the marked places (3) on Fig. 11

Table 4.
The results of quantitative chemical analysis of copper alloy in micro-square (3) on Fig. 11

Element	Wt%	At%
OK	14.53	43.09
SiK	05.35	09.03
PbM	21.05	04.82
FeK	03.67	03.12
CuK	42.82	31.97
AsK	12.58	07.97

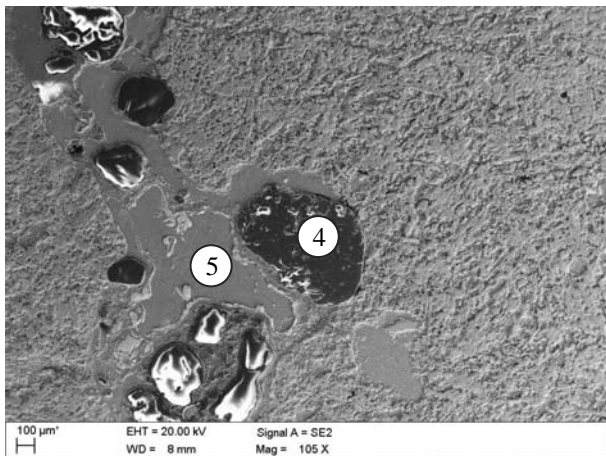


Fig. 15. Structure of the Element 1, SEM

Table 5.
The results of quantitative chemical analysis of copper alloy in micro-square (4) on Fig. 15

Element	Wt%	At%
OK	35.72	51.69
CuL	03.75	01.37
AlK	11.11	09.53
SiK	34.81	28.69
ClK	01.06	00.69
KK	13.55	08.03

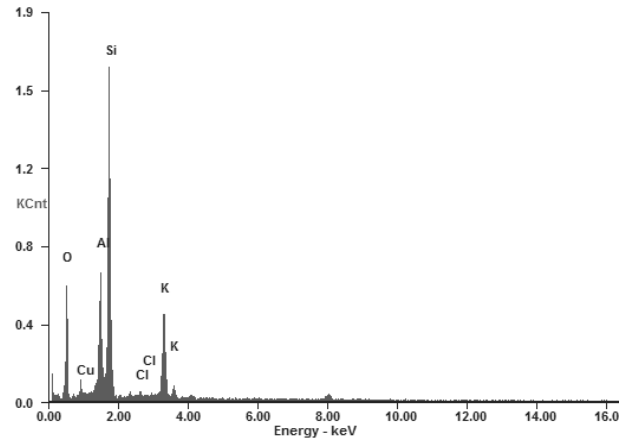


Fig. 16. EDX microanalysis performed on the marked places (4) on Fig. 15

The reason for the presence of aluminum in the chemical composition can be used in lining furnaces at that time (Fig. 17).

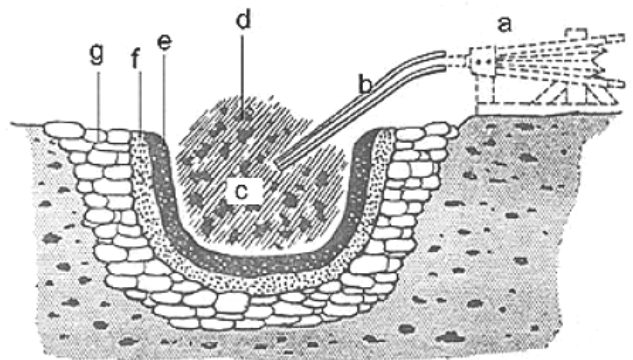


Fig. 17. Furnace for melting metal alloys from the Bronze Age: a - Smile, b - nozzle, c - charcoal, d - fine "grind" of copper and tin ore, e - lining of clay, f - priming with pen, g - stone lining

As shown in the Fig. 17 the furnace lining was clay which is sedimentary rock, which formed the most important ingredients in the process of weathering of feldspars in particular aluminosilicates of calcium, potassium and sodium. Very rarely, clay consists of pure kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$).
The large grains (7 and 8) shown in Figure 18 are

characterized with primarily high content of silicon (Si) over 50% and oxygen (O) above 35% and a small addition of copper (Cu) of about 6-8% (tabl. 7 and 8). The results of the analysis of chemical composition in micro-square conclusively demonstrate the presence of silica (SiO₂), which is plain sand. Silica is a compound very widespread in the earth's crust. As you clean its characters - mostly sand and sandstone - constitute about 12% of the Earth's crust, while also taking into account all the minerals which include it as part of their overall structure of the content is about 50% of the Earth's crust. Silica is an essential component of several commonly used materials.

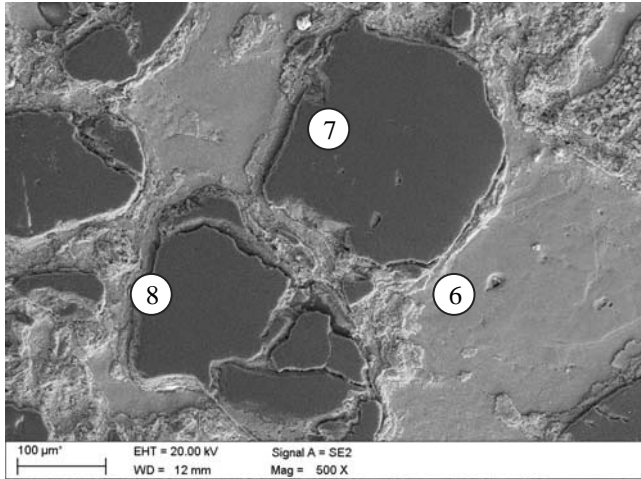


Fig. 18. Structure of Element 1, SEM

Table 6. The results of quantitative chemical analysis of copper alloy in micro-square (6) on Fig. 18

Element	Wt%	At%
ClK	34.85	48.95
CuK	65.15	51.05

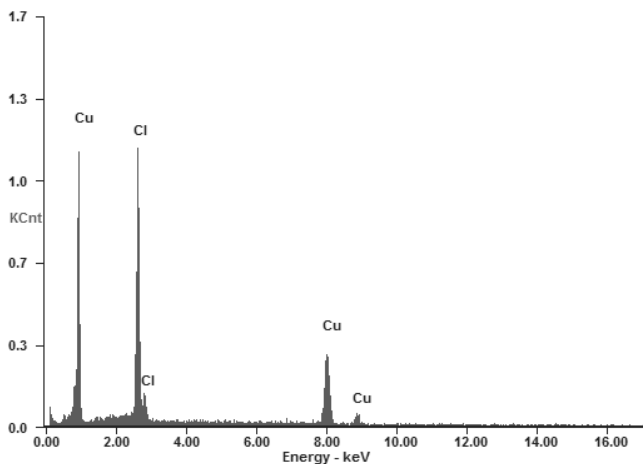


Fig. 19. EDX microanalysis performed on the marked places (6) on Fig. 18

Table 7. The results of quantitative chemical analysis of copper alloy in micro-square (7) on Fig. 18

Element	Wt%	At%
OK	38.25	54.01
SiK	53.53	43.06
CuK	08.23	02.93

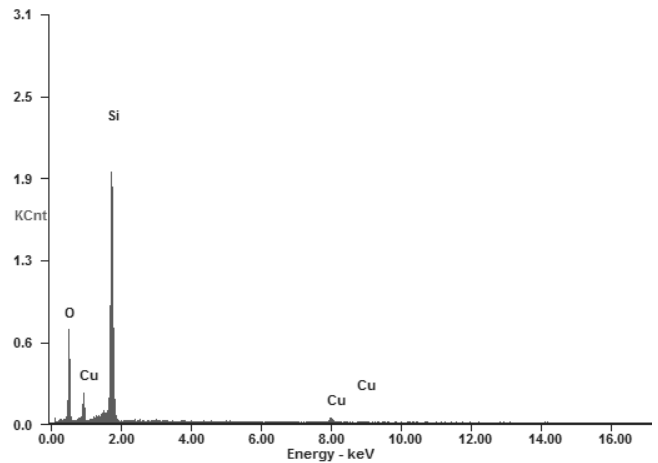


Fig. 20. EDX microanalysis performed on the marked places (7) on Fig. 18

Table 8. The results of quantitative chemical analysis of copper alloy in micro-square (8) on Fig. 18

Element	Wt%	At%
OK	39.71	55.05
SiK	54.26	42.84
CuK	06.03	02.11

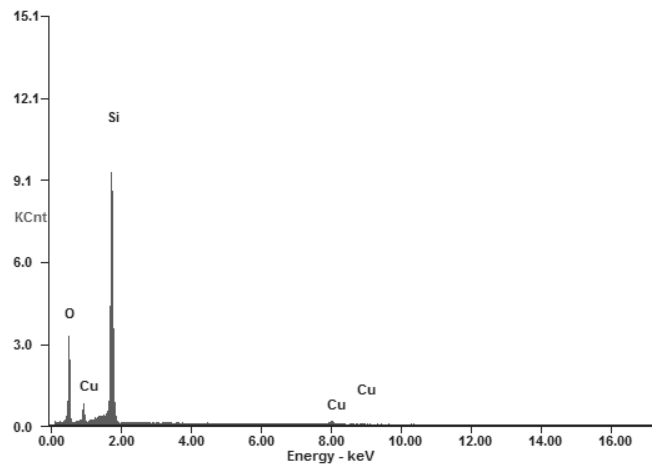


Fig. 21. EDX microanalysis performed on the marked places (8) on Fig. 18

The presence of silicon in such high concentrations may explain its occurrence in silicate ores: chrysocolla $Cu_2SiO_3 \cdot 2H_2O$ (common and widespread mineral silicates of the cluster), which is a mineral oxidation zone of copper deposits as well as in diopside $CuSiO_3 \cdot 2H_2O$ (mineral silicates of the cluster), which, like chrysocolla is secondary mineral, occurs in the zone of weathering of copper ore. Moreover, it is worth mentioning that diopside coincides with calcite, chrysocolla, malachite, limonite and azurite, or other ores containing copper. There is no information in the literature on the presence of potassium (K) and fluorine (F) in these alloys, can they can be used to identify the type of ore, mining, manufacturing or the dating of the item.

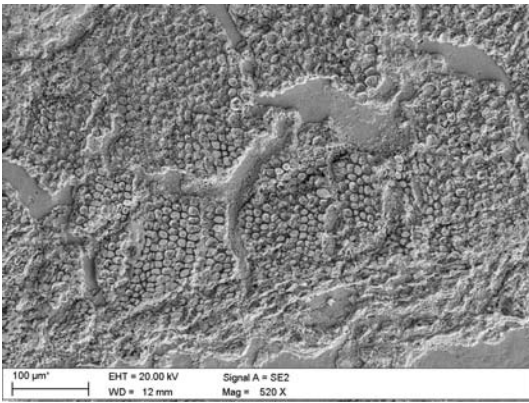


Fig. 22. Structure of Element 1, SEM

Table 9. The results of quantitative chemical analysis of copper alloy in micro-square Fig. 22

Element	Wt%	At%
CK	10.66	31.96
OK	11.70	26.34
SiK	02.24	02.88
PK	01.25	01.46
ClK	05.34	05.42
CuK	50.78	28.80
PbL	18.03	03.14

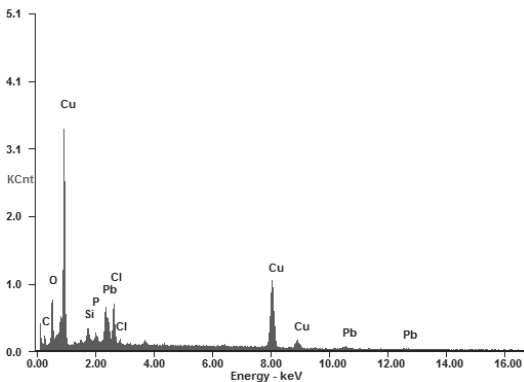


Fig. 23. EDX microanalysis performed on the marked places on micro-square like on Fig. 22

Analysis of chemical composition in micro-square shown in Fig. 22 showed the presence of primarily copper of about 50% as well as large quantities of lead - 18%, oxygen - 11.7%, carbon - 10% and small amounts of chlorine, silicon, phosphorus. The results are shown in Fig. 23 and Table 9. This analysis applies to a fairly large area.

However, the analysis of chemical composition in micro-square (9) also showed the presence of aluminum of about 3%, and calcium in an amount of more than 4%. But most importantly, that in the present micro-square analysis revealed the presence of almost 59% of carbon. This element is very common in all compounds and organic materials. The structure in Figs. 22 and 24 does not resemble the typical structures of copper alloys. Such a large concentration of carbon suggests that these are remnants of organic materials that were not removed from the material during the melting process and melt remains of charcoal being the fuel for metallurgical processes [27].

Moreover, the structure shown in Figures 22 and 24 shows the most likely unfired charcoal residue (commonly used in the smelting process) supersaturated liquid metal. During the process of melting metal brought to a liquid state flooded (saturated) charcoal, which had not completely burned.

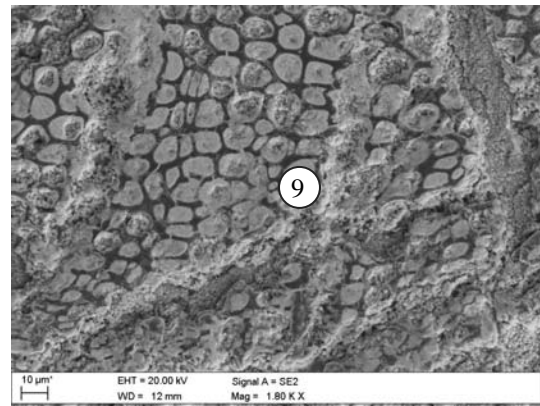


Fig. 24. Microstructure of Element 1, SEM

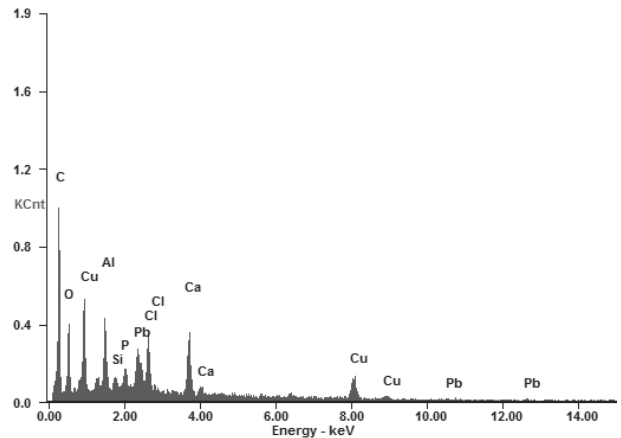


Fig. 25. EDX microanalysis performed on the marked places (9) on Fig. 24

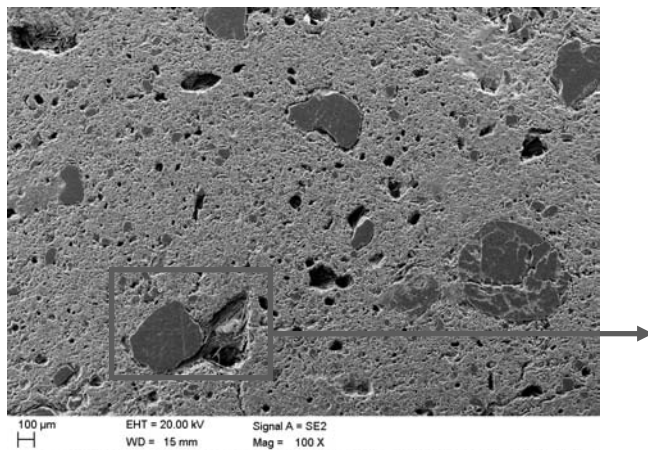


Fig. 26. Microstructure of Element 2, SEM

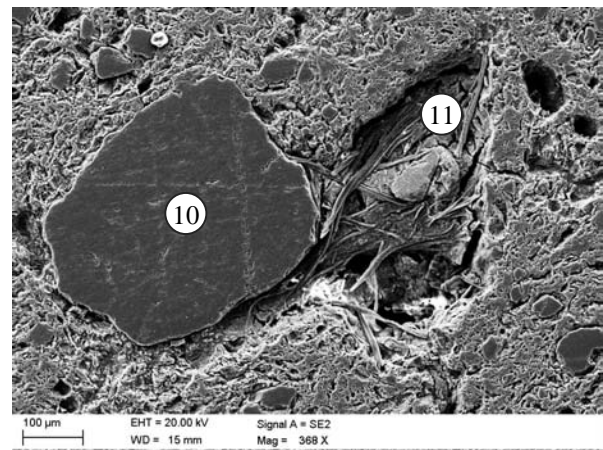


Fig. 27. Microstructure of Element 2 with visible of organic remains

Table 10.

The results of quantitative chemical analysis of copper alloy in micro-square (9) on Fig. 24

Element	Wt%	At%
CK	58.91	77.68
OK	13.80	13.66
AlK	03.19	01.87
SiK	00.59	00.33
PK	01.11	00.57
ClK	03.09	01.38
CaK	04.44	01.75
CuK	09.33	02.33
PbL	05.54	00.42

Shell material is characterized by high pollution. Two of the four phases practically do not contain copper or contain a small amount of it, is probably the third phase of copper chloride on the phase of the fourth part of Cu does not exceed 50%. This fact may indicate that the product is spent obtaining partially melted copper or copper ore.

Microhardness tests confirmed the heterogeneity of the structure as manifested by the large standard deviation of the mean value (Table 11). There have been two sets of 10 measurements each. Of all 20 measurements the lowest value was of 40.9 HV and highest value of 129.8 HV. Very large differences between minimum and maximum values suggest that the penetrator delve into every phase of the soft (eg, copper) and other times in the hard phase (eg, SiO).

Table 11.

The results of microhardness measurements of weight at different distances

1 series	2 series		
70.9	86.7	79.2	Mean value [HV]
17.4	29.2	25.0	Standard deviation
24.4%	33.6%	31.5%	
89.6	129.8	129.8	Max value
40.9	40.0	40.9	Min value

Also the Element 2 shown in Figs. 26, 27 with flush piece of pottery, charcoal and a small amount of patina were followed for scanning electron microscopy

Detailed analysis of organic residues (Fig. 28) that look like a leaf vein or fiber plants (13), trees can be revealed in addition to very large amounts of carbon, calcium, aluminum, silicon, oxygen, chlorine and iron, phosphorus, magnesium and sodium and, above all the elements present in organic compounds (C, O, N, S, F, Cl, Br, I) [28].

Figure 26 shows a fragment of the microstructure of Element 2 at relatively low magnification - only 100 times. However, the magnification of the selected area of the microstructure (Fig. 27) is clearly shows organic residues (most likely plant fragments). Analysis of the chemical composition of the separation of large darker spherical-shaped cross section (10) revealed only three elements: silicon, oxygen and small amounts of carbon. It is therefore assumed that it is a grain of sand. Slight concentration of carbon, which appeared as a result of the analysis will most likely come from neighboring organic residues. Another analysis of the chemical composition of micro-square (11) confirmed the presence of elements characteristic of organic substances such as carbon and calcium and aluminum, silicon, oxygen and chlorine.

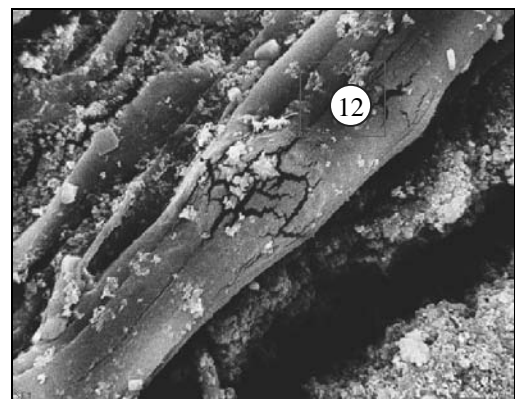


Fig. 28. View the remaining stalks in the microstructure Element 2

The case of the presence of organic residues in the analyzed Element 2 is not isolated. In other areas of the test material was also confirmed their presence (Figs. 29 and 30). Furthermore, as shown in Figure 30 the structure of the test material is very complex and shows a very high homogeneity and very low purity metallurgical material.

A lump of copper is probably slag coming from the furnace lining with fragments [19]. However, exact identification is very difficult due to the lack of research in this area

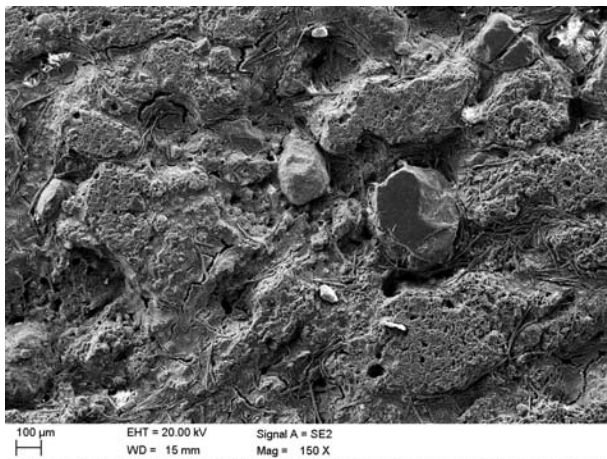


Fig. 29. Heavily contaminated by microstructure Element 2 with visible organic debris

Copper is a metal, which in addition to gold, was the earliest known and used by human being. Already the ancient peoples of Asia Minor, Egypt and Europe's acquire ability of smelting and casting of copper objects. In Europe, copper mining was developed in about 920 years in Saxony [21]. In Poland, the oldest surviving casting furnace was discovered on Mount Tumsk in Plock. Assessing by the patina coated metal pellets that are left in the casting mold, rediscovered near the furnace and foundry furnace bottom was covered with patina [28]. At the beginning of the twentieth century in the United States developed and implemented a more efficient method of extraction and enrichment of copper ores and above all, improved metallurgical processes [21].

The melting point of copper is 1084°C and boiling point 2595°C so as compared to iron, whose melting point is 1534°C, it is a metal that was easier to melt [20]. Obtaining a suitable temperature in order to liquidate the copper contained in the ore and then to smelting it could cast a lot easier to get the ancient blacksmiths, and therefore copper as the material appeared before in human history.

In ancient times, the bronze was a typical alloy of copper. It was a copper alloy with tin, copper, tin and zinc and copper with antimony. Bronze tin content of about 10% Sn was used mostly in a forged condition to manufacture swords, daggers and axes. Tin-tin bronzes and tin-zinc bronze due to the good castability used for making bracelets, ornaments or objects of worship as well as everyday objects [29].

Currently used copper ore enrichment processes are shown in Fig. 31 These processes, which were unknown in ancient times

did not allow produce alloys of copper with a purity of metallurgical comparable with the present.

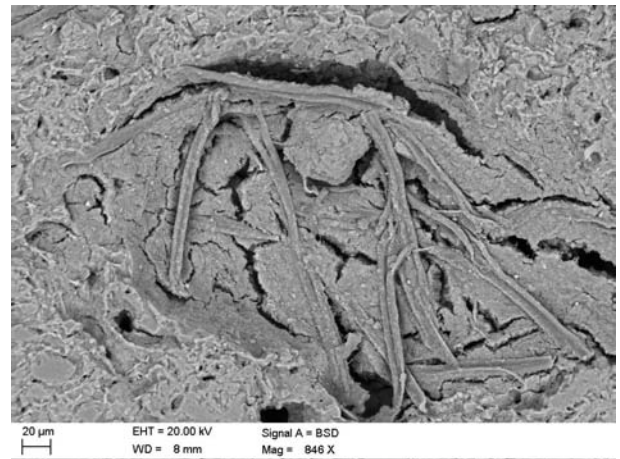


Fig. 30. Microstructure of Element 2 with visible of organic remains

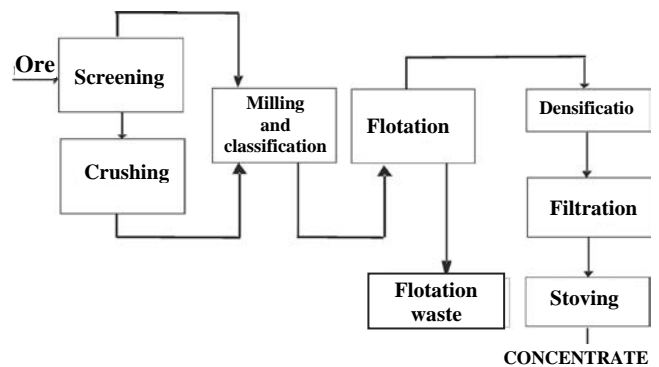


Fig. 31. Schematic of copper ore enrichment process [21]

Pictures of the microstructure shown in Figures 5-10 show a typical dendritic structure characteristic of the structure of castings, which were then subjected to any further heat treatment or plastic forming (eg, forging). This means that they were used in the raw state, also called the state provided. In the case of castings it is said also about the so-called, able to cast. Light blue separation in the shape of the bars are called dendrites and the direction in which they are arranged indicates the direction of solidification and crystallization of liquid metal.

3.2. Weight

From the weight was cut a piece of material and structural studies were performed, which included the qualitative X-ray phase analysis, observations of the structure using a scanning electron microscope (SEM) and the study of chemical composition in micro-square (EDX).

In the next phase of research carried out X-ray qualitative.

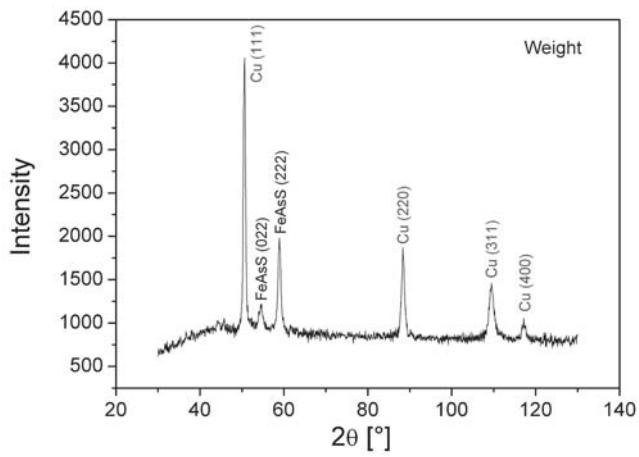


Fig. 32. X-ray diffraction of qualitative phase analysis of weight material



Fig. 33. Small "craters" on the surface of the investigated element

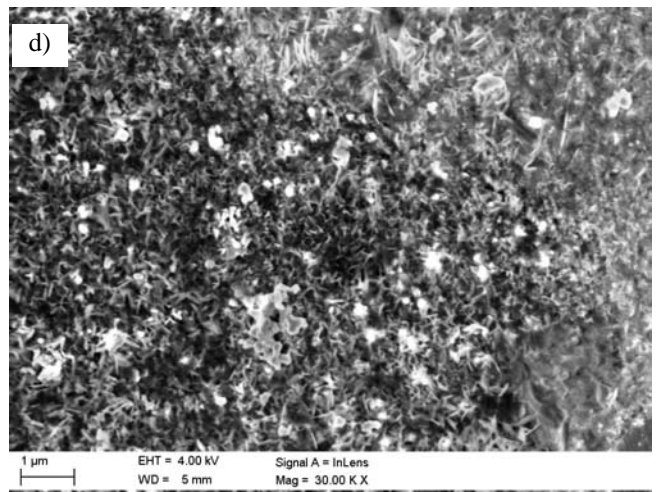
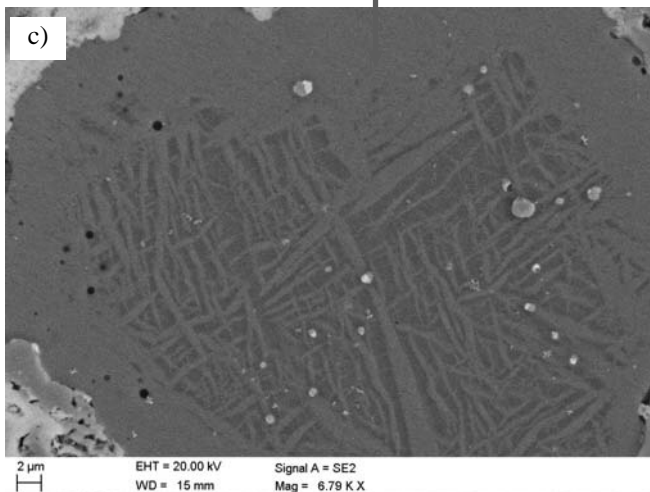
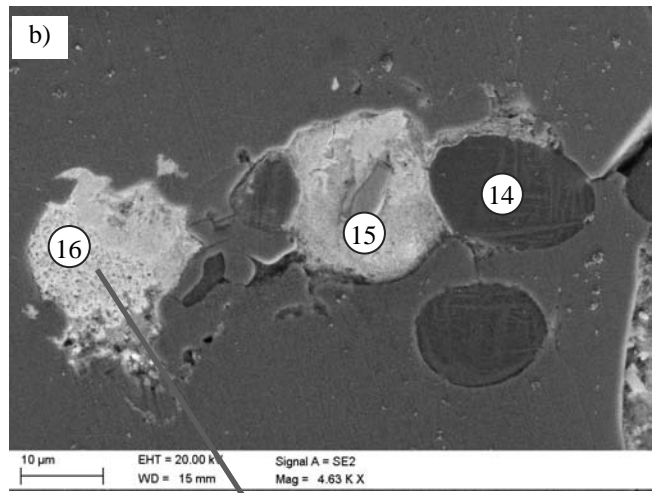
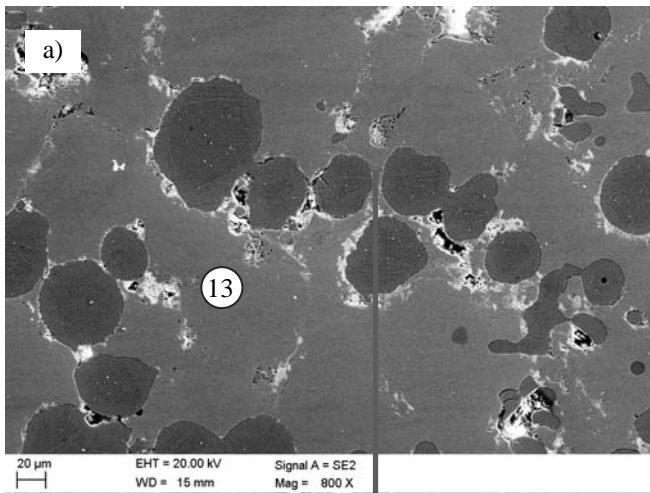


Fig. 34. The microstructure of the alloy weight, SEM

phase composition analysis of the material weight, to determine the chemical compounds (phases) that occur in it. The results of analysis (Fig. 32) confirms that the dominant element in the weight material is copper (Cu) crystallizes in the regular face-centered cubic system. In addition to the presence of copper in the material also confirmed the presence of phases FeAsS (arsenic), which crystallizes in the monocline system. However, as mentioned earlier (Element 1), X-ray qualitative phase analysis can reveal the presence of phase if its volume exceeds 3% of the tested material.

After preliminary observations, it was found that the structure of the alloy weight differs from the structure of the Element 1. The weight material structure (Fig. 33) can be divided into a separation of the large spherical shape as well as numerous smaller separation of the bright color and numerous voids. The presence of all the voids inside the weight material on its surface is explained by the imperfection of the casting process of that time and receive metal materials, which consisted in the inability to deoxidation and degassing of molten metal. Currently, copper is subjected to meticulous roasting process, which aims at removing such as sulfur, and then obtained by pyrometallurgical copper contains only 0.5-1% of impurities [20].

The analysis of chemical composition in micro-square (13) showed that the matrix of the test material is copper in an amount of more than 94% and small addition of arsenic 3.7% of the mass concentration. Occurrence of arsenic in copper alloys, even today it is not unusual, however, because of the large differences in atomic diameters of copper and arsenic, the element that causes a significant distortion of the crystal lattice of copper is usually removed in the metallurgical process (Fig. 34).

However based on the analysis of chemical composition in micro-square of large precipitates of spherical shape (14) found that the dominant element in this phase is also copper present in the mass concentration of about 64.7%. In addition, this confirmed the presence of sulfur in an amount of about 25.3%, iron at 9.3% and a small addition of cobalt in an amount of 0.7% of the mass concentration.

In turn, represent a very interesting analysis of chemical composition of very fine-particle longitudinal separation (15), which is located on a background of white spherical separation. The analysis showed only the presence of antimony at a concentration of 67.6% by mass, and nickel at a concentration of 32.4% by mass.

The results of analyzing the chemical composition of white spherical separation (16) also show very interesting. Not detected in the presence of copper, while the element with the greatest concentration of mass is 90% lead. In addition to Pb had the presence of oxygen in the amount of 8% and about 2% of aluminum.

Numerous voids (Fig. 35), whose presence was found in fact every area of the test material, to be the non-removal of gases from the molten metal during the metallurgical process. Analysis of chemical composition (17) helped determine the presence of lead in the amount of 56.7% of the mass concentration, antimony in an amount of 12.2%, oxygen at 9.3, copper in the amount of 8, 8%, chlorine in an amount of 5%, aluminum and arsenic at 3.4% each as well as iron at 1.2%.

In the next stage of testing the weight material hardness was measured on the inner surfaces of the samples. There have been three series of 10 measurements each and the results are shown in

Table 12 Of all 30 measurements of the lowest value was 159.6 HV and the highest value of 227.3 HV. The average value of all 30 measurements is 186 HV and the standard deviation is only 9.7% of the average value, which indicates that the hardness of the material is rather constant throughout the material.

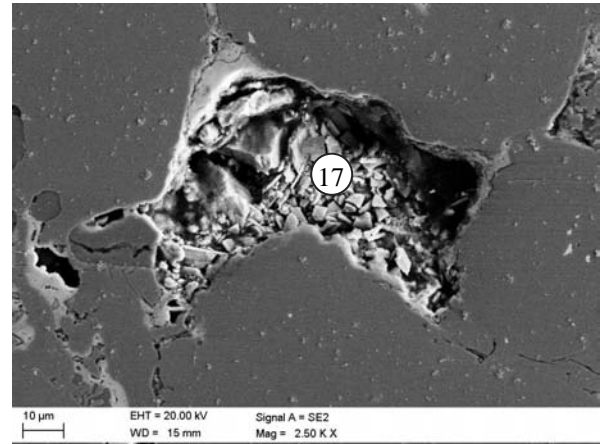


Fig. 35. Microstructure of weight alloy, SEM

Table 12. The results of microhardness measurements of weight at different distances

1 series	2 series	3 series		
188.7	179.0	190.5	186.0	Mean value [HV]
24.4	12.6	15.3	18.2	Standard deviation
13%	7%	8%	9.7%	

3.3. Nail

The study involved the nails, which probably joined beams with a layer of wood with thick filaments (18), in the color of rust. The study involved the nails, which probably combined with a layer of beams of wood with thick filaments (19), in the color of rust. Length: 180 mm, width varies from 3 mm to 25 mm, height: 30mm. They have a flattened shape, tapered towards the end. For the tested sample is characteristic of bending the nail in the arc (19), highlighted the lack of head and nesting at the end (Fig. 36 and 37). This allows the presumption that he was a strut stud nail: he was hammered in the intersection of two beams to hide. Some that stick out the other side bent.

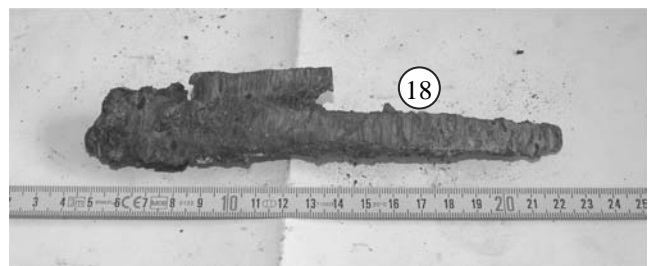


Fig. 36. Ceiling nail; side view



Fig. 37. Ceiling nail; side view

The tested nails exhibit a structure similar to the nails of the Żuraw village [1]. Inclusions are arranged in bands parallel to each other (Fig. 38). Inclusions, however, are smaller than those found in nail Żuraw (interjection had the greatest length of 357 microns), the overall share of the inclusions is much smaller (Fig. 39).

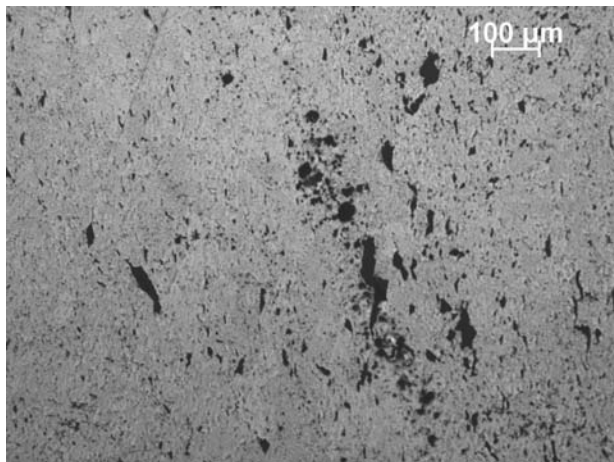


Fig. 38. Transverse metallographic specimen of nail, visible parallel stripes inclusions

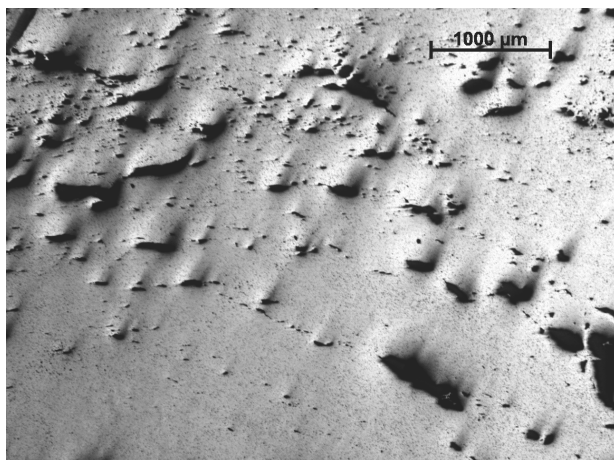


Fig. 39. Transverse metallographic specimen of nail, village Żuraw [24]

4. Conclusions

After analyzing the obtained results the authors came to the following conclusions:

1. In Element 1, (section forms surrounding weight), the main ingredient is copper, but it also contains other elements, sometimes in such large quantities that it indicates a very low-purity metallurgical material and thus proves that this is not what the typical brown that time produced, and is rather a byproduct of the process (eg, casting).
2. A large amount of impurities in the microstructure (Element 1) may also indicate that the item was made of "debris" from the production of relevant elements or batch was prepared for further melting.
3. Among the tested materials is characterized by the highest hardness of the copper material weight, and the lowest Element 1. If weight is probably due to a much greater purity metallurgical and added weight of antimony, which causes the strengthening of the alloy.
4. The tested metal nails are characterized by high purity metallurgical, more than nails investigated by the authors from the archaeological sites so-called "castle" cone in the village Żuraw, district Janow (near Częstochowa city) [24]. What manifests itself primarily lower microhardness test nails.

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