Physical and mechanical properties of ultrapure copper obtained by zone melting

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This paper presents the results of studies on the electrical conductivity, macro- and microstructure of ultrapure copper (5N3) obtained after zone melting of refined copper (99.96% Cu). The effect of residual concentrations of impurity metals on the electrical conductivity of ultrapure copper has been established. To assess the effect of low concentration impurities on the electrical conductivity of copper, the authors used a linear dependence of the increase in resistivity on the concentration of impurities (Ci), which was determined by the Mathyssen-Fleming rule. It is shown that low residual concentrations of impurity metals obtained in copper after its zone melting refining, ppm (ppm = 10^{-4} %): 0.2As; 0.06Sb; 0.006Ag; 0.07Bi; 0.006Sn; 0.02Pb; 1,1Ni have practically no effect on the electrical conductivity of ultrapure copper. The maximum electrical conductivity of M00K industrial grade copper (99.99% Cu) is 59 MSm/m, while zone-refined copper with a copper content of 99.999% has the electrical conductivity of 60.2 MSm/m. The values of the electrical conductivity of the obtained samples can serve to control the quality of obtained copper.
It is shown that, in contrast to the microstructure of the initial copper sample, the ultrapure copper microstructure is a densely packed structure consisting of fine grains. On the microstructure map of ultrapure copper, the presence of individual impurity metals in the form of rounded small balls was established. Elongated filaments in the form of continuous lines, which are associated with the formation of chemical compounds of impurity metals with each other, are also found. This phenomenon is clearly observed on the microstructure map of ultrapure copper, captured at a magnification of 1000x under conditions of etching of the sample under study.
The values of macro- and microhardness of the initial copper sample and ultrapure copper sample are established. The hardness of the initial copper sample is 84.42 HB (according to Brinell). After zone melting refining of copper from impurities, the hardness of the resulting ultrapure copper was 59.85 HB.
Measurements of the microhardness of samples of the initial copper sample and ultrapure copper obtained by zone melting showed the microhardness of 103.0 and 70.42, respectively.

Key words: electrical conductivity of copper, microanalysis, microstructure, hardness, microhardness, impurities, original sample, ultrapure copper.

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The use of copper in microelectronics, semiconductor devices, and other areas of high technology has significantly increased the demand for high purity copper [1, 2].

An effective technological method to create bulk nanostructured metallic materials with an ultrasmall grain size is the obtaining of single crystals from ultrapure metals. From the point of view of the efficiency of the growth and formation of single crystals, it is fundamental to obtain ultrapure metals themselves. From the degree of purity, changes in their structure, physicochemical, mechanical and other important properties of the metal or metal alloys are largely formed, which determine their use in high technologies [3].

Many researchers have tried to obtain ultrapure metals using various methods [4, 5]. To obtain various ultrapure metals and alloys based on them, the zone melting method is successfully used [6–14].

Improvement of the hardware and methodological support for zone melting has significantly expanded its capabilities. A high degree of copper refining by zone melting of in a mixture of argon and 20% hydrogen was achieved [8]: deep refining of copper from Zn, Pb, Mg, Cl, K, S, Ca, and Bi took place. The authors [10] showed that when refining copper by zone melting in a hydrogen atmosphere, a noticeable decrease in the concentrations of S, Se, Al, and Si is achieved.

One of the most important parameters that ensure the obtaining of high-purity metal is the content of impurities, temperature gradient, and liquid zone width. Optimal selection of each individual parameter and their mutual influence, as a whole, enable to obtain ultrapure metal.

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The purpose of this work is to study physical and mechanical properties of ultrapure copper (5N3) obtained using a new precision zone melting unit [15, 16].

Research methodology

To solve the problem, ultrapure copper obtained by zone melting was used. Technological experiments were carried out using a zone melting unit, whose design and operation principle are described in detail [15, 16].

Copper rods with a copper content of 99.96%, 800 mm long, and 30 mm in diameter were used as the starting material. Copper rods are made by remelting M2K grade copper cathode with the following composition, %: 99.94Cu; 0.001Bi; 0.002As; 0.002Sb; 0.002P; 0.005Pb; 0.002Sn; 0.003Ni; 0.005Fe; 0.004 Zn; 0.003Ag; 0.010S.

The essence of the experimental studies was to evaluate the change in the impurity metals concentration in the final metal depending on the ratio of the liquid zone width (X_i) to the rod length (L) at given temperatures of the molten zone, exceeding the melting point of copper by 100 °C, 150 °C and 200 °C.

The experimental procedure was identical to the experimental conditions, which are described in detail [16]. Refining of copper from impurities was carried out at different ratios of the liquid zone width (X_i) to the rod length (L) equal to: 0.35; 0.25; 0.15. From ultrapure copper, obtained as a result of zone refining from impurities, samples were prepared, which were subjected to further research.

The microstructure of ultrapure copper was studied using a Neophot 2 stationary metallographic microscope.

The hardness of copper samples was measured using a multifunctional stationary HBV-30A hardness tester designed to measure Brinell and Vickers hardness.

Microhardness testing of ultrapure copper was carried out using the currently widely used PMT-3 microhardness tester.

Experimental results and analysis

Influence of impurity metals on the electrical conductivity of copper

The content of impurities in copper can have a significant effect on the electrical conductivity of copper. Systemic studies on the influence of various impurities on the electrical conductivity of copper were carried out [17]. The authors have constructed dependencies that establish the change in the electrical conductivity of copper on the content of impurities. To assess the effect of impurities on the electrical conductivity of copper at their low concentration, the authors used a linear dependence of the increase in resistivity on the impurities concentration (C_i), which was determined according to the Mathyssen-Fleming rule:

$$\rho = \rho_o + \Delta\rho * C_i,$$

where: ρ_o is the main component resistivity, which depends on temperature (for high-purity copper, ρ_o = = 0.0168 μOm·m); $\Delta\rho$ is the temperature-independent residual electrical resistance proportional to the impurity concentration, induced by the presence of impurity metal atoms.

The effect of the content of impurities on the electrical conductivity of copper is shown in **Fig. 1.** It can be seen that As, Sb and metals of the first type — Ni, Fe, Co have the greatest influence on reduction the electrical conductivity of copper.

Comparative analysis of results of [17] with the data given in **Fig. 1** shows that the established minimum values of the residual contents of impurities obtained in copper after zone melting, ppm (ppm = 10^{-4} %): 0.2As; 0.06Sb; 0.006Ag; 0.07Bi; 0.006Sn; 0.02Pb; 1.1Ni, have no significant effect on reduction of the electrical conductivity of copper.

The maximum electrical conductivity of M00K industrial grade copper (99.99% Cu) is 59 MSm/m, while zone-refined copper with a copper content of 99.999% has an electrical conductivity of 60.2 MSm/m.

The values of the electrical conductivity of the obtained samples can serve to control the copper quality.

The ratio of the resistivity of the sample at 4.2 K (liquid helium temperature) and 273 K can also serve as an indicator of metal purity.

A sharp increase in this ratio with an increase in the content of impurities is explained by the Mathyssen-Fleming rule. This circumstance has found wide application to estimate the purity of copper by the value of its residual resistance near absolute zero. Thus, for copper with a high degree of purification from impurities (99.9994%), this ratio is 4647, and for copper with a purity of 99.9988%, it is 1432 [17].

Study of the ultrapure copper microstructure

In order to determine the shape and size of crystalline grains and change the internal structure of copper obtained by zone melting, a comprehensive study of copper samples was carried out using microanalysis.

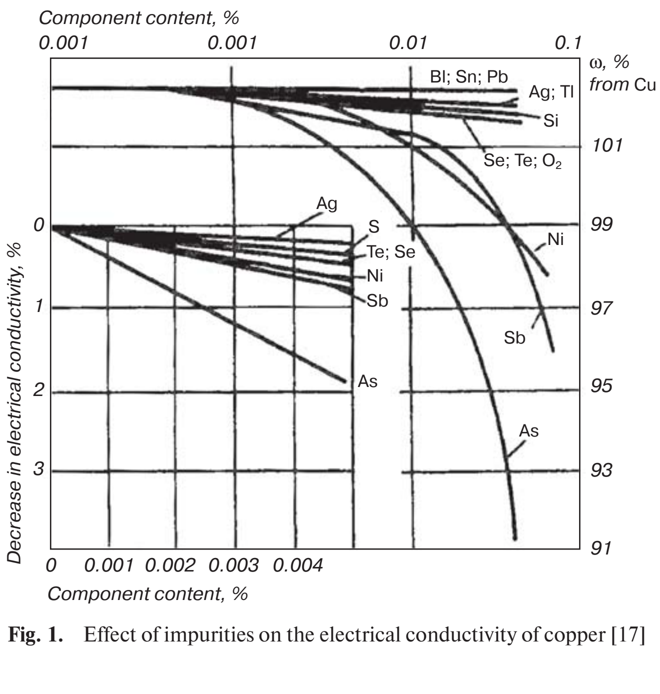

Fig. 1. Effect of impurities on the electrical conductivity of copper [17]

To conduct research, the samples of the initial and ultrapure copper were preliminarily carefully processed to a flat plane. Next, special samples (sections) were prepared by pouring them with epoxy resin, followed by further grinding and polishing of the surface under study. To reveal the grain boundaries and individual structural components, the sections were subjected to additional studies by etching them with a 6% solution of nitric acid in alcohol.

Macroscopic examination of the samples showed that small inclusions of shells and pores are observed in the initial copper sample, indicating chemical and structural heterogeneity. No pronounced anomalies were found in the sample of ultrapure zone-refined copper.

The microstructure of copper samples was studied using a Neophot 2 stationary metallographic microscope equipped with a computerized system for reproducing the results.

The research results are presented in **Figs. 2, 3**.

The map of microstructures of the initial copper sample sections **(Fig. 2 *a, b*)** shows pronounced defects (pores, cracks). In the structure of the studied sample, boundaries of large grains of copper crystals are noticeably distinguished **(Fig. 2, *b*)**. On the copper sample surface, captured on the etched section **(Fig. 2, *c*)**, the microstructure is a polycrystalline structure and is represented by macroscopically homogeneous equiaxed grains with an average size of about 0.25 μm. Small subgrains ~0.11 μm in size were found. Significantly elongated grains are observed in this structure. Surface and point defects of the crystal structure are clearly distinguished, apparently associated with the peculiarity of the formation of the crystal structure of the initial copper bar when casting and the presence of metal impurities.

A slightly different nature of the structure is established on the microstructure maps of ultrapure copper **(Fig. 3)**. In contrast to the initial copper sample microstructure, the microstructure map of ultrapure copper shows densely packed structure consisting of small grains **(Fig. 3, *a*)**. In the overall picture of the microstructure, pronounced segregations are observed with clearly defined boundaries, characteristic of the presence of impurity metals.

The nature and formation of residual concentrations of impurity metals in the microstructure of ultrapure copper

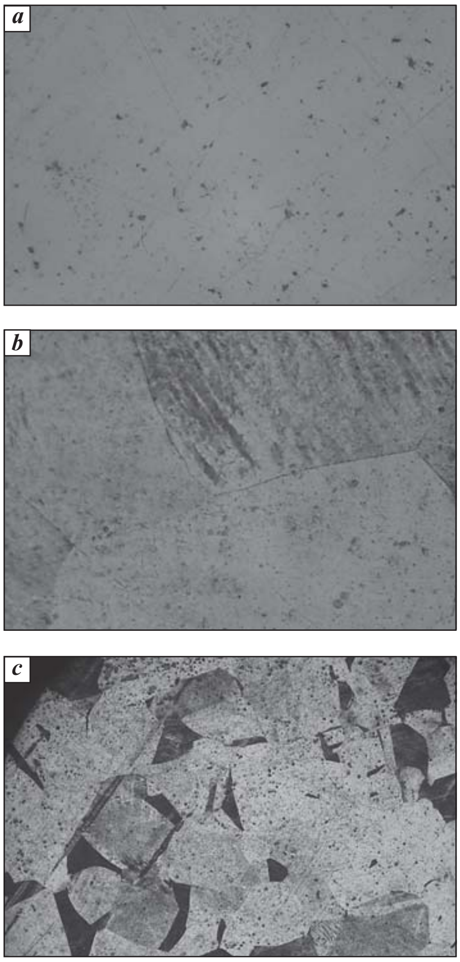

Fig. 2. Map of the initial copper sample microstructure
a — non-etched section sample, ×500; *b* — non-etched sample of the section, ×550; *c* — etched section sample, ×1000

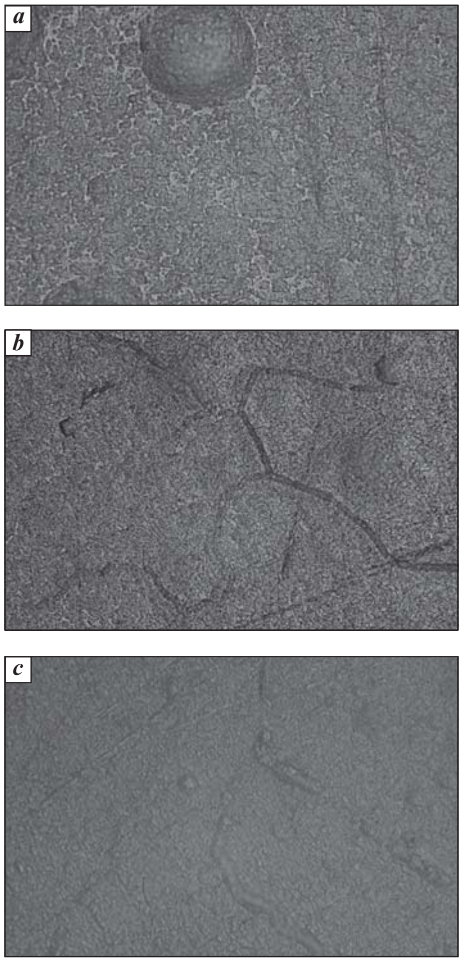

Fig. 3. Map of the ultrapure copper sample microstructure
a — etched sample of the section, ×500; *b* — etched sample of the section, ×550; *c* — etched section sample, ×1000

are clearly visible on the maps of the ultrapure copper microstructure taken under sample etching conditions **(Fig. 3, *b*)**. The presence of individual impurity metals in the form of rounded small balls is seen. Elongated filaments are also observed, presented as continuous lines, which may be associated with the formation of chemical compounds of impurity metals. This phenomenon is most clearly observed on the ultrapure copper microstructure map, captured at a magnification of 1000x under conditions of etching of the sample under study **(Fig. 3, *c*)**.

The results obtained on the study of the ultrapure copper microstructure show that during zone melting, the microstructure of the initial copper sample changes with the further formation of an ordered, densely packed fine-grained microstructure characteristic of ultrapure copper.

Study of the ultrapure copper hardness

The hardness of metal is one of the important characteristics, which is closely related to such basic mechanical properties of metals and alloys as strength, wear resistance, etc. The presence of impurities in metal has a significant effect on its strength and hardness. When obtaining ultrapure metals, in order to study properties and transformations, regardless of the method of their obtaining, it is necessary not only to know the “averaged” hardness - macrohardness, representing hardness as a result of the total influence of the impurity metals and structural components present in it, but also to determine their microhardness.

The established significant change in the ultrapure copper microstructure, associated with a decrease in the concentration of impurity metals, should also have a significant effect on its hardness. To confirm this assumption, we determined the hardness and microhardness of the initial copper sample and ultrapure copper sample obtained as a result of zone melting under optimal conditions [16]: the liquid zone temperature exceeds the melting temperature of copper by 150 °C; the ratio of the liquid zone width to the original rod length is 0.15; liquid zone movement speed — 200 mm; number of passes — 4.

Microhardness tests are carried out to determine the hardness of phases and to establish the effect of structural components on the hardening of metals and alloys. Microhardness testing is one of the static methods to determine hardness by indentation. It differs from other methods in the magnitude of the applied load: tests for microhardness (load less than 0.5 kgf), hardness at low loads (load in the range from 0.5 kgf to 5 kgf) and tests for macrohardness (load more than 5 kgf).

The hardness of copper samples was measured using a multifunctional stationary HBV-30A hardness tester designed to measure Brinell and Vickers hardness.

Microhardness of ultrapure copper

The main purpose of measuring microhardness is to determine the hardness of individual grains and structural components of multicomponent alloys (here, the microhardness method is the only one). The measurement of microhardness is of great importance in studying the properties and transformations in metals and alloys during their heat treatment in production, structural changes in operation, etc. [18].

To assess the properties of individual grains, phases and structural components, and to establish the effect of impurity metals on the strengthening of the ultrapure copper structure, we tested the microhardness of the initial copper and ultrapure copper samples using a PMT-3 microhardness tester.

The results of tests to determine the macro- and microhardness of the studied copper samples are summarized in the **Table.**

From the obtained results, it can be seen that the absolute decrease in the hardness of copper is 24.57 HB (Relative decrease in hardness ~ 71%).

The absolute decrease in microhardness is 32.58 or 3258 MPa (Relative decrease ~68%).

The data obtained well confirm the statement that if the metal has a relatively fine and uniform microstructure, then even small areas of the tested product are sufficient to assess its properties. In such cases, special tests for microhardness can be omitted, since their results will coincide with the results of tests for macrohardness.

Table

The results of measurements of the macro- and microhardness of the initial copper sample and ultrapure copper obtained after zone refining

No.	Parameter	Original copper, Cu – 99.96%	Ultrapure copper, Cu – 99.9993%
1	Amount of impurities, ppm	380	4.5
2	Impurity content, ppm:		
3	Pb	50	0.02
4	Bi	20	0.07
5	Fe	50	1.3
6	Cr	30	0.1
7	Mn	30	0.4
8	Ni	30	1.1
9	Zn	40	0.007
10	Ag	30	0.006
11	Co	20	0.9
12	Sb	20	0.06
13	As	20	0.2
14	Sn	20	0.006
15	P	20	0.004
16	B	10	0.3
17	Brinell hardness, HB	84.42	59.85
18	Microhardness, Pa	103.0	70.42

Conclusion

1. The effect of residual concentrations of impurity metals on the electrical resistance of copper has been established. Based on the data obtained from the Mathyssen-Fleming expression, it is shown that low residual concentrations of impurity metals obtained in copper after its zone melting refining, ppm (ppm = 10^{-4}%): 0.2As; 0.06Sb; 0.006Ag; 0.07Bi; 0.006Sn; 0.02Pb; 1.1Ni, almost have no effect on the electrical resistance reduction value.

2. Research has been carried out to study the mechanical properties of superlean copper (5N3) obtained after zone melting of refined copper (99.96% Cu). It has been established that during zone melting, the microstructure of the initial copper sample changes and the formation of an ordered and densely packed fine-grained microstructure characteristic of ultrapure copper takes place.

3. The macro- and microhardness values of the initial copper sample and ultrapure copper sample were determined. The hardness of the initial copper sample was 84.42 HB (according to Brinell). After zone melting refining of copper from impurities, the hardness of the resulting ultrapure copper is 59.85 HB.

4. Measurements of the microhardness of samples of the initial copper and ultrapure copper obtained by zone melting showed that their microhardness is 103.0 and 70.42, respectively.

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