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# STRUCTURE AND MECHANICAL PROPERTIES OF THICK COPPER CONDENSATES, DISPERSION-STRENGTHENED WITH CHROMIUM, ZIRCONIUM OXIDE AND THEIR MIXTURE

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#### ABSTRACT

The structure and mechanical properties of copper condensates with a thickness of 0.8-2.0 mm, dispersion-strengthened with chromium, zirconium oxide and their mixture, obtained by simultaneous electron beam evaporation of the selected components with subsequent condensation of the vapor phase onto flat steel substrates, were investigated. It is shown that the characteristics of the structure and the level of strength of the composites depend on the volumetric content of the strengthening phase, its dispersion and total action of the dispersoids.

**KEYWORDS:** electron beam vapour phase technology, thick vacuum condensates, copper-chromium, copper-oxide, copper-chromium-zirconium oxide systems, microstructure, hardness, strength, ductility

## INTRODUCTION

Copper-based composite materials are widely used in different sectors of modern industry, owing to a favourable combination of mechanical, thermal, thermal-physical and electric properties in such compositions, for instance, contacts of electrical equipment, electric motor commutators, electrodes for contact, spot and seam welding, part surfaces with a high resistance to arc erosion and wear at sliding friction, working surfaces of powerful laser mirrors, targets for neuron irradiation, etc [1–4]. Both metal (Cr, Mo, Nb, Be, Zr) and ceramic (Al<sub>2</sub>O<sub>2</sub>, ZrO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, ThO<sub>2</sub>, SiC, TiB<sub>2</sub>, AlN) materials are used as strengthening phases in copper compositions. At the same time, dispersion-strengthening copper alloys (for instance chromium bronzes), have certain disadvantages, such as a significant lowering of hardness and strength at higher temperatures that considerably limits their application. On the other hand, such dispersion-strengthened copper alloys, as Cu-Al<sub>2</sub>O<sub>3</sub>, Cu-ZrO<sub>2</sub>, demonstrate higher values of mechanical properties at higher temperatures that ensures a wider application of such compositions [5], which are usually produced by different powder metallurgy methods.

The objective of the proposed work is investigation of the structure and mechanical properties of Cu–Cr and Cu– $ZrO_2$  copper compositions, produced by electron beam vapour-phase technology, as well as studying the combined influence of two mechanisms

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of copper matrix strengthening by Cr and ZrO<sub>2</sub> particles on similar characteristics of binary systems.

# EXPERIMENTAL MATERIALS AND PROCEDURE

Composite materials of Cu-Cr, Cu-ZrO, and BrKh0.5- $ZrO_{2}$  systems in the form of  $120 \times 200 \times (0.8 - 2.0)$  mm plates with a variable content of the dispersed phase along their length were produced by simultaneous electron beam evaporation of copper or BrKh0.5 bronze and the strengthening phase from two independent water-cooled copper crucibles with further condensation of the vapour mixture on the steel substrates. The block diagram of this method is shown in work [6]. Used as initial materials were copper ingots of 69 mm diameter and 160-200 mm length, produced by electron beam remelting of copper of M0 grade, ingots of BrKh0.5 chromium bronze and chromium of VKh-1 grade of 49 mm diameter and 80-90 mm length, as well as compacted from commercially pure ZrO<sub>2</sub> + 5 % CaO powder and sintered cylinders of 49 mm diameter and 60 mm height. The substrate temperature was 750 °C, which was selected with the purpose of producing optimal mechanical properties and structure of the metal matrix. The metal condensation rate was  $5-7 \mu m/min$ , and for zirconium oxide it was 1.6-2.4 µm/min. The vacuum value was  $(1.33 \cdot 10^{-2})$ - $(0.66 \cdot 10^{-3})$  Pa. A thin layer of zirconium dioxide was pre-deposited on the substrates, in order to separate the condensates from them. The amount of the second phase in the condensates was determined by the chemical method.

Metallographic investigation of the condensate structure was conducted using MIN-7 and MIM-8 optical microscopes. The shape and dimensions of the second phase particles were studied in JEM-120 electron microscope. Mechanical properties of the condensates were determined by stretching the flat samples with 3 mm width and 10 mm length of the working part. The relative strain rate was  $1.67 \cdot 10^{-3} \, \text{s}^{-1}$ . Vickers hardness was measured in KhPO-250 instrument at 10 kg load for 30 s.

#### **INVESTIGATION RESULTS**

#### Cu-Cr SYSTEM

When considering the copper-chromium system it should be noted that in keeping with the constitutional diagram, the solubility of chromium in solid copper is quickly reduced with temperature lowering, and it is equal to 0.15 and 0.03 vol.% at 750 and 20 °C, respectively. Thus, in the presence of chromium in the above-mentioned amounts in copper in a slightly diluted solid solution of copper-chromium it will have the form of dispersed particles. Chromium content in copper in this study varied in the range from 0 to 3.0 vol.% Cr.

Metallographic investigation of the transverse microsections of Cu–Cr condensates allowed determination of the influence of the amount of strengthening chromium additive on the microstructural pattern of the two-phase condensate. Figure 1 shows the structures of copper-chromium vacuum condensates with Cr content from 0.3 to 2.7 vol.% produced at substrate temperature of 750 °C.

Comparison of the given structures with the microstructure of pure copper condensate formed at the same temperature shows that addition of even a small amount of chromium to copper leads to a significant reduction of the matrix crystallite size. For instance, at chromium content of 0.3 vol.% the size of Cu–Cr condensate grains is reduced 3 times. Increase of the concentration of the strengthening chromium phase causes further structure refinement and at chromium content of 2.7 vol.% and higher, the elements of the condensate microstructure become so dispersed that large magnifications have to be used to detect them (Figure 1, e, ×900).

Transmission electron microscopy studies of specially prepared foils of Cu–Cr condensates allowed determination of the size and shape of the dispersed chromium particles, depending on the amount of strengthening phase added to the copper matrix. Proceeding from experimental data, we can come to the conclusion that chromium particles are of a round shape and their size becomes larger with increase of the second phase concentration. For instance, while at 0.3 vol.% Cr content in copper the size of the strengthening particles is close to 30 nm, at the second phase amount of 2.5 vol.% the particle size becomes 7 times larger and it is equal to 210 nm. Figure 2 shows electron microscopy images of the structures of Cu–Cr condensates at different chromium concentrations.

The second phase greatly increases the copper hardness. Addition of chromium in the amount of 0.5 % increases the vacuum condensate hardness 1.5 times. At further increase of chromium concentration to 2.7 vol.%, the hardness increases in proportion to the strengthening phase content (Figure 3). Comparison of the hardness of Cu–0.5 % Cr condensate with







Tensile mechanical properties of condensates of Cu–Cr system were determined at room temperature and 700 °C in air and in vacuum of  $5 \cdot 10^{-5}$  mm Hg, respectively. Derived dependencies on strengthening phase content are shown in Figure 4. Strength characteristics of the two-phase condensates become higher with increase of chromium content. Chromium addition to copper in the amount of 3.2 vol.% increases the ultimate strength and yield limit by 1.9 and 2.0 times, respectively. Ductility of the two-phase condensates rises somewhat at addition of small amounts of chromium (up to 0.6–0.8 vol.%) into the copper matrix. At



**Figure 3.** Dependence of hardness of condensates of Cu–Cr (1) and Cu–ZrO<sub>2</sub>(2) systems on strengthening phase content

Comparison of ultimate strength, yield limit and relative elongation of Cu–0.5 % Cr condensates with similar characteristics of BrKh0.5 chromium bronze, produced by casting or powder metallurgy, is indicative of practical coincidence of absolute values of the above-mentioned mechanical properties of the condensed chromium and bulk bronzes in the hardened condition [7, 8].

Tensile tests at 700 °C indicate an increase of ultimate strength and yield limit with increase of chromium content to 0.8 vol.%. Further increase of chromium content leads to lowering of strength characteristics. Relative elongation of Cu–Cr condensates decreases from 41 to 21 % with increase of strengthening phase content to 0.8–1.0 vol.%, and then it increases in proportion to increase of chromium content. At 2.5 % chromium elongation of Cu–Cr condensates reaches 36 %.

The noted lowering of strength characteristics at simultaneous increase of ductility of condensates with chromium content in the range of 0.8–2.5 vol.% should be associated with coagulation of chromium particles as a result of a combined action of temperature (700 °C) and deformation. This fact is indicative of a comparatively low thermal stability of Cu–Cr materials at such temperature.

#### Cu-ZrO<sub>2</sub> SYSTEM

Metallographic investigations of Cu–ZrO<sub>2</sub> condensates indicate that addition of ZrO<sub>2</sub> oxide to copper leads to

reduction of the size of the crystallites in the matrix and formation of a columnar structure (Figure 5), as in the case of chromium addition. Oxide content in copper was varied in the range of 0-4.0 vol.% ZrO<sub>2</sub> in this study. The most marked grain refinement is observed in the region of second phase content of 0.2–0.7 vol.%. For instance, at oxide content of 0.6 vol.% in copper the composite grain size decreases 3.5 times, compared to the size of crystallites of pure condensed copper, formed at the same substrate temperature (750 °C). Increase of oxide phase content causes further refinement of the structure of copper-oxide composite, however, the rate of this process slows down significantly. At oxide content of 3-4 vol.% the condensate microstructure elements become so dispersed, that their detection requires application of high magnifications (Figure 5, d, ×900).

X-ray investigations of two-phase condensates of copper-zirconium oxide showed that the dioxide phase lines are not detected in the studied range of the second phase concentrations, copper lines are not blurred, and the matrix lattice parameter does not change depending on oxide content, and it coincides with that of pure copper condensate lattice. This is indicative of a practical absence of phase interaction at formation of condensates of Cu–ZrO<sub>2</sub> system. Absence of oxide lines in the roentgenograms can be accounted for by weak intensity of reflection of this refractory compound from the crystallographic planes and their subsequent absorption, in view of the small amount of the second phase in the composition. Transmission electron microscopy studies of foils of



Figure 4. Dependence of mechanical properties of Cu–Cr condensates on the amount of strengthening phase at test temperatures, °C: a - 20; b - 700



**Figure 5.** Microstructure of Cu–ZrO<sub>2</sub> vacuum condensates with different  $ZrO_2$  content, vol.%: a - 0.2; b - 0.3; - 0.5, ×350; d - 4.0, ×900



Figure 6. Microstructure of Cu– $ZrO_2$  condensates with different  $ZrO_2$  content, vol.%: a - 0.3; b - 2.5, ×40000

 $Cu-ZrO_2$  condensates showed that oxide particles are of a spheroidal shape and have rather uniform size (Figure 6). The size of strengthening particles also increases with increase of oxide content, similar to the case of copper-chromium composition.

It should be noted that at a small amount of  $ZrO_2$  phase (up to 0.8 vol.%), the oxide particles have larger dimensions, compared to chromium particles. For instance, at the second phase concentration of 0.3 vol.% the size of oxide and chromium particles is 60 and 30 nm, respectively. However, the growth rate of dispersed particles with increase of the second phase amount is much lower in copper-oxide compositions, compared to Cu–Cr condensates. As a result, at the second phase content above 0.8 vol. % the size of chromium particles will start exceeding the size



**Figure 7.** Dependence of mechanical properties of Cu–ZrO<sub>2</sub> vacuum condensates on strengthening phase content at test temperatures, °C: a - 20; b - 700

of oxide particles and at the second phase content of 3.4 vol.% chromium particles become much larger than oxide particles. The noted fact is attributable to a different extent of the second phase interaction with the copper matrix and different diffusion mobility of the strengthening phases in copper at formation of the condensed composition at the temperature of 750 °C, and chromium phase precipitation from the parent material in the matrix volume at substrate cooling from 750 °C to room temperature.

Addition of zirconium dioxide particles into copper causes an increase of its hardness from 40 for pure copper to 107 kg/mm<sup>2</sup> at 5.7 vol.% of oxide (Figure 3). Concentrational dependence of hardness of copper-oxide compositions is similar to hardness dependence on the phase amount for condensates of Cu–Cr system. The absolute hardness values of copper-oxide condensates, however, are somewhat higher at the same volumetric content of the strengthening phase. Comparison of the hardness of Cu–0.5 vol.% ZrO<sub>2</sub> condensate with that of samples of a similar composition, produced by powder metallurgy method of inner oxidation with further hot extrusion and cold drawing by 56% is indicative of practical coincidence of absolute values [9, 10].

Mechanical properties of Cu–ZrO<sub>2</sub> condensates were determined at room temperature in air and at 700 °C in the vacuum of  $5 \cdot 10^{-5}$  mm Hg. Derived dependencies are given in Figure 7. Addition of zirconium oxide particles into the copper matrix leads to increase of ultimate strength and yield limit of the two-phase condensates at simultaneous lowering of their ductility.

Concentrational dependence of strength of Cu–ZrO<sub>2</sub> condensates at room temperature is similar to the dependence of strength characteristics on the strengthening phase amount for condensates of Cu–Cr system. However, absolute values of ultimate strength and yield limit of the copper-oxide system are somewhat higher. At test temperature of 700 °C strength characteristics of Cu–ZrO<sub>2</sub> condensates also become higher with increase of oxide content in the studied range of second phase concentrations, and ductility decreases.



**Figure 8.** Microstructure of BrKh0.5–ZrO<sub>2</sub> vacuum condensates with different  $ZrO_2$  content, vol.%: a = 0.7; b = 1.7; c = 3.65, ×350; d = 5.7, ×900

Comparison of mechanical properties of condensates of Cu–Cr and Cu–ZrO<sub>2</sub> systems at test temperature of 700 °C shows that no drop of strength characteristics is observed in copper-oxide compositions with increase of the strengthening phase content in the concentration range above 0.8 vol.%, as in the case of Cu–Cr system, which is indicative of a higher thermal stability of copper-oxide condensates. This fact leads to the conclusion that in terms of operational reliability under the conditions of long-term action of higher temperatures the condensates of Cu–ZrO<sub>2</sub> system have an advantage over Cu–Cr system condensates. It is also known that dispersion-strengthened materials with a stable strengthening phase have extremely low creep rates at high temperatures.

#### Cu–0.5Cr–ZrO, SYSTEM

Metallographic studies of condensates of pure BrKh0.5 chromium bronze produced by electron beam evaporation from one crucible, showed that at its evaporation in a stable mode a condensate forms on the substrate with a structure, similar to the one obtained at simultaneous evaporation of pure copper and chromium from two crucibles. It allowed producing three-phase condensates of Cu–0.5Cr–ZrO<sub>2</sub> system with varying oxide content.



Figure 9. Structure of BrKh0.5–ZrO<sub>2</sub> condensates with different ZrO<sub>2</sub> content, vol.%: *a* — 0.3; *b* — 4.8, ×4000



**Figure 10.** Dependence of hardness of the studied copper condensates on the content of Cu–Cr (1), Cu–ZrO<sub>2</sub> (2), BrKh0.5 (3) strengthening phase

Addition of oxide phase to chromium bronze leads to further refinement of its structure (Figure 8). At 1.0 vol.% oxide content the grain size of bronze-oxide condensate decreases two times, compared to the size condensed bronze crystallites formed at the same substrate temperature (750 °C). Further increase of oxide concentration promotes refinement of the structure of bronze-oxide composite. However, the growth rate of such a process becomes somewhat slower.



**Figure 11.** Dependence of mechanical properties of BrKh0.5– ZrO<sub>2</sub> condensates on ZrO<sub>2</sub> content at test temperatures, °C: a - 20; b - 700

Transmission electron microscopy studies showed that simultaneous presence of strengthening particles of chromium and zirconium oxide in the copper matrix does not influence their morphology at different oxide content (Figure 9). As in the case of copper-based two-phase systems, an increase of the strengthening phase dimensions with increase of its content is also observed in three-phase condensates.

Addition of oxide particles to chromium bronze leads to an increase in its hardness from 60 to 160 kg/ mm<sup>2</sup> at 8 vol.% of the oxide (Figure 10), which exceeds the hardness of cast BrKh0.5 chromium bronze after dispersion hardening and 25 % cold deformation (150 kg/mm<sup>2</sup>) [7].

Tensile mechanical properties of three-phase condensates were determined at room temperature in air and at 700 °C in the vacuum of 5.10<sup>-5</sup> mm Hg (Figure 11). As one can see from the presented graphs, the concentrational dependencies of ultimate strength, yield limit and ductility of dispersion-strengthened bronze are characterized by the presence of a minimum at oxide content of 0.5 vol.%. Test temperature and ambient atmosphere do not influence its position. Simultaneous lowering of strength and ductility of BrKh0.5 bronze at increase of oxide content in it from 0 to 0.5 vol.% is attributable to unfavourable arrangement of the two types of dispersed particles on grain boundaries. Increase of oxide content from 0.5 to 1.8-2.0 vol.% results in an increase of the condensate mechanical properties, but their absolute values do not exceed those for condensates of Cu-Cr system. Further increase of oxide content lowers the mechanical characteristics of three-phase condensates, which is, most probably, due to brittle fracture of the samples.

## **DISCUSSION OF THE RESULTS**

Addition of chromium or zirconium oxide in the amount of 0 to 0.8 vol.% leads to refinement of the copper matrix structure, somewhat more abrupt in the



Figure 12. Dependence of crystallite width of the studied copper-based condensates on strengthening phase content: 1 - Cu - 0.5 % Cr–ZrO<sub>2</sub>; 2 - Cu–Cr; 3 - Cu–ZrO<sub>2</sub>

case of chromium (Figure 12). At higher concentrations of the second phase the pattern is reversed, that is attributable to higher dispersion of chromium particles at small amounts of this phase (up to 0.8 vol.%) and higher rate of their coagulation with increase of chromium content. Larger particles have a weaker influence on the structure. Simultaneous addition of strengthening particles of chromium and zirconium oxide to the metal matrix causes a summary refinement of the composite structure.

Hardness measurements of the studied systems indicate that the oxide particles more actively increase the hardness of the two-phase composition, than chromium particles do (Figure 10). At simultaneous addition of chromium and oxide particles to the matrix, the material hardness is increased more intensively, compared to the two-phase compositions that promotes its better polishability.

Investigations of tensile mechanical properties of the composites showed that dispersion-strengthened condensates of Cu–ZrO<sub>4</sub> system have better strength characteristics, compared to dispersion-hardening condensates of Cu–Cr system, particularly at higher test temperatures (700 °C), which is equal to  $0.7T_m$ of the matrix. Mechanical tests of three-phase copper-chromium-zirconium oxide condensates did not reveal any evident advantages of metal matrix strengthening by two types of particles, compared to two-phase Cu–Cr and Cu–ZrO, condensates.

## CONCLUSIONS

1. Cu–Cr, Cu–ZrO<sub>2</sub> and Cu–Cr–ZrO<sub>2</sub> compositions were produced by the method of electron beam evaporation with subsequent vapour mixture condensation on steel substrates.

2. Dispersion-strengthened  $Cu-ZrO_2$  systems have better strength characteristics, compared to dispersion-hardening Cu-Cr alloys.

3. A combination of two types of simultaneous strengthening of the copper matrix by coherent (Cr) and non-coherent ( $ZrO_2$ ) particles did not show any advantages, compared to two-phase Cu–Cr and Cu–ZrO<sub>2</sub> alloys.

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## **CONFLICT OF INTEREST**

The Authors declare no conflict of interest

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