Metal-Based Nanocrystalline Materials Condensed from the Vapor Phase

V. Grechanyuk, I. Grechanyuk, A. Kozyrev, A. Matsenko, V. Chornovol, and Yulia Kovalchuk

Abstract The research work is aimed at produced of metal-based nanocrystalline materials condensed from the vapor phase in the form of thin (up to 5 microns) and thick (more than 5 microns) films for use them as contacts in radio engineering, microelectronics, etc. Composite copper-based materials with nanocrystalline components of the second phase were produced on an electron beam installation by the evaporation–condensation method. Doping of the copper matrix with zirconium and yttrium with a total content of up to 0.1% in the composite material was carried out by evaporating copper from the cuprum, zirconium and yttrium alloy through an intermediary bath. It has been show that materials with copper matrix doped with molybdenum, tungsten or chromium have characteristics, which make them promising for widespread industrial applications. The source for such properties is the formation of supersaturated solid solutions at the submicron level due to deposition from the vapor phase, which, as a result of them decomposition, leads to the formation of a layered structure with a hierarchy of layers at the macro-, micro-, and submicron levels.

1 Introduction

It is impossible to achieve significant progress in any of the most important areas of science and technology without the creation of new materials with high characteristics. One of the most promising areas for creating of fundamentally new materials with predetermined properties is high-speed electron beam evaporation followed by condensation of metallic and non-metallic materials in a vacuum [1–3].

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Such evaporation–condensation processes make it possible form at the atomic–molecular level thin films (up to 5 microns) for radio engineering, microelectronics, computer technology, etc., as well as thick films (more than 5 microns) used as effective protective and wear-resistant coatings, and also as massive composite materials isolated from the substrates. Vapor flows do not have solubility limits, therefore, it is possible to regulate the structure and dispersion of the created materials over a wide range, by mixing their components according to a definite intention and controlling their subsequent condensation. In this way, it is possible to create compositions of a dispersed or layered type, even if this is not possible by other methods.

2 Research Materials and Methods

Composite copper-based materials with nanocrystalline components of the second phase were produced on a universal electron beam installation L-2 by the evaporation–condensation method [4]. The initial materials were evaporated from two independent sources onto a substrate made of steel St3 (GOST), which was stationary or rotating, depending on the tasks. To obtain gradient condensates with different concentrations of the reinforcing phase, a stationary substrate 700 × 400 × 15 mm was used. The scheme of this technological experiment is shown in Fig. 1.

The deposition of condensates with the required concentration of components was carried out on a substrate with a diameter of 800 mm and a thickness of 25–30 mm, rotating at a speed of 36 rpm (Fig. 2).

In this work, alloying a copper matrix with zirconium and yttrium with a total content of up to 0.1% in the composite material was carried out by evaporating copper from the Cu–Zr–Y alloy through an intermediary bath, which resulted in an increase in the copper evaporation rate by 2–3 times.

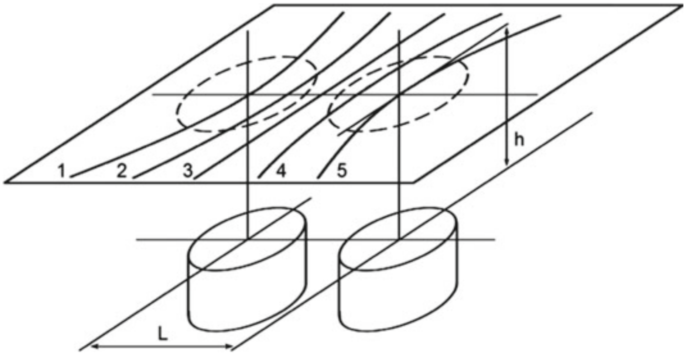

Fig. 1 The scheme of obtaining condensed composite materials with varying concentration along the length of the substrate by evaporation–condensation of components from two independent sources: 1, 2, 3, 4, 5—lines of constant concentrations of copper and molybdenum [5]

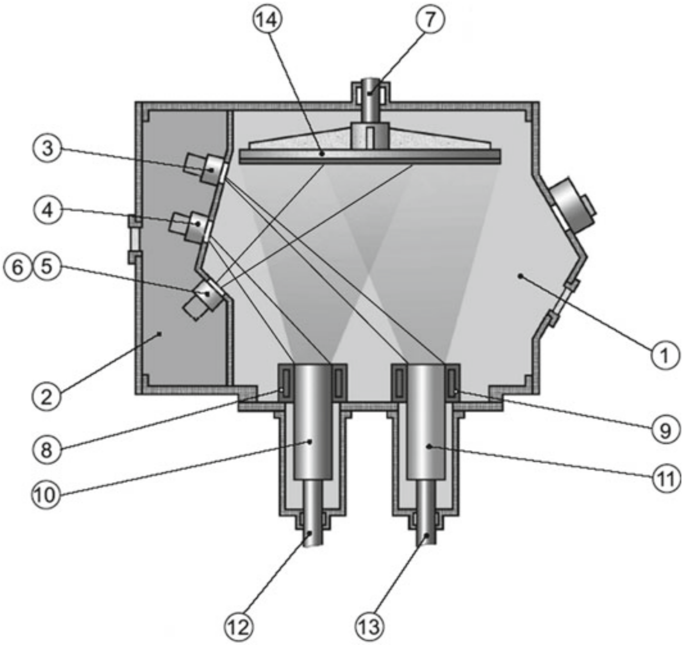

Fig. 2 The scheme of obtaining condensed composite materials on a rotating substrate by deposition of copper and molybdenum from two independent sources without separation of steam flows: 1—operational space, 2—space of equipment, 3–6—electron beam heaters, 7—substrate rotation mechanism, 8, 9—copper water-cooled crucibles, 10, 11—initial (evaporated) materials, 12, 13—feeding materials mechanisms, 14—substrate

This research was aimed at alloying a copper matrix with zirconium and yttrium with a total content of up to 0.1% in the composite material, by evaporating copper from the Cu–Zr–Y alloy through an intermediary bath, which resulted in an increase in the copper evaporation rate by 2–3 times. To separate the condensate from the substrate, it was covered with a separating layer of calcium fluoride. The resulting condensate was used to prepare test samples with the required dimensions.

3 Results and Discussions

The structure, physicochemical mechanical and operational properties of Cu–Mo, Cu–W, Cu–Cr, (Cu–Zr–Y)–Mo composite materials in the concentration range of refractory components up to 50% were comprehensively studied. The result of the research was finding the formation of supersaturated solid solutions in composite materials Cu–W, Cu–Mo, Cu–Cr at the submicron level. As a result of their decomposition, this leads to the formation of a layered structure with a hierarchy of layers at the macro-, micro- and submicron levels as it shown in Fig. 3.

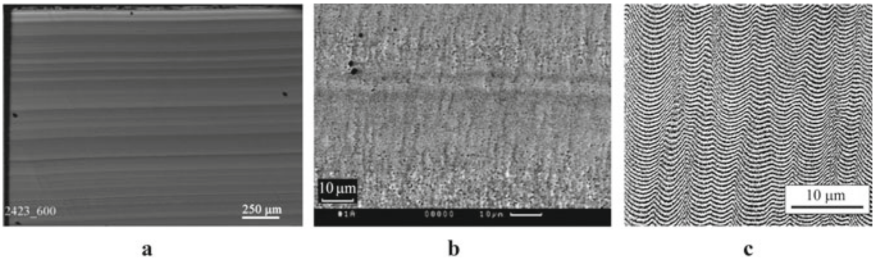

Fig. 3 Layered structure of a composite material based on copper and molybdenum on macro- (**a**), micro- (**b**) and submicron level (**c**)

At low concentrations of molybdenum (up to 7–8 wt%), tungsten (up to 4 wt%) layering is not very expressed. However, with an increase in the content of the refractory component, the contrast of the image increases, which indicates an increase in layering due to various factors. Layering at the macro-level is probably the result of the of electrical micro-breakdowns that occur during high-speed evaporation of the technical pure components (the deposition rate of copper on a rotating steel substrate with 1000 mm in diameter is 60–70 μm/min, molybdenum – 6–8 μm/min). Layering at the micro-level is caused by impurities present in the initial (evaporated) materials. The formation of layers at the submicron level is associated with the formation of supersaturated solid solutions, which, decomposing, form the corresponding micro-layers [6].

It has been experimentally confirmed that layered condensed composite materials based on low-alloy copper and molybdenum alloys up to 6 mm thick, obtained on a rotating substrate heated to 700 ± 30 °C, are bulk nanocrystalline materials. The grain size in them does not exceed 96 nm, and the size of dispersed inclusions of the reinforcing phase is 18 nm.

Transmission electron microscopic studies of layered composite materials (Cu-0.1 wt% Zr, Y)—Mo (8–12 wt%) showed that the average grain size of copper ranges from 58 to 96 nm, and the grain size of molybdenum is from 46 to 62 nm. Inside the grains, dispersed particles of reinforcing phases are evenly distributed. Their size ranges from 10 to 18 nm and depends on the nature of the reinforcing phases (oxides, metals) [7]. A typical electron microscopic image of the structure is shown in Fig. 4.

As can be seen in Fig. 4, the microelectron diffraction pattern of the composite has a characteristic annular shape inherent in nanocrystalline structures.

The composition and basic physical and mechanical properties of these materials are given in the Table 1.

Composite materials produced by the electron beam evaporation–condensation method are widely used in various industries due to their unique properties. Such materials of the (Cu–Zn-Y)–Mo system have mainly found industrial application as electrical contacts [8]. Switching tests have shown that in such a gradient layered nanomaterials, a change in the chemical composition of the layers significantly limits the zone of the thermal effect of the discharge. In some types of switching devices,

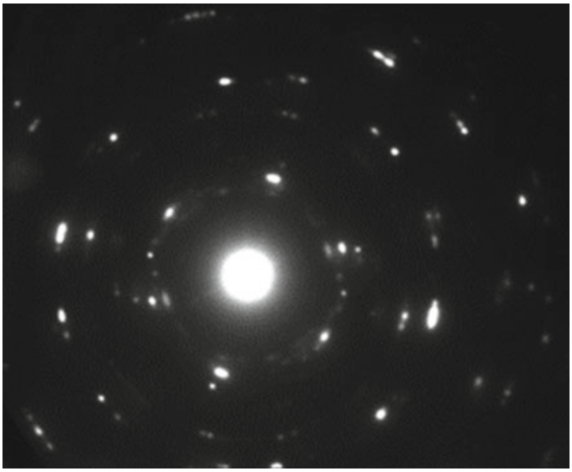

Fig. 4 Microelectron diffraction pattern of a composite material (Cu-0.1 wt% Zr, Y)—8–12 wt% Mo

Table 1 Chemical composition and physical and mechanical properties of (Cu–Zr–Y)–Mo composite materials containing Cu, 0.05–0.1 wt % Zr and Y, and various amounts of molybdenum (σ_B is the ultimate tensile strength, δ is the relative elongation)

Chemical composition (wt.% Mo)	Density (g/cm^3)	Electrical resistivity (μOhm × m)	Hardness H_V (MPa)	Mechanical characteristics			
				Before annealing		After annealing	
				σ_B (MPa)	δ (%)	σ_B (MPa)	δ (%)
3–5	8.9–9.0	0.021–0.022	1000–1500	300–430	10.3–7.3	295–420	17.6–9.3
5.1–8	9.0–9.05	0.022–0.024	1500–1650	440–630	7.25–3.4	425–600	9,45–4.9
8.1–12	9.05–9.1	0.024–0.028	1650–1800	635–785	3.25–1.8	605–730	4.85–3.9

when using these materials, there are smaller changes in the working layer of contacts and electrodes and an increase in erosion resistance compared to analogues obtained by powder metallurgy methods.

Composite materials (Cu–Zr, Y)–Cr with 0.05–0.1 wt % of Zr and Y, containing 35–50 wt % of chromium, are used for produced connectors in vacuum arc chutes [9]. Usability of condensed composite materials of this system is due to the features of the chemical composition and morphology of the "secondary" structure, which is formed on the surface of the contacts. In a non-equilibrium state of an arc discharge, the mutual solubility of copper and chromium increases and the decomposition of solid solutions take place with the formation of a dispersed structure. Condensates (Cu–Zr–Y)–Cr with such a chromium content have a layered structure at the macro-, micro-, and submicron levels. The layering of the last two levels is due to the anisotropy of normal grain expansion. This contributes to the formation of "pillars" within several layers of condensate. In such a structure, under the temperature and time, in the section of the layer perpendicular to the pillars, a structure is formed,

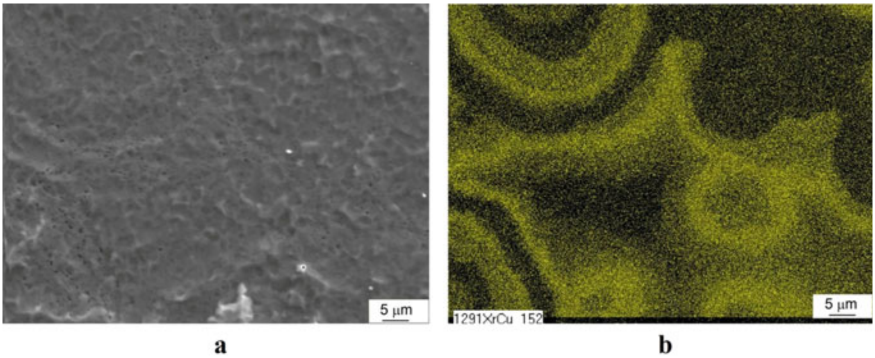

Fig. 5 Microstructure of a composite material (Cu-Zr,Y)–Cr with a chromium content of 35–50 wt % in secondary electrons (**a**) and in x-rays of copper (**b**)

which is characterized by a polygonal shape of grains (Fig. 5a), and contains signs of separation of the solid solution (Fig. 5b).

Hardness (by Vickers) varies with chromium content linearly. In the concentration range of 35–50% Cr, the hardness of the material is within 2069–2503 MPa. In a tensile test, the ultimate tensile strength increases to 550 MPa; however, the composite material in this case has zero plasticity.

Composite (Cu–Zr–Y)–Cr materials condensed from the vapor phase have many advantages: they are obtained in one technological cycle, they are cheaper than analogues obtained by powder metallurgy methods (by 1.5–1.7 times) and significantly (by 4 times) cheaper than the materials of silver-containing contacts.

Composite (Cu–Zr–Y)–Cr materials condensed from the vapor phase have several advantages, due to they are produced in one technological cycle. They are cheaper than analogues produced by powder metallurgy (by 1.5–1.7 times) and significantly cheaper (by 4 times) than the materials of silver-containing contacts. In terms of operational durability, condensed composite materials are no concede to materials based on silver-containing compositions. They are well processed by cutting, grinding, drilling, easily soldered by any of the known soldering methods using standard silver-containing and silver-free solders.

4 Conclusion

The studies have shown that composite materials with a metallic copper matrix doped with molybdenum, tungsten or chromium, produced by method condensation from the vapor phase, have a nanoscale structure that lend them characteristics, which make them promising for widespread industrial applications.

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