NEW SUBSTANCES, MATERIALS, AND COATINGS

The Effect of Aluminum-Oxide Powders on the Structure and Properties of Copper Electrodeposited Composite Coatings

I. R. Volkova[a, *], L. E. Tyryshkina[a, b], M. N. Volochaev[a], A. N. Zaloga[b], K. A. Shabanova[a, c], A. V. Ovchinnikov[c], and A. I. Lyamkin[a, b]

[a] Federal Research Center "Krasnoyarsk Science Center", Siberian Branch, Russian Academy of Sciences,
Krasnoyarsk, 660036 Russia

[b] Siberian Federal University, Krasnoyarsk, 660041 Russia

[c] Reshetnev Siberian State University of Science and Technology, Krasnoyarsk, 660037 Russia

*e-mail: Iriny_24@mail.ru

Abstract—Copper electrodeposited composite coatings containing two types of aluminum-oxide powders with different dispersities (alumina Al_2O_3-1 and electroexplosive aluminum-oxide nanopowder Al_2O_3-2) are obtained during the work. The studies show that introducing the powders leads to a change in the microstructure of the composites and a change in the grain growth principles during the formation of the coatings. Refinement and ordering of the grain structure of the coatings occurs and twinning defects and texture are formed. The change in the formation of the microstructure of the composites leads to a change in some operational characteristics: an increase in the microhardness (by 10% in the composites with the addition of alumina and by more than 30% in the coatings with electroexplosive aluminum oxide) and ultimate tensile strength (by 20% in the composites with Al_2O_3-1 and almost 1.5-fold in the samples with Al_2O_3-2).

INTRODUCTION

The undeniable advantages of copper, such as high electrical and thermal conductivity, plasticity, and resistance to corrosion, have found wide application in industry. Much attention is paid to the possibility of improving the operational characteristics of copper electrodeposited composite coatings (ECCs), including strength characteristics. Highly dispersed additives are most often used for this, which are introduced into the coating in the process of its preparation, which makes it possible to significantly affect its microstructure, grain size, and, hence, properties of the coating. In [1], the introduction of multilayered nanotubes decreased the sizes of the crystallites and changed the principle of formation of copper composite coatings, which led to an increase in their corrosion resistance and an increase in the microhardness by 30%. In [2], the introduction of 0.2 g/L graphene into a sulfate electrolyte bath led to an increase in the microhardness of copper composite coatings by about 21%. According to the authors, this is associated with a noticeable change in the sizes of the crystallites and a decrease in the grain size of the composite coatings. An increase in the roughness of the surface with the increase in the concentration of graphene in the electrolytic bath has also been noted. In [3], the effect of

highly dispersed additives on the microstructure of the obtained copper composite coatings and, as a consequence, increase in the hardness of composites based on copper and silicon nitride have also been noted. Analysis of the published sources showed that the number of works devoted to composites based on electrodeposited copper is quite high. However, there are very few studies devoted to copper ECCs containing aluminum-oxide powders as the dispersed phase. The aim of this work consisted in the preparation and investigation of the structure of copper composite coatings with the addition of aluminum-oxide powders with different dispersities.

EXPERIMENTAL

To obtain the coatings, a sulfate copper plating electrolyte with the following composition was used: 220 g/L $CuSO_4 \cdot 5H_2O$, 60 g/L H_2SO_4, pH 1. According to [4], an electrolyte with such a composition serves for depositing copper coatings onto steel with a sublayer of copper or nickel and copper alloys. The coatings were deposited onto brass and steel plates, the current density was 3.2–3.4 A/dm², and deposition time $t = 20$ min at $T = 293$–297 K. The composite coatings were obtained under these same conditions.

Powders of two types were introduced into the electrolyte as the dispersed additive:

(1) Al_2O_3-1—an alumina powder that is an amorphous highly defective phase χ-Al_2O_3 with an average median particle diameter of 5.2 μm; and

(2) Al_2O_3-2—electroexplosive aluminum-oxide nanopowder (OOO Tomskie nanoporoshki) with the phase composition γ- and δ-Al_2O_3 and the number average size of nanoscale particles of 40−60 nm.

The powders were introduced in the form of an aqueous suspension in the amount sufficient to achieve their concentration in the electrolyte of 13 g/L.

The porosity, thickness, and adhesion of the coatings were determined according to *GOST* (State Standard) 9.302-88 "USCAP. Metal and Nonmetal Inorganic Coatings. Control Methods." The thickness of the coatings was determined by gravimetry; porosity, by the method of filter paper application; and adhesion, by applying a grid of scratches.

The concentration of the dispersed phase in the composite coatings was determined by gravimetry after selective etching of the matrix of the coating in diluted nitric acid.

The microstructure of the surface of the coatings was studied on a Hitachi TM4000 scanning electron microscope (SEM) equipped with an accessory for energy-dispersive analysis (Bruker). The structure of the end cut was studied using a Hitachi FB-2100 focused-ion-beam system at an accelerating potential of 40 kV. The internal structure of the crystallites of the coatings was studied on an HT7700 transmission electron microscope (TEM) (Hitachi).

The microhardness was determined by the Vickers method on a PMT-3M microhardness tester at a load of 0.02 kg. The ultimate tensile strength of the samples was determined using an REM.1-5-U-A-1-2 tensile testing machine on the basis of tension to break, with the speed of tension being 1 mm/min.

X-ray diffraction analysis was performed under standard conditions: a CuK_α radiation, $U = 40$ kV, and $I = 40$ mA. The results were processed by the Rietveld method using the TOPAS 4.2 program.

RESULTS AND DISCUSSION

Pale pink dull copper electrodeposited coatings have been obtained during the work. The average thickness of all the coatings is 20 μm. It has turned out when determining the porosity of the samples that all the obtained coatings have almost no through pores. All the samples have demonstrated good adhesion on brass substrates.

On average, the concentration of Al_2O_3-1 in the copper composites is 0.4 wt % and the concentration of Al_2O_3-2 is 0.1 wt %.

A significant difference in the morphology is seen in the micrographs of the surface of the obtained coatings (Fig. 1). The coatings without additives (Fig. 1a)

have a pronounced globulelike structure of the grains and their aggregates and clear boundaries between them. The composite coatings, however, are distinguished by flatness of the grain boundaries and boundaries between the aggregates. The shape of the grains has changed, having lost roundness, but still the composites with Al_2O_3-2 as the additive (Fig. 1c) have a more structured grain structure than the composites with Al_2O_3-1 (Fig. 1b).
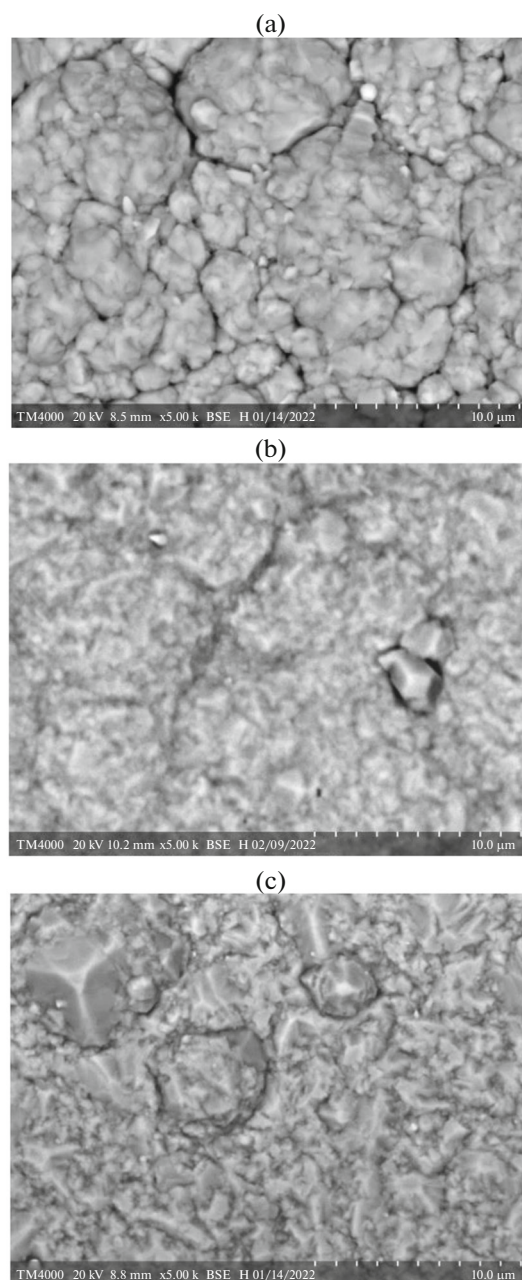

Fig. 1. Micrographs of the surface of the coatings: (a) a copper coating without additives, (b) a composite coating with Al_2O_3-1, and (c) a composite coating with Al_2O_3-2.
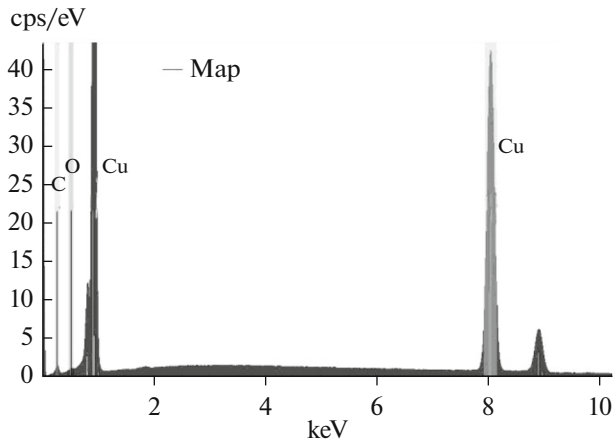
Fig. 2. Energy-dispersive spectrum of copper electrode-posited coatings.

The analysis of the energy-dispersive spectra (Fig. 2) has shown that all the samples are pure copper, which is expected taking into account the concentration of the dispersed phase in the composite samples. The insignificant presence of carbon and oxygen on the surface of the samples is associated with the open system of the instrument.

A change in the growth principle of the composite coatings in the process of their formation is seen in the micrographs of the end cut of the samples (Fig. 3). An unoriented grain structure is formed during the preparation of copper coatings without additives (Fig. 3a) [5]. Bushy fibrous vertical growth and refinement of the grain sizes can be noted in the composites containing Al_2O_3-1 (Fig. 3b). Also, both overgrowth of the existing grains and formation of new nuclei are observed with the growth of the coating. A more ordered refined narrow columnar structure directed along the normal to the substrate is seen in the composite coatings with Al_2O_3-2 (Fig. 3c), with the grain size of the composite samples increasing with the distance from the substrate. It should also be noted that the formation of crystal twins occurs in the process of formation of the grains of the coating, and their number is significantly higher in the composite coatings. The same effect of intercalation of a dispersed phase into an electrodeposited coating was noted in [6], where the effect of aluminum-oxide powders on the properties and structure of nickel electrochemical coatings was considered.

The micrographs taken on a TEM (Fig. 4) confirm that twinning defects are formed in the process of formation of coatings. The crystals are formed by the mechanism of lateral growth. Twinning apparently occurs by the Vaughan mechanism, in the case of which twins appear by incoherent nucleation against the background of growth layers [5]. The formation of twins occurs along the {111} plane, which is characteristic for crystals with a face-centered cubic (FCC) lattice.
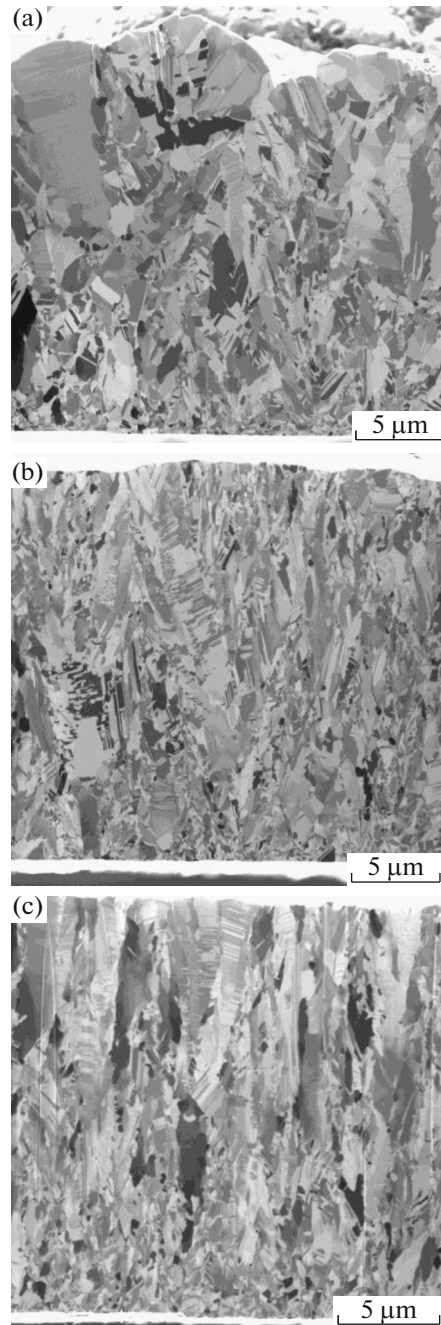

Fig. 3. Micrographs of the end cut of (a) a copper coating without additives, (b) a composite coating with Al_2O_3-1, and (c) a composite coating with Al_2O_3-2.

X-ray diffraction analysis of the samples (Fig. 5) has shown the presence of characteristic for copper with a face-centered cubic lattice (111), (200), (220), and (311) reflection planes. However, a difference is noticeable: the X-ray diffraction pattern of the coatings without additives (Fig. 5a) has a shape that is typical for copper and is comparable to the X-ray diffraction pattern of fully disordered powdered copper. The X-ray diffraction pattern of the composite with Al_2O_3-1
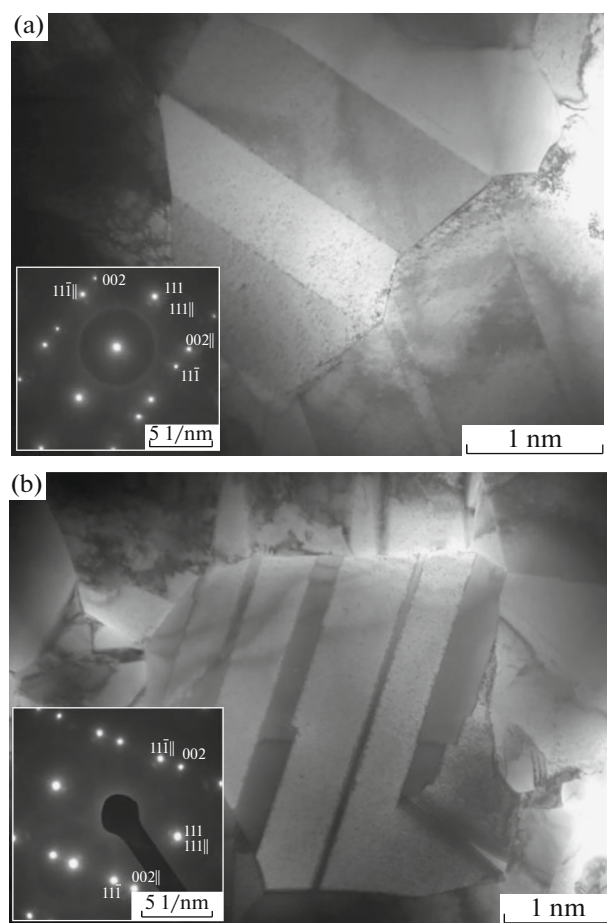
Fig. 4. Twinning defects in the grains and microelectron diffraction patterns of (a) composite coatings with Al_2O_3-1 and (b) composite coatings with Al_2O_3-2.

Fig. 5. X-ray diffraction patterns of the coatings: (a) a copper coating without additives, (b) a composite coating with Al_2O_3-1, and (c) a composite coating with Al_2O_3-2.

(Fig. 5b) also contains peaks corresponding to copper; however, redistribution of the intensities of the peaks has occurred, the intensity of the peaks at (111) and (200) has significantly decreased, and intercalation of Al_2O_3-1 particles has led to the appearance of a mixed predominant orientation of the copper crystallites along the (111) and (220) axes. A significant increase in the relative intensity of the peak at (111) in comparison with the two other samples is seen in the X-ray diffraction pattern of the composite with Al_2O_3-2; i.e., clearly pronounced predominant growth of the crystallites along the (111) plane is present. Formation of large crystallites is noted in all the samples.

The lattice parameters are the same in all the samples and are 3.615 Å, which suggests practical absence of point defects associated with the distortions of the crystal lattice of copper.

Therefore, the introduction of dispersed additives promotes the appearance of predominant growth of the coatings along the main crystallographic planes, which leads to the appearance of anisotropy of the properties of the coatings. It is known that one or
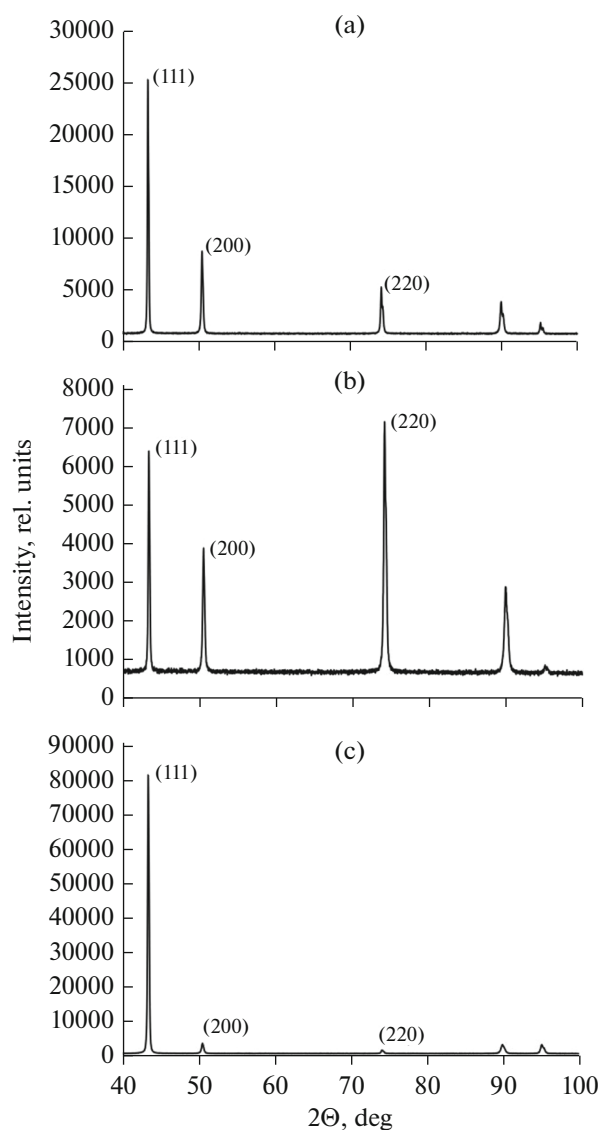
another texture affects the operational characteristics of electrodeposited copper [7]. The results of XRD, micrographs of the surface of the samples, and images obtained using a focused ion beam system are quite in agreement: the shape of the grains of the composite coatings and formation of columnar polyoriented (composites with Al_2O_3-1) and oriented directed perpendicular to the substrate (composites with Al_2O_3-2) structures is accompanied by the presence of predominant growth of crystallites (texturing) [8].

Figure 6 shows a characteristic stress–strain diagram of a sample of a copper coating.

The results of determination of the microhardness and ultimate tensile strength of the coatings are presented in Table 1.

Table 1. Microhardness and ultimate tensile strength of the coatings

Type of coating	Ultimate tensile strength, MPa	Microhardness, MPa
Cu	362.1 ± 45.3	487.6 ± 27.3
Cu + Al$_2$O$_3$-1	439.7 ± 27.6	539.8 ± 15.8
Cu + Al$_2$O$_3$-2	533.3 ± 59.7	645.3 ± 31.9
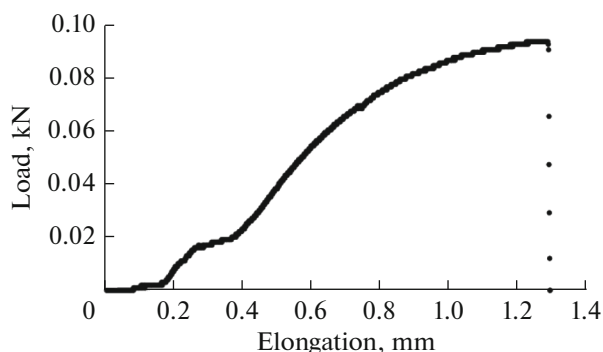
Fig. 6. Stress–strain curve of a sample of a copper coating.

Despite the fact that the concentration of Al$_2$O$_3$-2 particles in the coatings has been 0.1 wt %, the microhardness of such samples increased by more than 30%, and the ultimate tensile strength, almost 1.5-fold, while the microhardness and ultimate tensile strength of the composites with Al$_2$O$_3$-1 have changed not as significantly, by 10 and 20%, respectively (Table 1). This is associated with the different effects of the additives on the microstructure of the obtained composites: a more perfect texture in the composites with Al$_2$O$_3$-2 and more ordered growth of the grains in them. Since, most likely, the intercalation of the particles of the powders in the process of formation of the coatings occurs along the grain boundaries, an insignificant increase in the microhardness in the composites with the addition of Al$_2$O$_3$-1 can also be associated with the fact that, intercalating into the grain boundaries, the Al$_2$O$_3$-1 particles make them "looser" in comparison with the composites with Al$_2$O$_3$-2. According to [9], copper deposits with the {111} texture possess a high tensile strength. Also, the presence of twinning defects in a coating promotes an increase in the strength characteristics of the coatings [6].

CONCLUSIONS

The introduction of powdered additives of aluminum oxide with different dispersities to copper electrodeposited coatings differently affects their microstructure, principle of formation, and some characteristics. The intercalation of Al$_2$O$_3$-1 into a copper matrix has led to polyoriented growth of the grains and appearance of mixed predominant orientation of the growth of the crystallites along the (111) and (220) axes. However, this has insignificantly affected the microhardness and ultimate tensile strength of the samples of this type of coatings. At the same time, the introduction of Al$_2$O$_3$-2 into copper coatings has led to the formation of an oriented narrow columnar grain structure, and the strongest predominant growth of copper crystallites along the (111) axis has manifested itself, which has led to a change in the strength characteristics of these coatings: thus, the microhardness has increased by more than 30% in comparison with the coatings without additives, while the ultimate tensile strength has increased by 1.5-fold. In both cases, twinning defects have manifested themselves during the formation of the coatings, which also affect the properties of the coatings.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Ramalingam, S., Balakrishnan, K., Shanmugasamy, S., et al., *Surf. Eng.,* 2017, vol. 33, no. 5, p. 369.
2. Akanksha R. Shelke, J. Balwada, S. Sharma, et al., *Mater. Today: Proc.,* 2020, no. 28, p. 2090.
3. Eslami, M., Saghafiana, H., and Golestani-fard, F., *Appl. Surf. Sci.,* 2014, vol. 300, p. 129.
4. *GOST* (State Standard) *no. 9.305–84: Unified System of Corrosion and Ageing Protection. Metal and Non-Metal Inorganic Coatings. Technological Process Operations for Coating Production,* Moscow: Izd. Standartov, 1986.
5. Kovenskii, I.M. and Povetkin, V.V., *Metallovedenie pokrytii. Uchebnik dlya VUZov* (Metal Science of Coatings. Student's Book for Institutions of Higher Education), Moscow: Intermet Inzhiniring, 1999.
6. Goral, A., *Surf. Coat. Technol.,* 2017, vol. 319, p. 23.
7. Imaz, N., García-Lecina, E., Suárez, C., et al., *Trans. Inst. Met. Finish.,* 2009, vol. 87, no. 2, p. 64.
8. Gamburg, Yu.D., *Elektrokhimicheskaya kristallizatsiya metallov i splavov* (Electrochemical Crystallization of Metals and Alloys), Moscow: Yanus-K, 1997.
9. Brusnitsyna, L.A., Stepanovskikh, E.I., and Alekseeva, T.A., *Butlerov. Soobshch.,* 2021, vol. 67, no. 7, p. 39.

Translated by E. Boltukhina