

DEVELOPMENT OF NANOCOMPOSITES FOR COATING DEPOSITION BY FRICTION CLADDING METHOD

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ABSTRACT

The present paper is about development of copper matrix composites with nanoreinforcements as materials for coatings deposition by friction cladding method. Method of copper matrix composite fabrication is based on mechanical alloying of components mixture and compaction of obtained nanocomposite granules. Composite materials were produced by mechanical alloying in a planetary mill, in which drums with quasicylindrical milling bodies or balls were mounted. Nanodiamonds, onions, nanosilica, diatomite and particles of boron hydrides (boron–hydrogen compounds) were used as reinforcements. Main method of compaction for this study was cold and warm pressurizing with subsequent thermal treatment in protective atmosphere. Developed materials and coatings were investigated by optical and scanning electron microscopy. The study of the produced coating has shown that the quality of the coatings depends on the conditions of friction cladding and on the composition of the coating; each composition requires its own regimes of application to be developed. Optimization of regimes makes it possible to achieve a high quality of coating. With respect to thickness, the developed coating is continuous, without any defects. Study shows that coatings have very good adhesion to substrate; layers of coating materials and metal of substrate are mixed on interface without any pores, disintegrations or other defects. The study has shown that the technological scheme “mechanical alloying - friction cladding” makes it possible to produce high-quality coatings from nanocomposite materials.

1. INTRODUCTION

Long-term experience shows that endurance and reliability of metal products, equipment, machine components and tools are largely determined by the state of the surface and surface layers. The nature and state of the surface strongly determine adhesion and friction interaction, which play an exceptionally important role in friction and metal-working processes. A traditional way to increase the service characteristics of metal products is application of coatings, which possess a high corrosion resistance, hardness, wear resistance and other properties. Nanocomposites with copper matrix were proposed to be used as a coating material to increase the strength and hardness of coatings and to enhance the parameter variation range.

The aim of this paper is to investigate the possibility of development of copper matrix composites reinforcing nanoparticles for coating deposition on various work-pieces surfaces. The following reinforcing particles were used:

- nanodiamond powders;
- onion-like carbon particles produced from nanodiamond powders;
- silicon dioxide particles of 2 types: diatomite and silicon nanodioxide;
- boron hydrides (boron–hydrogen compounds).

2. INITIAL MATERIALS

Nanodiamond powders have a complex multilevel structure [1]. Primary nanodiamond particles (Fig. 1 a) with diameter around 4 nm [2] are combined into strong cluster aggregates 40 up to 400 nm in size (Fig. 1 b). In turn, primary aggregates are combined

into secondary aggregates and agglomerates of 0.4 μm in size. Nanodiamond powders belong to fractal systems; their most important structure-forming stages are fractal formation by the cluster-particle and cluster-cluster type to form multilevel macrostructures.

Onion-like carbon nanoparticles [3] were produced by thermal treatment of nanodiamonds (1300-1600 $^{\circ}\text{C}$ in vacuum) (Fig. 1 c).

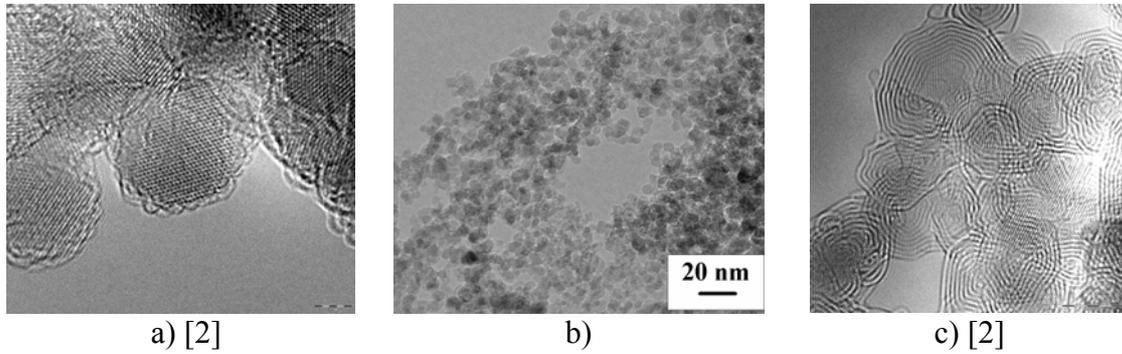


Figure 1: Appearance of nanodiamonds and onions

Of certain interest are applications of silicon dioxide nanoparticles for reinforcing the copper matrix. Figure 2 a, b presents the general view of these particles: a) nanoparticles of silicon dioxide; b) diatomite particles, which are frustules of diatomic algae and 97–98% of which is amorphous silicon dioxide. The primary particle of silicon nanodioxide is a sphere about 40–70 nm in diameter, however, these particles are strongly bound into agglomerates of a general size of 5–10 μm . Diatomite is represented by plates 100–300 nm thick and about 1 μm wide.

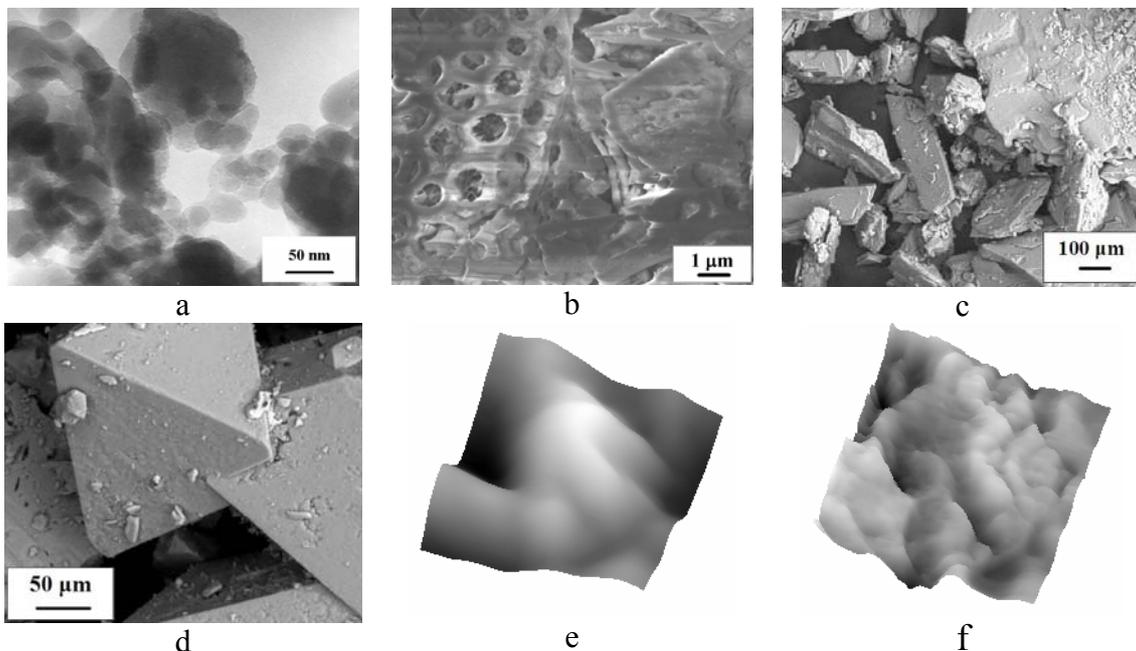


Figure 2: Appearance of applied reinforcements: a) diatomite; b) nanosilica; c) boron hydrides $((\text{C}_2\text{H}_5)_3\text{NH})[\text{CuB}_{10}\text{H}_{10}]$; d) boron hydrides $\text{Cs}_2\text{B}_{12}\text{H}_{12}$, e,f) results of scanning

a boron-compound particle on a Nanoscan installation (the scanning window was $4.9 \times 4.9 \times 0.3 \mu\text{m}$) (e) surface relief, (f) elasticity modulus map.

The shape and size of the boron compounds depend from chemical composition but they have one thing in common: all large crystals are not solid strong material, but consist of more fine particles (Fig. 2 c-f).

2.METHOD OF COMPOSITE PRODUCTION, INVESTIGATION OF STRUCTURE AND PROPERTIES

The use of the infiltration method widespread in production of aluminum composites becomes in the case of copper matrix rather problematic because of the following reasons:

- (1) the melting temperature of copper is considerably higher than that of aluminum;
- (2) infiltration methods can not change the size of the reinforcing particles, i.e., a more expensive initial material for reinforcing particles is required to produce a composite with a small size of reinforcing particles (the smaller the size, the more expensive the reinforcing material is).

Therefore, the following method of producing composite materials was investigated: mechanical alloying to produce granules of composite + subsequent consolidation to produce compact material. Mechanical alloying was performed in planetary mills in an argon atmosphere. The technological tools were either balls or special quasicylindrical milling bodies. The treatment time was varied from 0.5 up to 10 h. The share of second component of composite varied from 5 up to 50% (vol).

Studies have shown that kind of reinforcements influences on mechanism of composite formation. For example, during mechanical alloying the mechanism of incorporating nanodiamond particles has its peculiar features and depends on the treatment regimes, shape of milling bodies and amount of reinforcing particles (Fig. 3). Nanodiamond particles agglomerate to a size exceeding $1 \mu\text{m}$. If quasicylindrical milling bodies are used, and copper powder is processed together with 5–10% nanodiamond particles, in a short period of time these large agglomerates break down to very small agglomerates or even to separate diamond nanoparticles. Due to their high hardness, these small agglomerates of up to 20–30 nm in size incorporate into the surface layers of copper particles. The “blend” obtained splits away from large copper particles; comminution of the powders occurs. Particles obtained are combined into granules, which may contain particles of pure copper, so initially the structure of the granules is characterized by a significant inhomogeneity; an increased concentration of nanodiamond agglomerates is observed on the surface of many granules (Fig.3 b). However, as the treatment is continued, nanodiamond particles get uniformly distributed in the copper matrix owing to the alternation of the processes of comminution and fusion of particles, so that no increased concentration of nanodiamond particles on the surface of the granules is observed any more (Fig.3 c).

Increase of nanodiamonds proportion leads to difficulties of composite fabrication process. But it is possible to produce content of 35%(vol) nanodiamonds and more (Fig. 3 f) .

To confirm the uniform distribution of nanodiamond particles in the matrix, several granules of material obtained were cut by an ion beam. This was to ensure that the pattern on the cross section of a granule completely corresponded to a real situation and there was no change in the distribution of reinforcing particles during the preparation of specimens for the studies. These granules were investigated by a field emission

scanning electron microscope of high resolution. Figure 7 a shows that reinforcing nanodiamond particles are uniformly distributed in the bulk of the granule and their size does not exceed 10–15 nm, i.e., the initial agglomerates of over 1 μm in size are comminuted practically completely.

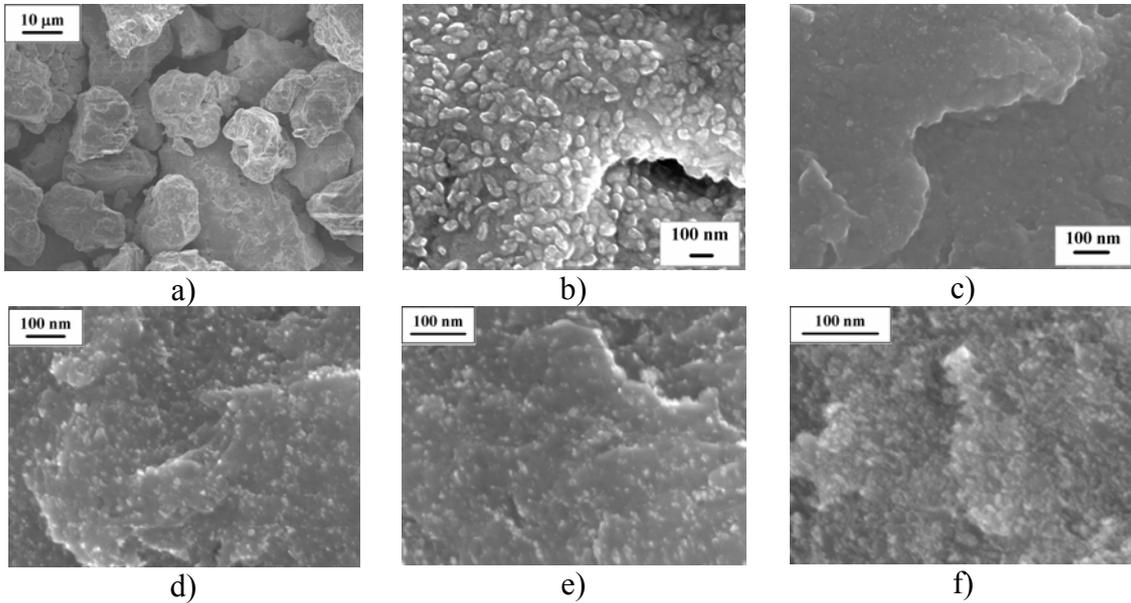


Figure 3: General view and surface morphology of composite “copper + nanodiamonds-ND” granules (SEM): a) general view of composite granules Cu+ND; b) Cu+5%ND, time of treatment in planetary mill $t=0,5\text{h}$; c) Cu+5%ND (surface of granule), $t=1,5\text{h}$; d) Cu+10%ND, $t=3\text{h}$; e) Cu+10%ND, $t=10\text{h}$; f) Cu+35%ND, $t=3\text{h}$

Increase of treatment time leads to hardening of composite material. Figure 4 shows increasing hardness of composite granules in dependence from time of treatment in planetary mill.

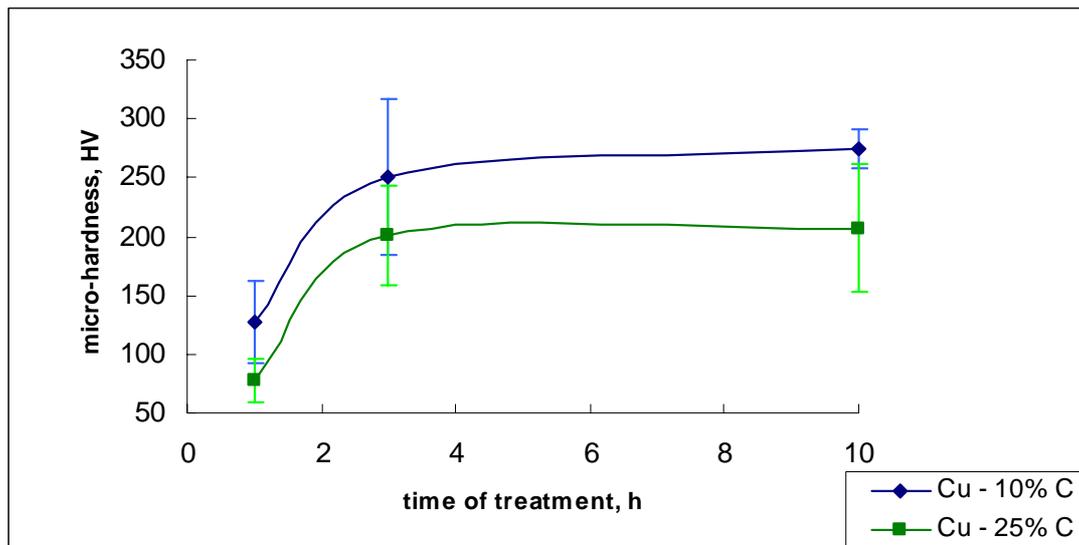


Figure 4: Dependence of hardness of composite granules Cu+ND from time of treatment

This study made it possible to determine the treatment regimes to obtain the copper–nanodiamonds composite material without graphitization of nanodiamonds.

However, a composite material with evenly distributed onion-like carbon nanoparticles (onions) can be fabricated, if such a material is required to be produced. It is possible to use two technological schemes for fabrication of composite “copper + onions”. First scheme is regular mechanical alloying of “copper + onions” mixture (Fig. 5 a, b), but it should be taken into account, that mechanical alloying of copper powder with onions sometimes cannot lead to positive results. According to second scheme, it is necessary first to achieve an even distribution of nanodiamond particles in the copper matrix, and then carry out their graphitization. This can be done in two ways: (a) by changing the technological regimes and tools, which would lead to graphitization of nanodiamond particles after their incorporation into the copper matrix and (b) heat treatment of the granules or compacted material. The structure produced may have individual particles of onion-like carbon (Fig. 5 c).

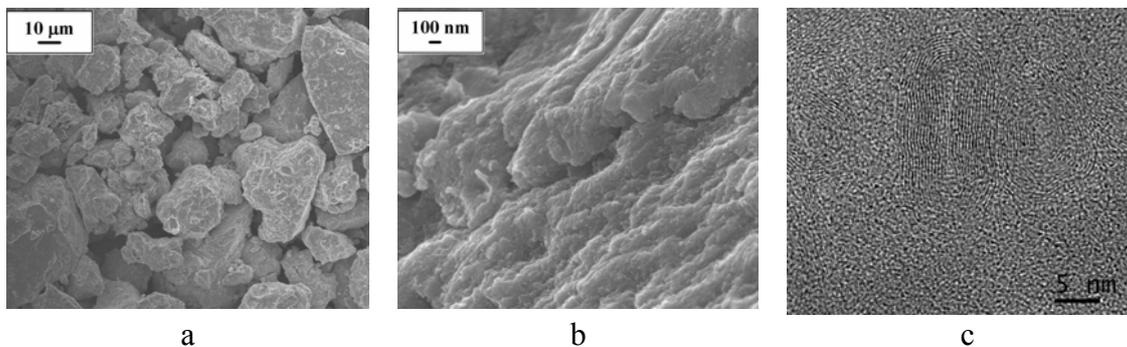


Figure 5: Appearance of copper composite granules with reinforcements from 20%(vol) onions (a, b) (SEM) and onions inside copper matrix (c) (TEM)

Granules are formed as the result of alternating processes of decomposition and fusion of treated particles. Therefore, their shape and morphology are determined by these processes, which, in turn, are defined by the properties of the material. The above is confirmed by studies of the appearance of granules by means of high-resolution scanning electron microscopy (Figs. 3, 5, 6). The figures present granules of copper composite materials with various reinforcing particles.

The fabricated granules of composite materials, as well as granules with nanodiamond reinforcing particles were cut by an ion beam to study the structure. Figure 7 demonstrates these structures. In their bulk, diatomite particles are broken down to smaller fragments not exceeding 100 nm. However, some amount of larger particles still remains. The granules are characterized by a high continuity and uniformity of the distribution of particles, which have a tight contact with the matrix (Fig. 7 b). Uniform distribution and, more importantly, comminution of agglomerated particles of silicon dioxide was achieved only by the treatment in a mill at a treatment time of over 90 min (Fig. 7 c). Studies of the surface and cross section of granules with boron–hydrogen particles indicated that in mechanical alloying boron–hydrogen compounds are comminuted such that they are difficult to observe even at magnifications of 100,000×. The largest size of separate particles does not exceed 100 nm. This degree of

comminution leads to decrease of granule fusion ability and require more intensive deformation during compaction (weak deformation lead to pore formation and even microcrack development) (Fig. 7 d).

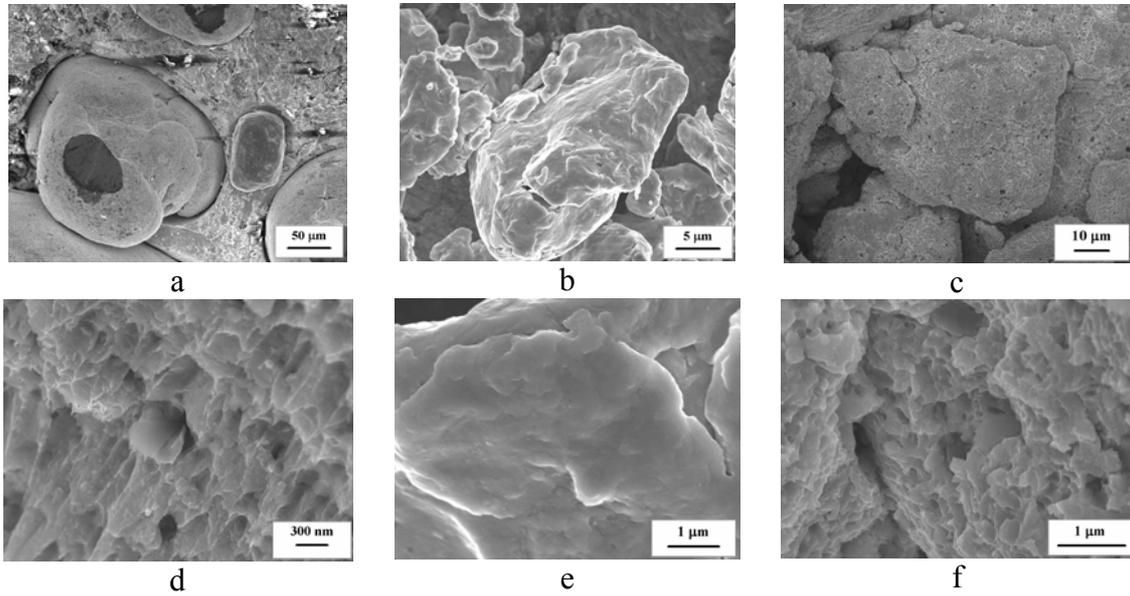


Figure 6: General view and surface morphology of composite granules (SEM); a, d – Cu + diatomite (5%); b, e – Cu + boron hydrides; c, f – Cu + nanosilica;

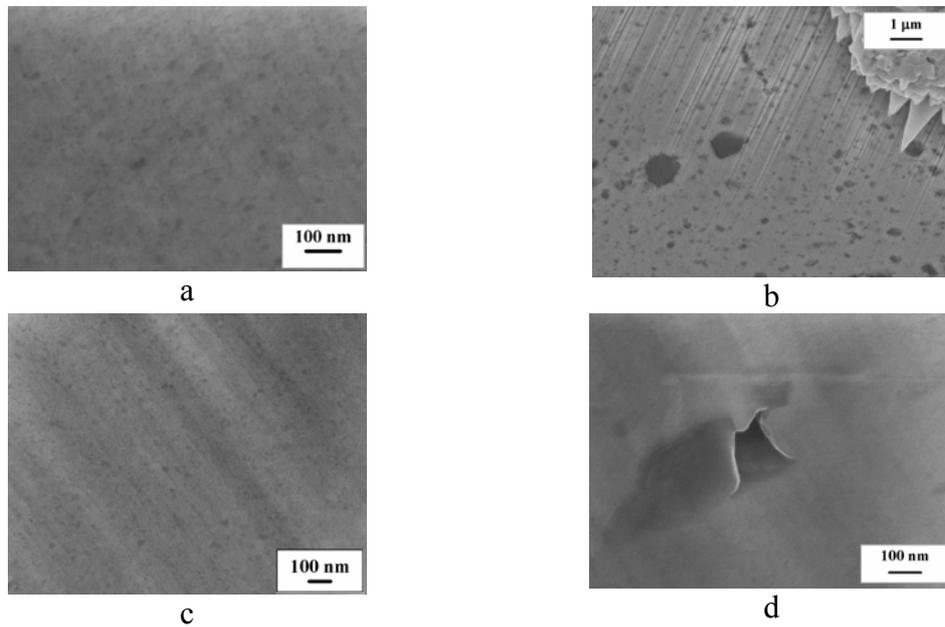


Figure 7: Cross section by ion beams of composite granules from copper with different reinforcements; a – nanodiamonds; b - diatomite; c – nanosilica; d – boron hydrides

As the result of studies, we developed mechanical alloying regimes to produce granules of composite materials with evenly distributed reinforcing particles for subsequent compaction.

3. COMPACTION AND FRICTION CLADDING

Main method of compaction for this study was cold and warm pressurizing with subsequent thermal treatment in protective atmosphere. Specimens of composite materials with copper matrix were prepared as rings of 50 mm in diameter, 20 mm in height; the diameter of the hole was 20 mm (Fig. 8). The specimens were compacted according to two procedures: (1) - pressed with a force of 1.7 MN, then annealed at 500 °C for 5 hours; (2) - the mixture of granules was cold-prepressed and then kept for a definite time in heated state under a load.

For friction cladding (FC) [4-6], a prepared ring was fixed in a holder, which was rotated to ensure a uniform pickup of composite material and its transfer to the treated surface. Studies of the surface of rings from various variants of composite coatings show that the brushes pick up an insignificant layer of material, many times smaller than the size of a granule (Fig. 9). The figure shows traces from separate wires, and individual granules are impossible to single out. This implies that composite material is additionally mixed up in FC, which ensures a uniform distribution of reinforcing particles in the coating material.



Figure 8: Specimens of composite materials with copper matrix for friction cladding

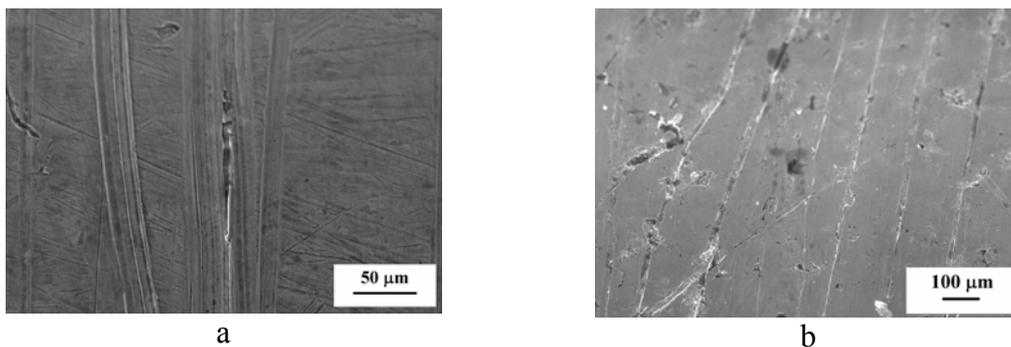


Figure 9: Surface of nanocomposite rings after application for friction cladding; a – copper + boron hydrides; b – copper + nanodiamonds

Study of the material was carried out at all process stages. Optical and scanning electron microscopy were used. The studies have shown that the quality of the coatings depends on the conditions of FC and on the coating composition; each composition requires its process regimes of application to be developed. Optimization of the regimes makes it possible to achieve a high quality of the coating. Figure 10 shows the surface of a

coatings based on copper with an addition of nanodiamond reinforcing particles. A slight change of the application regimes and rigidity of the metal brush may lead to some discontinuities on the surface of the coating (Fig. 10b), which can be eliminated by the re-run of the brush. It should be noted that uniformly distributed insignificant discontinuities play a positive role for some applications, as they make it possible to create conditions for accumulating increased amounts of lubricants on the surface of articles. In chrome plating, for instance, a network of cracks is specially produced for these purposes. The developed coating is of continuous thickness, without any defects. The high quality of the coating can be demonstrated both in the fracture and on cross-sectional specimens (Fig. 11).

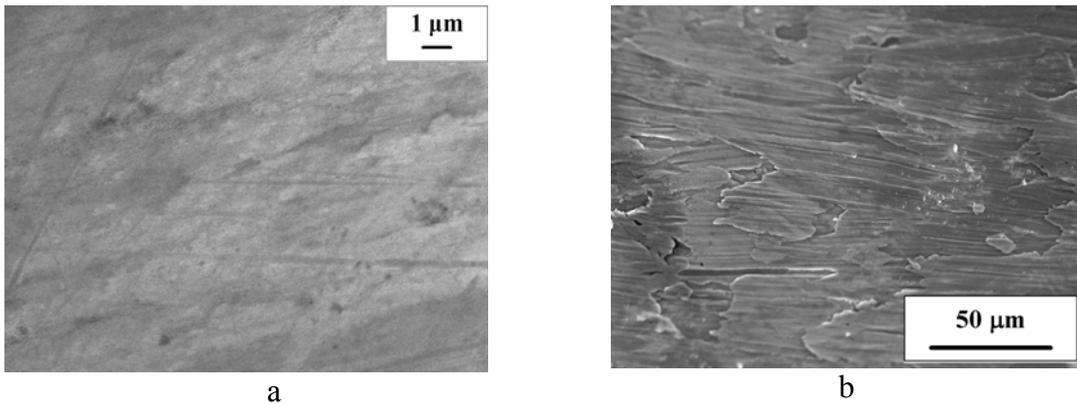


Figure 10: Surface of coatings from copper-nanodiamonds composite; a – without any defects; b – small discontinuities

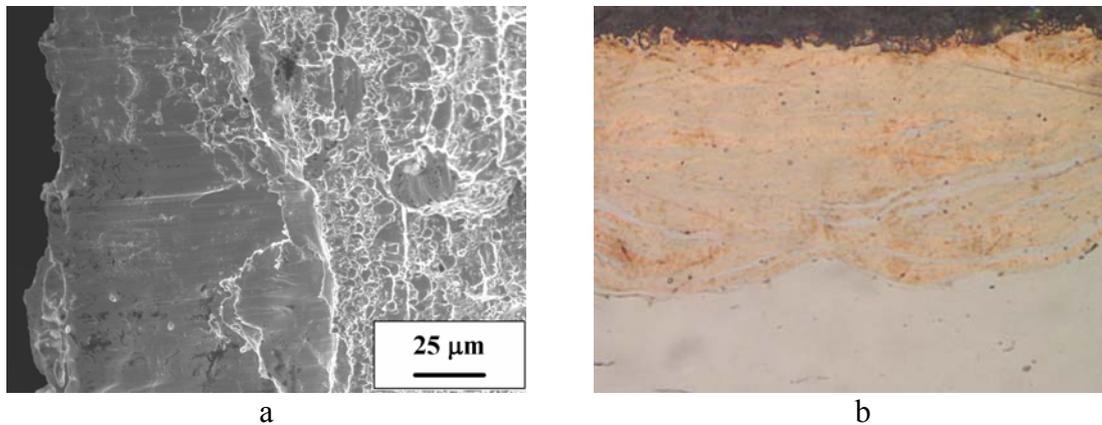


Figure 11: Nanocomposite coating deposited by friction cladding; a – fracture (SEM); b – cross section (optical microscopy), $\times 1000$

4. CONCLUSION

Thus, the studies have shown that the developed method enables fabrication of a high-quality coating from copper reinforced with various types of nanoparticles. Reinforcing nanoparticles are evenly distributed in the copper matrix. Friction cladding ensures a high adhesion of the coating to the base metal. No defects were found either in the mass of the coating or on the surface.

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