

## METAL MATRIX COMPOSITES WITH NANODIAMOND REINFORCEMENTS

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### **Abstract**

*This work deals with processes of production of particulate metal matrix composites. Nanodiamonds are used as reinforcing particles. Particulate MMC can be used as bulk materials and as coatings. The studies begin with the initial components subjected to mechanical alloying in planetary mills to produce granules of composite materials. This is followed by compaction of the granules into a bulk material. The coating is applied by friction cladding and electrochemically. It is shown that the methods developed make it possible to produce high-quality coatings from composite materials. Reinforcing particles are uniformly distributed in the metal matrix. The developed methods of applying coatings provide for high adhesion between the coating and the base. Defects are absent both in the bulk and on the surface of the coating.*

### **1 Introduction**

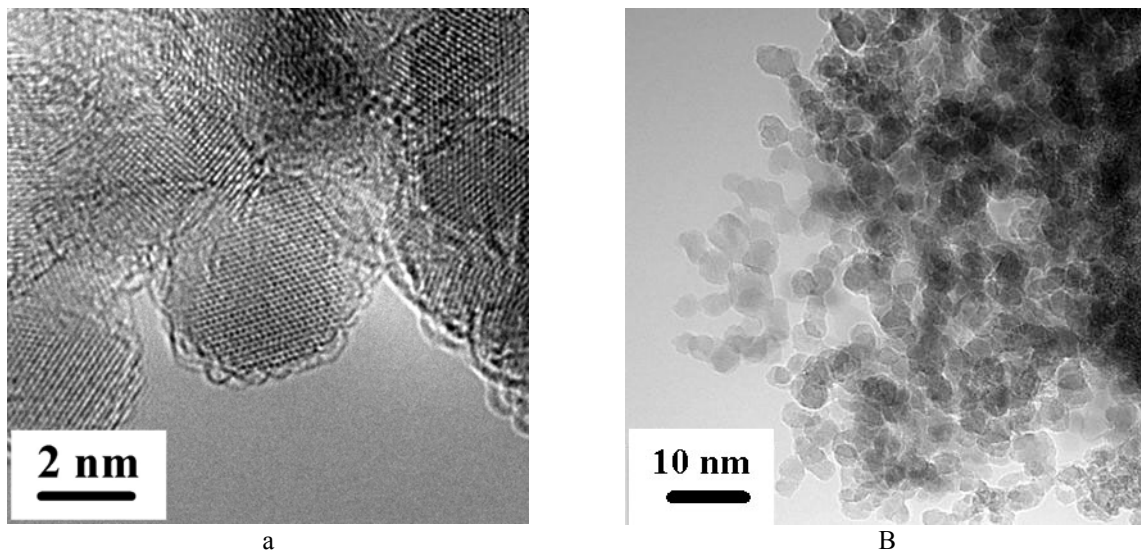
Modern industries require new materials with improved properties. For instance, Al+SiC – the classic composite – does not always satisfy the requirements for electronic packaging operated under severe conditions. Rubbing electrical contacts in various instruments and devices also require application of novel materials. One of the ways to solve this problem is to develop new metal matrix composites by mechanical alloying followed by consolidation of granules obtained in mechanical alloying [1]. In spite of significant research efforts, one of the problems, which impedes the widespread use of mechanical alloying as an industrial method of producing new materials, is lumping (fusion of granules into large lumps) of processed material and its sticking to process tools. For this reason, R&D of novel metal matrix composites and refinement of mechanical alloying processes are receiving considerable attention.

### **2 Development of Metal Matrix Composites with Nanodiamond Reinforcing Particles on the basis of Mechanical Alloying**

#### *2.1 Initial Materials and Equipment*

This work investigates the development of a method for producing metal matrix composites by mechanical alloying carried out in planetary mills. Copper, a copper–zinc alloy L62 (brass) and nickel were used as a matrix material. The matrix material was used as chips, which are pretreated in a planetary mill, after which the size of the particles was 0.5–2 mm. Nanodiamonds were used as reinforcing particles. Detonation nanodiamond (DND) powders have a complex multilevel structure [2, 3]. Primary nanodiamond particles 4–6 nm in

diameter (Fig.1 a) are combined into strong cluster aggregates from 40 to 400 nm in size. In turn, primary aggregates are combined into secondary aggregates and agglomerates of up to tens and hundreds of micrometers in size (Fig. 1 b).



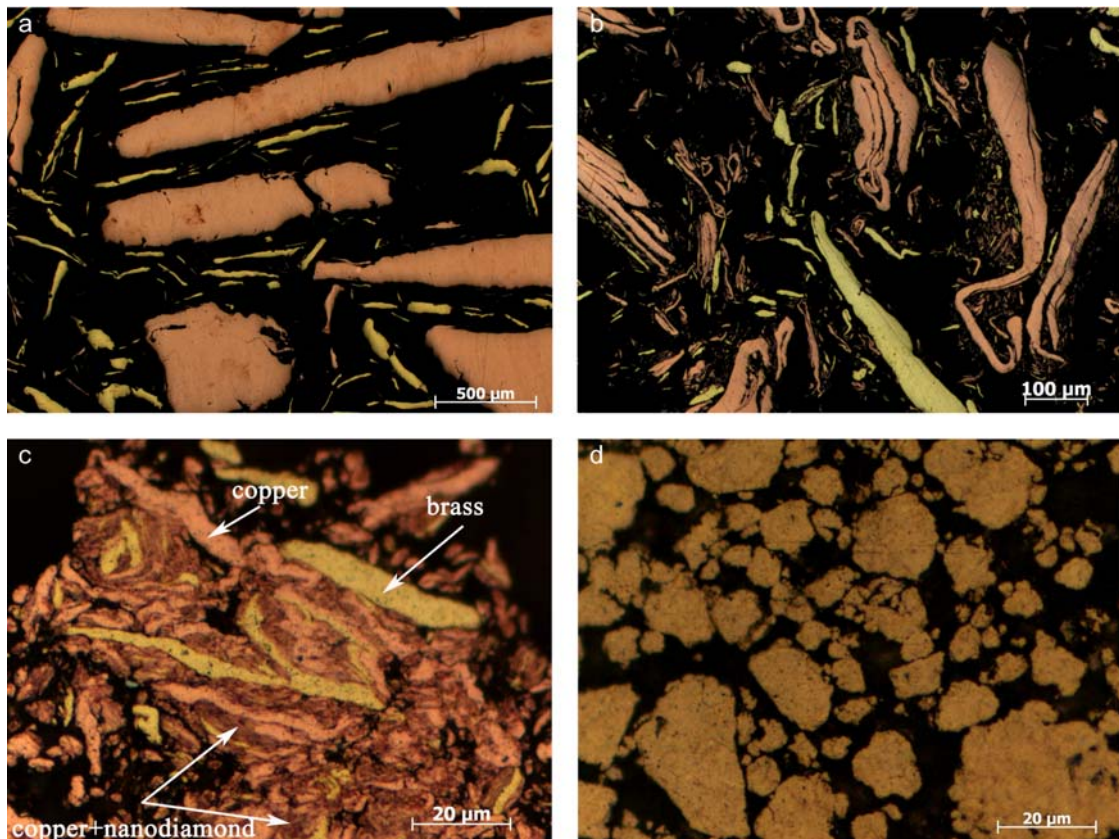
**Figure 1.** Detonation nanodiamonds

Mechanical alloying was carried out in Retsch PM400 and Gefest 11-3 planetary mills in an argon atmosphere, without using surfactants, in sealed steel grinding jars of 500-ml nominal volume. In both cases, powdered material was treated using fabricated from chromium steel milling balls 12 mm in diameter. The effects of the mechanical alloying regimes on the process and the properties of materials have been dealt with extensively. For this study, the following regimes were chosen. In the Retsch PM400 mill, the ratio of the weight of the balls to that of the treated mixture was 7:1. The rotation velocity of the grinding jars around the common axis (the rotation rate of the carrier) was 300 rpm. The jars were air-cooled during the operation. In the Gefest 11-3 mill, the ratio of the weight of the balls to that of the material was 4:1 at a carrier rotation velocity of 600 rpm. The jars were cooled with flowing water. In the Gefest 11-3 planetary mill, a quasicylindrical milling body was also used without the balls. An important advantage of mechanical alloying with the quasicylindrical milling body is an increased action force and contact area of unit impacts in the treatment, which in combination with low background temperature significantly facilitated mechanical alloying of large components of charge. The duration of treatment varied from 1 h up to 10 h for all materials. Compaction was done on hydraulic presses. The mechanical tests were conducted by the method of static compression for a Zwick Z250 test machine. The structures and properties of developed materials were studied by optical microscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffractometry (XRD).

## 2.2. Study of the Mechanical Alloying Process

The main stage of MMC formation was development of composite granules by mechanical alloying in planetary mill. The application of nanodiamond powders for metal matrix reinforcements has its specific features. And these small agglomerates started to embed into the surface layers of metal particles. Granules are formed as a result of alternating processes of breakdown and fusion of processed particles. For this reason, their structure, shape and surface morphology are determined by these processes, which, in turn, are determined by the properties of the material. This work investigated the processes of granule formation. For this purpose, a mixture of particles of copper M1 and brass L62 at the same ratio was used. Due to

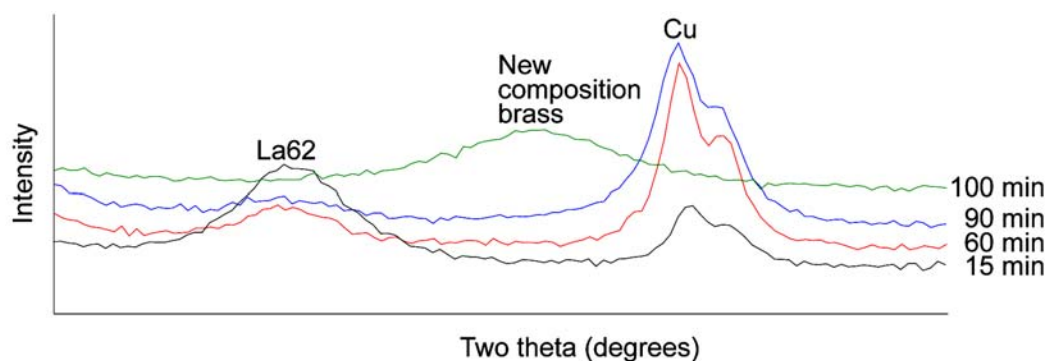
their difference in color, such particles were readily distinguishable from one to another by methods of optical microscopy, i.e., it was easy to follow particle shape formation during the treatment in a planetary mill. The mixture of copper and brass powders was supplemented with 20% (volume) nanodiamonds. After a treatment in a planetary mill for 15, 30, 45, 60, 90 and 100 min, samples taken from the jars of planetary mill were used for cross-sections (specimens for optical microscopy) preparation. Study by optical microscopy method showed that no significant changes in the shape of particles were observed after a 15-min treatment (Fig. 2a) – only individual particles were subject to deformation. The initial metal particles represented separate plain scales, the size of which in two directions was much larger than the size in the third direction.



**Figure 2.** Change of the structure of copper–brass–20% ND composite granules versus the treatment in a planetary mill: (a) 15 min treatment; (b) 60 min treatment; (c) 90 min treatment; (d) 100 min treatment

After a 30-min combined treatment, deformation of particles became some, but the mean area of the metal particles was  $1350 \mu\text{m}^2$ . After a 45-min treatment, heterogeneous scales began to layer up and twist into loose granules, such that each metal particle preserved its individuality. The size of the particles decreased. 60 min of treatment led to a greater mixing of the copper and brass particles, and consolidation of the granules. A layered structure began to form (Fig. 2b). Both purely metal areas and darker areas of metal-containing ND particles could be layered. Herewith, the mean size of scales changed little. After a 90-min treatment (Fig. 2c), granules had an equiaxial shape, where their area decreased to  $530 \mu\text{m}^2$ . The change of granule shape and size was readily seen from the comparison of Figs. 2a and 2c. However, areas with larger and smaller contents of ND particles (darker and lighter areas, respectively) were clearly seen. After a 100-min treatment (Fig. 2d), the components totally dissolved to form brass of a new composition. All granules of materials had a compact equiaxial shape with average size of  $165 \mu\text{m}^2$ . The structure of the composite granules was completely

homogeneous, where the initial components were indistinguishable. There were no copper and brass particles that had not interacted. X-ray phase analysis confirmed the results obtained in studies of the structure by optical microscopy. For a detailed analysis, reflections (222) within the interval of Bragg angles  $2\theta = 91\text{--}97$  angular degrees were chosen, which made it possible to avoid the possible influence of the change of stacking fault concentration on the position of diffraction reflections, and to increase the lattice-parameter measuring accuracy as the Bragg angle increased. Figure 3 shows fragments of diffractograms after 15-, 60-, 90-, and 100-min treatments. The positions of the diffraction peaks correspond to (222) reflections of brass and copper to an accuracy of  $0.001 \text{ \AA}$ . Reflections of copper and brass of cubic modification were present on the diffractograms of composite granules after 15-, 60-, and 90-min treatments in planetary mills. Treatments in planetary mills for 15–60 min led to a shift of reflections and to broadening, which was due to a change of the values of lattice parameters and an increase of the level of microstrains. However, the peaks corresponding to the initial materials were pronounced and remained so up to 90 min of treatment. After a 90-min treatment, the intensity of the (222) peak for brass decreased significantly, but its position did not change, and the reflection (222) of copper shifted towards smaller angles, which was due to an increase of the lattice parameter of the initial component from  $3.612$  to  $3.615 \text{ \AA}$ . The treatment for 100 min led to a phase transformation. As a result, the diffraction reflections of the initial copper and brass vanished, but a peak appeared corresponding to one phase – that of brass of a new composition, L81 (copper content, 81%).



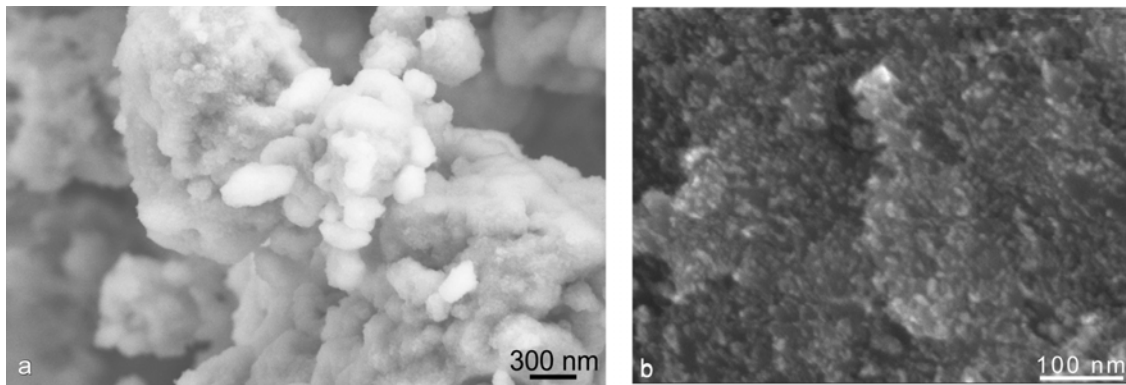
**Figure 3.** Diffractograms of L62+M1+20% ND composite granules after 15-, 60-, 90- and 100-min treatments

Studies of the development of composite materials with nanodiamond reinforcing particles have shown that nanodiamonds sharply reduce lumping of a treated material and its sticking to process tools. This makes it possible to suggest the use of nanodiamonds not only as reinforcing particles but also as process additives, which reduce sticking. Thus, “copper + silicon oxide” or “copper + silicon carbide” composite materials can be produced with the addition of 5–10% of nanodiamond powders. This enables a significant decrease of sticking, i.e., an increase of the yield of accepted product.

### 2.3. Effect of Increased Oxidation of High Nanodiamond Content Composites

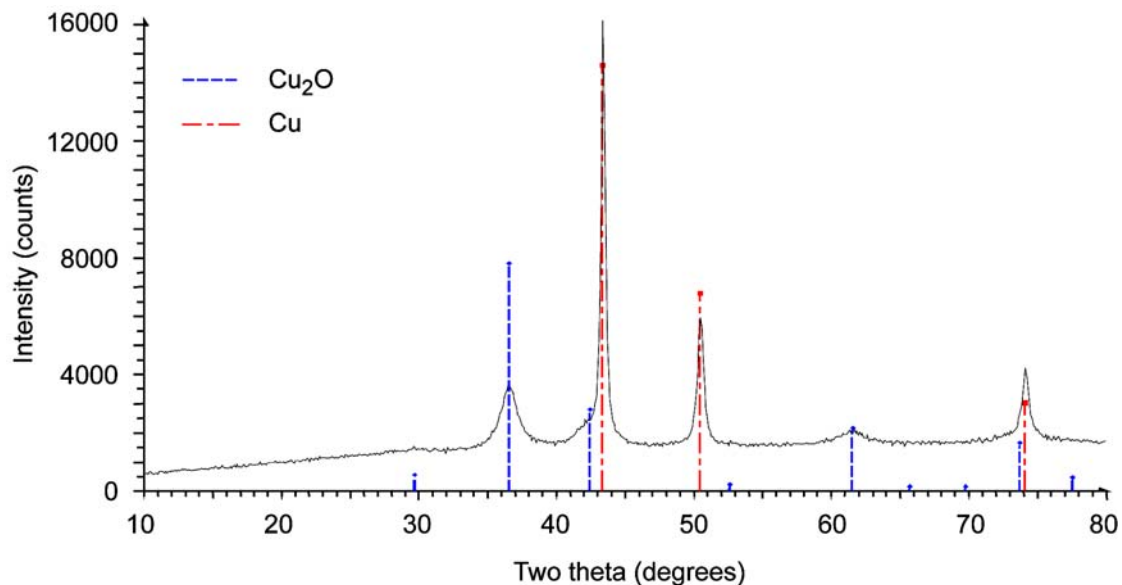
The studies revealed a characteristic feature that at a content of reinforcing nanodiamond particles greater than 20–25%, the nonuniformity of their distribution (and therefore the occurrence of an accumulation of broken, separately lying, and partially matrix-bound ND particles on the surface) led to increased oxidation of the composite in air (Fig. 4a). For the case of prolonged treatment in a planetary mill, i.e., for a uniform distribution of nanoparticles in the matrix and absence of free particles on the surface of granules, this effect was much smaller or almost absent (Fig. 4b).





**Figure 4.** View of Cu+35% ND composite granules treated in a planetary mill for 3 h (a) and 8 h (b)

Using the method of X-ray diffraction (XRD), it was found (Fig. 5) that on the surface on copper composite Cu+30%ND (time of treatment in planetary mill was 1,5h) mainly copper(I) oxide (monovalent copper oxide –  $\text{Cu}_2\text{O}$ ) was formed. Copper(I) oxide also appeared on composite granules in their contact with air and on specimens after compaction.



**Figure 5.** Diffractogram of a specimen of Cu+30% ND composite granules treated in a planetary mill for 2 h.

These results enable to propose the developed composite materials for use in coatings of marine facilities for protection from biofouling. As before, the most efficient for these purposes at present are copper oxides, predominantly monovalent copper oxide (copper(I) oxide). The application scheme of copper(I) oxide is simple: powders of copper(I) oxide are introduced into material of the coating. When marine organisms begin to erode the coating, particles of copper(I) oxide manifest themselves and, as a minimum, scare away those marine organisms. The problem is that particles of copper(I) oxide are quickly washed away during the contact with water. New marine organisms appear and destroy the coating to the next copper(I) oxide particle. This makes necessary application of a new coating in 1–2 years. The proposed composite material is not dissolved by water, is not fragile, so its washout by water is made difficult. Copper(I) oxide removed from its surface is formed there again. Thus, the life time of the protective coating can be greatly extended.

#### 2.4. Compaction

Granules produced by mechanical alloying are compacted by pressing at 400–600°C for up to 30 min. The press forms are cylinders (1) 10 mm in diameter and 20 mm in height and (2) 40 mm in diameter and 40–60 mm in height, and plates 10 mm wide, 30 mm long and 5–10 mm thick. The mechanical properties are determined on specimens 10 mm in diameter. Cylinders 40 mm in diameter are used for application of coatings by the method of friction plating; and plates for application of coatings by an electrochemical method. Information on the mechanical properties determined in the compression of specimens on an INSTRON tester is presented in Table 1. Composites with nanodiamond reinforcing particles are destroyed without a plastic strain, i.e.,  $\sigma_e = \sigma_{0.2}$ ; a composite with silicon oxide reinforcing particles is noted to have a plastic yield. For comparison, we have studied specimens of matrix materials for compression. The studies show that the yield strength of copper M1 is within the limits of 200–270 MPa, and of brass L62 within the limits of 320–350 MPa.

No	Material	Treatment in a planetary mill, h	Process tools	Yield strength $\sigma_e$ , MPa
1	Cu–20% ND	1	balls	114
2	Cu–20% ND	5	balls	540
3	L62–20% ND	1	balls	72
4	50Cu–50L62–20% ND	1.67	balls	576
5	Cu–35% ND	1	balls	89
6	Cu–35% ND	10	balls	520
7	Cu–35% ND	2	quasicylindrical body	510

**Table 1.** Strength characteristics of the “copper + nanodiamond (ND)” composite materials determined in the compression of specimens.

It is seen from the table that:

- an increase of the treatment time leads to an increase of the strength characteristics (*cf.* Nos. 1 and 2, 5 and 6, 8 and 9);
- phase transformations increase the uniformity of the distribution of reinforcing particles, which leads to an increase of strength (*cf.* Nos. 3 and 4);
- the use of a quasicylindrical milling body decreases the treatment time required to produce a homogeneous structure, which guarantees a high strength (*cf.* Nos. 6 and 7);

### 3 Deposition of coatings from developed composite materials

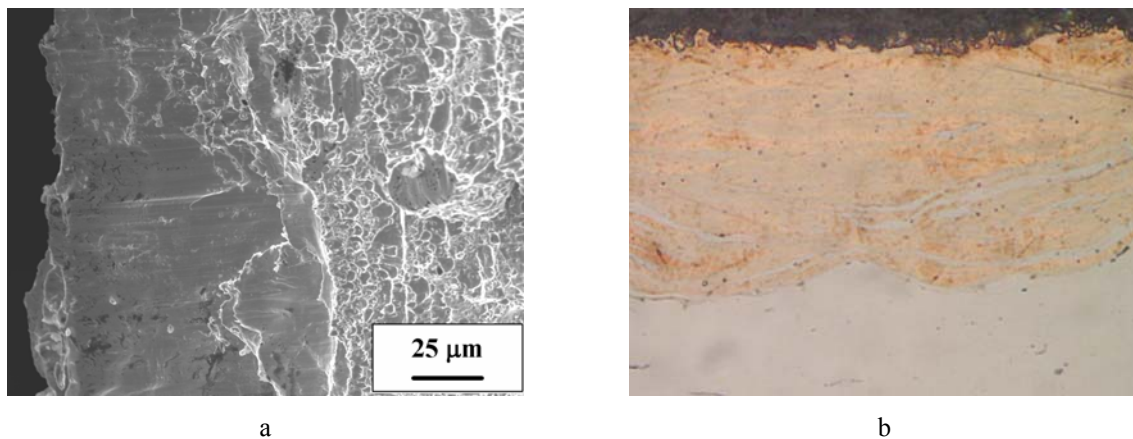
The present paper is about two methods of deposition of MMC coatings with nanodiamond reinforcements: friction cladding (FC) and electrochemical (galvanic).

#### 3.1 Deposition of composites coatings by friction cladding

A considerable number of coatings deposition methods have been developed. In our opinion, a promising approach is the friction method of applying MMC coatings by rotating wire brushes – the so called friction cladding [4]. Friction cladding is performed as follow. The coating material is a rod, ring or similar item. The main tool is a rotating cylindrical metal brush. The brush rotates with a high speed and is pressed to the processed surface. A rod (ring) of the coating material is pressed to the brush at a nearby point. By the ends of its wires, the brush scrapes metal particles fractions of a sub-micron in size off the rod and transfers them onto the treated surface. The high speed of rotation of the brush leads to a considerable strength of impact of a particle on the surface; the particle welds to the treated surface. A large number of wires in the brush and a high speed of rotation provide for a high performance and uniform transfer of the material of the rod onto the treated surface.

Elimination of oxide films and exposure of the pure surfaces at the combined plastic deformation of the surface layers and the coating-material particles provides for their strong adhesion to the substrate.

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. 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. 6).



**Figure 6.** Nanocomposite coating deposited by friction cladding; a – fracture (SEM); b – cross section (optical microscopy),  $\times 1000$

### 3.2 Deposition of composite coatings by the electrochemical method

One of the most complex problems, which impedes the wide use of nanocomposite electrodeposited coatings, is agglomeration of nanoparticles; it takes place both in the production of nanoparticles and application of the coating by the existing process schemes. If the size of a primary nanoparticle (depending on the material) is 4–50 nm, agglomerates can reach from several micrometers up to a millimeter in size. A detailed study of the disintegration process of a coating containing agglomerates of nanoparticles showed that it broke down in stress-concentration sites, i.e., defects that occurred in the breakdown of agglomerates under the action of cyclic loads. Thus, it is agglomeration of nanoparticles that is the main obstacle for a broad introduction of nanostructural electrodeposited coatings into practice. An electrochemical method of applying coatings was developed to eliminate these drawbacks. The method is applicable only for those electrochemical coatings which can be applied by transferring the material of the coating from one electrode to the other, such as one that is based on copper, nickel, gold, etc. The parts to be treated and shaped as plates were placed in a bath with an electrolyte; the components served as the cathode and plates from a copper+20% ND composite material served as the anode. During the passage of current through the bath with the electrolyte, the anode was dissolved and the composite material was transferred from the surface of the plates onto the surface of the treated part; that is, application of the coating was performed. There was practically no loss of reinforcing nanoparticles. During the transfer from the anode to the cathode, reinforcing nanoparticles were protected by the electrolyte from their interaction with one another and from agglomeration. A 5–7- $\mu\text{m}$ -thick coating was obtained. The study of the coating by a scanning electron microscope showed it to contain ND particles uniformly distributed in the matrix.

#### 4 Conclusions

The investigation has shown that nanodiamonds could be efficient reinforcing particles, increasing the mechanical characteristics of metal matrix composites. Developed MMC can be used as bulk materials and as coatings. Two methods of application of composite materials with nonagglomerated reinforcing nanodiamond particles has been developed: electrochemical way and friction cladding. The absence of agglomerates increases the quality of the coating and reduces the risk of its breakdown. The developed materials can be used in biofouling protection systems of marine facilities, as electronic packaging, and as wear-resistant coatings, for instance, on friction electrical contacts.

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