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New mechanical-alloying-based technological scheme for producing electrochemical composite coatings reinforced with non-agglomerated nanodiamond particles

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ABSTRACT

This study investigates the scheme "mechanical alloying for obtaining a uniform distribution of non-agglomerated nanodiamonds inside a copper matrix + compaction of mechanically alloyed granules into a bulk material in the shape of an anode + electroplating the composite coating by transferring the composite material from the dissolved anode to the cathode, which is the material to be treated". It is shown that mechanical alloying can be an effective method for producing metal matrix composites with non-agglomerated reinforcing nanodiamond particles. The production of electrochemical coatings from particulate copper matrix composites with non-agglomerated nanodiamond reinforcements is developed. The absence of nanodiamond agglomerates increases the quality of the coating and reduces the risk of its breakdown.

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1. Introduction

Coatings are very important modern materials. Many new effective methods of coating deposition have been developed, such as CVD and PVD processes, spraying, and different chemical and electrochemical methods, but electroplating remains very popular. The coating properties can be improved by the use of composite materials for coating application [1], and nanodiamonds are particularly promising reinforcements for composite coatings [2]. Individual nanodiamond particles are generally 5–6 nm in size, but they form agglomerates that are hundreds of micrometres in size. Existing techniques use nanodiamond powders in an agglomerated form as an electrolytic component [3]. As a result, coatings include nanodiamond agglomerates, which have many advantages for deformation-free conditions, including improved strength, wear resistance, hardness, and good adhesion to the substrate. However, under complicated loading conditions with coating deformation, the agglomerates can be destroyed, which can stimulate coating destruction. Therefore, the development of nanodiamond deagglomeration methods is very important. Mechanical alloying [4] is very effective for this purpose. Thus, this study investigates the

scheme "mechanical alloying for obtaining a uniform distribution of non-agglomerated nanodiamonds inside a copper matrix + compaction of mechanically alloyed granules into a bulk material in the shape of an anode + electroplating the composite coating by transferring the composite material from the dissolved anode to the cathode, which is the material to be treated".

2. Materials and methods

Technical-grade copper M1 (copper is more than 99.9%) was chosen as a matrix material. The matrix material was used as chips, which were pretreated in a planetary mill, after which the size of the particles was 0.5–2 mm. Nanodiamond (ND) powders were mainly used as reinforcing particles. Before the investigation, the nanodiamonds were checked and shown to be in compliance with the Russian Technical Specifications. Detonation-synthesised nanodiamond powders (also called ultradisperse diamonds) had a complex multilevel structure [5]. Primary ND particles were mainly of a close-to-spherical shape; however, particles of irregular shape were also observed. The size of the major part of the detonation synthesised nanodiamond particles (approximately 90%) was 4–6 nm, but particles of approximately 2 nm and 10–20 nm also occurred. Primary nanodiamond particles were combined into strong primary agglomerates of 40–400 nm in size, which in turn were combined into secondary and tertiary agglomerates. Their size could reach hundreds of micrometres.

Mechanical alloying has been carried out in Retsch PM400 planetary mill in an argon atmosphere, without use of surfactants, in sealed steel grinding jar containers of 500 ml nominal volume. The powdered material was treated using 12 mm-diameter chromium steel milling balls. The effects of the mechanical alloying regimes on the process and properties of the materials have been examined extensively [6], and

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the following regimes were chosen. 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. To prevent strong overheating, the mill was stopped for 5 min after every 10 min of operation. The real time, without accounting for stops, was considered to be the treatment time, which varied from 1 h to 10 h.

The granules produced by mechanical alloying were compacted into a bulk material as an anode-rod (10 mm × 10 mm × 80 mm) by pressing at 400–600 °C for up to 30 min using hydraulic presses of up to 100 T of force.

The electrochemical coating was applied in a bath with an electrolyte containing 80 g/l CuSO₄·5H₂O and 100 g/l H₂SO₄ at a cathode current density of 10 mA/cm² = 1 A/dm². The duration of the electroplating process was varied from 0.5 h to 3 h, and the thickness of the produced coatings was varied from 10 to 50 µm.

The structures and properties of the developed materials were studied by optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry (XRD) and microhardness measurements. Optical microscopy was performed using an Axiovert 200M MAT microscope (Carl Zeiss, Germany). SEM investigations were conducted using a JEOL JSM 6700 scanning electron microscope, and TEM investigations were carried out with a FEI TITAN 80-300 transmission electron microscope equipped with a GEOS-type aberration corrector for the objective lens. A Wolpert Wilson 402 MVD micro Vickers hardness tester was used for the measurement of the micro-hardness of the developed coating using a test load of 10 gf and a load duration (dwell time) of 10 s. The XRD analysis was carried out on a Bruker D8 ADVANCE diffractometer in monochromated Cu K α -radiation (with a diffracted-beam monochromator) using the EVA phase analysis software package and PDF-2-2006 database of interplanar distances of crystalline phases.

3. Experiment and discussion

A composite material of a copper matrix and 20 vol.% nanodiamonds was developed. During mechanical alloying, the application of nanodiamond powders for metal matrix reinforcement has specific features. During the treatment of a mixture of matrix particles and ND powders in a planetary mill, large ND agglomerates were broken down over a short period of time into very fine agglomerates of several primary spherical ND particles. Due to their high hardness, agglomerates of up to 20–100 nm in size were embedded into the surface layers of the copper particles. The obtained “mix” was exfoliated from large particles of copper, where the particles of the mix could combine into granules containing nanodiamonds and pure copper particles. Thus, the structure of the granules was initially characterised by a significant inhomogeneity, and the surface of many of the granules was observed to have an increased concentration of primary ND agglomerates. The compaction of such granules into a bulk material failed to produce high strength and hardness. However, increased treatment times resulted in a total breakdown of agglomerates into primary nanoparticles. Due to the alternating comminution and fusion of granules, the nanodiamond particles were evenly distributed in the metal matrix; increased concentrations of ND particles were not observed on the granule surfaces, as they had been earlier. Fig. 1

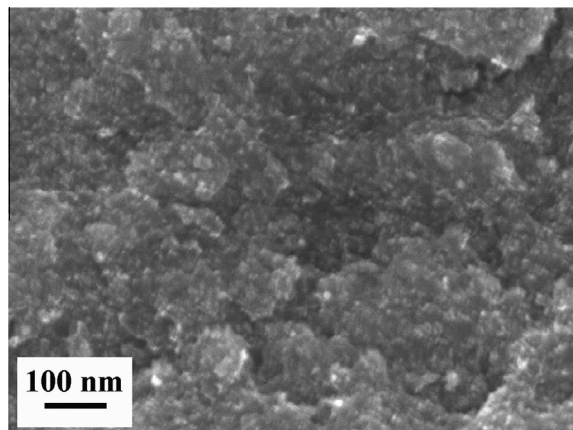


Fig. 1. View of the nanodiamond distribution on the surface of the Cu + 20 vol.%ND composite granules treated in a planetary mill for 8 h.

shows the surface of the composite granules with non-agglomerated uniform distributed nanodiamonds inside a metal matrix after 5 h treatment in a planetary mill. The compaction of these granules produced high-quality bulk composite materials.

The materials developed were used for coating deposition by electroplating. One of the most complex problems impeding the wide use of nanocomposite electrodeposited coatings is the agglomeration of nanoparticles, which occurs in both the production of nanoparticles and the application of the coating by the existing process schemes [3]. If the size of a primary nanoparticle (depending on the material) is 4–50 nm, agglomerates can range from several micrometres up to a millimetre in size. A detailed study of the disintegration process of a coating containing nanoparticle agglomerates showed that they broke down at stress-concentration sites, i.e., defects occurred in the breakdown of agglomerates under the action of cyclic loads. Thus, the agglomeration of nanoparticles is the main obstacle for the broad introduction of electrodeposited nanocomposite coatings in practice.

An electrochemical method of applying coatings was developed to eliminate these drawbacks. The method is only applicable for those electrochemical coatings that can be applied by transferring the material of the coating from one electrode to the other, such as copper-, nickel-, and gold-based materials. This work used a composite material with a copper matrix. The components to be treated and shaped as plates (other shapes are possible) were placed in a bath with an electrolyte; the components served as the cathode, and plates of the copper + 20 vol.%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 (the anode) onto the surface of the treated components (cathode), that is, the coating was applied. The reinforcing particles can move from the anode to the cathode as a consequence of the adsorption of matrix metal cations onto their surface [7]. There was practically no loss of reinforcing nanoparticles. During the transfer from the anode to the cathode, reinforcing nanoparticles were protected from interacting with one another, i.e., agglomerating, by the electrolyte. Several types of coatings with thicknesses from 10 to 50 µm were obtained. The study of the developed coatings by optical and scanning electron microscopy (Fig. 2) showed that the adhesion between the coating and substrate was very good (Fig. 2a), lacking defects (Fig. 2b) and containing uniformly distributed ND particles (Fig. 2c). Non-agglomerated nanodiamonds have very good adhesion to copper matrix. Destruction of the coating proceeds through the matrix metal and fracture of the coating very often consists nanodiamonds covered by copper (Fig. 2c). Measured at 10 points on a polished cross section, the microhardness of the developed 50-µm-thick “copper + 20%ND” composite coating is 1050 ± 50 MPa (the microhardness of pure electrolytic copper is 760 MPa). For study of wear resistance by described above method, rollers with developed “copper + nanodiamonds” coating and brass coating applied by friction cladding were used. Thickness of coatings was 50 µm. Results is presented in Table 1. It is possible to see that developed coating has better wear resistance properties in comparison with strong brass coating.

Electron microscopy was utilised because this method can reveal small voids on the boundary of the nanodiamond–copper matrix. Fig. 3 presents a scheme of the location of ND particles in the TEM specimen (a) and examples of aberration-corrected high-resolution TEM images of the developed composite showing the crystal lattices (b). Fig. 3a presents the difficulties in the structure investigation, which stem from the fact that the electron beam can pass through several nanoparticles. In Fig. 3b, the ND particles randomly oriented near the Bragg condition show clearly visible lattice reflections. The lattice fringes originating from the copper crystalline matrix are not visible because of the narrow depth of

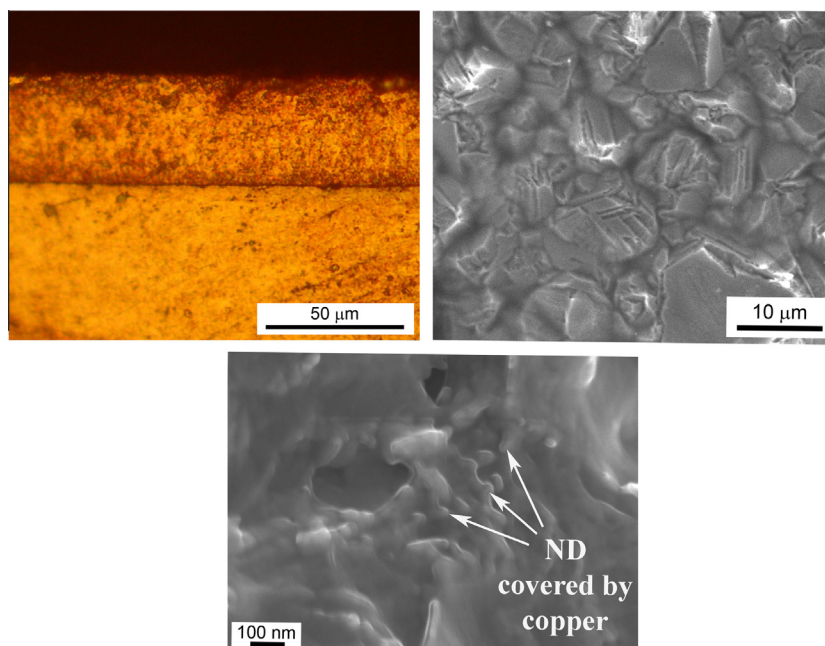


Fig. 2. Composite coating produced by an electrochemical method: (a) cross section after etching (optical microscopy image), (b) planar view of coating surface (SEM) and (c) cross section of coating on which nanodiamonds are distributed (SEM with high magnification).

Table 1
Wear resistance of coatings.

Time (min)	Coating “copper + nanodiamonds”		Coating from brass applied by friction cladding	
	Wear under loading 500 N (g)	Wear under loading 1500 N (g)	Wear under loading 500 N (g)	Wear under loading 1500 N (g)
10	0	0	0	0
20	0	0.01	0	0.01
30	0	0.01	0	0.02
60	0.01	0.02	0.01	0.04
120	0.02	0.03	0.03	0.06
180	0.03	0.06	0.04	0.09
240	0.03	0.08	0.04	0.13

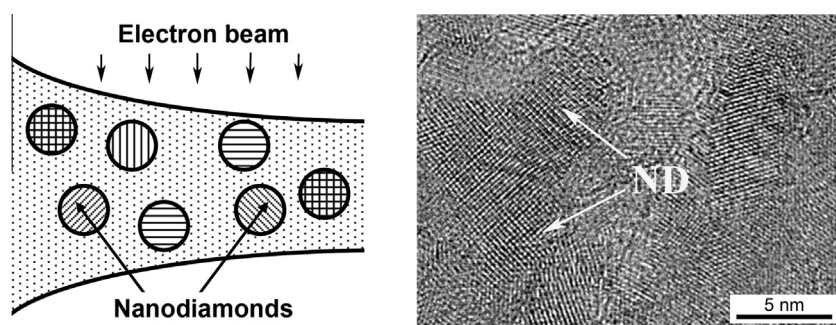


Fig. 3. Scheme of the location (a) and TEM image (b) of the nanodiamonds inside the copper matrix.

focus of aberration-corrected TEM. Moreover, the copper matrix was tilted slightly off-axes to suppress Cu lattice reflections. Importantly, no voids were revealed at different sample thicknesses (Fig. 3b), which indicates that the strength of the material should be high.

The size of the areas of the X-ray radiation coherent scattering is an important characteristic of a crystal material. In a copper matrix of “Cu + ND” composite coating it was defined by the XRD method for broadening of diffraction reflection (111) [8]. As the composite coating was on the copper substrate, there was used a

shooting in the “grazing beam”, changing angle θ from 3° to 0.5° in order to receive reflections from the coating material only. For every oblique angle there was received diffractogram in “Detector Scan” mode within the angle range of $2 = 41^\circ\text{--}45^\circ$. The results are shown in Fig. 4. Absence of diffractogram changes with the change of oblique angle means that the reflection is received only from the coating. The diffractogram 3 completely coincides with diffractogram 4. They were used as a basis for calculating the average size of the areas of coherent scattering of X-ray radiation by material of the composite coating matrix – copper. It was 20 nm.

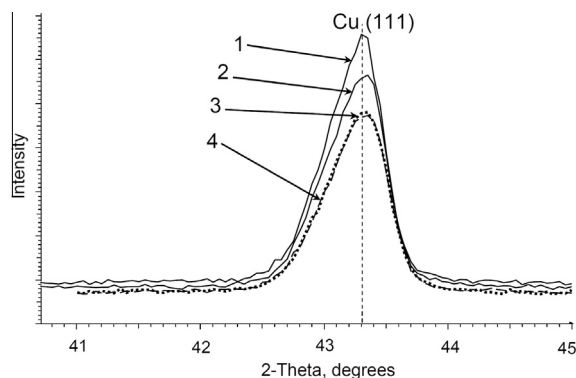


Fig. 4. Diffractograms received from the “Cu + ND” composite coating applied onto the copper substrate at various oblique angles of the X-ray beam: 1 – oblique angle of 3°; 2 – 2°; 3 – 1°; 4 – 0.5°.

4. Conclusions

It is shown that mechanical alloying can be an effective method for producing metal matrix composites with non-agglomerated reinforcing nanodiamond particles. The production of electrochemical coatings from particulate copper matrix composites with non-agglomerated nanodiamond reinforcements is developed. The

absence of nanodiamond agglomerates increases the quality of the coating and reduces the risk of its breakdown. It is shown that nanodiamonds can be efficient reinforcing particles for composite coatings.

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