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BRIEF
COMMUNICATIONS

Nanodiamonds Effect on Characteristics of Copper Galvanic Coatings

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Abstract—The introduction of nanodiamonds (Technical Specification TU 3974-001-10172699–94) into a sulfuric acid electrolyte of copper plating was shown to result in decreased porosity and the corresponding diminishing of the electric resistance of the copper coatings.

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Galvanic copper coatings are utilized in various fields: for local protection at selective carburization of steel parts, as substrate at applying protective, decorative, and functional coatings, in electrotyping, in the production of circuit plates as conducting layer etc. The introduction into the electrolytes of copper plating of highly dispersed additives, in particular, nanodiamonds of detonation synthesis (ND), affects the characteristics of the coatings. The unique State Standard for ND does not exist, different manufacturers produce ND according to the approved Technical Specification of the given enterprise. It was shown in [1] that the use of ND (TU 84-1124–87) in pyrophosphate electrolytes led to the formation of more fine-grain structure of coatings, their microhardness and corrosion resistance increased. In keeping with [2] the manufacturing of the coatings with ND (TU2-037-677–94) additives mostly the large crystalline structures were obtained with the size of some crystals up to 80 μm, the main amount of ND is found as conglomerations located between the crystals. The date from [3, 4] on sulfuric acid electrolytes and ND of the grade UDA-STV (TU05121441-275–95) showed that the characteristics of the diamond-containing copper coatings depended on the current density and on the concentration of the nanodiamonds in the electrolyte. For instance, at the current density of 0.7 and 1.2 A dm^{-2} and the Na content of 0.1–1 g l^{-1} the value of the specific resistance of the coatings increased from 21.9 to 24.2 mΩ mm^2 m^{-1}, respectively, by 5–10%, at the *N* concentration over 1g l^{-1} this increase reached 25–31%. At the current density 0.7 A dm^{-2} with the growing concentration of ND in the electrolyte the microhardness of the coatings increased, at 1.2 A dm^{-2} depending on the ND content both the increase and decrease in the microhardeness were observed. The introduction into the electrolyte of various ND concentrations can result in the increased as well as the decreased elasticity of the copper coatings. The main common advantage of the obtained diamond-containing copper coatings is their high wear resistance [3, 4].

At the utilization of the copper coatings in the manufacturing of the circuit plates as a conductive layer to the most important characteristics of the coatings belong the specific electric conductivity and the elasticity of the coating, the latter factor is important in the manufacturing, assembly, and exploitation. The sulfuric acid electrolytes of copper plating with special additives are characterized by a high scattering ability ensuring the uniform distribution of the deposit metal on the surface and the holes of the plates [5]. The usual technology applies the additives containing surfactants, operating current densities from 1 to 6 A dm^{-2}. The introduction of ND into the sulfuric acid electrolyte of copper plating also results in a significant growth of the scattering ability of the electrolyte [3, 4].

It is known that the characteristics of the galvanic coatings obtained with the use of nanodiamonds depend to a large extent on the surface composition and the size characteristics of the ND originating from the conditions of the detonation synthesis and the separation from the detonation products of the explosives or from the subsequent treatment of ND.

We formerly obtained and investigated the coatings with chromic [6] and nickel [7] matrices containing nanodiamonds corresponding to TU3974-001-10172699–94. These ND were obtained at the detonation of the alloy trinitrotoluene: RDX in the ratio 2 : 3 in the CO_2 atmosphere, and were purified from the nondiamond carbon by its thermal oxidation by the air oxygen in the presence of boric oxide along with the procedure in [8]. The composite coatings with a copper matrix containing ND corresponding to the given Technical Specification we have not studied before.

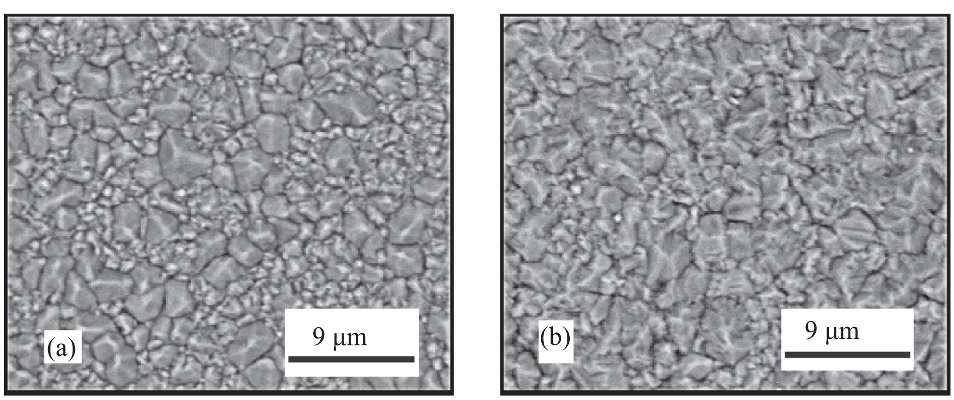
The aim of this study was the investigation of the effect of the introduction into the electrolyte of copper plating of nanodiamantes corresponding to TU3974-001-10172699–94 on the characteristics of the galvanic coatings.

EXPERIMENTAL

As the electrolyte of copper plating was used sulfuric acid electrolyte containing 220 g l^{-1} of copper sulfate and 60 g l^{-1} of sulfuric acid. This components ratio corresponds to the multi-purpose sulfate baths [9], in the copper coating of circuit plates with metallized holes a lower content of copper and a higher concentration of sulfuric acid are commonly used, but at the use of special additives these components ratios are also applicable in the technique of manufacturing the circuit plates [5].

The electrolysis was carried out at 293 K, current density 3.1–3.3A dm^{-2}. The coating deposition time was 15−29 min, its thickness 12–20 μm. For the preparation of diamond-containing coatings the water dispersions of ND were prepared by ultrasound dispersion of weighed samples of the powder in the distilled water (device UZDN-A, frequency 22kHz). The conductivity of the used nanodiamond powders was of the impurity origin, the energy barrier value was about 0.53 eV [10]. In the hydrosol the charge on the surface of ND particles was formed mainly as a result of the dissociation of the surface carboxy groups, therefore in the acidic electrolyte of copper plating the electrophoretic mobility of the ND particles virtually equals to zero. The number average size of ND particles in the hydrosol was 13 nm (size analyzed CPS 24000), the used ND concentration in the electrolyte was 13 g l^{-1}, same as in [7].

The microhardness estimation of the coatings was carried out according to State Standard GOST 9450–76 (microdurometer PMT-3), the porosity was measured in accordance with GOST 9.302–88. Microphotographs of the coatings were obtained on a focused beam electron microscope Hitachi TM-1000. For measuring electric resistance and ductility the coatings were applied to a stainless steel substrate with low roughness and easy peeling of coatings, the current values were 0.1 and 0.05 A, the voltage values were measured by a multimeter. Tensile test was conducted by coating on a single



Micrographs of coatings at 2000 magnification: (a) copper coating, (b) copper coated with ND.

cantilever bending device DMA 242 C (Netzsch). ND content of the coatings were determined gravimetrically after the election etching copper samples in nitric acid with monitoring dissolving of coatings produced without addition of ND to the electrolyte of copper plating. We used chemically pure reagents, the data are the average results of 3–6 replicates.

The content of ND in the composite coatings was 0.1 wt % in average. A large effect of ND introduction into electrolyte on the microstructure of the coatings was not observed (see figure), an average effective radius of the grains of copper coatings was 1.35 μm and the copper coatings containing ND was several higher, 1.45 μm. The porosity of the copper coating did not exceed 0.5 of pore per 1 cm^2 of surface area, for diamond-containing coatings the porosity was not higher than 0.25 of pore per cm^2. The microhardness of the samples differs only in the limits of experimental error, for copper coatings average microhardness was 640 MPa, which was in the range of values specified in GOST 9.303-84.

Data on the specific resistivity of four samples of the copper coating and coating with ND at a current of 0.1 A as well as mean values of conductivity for all measurements are given in the table.

According to GOST 9.303-84 the resistivity of copper coatings at 18°C is 1.68×10^{-8} Ω m. In view of the proximity of the microstructure and grain size characteristics of the diamond-containing coatings a decrease in the resistance of the coatings can be attributed to a decrease of the porosity, it is clear that at low levels of ND in the coating a porosity reduction prevails over the characteristic influence of impurities on the conductivity of metals.

When tested in tensile at maximum load (8 N) under conditions of the experiment no discontinuity of the coatings was observed, therewith the reached elongation of the copper coatings was 7.0% in average, that of the coating with ND, 6.6%. According to [11, 12] ductility of the copper deposition in the holes of modern printed circuit boards must be not less than 6%, i.e., the coatings meet these requirements.

Specific electrical resistance of the coatings

Coating type	ρ, 10^{-9} Ω m				$\langle\rho\rangle \pm \Delta\rho$, 10^{-9} Ω m
	1	2	3	4	
Copper	17.40	16.38	16.33	16.29	16.63 ± 0.32
Copper with ND	14.83	15.22	15.26	15.22	15.09 ± 0.52

CONCLUSIONS

The main effect of the addition of nanodiamond of the detonation synthesis in sulphate electrolyte of copper plating is to reduce the porosity of the coating. Thus, for the copper coatings containing 0.1 wt% nanodiamonds a decrease in electrical resistance occurs.

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