EFFECT OF SURFACANTS ON THE ELECTRODEPOSITION OF DIAMOND-BEARING COMPOSITE COATINGS

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In studies of the effect of surfactants on the growth of an electrodeposited metal around fine particles, special attention is usually paid to the charge and size of the particles and the degree of polarization of the cathode. Most authors are of the opinion that an increase in the overvoltage on the cathode is accompanied by an increase in the concentration of the second phase in the coating [1-3]. At the same time, there has not been enough study of the effect of the physicomechanical properties of the binder on the concentration of fine particles in composite electrochemical coatings (CECs), despite the importance of this index for predicting the wear-resistance and cutting characteristics of the coatings [4].

It was established earlier [5, 6] that electrically nonconducting particles of diamond powder are deposited firmly on the cathode from surfactant-free electrolytes by iron, cobalt, and nickel precipitated with a high level of polarization. The particles have a fine crystalline structure and high HV microhardness — 5060, 3510, and 2500 MPa, respectively. The surface concentration of diamond powder in the coatings reaches 50-55%. Copper obtained from a sulfate electrolyte without a surfactant is precipitated with low-level polarization and has a microhardness of just 1100 MPa. In this case, the particles are poorly secured to the surface of the horizontal cathode. At the same time, a tool with a soft copper coating that contains diamond particles can be used for the finish machining of hard materials.

In this study, we examine the relationship between the physicomechanical properties of the binder and the concentration of synthetic diamond powder in copper coatings obtained from electrolytes with and without additions of a surfactant.

We studied a surfactant-free sulfate copper-plating electrolyte of the following composition, g/liter: 200CuSO₄·5H₂O, 70H₂SO₄, (electrolyte 1); sulfate electrolytes with additions (of up to 50 mg/liter) of the ionic and nonionic surfactants most commonly used in copper-plating: sulfanol (electrolyte 2), thiocarbamide (electrolyte 3), avirol (electrolyte 4), sintamid-5 (electrolyte 5), gelatin (electrolyte 6), VIS-15 (electrolyte 7), and a pyrophosphate surfactant-free copper-plating electrolyte having the composition (g/liter) 40CuSO₄·5H₂O, 150Na₃P₂O₇·10H₂O, 90Na₃HPO₄·12H₂O (electrolyte 8). Process temperature was 298 K. We also studied the effect of the concentration of thiocarbamide and sulfanol on the content of diamond powder in the coating.

To perform the investigation, we used diamond powder from which electrically conducting impurities had previously been removed. The particles of the powder were 50 or 20-μm in size. The concentration of powder in the electrolyte was 5 g/liter. After mixing with a magnetic mixer, the powder was deposited on a horizontal 25-mm² cathode of bronze BrOF.6.5-0.15. The powders with 50-μm particles were covered with copper at a current density of 1 A/dm² over 60 min, while the powders with 20-μm particles were covered with copper at the same current density over 25 min. As a result, the size of the particles increased by an amount equal to approximately half their grain size.

The structure of the deposit and the surface concentration of powder were studied with an ORIM-1 microscope (on the basis of the amount of surface occupied by the powder in the field of view of the microscope). We used a PMT-3 hardness tester to measure the microhardness of a coating applied previously over 60 min at 1 A/dm² on bronze specimens.

Cathodic polarization curves were recorded on a P-5848 potentiostat. The polarization of the cathode Δφ was determined as the difference between the initial potential and the potential at the deposition current density of 1 A/dm² (it is at this density that quality copper coatings can be obtained from sulfate electrolytes). It can be seen from Fig. 1 (curve 1) that the polarization of the cathode is negligible in the sulfate electrolyte without a surfactant (electrolyte 1) and in the presence of such additions as sulfanol, thiocarbamide, and avirol (electrolytes 2, 3, 4); polarization is higher in the presence of sintamid-5, gelatin, and VIS-15 (electrolytes 5, 6, 7). The pyrophosphate electrolyte 8 had the highest polarization among the electro-
Fig. 1. Effect of the electrolyte on the microhardness of a copper coating (1), the polarizability of the cathode (2), and the concentration of diamond powder in the coating (3).

Fig. 2. Effect of the concentration of surfactant in electrolytes 3 (1) and 2 (2) on the concentration of diamond powder in the coating.

lytes that were examined. In accordance with [1, 2], we can expect that the concentration of diamond powder in the coating will increase in the same sequence. However, the character of the change in the concentration of diamond powder in relation to electrolyte composition (curve 2) corresponds roughly to the change in the microhardness of the coating (curve 3). The concentration of diamond powder reaches 30% in the presence of VIS-15, and it amounts to more than 50% in electrolytes with thiocarbamide and avirol and in the pyrophosphate electrolyte. Coatings from solutions with sulfanol, sintamid, and gelatin and sulfate solutions without a surfactant have a lower microhardness and contain a small number of inclusions (1-5%). It was noted in [7] that thiocarbamide and gelatin have a similar effect on the hardness of electrolytic deposits.

The microhardness of electrolytic deposits increases with a decrease in the grain size of the growing metal, which is related to an increase in the number of lattice defects [8]. It is known from [9] that the grain size of copper is reduced roughly sixfold by the addition of thiocarbamide to a sulfate electrolyte in the amount 20 mg/liter. This conclusion is consistent with our data: deposits obtained in the presence of thiocarbamide, avirol, and VIS-15 and from the pyrophosphate electrolyte have a higher microhardness and a more fine-grained structure. This structure prevents the diamond particles from being dislodged by the growing deposit and allows them to become fixed in the coating. Thus, the concentration of diamond powder is higher in the above-mentioned coatings than in coatings obtained in the presence of sulfanol, gelatin, and sintamid-5 and coatings obtained from the electrolyte without surfactant. The coatings with a lower concentration diamond have a lower microhardness and a coarser structure.

It was established [10] that surfactants can alter the total overvoltage for diffusion, phase transformation, and crystallization. As a rule, the crystallization overvoltage is negligible compared to the total overvoltage. It may be that even the crystallization overvoltage affects the fine structure and physomechanical properties of the coatings, and this facilitates or prevents the capture of fine particles by the growing deposit and their subsequent growth. The total overvoltage on the cathode may not unambiguously determine the concentration of the second phase in the coating. The exact mechanism by which the additions studied in this investigation act was not examined.

It is known that a decrease in the size of the diamond particles might be accompanied by a decrease in their concentration in the coating due to disjoining pressure or a deterioration in the freedom of movement of the electrolyte through the dense layer of fine particles on the horizontal cathode [5]. In fact, the content of diamond powder with 20-μm particles decreased by roughly 9% in the coating obtained from electrolyte 3 (curve 1 in Fig. 2) relative to the powder with 50 μm particles for the same thiocarbamide concentration — 50 mg/liter (curve 2 in Fig. 1, electrolyte 3). An increase in the concentration of thiocarbamide to 150 mg/liter did not increase the amount of diamond powder in the coatings (curve 1 in Fig. 2), but it did have an adverse effect on their quality: the coatings became spotty and exhibited poor adhesion. The grains of diamond were captured by the growing deposit only at the borders of the lustrous fine-grained and dull sections. An increase in the concentration of sulfanol in the electrolyte to 150 mg/liter did not change the content of 20-μm diamond powder in the coating — it remained below 1% (curve 2 in Fig. 2).