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THE USE OF PHOTOCHEMICAL PROCESSES FOR THE PRODUCTION OF CARBORUNDUM-CONTAINING COMPOSITE COATINGS

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ABSTRACT

To obtain carborundum-containing composite coatings on the copper surface by photochemical processes, it is proposed to use sorption layers obtained by wetting in appropriate solutions. Chemical and photochemical processes occurring in the sorption layer under the influence of electromagnetic waves of sunlight are considered. It is shown that as a result of such an impact, copper particles are formed that ensure the connection of carborundum particles with each other and with the copper base. It was found that when the soluble products of these processes are washed with water, strong agglomerate consisting of carborundum and copper particles remains on the surface of the sample. This agglomerate is the basis of the second phase of the composite coating. The processes of creating a matrix layer by chemical or galvanic nickel plating are considered. When studying the process of obtaining carborundum containing composite coatings on the surface of copper using an electron microscope, it was shown that the content of silicon carbide on the surface of copper can reach 10 wt. %. At the same time, the hardness of copper can be increased by 40 - 41 % by using photochemical processes.

Keywords: *copper, carborundum, binary semiconductor, photochemical processes, composite coating.*

INTRODUCTION

Increasing the surface hardness of the metal in order to ensure the necessary service life of individual parts and assemblies has not lost its relevance at the present time. One of the methods to solve this problem is to create a technology for applying composite coatings that contain substances of increased hardness. Technologies based on physical and chemical processes have been developed for their application.

The main physical method of obtaining such coatings is thermal spraying. The peculiarity of these processes is that the compounds used can be both a matrix and reinforcing filler in the form of continuous or discrete fibers, whiskers, plates (composites of the composition C/C, C/SiC, SiC/SiC) [1 - 4]. These processes require complex high-temperature apparatuses and are used mainly in aviation and space technology.

Of the chemical methods, coatings have become the most widespread, in which these characteristics are mainly determined by the dispersed phase, and the metal only binds the dispersed particles to each other and the surface of the product.

In this case, metal (the first phase or matrix) and powder particles (the second phase) are deposited on the surface of the coated product, which are cemented with a matrix.

Composite electroplating (electrochemical) coatings are obtained from suspensions, which are electrolytes with the addition of a certain amount of highly dispersed powder. When an electric current is applied on the surface of the coated product, metal (the first phase or matrix) and powder particles (the second phase) are deposited, which are cemented by the matrix. Similar processes occur during the chemical reduction of the matrix metal. But in this case, the metal is restored due to the influence of chemical reducing agents included in the electrolytes - suspensions.

Most often, nickel is used as a matrix in composite coatings. This is due to its physico-mechanical and anticorrosive properties, as well as the fact that the processes of galvanic and chemical nickel plating are well developed and widely used in engineering.

Refractory borides, carbides, nitrides and silicides, graphite and carbonaceous materials, abrasive powders are used as substances of the second phase.

Based on chemical methods, technologies have been developed for the production of composite coatings containing diamond powders [5, 6], carborundum [6, 7], boron and some of its compounds [8, 9], aluminum oxides, titanium, cobalt [10 - 12], graphene [13] as the second phase.

When using chemical nickel as a matrix, it is also necessary to take into account the positive effect of nickel phosphides formed along with nickel in the matrix, which belong to materials with increased hardness.

In addition, the introduction of certain substances of the second phase into such matrices can contribute to the production of materials with new physico-chemical properties. Thus, TiO_2/Ni-P composite coatings proved to be effective in water electrolysis [14].

The disadvantages of the chemical method of obtaining composite coatings include the following points: the need for intensive mixing and filtration of the electrolyte, which complicates the design of the devices used, the difficulty of obtaining coatings "rich" in the content of the second non-metallic phase.

A review of the technical literature shows that there is practically no data on the use of photochemical processes in technologies for the production of composite coatings. Meanwhile, the restoration of elements of the copper subgroup under the influence of the electromagnetic waves of sunlight is widely used in various fields of technology.

Therefore, in this work, chemical and photochemical processes were studied that allow to obtain composite coatings on copper by introducing carborundum, which is one of the hardest materials.

EXPERIMENTAL

Plates made of copper M0 were used as samples. Their preliminary preparation consisted in etching for several seconds in concentrated nitric acid, followed by rapid washing in water and drying. Degreasing of its surface was carried out with acetone.

The 63C carborundum used as the second phase was crushed in a porcelain mortar to a dust-like state. All chemical reagents used in the work were qualified as "chemical pure".

To create a sorption layer, a solution containing 50 g L^{-1} $CuCl_2$ and 10 wt. % carborundum and 1 g L^{-1} gelatin (suspension stabilizer) was prepared. Preliminary experiments have established that such a solution does not delaminate during photochemical studies. The copper plate was dipped into this solution immediately before photochemical studies.

Photochemical studies were carried out in a scientific laboratory. The density of the flux of sunlight penetrating through the window panes was determined by the SM 206-SOLAR solar radiation meter and was 800 - 1000 W/m^2.

Quantitative characteristics of photochemical processes were determined by changes in the intensity of the degree of blackness of the surface of the samples [15].

The structure and composition of films and coatings were studied using a scanning electron microscope JSM-6490-LV (JEOL, Japan). The device allows to obtain an electronic image of particles with a size of tens of nanometers, the elemental composition and the percentage of elements in the surface layers of the film.

Chemical nickel plating was carried out in a solution of the composition, g L^{-1}:

$NiSO_4 \cdot 7H_2O$ - 30, NaH_2PO_2 -10; CH_3COONa - 10; temperature - 90°C. Galvanic nickel plating was carried out in electrolyte, g L^{-1}: $NiSO_4 \times 7H_2O$ - 70, $NiCl_2 \cdot \times 6H_2O$ - 10, H_3BO_3 - 25, succinic acid - 1.5, pH 4.5 - 5.5, temperature 18 - 25°C, cathodic current density (A m^{-2}) - 200.

RESULTS AND DISCUSSION

When a sorption layer containing $CuCl_2$ is created on the copper surface, a layer of monovalent copper chloride is initially formed, which is a binary semiconductor,

$$CuCl_2 + Cu \rightarrow 2CuCl \qquad (1)$$

After the formation of the semiconductor layer, the electrons excited by the action of electromagnetic waves of sunlight (EWS) acquire the ability necessary for the recovery of monovalent copper:

$CuCl + e = Cu + Cl^-$, E= 0.137 V (2)

After that, vacancies remain in the semiconductor, for which only CuCl can be electron donors in this case.

$CuCl + Cl^- - e \rightarrow CuCl_2$, $E^o = 0.538$ V (3)

In this case, the total photochemical reaction will have the form:

$$2CuCl \xrightarrow{h\nu} Cu + CuCl_2 \qquad (4)$$

The study of the photochemical process occurring on the surface of a copper plate moistened with solutions of copper dichloride (Fig. 1) shows that not all the amount of $CuCl_2$ contained in the sorption layer participates in the formation of a black film of elemental copper according to the scheme of $CuCl_2 \rightarrow CuCl \rightarrow Cu$. Probably photochemical is limited by the time of complete drying of the sorption layer, which, regardless of the concentration of copper dichloride, is about 2 minutes. As can be seen from Fig. 1, the complete photochemical reduction of copper ions occurs at concentrations of copper bichloride 10 - 12 g L^{-1}, and the amount of copper in the reaction is insufficient to form a strong agglomerate with carborundum particles. Therefore, in the process of washing the sample, washing of carborundum particles with water is observed.

Therefore, if a higher content of copper particles is required to create a composite coating, substances with the necessary reducing properties must be introduced into the system. Such a reducing agent can be ascorbic acid. It is capable of chemically reducing copper bichloride to monochloride [16].

The redox potential of the ascorbic acid - dehydroascorbic acid system ($C_6H_8O_6$ -2e $\rightarrow C_6H_6O_6$ +$2H^+$) changes from -0.329 V to - 0.057 V with an increase in pH from 0 to 7 [16]. Therefore, it has a higher donor capacity than copper monochloride. Therefore, instead of reaction (4), the reaction will proceed:

$$2CuCl + C_6H_8O_6 \xrightarrow{h\nu} 2Cu + C_6H_6O_6 + 2\,HCl \qquad (5)$$

The photochemical nature of this reaction is confirmed by the fact that the formation of photochemical copper is not observed in the dark.

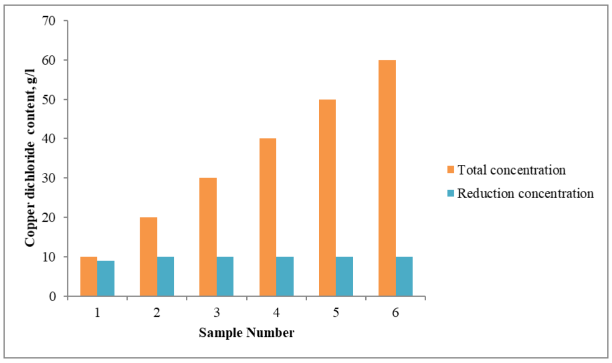

Fig.1. The degree of photochemical reduction of copper at different concentrations of copper dichloride in the sorption layer.

At the same time, if a layer of the second phase (in this case, carborundum) is previously created on the metal surface, photochemical copper particles fill the space between the individual particles of the second phase and the copper base. After washing the water-soluble products of chemical and photochemical processes, a relatively strong agglomerate consisting of carborundum and copper particles remains on the copper surface. This makes it possible to use conventional chemical or galvanic metallization plants to obtain composite coatings. The proposed technological scheme for obtaining composite films according to the above reactions is shown in Fig. 2.

To establish the formation of strong carborundum-containing agglomerates on the samples after the a, b, c, d operation according to Fig. 2, a layer of about 1 micron thick of chemical or galvanic nickel was applied. At the same time, the scanning electron microscope JSM-6490-LV allows to obtain the spectra and elemental composition of the surface layers of copper samples located under the nickel layer (Figs. 3, 4 and Tables 1 and 2).

Analysis of these SEM images shows that the Si content on the sample surface is about 8 %. This, in terms of SiC, is about 10 wt. %.

To measure the hardness, chemical and galvanic nickel with a thickness of 10 microns was deposited on the samples (Fig. 5), while the content of carborundum in the resulting coating is about 1 %. This is comparable to the data on the content of substances of the second phase in composite coatings obtained using conventional chemical or galvanic metallization.

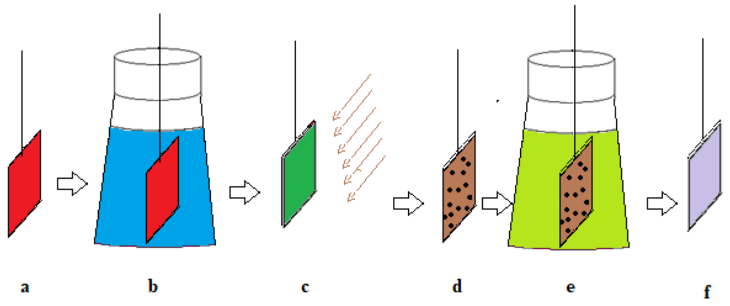

Fig. 2. Technological scheme of the process of obtaining carborundum containing films: a - initial copper plate; b - creation of a sorption layer containing $CuCl_2$, $C_6H_8O_6$, carborundum; c - exposure to sunlight; d- plate after washing; e - chemical nickel plating; f - finished plate).

Table 1. Elemental composition of a copper sample containing a layer of carborundum after chemical nickel plating.

Element	Weight (%)
C	16.88
O	6.70
Si	7.96
Fe	0.14
P	9.33
Cu	17.21
Ni	41.78
Total	100.00

Table 2. Elemental composition of a copper sample containing a layer of carborundum after galvanic nickel plating.

Element	Weight (%)
C	9.54
O	1.53
Si	7.85
Fe	0.29
Cu	5.92
Ni	74.87
Total	100.00

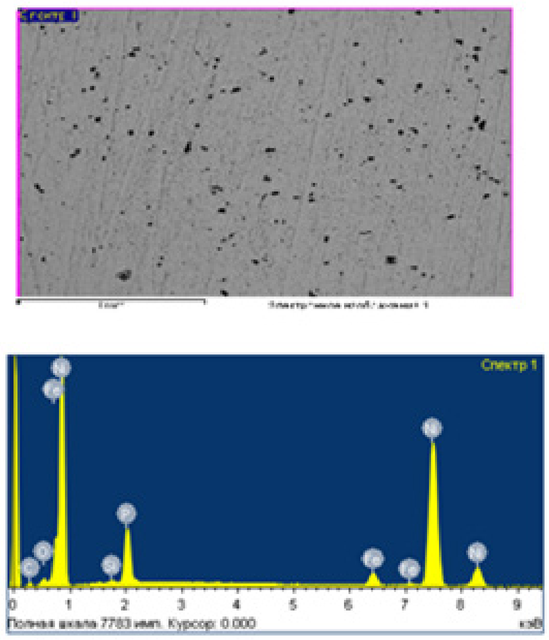

Fig. 3. SEM image and spectra of a copper sample containing a layer of carborundum after chemical nickel plating.

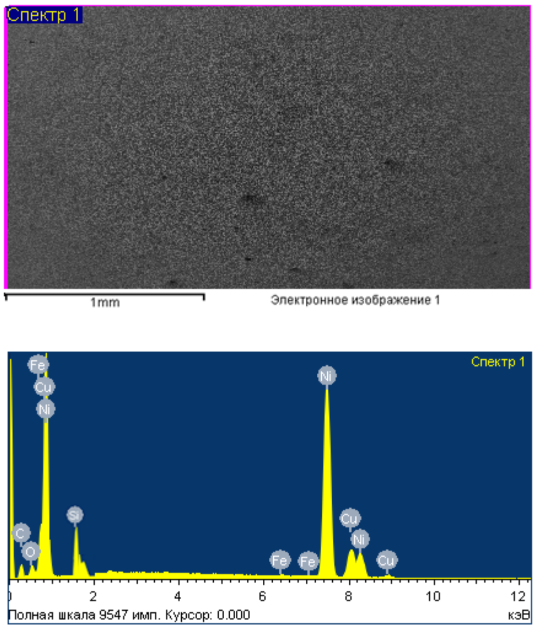

Fig. 4. SEM image and spectra of a copper sample containing a layer of carborundum after galvanic nickel plating.

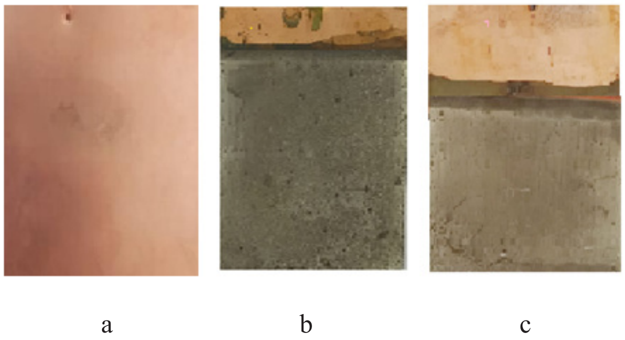

Fig. 5. Copper samples: a - initial, b - containing a coating of carborundum-copper-chemical nickel; c - containing a coating of carborundum-copper- galvanic nickel.

Table 3. Hardness of samples after application of a carborundum-containing composite coating.

Copper samples	HB value
Uncoated	767 ± 50
Containing a coating of carborundum -copper -chemical nickel	1110 ± 70
Containing a coating of carborundum -copper - galvanic nickel	1092 ± 70

The results of measuring the hardness of copper after applying a carborundum-containing composite coating are shown in Table 3.

The data obtained show that the application of a carborundum-containing composite coating increases the hardness of copper by 40 - 42 %. Moreover, the replacement of the matrix of "soft" galvanic nickel with a more "hard" matrix of chemical nickel practically has no effect on the overall hardness of the coating. Consequently, the presence of carborundum in the composite coating plays a decisive role in increasing the hardness of copper.

CONCLUSIONS

The application of a carborundum-containing composite coating was carried out in two stages. At the first stage, a thin layer of sorption film is obtained on the surface of the copper product, obtained by wetting the product with a suspension containing copper chloride and carborundum. In this sorption film, when exposed to electromagnetic waves of sunlight, chemical and photochemical processes occur leading to the formation of elemental copper. This fixes the carborundum particles on the surface of the product and allows further operations to apply a metal layer of the matrix in conventional stationary baths without changing the standard technology. At the same time, there is no change in the quality of carborundum-containing composite coatings. Such a separate technology makes it possible to regulate the content of carborundum in the composite coating with sufficient accuracy by changing the concentration of carborundum in the initial suspension. The technology can be used at small and medium-sized enterprises for the production of products of increased hardness.

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