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NANOSCALE AND NANOSTRUCTURED MATERIALS AND COATINGS

Features of Electroplating of Nanocrystalline Chromium Coatings from Electrolytes Based on Cr(III)

V. I. Bakanov, N. V. Nesterova*, and A. A. Yakupov
Tyumen State University, Tyumen, 625003 Russia
**e-mail: larina_nat@mail.ru*

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Abstract—It is shown that, for the development of new chrome-plating technologies, it is necessary to proceed from the complicated Cr(III) chemistry. The analysis of the complexation processes of Cr(III) with hydroxycarboxylic acids in aqueous solutions is given. The results of investigations of deposition processes of chromium coatings from sulfate, oxalate–sulfate, and formate–glycine electrolytes are presented. Thin chromium films, as well as chromium films alloyed with cobalt, are obtained from formate–glycine electrolyte. With the use of atomic-force microscopy, it is shown that the formed chromium films are bright and possess a nanocrystalline structure and codeposition of chromium and cobalt leads to the formation of a more uniform structure.

Keywords: electrolytes based on Cr(III) compounds, olated compounds, hydrolysis of Cr(III) salts, aqua complexes, mixed-ligand complexes, stability of complexes, nanocrystalline structure, coating-deposition rate, coating morphology, nanoparticles

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INTRODUCTION

In modern technology, chrome plating is one of the most popular galvanotechnical processes. This is due to the unique properties of chromium coatings: increased hardness, high reflection power, low friction coefficient, chemical durability, hydrophobic behavior, and heatproofness. These are the diverse and much valuable properties of chromium coatings that determined their applicability in various branches of industry, from space technology and aircraft building to medical instrumentation and household appliances. The fabrication of metal reflector mirrors that do not become dull in air is impossible without chromium coatings. Special functional properties are a feature of nanocrystalline coatings with a thickness of several micrometers.

At the same time, it is well known [1, 2] that conventional chrome-plating technologies are based on the use of rather concentrated and highly toxic Cr_2O_3 solutions, which have a carcinogenic and mutagenic effect.

To tackle the crucial issue of environmental protection, investigations of the development of efficient and low-toxicity processes based on Cr(III) compounds are underway [3–20].

The creation of nanostructured amorphous materials and coatings is a high-priority area of design of materials and technologies. To achieve this goal, composite electrochemical coatings [21] with metal-oxide nanoparticles, which make it possible to obtain coatings with a higher level of technological properties compared to the current conventional chrome-plating processes, have been proposed. Electroplating of composite chromium coatings has been carried out on the basis of the oxalate–sulfate electrolyte in the presence of 0.5 g/L of particles of aluminum oxide or silicon carbide [22]. Alternative technologies of cluster chrome plating are the core developments of the All-Russian Scientific Research Institute of Aviation Materials in research on cluster electroplating [23–25] starting in the late 1990s and still being developed actively today [26–28].

Deposition from trivalent chromium solutions allows obtaining coatings that are denser and cover the base metal better than does chrome plating based on Cr(VI), as well as providing higher current efficiencies. For the development of new chrome plating technologies, it is necessary to consider the complicated Cr(III) chemistry and mechanisms of electroreduction of Cr(III) complex compounds in detail.

THEORY

In the consideration of the Cr(III) electrochemistry, the hydration, hydrolysis, olation, polymerization, and oxolation processes, as well as penetration of anions into the coordination sphere, should be examined [29].

Chromium(III) salts in the form of chlorides, sulfates, and nitrates form violet $[Cr(H_2O)_6]^{3+}$ aqua ions in aqueous solutions. Depending on the pH value, there can be species with differing compositions in the solution: $[Cr(H_2O)_5OH]^{2+}$, $[Cr(H_2O)_4(OH)_2]^{+}$, or $[Cr(H_2O)_3(OH)_3]$. Due to Cr(III) aqua ion protolysis, the pH value of such solutions decreases:

$$[Cr(H_2O)_6]^{3+} + H_2O \leftrightarrow [Cr(H_2O)_5OH]^{2+} + H_3O^{+}.$$

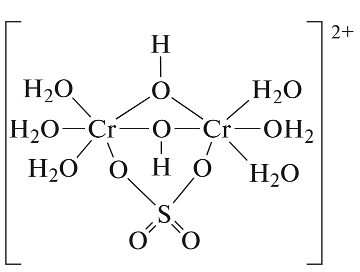
In chromium(III) chloride aqueous solutions, an equilibrium exists:

$$[Cr(H_2O)_6]^{3+} + 2Cl^{-} \leftrightarrow [Cr(H_2O)_4Cl_2]^{+} + 2H_2O.$$

With an increasing temperature and increasing concentration of halogenide ions, the equilibrium moves to the right and the solution turns green in color, whereas, with cooling and dilution of the solution, the equilibrium moves to the left (the solution becomes violet). One should note that the hydration energy (Gibbs energy change) of the Cr^{3+} ions is higher than 2000 kJ/mol. It is, therefore, natural that such species will not reduce to Cr^0 at the electrode.

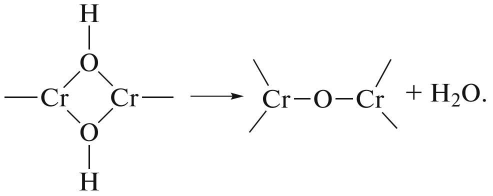
With an increasing pH value, the content of hydroxyl groups progressively rises, which leads to the deposition of the residue of aqua–hydroxy complexes. Taking into account that chromium deposition is accompanied by vigorous hydrogen evolution, it is not hard to suppose that such complexes form in the near-electrode layer.

However, in acid solutions (pH < 3), upon heating and long-term storage, polymerization with the formation of polynuclear complexes of the type $[Cr(OH)_2(H_2O)_8]^{4+}$, in which chromium atoms are connected to each other through bridging OH^- groups, takes place as well. In the case of chromium(III) salts, e.g., chromium sulfate, depending on temperature, pH value, and salt concentration, olated compounds of the type



or negatively charged species result, with the solution color changing from violet to green. To suppress the olation, one should cool the solution and decrease the Cr(III) concentration.

The hydrolysis of Cr(III) salts does not end with olation, but proceeds further, switching to the oxolation process; i.e., the bridging OH^- groups are changed to O^- groups:



The oxolation reaction is favored by the increased solution temperature and longer solution aging.

To hamper olation, one can add ligands forming complexes with Cr(III) to the solution. There are many familiar complex anions and complex cations of Cr(III) with such ligands as F^-, Cl^-, SCN^-, CN^-, and $C_2O_4^{2-}$. The role of ligands can be played by NH_3, CH_3NH_2, glycine, tartrate, malonate, citrate, and formate. In the process, a large part is played by the reactions of ligand penetration into the complex coordination sphere. Such penetration reactions are known to proceed extremely slowly. For instance, even in the most concentrated hydrochloric acid solution (12 M), complexation terminates at the third step:

$$[Cr(H_2O)_6]^{3+} + Cl^{-} \leftrightarrow [Cr(H_2O)_5Cl]^{2+} + H_2O,$$

$$[Cr(H_2O)_5Cl]^{2+} + Cl^{-} \leftrightarrow [Cr(H_2O)_4Cl_2]^{+} + H_2O,$$

$$[Cr(H_2O)_4Cl_2]^{+} + Cl^{-} \leftrightarrow [Cr(H_2O)_3Cl_3] + H_2O.$$

Not only Cr(III) aqua complexes, but also mixed Cr(III) aqua chlorides, are inert in the reactions of exchange of water molecules for chloride ions. The inertness of the mixed-ligand complexes decreases with an increase in the number of chloride ions in the complex coordination sphere.

Heating of the solution and increase in the chloride-ion concentration assists replacement of ligands, and the solution becomes green in color. However, one should keep in mind that heating accelerates the olation processes.

The difficulty in the investigation of Cr(III) complexes with hydroxycarboxylic acids (tartaric, citric, etc.) is that the studied ligands are the reagents which are polybasic and multidentate [30, 31] and the properties of chromium(III) salts are determined largely by the ionic composition of their solutions, which depends on the nature of anions and chromium(III) hydrolytic properties.

The choice of the optimal conditions for formation of complex species cause severe difficulties connected with the inertness of chromium(III) hexaaqua complexes. It is established that, in such systems, complexes with the composition 1 : 1 form and complexes with the composition 1 : 2 appear slightly in the pH range of 2–4.

To achieve complete yield of Cr(III) complexes, two-, three-, or even fivefold excess of the ligand is needed, depending on the ligand complexity; at the same time, the increase in the ligand concentration shifts the complex formation to a more acidic pH range. If we restrict the considered pH range to pH 2.5–4, then, for the Cr(III)–H_3Cit and Cr(III)–H_2Tart systems, chiefly $[CrHCit]^+$ and $[CrHTart]^{2+}$ complexes are formed under the assumption that the basicities of citric and tartaric acid are three and two, respectively. A maximum density of these acids is rarely achieved. For Cr(III), the formation of quite strong complexes is typical:

$$CrHCit^+ \log K = 29.59 \text{ and } CrHTart^{2+} \log K = 31.28.$$

One should take into account that the complexation between Cr(III) and hydroxycarboxylic acids proceeds very slowly. It was established that the rate of the formation reaction of Cr(III) complexes rises both with an increasing temperature and increasing pH of the solutions and ligand concentration.

One can surmise [31] that the complexation between Cr(III) and hydroxycarboxylic acids starts with the formation of outer-sphere complexes, e.g., $[Cr(H_2O)_6]H_2L^{2+}$, where L is ligand. At the next deprotonation step, protons are abstracted from both the ligand and water molecules of Cr(III) aqua complexes with the formation of conjugated bases $[Cr(H_2O)_6]HL^+$ and $[Cr(H_2O)_5OH]H_2L^+$. This step characterizes the dependence of the reaction rate on the pH value. The experimentally determined reaction rate is the rate of conversion of the outer-sphere complex into the inner-sphere one. This step occurs according to the scheme

$$[Cr(H_2O)_6]HL^+ \xrightarrow{k} [Cr(H_2O)_5HL]^+$$
$$\xrightarrow{\text{rapidly}} [Cr(H_2O)_4HL]^+ + H_2O,$$
$$[Cr(H_2O)_5OH]H_2L^+ \xrightarrow[-H_2O]{k} [Cr(H_2O)_5HL]^+$$
$$\xrightarrow{\text{rapidly}} [Cr(H_2O)_3HL]^+ + 2H_2O,$$

where k is the determined reaction-rate constant.

The rate-limiting step is the withdrawal of the water molecule from the aqua complex, with its site being rapidly occupied by the ligand.

The foregoing features of the Cr(III) chemistry should be taken into consideration in designing the technology of deposition of chromium coatings.

EXPERIMENTAL

Compared to the "hexavalent" chrome plating, the "trivalent" chrome plating allows introduction of varied organic additives and inorganic salts into the electrolyte, which makes it possible to enhance the electrolyte throwing power and lowers the edge effect.

The organic additives are selected experimentally; however, one should take into account that, at high negative potentials, they are desorbed from the electrode surface and are oxidized at the anode. Therefore, chromium electroplating when thick coatings (≥10 μm) are to be deposited should be conducted in an electrolyzer with separated electrode compartments.

In our studies, we employed electrolyzers with both separated and unseparated electrode compartments. For the separation of the cathode and anode compartments, we used a glass porous dividing partition.

The feature of the chrome plating is the use of high current densities ($i \geq 20$ A/dm^2) and low current efficiency (12–15%). The electrode process of chromium deposition belongs to processes in which the rate-determining step is the formation of a new phase (metal nuclei). For such processes, high overvoltages are inherent, which are the constituent part of the total overvoltage. This is suggested by the substantially facilitated chrome electroplating and noticeably higher current efficiency in the presence of an alloying metal (Co, Ni). There is no doubt that the formed alloying metal nuclei reduce the chromium nucleation work and chromium is deposited at lower current densities. Chromium alloyed with cobalt retains all the properties characteristic of pure chromium—high hardness, luster, and wear-resistance—and the resulting coatings are nonporous.

Another feature of chrome electroplating from aqueous solutions of its salts is that the majority of electricity (90% at times) is expended on discharge of hydrogen ions; as a result, vigorous hydrogen evolution is observed at the cathode. Therefore, the addition of the cationic or anionic surfactants leads mainly to foaming. As a consequence, the local increase in the pH value in the near-electrode layer encourages the formation of poorly soluble Cr(III) hydroxy compounds, impeding the chromium deposition, and degrading the quality of the coatings. Therefore, to prevent the formation of poorly soluble Cr(III) compounds, it is reasonable to introduce water-soluble polymer additives into the bath, as was demonstrated as early as in work [17]. The polymer additives generally affect the appearance of the coatings: the deposits are bright and cover the base surface uniformly. As the experiments showed, polymer additives and organic acids should be introduced into the electrolyte in moderate quantities. For instance, the PAA additive should comprise no more than 0.2 g/L. Any additives in high quantities result in worsened quality of the coatings, with the deposits beginning to darken.

Any substances of organic nature (tartrates, citrates, acetates, maleic and malic acids) lead to a remarkable increase in the overvoltage for chromium deposition. The increase in the overvoltage promotes intense hydrogen evolution, overexpenditure of electric power, and the chromium plating becomes insecure. In this case, one should be guided by the rule: the simpler the structure of the added substances, the more efficient the additive. This is why, for chromium electroplating from the solutions of Cr(III) salts, formate and glycine electrolytes are the most suitable. Sulfur-bearing compounds, such as rhodanides, sul-

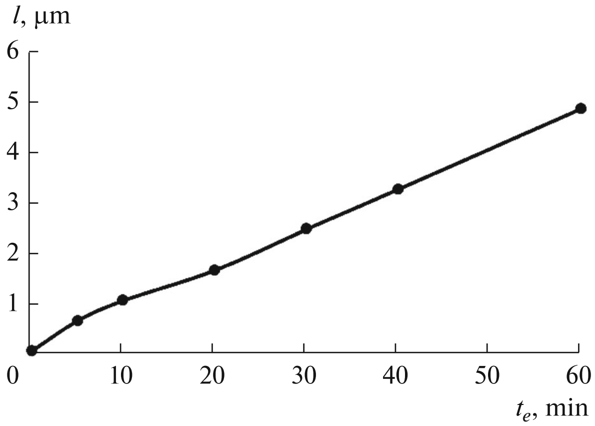


Fig. 1. Chromium-film thickness vs. electrolysis duration.

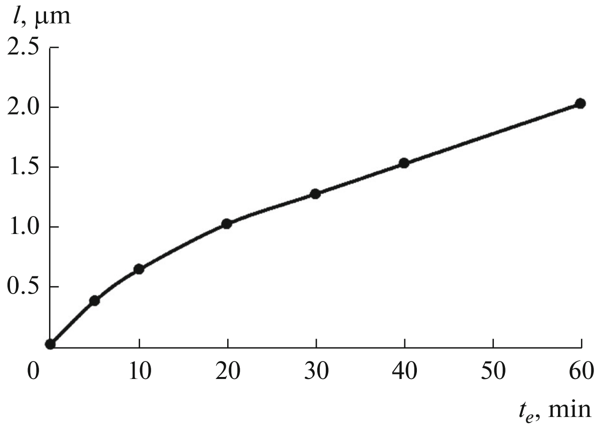


Fig. 2. Effect of electrolysis duration on the thickness of the chromium film deposited in electrolyte 1 in the presence of a water-soluble polymer.

foacids, thiourea, sulfides, sulfites, and thiosulfates, encourage the emergence of sulfur in the deposit, which is deleterious to the nanocrystalline films.

In the case of oxalate electrolytes [32], the chromium films are bright and deposit uniformly; however, they have no mirrorlike luster.

To prevent the formation of chromium(III) hydroxides, it is worthwhile to add boric acid, which serves as a buffer reagent, to the electrolyte. It can be surmised that a hydrogen bond is formed between the hydroxide of a compound Cr(III) complex and a hydrogen atom of the boric acid, thus averting olation. A discharge of the formed complex occurs with a high overvoltage. The chromium coating is uniform, and the resulting deposits are light in color.

The addition of urea has a favorable effect on the quality of the coating, and the deposits become bright. Urea molecules are readily adsorbed at the deposit surface and can passivate the spots of crystal growth. The introduction of urea into the solution is efficient only in acid solutions (pH < 2.0); however, at these pH values, the current efficiency decreases. At a high urea concentration (>30 g/L), the coating surface is delustered and then darkens gradually.

The addition of $Al_2(SO_4)_3$ does not result in a better chromium coating quality, and the film edges become mat but light in color.

Glycine is used as an efficient coordination-active compound in the electrochemical reduction of Cr(III) complexes [33, 34]. It is chosen because it combines varied electron–donor, bridging, and buffering properties. The reactivity of chromium(III) complexes is increased when a some of the coordinated water molecules in the inner coordination sphere are replaced by glycine anions. In the pH range of pH 2–3, due to the high buffering properties of glycine, it proved to be possible to increase a current density and avoid hydroxide formation upon the chrome electroplating. A bipolar behavior of the glycine ions makes possible their adsorption both at positively and negatively charged surfaces of the electrode [35, 36].

The modification of the inner coordination sphere of the chromium(III) aqua complexes via the exchange of water molecules for glycine anions was carried out by heating a chromium(III) sulfate solution with glycine at a temperature of 96–98°C for 2 h. The dominant complexes become the $[Cr(H_2O)_2Gly_4]^-$ ones with a stability constant of $\log K_{st} = 5.81$ at pH 2.5–3.5.

The direct-current value was maintained with a PI-50-1-1 potentiostat. The thickness and uniformity of the coating was examined with the help of a METAM RV–22 LOMO metallographic microscope. As electrodes, 0.5-mm-thick copper-foil plates 1 × 2 cm in size were used. The deposition rate and current efficiency were determined gravimetrically as a weight gain of the cathodes, and the total quantity of electricity was evaluated using the value of the current passed in a certain time.

The results of investigations of chromium deposition are given in the table.

Bright metal coatings were obtained from electrolyte 1. After 1 h of electrolysis, the solution pH increases to 3.2. The current efficiency did not exceed 4% at the $Cr_2(SO_4)_3 \cdot 6H_2O$ concentration of 120 g/L. With an increase in the Cr(III) concentration, the current efficiency rises; however, the deposits become less bright. Nevertheless, on the other hand, as the Cr(III) concentration is increased, a noticeable growth of chromium crystals in the coating takes place. Under these conditions, it is quite hard to obtain a nanocrystalline structure. The presence of Co(II) ions in the solution (electrolyte 6) enables a decrease in the chromium(III) salt concentration and a twofold increase in the current efficiency.

The addition of aluminum sulfate lead to darkening of the coatings with an electrolysis time; at a current

Results of investigation of chromium electrodeposition and compositions of electrolytes ($i = 20$ A/dm^2, $t_e = 20$ min, and $T = 30°C$)

No.	Electrolyte composition, g/L	l, μm	V, μm/min	Appearance
1	$Cr_2(SO_4)_3 \cdot 6H_2O$ – 120 Glycine – 36 HCOONa – 60 $(NH_4)_2SO_4$ – 75 H_3BO_3 – 30 pH 2,4 and $i = 10$ A/dm^2	1.6	0.08	Bright metal coatings
2	$Cr_2(SO_4)_3 \cdot 6H_2O$ – 200 Urea – 40 H_3BO_3 – 40 $Al_2(SO_4)_3 \cdot 18H_2O$ – 60 pH 2,4	1.8	0.10	Coatings with metallic luster; mat edges
3	$Cr_2(SO_4)_3 \cdot 6H_2O$ – 150 HCOONa – 60 H_3BO_3 – 42 pH 2,5	1.6	0.06	Coatings light in color; however, with mat edges
4	$Cr_2(SO_4)_3 \cdot 6H_2O$ – 120 $Na_2C_2O_4$ – 30 $(NH_4)_2SO_4$ – 60 H_3BO_3 – 40 Glycine – 30 pH 2,6	1.6	0.08	Bright coatings
5	$Cr_2(SO_4)_3 \cdot 6H_2O$ – 120 $Na_2C_2O_4$ – 30 Na_2SO_4 – 60 $Al_2(SO_4)_3$– 90 pH 2,4	1.8	0.10	Coatings light in color with metallic luster; mat edges
6	$Cr_2(SO_4)_3 \cdot 6H_2O$ – 50 $CoCl_2$ – 13 NH_4Cl – 30 Glycine – 40 HCOONa– 30 pH 3,6 and $i = 10$ A/dm^2	3.7	0.21	Bright metal coatings

density of $i > 20$ A/dm^2, the coatings became dark and cinder patches appeared at the edges of the samples. In addition, at pH > 3, $Al(OH)_3$ residue deposits. At higher current densities, deposition of this residue is not observed by the eye.

Bright chromium films are also deposited when chrome alum $KCr(SO_4)_2 \cdot 12H_2O$ is substituted for the chromium (III) salt in electrolyte 1.

The dependence of the chromium-film thickness of the electrolysis duration in electrolyte 1 is shown in Fig. 1. It is seen that the deposition rate evens out to the value of 0.08 μm/min.

In the presence of the water-soluble polymer, the deposition rate diminishes and becomes 0.03 μm/min. The film remains bright.

The surface of the chromium deposited electrolytically onto a brass substrate at a direct current of 20 A/dm^2 for 10 min was studied by scanning probe microscopy. An INTEGRA-AURA probe nanolaboratory operating with the NOVA program was employed. In the measurements, images of contrast were recorded, which allows one to determine the grain boundaries and characterize the structure and growth clusters of the coatings. To obtain nanocrystalline coatings, the brass base was polished thoroughly

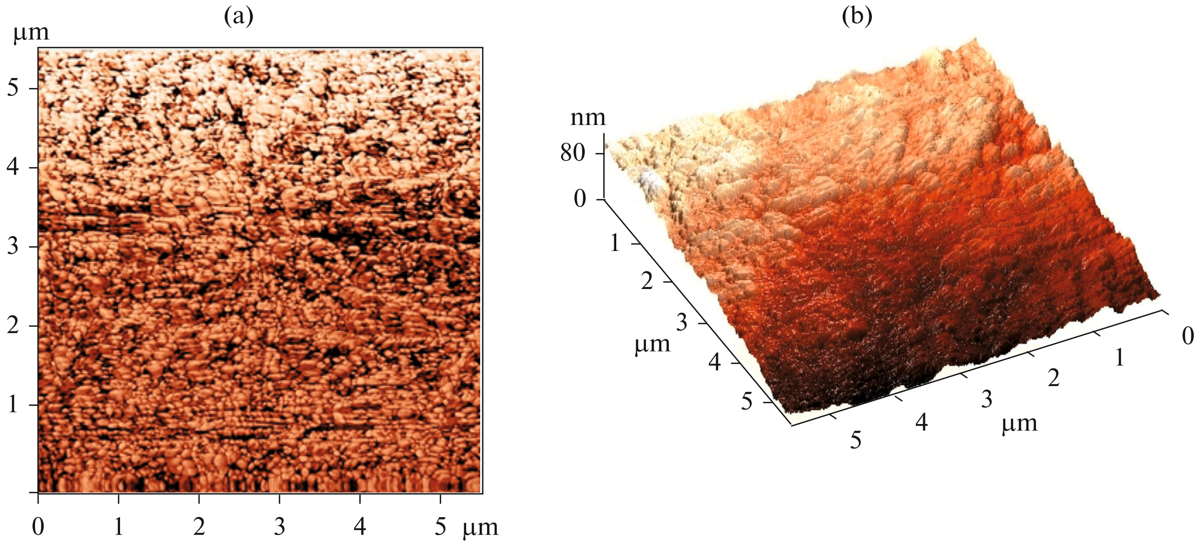


Fig. 3. Surface morphology and topography of the chromium film on a brass substrate: (a) morphology and (b) topography.

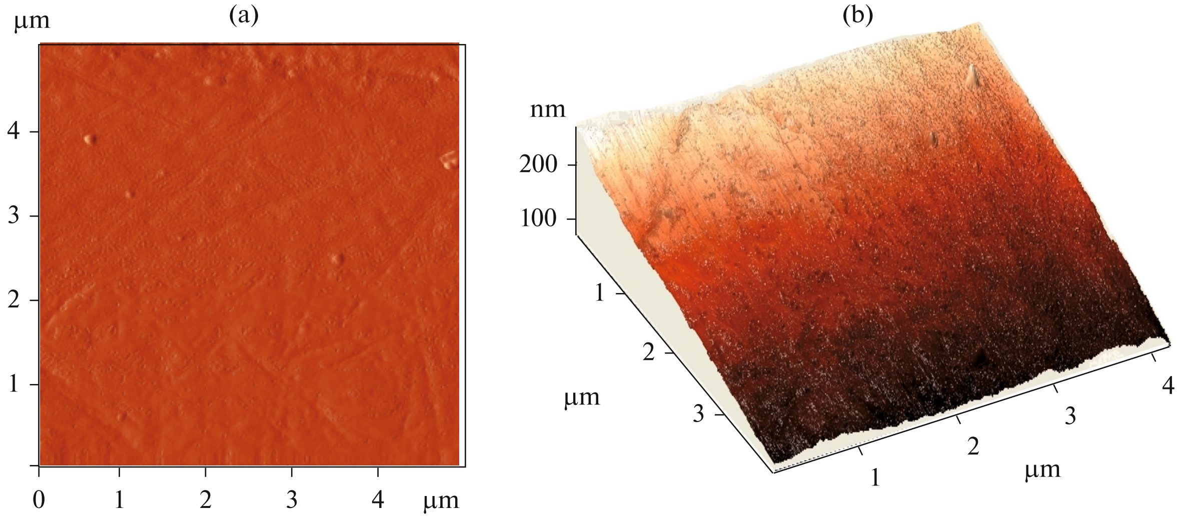


Fig. 4. Surface morphology and topography of the Co–Cr film on a brass substrate: (a) morphology and (b) topography.

and a thin bright copper film was next deposited onto it. Chromium was electroplated from electrolyte 1 (table) with the addition of 0.01 g/L of water-soluble polymer. The scan size was 5 × 5 μm.

Figure 3 displays the results of the investigations of the chromium-coating surface: the structure and image of topography of the film surface in a 3D format. The coating obtained at a direct current is formed by ordered structures. The minimum grain size is 20 × 30 nm. The smoothness of the surface is rather high. A rounded shape of crystalline grains is evidence that the film surface is bright. In fact, a bright film with a smooth surface containing separate microspheroids was obtained. The coating structure replicates the initial substrate-surface relief quite closely; therefore, the grain size depends of the quality of substrate-surface preparation. In Fig. 3b, growth patterns can be seen.

The addition of cobalt to the coating material changes the coating structure appreciably. The formed grains become more isotropic, and their size decreases significantly. The results of scanning are displayed in Fig. 4, which also shows the film surface in a 3D view (Fig. 4b). The electrodeposition was performed from electrolyte 6 (table).

The surface structure of the Co–Cr alloy features an ordered nanocrystalline structure. In the case of the Co–Cr alloy, the role of a stabilizer for separate nanoparticles may be played by the cobalt hydroxide amorphous phase.

CONCLUSIONS

For the development of new chrome plating technologies, it is necessary to take into account the formation of kinetically inert chromium(III) octahedral complexes.

The use of formate–glycine electrolytes allows a decrease in the minimum current density at which chrome electroplating commences.

Using atomic-force microscopy, it was shown that bright chromium films with a nanocrystalline structure form in this electrolyte. Deposition of chromium alloyed with cobalt leads to the formation of a more uniform structure.

The adjustment of the current value used in the coating deposition can serve as an efficient way of controlling the size and shape of nanocrystalline structures.

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