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Electroplating of Wear-Resistant Nanocrystalline Coatings from a Bath Containing Basic Chromium(III) Sulfate (Chrome Tanning Agent)

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Abstract—Regularities of the electroplating of chromium–carbon alloy coatings from a bath containing basic chromium(III) sulfate, carbamide, formic acid, sodium sulfate, aluminum sulfate, orthoboric acid, and sodium dodecyl sulfate are studied. Replacement of chromium sulfate as a source of trivalent chromium ions in the solution with basic chromium sulfate (chrome tanning agent) results in a decrease in the current density when metal deposition begins. As a result, the covering power of the bath increases. The effects discovered are determined by changes in the composition of the discharged chromium complexes. A certain excess of OH[−] groups in the inner sphere of electroactive chromium complexes results in acceleration of electroplating. The studied electrolyte based on chrome tanning agent enables one to produce thick high-quality nanocrystalline Cr–C alloy coatings with improved tribological characteristics.

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INTRODUCTION

In the last decade, the development of theoretical principles of new deposition techniques of individual chromium and chromium alloy coatings from ecologically safe baths based on Cr(III) compounds is attracting progressively increasing attention from researchers [1–10]. One topical problem is the production of thick deposits (up to several tens or hundreds of microns) that can be used as wear-resistant coatings [9, 10]. To solve the problem, we have proposed a bath based on chromium(III) sulfate and containing formic acid and carbamide as organic components [10–15]. The bath enables one to obtain high-quality solid nanocrystalline chromium–carbon alloy coatings with a thickness no smaller than several hundreds of microns. Unfortunately, this method has particular drawbacks, such as the low covering power of the bath and the noticeable cost of chromium(III) sulfate used.

At the same time, there is another, much cheaper source of trivalent chromium that can be used in baths of this kind, namely, Cr(OH)SO₄ basic chromium(III) sulfate (chrome tanning agent). The large-scale production of chrome tanning agent is chiefly because of its use in the tanning industry [16, 17]. As was shown previously, Cr₂(SO₄)₃ can be replaced with basic chromium(III) sulfate in a plating bath for the deposition of Cr–C alloys; and the resulting increase in the covering power of the electrolyte was noticed [18–20]. The object of this work is to clarify the physicochemical regularities of the electroplating, as well as certain characteristics of the coatings deposited from a bath contain-

ing chrome tanning agent compared to those from a chromium(III) sulfate-based bath.

EXPERIMENTAL

Two electrolytes of the following general composition were taken in this study for the electrodeposition of chromium–carbon coatings: 1 M Cr³⁺, 0.5 M HCOOH, 0.5 M CO(NH₂)₂, 0.15 M Al₂(SO₄)₃ · 18H₂O, 0.3 M Na₂SO₄, 0.5 M H₃BO₃, and 0.1 g/L sodium dodecyl sulfate [10–15, 18–20]. In one bath, chromium(III) sulfate was used as a source of Cr³⁺ ions (CS electrolyte); in the other bath, basic chromium(III) sulfate was used (BS electrolyte). Note that the basicity of chrome tanning agent was ~34%. Formic acid and carbamide served as complexing agents. Sodium sulfate, aluminum sulfate, and boric acid acted as conducting salts and buffer additives, respectively. Sodium dodecyl sulfate played the role of a surfactant.

The acidity of the solution (pH 1.5) was set by adding a certain amount of concentrated H₂SO₄ or Na₂CO₃ solution. Coatings were plated on the surface of a disc electrode made of degreased copper foil placed in a plastic holder in a thermally controlled glass cell. Electroplating was carried out under galvanostatic conditions with the use of titanium–manganese dioxide anodes without separation of the electrode spaces.

The chemical composition of deposits was determined with the use of X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 unit. Additionally, chemical analysis according to a technique described in [10, 15] was carried out.

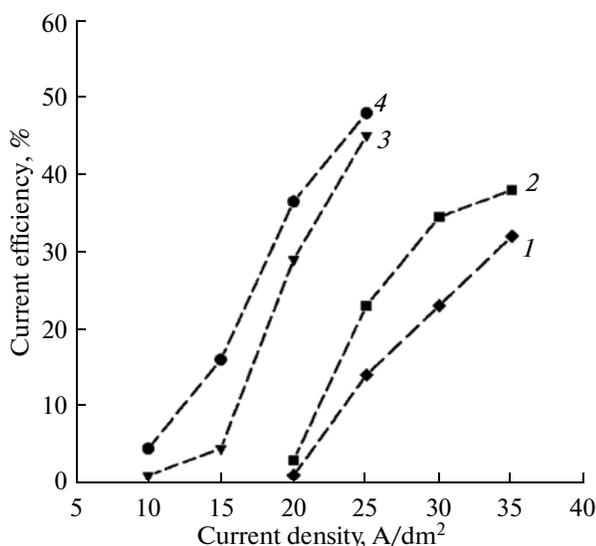


Fig. 1. The effect of the current density on the current efficiency of Cr–C alloy in (1, 2) CS and (3, 4) BS bath at a temperature, °C: (1, 3) 35 and (2, 4) 40.

Steady-state partial polarization curves of chromium deposition were recorded under potentiostatic conditions with a Potentiostat/Galvanostat Reference 3000 (Gamry) according to a technique outlined in [22]. Electrode potentials were measured with respect to the saturated silver-chloride reference electrode and recalculated to the standard hydrogen electrode scale.

The covering power of the baths was estimated from plating experiments in a Hull cell ($V = 250$ mL, $I = 5$ A, $t = 3$ min) judging from the length of the cathode segment covered with a electrodeposit.

Absorption spectra of the solutions in the visible range were recorded with an SF-46 spectrophotometer. The thickness of a glass cuvette was 1 cm, and the reference liquid was water.

Small-angle diffraction patterns were obtained on a DRON-3.0 X-ray diffractometer supplemented with a KRM-1 small angle camera in monochromatic Mo K_{α} radiation.

Tribological tests were carried out with an SMTs-2 unit in a dry friction regime. In these experiments, a galvanic Cr–C deposit with a thickness of 20 μm was applied on the surface of a steel stock with an outer diameter of 50 mm. A quenched steel disc was taken as a counterbody. The fretting wear and friction coefficients were determined at a sliding velocity of 0.79 m/s and a load of 1 MPa. The mean wear of coatings was estimated from the results of gravimetry.

RESULTS AND DISCUSSION

Current Efficiency and Covering Power of Electrolyte

As was shown previously [12], in chromium–carbon alloys obtained from a bath of the selected composition, carbon is present in the form of carbide. The carbon

content in the deposit decreases with an increase in the cathodic current density and temperature, although the corresponding changes are relatively small. We can accept that the contents of chromium and carbon in the deposits are ~90–91 and 9–10 wt %, respectively, independently of the nature of the chromium source in the bath (chromium(III) sulfate or chrome tanning agent). The possible mechanism of the codeposition of carbon and chromium and the reasons for the independence of the alloy composition of different factors were discussed in [14].

Figure 1 illustrates the effect of the current density on the current efficiency of the alloy plating from CS and BS electrolytes.¹ As can be seen, an increase in the current density and a decrease in the temperature of the bath result in an increase in current efficiency. The difference between the upper and lower boundaries of the current density range where high-quality coatings can be produced is a substantial difference between CS and BS electrolytes.

In fact, deposition from a CS bath begins at a current density of about 20 A/dm² (an accurate value depends on temperature), while, in a BS bath, deposition proceeds at a noticeable rate already at 10 A/dm². Thus, it is effective to carry out plating in CS and BS baths in current density ranges of 25–35 and 15–20 A/dm², respectively.²

Production of thick chromium deposits from baths based on chromium(III) salts is known to be a difficult problem, since the deposition rate rapidly decreases with time, and, in several tens of minutes of electrolysis, the deposition stops [23]. Practically constant (time-independent) deposition rate, which enables one to produce bright Cr–C deposits with a thickness of several hundreds of microns, is an advantage of the baths proposed [18].

It is worth noting that the current efficiency of chromium plating from conventional acidic chromium electrolytes is typically no higher than 10–20%. As can be seen, under certain conditions of electrolysis, much higher current efficiencies can be reached in the electrochemical system studied and the electroplating rate can be as high as 0.7–0.8 $\mu\text{m}/\text{min}$.

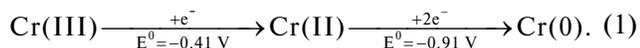
Lower current densities of the beginning of the metal deposition indicate the larger covering power of the BS bath (compared to CS electrolyte). Tests in a Hull cell confirm this conclusion (Table 1).

¹ Note that, in contrast to the results considered in [11, 12, 18], in this study, the current efficiency was calculated for the Cr–C alloy deposition rather than for a partial reaction of chromium deposition.

² When the cathodic current density is higher than the given upper boundaries, the exterior of coatings sharply deteriorates, namely, the surface becomes gray and rough, and burning can be noticed at the specimen edges.

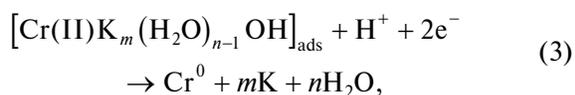
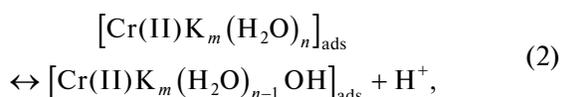
Kinetics of Electrode Processes

In order to clarify the peculiarities of the deposition kinetics of chromium from the selected baths, partial polarization curves were recorded under potentiostatic conditions (Fig. 2). It is well known that the deposition of chromium proceeds in stages via the formation of relatively stable intermediate Cr(II) complex particles [22, 24, 25]:



Electroreduction of Cr(II) complex particles is the rate-determining stage of the total process [14, 22]; therefore, the partial current density of the metal deposition was calculated for the second stage of reaction (1) (for the $\text{Cr(II)} + 2e^- \rightarrow \text{Cr(0)}$ stage).

As was found previously, OH^- ions can catalyze the deposition of chromium due to the formation of electroactive hydroxo complexes of bivalent chromium in the layer near the electrode [6–10, 22, 25]. The corresponding reaction scheme can be written as follows:



where K is an organic ligand.³

As can be seen, there is a current peak in the partial polarization curves. The decrease in the current of the partial chromium deposition can be caused by blockading the electrode surface with difficultly soluble Cr(III) hydroxide compounds [22, 26–28].

As follows from the data obtained, using chrome tanning agent instead of chromium(III) sulfate as a source of Cr(III) ions results in a shift in the partial polarization dependence toward more positive potentials, i.e., in the increase in the deposition rate. Obviously, this feature accounts for the difference in the current densities at which chromium is plated from CS and BS baths.

The discovered effect may be related to the difference in the composition of complex chromium ions in the corresponding solutions. This hypothesis is confirmed by the differences in the absorption spectra of diluted CS and BS electrolytes in the visible spectral range (Fig. 3).⁴

In the absorption spectra of aqueous solutions of complex trivalent chromium ions, there are two absorp-

³ Accurate compositions of complexes involved in a transformation on the electrode are obviously unknown. Therefore, for simplicity, charges of K particles and complexes are not shown in schematic Eqs. (2) and (3).

⁴ For measuring the absorbances, upon 100-fold dilution of the electrolyte samples, the concentration of all components except for Cr(III) ions was increased to the values of the original bath used for electroplating.

Table 1. Covering power of Cr(III)-based baths estimated according to the Hull method

Bath	Covering power, mm
CS	24
BS	47

Note: Temperature 35°C.

tion peaks at wavelengths of ~410 and ~570 nm, respectively. The peaks correspond to two possible spin-allowed transitions, namely, ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$ and ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$, the former (in the low-frequency range) being determined by the electronic excitation of the central ion, while the latter is determined by the excitation of the ion and its first coordination shell [29, 30]. In the solution that contains chrome tanning agent as a source of chromium ions, the absorption intensity is substantially higher (the so-called hyperchromic effect) and the absorption peaks are red shifted by 2–3 nm (compared to the chromium(III) sulfate solution). Thus, the natures of complex trivalent chromium ions contained in CS and BS baths differ. Obviously, in solutions prepared from basic chromium(III) sulfate, hydroxide ions are kept in the inner sphere of the complexes. In fact, according to the data of [29], a substantial hyperchromic effect at the concurrent red shift of the absorption peaks is typical of the formation of Cr(III) hydroxo complexes.

Basic chromium(III) sulfate differs from chromium(III) sulfate in having increased basicity, which is determined by the mean number of OH^- groups involved in the inner sphere of the chromium ion complex [21]. A certain excess number of hydroxide ions,

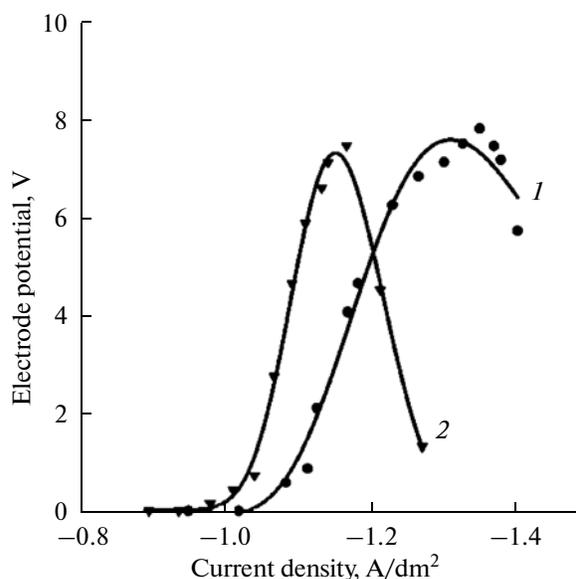


Fig. 2. Partial polarization curves of the chromium plating from (1) CS and (2) BS baths at a temperature of 35°C.

Table 2. Results of tribological tests

Bath and plating conditions	Tribological characteristics	
	friction coefficient	fretting wear, g/(cm ² h)
Conventional acidic chromium bath (2.5 M CrO ₃ , 0.025 M H ₂ SO ₄ ; $i = 35$ A/dm ² ; $t = 50^\circ\text{C}$)	0.17	0.00210
CS bath ($i = 35$ A/dm ² ; $t = 35^\circ\text{C}$)	0.14	0.00083
BS bath ($i = 20$ A/dm ² ; $t = 35^\circ\text{C}$)	0.15	0.00150

which are liberated at the discharge of trivalent chromium ions from a BS bath, may result in an additional increase in pH_S in the layer near the electrode (compared to CS electrolyte) even at the same pH value in the bulk solution. According to the proposed concept of the catalytic effect produced by OH⁻ ions on the discharge of Cr(II) ions, the discovered acceleration of the chromium deposition becomes natural.

Structure and Tribological Characteristics of the Coatings

Small angle X-ray scattering experiments [12, 18] showed that the studied chromium–carbon coatings have nanocrystalline structures and there are 3- to 6-nm domains with an ordered arrangement of atoms in the deposit.

Tribological characteristics are among the most important functional properties of thick galvanic chromium-based coatings. Cr–C deposits obtained from the studied baths based on Cr(III) compounds differ from the coatings deposited from conventional acidic chromium electrolytes in higher wear resistance and smaller friction coefficient (Table 2), which can be determined by their nanocrystalline structure [15].

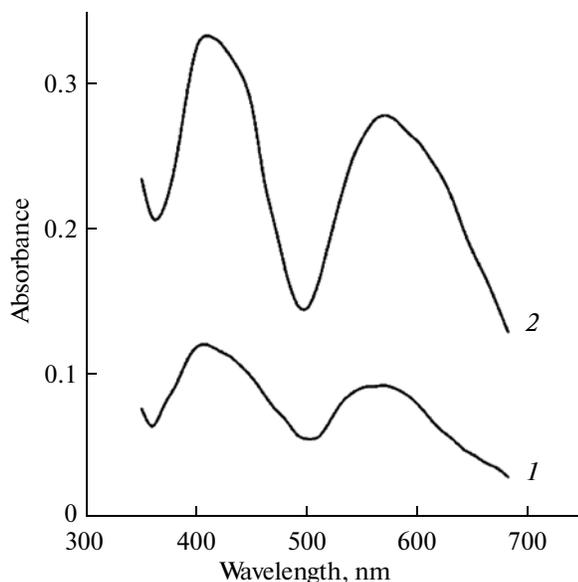


Fig. 3. Absorption spectra of diluted (1) CS and (2) BS electrolytes at a Cr(III) concentration of 0.01 M.

Note that a somewhat lower wear resistance of the coatings obtained from a BS bath compared to those from a CS bath is likely to be caused by the differences in the deposition current densities (see Table 2).

CONCLUSIONS

Replacing chromium sulfate as a source of Cr(III) ions with basic chromium sulfate (chrome tanning agent) in a chrome-plating bath enables one to decrease the lower boundary of the current density range within which the metal deposition takes place and, hence, increase the covering power of the bath. The data obtained can be interpreted in terms of the previously proposed mechanism of chromium plating, according to which Cr(II) hydroxo complexes are electroactive intermediate particles. A certain additional amount of OH⁻ ions that are present in the inner spheres of chromium complexes in the bath based on chrome tanning agent seems to promote accelerated discharge of intermediate Cr(II) ions.

The proposed bath enables one to produce high-quality nanocrystalline chromium–carbon alloy coatings with a substantial thickness that have higher wear resistance and smaller friction coefficients compared to conventional chromium electrodeposits.

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