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Electrodeposition from trivalent chromium baths as an environmentally friendly alternative to electroplating from hazardous hexavalent chromium baths

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Abstract : The paper deals with the generalization of investigations concerning current state in development of trivalent chromium baths as environmentally friendly alternative to hazardous electroplating baths containing toxic hexavalent chromium. The main technological properties of trivalent chromium baths containing carbamide and formic acid are described and compared with those typical of common Cr(VI)

plating bath. Thick nanocrystalline chromium-carbon deposits may be obtained from the Cr(III) electrolytes, some physicochemical and service properties of such coatings exceeding those of "usual" chromium deposits. © Global Scientific Inc.

Keywords : Trivalent chromium; Electroplating; Electrodeposition; Nanocrystalline coating.

INTRODUCTION

Chromium electrodeposits are widely used for improving hardness, wear resistance, corrosion resistance and decorative appearance of engineering tools and components. Usually, Cr coatings are deposited from electrolytes based on chromic acid which are highly toxic and oxidative^[1]. With increasing close attention to environmental problems throughout the world, hexavalent chromium electroplating faces possible extinction as a result of its serious health and environmental hazard. In 2006, EU adopted the Restriction of Hazardous Substances (RoHS) which extremely restricts the use of

hexavalent chromium in electrical and electronic equipment. Therefore, developing ecologically desirable alternative surface treatment technologies to replace hexavalent chromium electroplating is a key problem in modern surface engineering.

In the past decades, strenuous attempts have been made to obtain a commercially viable trivalent chromium plating bath as a replacement for the conventional toxic hexavalent bath^[2-5]. However, trivalent chromium cannot be readily deposited from aqueous solution and there are still many problems that need to be solved in the trivalent chromium plating processes. Firstly, it is difficult to improve the thickness of chromium deposits

in trivalent chromium plating^[6]. Secondly, highly complicated chemistry of Cr(III) compounds results in complexity of bath composition and difficulties in bath maintenance^[7,8]. Furthermore, Cr(III) ions are easily oxidized to Cr(VI) ions near the anodes which would contaminate the bath^[9]. All these problems restrict the application and expansion of the trivalent chromium plating process.

Nevertheless, a great number of trivalent chromium baths have been reported in recent years^[10-27]. Recently, a novel trivalent chromium bath containing formic acid and urea was proposed which allows obtaining thick coatings with a relatively high deposition rate^[23-30]. However, all above-mentioned papers are devoted to various and separate physicochemical and technological aspects of the electrodeposition process from the plating bath involved, and there is a vital need to summarize the data obtained and to provide information on current state in the problem of the development of eco-friendly trivalent chromium baths. The aim of this paper is to generalize the main technological characteristics of the state-of-the-art process of electroplating from a trivalent chromium bath in comparison with hexavalent chromium baths.

EXPERIMENTAL

Chromium electrodeposition was performed galvanostatically in a usual glass cell. Coatings were deposited on a disc electrode of copper foil fixed in a plastic holder. Prior to each experiment, the surface of copper foil was treated with magnesium oxide and then rinsed with hydrochloric acid solution and distillate water.

Two trivalent chromium baths with the following composition were applied in the present study: 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⁻¹ of sodium dodecyl sulfate^[23,24]. "Common" chromium sulfate was used a source of Cr(III) ions in the first bath. The second plating bath was prepared utilizing basic chromium sulfate (i.e. chrome tanning agent)^[25,28,30]. The basicity value of the chrome tanning agent was about 34%^[31]. Formic acid and carbamide act as complexing agents. Sodium sulfate, aluminium sulfate and boric acid are conducting salts and

buffer agent, correspondingly. Sodium dodecyl sulfate is used as surfactant. Let us designate for convenience the bath containing chromium (III) sulfate as Bath "A" and the bath containing basic chromium sulfate as Bath "B".

Common hexavalent chromium bath was applied in this work (250 g L⁻¹ CrO₃, 2.5 g L⁻¹ H₂SO₄).

The electrolysis was carried out either with titanium-manganese dioxide anodes (TMDA) or with composite TiO_x/PtO_y anodes^[9,32]. Lead anodes were applied in the hexavalent chromium bath.

The current efficiency and rate deposition were calculated using Faraday's law by comparing the weight gain of the cathode placed in the chrome-plating bath with that of a copper coulometer connected in series.

The content of Cr(III) and Cr(VI) ions in the bath was determined by spectrophotometric method. The pH value was controlled by means of common potentiometric method.

The chemical composition of the coatings under study was determined by XPS investigations which were described in detail in our previous work^[23]. In addition, the chemical composition of electrodeposits was established by means of a spectrophotometric analysis^[26].

The covering power of the plating bath was determined using a usual Hull cell (V = 250 mL, I = 5 A, t = 3 min). Copper-foil plates (75×100 mm) served as the working electrodes. The covering power of the chromium bath was estimated measuring the length of deposited area (mm).

Small-angle X-ray scattering (SAXS) experiments were performed using an X-ray diffractometer DRON-3.0 with a small-angle X-ray camera KRM-1 in the monochromatized Mo-K_α radiation^[23]. The tribological tests were conducted on the SMC-2 wear tester under unlubricated conditions^[26]. The hardness of chromium coatings was determined using a PMT-3 set-up at a load of 100 g and the coating thickness of about 20 μm.

The conductivity of chromium electrolytes was measured by means of usual ac Wheatstone bridge at a frequency of about 510 Hz. A thermostated glass cell with two Pt-electrodes, on which a layer of spongy platinum has been electrolytically deposited, was used in these experiments.

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RESULTS AND DISCUSSION

It is stressed that chromium-carbon alloy deposits from the Cr(III) plating bath containing organic components^[23,26-28] whereas “pure” chromium is obtained from the hexavalent chromium plating baths. According to our XPS-investigations, carbon is present in the coatings as chromium carbide^[23]. The mechanism of carbon co-deposition was described and discussed earlier^[27,28]. According to this mechanism, carbon is included in the deposits by a chemical interaction of active chromium ad-atoms with adsorbed organic molecules (carbamide and formic acid). With changing in current density and bath temperature carbon content variation is relatively weak, chromium and carbon content in the deposited alloys being close to ~90÷91% and 9÷10% (wt.), respectively.

Figure 1 shows the effects of current density on current efficiency (CE) of electrodeposition process in the plating baths containing chromium sulfate or basic chromium sulfate. As can be seen, an increase in the current density and the decrease in the bath temperature lead to an increase in the current efficiency. Let us note that, in contrast to data reported in works^[23,24], in

this communication the values of CE for overall Cr-C alloy electrodeposition (but not for the partial process of the chromium electrodeposition reaction) are presented. A fundamental difference between two trivalent chromium baths under consideration consists in dissimilarity between the values of operating values of cathodic current density. Indeed, when in case of the bath “A” chromium deposition starts at ~20 A dm⁻² (depending upon electrolyte temperature), chromium electroplating process in the bath “B” begins at ~10 A dm⁻². Thus, the most suitable values of current density seem to be close to 30÷35 A dm⁻², and 15÷20 A dm⁻² for the baths “A” and “B”, respectively. When cathodic current density exceed indicated values, the surface appearance of deposits becomes worse—the coatings surface is rough and the “burning” occurs on the deposits surface.

It is well known that bright coatings may be obtained from the bath containing Cr(VI) compounds only if the bath temperature is in the range from about 45 °C to about 55 °C^[1]. Curve 5 in Figure 1 gives the dependence of CE upon current efficiency for the case of common hexavalent chromium bath. As can be seen, the values of CE in the trivalent chromium baths are

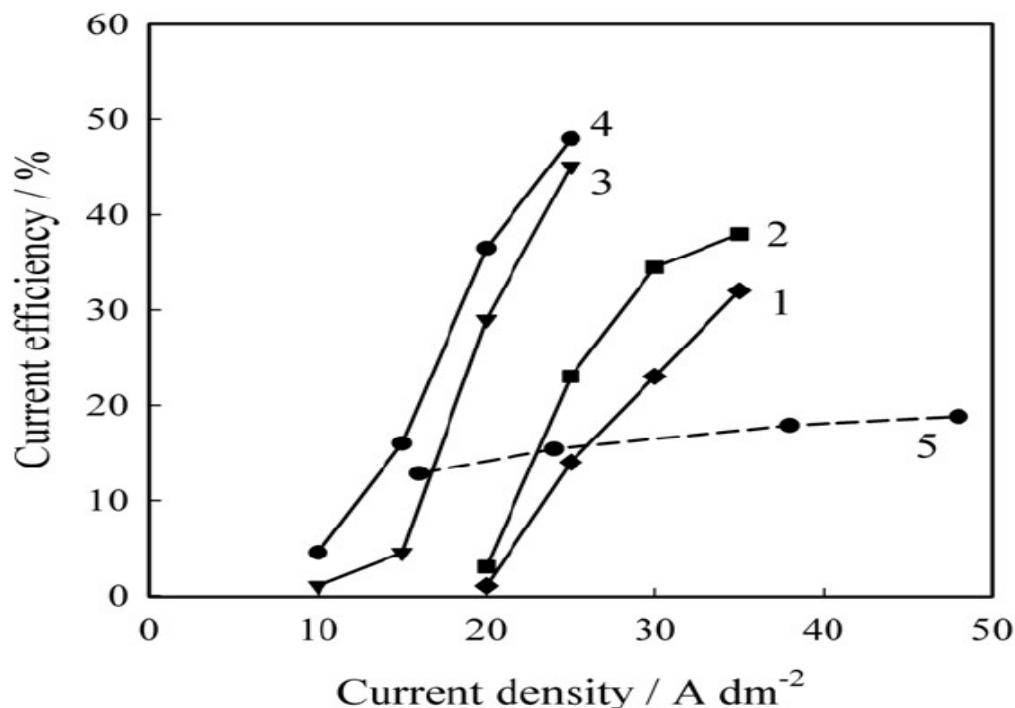


Figure 1 : Effect of current density on current efficiency of Cr and Cr-C alloy deposition processes for the bath “A” (1), (2), for the bath “B” (3), (4), and for the hexavalent chromium bath (5). Bath temperature 40 °C (1), (3); 35 °C (2), (4); 50 °C (5). (Lines are drawn only to guide the eye)

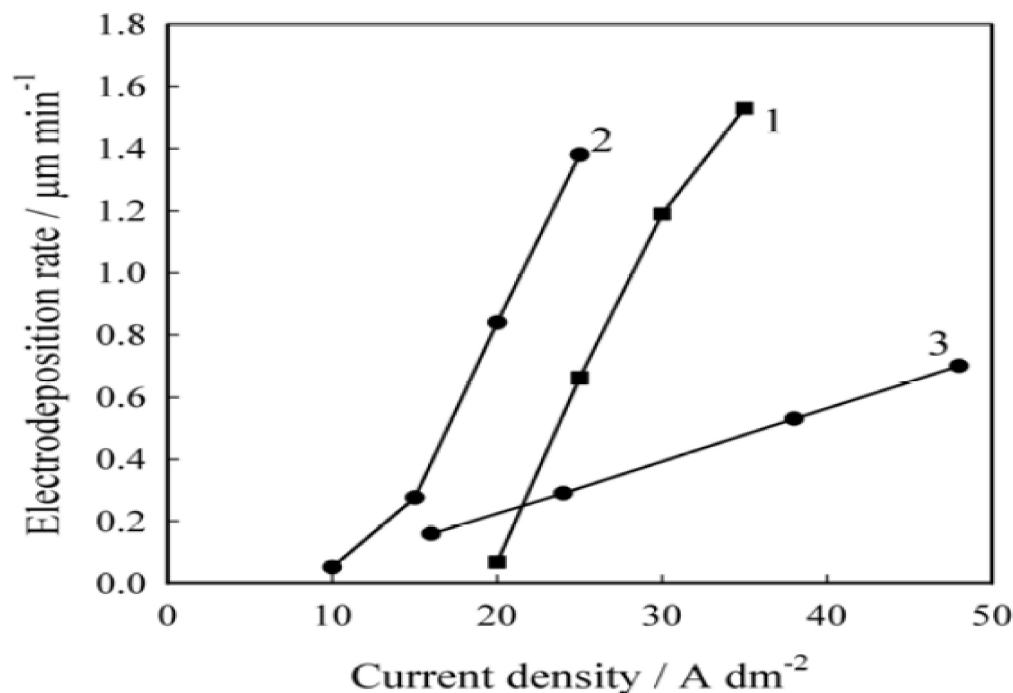


Figure 2 : Effect of current density on electrodeposition rate of Cr and Cr-C coatings for the baths: “A” (1), “B” (2), hexavalent chromium bath (3). Bath temperature 35 °C (1), (2), or 50 °C (3). (Lines are drawn only to guide the eye)

appreciably higher than those typical of the Cr(VI) plating bath.

As is known it is too difficult to deposit thick chromium layers from trivalent chromium baths. The rate of chromium deposition was reported to be rapidly diminished with deposition time and after several ten minutes of electrolysis no mass gain was observable^[6]. On the contrary, the value of electroplating rate as well as current efficiency does not practically change in the trivalent chromium bath proposed during electrolysis and thick electrodeposits may be easily obtained. This feature is very favorable for practical use.

The baths under consideration is distinguished by a relatively high electrodeposition rate ($\sim 0.5 \div 1.5 \mu\text{m min}^{-1}$), therefore thick chromium-carbon layers are deposited during relatively short time. It should also be stressed that the electrodeposition rate in case of Cr(III) baths is considerably higher than that in case of Cr(VI) bath (Figure 2). Such a feature of trivalent chromium baths is their essential advantage.

The lower value of minimal current density, at which Cr deposition reaction begins, points out that the covering power of the bath “B” is better. The results of the Hull cell test confirmed this conclusion (TABLE 1).

Comparing trivalent and hexavalent chromium baths

(TABLE 2), in the first place, environmental safety of trivalent baths should be emphasized. The baths on the base of Cr(III) salts include only traces of Cr(VI) ions which are formed in a very small quantity on the anodes and can be further reduced on the cathode. As the Cr(VI) content in such baths is negligible, mist evolution and waste water are practically Cr(VI)-free. The Cr(III) plating bath has a lower concentration of chromium in electrolyte (generally, 52 g dm^{-3}) compared to $\sim 125 \text{ g dm}^{-3}$ for hexavalent chromium. Therefore, there is much less chromium in the wastewater. The reduction step in wastewater treatment is not required. As waste management costs continue to rise, the savings that trivalent chromium systems offer will increase markedly.

Further, it must be noted the trivalent baths distinguish by higher current efficiency and electrodeposition rate, the operating current density and bath temperature being appreciably lower than in the case of Cr(VI) bath. It is profitable in terms of economic considerations.

In case of Cr(III) bath, the electrolysis is carried out using titanium-manganese dioxide anodes (Ti/MnO₂) or, as showed in work^[32], composite TiO_x/PtO_y anodes. On these anodes the electrooxidation of Cr(III) ions to Cr(VI) occurs with a rather small rate^[9].

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TABLE 1 : Covering power of plating baths estimated by Hull cell test

Type of the plating bath	Covering power, mm
Trivalent chromium bath "A"	24
Trivalent chromium bath "B"	47
Hexavalent chromium bath	60

Bath temperature was 35 °C for both trivalent chromium baths and 50 °C for hexavalent chromium bath

Therefore, electroplating can be performed without separation of anode and cathode compartments. Although titanium-based anodes are relatively expensive, they are very long-lived and can be stably operated during several years. Toxic and expensive lead anodes, which are utilized in hexavalent baths, are unworkable.

The trivalent chromium baths proposed are operated at higher pH values as those based on Cr(VI) compounds (see TABLE 2). Therefore, the former show lower corrosion activity to constructional materials and

equipment.

A trivalent chromium bath can be prepared both on the base of chromium sulfate and on the base of chrome tanning agent. As shown above, applying basic chromium sulfate (instead of chromium sulfate) leads to a decrease of the current density at which chromium begins to electrodeposit. As a result, the covering power of the bath improves. Such a feature has been explained by changing in the composition of electroactive chromium complexes^[29]. Excessive amount of OH⁻ groups in the inner sphere of the electroactive chromium complexes leads to accelerating the chromium electrodeposition reaction. Chrome tanning agent is produced on a large scale by modern chemical industry. It is widely used to tan the leather and is much cheaper than chromium sulfate.

It is important and interesting that, in accordance with the results of our SAXS investigations^[23,26],

TABLE 2 : Comparison table of the main characteristics of trivalent and conventional hexavalent chromium baths

Parameter	Conventional hexavalent chromium bath	Trivalent chromium bath	
		On the base of Chromium sulfate ("A")	On the base of chrome tanning agent ("B")
Total chromium content (Cr(III)+Cr(VI)), g L ⁻¹	~125	~52	
Hexavalent chromium content, g L ⁻¹	~125	~0.4	
pH	< 0		1.5
Cathodic current density, A dm ⁻²	~40-60	30-35	15-20
Bath temperature, °C	~45-55		35
Current efficiency, %	~12-18	~30-35	~28-30
Electroplating rate, μm min ⁻¹	~0.2-0.6	~1-1.5	~0.8-1
Bath life	From several months to several years	At least two months	
Application of toxic lead and its alloys	Yes (as anodes)	No	
Anodes	Pb or its alloys	Ti/MnO ₂ or composite TiO _x /PtO _y	
Cr(VI) mist evolution	Intensive	Non detectable	
Structure of deposits	Crystalline	Nanocrystalline (with average grain size ~ 3-5 nm)	
Surface hardness, HV	800-900 (diminishing after annealing)	800-900 (after annealing may be increased up to 1800-1900)	
Friction coefficient	0.06-0.5 (dependent on the type of friction pair)	0.14	0.15
Maximal current density of anodic active dissolution (critical current density) in 0.5 M H ₂ SO ₄ + 0.2 M NaCl, A dm ⁻²	0.0236	There is no active dissolution region	
Passive current density in 0.5 M H ₂ SO ₄ + 0.2 M NaCl (at E = 0.0 V), A dm ⁻²	1.41·10 ⁻³	4.85·10 ⁻⁴	7.70·10 ⁻⁴
Electrolyte conductivity, Ω ⁻¹ m ⁻¹	~60		~6

nanocrystalline Cr-C coatings are formed when proposed trivalent chromium baths are applied. The average grain size is about 3-5 nm. Some physicochemical and service properties of deposits from Cr(III) baths are close to those obtained from Cr(VI) bath and fulfill all requirements which are claimed to hard chromium plating. It should be stressed that the hardness of Cr-C deposits increases when annealing in contrast to the coatings from hexavalent baths; in addition, the corrosion resistance of the coatings considered is extremely high^[23].

A long-continued test has been performed in which electrolysis lasted for 2 months with periodical bath correction^[25], the trivalent chromium bath "B" being used in these experiments. The possibility of continuous service of the trivalent chromium bath under consideration was confirmed.

Let us note that the trivalent chromium baths have also some shortcomings along with the obvious advantages. First of all, it is their relatively low covering power in comparison with the baths on the base of hexavalent chromium, though the covering power of the bath containing chrome tanning agent approaches to that typical of the conventional Cr(VI) bath.

Another grave shortcoming of the trivalent baths proposed is their low conductivity compared with the hexavalent one (see TABLE 2). It leads to an appreciable increase in the bath potential. Among other things, small conductivity should result in an increase in energy consumption. At the same time, higher deposition rate and lower operating current density promote diminishing energy consumption in case of trivalent bath in comparison with hexavalent one. In addition, it must be noted that the trivalent bath is operated at lower temperature, i.e. heating expenses become lesser. Taking in consideration all these facts and on the ground of our rough estimations, we suppose that the total energy consumption would be similar in cases of using both hexavalent and trivalent chromium baths.

CONCLUSIONS

Some functional advantages and disadvantages of eco-friendly trivalent chromium baths are summarized in comparison with extremely toxic and hazardous hexavalent chromium bath. The investigations performed

show that developing Cr(III) plating baths is a promising area in modern surface engineering. A remarkable progress achieved in recent years is connected with the development of trivalent chromium baths which allow obtaining thick hard coatings (with a thickness of several hundred micrometers). In spite of evident advantages of such electrochemical systems, they possess several shortcomings (first of all, relatively low covering power and conductivity); further investigations should be focused on solving these problems.

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