M.V. TOMIĆ[1], LJ.J. PAVLOVIĆ[2],
M.G. PAVLOVIĆ[1], V. MIĆIĆ[1], B. ĐUKIĆ[1]

Catalytic effect of sulphuric acid in the process of deposition of chromium coatings

This paper analyzes the catalytic effect of sulphuric acid on current efficiency, the coating thickness and the rate of deposition of electrochemical chromium coatings. According to the properties of chrome, there are three types of chrome coatings: decorative, hard and porous. The quantitative composition of baths and working conditions are the factors which determine which type of a coating will be obtained.

The cathodes are made of copper electrolitical plates (99.99%), which are submitted to mechanical smoothing and chemical preparation. Electrochemical chromium coatings were deposited galvano-staticaly from bath I (250 g/dm³ CrO₃ + 2.0 g/dm³ H₂SO₄), are then deposited on the cathodes prepared in this way, also from bath II (250 g/dm³ CrO₃ + 2.5 g/dm³ H₂SO₄), and from bath III (250 g/dm³ CrO₃ + 3.0 g/dm³ H₂SO₄), at current densities of 10 A/dm², 15 A/dm² and 30 A/dm². Deposition was performed for 5, 10 and 15 minutes intervals in all three baths and for all three current densities. The difference in samples mass before and after electrochemical deposition was measured on the analytical scale.

Cathodic current efficiency, the coating thickness and deposition rate increase with the increase of acid concentration, current density and deposition time. The average deposition rates are appro-ximately the same for baths II and III, for the same deposition time, at the same current densities. This shows that the increase of the concentration of sulphuric acid above 2.5 g/dm³ is not justifiable. The ratio of these parametres, according to the quantity of the sulphuric acid used is the best for bath II, which makes deposition of electrochemical chrome coatings from this bath most profitable, from the aspect of current efficiency, deposition rate, coatings quality and chemicals consumption of bath.

Key words: *catalytic effect, coating thicknes, current density, electrochemical chromium coatings, electrochemical deposition.*

INTRODUCTION

Applying coating for protection or decorations, most frequently on metal objects, is done by electrolytic deposition.

By applying a relatively thin layer, the product with significantly altered characteristics of the surface is obtained. That provides production of some objects from cheaper metals and alloys, which physical - chemical properties and aesthetic appearance are latter improved by coating with suitable metal or alloy.

Because of destinguished properties of chromium coatings, their application is very common in practice. Chromium coatings are resistant toward atmospheric corrosion at normal and elevated temperatures, they are very compact and wear resistant, have low coefficient of friction and could be obtained bright and without previous treatment.

Author's address: [1]University of Eastern Sarajevo, Faculty of Technology Zvornik, Republic of Srpska, [2]Univesrity of Belgrade, ICTM – Centre for Electrochemistry, Belgrade, Serbia

Thanks to these characteristics, there are three types chromium coatings [1-7]:

1. Decorative chromium coatings, which are usually applied on coating of copper, nickel, zinc and brass in order to decorate object and protect it from corrosion;

2. Hard chromium coatings, which aim is to increase the durability of the object surface that are exposed to wear (pistons, cutting tools, etc.) or such coatings are used for battered parts of machinery or tools in order to bring them into original measurment (state). Electrolytes for deposition of hard chromium coatings were similar to those for bright chromium plating, except that concentrated solutions are not used. Baths for hard chromium coatings, unlike the bath for protective - decorative chromium plating, must be designed for work at high current densities, which are able to provide considerable deposit thickness, and extraordinary hardness;

3. Porous chromium coatings, which are intended for surfaces (in whose exploatation oils have to be used)) which in exploatation must be lubricated by oil.

Quantitative composition of the bath and working conditions determine the type of coating. During

experimental part of this paper three baths of different contents of sulphuric acid were examined, that have a catalytic effect during chromium deposition [8-11].

The aim of this study was to examine the effect of concentration of catalyst, current density and deposition time on current efficiency, the thickness of chromium plating and electrochemical deposition speed.

EXPERIMENTAL PART

For electrochemical deposition of chromium coatings three baths were used whose quantitative composition differ in concentration of sulphuric acid, while the concentration of CrO_3 was the same in all three baths:

Bath I: $250 \ g/dm^3 \ CrO_3 + 2.0 \ g/dm^3 \ H_2SO_4$
Bath II: $250 \ g/dm^3 \ CrO_3 + 2.5 \ g/dm^3 \ H_2SO_4$
Bath III: $250 \ g/dm^3 \ CrO_3 + 3.0 \ g/dm^3 \ H_2SO_4$

In preparation of the baths analytical grade purity chemicals and distillated water were used. Electrochemical chromium coatings are deposited galvanostaticaly for 5min, 10 min and 15 min at current densities of $10 \ A/dm^2$, $15 \ A/dm^2$ and $30 \ A/dm^2$ at temperature 45˚C. As an anode the Pb-Sb over the wall of electrochemical cell, volume $0.5 \ dm^3$ was used. As cathode copper electrolitical plates (99.99%), dimensions (3x3x0.05)cm were used. All plates were prepeared in the same way, because the

quality of the deposited coatings differ from sample preparation: degreasing in alkaline medium at a temperature of 70˚C, rinsing with flowing water, mechanical polishing by abrasive agency at room temperature, then rinising by flow and distilled water, etching in concetrated nitric acid ($HNO_3:H_2O = 1:1$) for 5 seconds, and rinsing with flow water and distilled water. Mechanical polishing of copper plates composited of wet grinding silico-carbide emery paper with a finess of: 320, 500 i 1.000, and then fine grinding with water suspension of surface active mean for grinding „Extra Polish". Suspension was applied on polishing cloths.

On such prepared samples electrochemical chromium coatings were deposited. After electrochemical deposition of chromium coatings, the samples were thoroughly rinsed in the flowing and distilled water and then dried by hot air for 10 minutes.

RESULTS AND DISCUSSION

In tables 1-3, an overview of the results obtained by electrochemical deposition of cromium coatings from tested baths is given. As already mentioned above, the deposition time of coatings was 5, 10 and 15 minutes, at a temperature of 45˚C and cathodic current densities of $10 \ A/dm^2$, $15 \ A/dm^2$ and $30 \ A/dm^2$.

Table 1 - Results of chromium coatings deposited from bath I: $250 \ g/dm^3 \ CrO_3 + 2.0 \ g/dm^3 \ H_2SO_4$

Bath I ($250 \ g/dm^3 \ CrO_3 + 2.0 \ g/dm^3 \ H_2SO_4$)									
Current density, j (A/dm^2)	10			15			30		
Time, τ (min)	5	10	15	5	10	15	5	10	15
Mass yield, Δm (g)	0,001	0,003	0,014	0,008	0,022	0,034	0,027	0,049	0,084
Current efficiency, η (%)	2,07	3,03	9,64	11,05	14,84	15,59	18,65	16,53	19,26
Average current efficiency, η_{av} (%)	4,91			13,83			18,15		
Coating thickness, d (μm)	0,076	0,226	1,058	0,605	1,663	2,570	2,041	3,704	6,350
Deposition speed, v (μm/min)	0,015	0,023	0,071	0,121	0,166	0,171	0,408	0,370	0,423
Average deposition speed, v_{av} (μm/min)	0,036			0,153			0,400		

Table 2 - Results of chromium coatings deposited from bath II: $250 \ g/dm^3 \ CrO_3 + 2.5 \ g/dm^3 \ H_2SO_4$

Bath II ($250 \ g/dm^3 \ CrO_3 + 2.5 \ g/dm^3 \ H_2SO_4$)									
Current density, j (A/dm^2)	10			15			30		
Time, τ (min)	5	10	15	5	10	15	5	10	15
Mass yield, Δm (g)	0,005	0,013	0,020	0,011	0,021	0,036	0,032	0,060	0,084
Current efficiency, η (%)	10,36	13,15	13,76	15,20	14,16	16,51	22,10	20,24	19,26
Average current efficiency, η_{av} (%)	12,42			15,29			20,53		
Coating thickness, d (μm)	0,378	0,983	1,512	0,831	1,587	2,721	2,419	4,535	6,349
Deposition speed, v (μm/min)	0,076	0,098	0,101	0,166	0,159	0,181	0,484	0,454	0,423
Average deposition speed, v_{av} (μm/min)	0,092			0,169			0,454		

Table 3 - Results of chromium coatings deposited from bath III: 250 g/dm^3 CrO$_3$ + 3.0 H$_2$SO$_4$ g/dm^3

Bath III (250 g/dm^3 CrO$_3$ + 3.0 g/dm^3 H$_2$SO$_4$)									
Current density, j (A/dm^2)	10			15			30		
Time, τ (min)	5	10	15	5	10	15	5	10	15
Mass yield, Δm (g)	0,005	0,012	0,023	0,012	0,025	0,035	0,030	0,063	0,081
Current efficiency, η (%)	10,36	12,14	15,82	16,58	16,86	16,05	20,72	21,25	18,58
Average current efficiency, η$_{av}$ (%)	12,77			16,49			20,18		
Coating thickness, d (μm)	0,378	0,907	1,738	0,907	1,890	2,646	2,268	4,762	6,122
Deposition speed, v (μm/min)	0,076	0,091	0,116	0,181	0,189	0,176	0,454	0,476	0,408
Average deposition speed, v$_{av}$ (μm/min)	0,094			0,182			0,446		

The efficiency of deposition of chromium coatings increases with the incrase of current density deposition, and deposition speed of metal ions on chatode is faster, once it comes to nucleus growth. This probably explains deficiency and growth of crystallizing centers in these conditions. Second phase of deposition implies renucleation at the starting surface, or the already exsisting nuclei. The result of the further growth is well defined crystal forms which can hold on during increase of depostion time [5].

Figure 1 (a-c) shows the effect of concentration of catalyst (sulphuric acid) on current efficiency during electrochemical deposition of chromium coatings, in the function of current density and deposition time. Figure 2 shows the dependence of the average current efficiency on current density and catalyst concentration.
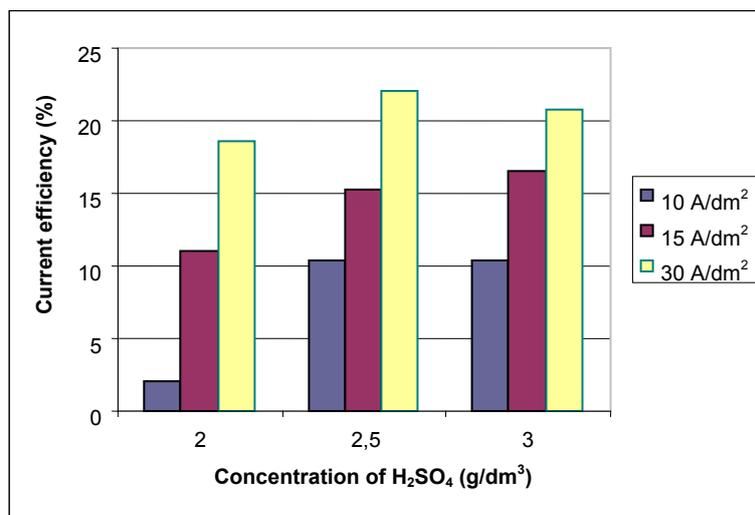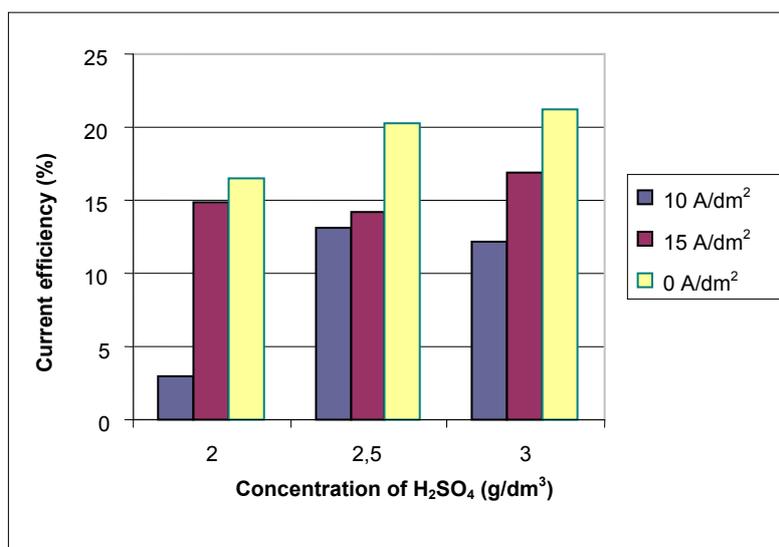

a)

Figure 1a - Dependence of current efficiency on sulphuric acid concentration with deposition time: a) 5 minutes

On figure 1a, it can be seen that for same deposition time, with increase in chatode current density at electrochemical deposition of chromium coatings, current efficiency rises. The same conclusion can be drown from Figures 1 b,c.

It is known that throwing power of electrolyte for chroming is very bad. At the same time it implies low current efficiency. The best substrate cover is obtained when a good ratio of chromic acid anhydride (CrO$_3$), sulphuric acid catalyst (H$_2$SO$_4$), bath temperature and anode position (which has to be designed in accordance with the shape of object on which the chromic coatings are deposited), is found. In order to satisfy above mentioned requirements, trying to get an answer, how to obtain satisfactory coating, electrolyte stability and maximum current efficiency in constant (tested) conditions of electrolysis.

b)
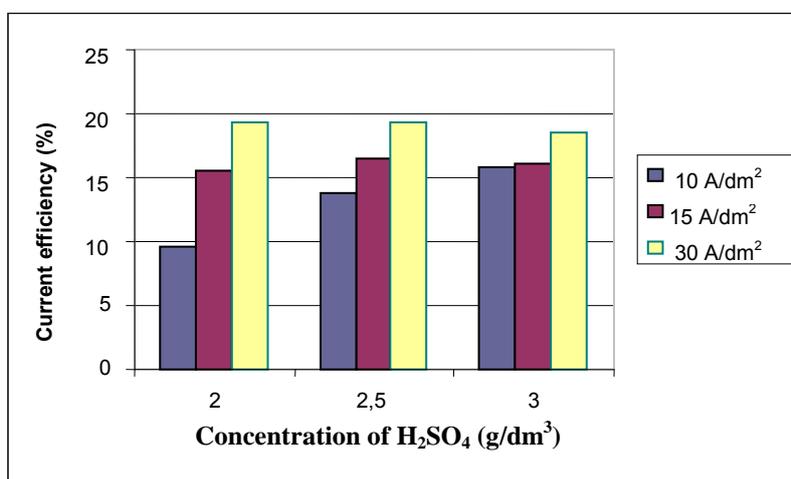
c)

Figures 1 b, c - Dependence of current efficiency on sulphuric acid concetration with deposition time: b) 10 minutes; c) 15 minutes

Besides, by changing set parameters, an answer is tried to be given, what is the role of catalyst, why does the current efficiency vary with current density, that is what is the best ratio of $CrO_3:H_2SO_4$ for given conditions. In other words why the same catalyst, introduced in electrolyte in such a small quantity, gives wide spread of scattered results.

From Figures 1 (a-c) can be concluded that the increase in current efficiency is expressed during shorter period of deposition. It is noticable a small increase in current efficiency, with increase in current density for deposition time of 15 minutes, while for deposition time of 5 minutes, this increase is significant for all three baths. The highest current efficiency is achieved in the bath II (22.10%), at the current density of 30 A/dm^2 and for deposition time of 5 min.

From Figure 2 it can be seen that the highest values of average current efficiency for all three baths are obtained for cathodic current density of 30 A/dm^2, and maximum value of the average current efficiency is for bath II, for current density also of 30A/dm^2 and it stands at 20.53%. This fact indicates that increase in concentration of sulphuric acid above 2.5 g/dm^3 is not justified, and that the optimal concentration of catalyst is 2.5 g/dm^3 compared to CrO_3 (250 g/dm^3). The obtained experimental results confirm the fact that the optimal ratio of CrO_3 and H_2SO_4 is 100:1 [1,5,6].
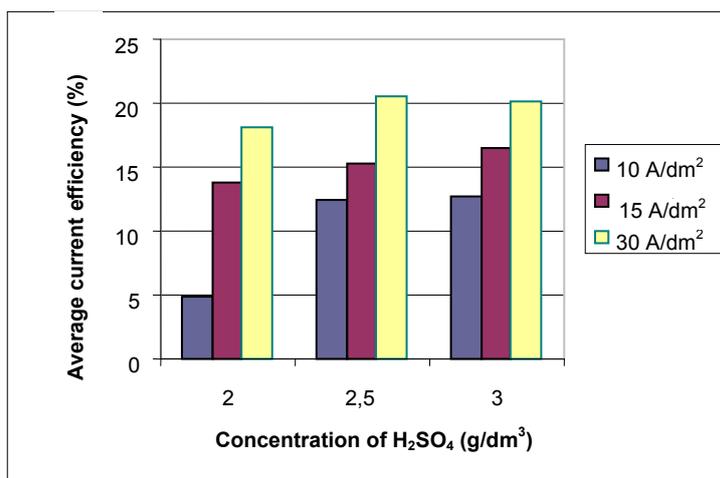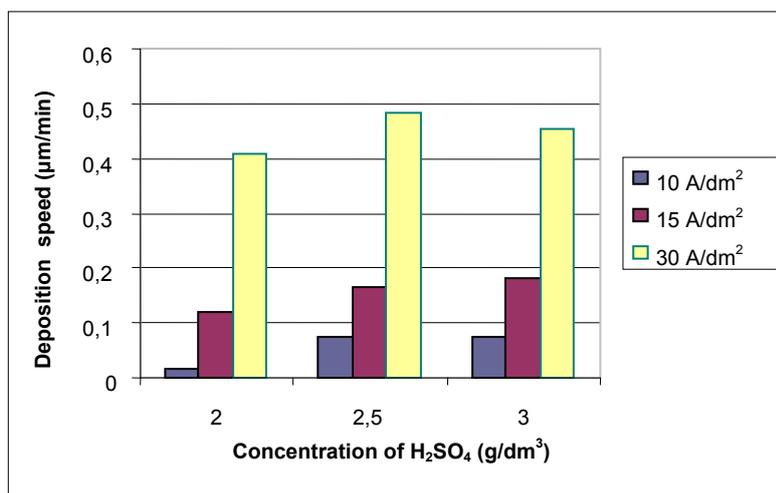
Figure 2 - Dependence of average current efficiency vs. catalyst concentration and cathodic current density

Based on the average current efficiency dependence on concentration of sulphuric acid, it can be seen that the bath II is the best, since it has the best ratio of current efficiency and the amount of used sulphuric acid.
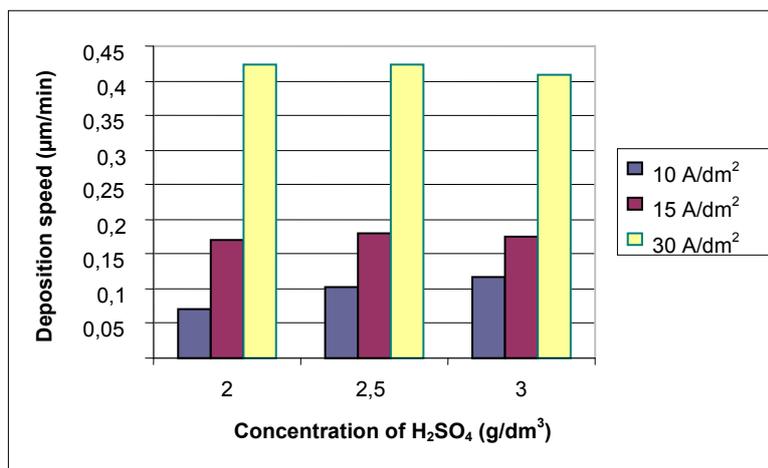

a)

Figure 3a - Dependence of deposition speed of chromium coatings on sulphuric acid concentration and current density for deposition time: a) 5 minutes
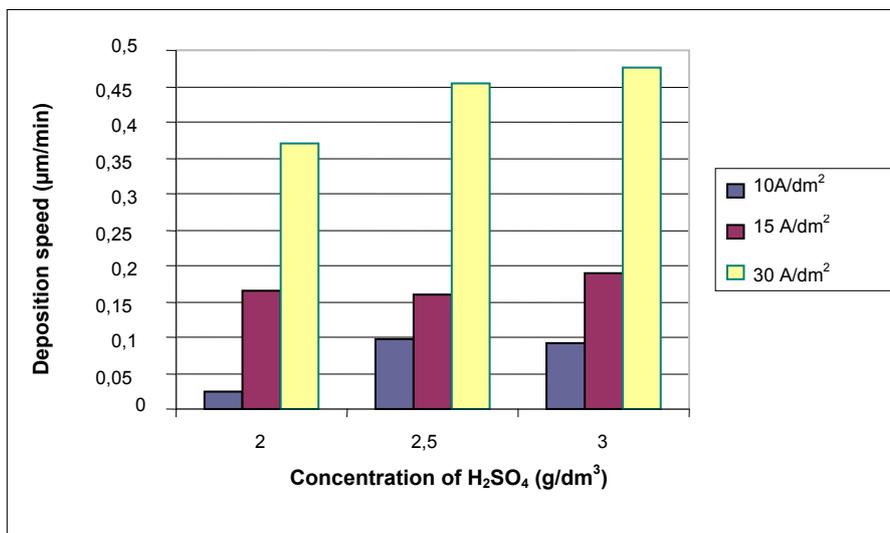
b)

c)

Figure 3 b, c. Dependence of deposition speed of chromium coatings on sulphuric acid concentration and current density for deposition time: b) 10 minutes c) 15 minutes

Figure 3 (a-c) shows the effect of sulfate content on the rate of chromium coatings deposition for all three baths, for different deposition time. Figure 4 presents the dependence of average depositon speed, for three times (5, 10 and 15 minutes), on concentration of sulphuric acid at different current densities.

Figure 3 (a-c) shows that speed of electrochemical deposition on chromium coatings is approximately the same for all baths, but for the current density of 30 A/dm^2 it is significantly higher compared to the other two values of cathode current density (10 A/dm^2 and 15A/dm^2).

Deposition time of electrochemical chromium coatings from all three baths, for current density of 30 A/dm^2 has no significant inffluence on the current efficiency. Analyzing obtained results, it can be concluded that deposition time has larger effect on current efficiency at lower current densities, while with its increasment, the electrolysis time slightly effects its efficiency.

As already pointed out, current efficiency for chromium baths is very small, compared to baths which owns most of the other metals. Usual chromium baths have current efficiency between 6 and 16%: more diluted baths have higher efficiency [5-7]. This is closely related to temperature of electrolyte and current density required to produce a satisfactory coating. Since in this paper the temperature of the baths was a constant value, it can be concluded that the experimental conditions could give the correct answer only for the specified operating parameters. Also, it is reasonable to assume that if higher current densities deposition are applied, it would require higher baths temperatures, in order to obtain a satisfactory coating. From the above mentioned, it follows that any concetration ratio of chromium anhydride and sulphuric acid „recommends" optimal temperature, which provides widest field of current density, and which gives „optimal" deposit.
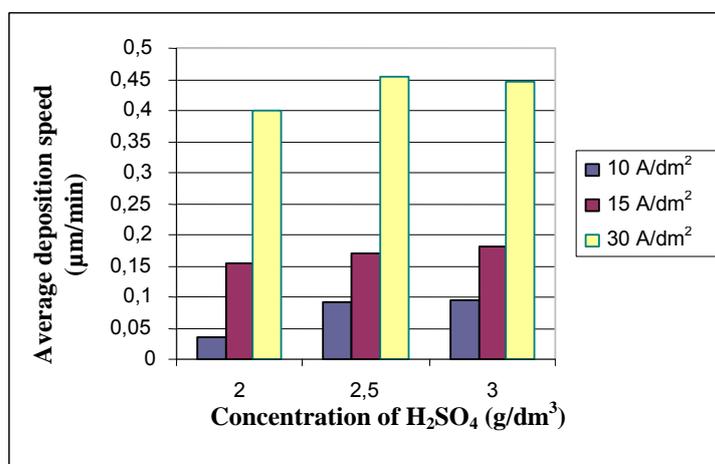

Figure 4 - Dependence of average deposition speed on sulphuric acid concentration for all three current densities

Based on dependence of average deposition speed on sulphuric acid concentration, it can be seen that deposition speed increases with increase in current density, regardless of bath that is beeing used (Figure 4). It can also be seen, that the average deposition speed are approximately the same for the baths II and III for the same deposition time, at the same current densities (i.e. at the same deposition conditions).
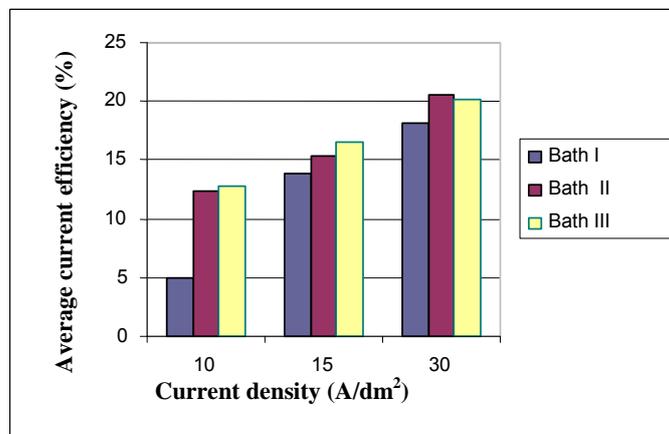

Figure 5 - Dependence of average current efficiency on current density for all three baths

Figure 5 presents the dependence of average current efficiency for all three times on concentration of sulphuric acid, for different current densities.

From Figure 5 it can be seen that with increase of cathodic current density, current efficiency increases for all three baths. The highest values of current efficiency are obtained by electrochemical deposition of chromium coatings at current density of 30A/dm^2 from bath II (20.53%) and bath III (20.18%). This data also leads to conclusion that the optimal concentration of catalyst (sulphuric acid) is 2.5 g/dm^3 and cathodic current density is 30 A/dm^2.

In Figure 6 it is shown dependance of average deposition speed for all three times of electrochemical deposition of chromium coatings in the function of current density.
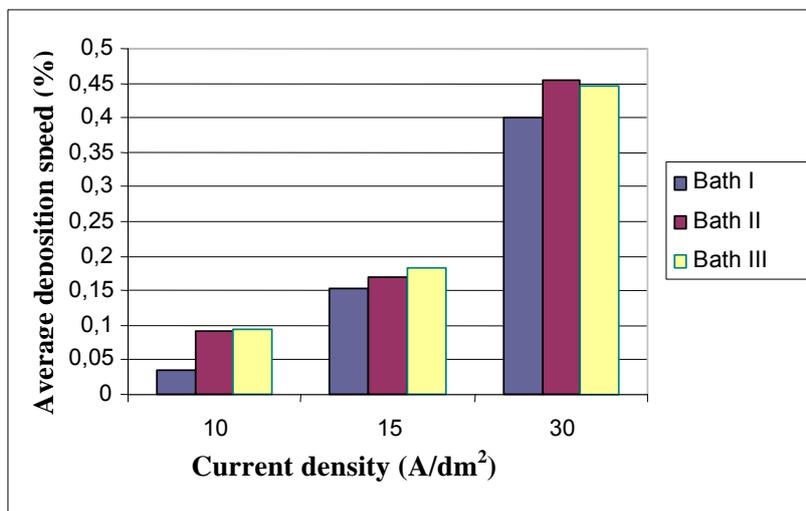

Figure 6 - Dependence of average deposition speed on current density for all three baths

With increase of cathodic current density, increases average deposition speed of electrochemical chromium coatings. Increase in average deposition speed is significantly higher at the current density of 30 A/dm^2 compared to the other two values (10 A/dm^2 and 15 A/dm^2). It can be concluded that by deposition of electrochemical chromium coatings, at current density of 30 A/dm^2, the best results are ac- hieved, that is the deposition speed is the greatest. It should be noted that the microscopic images of the chromium coatings surface (optical and SEM micro- scopy) were not given., but by visual observation of the surface of chromium coating, it can be concluded that the previous explanation is in good correlation with the bright mirror surface.

CONCLUSIONS

With increase of cathodic current density during deposition of electrochemical chromium coatings, for the same deposition time, the cathodic current efficiency increases. In lane with expectations, increase in current efficiency is more expressed at shorter deposition time. The highest current efficiency is recorded during deposition of coatings in bath II (22.10%) at current density of 30 A/dm^2 and deposition time of 5 minutes.

The highest values of average current efficiency for all three baths are obtained at cathodic current density of 30 A/dm^2, and maximum value of average current efficiency is in bath II, also at the current density of 30 A/dm^2 and it stands at 20.53%. This fact indicates that increase in concentration of catalyst (sulphuric acid) above 2.5 g/dm^3 is not justified and that the optimal concentration of sulphuric acid is 2.5 g/dm^3 compared to CrO$_3$ (250 g/dm^3).

Average deposition speed of electrochemical chromium coatings increases in all three baths, with increase in current density, regardless of the concentration of sulphuric acid. However, average deposition speeds are approximately the same for the baths II and III, for the same deposition time, at the same current densities. Therefore, in this case, optimal concetration of sulphuric acid is 2.5 g/dm^3.

Deposition time of electrochemical chromium coatings from studied baths, at current densities of 30 A/dm^2 has no significant impact on current efficiency. Deposition time has greater influence at lower densities, while with its increasment, the time of electrolysis slightly effects its efficiency.

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IZVOD

KATALITIČKI UTICAJ SUMPORNE KISELINE U PROCESU
TALOŽENJA PREVLAKA HROMA

Ispitivan je katalitički uticaj sumporne kiseline na iskorišćenje struje, debljinu i brzinu taloženja prevlaka hroma dobijenih elektrohemijskim putem. Zahvaljujući osobinama hroma razlikuju se tri vrste prevlaka: dekorativne, tvrde i porozne. Kvantitativni sastav kupatila i radni uslovi su faktori koji određuju koji tip prevlaka će biti dobijen.

Katode su bile od tehničkog bakra nepoznatog sastava, koje su mehanički glačane pa zatim hemijski pripremljene. Za elektrohemijsko taloženje prevlaka hroma, koje su taložene galvanostatski, ispitivana su tri elektrolita čiji se kvantitativni sastav razlikuje u koncentraciji sumporne kiseline, dok je koncentracija CrO$_3$ bila ista u sva tri kupatila i to: kupatilo I (250 g/dm^3 CrO$_3$ + 2.0 g/dm^3 H$_2$SO$_4$), zatim kupatilo II (250 g/dm^3 CrO$_3$ + 2.5 g/dm^3 H$_2$SO$_4$), i na kraju kupatilo III (250 g/dm^3 CrO$_3$ + 3.0 g/dm^3 H$_2$SO$_4$), pri gustinama struje 10 A/dm^2, 15 A/dm^2 i 30 A/dm^2.

Katodno iskorišćenje struje, debljina prevlaka i brzina taloženja se povećava sa povećanjem koncentracije sumporne kiseline, gustine struje taloženja i vremena taloženja.

Srednje brzine taloženja prevlaka hroma su približno iste za kupatila II i III, pri istim vremenima taloženja i pri istim gustinama struje. S tim u vezi, povećanje koncentracije sumporne kiseline iznad 2,5 g/dm^3 nije opravdano.

Odnos ovih parametara, prema koncentraciji sumporne kiseline, je najbolji za kupatiko II, koje daje optimalne prevlake hroma dobijene elektrohemijskim putem, u pogledu iskorišćenja struje, brzine taloženja, kvalitata prevlake i hemijskog sastava kupatila.

Ključne reči: *katalitički efekat, debljina prevlake, gustina struje, elektrohemijske prevlake hroma, elektrohemijsko taloženje*