ON THE EFFECT OF STIRRING ON THE PROPERTIES OF ELECTROLYTICALLY DEPOSITED Cr-Co PLATINGS

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Abstract: Chromium electroplating is one of the most important electrochemical processes. Due to the unique properties of chromium platings, this process is used very widely in various industries and in medicine. Cobalt, nickel and chromium alloys of the type Co-Ni-Cr-Mo-Fe, Ni-Cr, Co-Cr, etc., are used in dentistry and orthopedic surgery. The specific requirements to the properties of these alloys are very strict. It is, therefore, necessary to know the factors which have a significant effect on the properties of the alloys obtained.

The process of electrochemical deposition of chromium alloy platings is complex and very sensitive. It depends strongly on the operating conditions - temperature, current density, electrolyte composition, etc. We have already studied the effect of some factors - cobalt salt concentration, current density, nature of the cathode material. Stirring of the electrolyte is also very important for the structure and properties of the plating obtained. This study discusses that particular factor.

The effect of stirring of the electrolyte in the plating bath on the properties of Cr-Co alloys deposited by electrochemical crystallization using electrolytes of "Chromispel" type has been studied. To date, classical sulphate electrolytes are predominantly used for the production of electroplated chromium alloys. Their main disadvantage is the low cathode current yield - approximately 10%. "Chromispel" electrolytes are a new type of non-standard and more efficient electrolytes. Depending on the operating conditions and chromium anhydride concentration, the current yield is 30-60%. The deposition of the chromium platings studied was carried out using direct current in galvanostatic mode, on substrates of different nature (copper and steel), in a wide range of current densities and with various contents of $CoCl_2.6H_2O$. In order to study the effect of homogenization on the properties of chromium platings, stirring at a rate of 600-1,000 rpm was applied.

The changes in some of the properties of electrolytically deposited Cr-Co platings, such as texture of platings, internal stresses, reflectivity, surface morphology and cobalt content, were investigated. Conclusions have been made about this effect on the structure and the properties of the deposited platings.

Keywords: chromium plating, electroplated Cr-Co alloys, "Chromispel" electrolytes

INTRODUCTION

Chromium alloys of the type Co-Ni-Cr-Mo-Fe, Ni-Cr, Co-Cr, etc., are widely used in industry, medicine and dentistry. The specific requirements to the properties of these alloys are very strict. It is, therefore, necessary to know the factors which have an effect on the properties. We have already studied the effect of some factors - cobalt salt concentration, current density, nature of the cathode material.

Homogenization of the electrolyte is also very important for the structure and properties of the plating obtained. This study discusses that particular factor.

The effect of stirring of the electrolyte in the plating bath on the properties of Cr-Co alloys deposited by electrochemical crystallization using electrolytes of "Chromispel" type has been studied. The changes in some of the properties of electrolytically deposited Cr-Co platings, such as phase composition and texture of platings, internal stresses, reflectivity, surface morphology and cobalt content, were investigated. Conclusions have been made about this effect on the structure and the properties of the deposited platings.

MATERIALS AND METHODS

The deposition of the chromium platings studied was carried out using direct current in galvanostatic mode, on substrates of different nature (copper and steel), in a wide range of current densities and with various contents of $CoCl_2.6H_2O$.

The *"Chromispel"* electrolytes used contain chromic anhydride and halide anions. Additional anions were introduced into the electrolyte by $k.\ HI$ or $k.HCl$.

In order to study the effect of homogenization on the properties of chromium platings, stirring at a rate of 600-1,000 rpm was applied.

Reflectivity data was obtained using a Lange type gloss meter. The root mean square roughness and grain size were determined using a high-power electron microscope. Internal stresses were determined by the bending cathode method and their values were calculated using the Stoney equation. The percentage composition of cobalt in the platings was determined using the instrument **Fischerscope® X RAY XDAL.** The texture of metal chromium deposited was examined using a texture diffractometer, by the Schulz method, under different electrolysis conditions.

RESULTS

1. Phase composition and structure of alloy chromium platings

Regarding the phase composition of chloride chromium platings deposited using "Chromispel" electrolytes, it was found that only $\alpha - Cr$ is deposited (1).

By X-ray analysis of crystal structure, we determined the lattice constant "a". The data shows that stirring of electrolyte has almost no effect on the numerical values of the parameter "a". They are the ones typical of stable crystalline modification $\alpha - Cr$ - Table 1.

Table 1. *Data from X-ray analysis of Cr-Co platings deposited using modified "Chromispel" electrolyte with and without stirring of the electrolyte*

No.	$CoCl_2.6H_2O$ $g.L^{-1}$	I, $A.dm^{-2}$	stirring	Co %	Lattice constant, Å
1	3	15	no	0.172	2.888
2	3	15	yes	1.140	2.885

2. Texture

For standard sulphate electrolytes at room temperature 18-20°C, a texture axis <001> was recorded, and at 50-80°C the orientation of platings was on axis <111>. For a body-centered cubic lattice, a texture axis <001> was detected (2).

Our studies show that platings deposited by "Chromispel-C" electrolytes at lower densities (from 15 $A.dm^{-2}$ to 50 $A.dm^{-2}$) and with small thickness in the range of 0.5 - 3 μm have a predominant orientation on texture axis <011>. We found that stirring does not affect the texture axis - Fig. 1.

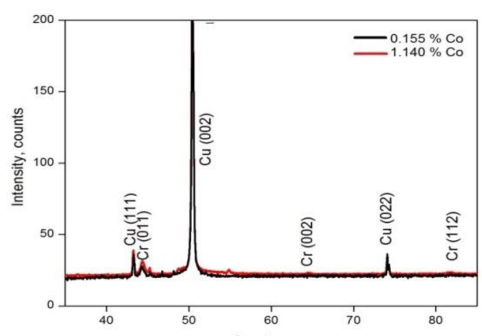

Fig. 1. *X-ray diffraction patterns of chromium platings deposited under different electrolysis conditions with and without stirring of the electrolyte.*

3. Internal stresses

Chromium platings are characterized by high internal stresses. These result from structural transformations associated with the transition of unstable crystalline modification into stable.

The internal stresses we determined in the chloride chromium layers are shrinkage stresses, i. e. /-/. A criterion for this is the observed effect of bending of the flexible cathode towards the anode.

The effect of stirring is contradictory. For electrolytes containing 1-3 $g.L^{-1}$ $CoCl_2.6H_2O$, it is favourable and reduces internal stresses. However, an adverse effect is observed with 5 $g.L^{-1}$ $CoCl_2.6H_2O$ - Fig. 2.

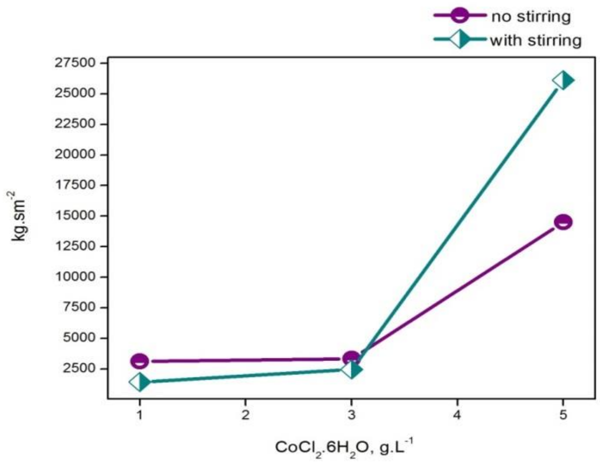

Fig.2. *Relationship between internal stresses and stirring.*

4. Surface morphology and reflectivity

According to (3), the surface of a glossy chromium plating looks dense and smooth to the naked eye. However, when observed under a microscope, it features characteristic cones and micro cracks. This can be explained by the presence of unstable chromium hydrides formed in the electrocrystallization process. Some of these crystallize in the form of unstable hexagonal crystals Cr_2H-CrH, while others - in the form of face-centered cubic CrH-CrH_2 structures. Part of the hydrogen escapes, while another part is included in the plating and changes its structure and properties. Table 2 shows the relationship between roughness class and reflectivity.

Table 2. *Roughness class and reflectivity of coatings deposited for a period of 5 minutes with* $i_k = 35A.dm^{-2}$ *and different concentrations of* $CoCl_2.6H_2O$

No.	$CoCl_2.6H_2O$, $g.L^{-1}$	S_q *nm*	Grain size, *nm*	δ %	Note
1	1	5.84	458.60	87.5	without stirring
2	3	6.80	1,122.00	76.04	
3	5	10.88	1,280.00	25.56	
4	1	6.11	658.20	77.92	with stirring
5	3	11.35	674.60	64.24	
6	5	14.61	1,140.00	20.28	

The diagrams and 3D images in Fig. 3 and Fig. 4 show the root mean square roughness of platings obtained from compositions containing 5 $g.L^{-1}$ $CoCl_2.6H_2O$. With stirring of the electrolyte, the layers become more rough - Fig. 4.

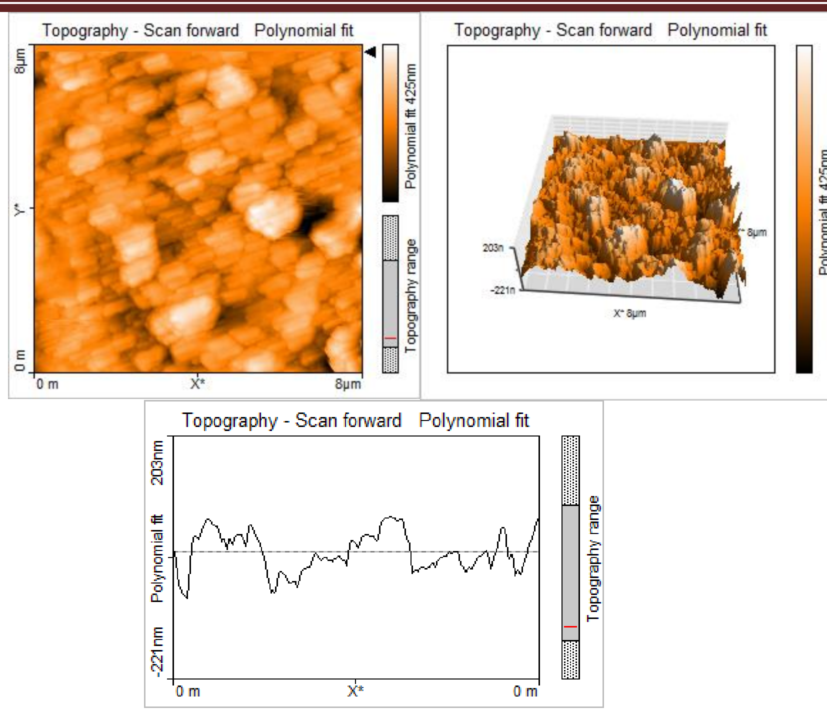

Fig. 3. *S_q values for platings deposited without stirring, S_q= 10.88 nm.*

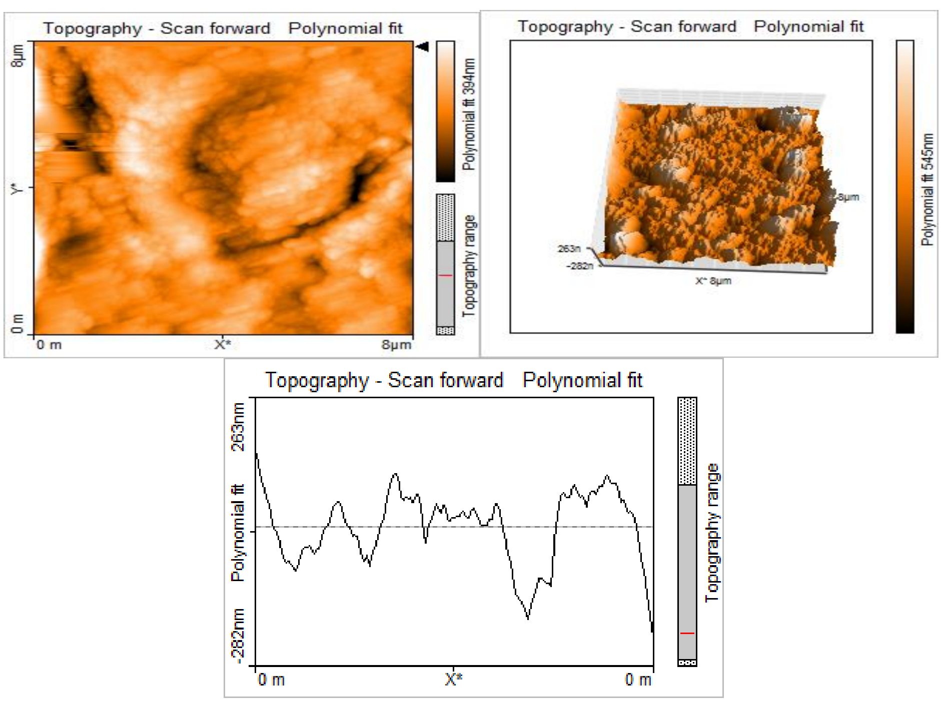

Fig. 4. *Sq values for platings deposited with stirring, Sq = 14.61 nm.*

5. Cobalt content in alloy chromium platings

Literature and practical experience show that stirring of electrolyte results in predominant deposition of the more electropositive metal (4). If the modified "Chromispel" electrolyte is subject to stirring, platings with a lower cobalt content are deposited when using compositions containing 1 $g.L^{-1}CoCl_2.6H_2O$. The other electrolytes with 3-

5 g.L^{-1} $CoCl_2.6H_2O$ show different behavior - with them, the cobalt content in the alloy increases. Cobalt content is highest in samples plated at a density of 40 A.dm^{-2} from electrolyte with 5 g.L^{-1} $CoCl_2.6H_2O$.

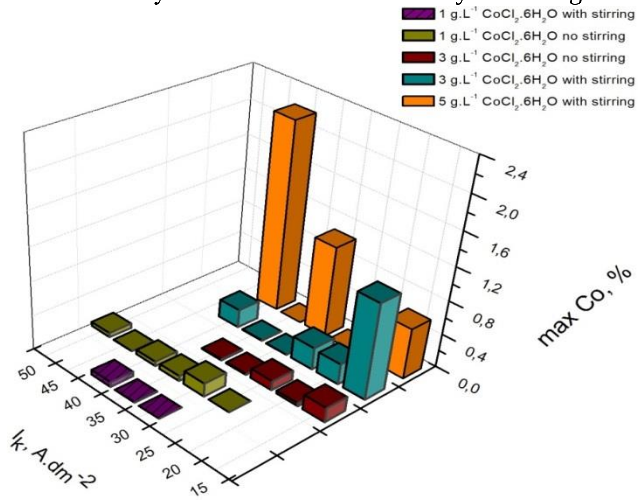

Fig. 5. *Effect of stirring on cobalt content in platings.*

Using fluorescence analysis, it has been shown that the effect of stirring is controversial - the compositions containing 1 g.L^{-1} $CoCl_2.6H_2O$ deposited coatings with low cobalt content, and other electrolytes with 3-5 g.L^{-1} $CoCl_2.6H_2O$ increase the inclusions of cobalt. Cobalt content is highest in samples plated at a density of 40 A.dm^{-2} from electrolyte with 5 g.L^{-1} $CoCl_2.6H_2O$

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