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Nanocomposite chromium coatings on aluminum alloys

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Abstract

Chromium coatings modified with nanodiamond particles were deposited on aluminum alloys. The concentration of the nanodiamond particles in the chrome plating electrolyte was from 5 to 25 g/l. The thickness of the layer varied between 30 and 70 µm. The layers were prepared with the same electrolytic conditions and were measured with a metallographic microscope. The maximum microhardness of the coating was 840 kg/mm². X-ray diffraction analysis was performed with a Siemens D500 apparatus using the Bragg-Brentano technique. The distribution of Cr, Al and O in the cross section was studied by SEM-EDS. It was found that the layers were homogenous - only consisted of chromium. The coatings were also studied for non-destructivity by X-ray 3D computed tomography. It was found that the coatings were intact and continuous along the section. In order to obtain the maximum yield of chromium and maximum thickness of the layer, the optimum nanodiamond particle concentration was 10 g/l.

<u>Keywords</u>: chromium coating, aluminum, nanodiamond particles, electrochemical plating

1. Introduction

Aluminum is an easily oxidized metal so generally there is an oxide, AI_2O_3 , layer on its surface, strongly bonded to the matrix. The free energy formation of AI_2O_3 , $G^0_{298} = -1582.94$ kJ/mol shows high stability, therefore low reducibility of this oxide layer. An additional difficulty is a significant hydrogen overvoltage on the aluminum surface during electroplating of metals from acidic electrolytes. Due to these difficulties, an intermediate layer must be applied on the aluminum surface before metals such as chromium, nickel and the like are electrochemically deposited. Most often this intermediate layer is copper or copper containing alloys [1]. Applying coatings of chromium, nickel, etc., on aluminum alloys increases their hardness, wear and corrosion resistance [2]. This combines the high chemical and mechanical properties of the metal coating with the low weight of aluminum products, which is particularly important for engineering design [3].

The objective of the present study was to study the characteristics and properties of chromium coating, modified with nanodiamond particles, deposited on an aluminum alloy.

2. Experimental

The samples were of aluminum alloy grade 2017 - T451 of chemical composition shown in Table 1.

Table 1. Chemical composition of aluminum alloy grade 2017 - T451, wt. %

| Si | Fe | Cu | Mg | Cr | Zn | AI |
|------|------|------|------|------|------|---------|
| 0.40 | 0.34 | 3.96 | 0.63 | 0.02 | 0.13 | Balance |

The samples were cylindrical with dimensions diameter/height: 6/60 mm. They were degreased successively in 1.2 $C_2H_4Cl_2$ and C_2H_5OH , then weighed and measured. Prior to galvanization they were etched by treating with acidic mixtures of different compositions, but always containing toxic HF. A systematic cleaning process of the surfaces of the samples, with sufficient reproducibility, was developed. It resulted in modified with nanodiamonds electrochemical chromium coating adhereing well to the matrix.

The chromium electrolyte was standard composition: $\text{CrO}_3 - 220 \text{ g/l}$ and $\text{H}_2\text{SO}_4 - 2.2 \text{ g/l}$. The nanodiamond particles were produced by detonation synthesis (NDPs). Their grain size varied from 4 to 40 nm. NDPs are added to the electrolyte as an aqueous suspension after ultrasonic activation treatment in order to obtain a dense composite coating. The current densities were in the range of 40–60 A/dm². The galvanization was carried out for 65 minutes using a lead anode. The temperature of the electrolyte was 50–55°C. The galvanization parameters were constant.

3. Results and discussion

The microstructure and the microhardness of the coatings were examined by a metallographic method. The thickness of the layer was measured by Olympus Image System for Quantitative Analysis. The average coating thickness was 40 μ m (Fig. 1).

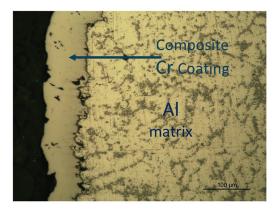


Fig. 1. Microstructure of electrodeposited composite chromium and NDPs coating

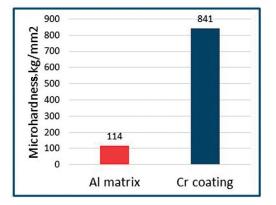


Fig. 2. Comparison of the microhardness of the composite chromium coating and the aluminum matrix

The coatings were well formed, visibly tightly adhering to the matrix, e.g. Figure 1. The microhardness was measured with a Micro-Duromat 4000 testing device at a load of 10 g and time 10 s (Fig. 2). The average microhardness was 114 kg/mm² and 840 kg/mm², for the matrix and the layer, respectively. This means that the increase of the hardness was 7.4 times.

The phase compositions of the coatings were examined by X-ray Bragg-Brentano diffraction technique using Siemens D 500 diffractometer. The phase composition of the composite coatings remains constant with increasing concentration of nanodiamond particles in the electrolyte (Figs. 3a-c). The phases in the layer were Cr and Al. According to the phase diagram of the Cr-Al system [4] Al and Cr form several intermetallics. There is an eutectic mixture of the solid solution of Cr in Al and CrAl, phase present in the zones rich in AI. The AI content in the eutectic is 0.4 at. %. Al and Cr have face cubic centered (fcc) and body centered cubic (bcc) crystal lattices, respectively. The parameters of the crystal lattice of Al and Cr in the composite coating were measured. They have the following average values: for fcc Al lattice, a =0.2883 nm and for bcc Cr lattice, a = 0.4044 nm. These differences make it difficult to plate aluminum directly with chromium. The composite coating (Cr + NDPs) has good adhesion to the substrate. The thickness of the layer can reach as much as 75–80 µm (Fig. 4). The stable deposition of the composite coating on the aluminum alloy is due to its chemical and phase compositions. The aluminum is alloyed with about 4 wt. % copper (0.089 at. %). It is located in the eutectic zone Cu in Al solid solution and the Al₂Cu phase according to the Cu-Al phase diagram [4].

3D X-ray tomography image of the composite coating (Cr + NDPs) on an aluminum sample is shown in Figure 4. The coating is intact and continuous along the section. Its thickness is about 70 μ m.

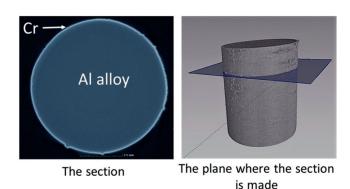


Fig. 4. X-ray tomography of aluminum item coated with the composite chromium coating

The morphology and the depth distribution of Cr and Al in a layer was investigated by SEM-EDS technique. The coating was prepared by an electrolyte with 10 g/l

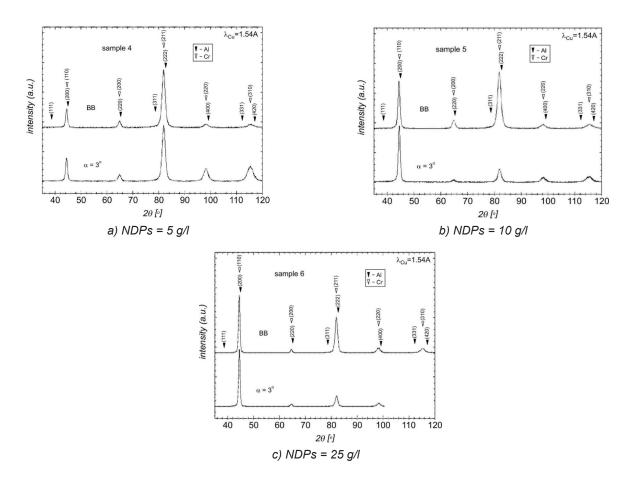


Fig. 3. X-ray diffraction analysis of electrodeposited chromium coating with different concentration of nanodiamond particles in the electrolyte

content of NDRs. The concentrations of chromium and aluminum have constant values over the entire thickness of the layer (Fig. 5). On the surface of the aluminum sample the concentration of Cr decreases and that of Al increases. The changes in their concentrations are not abrupt; they are of a diffusive character. The concentration of oxygen is almost zero, which shows that the surface of the aluminum is not oxidized. This determined the good adhesion of the chromium coating to the surface of the aluminum alloy.

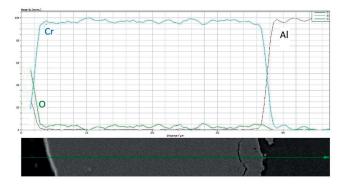


Fig. 5. Distribution of Cr, Al and O across the electrodeposited composite chromium coating

Dry friction wear resistance of the composite coating was investigated by block-on-ring tester and was measured by the loss of mass of the sample [5]. The composite coatings (Cr + NDPs) were prepared with contents of diamond nanoparticles in the electrolyte of 5, 10 and 25 g/l and the same galvanization parameters. The composite chromium coating possessing the highest dry friction wear resistance was deposited with electrolyte containing NDPs – 10 g/l (Fig. 6).

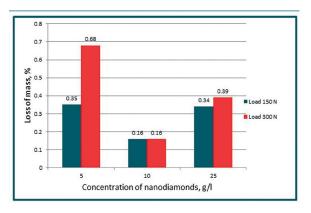


Fig. 6. Wear resistance at dry friction of electrodeposited chromium coating with different concentrations of nanodiamond particles in the electrolyte

4. Conclusions

- 1. The presence of nanodiamond particles in the electrolyte facilitates the process of chromium deposition on aluminum items.
- 2. The chromium coating adheres very well to the aluminum substrate with thickness of up to 70–80 $\mu m.$
- 3. The chromium coating increases wear resistance and improves friction of the aluminum products.
- 4. New applications are possible using lightweight aluminum combined with the durability of a hard chromium coating.

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