



# Electrodeposition of Cr–Al<sub>2</sub>O<sub>3</sub> Nano-composite Coatings from Trivalent Chromium Bath: Evaluation of Current Efficiency and Electroplating Characteristics

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## ABSTRACT

Nano-composite Cr–Al<sub>2</sub>O<sub>3</sub> coatings with different molar ratios were co-deposited from trivalent chromium baths containing Al<sub>2</sub>O<sub>3</sub> nanoparticles via conventional electrodeposition technique. Effects of bath concentration and average current density on deposition efficiency and coating composition were determined. With a low Al<sub>2</sub>O<sub>3</sub> bath composition, the Al<sub>2</sub>O<sub>3</sub> distribution in the coatings was uniform. At high concentrations, the nano-particles were agglomerated on the surface. Cathodic current efficiency was increased with Al<sub>2</sub>O<sub>3</sub> bath concentration.

**Keywords:** Nano-composite; Trivalent chromium bath; Al<sub>2</sub>O<sub>3</sub> nano-particles; Electrodeposition

## INTRODUCTION

Electroplating is an appropriate method for co-deposition of metallic, non-metallic and polymeric fine particles into a metallic matrix to produce functional coatings. Particle-reinforced metal matrix composites commonly exhibit wide engineering applications due to their improved hardness, higher wear and corrosion resistance when compared to pure metals or alloys [1–8]. In recent years, successful co-deposition of ultra-fine particles such as metallic powders, hard oxides (like Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>), carbides (like WC and SiC), diamond and polymers with metal or alloy matrices have been practiced and their corresponding structures and properties extensively have been investigated [3–5,9].

Traditional chromium coatings electroplated from Cr(VI) baths have been widely used for decoration, abrasion prevention, corrosion exclusion and hardness enhancement [10,11]. Electrodeposition of Cr(VI) needs to be substituted for its high toxicity and carcinogenicity by other non-toxic ions [10–14]. Chromium plating from trivalent baths has received renewed interest because of domestic regulations prohibiting discharge of toxic hexavalent chromium ions into the waste streams. In the United states, Cr(VI) will be completely banned from industry by 2010 and also In the European Union, the “waste of electric and electronic equipment” (WEEE) and “restriction of the use of certain hazardous substances in electrical and electronic equipment” (RoHS) directives have been passed to restrict the use of certain hazardous substances including Cr(VI) in electrical and electronic equipment. Countries such as China and Japan have also passed some corresponding directives to restrict the use of Cr(VI) [2,11]. The main advantage of trivalent chromium plating bath is the existence of non-toxic Cr<sup>3+</sup> ion. As is reported in the literature, thick trivalent chromium deposits cannot easily be obtained. The maximum chromium thickness achieved from the commercial trivalent baths is generally less than 10 μm, making the deposit undesirable as a hard and wear-resistant layer suitable for functional applications [14].

During past decades, many researches have concentrated on deposition of composite coatings with improved mechanical, corrosion and tribological properties, but very few have investigated co-deposition of composite coatings from trivalent chromium baths. In this study, the electrolytic co-deposition of nano-sized Al<sub>2</sub>O<sub>3</sub> particles from trivalent chromium bath to disperse into a chromium matrix is investigated. Hardness, wear resistance and morphology of the electrodeposited chromium composite are all strongly influenced by the amount of ceramic particles embedded within the chromium layer. The Al<sub>2</sub>O<sub>3</sub> layer content, efficiency of the current and microstructure of the coatings were of the most important parameters to be investigated. Pure chromium deposits were produced under the same experimental conditions for comparison.

## EXPERIMENTAL PROCEDURE

Table 1 illustrates the electrolyte composition and the operational conditions of the electrodeposition process performed in this research. Chromium and Cr–Al<sub>2</sub>O<sub>3</sub> composite coatings were electrochemically deposited from a trivalent chromium bath. The average size of the α-Al<sub>2</sub>O<sub>3</sub> particles added into the bath in these experiments was about 50 nm (α-Al<sub>2</sub>O<sub>3</sub>, Nanostructured & Amorphous Materials Inc.). The solution contained Al<sub>2</sub>O<sub>3</sub> particles ultrasonically dispersed for 15 minutes and then was stirred for 2 hours before the co-deposition process. During the co-deposition experiments, the bath was stirred out by a magnetic stirrer having a rate of 200 rpm in order to keep the particles dispersed and the possible sedimentation of the dissolved substances be prevented.

Copper plate with a hardness of 100 HV was used as the cathode. Before the deposition, the substrates were mechanically polished to 0.05–0.1 μm surface roughness. Before each experiment, the cathode was sequentially cleaned in ethanol and in a distilled water, activated in 5 wt% HCl solution for 20 seconds, washed in distilled water and then immediately immersed in the plating bath to allow the electrodeposition. A platinum plate was used as the anode. Areal ratio of anode to cathode was about 2:1 and the distance between the anode and the cathode was 2 cm.

## EXPERIMENTAL PROCEDURE CONT'D

A galvanostatic DC power supply was used in the experiments. The surface morphology of nano-composite coatings were observed by using field emission scanning electron microscopy (FESEM) and the percentage of the co-deposited Al<sub>2</sub>O<sub>3</sub> particles was evaluated by using energy dispersive X-ray spectroscopy (EDS) system attached to the scanning electron microscope (HITACHI model HIT-S4160 operated at 15 kV). All chemical compositions quoted in volume percentage represented the average of at least three measurements.

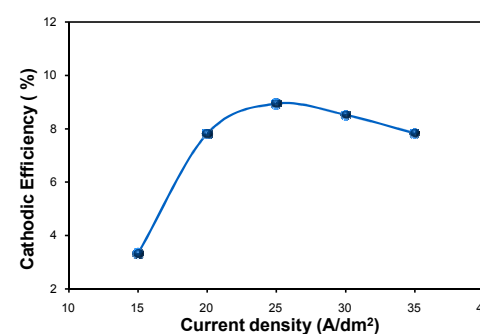
**Table 1.** Composition and deposition parameters of the nano-composite bath used in this research.

Solution composition	
CrCl <sub>3</sub> .6H <sub>2</sub> O	0.4 M/L
Glycine	0.5 M/L
H <sub>3</sub> BO <sub>3</sub>	0.5 M/L
NaCl	0.5 M/L
NH <sub>4</sub> Cl	0.5 M/L
NH <sub>4</sub> Br	0.2 M/L
AlCl <sub>3</sub> .6H <sub>2</sub> O	0.1 M/L
Electrodeposition conditions	
Al <sub>2</sub> O <sub>3</sub> powder	1 g/L
temperature	30 ± 1°C
pH	2.7
Electrolyte agitation	Magnetic stirring (200 rpm)
Current type	Direct (DC)

## RESULTS AND DISCUSSION

### 1. Effect of average current density on volume percent of alumina nano-particles

Fig. 1 indicates the variation of cathode efficiency of the chromium bath with current density. It can be seen that up to 25 A/dm<sup>2</sup>, the cathode efficiency increases with the current density. As the current density surpasses 25 A/dm<sup>2</sup>, the cathode efficiency for pure chromium deposition decreases. Current densities lower than 15 A/dm<sup>2</sup> were not considered in the present study due to the extremely slow plating rates they yielded.

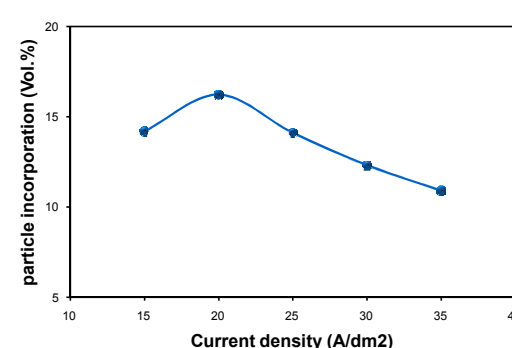


**FIGURE 1.** Effect of current density on efficiency of pure chromium cathodic deposition.

Figure 2 shows the relationship between the amount of incorporated alumina nano-particles and the average current density. It is observed that the volume percentage of the alumina nano-particles embedded into the composite coating increases initially with increasing of the average current density at lower current densities and reaches to its maximum at 20 A/dm<sup>2</sup>. This volume percentage decreases, however, when the average current density exceeds 20 A/dm<sup>2</sup>. To explain this effect, the Guglielmi's model [16] which is of the earliest ones, assumes that co-deposition is based on two successive adsorption processes:

- In the first step which has physical nature, the particles loosely connect to the cathode surfaces. These loosely adsorbed particles are in equilibrium with the particles in suspension which surround the adsorbed ions.
- In the second step, which is thought to be electrochemical in nature, the particles lose their ionic cloud and become strongly absorbed onto the cathodically deposited layer.

Generally, the step before the maximum strengthening of the adsorbed particles is the rate determining step. The amount of the incorporated alumina nano-particles in the composite coating throughout this step is small because of loose adsorption potential of the chromium electrodeposited layer. The cathode efficiency of the chromium deposition is very low during this step. After reaching the maximum particle incorporation, a loose adsorption will be the rate determining step again. When current density is greater than 20 A/dm<sup>2</sup>, the decreasing amount of the incorporated alumina nano-particles in the composite coating can be explained by the fact that an increase in the current density results in more rapid deposition of the metal matrix and fewer chance for the particle embedding into the coated layer.

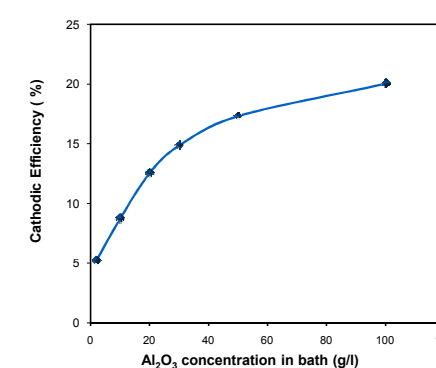


**FIGURE 2.** Effect of Current density on volume percentage of the alumina nano-particles incorporated in the Cr deposited layer.

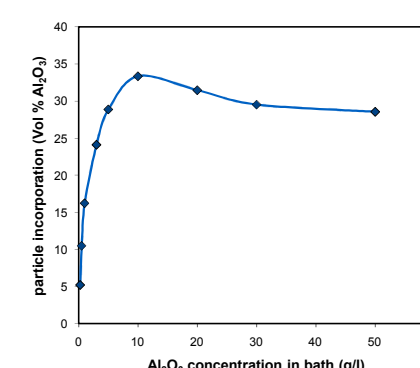
## RESULTS AND DISCUSSION CONT'D

### 2. Effect of Al<sub>2</sub>O<sub>3</sub> concentration of the bath on the cathodic efficiency and layer morphology

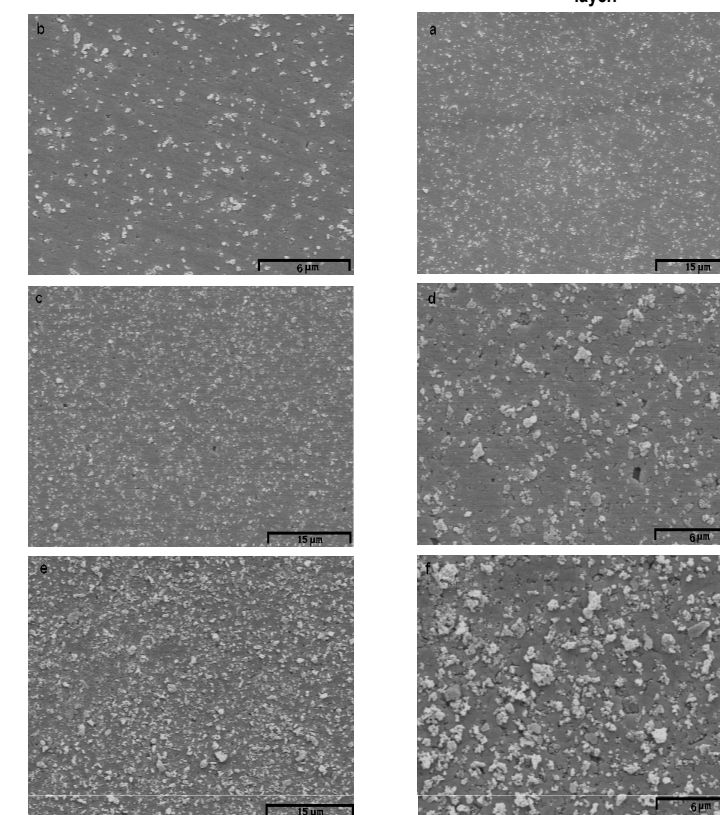
Fig. 3 shows the change of the cathodic efficiency with the bath concentration of the alumina nano-particles. When the alumina nano-particles collide at the cathode surface, the conditions for deposit formation are established and the cathodic efficiency increases. The alumina volume percentage in composite coating is plotted as a function of alumina concentration, stirring rate, current density and the bath temperature, as shown in Fig. 4. Morphology of the deposited layer is shown in Fig. 5 against the alumina content of the suspension.



**FIGURE 3.** The change in cathodic efficiency with addition of alumina nano-particles.



**FIGURE 4.** Relationship between the alumina contents of the suspension and of the composite layer.



**FIGURE 5.** SEM surface morphology of Cr–Al<sub>2</sub>O<sub>3</sub> composite coatings with different alumina content in the suspension: (a) and (b) 0.5 g/l; (c) and (d) 1 g/l and (e) and (f) 5 g/l.

## CONCLUSION

Cr–Al<sub>2</sub>O<sub>3</sub> nano composite coatings were deposited from the trivalent chromium baths under direct current conditions. The maximum cathodic efficiency was achieved at 25 A.dm<sup>–2</sup> for pure chromium coatings. It was observed that the content of the co-deposited Al<sub>2</sub>O<sub>3</sub> nano-particles can reach a maximum at 20 A.dm<sup>–2</sup>. The increase in the current density during the co-deposition process has two consequences: (a) the reduction of the loose adsorption coverage and (b) the higher probability of transfer from the loose adsorption step to the strong adsorption step. The existence of an optimum value for co-depositing of the Al<sub>2</sub>O<sub>3</sub> by increasing of the current density was attributed to the result of the decreasing trend in the loose adsorption coverage and increasing trend in the transference probability from the loose adsorption step to the strong adsorption step. It was found that the cathodic efficiency increased with increasing of the bath Al<sub>2</sub>O<sub>3</sub> concentration. The two-step co-deposition mechanism proposed by Guglielmi was valid in the ultra-fine Cr–Al<sub>2</sub>O<sub>3</sub> composite plating process which occurred in this research.

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