

Electrochemical deposition and characterization of Fe–Zn alloys

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ABSTRACT

Structural and microstructural characterization was performed on Fe- Zn thin films on aluminum oxide templates. Thin films have been prepared using an electrodeposition device with uniform cylindrical deposition ability. Plating baths, containing iron sulphate and zinc sulphate. The microstructural characterization and composition analysis were performed using SEM. Energy dispersive x-ray analysis of the deposit confirmed the presence of iron and zinc in the deposit. The results show that Fe-Zn alloys can be produced with good adhesive and anticorrosive properties, and all films have the same crystallographic structure as zinc, but with different crystallographic orientations.

Keywords: Thin films, Electrodeposition, Microstructural characterization.

I. INTRODUCTION

Among variety of coating types, zinc coating is widely used as a protective coating on steel and one of the very important problems in galvanizing is the improvement of the protective and functional properties of Zn coatings. According to literature¹⁻³ Zinc alloys can provide improved corrosion resistance compared to pure zinc in the protection of ferrous- based metals. This is easily achieved by alloying Zn with more noble metals, mostly with metals of the iron group (Ni, Co and Fe)^{4,5}. Among them, zinc-iron alloys have been used a lot recently, since they showed excellent corrosion resistance (due to the nature of the zinc-iron phase), good paint ability, formability and weldability (due to the high hardness and melting point of the zinc-iron phase in comparison to pure zinc) and ease of formation of the coating^{6,7}. The co-deposition of iron group metals with zinc has several unique features. As reported in refs^{8,9}. Alloy electrodeposition is widely used in the production of new materials that require mechanical, chemical, and physical properties^{10,11}. The electrodeposition method is suitable for producing reproducible electrodeposited films at the same conditions. Zn coatings have been applied as the first protection layer on steel, mainly in automobile industry¹². In particular, Fe- Zn crystalline electrodeposits are promising alternative to pure Zn and galvanized steel, due to their improved mechanical properties and corrosion resistance^{13,14}. Iron - Zinc alloy coatings have been widely used by the automotive industry because of some advantages which zinc coatings cannot provide. It has been reported that zinc-iron coatings

not only provide excellent corrosion resistance but also exhibit improved mechanical properties compared to zinc coatings. The microstructure of zinc alloy coatings is closely related to the alloy content and phase composition of the deposit. It has been known that two or more metals can be co-deposited on a steel substrate under proper conditions. Since alloy electrodeposition is more complicated than the deposition of pure metal, two conditions are critical for the alloy deposition: (1) at least one of the metals must be capable of being deposited independently, and (2) their deposition potentials must have similar values. The electrodeposition of zinc-iron coatings provides various textural and morphological characteristics based on the different alloy composition of the deposits. The alloy composition of the coatings is not only governed by the bath composition but also by the applied current density, because the current density is responsible for the anomalous codeposition behaviour.

II. EXPERIMENTAL METHODS

Aluminum foil of 99.95 % purity and thickness 300 microns (size 3 cm × 2 cm) was ultrasonically cleaned in trichloroethylene to remove oil, grease and dust particles present on the surface. Electro-polishing of the specimen was carried out in a solution of ethanol (95%) and perchloric acid (70%) taken in the ratio 5:1 respectively to facilitate formation of ordered pores during anodization [28]. The polishing was done at 18 V DC for two minutes at a temperature of 8 – 9°C. Stainless steel cathode was used to complete the circuit. Brook field TC 500 constant temperature bath was used to maintain the

temperature of the electro-polishing solution during operation. The electro-polished specimen was oxidized anodically in 3% oxalic acid at 17 volts DC for one hour using lead as counter electrode. The temperature of the anodizing bath was maintained at $24 \pm 0.5^\circ\text{C}$ by circulating chilled water through titanium cooling coil immersed in the solution. The pores formed during anodization were widened by dipping for 30 minutes at $37 \pm 0.5^\circ\text{C}$ in 0.1M phosphoric acid [2]. Iron zinc was deposited inside these pores from an aqueous electrolyte containing iron sulphate (0.1 M) and zinc sulphate (0.01 M) and boric acid by applying high frequency (200 Hz) alternating current ($19 \text{ V}_{\text{rms}}$) using graphite as counter electrode. After electro deposition, the oxide layer was removed partially in 0.5 M phosphoric acid at 87°C for 15 seconds to expose the shape of iron zinc deposited on the porous AAO templates. Scanning electron microscope (SEM), XL30 CP Philips was used for characterization during each stage of pore formation and nanowire growth. Energy dispersive x-ray (EDX) analyzer, Bruker make, was used for identification of elements present in the deposit. Fe-Cu alloy were obtained by electrodeposition from the solutions shown in Table I.

Table 1: The Solution composition and operating parameters for Fe-Cu Alloy

Composition of solution	I
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	0.1M
$\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$	0.1M
H_3BO_3	4.5g
Solution pH	4.5
Temperature ($^\circ\text{C}$)	50
Time (sec)	30
Frequency (Hz)	200
Voltage (V)	19

III. RESULTS AND DISCUSSION

SEM Analysis

Scanning Electron Microscopy was used for the microstructural characterization and the composition analysis. The morphological characterization was studied by SEM. These investigation are limited by resolution of the SEM, satisfactory quality of SEM image was possible when the thickness of single Fe-Zn alloy layer exceeds $300\mu\text{m}$. Based on SEM investigation high efficiency of the deposited thickness measured by SEM was similar to that predicted from deposition charge. The variation in the surface morphology of the deposit with concentration difference is shown in Fig.1.

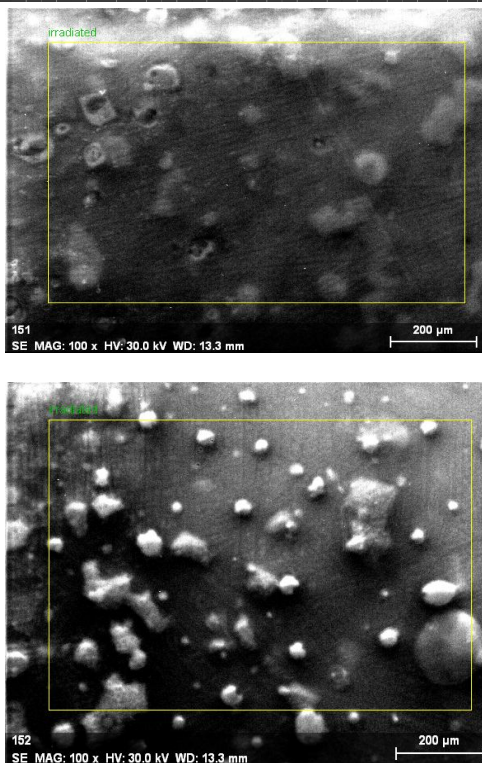


Fig.1: SEM image of Fe-Zn alloy deposit at 0.1 M concentration

Figure 1 shows the scanning electron microscope (SEM) image of top surface of porous aluminum oxide formed after anodizing the aluminum foil in 0.24M oxalic acid. Pores having diameter in the order of 25 to 35 nm were seen uniformly through out the surface. After pore widening in phosphoric acid, the diameter of the pores increased to the order of 35 to 40 nm. This specimen was used as a template for the deposition of cadmium selenide from aqueous solution consisting of cadmium sulfate and selenium dioxide using a high frequency alternating current (AC). AC electro deposition technique was preferred because direct current cannot pass through the highly resistive barrier oxide layer present under the pores of AAO membrane and needs a conductive gold coating. The positive cycle of the alternating current removes the resistive barrier layer of aluminum oxide film and facilitates deposition of metals / semiconductors into the pores during the negative cycle.

EDAX Analysis

Energy dispersive x-ray (EDX) analysis was carried out on both the locations for identifying the constituents present in the deposit EDX spectrum shows the presence of aluminum and oxygen which are from the base substrate and its conversion to aluminum oxide.

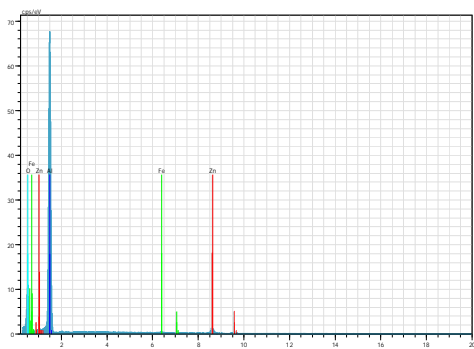


Fig. 2: EDAX image of 0.1 M Fe/Cu film

El AN Series un. C norm. C Atom. C Error
[wt.%] [wt.%] [at.%] [wt.%]

Al 13 K-series	48.88	50.62	39.15	2.5
O 8 K-series	44.17	45.74	59.66	5.6
Zn 30 K-series	3.10	3.21	1.02	0.1
Fe 26 K-series	0.41	0.43	0.16	0.0

Total: 96.57 100.00 100.00

CONCLUSION

AC electro deposition technique was preferred because direct current cannot pass through the highly resistive barrier oxide layer present under the pores of AAO membrane and needs a conductive gold coating. (SEM) image of top surface of porous aluminum oxide formed after anodizing the aluminum foil in 0.24M oxalic acid. Pores having diameter in the order of 25 to 35 nm were seen uniformly throughout the surface. Pores having diameter in the order of 25 to 35 nm were seen uniformly throughout the surface.

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