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Development of compositionally modulated multilayer Zn–Ni deposits as replacement for cadmium

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Abstract

Compositionally modulated multilayer (CMM) Zn–Ni deposits were electrodeposited from single acidic bath (pH=4.7) by using a potentiostatic sequence. The Zn and Ni composition in the alloy was tailored as a function of distance from the steel substrate. X-ray diffraction studies of the deposit showed the presence of γ-phase with a composition of Ni_5Zn_{21}. The corrosion properties of modulated multilayer coatings were studied in 5% NaCl solution using electrochemical corrosion techniques. The polarization resistance of the deposits varied as a function of Ni content between 1700 and 3440 Ω. CMM Zn–Ni with 20 wt% Ni exposed in ASTM B117 salt spray test did not show any red rust formation after 400 h.

Keywords: Compositionally modulated multilayer; Zn–Ni alloy; Cadmium replacement; Corrosion rate; Microhardness

1. Introduction

Cadmium has been used for years as a corrosion resistant coating in aerospace, electrical, and fastener industries owing to its excellent corrosion resistance and engineering properties [1]. Currently, efforts are being made to find a suitable alternative because of toxicity of the metal and its salts, risk of failure due to hydrogen embrittlement and to avoid cyanide baths for plating cadmium [2–5]. Hydrogen embrittlement in steel occurs due to the absorbed atomic hydrogen which is discharged as an unavoidable electrode reaction during electrodeposition. Zinc–nickel alloy coatings are being extensively studied as a replacement for cadmium coating due to their good corrosion protection property [6–8], superior formability, and improved welding characteristics [9–11]. Zn–Ni alloys containing 15–20 wt% nickel have been shown to possess four times more corrosion resistance than cadmium–titanium deposit [12]. However, Zn–Ni alloys have more negative potential than cadmium due to the high zinc content in the deposit and hence dissolve rapidly in corrosive environments. Although Ni is nobler than Zn, the co-deposition of Zn–Ni is anomalous and a higher percent of Zn is present in the final deposit [13,14].

Typical nickel composition in the alloy is approximately 5–10%, and further increase in nickel content has been achieved by using a higher Ni amount in the plating bath [15–17]. An enhancement in the nickel composition would lead to more positive open-circuit potential, which in turn will reduce the driving force for the galvanic corrosion. The barrier properties associated with nickel-rich deposits are also superior compared to other coatings [18–20]. Zn–Ni alloys prepared by the pulse process [21] and a multilayer approach [22] were also adopted in order to obtain high corrosion resistant alloys. Several attempts have been made to decrease the anomaly and increase the nickel content either by introducing inert species in the bath or by developing a ternary alloy [23–27]. Co-deposition of phosphorous along with Zn–Ni improves the corrosion [25] and hydrogen permeation [26] characteristics of the electrodeposits. Zhou and Keefe [32] studied the effect of tin addition on the anomalous deposition of Zn–Ni alloy. The nickel ratio increased from 6 to 8% with the addition of small amounts of tin. However, the observed small increase of Ni content in the alloy did not improve the Zn–Ni barrier properties. Other alloys studied as corrosion protection coatings include Zn–Mn [28–30] and Zn–Sn [31,32].

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The objective of the present investigation is to synthesize compositionally modulated Zn–Ni multilayer deposits with varying nickel concentration (from 15 to 30 wt.%) on carbon steel substrate. The goal is to deposit a zinc rich deposit close to the steel substrate and nickel rich deposit on the surface. Also, the goal of the present study is to evaluate the physical properties of the prepared coatings such as adhesion and microhardness and compare their corrosion properties in 5% NaCl solution with commercial Zn–Ni (13–15% Ni) and cadmium coatings.

2. Experimental

2.1. Electrolyte preparation and deposition

The deposition was performed using chloride electrolyte (pH=4.7) consisting of nickel chloride ($NiCl_2.6H_2O$), zinc chloride ($ZnCl_2.7H_2O$), ammonium chloride and boric acid. Plating and subsequent corrosion studies were done on low-carbon cold-rolled steel plates (Q-Panels, USA) of 0.8 mm thick and 4×2.5 cm^2 in area. Initially, the steel samples were mechanically polished with successively finer grades of emery paper. Next, they were degreased with soap water and rinsed with de-ionized water followed by treatment in 10% (v/v) sulphuric acid solution for 1 min to remove any adherent oxide layer present on the surface. Finally, the samples were washed in de-ionized water. This procedure was repeated until a clean and smooth surface was obtained. The plating was carried out initially at different potentials followed by a potential sequence shown in Fig. 1.

2.2. Material characterization and mechanical properties evaluation

Energy Dispersive Analysis using X-rays (EDAX) was used to analyze the distribution of the elements in the final deposit. To ensure accuracy of the element distributions, EDAX was done at several points on the surface of the substrate. The surface morphology and the microstructure of the coating were analyzed using Scanning Electron Microscopy by means of a Hitachi S-2500 Delta Scanning Electron microscope. Backscattering scanning electron microscope (BSEM) and electron microprobe analysis (EMPA, Cameca SX50) were used to determine the distribution of the elements across the thickness of the deposits.

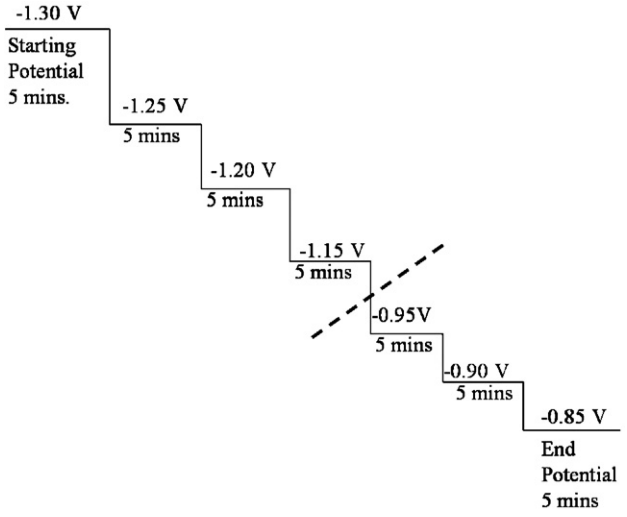

Fig. 1. Schematic of the potential sequence used for the CMM Zn–Ni deposits.

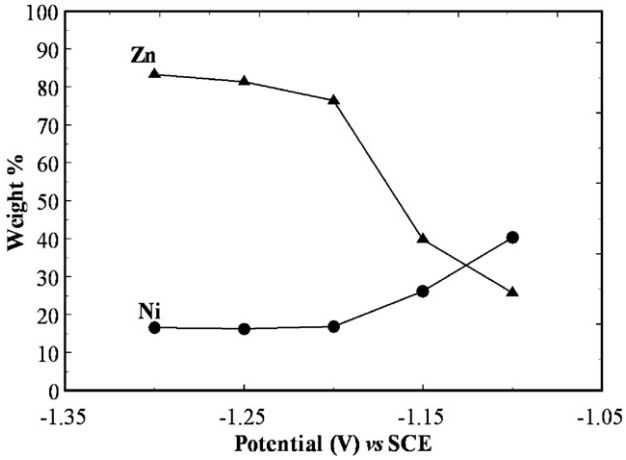

Fig. 2. Effect of applied potential on the composition of Zn–Ni deposits.

The mechanical characterization studies such as adhesion and micro-hardness were performed according to ASTM B 571-97 and ASTM B 578-87 respectively. A Vickers hardness indenter (Buehler Micromet 1 Microhardness Tester) was used to indent the prepared Zn–Ni alloys with a diamond tip. Commercial Zn and Zn–Ni deposits were also subjected to hardness measurements for comparison. The physical deformation that occurs during the indentation process at an applied load of 100 g for 10–15 s was observed under a microscope and the dimensions of the depression were marked. Vickers hardness number (VHN) was calculated based on the observations made on the indent using the formula

$$\mathrm{VHN} = \frac{2P}{d^2}\sin\left(\frac{\alpha}{2}\right) \quad (1)$$

where, d is the diagonal length left by the diamond shaped pyramid indenter. The angle between the phases of the pyramid is $\alpha=136°$. P is the load used in kilograms and the units of d are in millimeter.

2.3. Electrochemical characterization and ASTM B 117 Salt Spray Test

A variety of electrochemical techniques such as linear and Tafel polarization studies were used to evaluate the barrier resistance properties of the coating. The electrochemical characterization was performed using an EG&G PAR model 273 A potentiostat/galvanostat interfaced with a computer and a three-electrode setup in 5% NaCl solution. The steel substrate with the coating was used as the working electrode and a platinum mesh was used as the counter electrode. A saturated calomel electrode (SCE) was used as the reference electrode. All potentials mentioned in this study are referenced to the SCE.