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The effects of duty cycles on pulsed current electrodeposition of Zn–Ni–Al_2O_3 composite on steel substrate: Microstructures, hardness and corrosion resistance

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ABSTRACT

In this study, we examine the effect of duty cycles (33%, 50% and 67%) under square-wave galvanostatic pulses on the electrodeposition of zinc-nickel-alumina (Zn–Ni–Al_2O_3) composites from a sulfate bath. XRD results showed that the dominant phases of the Zn–Ni–Al_2O_3 electrodeposits were mixtures of $Zn_{21}Ni_5$ and $Zn_{22}Ni_3$ phases together with as Al_2O_3. The Ni content measured in the electrodeposits using EDS varied from 9.73 to 13.47 wt%. SEM results showed that finer and smoother surface electrodeposits were obtained by pulsed current electrodeposition at a low (33%) duty cycle. In addition, the corrosion properties of the electrodeposits were characterized by Tafel plots and electrochemical impedance spectroscopy (EIS), while the microhardness of the electrodeposits was measured by a Vickers hardness tester. In summary, this study revealed that pulsed current electrodeposition at a 33% duty cycle led to a finer and smoother surface morphology, an enhanced strength, a greater corrosion resistance, and a higher Ni content in the Zn–Ni–Al_2O_3 composite coatings compared to plating at higher duty cycles or plating through DC electrodeposition.

Introduction

Due to the energy shortage and environmental concerns, fuel cells are expected to be one of the most promising renewable source of energy [1–3]. Despite of its great advantages such as high efficiency, modular and environmental acceptability [4], corrosion still exists a problem especially the bipolar plates for proton exchange membrane fuel cells (PEMFC) and the interconnect in the a working solid oxide fuel cell (SOFC) stack [5].

Great efforts are being made to improve the corrosion resistance of zinc and zinc alloy coatings for use under harsh conditions. Zn–Ni alloys have attracted much attention due to their high corrosion resistance and mechanical erosion durability. Electrodeposition of zinc and nickel alloys offers an attractive and alternative method for producing coatings with

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a high Ni content in the form of a thin and uniform deposit on substrates. Coatings of Ni exhibit good mechanical properties as well as high corrosion resistance, thus increasing demand for industrial applications such as fuel cell, petroleum pipe line and high temperature electrochemical devices [6–18].

Metal matrix composites (MMCs) are known for their superior properties, e.g., they are hard, self-lubricating and resistant to oxidation, wear, high temperatures and corrosion. Plating, hot dipping or chemical/physical vapor deposition may be used for the production of MMCs. MMC production in electrolytes should be designed bearing in mind the ease of use, the production cost, and pollution control [19–26].

Zn–Ni coated composites reported in the literature include Zn–Ni–Al_2O_3, Zn–Ni–TiO_2, and Zn–Ni–SiC [19–26]. Integration of micro or nano-ceramic particles in an electrodeposit suspension during electrodeposition allows the particles to be encapsulated into the coating matrix. This process, however, has been found to be problematic as a result of the particles' large surface area and high surface energy, which contribute to uneven nano-particle deposition with detrimental consequences [19–23].

Newer methods, such as pulsed electrodeposition, are designed to produce coatings better mechanical and anti-corrosion properties. It has been observed that pulse plating improves coating quality by reducing grain size and improving corrosion resistance compared to that of DC electro-plating. Moreover, pulse electro-deposition was reported to allow for a better control of deposit composition as it has been shown that by increasing Ni content, the coating's grain refinement can be accomplished down to the nano scale. Pulse electro-deposited Zn–Ni coatings had been found to have increased surface smoothness with reduced porosity and increased hardness as well as better ductility [24–32].

The process of pulsed electrodeposition involves the use of a pulsed current. The average current is calculated as:

$$I_m = I_c\left(T_{on}/T_{on} + T_{off}\right) \quad (1)$$

where I_m is the average current density, I_c is the cathodic current density, T_{on} is the time of the cathodic pulse (on-time) and T_{off} is the time between pulses (off-time). The duty cycle is the fraction of a period or cycle during which the current is applied, as shown in Fig. 1.

The pulse electrodeposition technique is capable of co-depositing oxide nano-particles, thereby reinforcing metal coatings. In the research of Ghaziof and co-workers [25–28], the electrodeposition of MMCs by DC and pulsed plating methods was compared by varying the pulse frequency at a fixed duty cycle of 50%. They found that although pulse frequency did not significantly affect the chemical and mechanical properties of the deposited Zn–Ni–Al_2O_3 composite coatings, it increased microhardness, reduced through-thickness microcracks and enhanced corrosion resistance relative to that of DC plated MMCs. However, to the best of our knowledge, the effects of duty cycle, changing the ratio of on and off time under the same or controlled frequency, on Zn–Ni–Al_2O_3 composite electrodeposition have not yet been investigated. It is expected that the duty cycle will influence the deposit properties.

Therefore, in this paper we examine the effects of the duty cycle on the nano structures and properties of Zn–Ni–Al_2O_3 composite coatings. Details such as the surface morphology, Ni content, phase structure, microhardness and corrosion resistance of Zn–Ni–Al_2O_3 composite coatings from each duty cycle are discussed. In addition, the effect of the duty cycle on the phase transformation of Zn–Ni is reported.

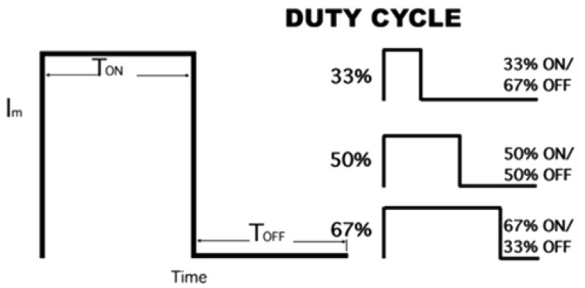

Fig. 1 – Diagram of the pulsed current electrodeposition.

Experimental

Materials and electrodeposition electrolyte

Mild steel with a thickness of 1 mm was cut into 1 cm × 1 cm samples and a nickel plate with a thickness of 2 mm was cut into 5 cm × 2 cm samples. The chemical compositions of the respective plates using a spectrometer (Thermo Scientific, ARL3460) are as shown in Table 1. Mild steel was used as a substrate while the nickel plate samples served as anodes on both sides of the electrolysis cell. Both the mild steel and nickel plates were prepared by polishing with 120, 240, 400, 600, 1200 emery grade paper before washing with distilled water and then with acetone.

An electrolyte for electrodeposition was prepared by mixing a solution containing 35 g/l $ZnSO_4{\cdot}7H_2O$ (Alpha; 99% purities), 35 g/l $NiSO_4{\cdot}6H_2O$ (Alfa aesar; 98% purities), 80 g/l H_3BO_3 (Daejung; 99.5% purities), 80 g/l Na_2SO_4 (Carloerba; 99% purities) with a solution containing 6 ml/l of Al_2O_3 solution (Alfa aesar; 97% purities) and 2 g/l p-toluene sulfonic acid monohydrate (Fluka; 98% purities). Note that Al_2O_3 solution was prepared by slowly adding distilled water into the 97% Al tri-*sec*-butoxide (ATSB) at a mole ratio of 12.4:0.01. Then pH of the solution was adjusted to 3.5 using 30% nitric acid. To dissolve the precipitates, the solution was stirred at 60 °C until it turned clear. The average size of the Al_2O_3 particles by this method was reported to be about 10 nm [25–28].

Co-electrodeposition

Fig. 2 shows a diagram of a two-electrode cell used for the electrodeposition. The galvanic electrode cell consists of a

Table 1 – Chemical compositions of mild steel and nickel plate.

	Composition (Avg.)				
Mild steel	Fe 99.50%	C 0.07%	Mn 0.24%	S 0.01%	P 0.06%
Ni plate	Ni 99.95%	Al 0.04%	Other 0.01%		

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