Journal of Magnetism and Magnetic Materials 345 (2013) 48–54

Contents lists available at SciVerse ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Magnetically induced electrodeposition of Zn–Ni alloy coatings and their corrosion behaviors

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ARTICLE INFO

Article history:
Received 18 March 2013
Received in revised form
21 May 2013
Available online 18 June 2013

Keywords:
Magnetically induced deposition
Zn–Ni alloy
Corrosion study
SEM and XRD

ABSTRACT

The less magnetic features of Zn–Ni alloy compared to Fe–Ni and Fe–Co alloys made it interesting to develop them under the influence of applied magnetic field. In this regard, the effects of a magnetic field (B) applied in a direction parallel and perpendicular to the nominal current, during electrodeposition process of Zn–Ni alloy have been investigated by means of X-ray diffraction and EDX analysis. The modification of crystal orientation by superimposition of a varying magnetic field is studied for alloys of constant nickel content (8 a %.), deposited at optimal current density (j) of 3.0 A dm^{-2}. The effect of magnetic field on crystallographic orientation and hence the corrosion behaviors of the coatings were studied. The preferential orientations (101) and (002) of the zinc phase and (330) γ-Ni_5Zn_{21} phase are always favored to exist with parallel and perpendicular magnetic field. The preferential (321) γ-Ni_5Zn_{21} orientation is found to be the characteristic of perpendicular magnetic field. Further, Zn (100) orientation is found to be non-responsive to the effect of parallel magnetic field. The coatings developed using perpendicular magnetic field is more corrosion resistant compare to that for parallel magnetic field. This is attributed to the additional (321) γ-Ni_5Zn_{21} orientations. The changes in the phase structure of the coatings deposited at different magnetic field are attributed to the effect caused by the magnetic convection induced in the electrolytic solution, called MHD effect (magneto-hydrodynamic effect). The chemical composition of the alloy was found to be same in both natural and magnetically induced deposition due to constant Ni content in the bath. The variation in the surface morphology of the coatings was studied by scanning electron microscopy (SEM). The Zn–Ni alloy coating deposited at 0.8 T perpendicular B showed the highest corrosion resistance (with corrosion rate $= 0.26 \times 10^{-2}$ mm y^{-1}) compared to the one with no B (corrosion rate $= 14.46 \times 10^{-2}$ mm y^{-1}). The improved corrosion resistance of the coatings was discussed in the light of magnetic field effect on crystallographic orientation.

1. Introduction

The electrodeposition of Zn–Ni alloy is the most volume consuming in modern electroplating industries due to its wide spread applications, such as in aerospace, oil, gas and automotive industries [1–5], even in construction industries [6], electrical and electronic components [7,8]. The mechanism of Zn–Ni alloy deposition has been discussed from experimental and theoretical points of view and the effects of different parameters such as pH, polarization and bath composition on the properties of the alloy has been widely investigated [9–12]. Natural and forced convections are important parameters that influence the electrodeposition process and properties of the electrodeposited material. Natural convection depends on the geometric configuration of the working electrode and a forced convection can be generated by various means as stirring, rotating disc or a magnetic field applied onto the electrolytic cell. Magnetohydrodynamic (MHD) convection is considered as one of the characteristic phenomena in magneto-electrochemistry (MEC, electrochemistry realized with a magnetic field superimposed onto the cell). A magnetic field generally induces an enhanced convection, attributed to the Lorentz force when it is applied in a direction parallel to a plane electrode and various phenomena caused by the Lorentz force as well as by the magnetization forces are actually expected; it can be highlighted that the electrodeposition growth is highly sensitive to the magnetic field when Lorentz force and natural convection interfere. Electroactive species mass transport towards the electrode can be increased and therefore the deposition current can be modified [13].

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http://dx.doi.org/10.1016/j.jmmm.2013.06.014

Table 1
Bath composition and operating parameters of the optimized bath.

Bath ingredients	Composition (g L^{-1})	Operating parameters
$ZnCl_2$	27.2	Anode: pure zinc
$NiCl_2 \cdot 6H_2O$	94.9	Cathode: mild steel
Boric acid	27.7	pH: 4.0
NH_4Cl	100	Temperature: 30 °C
Gelatin	5.0	
Glycerol	2.5	

The MHD effect arises due to the Lorentz force, which is the total force on a charged particle like electron or an ion, moving in an electromagnetic field and is given by,

$$F_L = q(E + vB) \quad (1)$$

where F_L is the Lorentz force, q the charge of an ion, E the electric field strength, v the velocity of the ions and B the magnetic flux density. The Lorentz forces significantly affect the usual diffusion-controlled process by increasing the mass transport effect of the ions due to the induced convections in the electrolytic solution. It has been shown that the superimposition of a magnetic field during the electrodeposition of metals and alloys induces modifications on the deposition mechanism and on properties of the deposit (morphology, crystal orientation or crystal texture) [14,15]. The phase structure of Zn–Ni alloy coating is found to be the major determining factor of its anti-corrosive property [16,17]. For the coatings containing upto 13% Ni, electrochemically obtained phases do not correspond to the thermodynamic diagram phases and change according to the thickness of the deposit [18]. However, Brooks et al. have reported that the single phase structure usually appears in the coatings containing ~13 at% of nickel, i.e., γ-Ni_5Zn_{21} phase [19]. The variation in the phase composition of the alloy coating can be induced by applying magnetic field during co-deposition process [20–22].

The magnetoelectrolysis is also found to enhance the surface smoothness of the electrodeposit [23,24]. Ganesh et al. have observed grain refinement of the nickel electrodeposited at 10 mA cm^{-2} from nickel sulfamate bath in the presence of magnetic field upto 1 T. It was further observed that the magnetic convections increased the mass transfer rate and reduced the concentration polarization [25]. For nickel, the variation in the pH near the cathode surface due to MHD convection found to cause the change in the preferred orientation parallel to the substrate plane with the amplitude of the magnetic field affecting the hydrogen evolution [26]. The visible convection and magnetic properties of nickel caused by the Lorentz force was reasoned to be responsible for the preferential orientation of nickel. The magnetic field of order 1 T was found to increase the mass transport limited current of the order of 100%. It has also been reported that when magnetic field is uniform, the contribution of the Lorentz force as well as electrokinetic force was found to be equal [27]. However, Hinds et al. have reported the copper magnetoelectrolysis studies which demonstrated that the mass transfer controlled deposition current is almost double on applying external magnetic field of 0.6 T and observed that the deposition process is independent of field direction and electrode orientation [28,29]. Coey and Hinds reported that the enhanced deposition rate with the superimposed magnetic field influenced the morphology of the radially grown electrodeposit due to their sensitivity towards magnetic field [30]. Yang et al. studied the effect of the magnetic field on the deposition of iron, nickel and cobalt based on the reflection high-energy electron diffraction (RHEED) study. They observed that the magnetic field had a little effect on their preferred orientation. However, the roughness of the deposit has increased with projections protruding in the direction of the applied perpendicular field [31]. The polarization effect on the cathode potential of the nickel, iron–nickel alloy and magnetic metals was found to be greater when the magnetic field was perpendicular to the electrolyte flow, than when the two fluxes were parallel [32]. Although much investigation have been done on the magnetoelectrodeposition and characterization of Zn–Ni alloy, relatively less work have been reported with regard to the effect of magnetic field (B) on their corrosion behavior. Hence, the present paper looks at the effect of B on crystallographic phase composition, consequently on corrosion protection ability of the electrodeposited Zn–Ni alloy coatings.

2. Experimental

The electrodeposition was carried out using acid chloride bath consisted of $ZnCl_2$, $NiCl_2 \cdot 6H_2O$ (as metal salts), NH_4Cl (as conducting salt), boric acid (as buffer), and gelatin+glycerol (as additives), prepared using analytical grade reagent and double distilled water. The bath constituents and operating parameters were optimized using the conventional Hull cell method [33]. The optimal bath composition and operating parameters of the binary Zn–Ni alloy bath is given in Table 1. The electroplating process was carried out in a stirred solution on a pre-cleaned mild steel (MS) panel, having 7.5 cm^2 active surface area. The surface was degreased by alkali cleaning prior to coating. A constant bath pH = 4.0 was maintained using dilute solution of HCl/NH_4OH, and temperature was maintained at 303 K. No inert gas purging was done during the process of deposition.

It was found that when glycerol alone was used as additive, no bright and homogenous Zn–Ni alloy coating was observed. Hence, a known amount of primary additive, namely gelatin was dissolved in hot water (being insoluble in cold water) and added into the bath to impart uniformity to the coatings. The Zn plate was used as anode with the same exposed area as that of cathode. The electroplating was accomplished for 10 min under the influence of natural and magnetically induced (both perpendicular and parallel) convections using computer controlled DC power Analyzer (N6705A, Agilent Technologies). The deposition was carried out with and without superimposed B with amplitudes up to 1 T (T), using electromagnet (Polytronics Electromagnet, Model: EM 100, Flat pole pieces with 100 mm diameters). The cell was kept in the gap of these electromagnet and constant distance between the cathode and anode was maintained. The magnetic field was constant, uniform and homogeneous onto the whole cell. While thickness of coatings was estimated by Faraday's law it was verified by measuring using Digital Thickness Meter (Coatmeasure, M&C, AA Industries/Yuyutsu Instruments). The hardness of coatings was measured using Digital Micro Hardness Tester (CLEMEX). The corrosion performances of the coatings have been evaluated in 5% NaCl at 298 K by electrochemical AC and DC methods (ACM Instruments, Gill AC Series No-1480). The measurement was done with same active surface area of 1 cm^2. A standard three electrode system was used. Electroplated specimens were used as the working electrode, and platinum electrode as the counter electrode. All potentials expressed in this study are with referring to Saturated Calomel Electrode (SCE). The electrochemical impedance spectroscopy (EIS) study was made in the frequency range of 100kHz–10 mHz using a perturbing voltage of $\pm$ 10 mV. No DC potential was applied during the EIS measurements, i.e. for free corrosion at OCP. The potentiodynamic polarization study was carried out at scan rate of 1 mV s^{-1}, in a potential ramp of $\pm$ 250 mV from OCP. The corrosion rates were evaluated by Tafel's extrapolation method. The topographical image of the coatings was studied using Scanning Electron Microscopy (SEM) (model JSM-6380 LA from JEOL, Japan) interfaced with EDXA facility. The