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Amorphous Al–Mn coating on NdFeB magnets: Electrodeposition from $AlCl_3$–EMIC–$MnCl_2$ ionic liquid and its corrosion behavior

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ABSTRACT

Amorphous Al–Mn coating was electrodeposited on NdFeB magnets from $AlCl_3$–EMIC–$MnCl_2$ ionic liquid with the pretreatment of anodic electrolytic etching in $AlCl_3$–EMIC ionic liquid at room temperature. The microstructure, composition and phase constituents of the coatings were investigated by scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDS), X-ray diffraction (XRD) and transmission electron microscopy (TEM). The corrosion resistance of the coatings was tested by means of potentiodynamic polarization and immersion test in 3.5 wt. % NaCl solution. The results show that anodic electrolytic etching in $AlCl_3$–EMIC ionic liquid is a satisfactory pretreatment to remove the surface oxide film and favor the adhesion of the Al–Mn alloy coating to the NdFeB substrate. The amorphous Al–Mn alloy coating provides sacrificial anodic protection for NdFeB. It exhibited good corrosion resistance and significantly reduced the corrosion current density of NdFeB by three orders of magnitude at potentiodynamic polarization.

1. Introduction

It is well known that NdFeB permanent magnets possess excellent magnetic properties [1]. However, the presence of rare earth element neodymium in the magnets drastically accelerates the corrosion process, which in turn greatly deteriorates the magnetic properties of NdFeB [2]. To improve the corrosion resistance of NdFeB, the electrodeposition technique, which is less energy consuming, of lower cost and easier to be controlled as compared to other techniques such as physical vapor deposition and chemical plating, has been widely used in industry. Nowadays, the electrolytes are almost always aqueous solution [3–7]. However, it is not easy to electrodeposit coatings with excellent adhesion and lack of porosity on NdFeB in aqueous solution because of their active nature in aqueous environment. The use of room temperature ionic liquids (RTILs) as a substitute for aqueous electrolytes is thus of interest and worth of study. As novel green electrolytes, RTILs have been extensively investigated for the electrodeposition of metals and alloys [8]. Among RTILs, aluminum chloride-1-ethyl-3- methylimidazolium chloride ($AlCl_3$–EMIC) ionic liquid, which is water- and oxygen-free, has been widely used for the electrodeposition of protective Al coatings on reactive metals, such as Mg alloys [9] and rare earth alloy [10]. Therefore, electroplating using $AlCl_3$–EMIC ionic liquid may be feasible for active NdFeB.

Generally, the free corrosion potential of NdFeB in neutral solution is approximate $-0.75 \pm 0.05 V_{SCE}$. Most of the reported coatings such as Ni and Ni alloys on the NdFeB are cathodic coatings [4,5]. Once these coatings suffer physical deterioration and electrochemical corrosion, a larger cathode versus smaller anode situation occurs, which could accelerate the corrosion of NdFeB. Although there are anodic coatings reported on NdFeB, such as Zn and Zn alloys [6,7], the hydrogen damage and incomplete protection to NdFeB still limit the application of these coatings [11]. As reported in literature [12–14], amorphous Al–Mn alloy coatings have promising chemical, electrical and corrosion resistance as well as mechanical properties, and they have been utilized to protect metals like steels and magnesium alloys from corrosion. The free corrosion potential of amorphous Al–Mn alloy coatings can vary from $-0.713 V_{SCE}$ to $-1.271 V_{SCE}$ in neutral solution with various Mn contents [13]. The large range of free corrosion potential shows there will be a high possibility to fabricate anodic amorphous Al–Mn alloy coating on NdFeB.

The purpose of this paper is to investigate the electrodeposition of amorphous Al–Mn alloy coating on NdFeB magnets from $AlCl_3$–EMIC–$MnCl_2$ room temperature ionic liquid. To improve the adhesion of the deposited coating, the pretreatment of anodic electrolytic etching was specifically investigated. The protection behavior of amorphous Al–Mn alloy coating to the NdFeB substrate was also discussed.

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2. Experimental

The commercial powder-sintered NdFeB magnets for this investigation were purchased from Hangzhou Permanent Magnet Group Co. Ltd. They were composed of 67.5% Fe, 29.5% Nd, 1.0% B, 1.1% Dy, 0.4% Nb, 0.4% Al, and 0.1% Cu (mass fraction). The NdFeB magnets were mechanically polished with dry emery paper, cleaned with acetone in an ultrasonic bath. The typical exposed area was 1 cm^2.

An acidic $AlCl_3$–EMIC ionic liquid (2:1 M ratio $AlCl_3$ to EMIC) was prepared by slow addition of $AlCl_3$ (anhydrous powder, $\geq$99.99%, Alfa Aesar) to EMIC (homemade according to a previous paper [15]) in a beaker at room temperature. The mixture was continuously stirred by a magnetic bar for one day to ensure uniformity. The $AlCl_3$–EMIC–$MnCl_2$ electrolyte was prepared by adding anhydrous $MnCl_2$ (anhydrous powder, $\geq$99.99%, Alfa Aesar) directly into $AlCl_3$–EMIC ionic liquid. The content of $MnCl_2$ was 0.2 mol/L. All experiments referring to ionic liquid were handled under a purified argon atmosphere in a glove-box at room temperature, in which the moisture and oxygen content were maintained below 1 ppm.

A three-electrode electrochemical system controlled by a CHI660C electrochemical workstation was employed for the anodic polarization measurements. The electrolyte was 2:1 M ratio $AlCl_3$–EMIC ionic liquid. The working electrode was the polished NdFeB while the reference electrode was an Al (99.999%) wire placed in a separate fritted glass tube sealed by a porous ceramic mesh containing the 2:1 $AlCl_3$–EMIC ionic liquid. The counter electrode was a pure Al (99.999%) plate.

NdFeB was electrolytic etched in $AlCl_3$–EMIC ionic liquid at the current density of 25 mA/cm^2 for 20 min to remove the native oxide layer. Then Al–Mn coating was deposited from $AlCl_3$–EMIC–$MnCl_2$ ionic liquid at the selected parameters of 6 mA/cm^2 for 4 h according to ref. [16].

The morphologies of surface and cross-section were examined by a scanning electron microscope (SEM, Philip XL-40FEG). The chemical composition of the samples was identified by means of an energy-dispersive X-ray (EDX) analyzer coupled to the SEM instrument. The phase constituents of the coatings were determined by a Bruker AXS D8 X-ray diffraction (XRD) system with a Cu Kα radiation. Transmission electron microscopy (TEM) characterization was performed to identify the crystallization of the coatings using a Tecnai G2 F30 S-Twin field-emission transmission electron microscope operating at 300 keV. The TEM specimens were prepared by stripping the coating from the substrate and then grinding into powders. The powders were ultrasonically suspended in alcohol and then spread on copper grids covered with carbon films for TEM observation.

The corrosion behavior of the coatings was evaluated by potentiodynamic polarization measurements in 3.5 wt. % NaCl solution. The potential was scanned from −1.3 V to 0.2 V (vs. SCE) with a sweep rate of 0.5 mV/s. A platinum sheet and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. The protection behavior of the coatings was evaluated by immersion tests in 3.5 wt. % NaCl solution. Prior to the immersion tests, a simple mechanical scratch with a steel knife was deliberately imposed across the coated surface to make the NdFeB substrate exposed. Then the specimens were wholly immersed in 3.5 wt. % NaCl solution at 25 ± 2 °C for 7 d. The NaCl solution was refreshed every day.

3. Results and discussion

3.1. Anodic electrolytic etching pretreatment

Fig. 1 shows the anodic polarization curve of NdFeB in $AlCl_3$–EMIC ionic liquid. At the start of the curve, there was a rectilinear portion AB where the current density increased proportionally to the voltage. Then the current density decreased rapidly from 20 to 5 mA/cm^2. In portion CD, current density remained. Then it increased regularly and rapidly along DE where the solution was accompanied by a more and more vigorous evolution gas.

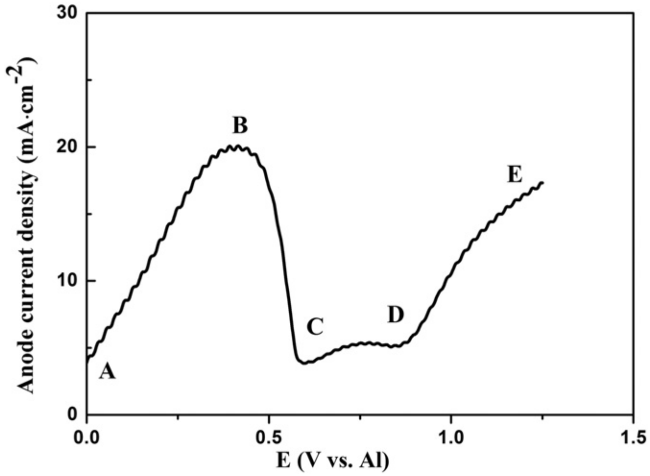

Fig. 1. Anodic polarization curve of NdFeB in the 2:1 $AlCl_3$–EMIC ionic liquid with scan rate of 10 mV/s.

The cell voltage variations versus the time of electrolytic etching under different current densities are shown in Fig. 2. When the current density values were 5 and 15 mA/cm^2, the cell voltage had a slight initial increase and then remained stable (Fig. 2a, b). When the current density increased to 20 mA/cm^2, the cell voltage showed a sudden increase from 7 to 27 V after 300 s and then remained stable (Fig. 2c). Meanwhile, an obvious brown liquid layer on the substrate surface can be observed, which was considered to be a viscous layer formed in ionic liquid according to the results of preliminary studies [17]. There were similar features when the current density was 25 mA/cm^2 (Fig. 2d). The brown liquid layer can dissolve in the $AlCl_3$–EMIC ionic liquid. The rapid increase of the cell voltage is due to the formation of brown layer

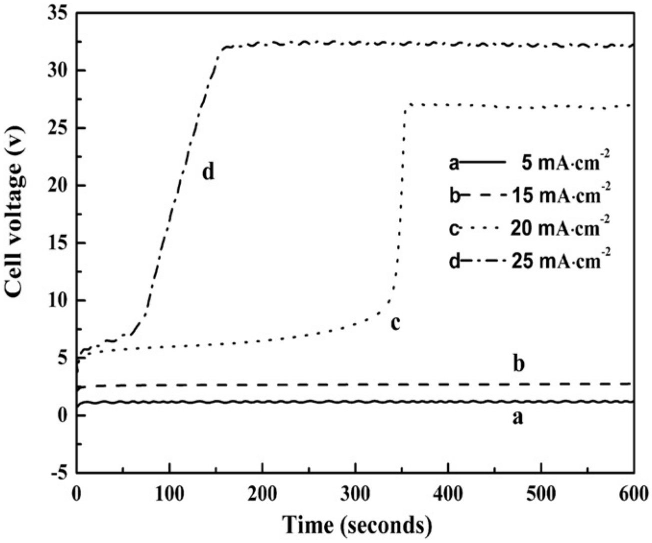

Fig. 2. Cell voltage–Time curves for NdFeB etched in $AlCl_3$–EMIC ionic liquid under different current densities.