



Effects of glycine and current density on the mechanism of electrodeposition, composition and properties of Ni–Mn films prepared in ionic liquid

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ARTICLE INFO

Article history:

Received 14 November 2015
Received in revised form
23 December 2015
Accepted 31 December 2015
Available online 4 January 2016

Keywords:

Ionic liquid
Electrodeposition
Glycine
Film
Corrosion

ABSTRACT

The effects of glycine on the mechanism of electrodeposition of Ni–Mn alloy film prepared in ChCl–urea ionic liquid were studied in order to control the composition, microstructure and properties of the film. The cyclic voltammograms revealed that the presence of glycine in the ionic liquid can inhibit the reduction of Ni²⁺ ions but promote the reduction of Mn²⁺ ions in the cathodic scan. However, it promoted the dissolution of both Ni and Mn deposits in the ChCl–urea ionic liquids during the reverse scan. Glycine changed the mode of Ni–Mn film growth from Volmer–Weber mode into Stranski–Krastanov mode. The Mn content in the Ni–Mn film increased with the increase of concentration of glycine and current density. The Ni–Mn alloy film with 3.1 at.% Mn exhibited the lowest corrosion current density of 3×10^{-7} A/cm² compared with other films prepared and exhibited better corrosion resistance than pure Ni film in 3.5 wt.% NaCl solution.

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1. Introduction

Electrodeposited nickel and nickel-based alloy films are widely used to improve the corrosion resistance in engineering application due to their chemical stability, good physical properties and attractive appearance. It was reported that Ni co-deposition with some transition metals such as Cu, Zn and Cr could significantly improve its corrosion resistance and reduce the grain size compared to the pure Ni film. The reason was ascribed to the formation of dense and crack-free film structure. Manganese as the VII B element was usually incorporated into Ni to improve its strength and temperature resistance [1–7]. Ni–Mn films also show considerably better mechanical strength and plasticity than pure sulphamate-plated Ni film does [8]. However, few literatures about the corrosion behavior of Ni–Mn films have been reported due to the large difference of standard electrode potential between Ni ($E_{\text{Ni}^{2+}/\text{Ni}}^{2+} = -0.257$ V vs. SHE) and Mn ($E_{\text{Mn}^{2+}/\text{Mn}}^{2+} = -1.185$ V vs. SHE) in aqueous solution and the resulting difficult to prepare the uniform alloy films. Mn is generally regarded as the least noble metal that can be electrodeposited

from aqueous solutions on a broad scale although its more negative deposition potential than that of hydrogen ions H⁺ [9–11]. However, it is well known that the electrodeposition of Ni–Mn films often accompanies with hydrogen evolution reaction which leads to some drawbacks, such as low current efficiency, poor adhesion, poor stability of electroplating bath and so on [2,9]. In order to eliminate these drawbacks, novel solution system (e.g., ionic liquid) was used to prepare metals and alloys which are hard to be electroplated in aqueous solutions [12]. A mixture of choline chloride (ChCl) and urea in a 1:2 mole ratio has a melting point of 12 °C (far less than the melting point of choline, 302 °C and urea, 133 °C), which makes it liquid at room temperature and one of the most significant deep eutectic solvent (DES). Compared to aqueous solution, ionic liquids (ILs) show some unique properties like low vapor pressures, high thermal stability, high electrical conductivity, high current efficiency as well as wide electrochemical window [12–15]. Actually, ILs can dissolve most metallic oxide and metal chloride easily because of their strong solvation properties. It is important that metal ions electrodeposition potential can get much closer in ionic liquid compared with that in aqueous solution, which makes the preparation of alloy much easier and more possible in a single bath of ionic liquid. In aqueous plating baths, complexing agents and grain-refinement additives are usually used to produce a brighter and harder coating. However, researches on the effects of additives

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or complexing agents on the electrodeposition in the DES (such as ChCl–urea) based solution are rather limited. Abbott et al.'s work has indicated that the additives in the DES based solution would greatly affect the nucleation mechanism and morphologies of zinc or nickel films [16]. Meanwhile, Gu et al. also have investigated the effect of ethylenediamine (EDA) on the deposition mechanism, microstructure and corrosion resistance of Cu films prepared from DES based solution [17]. However, their works are mainly focused on the pure metal film, and the effects of additives on the composition and morphology of binary alloy are less studied.

The aim of this work was to study the effect of additive agent, namely glycine ($\text{H}_2\text{NCH}_2\text{COOH}$), on the mechanism of electrodeposition of Ni–Mn binary alloy films prepared in ChCl–urea ionic liquid, which was important to control the film morphology, composition and structure. The effects of glycine concentration on the reduction mechanisms of Ni^{2+} , Mn^{2+} ions in pure Ni bath, Mn bath and Ni–Mn bath were studied by cyclic voltammetry. Surface morphology and chemical composition of the Ni–Mn films were also studied by scanning electron microscope (SEM) combined with energy dispersive X-ray spectroscopy (EDX). Potentiodynamic polarization measurements were further used to characterize the corrosion properties of the Ni–Mn film in 3.5 wt.% NaCl solution.

2. Materials and methods

2.1. Preparation of specimens and electrolytes

The specimens for electrodeposition were pure copper (99.99% Cu) plates with a size of 20 mm \times 15 mm \times 5 mm and were wet-ground by SiC papers down to 3000 grit, and then degreased ultrasonically in acetone for 10 min. Before being electrodeposited, the specimens were etched in 40 wt.% HNO_3 solution for 1 min, then cleaned with deionized water, and subsequently dried in hot air.

Analytic pure choline chloride (ChCl) [$\text{HOC}_2\text{H}_4(\text{CH}_3)_3\text{Cl}$], urea [CON_2H_4], nickel chloride hexahydrate [$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$], manganese chloride tetrahydrate [$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$] and glycine [$\text{C}_2\text{H}_5\text{NO}_2$] were purchased from Sinopharm Chemical Reagents Co. Ltd. and used as received without further purification. The eutectic ionic liquid was prepared in air by mixing ChCl and urea with a mole ratio of 1:2 in a beaker, and then stirred continuously at 60 °C until a homogenous and colorless liquid was formed. 0.20 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ was added into the above eutectic ionic liquid with gentle stirring until a transparent green liquid was obtained, for the convenience of narrative, this electrolyte was hereafter called Ni bath. In the same way, the Mn bath means a solution of 1.50 M $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in the above eutectic ionic liquid which presents a transparent pink appearance. For Ni–Mn bath, both 0.20 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 1.50 M $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were simultaneously added into the eutectic ionic liquid with gentle stirring until a transparent yellow green liquid was obtained. Glycine additive was added to the three baths with a concentration of 0.10, 0.15 and 0.20 M, respectively.

2.2. Electrochemical measurements and characterization

Cyclic voltammetry tests were carried out by PARSTAT 2273 electrochemical system in a three-electrode cell system. In order to investigate the electrodeposition mechanism, a pure Pt wire with 0.5 mm diameter was used as a working electrode, and an Ag wire with 0.5 mm diameter which has been shown having a stable reference potential in eutectic-based ionic liquid was used as a quasi-reference electrode (QRE) [18], and a pair of parallel Ni plate (50 mm \times 25 mm \times 3 mm) was used as counter electrode to ensure a homogeneous electrical field around the working electrode. All experimental electrodes were cleaned enough and dried before all measurements. All cyclic voltammeteries were performed at a scan

rate of 10 mV/s and the operation temperature was maintained at 70 °C.

The Cu specimen to be electrodeposited was used as a working electrode instead of the said Pt wire for electrodepositing Ni–Mn films and the electrodeposition current density was ranged from 1 to 9 mA/cm² under a galvanostatic mode. For all experiments, the charge density was kept at 10.8 C/cm² to ensure the relative constant nominal thickness of the films. The temperature was also maintained at 70 °C during electrodeposition process. After electrodeposited, the specimens were thoroughly cleaned with distilled water, ethanol and then dried in air.

The surface morphologies and chemical composition of Ni–Mn films were evaluated by scanning electron microscope (SEM, JSM7600F, Japan), coupled with energy-dispersive X-ray spectrometry (EDX). Grazing incidence X-ray diffraction (XRD, D/MAX 2000V, Rigaku, Japan) with a Cu–K target was used to determine the structural properties of Ni–Mn thin films in order to effectively reduce the interference of substrate diffraction peak. $2\theta/\theta$ scanning mode was executed in the range of $2\theta = 20\text{--}80^\circ$ at a scan speed of $4^\circ/\text{min}$ and the grazing angle was 5° . The potentiodynamic polarization (PD) tests were performed in 3.5 wt.% NaCl solution at $25 \pm 2^\circ\text{C}$ without stirring to evaluate the corrosion resistance of Ni–Mn films. Three-electrode cell was also used in these tests with a graphite electrode as counter electrode, a saturated calomel electrode as reference electrode and the specimen as working electrode, respectively. The specimens to be tested were packaged by silica gel and the exposed area was 0.5 cm². To achieve a stable value, the time interval between beginning of immersion and start of electrochemical measurements was assumed as 1 h, which was kept constant for all tests. The scan rate of potentiodynamic polarization curve was 1 mV/s.

3. Results and discussion

3.1. Cyclic voltammetry

The cyclic voltammetry was carried out to determine the reduction potential for individual Ni^{2+} and Mn^{2+} ions in Ni bath and Mn bath and the reduction potential for Ni–Mn alloy in Ni–Mn bath, which contains or not contains glycine respectively. Curve (a) in Fig. 1 reports the cyclic voltammogram (CV) for Ni^{2+}/Ni redox couple in Ni bath on Pt wire electrode at 70 °C. For a cathodic scan, the electrode potential was initially scanned from 0 V to -1.50 V (vs. Ag QRE). An onset reduction potential -0.37 V of Ni^{2+} ions was observed and a reduction peak potential occurs at approximately -0.64 V. The formation of a black Ni deposit on the Pt wire electrode was clearly visible at this moment. The current density increases dramatically at around -1.25 V, which can be attributed to the decomposition of ChCl–urea ionic liquid [13,15]. In the reverse scan, the oxidation current rapidly increases at -0.12 V and an oxidation

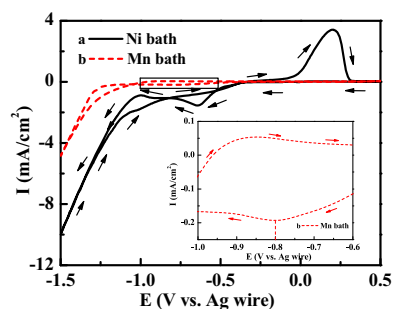


Fig. 1. Cyclic voltammograms of 1:2 (mole ratio) ChCl–urea ionic liquid containing (a) 0.20 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; and (b) 1.50 M $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ on Pt wire at 70 °C, respectively. Both scan rates are 10 mV/s.

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