Available online at www.sciencedirect.com
SCIENCE DIRECT
Electrochimica Acta 51 (2006) 3652–3657
ELECTROCHIMICA Acta
www.elsevier.com/locate/electacta

Reversal pulsing electrodeposition of Ni/polypyrrole composite film

Yoshihiro Haseko, Nabeen K. Shrestha, Shuichiro Teruyama, Tetsuo Saji *

Department of Chemistry & Materials Science, Tokyo Institute of Technology, 2-12-1 S-44, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Received 20 August 2005; received in revised form 7 October 2005; accepted 13 October 2005
Available online 28 November 2005

Abstract

A uniform composite film of Ni/polypyrrole was deposited on a copper substrate, without any preliminary chemical and electrochemical surface treatment of the substrate, by reversal potential pulsing technique. The influence of pulse potential, pulse frequency and electrolysis time on the formation of a uniform composite film was investigated. These films were characterized using SEM, EDX, EPMA, and GD-OES. The composite films produced under the optimized conditions exhibited a strong adherence to the substrate and exhibited the better corrosion resistance in a marine environment than that of the electrodeposited nickel coating without any incorporated polymer.

Keywords: Reversal pulse; Plating; Nickel; Polypyrrole; Composite film

1. Introduction

Pulse plating is an electrodeposition technique by which various metals [1–3], metal alloys [4–7] and the metal matrix composites containing various ceramic particles [8–11] are deposited using pulse current or potential. These deposits generally possess a better property than the deposits produced by a direct current electrodeposition technique [12]. Since a high current or a high potential can be applied for a short time and even the direction of these parameters can be reversed in the pulse plating, this technique produces the crystals with lattice defects which might have a hybrid character and might exhibit a better property than by the crystals with regular lattices. On the other hand, applying a current for short time and then keeping the current in rest for another short time and repeating this process during electrodeposition, each cycle of this process may generate a new crystal. Therefore, by controlling the magnitude of the current and pulse width, production of nano-crystals is also possible [13]. Recently, investigation on electrodeposition of conducting polymers is growing [14–18] due to their applications in various fields [19,20]. Deposition of conducting polymers by electro-polymerization takes place at a potential region where most of the metals undergo oxidation. Therefore, simultaneous co-deposition of metals especially less noble metals and conducting polymers is difficult. Composite plating of metals and polymer can be carried out in two steps by depositing conducting polymers in the first step followed by deposition of metals over the polymer film in the second step [21]. However, the conducting polymers in this case lose their doping ions and become insulator during the deposition of metals. On the other hands, to prevent the dissolution of the substrate in the case of oxidizable metals like nickel, copper, zinc, iron, etc., which are usually used in industries as the base metals, pre-surface treatment or some electrolytes that can form a passive layer on the surface of the substrate during electrolysis, are required [22–24]. In such cases, reversal pulse-plating technique can be applied to preserve the conductivity of the polymer because by adjusting the pulse width, it is possible to control the rate of charge transfer in oxidation and reduction reactions in which polymerization and metal deposition takes place, respectively. By choosing a suitable pulse width for cathodic and anodic potentials, it can preserve the conductivity of the polymer during the deposition of metals in such a way that polymer can be kept still in the partially conducting state by making the slow charge transfer reaction in the anodic cycle which hinders the complete transformation into the insulating state. On the other hand, the dissolution of metal substrate and metal deposits can be controlled by the pulse width, and hence this technique avoids the pre-surface treatment of the substrate in order to passivate the surface, which can prevent the substrate from dissolution during the polymerization reaction. Although pulse plating has already been a well-established

* Corresponding author. ISE member. Tel.: +81 3 5734 2627; fax: +81 3 5734 2627.
E-mail address: tsaji@o.cc.titech.ac.jp (T. Saji).

0013-4686/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2005.10.032

technique for plating metals and their composites with ceramic particles, research on the co-deposition of metals and polymers especially conducting polymers for the synthesis of composite film by pulse plating technique seems still on the early stage. In the present study, composite plating of nickel and polypyrrole (PPy) on a copper substrate by reversal pulse potential technique was performed. The objective of the present study is to search the optimal pulse conditions to produce a uniform Ni/PPy composite film on an oxidizable substrate and to investigate the electrochemical behaviors of this composite film.

2. Experimental

Cyclic voltametry experiment was performed under nitrogen atmosphere in a one-compartment cell consisting of three electrodes system using an electrochemical workstation (*CV*-50 W, BAS, Inc., USA). A potentiostat/galvanostat device (*HA*-305, Hokuto Denko Ltd., Japan) was used to deposit the composite film and this system was coupled to a function generator (*HB*-104, Hokuto Denko Ltd., Japan) to generate the pulse. During the deposition, a reversal pulse potential against the reference electrode in the rectangular waveform was imposed on the working electrode. A 0.3 mm thick copper plate with the dimension of 10 mm × 30 mm was polished to a mirror finish using metal polishing reagent (*PIKAL*, Nihon Maryo-Kogyo Co., Ltd., Japan) and it was washed by ultrasonic agitation in chloroform for 5 min followed by acetone for another 5 min. A 10 mm × 15 mm of this copper substrate was used for the deposition and this substrate was used as a working electrode, whereas a nickel plate and SCE were used as counter and reference electrodes, respectively. An aqueous solution containing 0.2 mol dm^{-3} $Ni(CH_3COO)_2$ (Kanto Chemicals, Japan), 2 cm^3 dm^{-3} pyrrole (Py) (99% purity, Kanto Chemicals, Japan) and 0.8 mol dm^{-3} sodium *p*-toluenesulfonate (Tokyo Kasei Kogyo Co. Ltd., Japan) was used as the plating bath. The pH of this plating bath was initially adjusted to 5 with *p*-toluenesulfonic acid (Kanto Chemicals, Japan) and electrodeposition was carried out for 10 min under slow stirring condition. The scheme of the pulse potential applied for the deposition of composite film in the present investigation is shown in Fig. 1. All experiments were performed at 25 °C unless otherwise stated. The surface and cross-sectional morphologies of the composite film were investigated using a scanning electron microscope (SEM, *JSM*-5310, JEOL, Japan). The content of the PPy in a composite film was determined gravimetrically by dissolving five replicas of the composite film in 30% aqueous solution of nitric acid and separating the PPy using a membrane filter. On the other hand nickel content in the filtrate was also determined using an ICP-optical emission spectrometer (*Prodigy*, JEOL, Japan). The average weight of the PPy determined from these two investigations was assumed here as the content of PPy in the composite film. The composition of the composite film was analyzed semi-quantitatively using an electron probe micro-analyzer (EPMA, *JXA*-8200, JEOL, Japan) and an energy dispersive X-ray micro-analyzer (EDX, *PV*-9900 *I*, Philips). The depth profile of the composite film was investigated qualitatively using a glow discharge optical emission spectrometer (GD-OES, *JY*-5000*RF*, Horiba/Jobin Yvon).

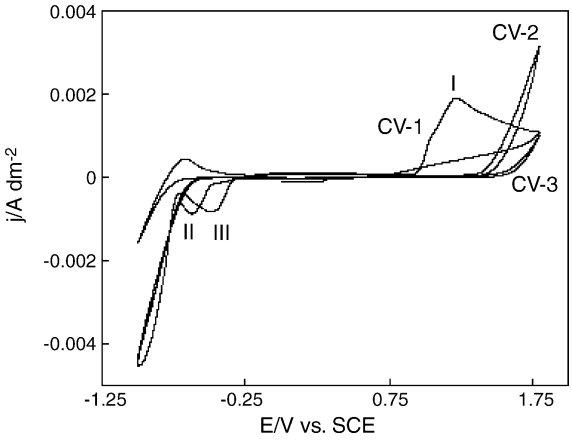

Fig. 1. Cyclic voltammogram of an aqueous electrolyte containing (CV-1): 0.2 mol dm^{-3} $Ni(CH_3COO)_2$, 2 cm^3 dm^{-3} pyrrole, and 0.8 mol dm^{-3} sodium *p*-toluenesulfonate; (CV-2): 0.2 mol dm^{-3} $Ni(CH_3COO)_2$ and 0.8 mol dm^{-3} sodium *p*-toluenesulfonate; (CV-3): 0.8 mol dm^{-3} sodium *p*-toluenesulfonate at 25 °C. WE: Pt, CE: Pt, and scan rate: 2 mV $s.^{-1}$.

The adherence of the composite film was evaluated by applying the Cross-Cut Tape Test method according to the *ASTM D* 3359 standard.

Electrochemical behavior of the composite film was studies in a 0.8 mol dm^{-3} sodium *p*-toluenesulfonate using cyclic voltametric technique. Similarly, corrosion behaviour of the composite film was briefly investigated in a 0.1 mol dm^{-3} NaCl aqueous solution (pH 7.8) using potentiodynamic polarization technique. The polarization of the coated substrates was carried out by sweeping the potential anodically from −0.8 V to +0.8 V versus SCE at 1 mV s^{-1}.

3. Results and discussion

The cyclic voltammogram (CV) of the plating bath is shown in Fig. 1 (CV-1). As evident from CV-1, there is an oxidation peak at about +1.2 V versus SCE (peak-I). This oxidation peak disappeared when the CV of the above plating bath without Pyrrole (CV-2) was measured. Therefore, the above oxidation peak-I can be ascribed to the oxidation of pyrrole. In the above CV, *p*-toluene sodium sulfonate acted as a supporting electrolyte. However, the main objective of sodium *p*-toluenesulfonate was to dope PPy with the sulfonate ion. A large variety of anions [25] can act as doping ions, which are entrapped with polymer during polymerization. Therefore, without adding such external source of doping ions in the nickel-plating bath, the counter ions of nickel in some cases, e.g. nitrate [26] and chloride [27] ions, also can work as doping ions. However, in the present investigation, no oxidation peak of pyrrole was observed when the CV of an electrolyte without sodium *p*-toluenesulfonate was run. On the other hand, this CV experiment did not deposit the black film of PPy on the working electrode. Therefore, these results revealed that the acetate ion, which was the counter ion of nickel in the present investigation, could not act as a doping ion for polymerization of pyrrole. During the cathodic sweep, the CV-1 exhibited a small reduction peak at about −0.65 V versus SCE (peak-II). This reduction peak is due to the reduction of