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# Electrodeposition of nickel-iridium alloy films from aqueous solutions

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ABSTRACT

Nickel–iridium (Ni-Ir) alloy films were electrodeposited from aqueous solutions on copper substrates under galvanostatic conditions. The effects of bath composition and deposition time on the faradaic efficiency (FE), partial current densities, chemical composition, morphology and crystallographic structure of the films were studied. The results show that the Ni–Ir alloys with Ir content as high as 37 at% and FE as high as 44% were obtained. Increase in concentration of citric acid had little or no effect on the composition of the alloys, but resulted in a significant decrease in FE and partial current densities of Ni and Ir. The FE and the partial current density of Ni slightly decreased with increasing $Ir^{3+}$ concentration, however, Ir content increased while partial current density of Ir remained stable. The increase of $Ni^{2+}$ concentration could result in the increase of the FE and the rate of Ni–Ir deposition, and even no cracks formed on the surface. The surface average roughness and root mean square roughness of the film were $6.8 \pm 0.3$ nm and $5.4 \pm 0.3$ nm, respectively. The mixture phases contained significant amounts of Ni oxides and a small amount of metallic Ni, Ir and Ir oxides on the surface. After argon ion sputter cleaning, the film was mainly composed of metallic Ni and Ir. The film consisted of the amorphous and nanocrystalline phases. The Ni content in the deposits was higher than that in the electrolyte, the co-deposition of Ni–Ir alloy was a normal deposition.

## 1. Introduction

Nickel (Ni) and its alloys enjoy a lot of interest in many fields, mainly due to its wide range of potential applications in corrosion resistance and catalysis [1–3]. Although Ni has some remarkable physical and chemical properties, the performance of Ni in high temperature air environment is limited due to the formation of Ni oxides. In order to protect Ni and its alloys from high temperature oxidation, a top layer such as rhodium (Rh) or iridium (Ir) is often applied. Ir has a high melting point, a low oxygen permeability, good chemical compatibility and superior oxidation resistance, which renders it as one of the most promising candidates for protective film of refractory materials against extreme environments [4–6].

Ir film can be prepared by metal organic chemical vapor deposition [7], chemical vapor deposition [8], magnetron sputtering [9], double glow plasma [10,11] and electroplating [12,13]. For vapor deposition processes, the films are produced by relatively expensive devices at a high-vacuum condition. Electroplating is a powerful cost-effective and reliable film process without vacuum condition. The electroplating of Ir and its alloys may become an alternative, which is widely employed in the deposition of pure, uniform, adherent metals and alloys in low-temperature aqueous solution bath [14–19]. However, the electroplating of Ir from aqueous solution has some disadvantages with respect to the stability of electrolyte and quality of deposits [13]. Significant hydrogen evolution might lead to deterioration of the Ir films with cracking and low faraday efficiency (FE) [14]. The binary alloys between platinum-group and iron-group metals could be electrodeposited from aqueous solutions. Platinum-group metals have high melting points, excellent catalytic activity and superior corrosion resistance [20,21], which could compensate for the shortage in certain characteristics of iron-group metals. Pd–Ni and Ir–Co alloys for the use as catalysts could be electroplated from aqueous solutions [20,21]. Cohen-Sagiv et al. [22] developed suitable plating baths for electroplating of Re-Ir-Ni alloys and pointed out that Ni-Ir alloys could be electroplated from aqueous solutions, but only studied the effect of citric ions concentration on the electrodepostion of Ni-Ir alloys.

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Electrodeposition of alloy involves more complicated process than the deposition of individual metals. It is well known that the complexes of citrate with metal salts could have an impact on the overall deposition process and the nature of the deposits [23]. Therefore, the electrodeposition of Ni–Ir alloy from citrate aqueous solution has to be studied. The present work investigates the effects of bath chemistry and deposition time on the FE, partial current densities, chemical composition, morphology and crystallographic structure of Ni–Ir alloy films, and also addresses the proposed mechanism of Ni–Ir electrodeposition.

## 2. Experimental

In the experiment, a copper (Cu) disc (ϕ 10 mm × 0.5 mm) with exposed surface area of ~1.6 cm$^2$ was welded with a Cu wire (ϕ 0.9 mm × 100 mm) by a spot welder machine. The Cu disc was used as the working electrode. Before each experiment, the surface of Cu disc was cleaned with surfactant soap water in an ultrasonic bath for 5–10 min in order to remove major contaminants, and subsequently immersed in a mixture solution of $HNO_3$-$H_2O$ (1:1) at room temperature for ~1 min in a fume hood, then rinsed and cleaned with deionized water by a plastic squeeze bottle, and finally followed by cleaning with acetone in an ultrasonic bath for 3–5 min.

Ni–Ir alloy films were electroplated on the working electrode in a three-electrode cell. The three electrodes consisted of a working electrode (the cathode), two platinum foils (ϕ 10 mm × 0.25 mm) as the counter-electrode placed ~5 mm away from both sides of the working electrode, and a reference electrode of Ag/AgCl 3 M KCl. The deposition conditions of Ni-Ir alloy films were: current density of 50 mA cm$^{-2}$, bath pH of $5 \pm 0.1$ and plating temperature of $70 \pm 1$ °C. The volume of the electrolyte in the cell was approximately 12 mL. The deposition process was typically run for 60 min, although the shortest deposition time was 10 min. In a typical preparation process, 17–70 mM $IrCl_3 \cdot nH_2O$, 17–115 mM $Ni(NH_2SO_3)_2$ and 35–105 mM $C_6H_8O_7$ were stirred and dissolved completely in 25 mL of deionized water for about 3 h using a magnetic stirring apparatus. The solution pH was examined by a PHS-3C pH meter at room temperature, and was adjusted to the desired value by adding 5.0 M NaOH while being stirred. The bath solution was purged with pure $N_2$ for 15 min before turning on the current. A $N_2$ blanket was passed over the solution during electroplating. In all experiments, a magnetic stir bar was used to stir the solution. The bath temperature was controlled by a HH-501 thermostatic bath. The galvanostatical electrodeposition and electrochemical process were carried out in the cell, using an electrochemical workstation (CHI 660E) coupled to a computer with specific data acquisition software installed. The cyclic voltammetry was performed at scanning rate of 10 mV s$^{-1}$. The working electrode of Cu with a surface area of 0.8 cm$^2$ was cold covered in epoxy resin on one side for electrochemical analysis.

The mass change of the specimens before and after deposition was recorded by an analytical balance (FA2004B, resolution 0.1 mg). The average FE was calculated from the added mass, the charge passed and the chemical composition of the films. The partial current densities of Ni and Ir metals were calculated from the added mass and the chemical composition of the deposits. Further details can be found in Ref. [22].

The crystallographic structure of the selected deposits was determined by X-ray diffraction (XRD, Scintag, USA) equipped with a Cu-Kα radiation source. Typical morphology of the top surface and metallographic cross section of selected deposits were observed by a scanning electron microscopy (SEM, JSM-6360) operated in the high-vacuum mode, equipped with an energy dispersive spectroscopy (EDS) detector. The chemical composition of alloys was measured at five locations to confirm uniformity by the EDS detector. The surface roughness of the alloy was characterized by an atomic force microscopy (AFM, Nanoscope V, Bruker) taking an average of the values obtained at three different locations on each specimen. At the same time, the average roughness ($R_a$) and root mean square roughness ($R_q$) were reported.

X-ray photoelectron spectroscopy (XPS) measurements were performed in ultrahigh vacuum ($3.3 \times 10^{-8}$ Pa base pressure) using a 5700 ESCA System (PHI, USA). The samples were irradiated with an Al-Kα monochromatic source (1486.6 eV), and the outcome electrons were analyzed by a spherical capacitor analyzer using the slit aperture of 0.8 mm. The samples were analyzed either at the surface or after sputter cleaning with a 4 kV Ar$^+$ ion gun (sputtering rate on $SiO_2$/Si was 3.3 nm·min$^{-1}$). The area and current of the sputtering were 5 mm × 5 mm and 0.5 μA, respectively. The carbon signal for C–1s at 285 eV was taken as an energy reference for the measured peaks. In order to identify the elements present on the surface of the alloy film, a low-resolution survey spectrum was first taken over a wide energy range (0–1400 eV). High-resolution spectra were acquired with a pass energy of 23.5 eV at increments of 0.1 eV step$^{-1}$, to allow precise determination of the position of the peaks and their shape. Curve-fitting was done with Gaussian–Lorentzian function, using the XPSPEAK software. Two fitting parameters – the position of the peak and its full width at half-maximum (FWHM) – were fixed within less than about ± 0.2 eV.

## 3. Results and discussion

In the framework of this work, the effects of the analytical concentrations of citrate, Ni and Ir ions on the FE, partial currents densities and Ir content in the deposits are firstly shown in Section 3.1. Subsequently, Section 3.2 presents the effect of deposition time on the FE, partial deposition current densities and Ir content in the alloys, at the same time the surface roughness of the film was also studied. Then, Section 3.3 provides a hypothesis for the deposition mechanism of electrodeposited Ni-Ir alloys. Finally, Section 3.4 describes and analyses the characterization of alloys, including the morphology, chemical composition and crystallographic structure of representative alloy films.

### 3.1. *The effect of bath chemistry*

#### 3.1.1. *The effect of the concentration of citrate ions*

Fig. 1 shows the plots of the Ir content and the FE, the partial current densities of Ni and Ir as a function of the concentration of citrate ions. The concentrations of Ni$^{2+}$ and Ir$^{3+}$ ions were the same, 35 mM. As shown in Fig. 1**a**, the Ir content in the deposits remained a stable value of ~20 at% with an increase in concentration of citrate ions, except at Cit$^{3-}$/Ni$^{2+}$ concentration ratio of 3.0. Here citrate is abbreviated to Cit. The FE for the deposition decreased remarkably with increasing the concentration of citrate ions. As the concentration of citric acid was 105 mM, the FE was about 1% and the Ir content increased slightly. Fig. 1**b** shows the partial current densities of Ni and Ir. The partial current densities of Ni and Ir decreased steadily with increasing the concentration of citrate ions. The partial current density of Ni metal was higher than that of Ir metal, although the concentrations of Ir$^{3+}$ and Ni$^{2+}$ were the same.

#### 3.1.2. *The effect of the concentration of Ni ions*

Fig. 2 shows the plots of the Ir content, the FE and the partial current densities of Ni and Ir as a function of Ni$^{2+}$ concentration. The concentrations of citric acid and Ir$^{3+}$ were 90 mM and 35 mM, respectively. As shown in Fig. 2**a**, although the Ir content decreased from 34 at% to 10 at% with increasing Ni$^{2+}$ concentration, the FE showed a significant increase in the same range. As the concentration of Ni$^{2+}$ ions was 35 mM, the FE was very low, because the