

Electrochemical deposition and characterization of Ni–P alloy thin films

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Abstract

Nickel phosphorus (Ni–P) alloy thin films were prepared by electrodeposition on pre-cleaned copper substrates using a potentiostatic cathodic electrodeposition method from sulfate electrolyte baths at various sodium hypophosphite (NaH_2PO_2) concentrations. X-ray diffraction studies reveal polycrystalline cubic alloys at low concentrations of phosphorus (<13.5 at.%) and these transformed into amorphous alloys at higher concentrations. X-ray photoelectron spectra show the presence of Ni_{2p} and P_{2p} lines corresponding to their binding energies. Scanning electron microscopic studies reveal spherical shaped grains at low phosphorus contents and modules of cauliflower type morphology at higher phosphorus concentrations. The effects of phosphorus concentration on the crystal structure, composition and morphology are studied and discussed.

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1. Introduction

In recent years, the iron group of alloys has attracted a great deal of attention owing to their promising mechanical, chemical and magnetic properties [1]. In particular nickel phosphorus (Ni–P) alloys systems are very attractive due to their good corrosion and wear resistance behavior which make them suitable for important technological applications [2]. Electrochemical methods such as electroless deposition and electrodeposition are

identified as the most practical and inexpensive techniques to synthesize Ni–P alloy thin films [3]. Electrodeposited Ni–P alloys are reported to be mirror-bright and corrosion resistant when the phosphorus content of the deposits is above 18 at.% [4]. The mechanism of Ni–P deposition in a Ni-citrate bath was discussed by Morikawa et al. [5]. Li [3] and Li et al. [6] studied the effect of ammonium on low temperature electrodeposition of Ni–P amorphous alloy thin films prepared by electroless plating. Lu and Zangari [7] studied the corrosion behavior of Ni–P based alloy films synthesized using an autocatalytic deposition. Seo and co-workers [7,8] reported the characteristics of a Ni–P alloy electrodeposited from a sulfamate bath. Even though several reports are available on Ni–P alloy

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Table 1
Bath composition and deposition conditions used for Ni–P coatings

Electrolyte	Concentration	Deposition conditions	
		Parameters	Value
NiSO ₄ ·7H ₂ O	0.2 M		
NaH ₂ PO ₂	0.10 to 0.3 M	Bath temperature	70°C
H ₃ BO ₃	0.4 M	Current density	7.5 to 10 mA/cm ²
NaCl	0.7 M	Deposition time	30 min
Saccharin	0.005 M	Solution pH	2.5±0.1

films, systematic studies on the synthesis conditions for phosphorus inclusion are scarcely found in the literature. Hence, the present work is aimed to carry out a few systematic studies on the effect of phosphorus concentrations on the electrochemical preparation and characterization of Ni–P alloy films.

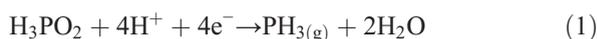
2. Experimental details

Ni–P thin films were prepared by galvanostatic electrodeposition. A conventional three-electrode cell and a Potentiostat/Galvanostat [(EG & G, Model 362, USA)] were used for the electrodeposition. The pre-cleaned copper substrates were used as working electrodes. The counter electrode and reference electrode were a graphite plate and a saturated calomel electrode (SCE), respectively. Analytical grade reagents (Merck) were used for the electrodeposition of Ni–P alloy thin films. Prior to deposition, the substrate was polished mechanically with silicon carbide emery paper and chemically treated in 10% sulfuric acid for 1 min. After these pretreatment steps, the substrates were cleaned in acetone and then rinsed thoroughly in double distilled water. The distance between the anode and cathode was maintained at 1 cm to ensure uniform deposition. During deposition the electrolyte was stirred with a magnetic stirrer. The bath compositions and deposition conditions are represented in Table 1 Sodium chloride (NaCl) and boric acid (H₃BO₃) were added as supporting electrolyte and pH buffer, respectively. Saccharin was added in the deposition bath to reduce the deposit stress. Copper foil was used as the working electrode for cyclic voltammetry as well as for constant current plating.

An X-ray diffractometer system [Model-Brucker, Discover D8] using CuK α radiation with $\lambda=0.15418$ nm was used to identify the crystal structures of the films. Surface morphological and compositional analyses were carried out using a scanning electron microscope and an energy dispersive X-ray analysis (EDAX) set up attached to an SEM (Philips, Model XL 30). XPS spectra were recorded on a Perkin-Elmer 5600-CI spectrometer using monochromized Al K α radiation (1486.6 eV).

3. Results and discussion

In aqueous solutions, phosphorus could not be deposited alone [1]. However, it can be deposited in the presence of a metal of the iron group such as nickel and this phenomenon is known as induced co-deposition [9]. Since the direct incorporation of phosphorus with nickel is not feasible, the indirect mechanism proposed by Ratzker et al. [10] is the likely reaction for the formation of Ni–P alloy films. The indirect mechanism suggests that the phosphorus oxyacid reduction depends on H⁺ reduction with the formation of a gaseous intermediate phosphine (PH₃). The following two possible reactions lead to the simultaneous deposition of Ni and P in our present work:



A typical cyclic voltammogram (CV) on pre-cleaned copper substrates at various NaH₂PO₂ concentrations (0.1 to 0.3 M) and with a scan rate 50 mV/s in the potential range from –1.0 V to +1.0 V is shown in Fig. 1. The scanning direction of the switching potential E_{λ} change from cathodic to anodic was fixed at –800 mV in order to eliminate possible interference from the hydrogen evolution reaction. The polarization during cathodic scan reveals different polarization values in the C–V studies. Dini [11] showed that the polarization has a close correlation with the size of grains in the electrodeposited alloys. He reported that when the alloy is electrodeposited at high polarization conditions, the deposits contained small grains. Cyclic–Voltammetric

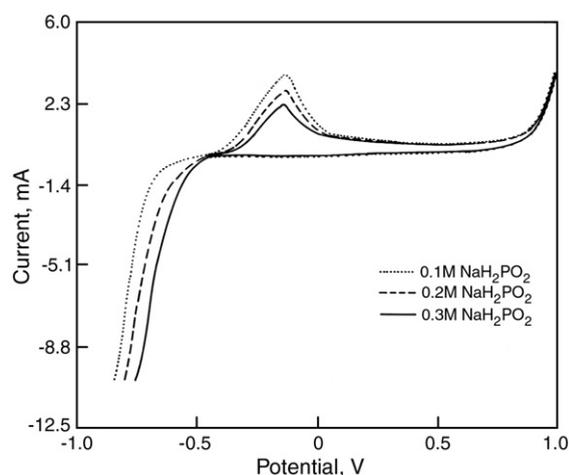


Fig. 1. Cyclic voltammetric behavior of Ni–P alloy films deposited at various NaH₂PO₂ concentrations.

studies reveal that the polarization decreases with an increase of NaH_2PO_2 concentration in the Ni–P electrolyte solution. The over crossing potential E_c was measured by cyclic voltammetry with E_λ ranging from -750 mV to -810 mV by a step of 15 mV. In the case of a solution containing 0.3 M NaH_2PO_2 , E_c stays near -450 mV or shifts a little to the anodic direction. The E_c stays near -530 mV to -500 mV and moves to the cathodic direction in a NaH_2PO_2 solution concentration between 0.1 M and 0.2 M.

X-ray diffraction patterns of Ni–P alloy films deposited at various NaH_2PO_2 concentrations (0.10 M to 0.20 M) are shown in Fig. 2. Ni–P alloy electrodeposited in a solution containing 0.10 M of NaH_2PO_2 exhibits the FCC structure with three nickel peaks (111), (200) and (220). As the NaH_2PO_2 concentration increases to 0.15 M, the peaks become broad indicating the continuous refinement of Ni grains. It is also observed that the 2θ values are slightly shifted to higher angles indicating the presence of phosphorous in the films. When the NaH_2PO_2 concentration is further increased to 0.20 M, the (200) and (220) peaks disappear and the film became amorphous leaving a broad peak around $2\theta=45^\circ$ corresponding to the prominent (111) peak of pure nickel. These studies reveal that the Ni–P alloy films deposited above 0.15 M NaH_2PO_2 concentration are amorphous. The structural transformation from crystalline into an amorphous phase with an increase of phosphorous content is in agreement with the results reported earlier [12,13].

The quantitative analyses of the Ni–P electrodeposits were performed with an aim to determine the compositional relationship between different NaH_2PO_2 concentrations and are shown in Fig. 3. Through EDAX studies, the compositions of Ni–P electrodeposits (in

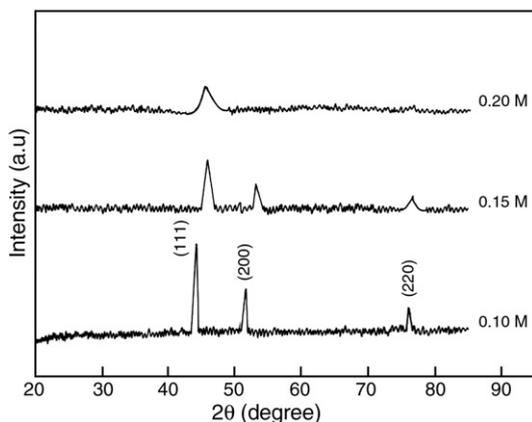


Fig. 2. XRD patterns of Ni–P alloy films electrodeposited at various NaH_2PO_2 concentrations.

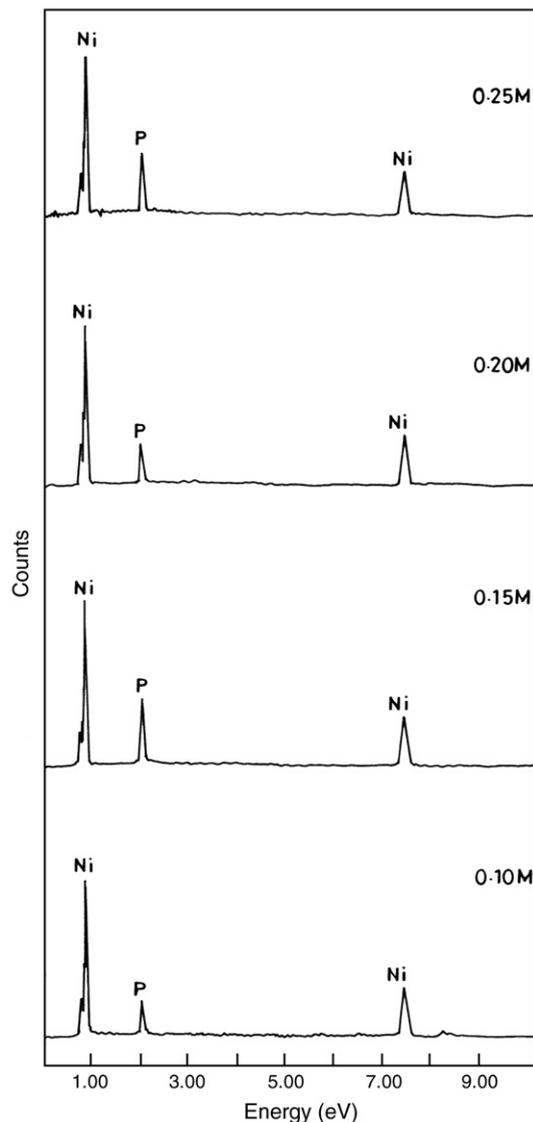


Fig. 3. EDAX patterns of Ni–P alloy films electrodeposited at various NaH_2PO_2 concentrations.

atomic percent) obtained at different NaH_2PO_2 concentrations (0.10–0.25 M) are shown in Table 2. The EDAX results revealed that the nickel content (Ni) decreases whereas the phosphorous (P) content increases with an

Table 2
Compositional analysis of Ni–P electrodeposits

S. no.	NaH_2PO_2 concentrations (M)	Ni (at.%)	P (at.%)
1.	0.10	88.02	11.98
2.	0.15	86.48	13.52
3.	0.20	78.95	21.05
4.	0.25	78.28	21.72

increase in the NaH_2PO_2 concentration in the electrolyte bath. The increase in NaH_2PO_2 content gradually leads to the refinement of grains and eventually the phosphorus content reaches saturation in the Ni–P alloy films.

Fig. 4a and b presents the XPS spectra of nickel 2p and phosphorus 2p crystalline lines respectively for the Ni–P sample electrodeposited at 0.25 M NaH_2PO_2 concentration. Fig. 4a exhibits one peak with the binding energy observed at 129.9 eV corresponding to $\text{P}_{2p_{3/2}}$ exhibiting that almost all the phosphorous in the alloy existed in an elemental state. Fig. 4b shows two peaks with the binding energies at 870.1 eV and 852.9 eV corresponding to $\text{Ni}_{2p_{1/2}}$ and $\text{Ni}_{2p_{3/2}}$, indicating that almost all the nickel in the alloy films existed in its elemental state [14].

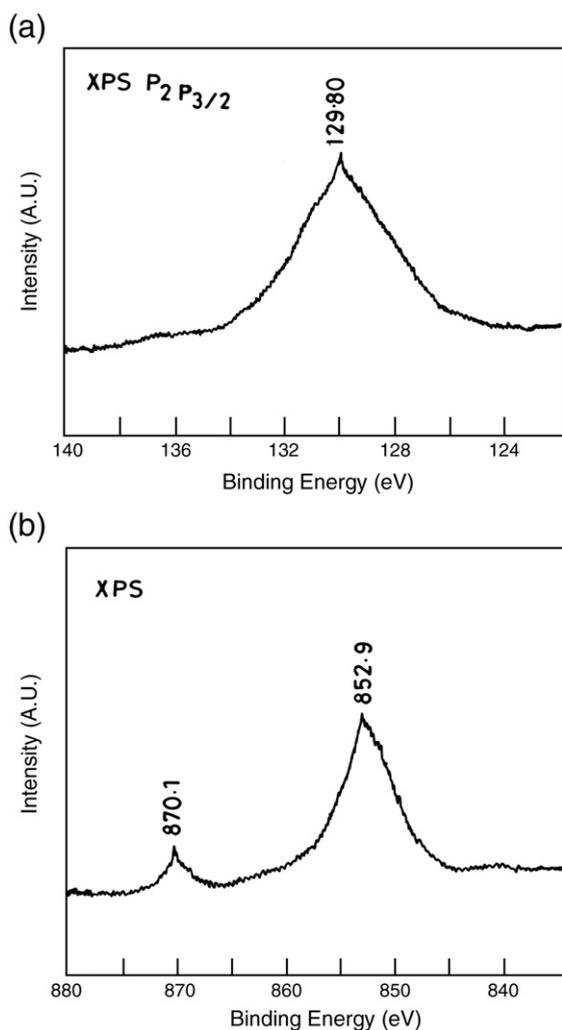


Fig. 4. XPS spectra of Ni–P alloy films deposited at 0.25 M NaH_2PO_2 (a) P_{2p} line (b) Ni_{2p} line.

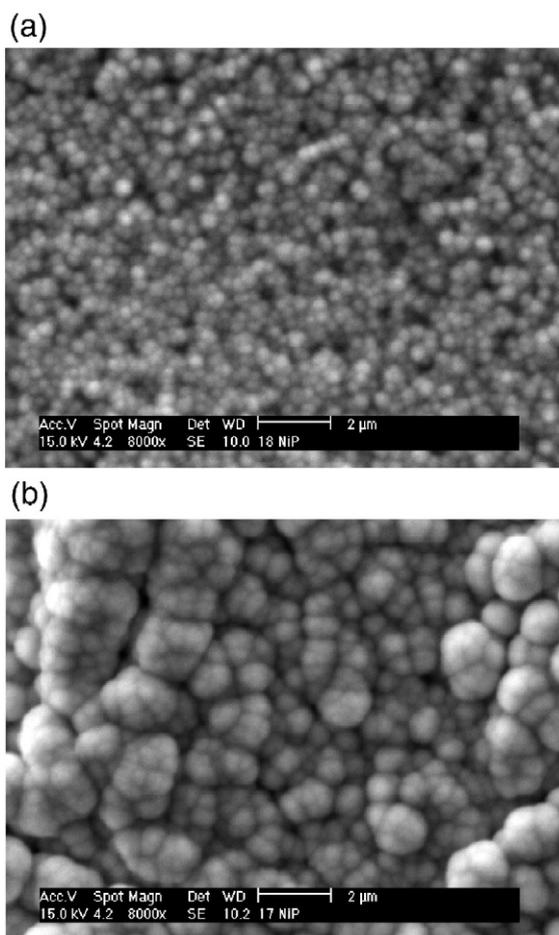


Fig. 5. Scanning electron micrograph of typical Ni–P thin films deposited at various NaH_2PO_2 concentrations (a) 0.15 M and (b) 0.25 M.

Scanning electron micrographs of Ni–P films deposited at different phosphorous concentrations were recorded. A typical scanning electron micrograph obtained for a film deposited at a NaH_2PO_2 concentration of 0.15 M is shown in Fig. 5(a). The surface morphology is found to be uniform with spherical shaped grains. The average grain size is found to be in the range between 0.2 and 0.30 μm. An SEM picture of a typical Ni–P film deposited with a NaH_2PO_2 concentration of 0.25 M is presented in Fig. 5(b). The surface morphology appears to be composed of larger nodules of “cauliflower” type structures typical for amorphous materials [15]. As the NaH_2PO_2 concentration was increased to 0.25 M, the grain size increased. The small crystallites are aggregated into larger nodules with an average size between 0.75 and 1.0 μm. Our X-ray diffraction results indicate that Ni–P alloy films deposited at 0.25 M NaH_2PO_2 concentration are amorphous. Also, a similar morphology of

electroless deposited Ni–P based ternary alloy films with a phosphorus content of 21 at.% was reported by Lu and Zangari [7].

4. Conclusions

Ni–P alloys were electrodeposited from sulfate baths to investigate the dependence of the structural, compositional, electronic and morphological properties at various phosphorous concentrations. The properties of Ni–P alloy films were strongly influenced by NaH_2PO_2 concentrations. Cyclic voltammetry studies revealed the variation of interfacial polarization at different phosphorous contents in the solution bath.

At lower phosphorus concentrations (<13.5 at.%) a polycrystalline FCC structure is observed which transformed into an amorphous structure as the phosphorus content in the deposit is increased. EDAX studies of Ni–P alloys reveal an increase of phosphorus content in the film with an increase in the NaH_2PO_2 concentration in the deposition bath. An XPS study reveals the presence of predominantly Ni_{2p} and P_{2p} phases. Spherical-shaped grains and nodules of a “cauliflower” type morphology are observed for films deposited at low and high concentrations of NaH_2PO_2 in the solution bath, respectively.

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