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Mechanical Properties of Electrodeposited Ni-W ThinFilms with Alternate W-Rich and W-Poor Multilayers

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ABSTRACT

Nickel-tungsten (Ni-W) alloys with tailored composition were electrodeposited by controlling the pH of electrolytes and the applied current density. The current efficiency for the electrodeposition of Ni-W alloys was dependent on the pH of the employed electrolytes. The surface morphology and crystallinity of the electrodeposited Ni-W with controlled compositions were characterized. Based on the electrochemical studies of Ni-W alloys, Ni-W thin films with alternate W-rich and W-poor multilayers were produced by applying alternate current densities. The number and dimensions of the deposited layers were well controlled by the programmed frequency of the applied current and period time, respectively, in the electrochemical cell. In addition, the mechanical properties, such as hardness and internal stress of the Ni-W electrodeposits, were investigated as a function of the composition and number of deposited layers. Compared to the single layer Ni-W films showing the increase of cracks and interal stress with increasing the hardness, the modulated Ni-W multilayers without surface cracks demonstrated the enhanced hardness without an increase in the internal stress.

1. Introduction

Coating techniques with enhanced mechanical and chemical properties have been developed to protect the surface of functional components for various applications. Various metals, metal oxides, and alloys have been utilized as the coating materials to improve the properties such as hardening, self-lubricity, wear resistance, corrosion resistance, and high temperature oxidation. In addition, an enhancement of mechanical and chemical properties has also been achieved by controlling microstructures such as density, pores, grains, dislocations, and inclusions in the deposited thin films [1–3]. Recently, multilayered thin film, double-layered thin film, and graded-layered thin film technologies have been proposed in the three dimensional concept as solutions to improve the properties of thin films [1,4,5].

Deposition of thin films for protective applications has been performed by various techniques such as magnetron sputtering, plasma/thermal spraying, and electrodeposition [1,4,6]. Electrodeposition is considered to be one of the most important techniques for thin films, especially alloy thin films, because the composition, microstructure, and dimensions of the deposited materials can be controlled by adjusting electrochemical parameters including the current density, electrolyte composition, and temperature. Further, electrodeposition is a cost-effective technique [7,8].

As one representative of alloy thin films, chromium-based thin films have been used extensively in a wide range of engineering industries due to the excellent properties against wear and corrosion [9]. However, hexavalent chromium thin films were banned from use in industries due to the hazardous waste associated with their use (*e.g.*, barium sulfate and lead chromate). The trivalent chromium thin film process, an alternative approach, showed limitations such as discoloration and high cost. Recently, a comparative investigation of thin films employing Ni alloys has been carried out to demonstrate improved mechanical properties. Ni thin films with similar grain sizes have typically demonstrated better mechanical properties than Co thin films; this behavior was attributed to the difference in crystal structure between face-centered-cubic (FCC) Ni and hexagonal-close-packed (HCP) Co [10,11]. Compared to elemental Ni thin films, the thin films of Ni-W alloys have shown excellent mechanical properties in terms of hardness, wear resistance, corrosion, and thermal stability [12–14]. However, the internal stress of the film increased with the introduction of W, which can lead to detrimental effects such as

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fatigue, cracking, and delamination [15–17]. Thus, the promise of high performance Ni-W thin films has been derailed by this increase in the internal stress.

Incorporation of less brittle metallic interlayers between two layers with high internal stress has been investigated as an advanced thin film technique to relieve the internal stress in thin films. Conventional physical vapor deposition techniques have mainly been utilized to deposit multilayered thin films with well-controlled dimensions [4,5,18,19]. However, the composition of the deposited alloys in each layer is difficult to control using this method. In contrast, electrodeposition is a powerful technique to deposit multilayered films with the designed composition in a cost-effective way.

Although W cannot be generally electrodeposited in an aqueous solution, Ni-W alloys can be co-electrodeposited by utilizing Ni precursors and complexing agents such as citrate, ammonia, glycine, and triethanolamine(TEA). The complexing agents also reduce the residual stress of Ni-W deposits [8,20]. The composition, crystallinity, and microstructure of the electrodeposits can be controlled by various electrochemical parameters [2,21–23].

In this paper, Ni-W electrodeposition resulting in tailored crystallinity and composition was systematically investigated. Based on the electrochemical study of Ni-W single-layer thin films, Ni-W multilayered films with alternate amorphous W-rich Ni-W and polycrystalline W-poor layers were electrodeposited with control over the thickness and number of layers. Mechanical properties (*i.e.*, hardness and internal stress) of the electrodeposited Ni-W thin films were characterized for various W amounts in the Ni-W alloys. Additionally, the mechanical properties of multilayered Ni-W thin films were analyzed as a function of the number of layers.

2. Experimental

2.1. Electrodeposition of Ni-W alloys

The electrolyte for the electrodeposition of Ni-W alloys consists of 0.2 M $NiSO_4{\cdot}6H_2O$ (Daejungchem), 0.6 M $Na_2WO_4{\cdot}2H_2O$ (Daejungchem), and a complexing agent of 1 M $C_6H_5Na_3O_7{\cdot}2H_2O$ (Daejungchem). The pH of the solution was adjusted by addition of H_2SO_4 (Junsei). Electrodeposition of Ni-W alloy was performed in a two-electrode configuration using a potentiostat (VersaSTAT 3, AMETEK PAR). A copper-sputtered Si wafer with an exposed area of $10 \times 10\,mm^2$ and a platinum plate with an exposed area of $10 \times 10\,mm^2$ were utilized as a cathode and an anode, respectively. The space between the cathode and anode was 30 mm. The applied current density and the pH of electrolytes for the electrodeposition of Ni-W alloys were varied from $10\,mA\,cm^{-2}$ to $40\,mA\,cm^{-2}$ and 4 to 8, respectively. The multilayered Ni-W thin films with alternate W-rich and W-poor phases were galvanostatically deposited by applying an alternating current density of $10\,mA\,cm^{-2}$ and $40\,mA\,cm^{-2}$ with tailored deposition time at room temperature in the electrolytes with a fixed pH of 6. Loops ranging from 1 to 16 and various deposition period times with the alternate current density were applied to control the number and the thickness of the deposited layers.

2.2. Characterization

Top and cross-sectional morphologies, selected area electron diffraction (SAED), and compositions of Ni-W thin films were observed with a field emission scanning electron microscope (FE-SEM, HITACHI model S-4800), a transmission electron microscope (TEM, JEOL JEM-2010), and energy dispersive spectroscopy (EDS). The composition-dependent crystal structures of Ni-W thin films were characterized by X-ray diffraction (XRD, Rigaku D, MAX-2500), which was swept in the range of 2θ from 30° to 70° operating at 40 kV and 100 mA with Cu Kα radiation.The hardness and internal stress of the deposited Ni-W thin films was analyzed by using a nano-indentation test (Nanoindenter G200, Agilent Technologies) and a copper strip test (model 683, Specialty Testing & Development,Inc.), respectively.

3. Results and Discussion

3.1. Electrodeposition of Ni-W alloy

The electrodeposition of Ni-W alloys was carried out by the induced co-deposition process. Therein, the deposition potential of the alloy is determined by the reduction potential of the less noble component and an additional potential shift due to the alloy compound formation, making the overall potential more positive than the reduction potential of the less noble component [6]. In the case of Ni-W alloys, the less noble W cannot be electrodeposited alone in an aqueous solution because of the evolution of H_2 (g) prior to reaching the required reduction potential. However, Ni-W alloys can be electrodeposited in an electrolyte including the complexing agent, citrate (Cit), since the formed complexes can induce the deposition potential shift as described in Eq. (1) and Eq. (2). Citrate as a complexing agent was employed because citrate rather than other complexing agents such as ammonia, glycine and TEA can increase W contents in Ni-W films.

$$[(Ni)(Cit)]^{-} + [(WO_4)(Cit)(H)]^{4-} \rightarrow [(Ni)(WO_4)(Cit)(H)]^{2-} + Cit^{3-} \quad (1)$$

$$[(Ni)(WO_4)(Cit)(H)]^{2-} + 8e^{-} + 3H_2O \rightarrow NiW + 7OH^{-} + Cit^{3-} \quad (2)$$

As previously reported, the structure of the complexes in the electrolyte for the Ni-W electrodeposition was determined by the pH of the solution. The $[(WO_4)(Cit)(H_2)]^{3-}$complexes are dominant in the approximate pH range between 3 and 5. In the range of pH from approximately 5 to 8, the concentration of $[(WO_4)(Cit)(H_2)]^{3-}$complexes decreased and the concentration of $^{-}[(WO_4)(Cit)(H)]^{4-}$ complexes gradually increased [24,25]. The concentration of $^{-}[(WO_4)(Cit)(H)]^{4-}$ complexes decreased and $(WO_4)^{2-}$ ions began to be formed for pH values above 8. The variation of W content in Ni-W alloys and current efficiency with pH were investigated by varying pH from 4 to 8 at a fixed current density of $10\,mA\,cm^{-2}$, as described in Table 1. The current efficiency of the deposits was analyzed based on Eq. (3).

$$CE = \frac{W}{it}\left(\frac{C_{Ni}n_{Ni}F}{M_{Ni}} + \frac{C_W n_W F}{M_W}\right) \times 100 \quad (3)$$

Here, *W*,*i*, *t*, and *F* are the weight of the deposit, passed current, deposition time, and Faraday constant, respectively. Further, *c*, *n* and *M* indicate the weight fraction, number of electrons transferred in the reduction of 1 mole of atoms, and the atomic

Table 1
Electrochemical parameters for the deposition of single-layered Ni-W thin films.

Solution	pH	Current density ($mA\,cm^{-2}$)	Deposition time (sec)
	4		
	5		
$NiSO_4{\cdot}6H_2O$ 0.2 M	6	10	5000
$Na_2WO_4{\cdot}2H_2O$ 0.6 M	7		
$C_6H_5Na_3O_7{\cdot}2H_2O$ 1.0 M	8		
	6	20	2500
		30	1665
		40	1250