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Study of the electroplating mechanism and physicochemical proprieties of deposited Ni-W-Silicate composite alloy

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ABSTRACT

In this work, layers based on Nickel-Tungsten (Ni-W) were electroplated from citrate-ammonia bath with and without silicate addition. Firstly, Electrochemical Quartz Crystal Microbalance (EQCM) and Global Discharge Optical Emission Spectroscopy (GDOES) were used to investigate the electroplating mechanism of both coatings. The gain mass was 14 and 4.13 $\mu g\,cm^{-2}$ for Ni-W-Sil and Ni-W coatings, respectively. Secondly, the morphology of the composite alloy shows a smooth and homogenous surface with compact cauliflower like-structure identified as silicate incorporation. Finally, after a long immersion into chloride solution, Ni-W-Sil composite film showed a good surface stability and a remarkable mechanical hardness. These proprieties enhanced the electrochemical behavior of the composite alloy.

1. Introduction

The electrodeposition of Ni-W alloys was anomalous in nature, with the co-deposition resulting in a higher amount of Ni in the final deposit [1–3]. Therefore, deposit characteristics of Ni-W as compared to the conventional nickel include benefits of extended corrosion resistance and significantly harder coatings. Moreover, the presence of tungsten imparts a good barrier resistance to the coating. However, most previous papers reported that the increase of W content into layer produce amorphous structure. Indeed, crystal lattices of films could be distorted due to larger atomic radii of W (0.1270 nm) which substituted the Ni atom with the atomic radii of 0.1245 nm. This crystal structure increases the appearance of pores and imperfections on final Ni-W coating [3–5]. Attempts were made to enhance the Ni-W alloy compactness by either introducing adsorbed species in the bath or by developing a ternary alloy [6–8].

The use of additives in electrodeposition bath is extremely important due to their influence on the growth and structure of the resulting deposited films. The presence of Diethanolamine and Triethanolamine such as additives during Ni-Zn electroplating had been shown to influence physical and mechanical properties of the electrodeposits (grain size, brightness, internal stress, pitting and even chemical composition) [9]. In addition, the codeposition of phosphorous along with Zn–Ni improves the corrosion [10] and hydrogen permeation [11] characteristics of the coating.

On the other hand, composite coatings based on silicate were also quoted to provide a higher barrier resistance and better stability than others composites [12–15]. Previous studies [12–15] had shown that the presence of silicates into the electroplating bath of zinc allowed the formation of a physical barrier preventing the penetration of aggressive ions. Moreover, the reactions of the film formation were reported incomplete during electroplating and continued during immersion in NaCl solution resulting in a decrease of the corrosion rate [16]. Furthermore, the addition of silicate content into electrolyte bath during DC electroplating of Ni-Zr coating increase its wear resistance [17]. While there is wealth of information on the effect of Silicate species on the electroplating of various metals specially Ni, information on Ni-W electroplating is absent. Hence, it was felt that it would be interesting to carry out a comprehensive study in an extended area, regarding the effect of sodium silicate addition in the plating bath on the properties of the produced Ni-W coatings.

Thus, the objective of the current work is to study the effect of Silicate addition on the electroplating mechanism and corrosion behavior of Ni-W alloy obtained from citrate-ammonia bath and electrodeposited onto copper substrate.

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2. Material and Methods

2.1. Optimization

The pH of the electroplating bath and silicate content (C_{Sil}) are very important to synthesize a resistant composite layer against chloride ions penetration and make the electroplating successful in the shortest time possible.

A Doehlert design, with 9 experiments for 3^2 (3 levels and 2 factors), was carried out as a screening approach to optimize those experimental conditions using NEMROD software program (L. P. R. A. I, Marseille, France). The polarization resistance values Rp of Ni–W alloy and Ni-W-Sil composite alloy electrodeposited on copper used as responses in Doehlert design were investigated and describes elsewhere [18].

2.2. Operating Conditions

Experiments were conducted at room temperature (20 ± 2 °C) and at a constant current density of 20 mA cm^{-2}. Ni-W alloys were electroplated from aqueous solutions containing $NiSO_4{\cdot}6H_2O$ (nickel sulfate hexa-hydrate, Merck #06727, 0.10 M) and $Na_2WO_4{\cdot}2H_2O$ (sodium tungstate dihydrate, Fluka #72070, 0.40 M) as the electro-active species. $C_6H_5Na_3O_7{\cdot}2H_2O$ (citric acid, Merck #06442, 0.35 M) and NH_4OH (ammonia hydroxide, Merck #06448, 0.01 M) as the complexing agents. The additive concentration in the electrolytic baths was achieved by adding aliquots of Na_2SiO_3 (silicate sodium) from a stock solution of 10 g dm^{-3}. All the solutions were prepared from ultrapure water. Electrodeposition was carried out on a pure copper (99.99%) stationary disk electrode of 1 cm^2 surface area. The surface of copper samples was polished with SiC paper, washed with anhydrous acetone, and dried.

The electrochemical cell was platinum as counter electrode and the copper as working electrode. For electrodeposition, the saturated sulfate reference electrode (SSE) was used to prevent presence of chloride ions in citrate-ammonia bath. However, for the corrosion test in 3% NaCl solution, reference electrode was the saturated calomel electrode (SCE).

2.3. Apparatus and methods

2.3.1. Electroplating conditions

To characterize the adherence of coatings, we have subjected them to a thermal shock [19]. Coated samples were placed into a furnace for 30 min at 500 °C and subsequently quenched in water at ambient temperature. Proper adherence of films is indicated when quenching does not result in cracks in the film.

For electrochemical quartz crystal microbalance (EQCM) experiments, the Ni-W layer and Ni-W-Sil composite layer were electrodeposited by chronopotentiometry (at constant current density 20 mA cm^{-2} during 30 minutes) on a quartz crystal blade (6 MHz AT-cut) upon which a thin copper layer has been vacuum deposited previously. The surface area of EQCM electrode was 1 cm^2. All additional information is described elsewhere [20]. For the gravimetric measurements, the results are presented as the mass variation with respect to time. The mass changes were derived from the observed frequency changes using the Sauerbrey equation [20]:

$$\Delta f = -K_s \Delta m \qquad (1)$$

Where Δf is the frequency change, Δm mass change and K_s the constant depending upon the resonant frequency of the quartz. In this study, the nominal frequency was 6 MHz, K_s for the electrodeposition of Ni alloys was equal to 52 Hz μg^{-1} cm^2 according to the relative data of the EQCM instrument.

Scanning Electron Microscopy (SEM) was carried out using a JEOL type 5600 associated to an Energy Dispersive Spectroscopy (EDS) FONDIS model to determine the approximate composition of the alloy.

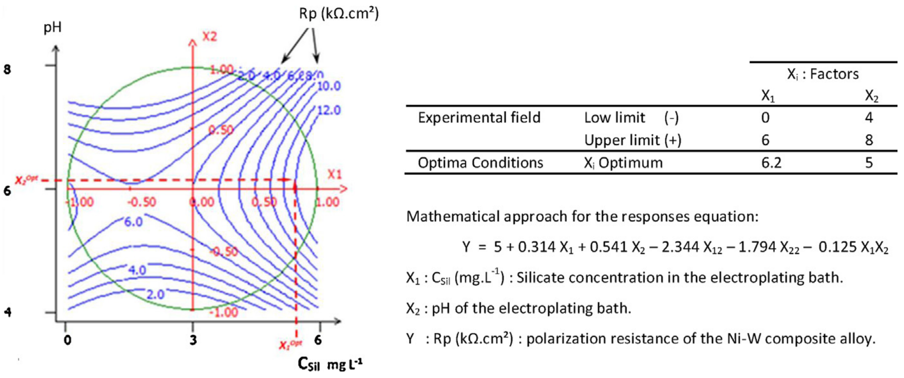
The distribution of species in the deposit was determined by depth profiling with Glow discharge optical emission spectroscopy (GDOES) technique. The instrument was a Jobin Yvon GD-Profiler equipped with a 4 mm diameter anode and operating after optimization at a pressure of 650 Pa and a power of 30 W in an argon atmosphere. This low power was retained to decrease the speed of abrasion of the layers with low thickness and to obtain maximum information at the surface.

The preferred orientations of the coatings were determined by an X-Ray Diffraction under shaving incidence (XRD-Ras) using a D8 advance Bruker (with Bragg–Bretano configuration) with Cu-K_α radiation (λ=1.54 Å). The 2θ range of 30° to 95° was recorded at a rate of 0.02° s^{-1}.

Measurements of the Vickers microhardness (HV) of coatings were performed in the surface by using a HMV-M3 SHIMADZU Microhardness tester under 25 g to 100 g load for 10 s and the corresponding final values were determined as the average of 5 measurements. The porosity was determined by image analysis from the optical micrographs [21].

2.3.2. Electrochemical behavior

The polarization curves were obtained by means of a potentiostat–galvanostat Radiometer Copenhagen PGZ 402 model, piloted by software Voltlab4. The test was a linear scan from E_1 cathodic potential (-1400 mV/SCE) to an anodic potential E_2 (1000 mV/SCE) using a scanning rate of 25 mV/min. The



		X_i : Factors	
		X_1	X_2
Experimental field	Low limit (-)	0	4
	Upper limit (+)	6	8
Optima Conditions	X_i Optimum	6.2	5

Mathematical approach for the responses equation:

$$Y = 5 + 0.314 X_1 + 0.541 X_2 - 2.344 X_{12} - 1.794 X_{22} - 0.125 X_1X_2$$

X_1 : C_{Sil} (mg.L^{-1}) : Silicate concentration in the electroplating bath.

X_2 : pH of the electroplating bath.

Y : Rp (kΩ.cm²) : polarization resistance of the Ni-W composite alloy.

Fig. 1. Isoresponse curves for the modeling polarization resistance Rp (kΩ cm^2) of Ni–W coatings on copper substrate function of sodium silicate concentration (C_{Sil}) and pH of the electroplating bath.