Morphology and Impedance Characteristics of Nickel Electroplating from Watts Bath

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The electroplating of bright nickel from Watts bath with stepwise additives of gelatin, benzene sulphonic acid and its sodium salt was investigated. Electroplating of fine dispersed nickel layer from the same bath with inclusions of gelatin, benzene sulphonic acid sodium salt, $\text{Al}_2(\text{SO}_4)_3$ and SiO_2 was also examined. The effects of bath constituents on the cathodic polarization and the interfacial impedance response during deposition of both forms of nickel was discussed. The surface morphology of the deposits was examined by scanning electron microscopy (SEM) and the crystal structure was elucidated by X-ray diffraction.

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I. Introduction

Nickel has long been electroplated from several baths, frequently chloride⁽¹⁾⁽²⁾, sulphamate⁽³⁾, fluoroborate⁽⁴⁾, chloride-acetate⁽⁵⁾ and acetate⁽⁶⁾ baths. However, the Watts bath has been utilized in most industrial applications, because of its attractive features, *e.g.*, it maintains a cathodic efficiency close to unity for a large range of current densities and allows the addition of organic compounds up to relatively high concentrations. There is a wealth of data reported on the electroplating of bright nickel in the presence of brighteners⁽⁷⁾⁽⁸⁾.

Bright and dispersed silica containing nickel layers have been widely used as supports for highly porous chromium plate to improve its brightness and corrosion resistance. In the previous studies⁽⁹⁾⁻⁽¹¹⁾, it was found that the corrosion behaviour of bright and dispersed SiO_2 -nickel plates depended on the electroplating bath additives.

The objective of the present work is to investigate the quality of electroplated of bright and dispersed SiO_2 -nickel from the Watts bath in presence of different organic and inorganic additives to produce suitable bright and dispersed nickel layer to be used as supports for porous chromium, plating.

II. Experimental

All the plating baths were freshly prepared from distilled water and AR grade chemicals (BDH). The symbols, numbers and compositions of bright nickel (B-Ni) and dispersed nickel (D-Ni) Watts baths are given in Tables 1 and 2, respectively. The experimental set-up for

the electrodeposition process consisted of a rectangular plating cell provided with a copper sheet cathode placed midway between two plane-parallel nickel sheet anodes, all electrodes were of the same area ($2.5 \text{ cm} \times 3 \text{ cm}$). Before each run, the electrodes were mechanically polished with 600 grit emery paper, washed with distilled water and rinsed with ethanol. Air agitation was provided by means of an air pump. The electric current was supplied by a 12 V battery. The plating duration was 30 min. Experiments were carried out at the required temperature with the help of an air thermostat. Potentiodynamic cathodic polarization measurements were performed via a potentiostat (Wenking ModelPOS 73).

Potentials were measured against a saturated calomel electrode (SCE) and the counter electrode was a platinum sheet. To avoid contamination, the reference electrode was connected to the working copper cathode via a bridge filled with the solution under test. The potential-current density curves were recorded using an X-Y recorder (Series 2000, Ominegraphic).

X-ray analysis of the as-plated nickel was carried out using a Philips diffractometer (40 kV, 25 mA) with nickel filter and copper radiation. The morphology of the surface and cross section of the deposits were examined using a scanning electron microscope (JEOL SEM T200).

The electrochemical impedance spectroscopy of nickel electrodeposition from Watts baths was measured under the same plating condition, without agitation. The impedance measurement unit (CNF-6378 Circuit Design Block Co., LTD) was used. The instrument was consisted of a Frequency Response Analyzer (FRA) model S-5720, NF circuit Design Block Co., LTD, serving to make the frequency sweep measured on a logarithmic scale from 0.1 Hz to 10 KHz, using a small sinusoidal perturbation signal. The measurements were controlled by a personal computer (PC-9801F, Nippon Electronic Corporation), and the data were promptly memorized. Complex plane graphs of Cole-Cole plot were obtained

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Table 1 Composition of bright nickel (B-Ni) electroplating solutions. ($I=300 \text{ A/m}^2$, $T=60^\circ\text{C}$, pH 4.5)

Solution	Concentration/ $\text{kg} \cdot \text{m}^{-3}$					
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	H_3BO_3	Gelatin	BSA	BSAS
B-Ni-1	250	75	45	—	—	—
B-Ni-2a	250	75	45	10^{-2}	—	—
B-Ni-2b	250	75	45	5×10^{-2}	—	—
B-Ni-2c	250	75	45	10^{-1}	—	—
B-Ni-3a	250	75	45	10^{-1}	5×10^{-3}	—
B-Ni-3b	250	75	45	10^{-1}	10^{-2}	—
B-Ni-3c	250	75	45	10^{-1}	10^{-1}	—
B-Ni-4a	250	75	45	10^{-1}	10^{-2}	10^{-3}
B-Ni-4b	250	75	45	10^{-1}	10^{-2}	5×10^{-2}
B-Ni-4c	250	75	45	10^{-1}	10^{-2}	10^{-1}

BSA: Benzene sulphonic acid

BSAS: Benzene sulphonic acid sodium salt

Table 2 Composition of dispersed nickel (D-Ni) electroplating solutions. ($I=150 \text{ A/m}^2$, $T=55^\circ\text{C}$, pH 4.5)

Solution	Concentration/ $\text{kg} \cdot \text{m}^{-3}$						
	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	H_3BO_3	Gelatin	BSAS	$\text{Al}_2(\text{SO}_4)_3$	SiO_2
D-Ni-1	250	65	40	—	—	—	—
D-Ni-2a	250	65	40	10^{-1}	—	—	—
D-Ni-2b	250	65	40	10^{-2}	—	—	—
D-Ni-2c	250	65	40	10^{-3}	—	—	—
D-Ni-3a	250	65	40	10^{-1}	10^{-1}	—	—
D-Ni-3b	250	65	40	10^{-1}	10^{-2}	—	—
D-Ni-3c	250	65	40	10^{-1}	10^{-3}	—	—
D-Ni-4a	250	65	40	10^{-1}	10^{-1}	0.5	—
D-Ni-4b	250	65	40	10^{-1}	10^{-1}	1	—
D-Ni-4c	250	65	40	10^{-1}	10^{-1}	3	—
D-Ni-5a	250	65	40	10^{-1}	10^{-1}	1	1
D-Ni-5b	250	65	40	10^{-1}	10^{-1}	1	2
D-Ni-5c	250	65	40	10^{-1}	10^{-1}	1	3

using an X-Y plotter (MP3300 Graphec Corop.).

III. Results and Discussion

1. Cathodic polarization

Figures 1 and 2 show the potentiodynamic cathodic polarization curves for bright and dispersed nickel electroplating from Watts solutions with compositions given in Tables 1 and 2. The compositions of both baths fulfill the essential requirement of electroplating with respect sufficient Ni^{2+} content, acidic medium to avoid the formation of nickel hydroxide or basic oxides at the cathode, and a buffering agent (boric acid) to maintain a constant pH in the cathode layer⁽¹⁾. It is noteworthy that the cathodic polarization was carried out at optimum concentration of the constituents, leading to the formation of nickel electroplating of the best quality.

Inspection of Fig. 1 (curve 2) reveals that the addition of $10^{-1} \text{ g} \cdot \text{L}^{-1}$ gelatin to B-Ni-1 solution increased the cathodic potential by about 120 mV than that recorded in the absence of gelatin, (curve 1, Fig. 1). This behaviour may be ascribed to the formation of a very thin protein membrane upon the cathode compartment⁽¹²⁾. This mem-

Fig. 1 Potentiodynamic cathodic polarization curves for bright nickel electroplated from (1) B-Ni-1, (2) B-Ni-2c, (3) B-Ni-3b and (4) B-Ni-4c.

Fig. 2 Potentiodynamic cathodic polarization curves for dispersed nickel electrodeposited from (1) D-Ni-1, (2) D-Ni-2a, (3) D-Ni-3a, (4) D-Ni-4b and (5) D-Ni-5c.

brane hinders the migration and discharge of Ni^{2+} ions. A small negative polarization shift is observed (curve 3, Fig. 1) as a result of the combined effect of gelatin and benzene sulphonic acid (BSA) in B-Ni-3b solution. The effect of BSA may be ascribed to the adsorption and consequent hydrogenolysis at the cathode surface yielding benzene and bisulphite anion, the latter being reduced at the freshly formed nickel layer to sulphide ion, which is incorporated into the nickel plate as nickel sulphide⁽⁷⁾⁽¹³⁾, while benzene is desorbed from the surface⁽¹⁴⁾, on the other hand, the combined effect of gelatin, BSA and benzene sulphonic acid sodium salt (BSAS) in solution B-Ni-4c (curve 4, Fig. 1) leads to a slight positive polarization shift compared with that observed in the presence of gelatin only (curve 2, Fig. 1), due to the adsorption of both BSA and BSAS leading to increase of the brightness of the nickel plate.

Figure 2 shows the potentiodynamic cathodic polarization curves for D-Ni-1, D-Ni-2a, D-Ni-3a, D-Ni-4b and D-Ni-5c solutions. It is interesting to note that the addition of $10^{-1} \text{ g} \cdot \text{L}^{-1}$ gelatin in solution D-Ni-2a causes a shift in the cathodic polarization potential to a more negative value (curve 2, Fig. 2), while the combination of gelatin and BSAS in solution D-Ni-3a (curve 3, Fig. 2) shifts the cathodic polarization potential to a less negative value. These effects are likely related to the formation of protein membrane and the adsorption of BSAS molecules on the cathode surface. The inclusion of fine particles of $\text{Al}_2(\text{SO}_4)_3$, observed in solution D-Ni-4b to form a composite matrix with the nickel plate, has not enhanced the cathodic polarization (curve 4, Fig. 2). Also the combination of $\text{Al}_2(\text{SO}_4)_3$ and SiO_2 particles in D-Ni-5c solution, has led to a decrease in the cathodic polarization potential (curve 5, Fig. 2). This behaviour in-

dicates that the presence of $\text{Al}_2(\text{SO}_4)_3$ and SiO_2 particles in the bath facilitates the deposition of nickel at lower current density.

2. Surface morphology and structure of the deposits

Figure 3 shows scanning electron micrographs (SEM) of the surface of as-plated nickel obtained from some bright nickel solutions under test, at a current density of 300 A/m^2 , at 60°C and 30 min plating duration. The nickel electroplate obtained from solution B-Ni-1 consisted of large irregular shaped porous crystals (Fig. 3(a)). The formation of such pores may be caused by discharge of H^+ ions at the cathode layer yielding hydrogen gas bubbles which would cling to the growing nickel deposit⁽⁴⁾.

Figure 3(b) shows the SEM micrograph of nickel electroplated from solution B-Ni-2c, which contains $10^{-1} \text{ g} \cdot \text{L}^{-1}$ gelatin, reveals the formation of nonlevelled, fine nodular shaped nickel crystals covering the cathode surface. The morphology may be attributed⁽¹²⁾ to the formation of a slightly thicker protein membrane like film at the higher current density than that formed at lower current density areas of the cathode diffusion layer. This film would be formed not only by cataphoresis, but also as a result of the decrease in H^+ ion concentration in the cathode layer associated with the cathodic discharge. Consequently, the permeability of such membrane would be decreased at the higher current density areas mainly for the Ni^{2+} ions, but not appreciably for H^+ ions⁽⁶⁾.

The presence of BSA in solution B-Ni-3b seems to bring about the formation of more or less levelled, finer-grained texture which completely covers the cathode surface (Fig. 3(c)). This may be achieved due to the adsorption of BSA on growth sites of crystals thus inhibiting the most active growing sites⁽¹⁵⁾⁽¹⁶⁾. This indication is in agreement with the observed increase in the nucleation density⁽¹⁷⁾.

Figure 3(d) reveals that the combination of BSA and BSAS during the electroplating of nickel from solution B-Ni-4c (optimum bath) leads to the formation of a smooth deposit exhibiting mirror-like appearance without visible pits. This behaviour shows that BSA and BSAS, which are classified as class I brighteners⁽¹⁾, also act as anionic wetting agents, thus preventing the formation of pits which are caused by clinging hydrogen bubbles. It can be seen from the cross-section micrograph of nickel electroplate obtained from the optimum bath (Fig. 3(e)) that the large grains consisted of several small compact grains without leaving pores or cracks between them.

The surface morphology of the as-plated nickel deposits obtained from dispersed nickel solutions (Table 2), at a current density of 150 A/m^2 , temperature of 55°C and duration of 30 min, is exhibited by the micrographs shown in Fig. 4. The nickel electroplated from solution D-Ni-1 consists of a coarse-grained deposit which leaves some bare areas on the cathode surface (Fig. 4(a)). The inclusion of $10^{-1} \text{ g} \cdot \text{L}^{-1}$ gelatin in solution D-Ni-2a improves the fineness of the deposit (Fig. 4(b)), presuma-

Fig. 3 Electron micrographs of nickel electroplated from (a) Solution B-Ni-1, (b) Solution B-Ni-2c, (c) Solution B-Ni-3b, (d) Solution B-Ni-4c and (e) The cross-section of the deposit shown in (d).

bly due to the formation of membrane-like film on the cathode layer⁽¹²⁾. The combination of both gelatin and BSAS in D-Ni-3a solution yields a still finer grained deposit with better coverage (Fig. 4(c)). This effect is due to the increase of nucleation density resulting from the adsorption of BSAS during the electroplating process⁽⁶⁾.

The morphology of nickel electroplate obtained from solution D-Ni-4b including gelatin, BSAS and $\text{Al}_2(\text{SO}_4)_3$, (Fig. 4(d)), is very similar to that obtained from solution D-Ni-1, except that the grain size of latter deposit was smaller. This effect indicates that the random codeposition of $\text{Al}_2(\text{SO}_4)_3$ particles by agitation during the electroplating of nickel leads to the formation of larger crystals.

Inspection of Fig. 4(e) reveals that the inclusion of fine particles of $\text{Al}_2(\text{SO}_4)_3$ and SiO_2 in the plating bath D-Ni-5c has given rise to a microcraze-cracking. In the practical application of the multi-nickel layers as support for porous chromium plating, the cracks in the dispersed nickel layer should not reach the surface of the substrate to avoid the galvanic corrosion. Figure 4(f) shows the cross-section of the dispersed nickel plate which reveals that the microcrack did not reach the substrate. Such a layer would be quite suitable for use as an under-layer for chromium plating.

Table 3 gives the X-ray diffraction data for deposits obtained from solutions B-Ni-4c and D-Ni-5c. Regardless of the composition of the examined bath, the results

reveal that nickel electroplates possess the cubic structure exhibiting the orientations (111), (200) and (220). Moreover, the results showed a good agreement between the calculated values and the standard lattice parameters. However, Pangarov⁽¹⁸⁾ and Haruyama⁽¹⁹⁾ showed that the preferred orientation of deposits would depend on the current density which changed in case of solutions with additives, which would adsorb easily at a high energy face, preventing thus the growth of Ni deposits on that surface, accelerating thus the film growth on other faces according to the inhibition theory⁽²⁰⁾.

3. Impedance response during the electrodeposition

The interfacial impedance spectra were measured during the electroplating of nickel from various B-Ni and D-Ni baths under the operating conditions (current density, pH and temperature) as mentioned in Tables 1 and 2 without agitation. Schematic diagrams of the electrochemical equivalent circuit and the impedance locus of nickel electroplating from those baths are given in Fig. 5(a) and (b).

Figure 5(b) shows that the dispersion of impedance spectrum on a complex plane is generally semicircular with its center below the real axis. The angle θ between the real axis and the central line of the semicircle through the intercept obtained at high frequency has been considered as a parameter corresponding to the reaction homogeneity on the surface⁽²¹⁾⁽²²⁾, so that when θ is small,

Fig. 4 Electron micrographs of nickel electroplated from (a) Solution D-Ni-1, (b) Solution D-Ni-2a, (c) Solution D-Ni-3a, (d) Solution D-Ni-4b, (e) Solution D-Ni-5c and (f) The cross-section of the deposit shown in (e).

Table 3 X-ray diffraction data of nickel plates from B-Ni-4c and D-Ni-5c solutions.

Sample	Observed		I/I_0	hkl	Lattice parameters/nm	
	2θ	d/nm			Observed a	Standard a
B-Ni-4c	44.5	0.2034	100	111	0.3522	0.3523
	51.9	0.1762	11	200		
	76.3	0.1247	4	220		
D-Ni-5c	44.7	0.2024	100	111	0.3522	0.3523
	51.88	0.176	15	200		
	74.44	0.123	3	220		

the surface reaction is uniform. The interval between intercepts of the semicircle with the real axis is R_t and the inverse of the top angular frequency is the mean reaction time constant (τ_0), where $\tau_0 = R_t \cdot C$. Parameters R_t and τ_0 refer to the reaction facility and reaction activity⁽¹⁹⁾. Small magnitude shows that the reaction takes place easily with high homogeneity.

The typical change of the impedance spectra with change of the bath composition is represented by Fig. 6,

Fig. 5 (a) Schematic diagram of the electrochemical equivalent circuit for nickel electrodeposition. R_e =the solution resistance, C =Capacity of the electrochemical double layer, R_t =Transfer resistance, ρ =Faradaic resistance, L =Self inductance. (b) Schematic diagram of impedance locus for nickel electrodeposition from Watts bath.

Fig. 6 Cole-Cole plot corresponding to the electroplating of nickel from solutions (a) B-Ni-1, (b) B-Ni-2c, (c) B-Ni-3b and (d) B-Ni-4c, under the conditions of J , 300 A/m², 10 min, pH 4.5; frequencies are expressed in Hz.

obtained with bath B-Ni. In general, the spectra are characterized by a capacitive semicircle at higher frequency region and an inductive loop at lower frequency region. It is interesting to note that the parameters R_t , θ and τ_0 to some extent depend on the solution additives, whereas the inductive loop at lower frequency has been believed to be a response adsorption and desorption reactions of a nickel intermediate compound, $(\text{Ni OH})_{\text{ad}}$, consumed at the electrode⁽²³⁾. A similar behaviour has been reported for the dissolution of iron⁽²⁴⁾. It has been argued⁽²⁵⁾ that the shape of the impedance spectra of nickel electroplated from the Watts bath depends on the current density and the agitation of the bath, so that the presence of inclusion of either $\text{Al}_2(\text{SO}_4)_3$ or SiO_2 in the solution diminishes the inductive loop at the low frequency region.

IV. Conclusion

Bright nickel layer was electroplated on copper sheet cathode from Watts bath with additives of gelatin, benzene, sulphonic acid and its sodium salt at a current density of 300 A/m², at 60°C and 30 min plating duration. Also electroplating of fine non metallic dispersed nickel layer was achieved from the same bath in the presence of $\text{Al}_2(\text{SO}_4)_3$ and SiO_2 at a current density of 150 A/m², at 55°C and 30 min plating duration. It was found that both nickel plates exhibited the crystal orientations of (111), (200) and (220). The interfacial impedance response during the electrodeposition of both forms of nickel showed that the electrocrystallization of nickel takes place through intermediate compound.

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