Properties of Nickel Electrodeposits Obtained from Ethylene Glycol Baths

By A. A. Sarabi* and V. B. Singh*

Nickel electrodeposition was carried out in Ethylene Glycol (EG) solution using chloride and sulphate baths. The physical properties and structure of the deposits under different plating conditions have been studied. Nickel deposits free of cracks and porosity with sound physical properties have been obtained. Transmission electron microscopic examination revealed some interesting results with respect to dislocation, texture and twinning in the nickel deposits. The microhardness variation with bath temperature and annealing temperature has been studied. Influence of interrupted direct current also has been investigated.

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I. Introduction

Recently⁽¹⁾⁻⁽⁵⁾ there has been much interest in the electrodeposition of metals and alloys from organic solvents, because of the possibility of enhancing ion solvation/ion complex formation owing to different dielectrical properties, the different natures of hydrogen bonding, alter ion size and resonance, etc. Furthermore, the metal can be obtained at high current efficiency in high purity and with good physical properties.

In most electroplating systems in which the cathodic reaction involves both metal deposition and hydrogen evolution, therefore, the incorporation of hydrogen affects the properties of the deposits significantly. Nakahara and co-workers⁽⁶⁾⁽⁷⁾ have reported the defect observed in nickel electrodeposits due to hydrogen inclusion. Recently Kaja *et al.*⁽⁸⁾ have studied the effect of pH on the microstructure of the nickel electrodeposits and found high density of dislocation in the deposits with twinning and texture formation at low pH 1.5 though at pH 4.2 the deposits were relatively dislocation free. Many other workers⁽⁹⁾⁽¹⁰⁾ have discussed the role of hydrogen on the structure and prop-

erties of the electrodeposits. The role of hydrogen in electrodeposits have aroused the interest of the authors. A systematic investigation has been undertaken to study the deposition of nickel from organic solvents in this laboratory. The successful deposition of nickel from Ethylene Glycol has already been reported⁽¹¹⁾⁽¹²⁾ in which the deposits were obtained at high cathode current efficiency with improved physical properties. The effect of heat treatment of the deposits obtained particularly from organic solvents and influence of interrupted direct current in organic solvents for nickel deposition has not been reported in the literature. This may reveal some interesting characteristics. Since the heat treatment affects the microhardness and other physical properties which are also related to the hydrogen or other inclusions to some extent.

It would be worthful to investigate such effects for the deposits obtained particularly from organic solvents (EG). The structural studies of the nickel deposits have been examined by a scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-rays.

II. Experimental

The general experimental procedures and set-up are described in earlier publications⁽¹²⁾⁽¹³⁾.

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Table 1 Composition and operation conditions for nickel electrodeposition from Ethylene Glycol bath.

	Chloride bath	Sulphate bath
Nickel salt (kmol/m ³)	0.3	0.05
Boric acid (kmol/m ³)	0.2	0.2
Current density (A/m ²)	15–130	15–75
Temperature (K)	293–413	293–413
Time (second)	1200–4800	1200–3600

For each experiment the above composition of the electrolyte has been used.

The plating solutions were prepared from nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and nickel sulphate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) separately in extra pure ethylene glycol (Table 1). A mechanically polished scratch free rectangular copper sheets ($0.02 \times 0.01 \times 0.0001$ m) degreased and pickled, were used as a cathode in the plating solution. The nickel plated specimens were vacuum sealed in a glass tube and annealed them at various temperatures for 2 h and then allowed to cool slowly at room temperature. The direct current was interrupted at the highest frequency 10000 cycles/s by inserting an electronic chopper in the electrical circuit.

Microhardness of the deposits was measured by using a Tukon Wilson microhardness tester with a 136° diamond pyramid indenter, applying 10 gf load (0.098 N), the surface hardness values are the average of several measurements which did not vary much. The specimens for the TEM were prepared and then thinned by electropolishing, as adopted earlier⁽¹⁴⁾. Microstructure was examined by a scanning electron microscope (PSEM-500) and a transmission electron microscope (CM-12 philips), operated at 100 kV. X-ray diffraction was performed by (PW 1710) at an accelerating voltage 30 kV and 20 mA.

III. Results and Discussion

1. Effect of current density and temperature

The microhardness of the electrodeposited nickel was measured at different current densities (Fig. 1). The microhardness increased

Fig. 1 Effect of current density on the microhardness. ●—Nickel chloride (0.3 kmol/m³), temperature 313 K. ○—Nickel sulphate (0.05 kmol/m³), temperature 313 K.

considerably with an increase in the current density for the deposits obtained from chloride and sulphate bath. Due to low solubility of sulphate higher current density could not be employed. The enhanced microhardness of the deposits can be attributed to the considerable reduction of grain size at increasing current density. Butts and De Nora⁽¹⁵⁾ have reported that at a low current density the rate of discharge of ions is small, the rate of crystal growth can easily match the rate of liberation of metal atoms, so it is easier for crystals to grow than that of fresh nuclei form and produced a large grain size, therefore, at higher current densities the rate of crystal growth may not be sufficient to provide for the faster rate of liberation of atoms, so fresh nuclei are formed and consequently fine grained deposits are produced.

The microhardness of the deposit was observed to be higher in the case of chloride bath than sulphate bath (Fig. 1). This can be attributed to the presence of chloride ion which decreases the grain size of the deposit⁽¹⁶⁾.

The effect of the bath temperature on the cathode current efficiency (CCE) was studied between 293 and 413 K for chloride and sulphate baths under the optimum current densities 100 and 40 A/m², respectively, (Fig. 2).

Mirror bright, adherent and uniform deposits without porosity were obtained from

Fig. 2 Effect of bath temperature on the CCE.

- Nickel chloride (0.3 kmol/m^3), c.d. 100 A/m^2 .
- Nickel sulphate (0.05 kmol/m^3), c.d. 40 A/m^2 .

chloride up to 373 K, above which the deposits turned to semibright but were adherent and uniform with large grain size. The cathode current efficiency remained almost constant within the temperature range studied.

Bright and adherent deposits were obtained from sulphate bath up to 353 K. Beyond this temperature the deposits turned to semibright but remained smooth and adherent. The CCE increased with an increase in the temperature of the bath (Fig. 2) which may be due to the increase in the rate of diffusion of metal ions with temperature.

The variation of the microhardness of the deposits obtained from chloride and sulphate baths at different temperatures is shown in Fig. 3. Initially the microhardness increased with

Fig. 3 Effect of bath temperature on the microhardness.

- Nickel chloride (0.3 kmol/m^3), c.d. 100 A/m^2 .
- Nickel sulphate (0.05 kmol/m^3), c.d. 40 A/m^2 .

an increase in temperature up to 333 K, but above this temperature it decreased regularly with increasing temperature. The higher hardness value at 333 K can be explained in terms of reduced grain size of the deposits. It can be added that the fine grained deposits are formed only up to a certain temperature ($\approx 333 \text{ K}$), while at higher temperatures the large grains formed as is evident from SEM micrographs (Fig. 4(a), (b)). The bath temperature affects the diffusion reaction velocity, the polarization and the relative rates of nucleus formation and crystal growth. The ions are mobile at higher temperatures which favours equilibrium

Fig. 4 SEM micrograph of electrodeposited nickel from a 0.3 kmol/m^3 nickel chloride bath at c.d. 100 A/m^2 (a) 313 K (b) 413 K.

Fig. 5 Effect of annealing temperature on the microhardness.

- Nickel chloride (0.3 kmol/m^3), c.d. 100 A/m^2 .
- Nickel sulphate (0.05 kmol/m^3), c.d. 40 A/m^2 .

deposition and the formation of large grains with a low free energy. This is the probable reason for the production of large grains at higher temperatures.

The microhardness of the deposits decreased with an increase in the annealing temperature (Fig. 5). A sharp decline in the hardness is observed up to 773 K and thereafter decreases gradually. This indicates that probably complete annealing has occurred. Similar observation⁽¹⁷⁾ has been reported for nickel deposits.

The SEM micrographs Fig. 6(a) and (b) show a significant structural changes with respect to initial structure (Fig. 4(a), (b)). As

the annealing temperature increased the deposits passed through a process of recrystallization and finally well defined grain growth has been observed. It is clearly marked with distinct growth boundaries. The process of recrystallization of grains has been reported in the literature⁽¹⁸⁾. The deposits obtained from either sulphate or chloride bath possessed almost the same microhardness value after annealing at 973 K .

2. Interrupted direct current effect

Figure 7(a) and (b) are the SEM micrographs of nickel deposits obtained from chloride bath by using direct current and interrupted direct current at current density 130 A/m^2 , respectively. Figure 7(a) shows that the central portion of the deposited nickel is crack free and almost free of porosity and pitting or voids. The microcracks are observed near the edges and corners which may be due to high internal stress. The microcracks have nearly completely disappeared when the current was interrupted at 10000 cycles/s (Fig. 7(b)). The stress reduction for nickel deposition by pulse plating has been reported⁽¹⁹⁾. The structure of the deposits appears to undergo a change due to high interruption frequency. It tended more towards a columnar than lamellar structure in the case of chloride bath and also the smoothness and grain refinement were considerably improved. The cathode current efficiency also improved (8% to 10%) due to such an interruption.

Fig. 6 SEM micrograph of electrodeposited nickel. (a) Nickel chloride (0.3 kmol/m^3); c.d. 100 A/m^2 and annealing temperature 973 K . (b) Nickel sulphate (0.05 kmol/m^3); c.d. 40 A/m^2 and annealing temperature 973 K .

Fig. 7 SEM micrograph of electrodeposited nickel from 0.3 kmol/m^3 nickel chloride at c.d. 130 A/m^2 , temperature 313 K , (a)—direct current (b)—Interrupted direct current.

3. TEM studies

TEM studies performed for the nickel deposits obtained from chloride bath presented some peculiar structural features. The micrographs (Fig. 8(a)–(d)) show that the deposits are fine-grained and polycrystalline which is evident from the observed numerous spots on the ring diffraction (Fig. 8(d)) and also from the measurement of grain size ($0.75\text{--}1.4 \mu\text{m}$) in microstructure revealed by bright field image (Fig. 8(a)–(c)). A careful examination of the micrographs (Fig. 8(a)–(c)) indicates that the deposits are almost free from dislocation and twinning. It is also inferred from the continuity of the ring that preferred orientation in deposits is not clearly realized. Such an absence of texture in the deposit is probably due to the fact that a critical grain size above which preferred orientation can develop has not been attained in the present case. Texture free copper deposits have been obtained from cyanide bath⁽²⁰⁾. Lee and co-workers⁽²¹⁾ have reported that in the bright nickel deposits the $[110]$ texture developed in most cases except during a few experiments at low temperatures and high current densities when a random distribution of crystals appeared. Furthermore, the f.c.c. structure of the deposits revealed by TEM in the present studies was also confirmed by X-ray diffraction which gave the lattice constant (0.3520 nm). Our TEM (micrographs) observations with

respect to dislocation, twinning and texture are not in agreement with those reported in the literature⁽⁶⁾⁽⁷⁾. Yang⁽⁹⁾ has reported that hydrogen may be one of the principal factor for the formation of the mixed structure or h.c.p. structure in nickel deposits. Kapusta *et al.*⁽²²⁾ observed that hydrogen evolution at a single crystal iron foil increased the dislocation density.

The main reason for the observed defects in the metal deposits by the above workers have mainly been correlated due to the evolution/occlusion of the hydrogen in the matrix. The present results can be examined in the light of hydrogen interference in the nickel deposits. It is anticipated that since in the present case deposits have been obtained from organic solvent the consequences of hydrogen evolution/occlusion may not be effective because hydrogen would be available to a negligible extent here. Even if nominal hydrogen evolution is taken into consideration, there is the possibility that it is not occluded in the deposits and therefore does not affect the structure of nickel.

The nickel deposits obtained from ethylene glycol bath show moderately high hardness and good ductility. The moderate hardness of the deposits obtained can possibly be correlated to the absence of dislocation in the deposited nickel. Moreover, the deposits are free of any impurity/inclusion (hydride/hydroxide) and therefore its hardness matches

Fig. 8 TEM micrograph of electrodeposited nickel from 0.3 K mol/m^3 nickel chloride at c.d. 100 A/m^2 , temperature 313 K . (a) 12×5900 , (b) 10×10500 , (c) 14×10500 , (d) selected area diffraction pattern.

to the pure usually electrodeposited nickel.

IV. Conclusions

It is found that satisfactory nickel deposits can be obtained with high cathode current efficiency from ethylene glycol solvent and bath can be operated at elevated temperatures. Sound and uniform deposits free of porosity, cracks and voids were obtained. The moderately high hardness could be obtained without using addition agents. Recrystallization of grains in the deposits is clearly observed at high annealing temperatures. With high frequency interruption of the direct current the quality of deposits improved. TEM studies have hardly revealed the presence of any dislocation, twinning and texture in the nickel deposit and no interference of hydrogen is thus inferred.

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