

Studies on plating, physical properties and structure of nickel electrodeposited from sulphamate/dimethyl sulphoxide

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Electrodeposition of nickel has been carried out in a nickel sulphamate/dimethyl sulphoxide bath. Physical properties and structure of the deposits under different plating conditions have been studied. Nickel deposits without cracks are obtained at a current density of 0.6 Adm^{-2} and at 70°C . The microhardness of deposits increased with increasing current density. The bath seems to be advantageous compared to the earlier reported dimethyl sulphoxide baths with respect to quality, cathode current efficiency and microhardness. The variation of microhardness with bath temperature and annealing temperature is reported.

Earlier investigation¹ on nickel deposition from $\text{NiCl}_2/\text{DMSO}$ and $\text{Ni}(\text{BF}_4)_2/\text{DMSO}$ indicated that dimethyl sulphoxide (DMSO) was not a suitable solvent for depositing nickel as it led to non-adherent and black deposits, although other metals such as titanium² and manganese³ were successfully deposited from DMSO based baths. Later it was found⁴ that with additions of small quantity of cobalt acetate or cadmium acetate in DMSO bath, the quantity and physical properties of nickel deposits improved upto some extent. Electrodeposition from aqueous bath suffers some disadvantages due to hydrogen evolution and its inclusion in the deposits. Nakahara and Felder^{5,6} reported that incorporation of hydrogen, hydroxide or other inclusions in the deposits altered the properties and crystallographic structure of the metal deposits. Absorption of hydrogen can be best prevented by using non-aqueous solvents for electroplating and from this point of view the electrodeposition of nickel was carried out from organic solvents. Since nickel sulphamate-aqueous bath produced nickel deposits exhibiting high hardness and low internal stress⁷, therefore, it was of interest to deposit nickel from DMSO bath and then to study its physical properties and structure under different plating conditions.

Experimental procedure

Dimethyl-sulphoxide (A R grade) was purified as noted in literature⁸. Mechanically polished scratch-free copper strips ($2.0 \times 1.0 \times 0.01 \text{ cm}$) degreased and pickled, were used as cathodes. The experimental set up was the same as described

earlier^{9,10}. Sulphur depolarized electrolytic nickel sheets were chosen as anodes. The plating solution was prepared by dissolving required amounts of nickel sulphamate (Fluka AG) and boric acid (AR grade) in purified DMSO solution. The bath composition and operating conditions are given in Table 1. Microhardness of electrodeposits was measured using a $\pi\text{MT-3}$ microhardness tester with a 136° diamond pyramid indenter, applying 20 g load. Each hardness-value is the average of several measurements. The deposited nickel was annealed in vacuum for 2 h at various temperatures (200, 300, 400, 500, 600, 700 and 800°C) then allowed to cool slowly to room temperature. Structures were characterized by using SEM (Jeol 840 A). The cathode polarization was carried out potentiostatically (POS 73, Wenking) using saturated calomel reference electrode.

Results and Discussion

Effect of electrolyte concentration and current density—Effect of different concentrations of

Table 1—Composition and operating conditions of electrolysis for nickel deposition in dimethyl sulphoxide (DMSO)

Parameter	Value
Nickel (II) Sulphamate, [Ni (SO_3NH_2) ₂ .2H ₂ O], M	0.05, 0.1 & 0.2
Boric acid, M	0.2
Bath temperature, $^\circ\text{C}$	20-80
Annealing temperature, $^\circ\text{C}$	200-800
Current density, Adm^{-2}	0.2-1.2
Duration of electrolysis, min	60
Agitation	Nil

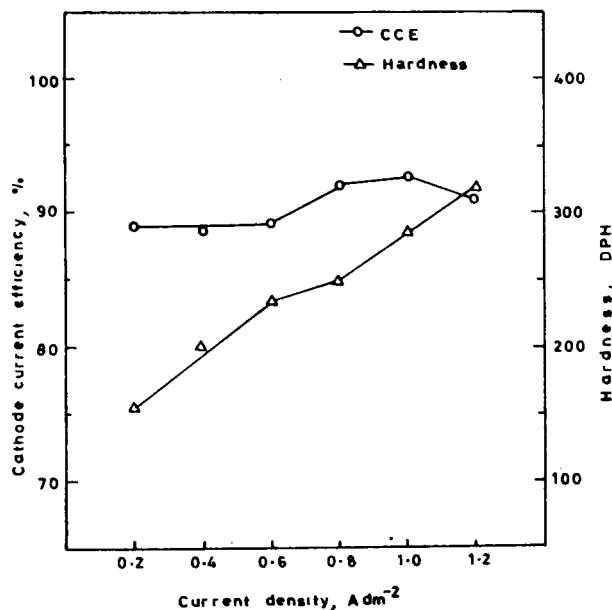


Fig. 1—Effect of current density on CCE and microhardness (0.2 M Nickel Sulphamate; 0.2 M boric acid, 40°C)

electrolyte (0.05, 0.1 and 0.2 M) and current density on the cathode current efficiency (CCE), quality and hardness of nickel deposits was investigated. It was observed that 0.2 M concentration of nickel sulphamate, the maximum soluble amount of electrolyte at 40°C, led to highest cathode current efficiency and hardness with better quality (light gray, smooth and adherent) at a current density (CD) of 0.6 Adm^{-2} . Influence of current density was studied between 0.2-1.2 Adm^{-2} using a bath of composition 0.2 M nickel sulphamate and 0.2 M boric acid/DMSO at 40°C (Fig. 1). The cathode current efficiency remained almost constant upto 0.6 Adm^{-2} and, thereafter, increased upto some extent and above 1.0 Adm^{-2} it decreased slightly. Nature of the deposits was light gray and adherent at optimum CD (0.6 Adm^{-2}) but with further increase in current density it turned to be dull gray, black and powdery on the edges. The non-adherent and black deposits obtained at higher current densities may be attributed to the high rate of nucleation, hydrogen evolution with lower activity of nickel ion near the cathode.

Microhardness of the as deposited nickel increased considerably with an increase in the current density (Fig. 1) and maximum microhardness (318 DPH) was obtained at the highest current density (1.2 Adm^{-2}). Such improvement in the microhardness can be attributed to the progressive grain refinement of the deposits. Enhancement of microhardness with increase in current density, is also due to adsorption and inclusion of basic colloidal hydroxide⁶ which is formed in a higher but appropriate amount in the

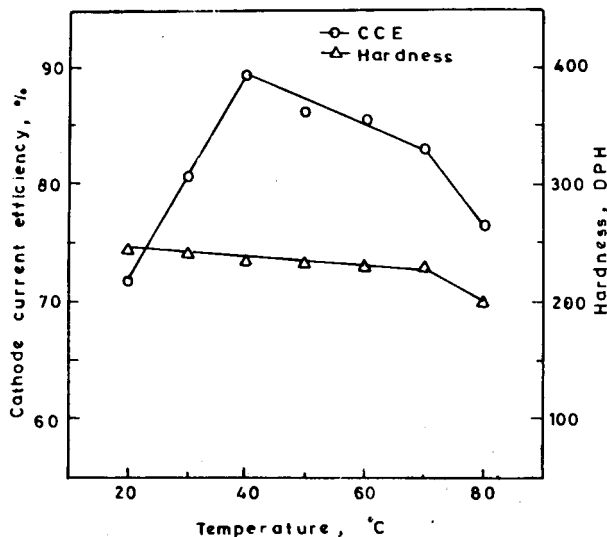


Fig. 2—Effect of bath temperature on CCE and microhardness (0.2 M Nickel Sulphamate, 0.2 M boric acid, CD 0.6 Adm^{-2})

catholyte, at higher current densities¹¹. The basic colloidal hydroxide is likely to be entrapped on the growth steps during film formation¹².

Effect of bath and annealing temperatures—It was observed that the CCE increased upto 40°C and, thereafter, declined with increasing bath temperatures (Fig. 2). The studies at optimum CD (0.6 Adm^{-2}) showed that 70°C to be the best operating temperature at which semi-bright, adherent and crack-free deposits were produced from this bath. When the temperature of the bath was raised beyond 70°C, the quality of the deposits tended to deteriorate slightly; the deposit was semi-bright at central portion with black streaks at the edges of nickel plate at 80°C.

Microhardness of the deposits gradually decreased with raising the bath temperature upto 70°C and then decreased (Fig. 2). Moderately high temperature seems to be advantageous because of enhancement of the mobility of metal ions and reduction in viscosity of the solution. The bath temperature affects the diffusion rate, polarization and the relative rates of nucleus formation and crystal growth¹¹. The ions are mobile at higher temperature which favours equilibrium deposition and the formation of large grains with a low free energy. This may be the probable reason for the production of larger grains at higher temperatures which, generally, are softer. Similar trend of variation of hardness with temperature has been reported earlier¹³. The microhardness measurements of nickel deposits produced under optimum conditions (CD 0.6 Adm^{-2} and 70°C) which were subjected to annealing at various temperatures (200-800°C) shows

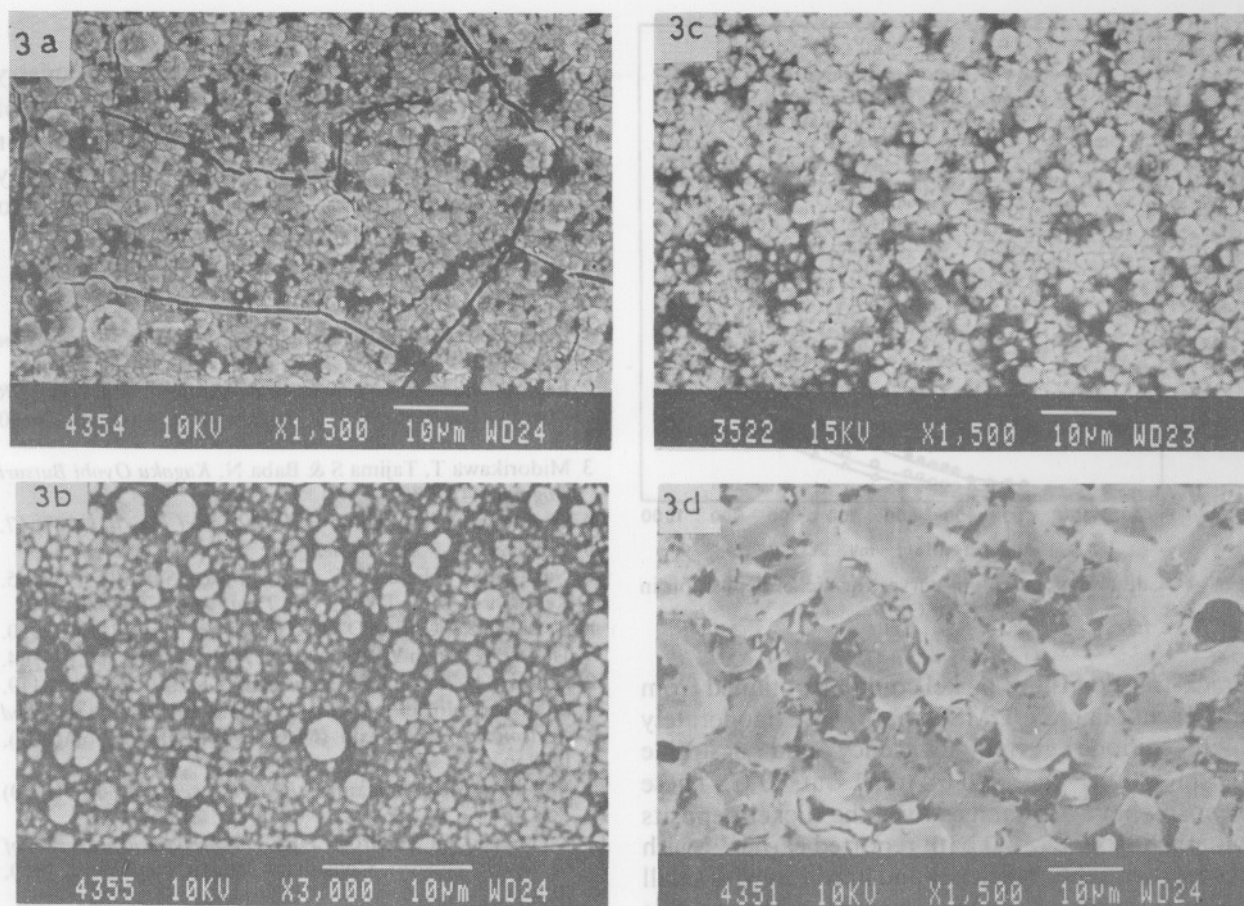


Fig. 3—SEM micrographs of electrodeposited nickel; (a) deposited under optimum current density (0.2 M Nickel Sulphamate, 0.2 M boric acid, CD 0.6 Adm^{-2} and 40°C) (b) deposited under optimum condition (0.2 Nickel Sulphamate, 0.2 M boric acid, CD 0.6 Adm^{-2} and 70°C) (c, d) deposits obtained under optimum conditions subjected to annealing temperature (c) 500°C , (d) 800°C

decreasing trend (225-141 DPH) with increase in annealing temperature. Such observation of decrease in hardness with increasing annealing temperature for nickel deposits have also been reported elsewhere^{14,15}.

Microstructure of the electrodeposits, SEM studies—Scanning electron microscopy indicated existence of cracks and pits in the deposits obtained at optimum CD (0.6 Adm^{-2}) and 40°C (Fig. 3a). The microstructure obtained at higher bath temperature (70°C) revealed a remarkable difference in structure that the deposits are fine-grained, though the distribution of particles is generally at random, the finer ones form line patterns which may serve as points of stress (Fig. 3b). The bath operated at higher temperatures is useful from the point of view that absorption of gas bubbles (hydrogen) would decrease with increasing temperature and, thereby, likely to result in a structure, free of any cracks or other defects. SEM micrographs of the annealed deposits showed that at 500°C (Fig. 3c), a definite change of structure occurred and there was clear indication of

recrystallisation at this temperature. However, at higher temperature the deposits showed some sign of grain growth with a tendency to undergo partial or soft sintering (Fig. 3d). It is inferred from the rounded amorphous structure that the deposits do not show a simple grain growth but is accompanied by soft sintering.

Cathodic polarization—The cathodic polarization curves for nickel deposition from DMSO bath using nickel sulphamate as electrolyte at different concentrations are illustrated in Fig. 4. It is seen that current initially does not increase noticeably with enhancement of the cathodic potential in all concentrations, but after certain potential ($> -480 \text{ mV}$) it started increasing steadily. A sharp increase in the current density occurred at higher potentials which indicated the metal deposition to commence with a measurable rate and the deposition is associated with appreciable polarization.

Conclusion

It is found that semi-bright, adherent and

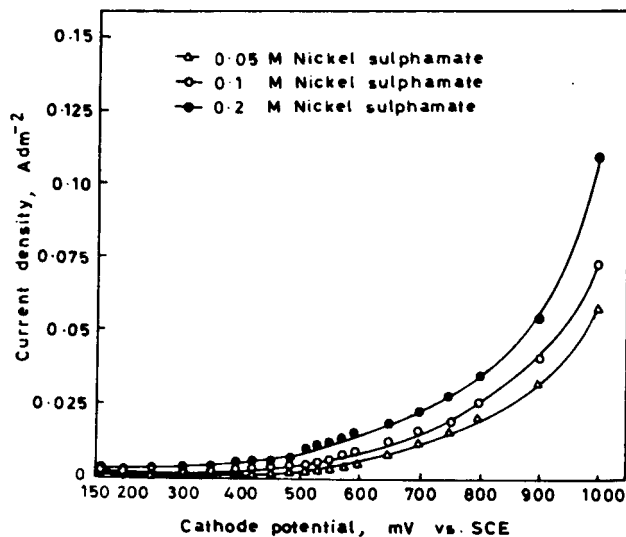


Fig. 4—Cathodic polarization curves for nickel deposition in DMSO

crack-free deposit of nickel could be obtained from nickel sulphamate/DMSO bath with moderately high cathode current efficiency and desirable hardness at a CD of 0.6 Adm^{-2} at 70°C . These deposits have advantages over the nickel deposits obtained from DMSO bath reported earlier¹⁻⁴ with respect to quality, efficiency and hardness with small defects in surface structure. Hardness of the deposits declined with increasing annealing temperature.

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