Vickers diamond. The measured, scratch current density (i_s^{m}) of the cylindrical electrode is represented as follows

$$i_{\rm s}^{\rm m} = i_{\rm s}^{\rm a} + i_{\rm surr} \frac{A_{\rm surr}}{A_{\rm scar}}$$
 [2]

where i_{s}^{a} is the current density from the scar and i_{surr} is the current density of the surroundings. The second term on the right side of Eq. [2] incorporates the contribution from shear bands and ridging associated with the scribing. The foregoing results suggest that the current rise derives from the activation of the scar and the surrounding region, and the current rise is not simply related to the area within the scratch.

Conclusions

The transient current rise of passivated, rotating cylindrical electrodes have been measured after scribing the surface with a Vickers diamond. For lightly loaded scribing (<13N), the maximum current density acquired from scribing increased linearly with increasing scribing loads. For heavily loaded scribing (>13N), the measured, scratch current density reaches a plateau of 373 mA/cm². In addition, the surrounding region of the scar shows evidence of plastic deformation in the form of ridging and shear bands which activate the surface. The measured, scratch current density consists of the current density of the interior scratched surface and that of the surrounding region.

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Study of Some Physical Properties and Structure of **Electrodeposited Nickel from 2-Methoxy Ethanol**

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Nickel is most commonly electrodeposited from aqueous baths. However, it suffers from some limitation due to inclusion of either addition agents or hydrogen/ hydroxide, etc., which influence the properties and structure of the deposits and also CCE. Inclusion of hydrogen in the deposits and its evolution during electrodeposition, in general, is not beneficial. Nakahara and co-workers (1, 2) reported that incorporation of hydrogen or hydroxide or other inclusions in the deposits altered the properties of the metal deposits and crystallographic structure. The role of hydrogen inclusion in modifying the properties and particularly the structure of the deposited metals have been reported by other workers (3, 4-7) also. They observed high density of dislocation (2, 3, 8), twinning (9, 10), texture (11), and other defects (12) in the deposits under different experimental conditions.

In view of this, it was planned to electrodeposit nickel using suitable organic solvents with the purpose of conveniently minimizing/checking the hydrogen evolution/ occlusion in the deposit to a maximum possible extent during extrodeposition. Moreover, the electrodeposition of metals from organic solvents has attracted the attention of the workers (13-20) in the past due to many other specific reasons. However, these baths have not fully met the commercial rigor. Thus electrodeposited nickel from nonaqueous/organic solvents may reveal significant changes in physical properties and structure under different experimental conditions.

The present paper deals with the investigations on nickel deposits obtained from 2-methoxy ethanol with a particular aim of examining the structural aspects (crystallographic and microstructure) and microhardness due to the variation of bath temperature, annealing temperature, and current density.

Experimental

The experimental setup was the same as described earlier (13, 21). The plating solutions were prepared using nickel chloride (NiCl $_2 \cdot 6H_2O$) in extra pure 2-methoxy ethanol (Table I). A mechanically polished scratch-free rectangular copper sheet $(2.0 \times 1.0 \times 0.01 \text{ cm})$, degreased and pickled, was used as a cathode in the plating solution. All experiments were carried out for 25 min without agitation unless otherwise mentioned. Bath composition, operating conditions, and other results are summarized in Table I. The nickel-plated specimens were vacuum sealed in a glass tube and annealed at various temperatures (200°-700°C) for 2h and then allowed to cool slowly up to the room temperature. Microhardness was measured on the surface of the as deposited nickel using a Tukon Wilson microhardness tester with a 136° diamond pyramid indenter, applying 10g load. Each recorded value is an average of at least five to seven measurements. At lower current densities the plating time was prolonged to give

Table I. Bath composition and conditions of electtroysis for nickel electrodeposition in 2-methoxy ethanol



Fig. 1. Variation of microhardness (DPH) with current density, 0.5M nickel chloride, 0.2M boric acid at 40°C.

suitable thickness for the hardness measurements to ensure that the hardness of the substrate did not affect the measurements. The specimens for the TEM studies were prepared by thinning the as deposited nickel by electropolishing, as reported earlier (22). The specimens were cleaned ultrasonically before use.

Microstructure was examined using scanning electron microscope (PSEM-500) and transmission electron microscope (TEM) operated at an accelerating voltage of 200 kV. X-ray diffraction was performed by (PW-1710) at an accelerating voltage 30 kV and 20 mA.

Results and Discussion

Effect of current density.—The microhardness of the as deposited nickel significantly increased with an increase in the current density (Fig. 1). Initially the microhardness of the deposits gradually increased up to 0.4 A/dm^2 , thereafter, it sharply increased and maximum microhardness (360 DPH) was obtained at 1.0 A/dm^2 . An improvement in microhardness with an increase in current density can be understood as being due to the grain refinement of the deposits which actually occurs at higher current densities. The trend of variation of hardness with current density is similar to that usually reported in the literature (23, 24).

The SEM micrographs (Fig. 2a, b) revealed very smooth, uniform, crack-free, and fine-grained deposits with lamellar structure. The lamellar structure of nickel deposits has been reported by Lee and Ye (11).

Effect of bath and annealing temperatures.—The temperature of the bath was varied between 20° and 80°C and its influence on the quality, structure, and microhardness of the nickel deposits was investigated. Bright, uniform, and fine-grained deposits without cracks were obtained up



Fig. 3. Variation of the microhardness (DPH) with bath temperature and annealing temperature (0.5M nickel chloride, 0.2M boric acid at c.d. 0.6 A/dm²).

to 70°C. However, above 70°C it tended to be nodular. It is observed that the microhardness gradually decreased with an increase in the bath temperature (Fig. 3). The trend of variation of microhardness agrees with the usual trend reported in the literature (24).

The microhardness of the deposits decreased with an increase in the annealing temperature (Fig. 3). It is seen that initially the microhardness decreased sharply between 200° and 500°C, and above this temperature decrease in the microhardness of the deposits was relatively lower up to 700°C. It appears that the annealing of the deposits at lower temperatures resulted in the relief of internal micro-stresses in the deposits which existed in the metal as a result of cold working. Therefore, the deposits turned increasingly softer and ductile as the annealing temperature is increased up to 500°C. At 600°C and above probably it resulted in the process of recrystallization.

SEM micrographs revealed almost insignificant structural changes and a very slow recovery at comparatively low temperatures. But at 600°C some small grains grew and at 700°C definite changes (Fig. 4a-c) with respect to initial structure (Fig. 2a and b) has occurred and a number of recrystallized nuclei grew rapidly (Fig. 4c). This shows the recrystallization between 600°-700°C. The present study agrees with results reported earlier (25). The insignificant change in structure, observed nominal recovery of the deposits, and trend of microhardness variation with respect to the annealing temperature up to 600°C indicate that as obtained nickel deposits were almost free from defects, microcracks, and inclusions. This has been further investigated by TEM.



<u>5μm</u>





Fig. 4. SEM micrographs of electrodeposited nickel (0.5M nickel chloride, 0.2M boric acid at c.d. 0.6 A/dm^2 and annealing temperature 700°C).









Fig. 5. TEM micrographs of electrodeposited nickel (0.5M nickel chloride at c.d. 0.6 A/dm², 40°C, and selected area diffraction pattern)

TEM studies.—TEM studies performed for the as deposited nickel showed some interesting structural features. Figures (5a-d) are the TEM micrographs, Fig. 5a and b are micrographs of the bright field, and Fig. 5c and d are the selected area diffraction (SAD) pattern, respectively. The micrograph showed that grains are finer (0.02-0.1 µm) and are almost free from any defect. The bright-field image does not show any indication of dislocation or twinning. The finer grains are realized by the continuity of ring (SAD) and hardly any evidence of the development of preferred orientation in the deposits is observed (Fig. 5c and d). The refinement of grains and polycrystalline nature is also indicated by numerous spots on the sharp ring diffraction pattern. The measurement of d values showed fcc structure of nickel. Furthermore, the fcc structure of the deposits was also confirmed by x-ray diffraction which gave the lattice constant (3.520Å), in close agreement with the literature value. High density of dislocation (1, 8), twinning (9, 10), texture (11), and stacking faults (26) exhibiting by metal deposits obtained from the aqueous bath, have been mainly attributed to the evolution/and occlusion of the hydrogen in the matrix of the deposits. The dislocation created by the evolution/absorption of hydrogen gas could act as nucleation sites, thereby explaining the fine grained (2) nature of nickel electrodeposited at the lower pH. The film contained numerous growth twins but was relatively free from dislocations.

It emerges from the above discussion that the situation is expected to differ when either the hydrogen evolution is small or there is no hydrogen evolution. In the present case nickel deposition has been carried out in an organic solvent, the consequences of hydrogen evolution/occlusion may not be effective because hydrogen would be available to a negligible extent only. Even if nominal hydrogen evolution is taken into consideration, perhaps it is not occluded in the deposits and therefore does not affect the structure and properties of nickel deposits, as a result of which pure and randomly orientated crystalline nickel deposits free from defects have been obtained. Since TEM studies do not indicate the existence of defect and texture in the metal deposit obtained from this bath and thus the hydrogen interference in the deposition is not inferred.

The observed moderate microhardness of the deposits can be correlated to the possible absence of dislocation in the deposited nickel. Moreover, the deposits are free from any impurity/inclusion (hydride/hydroxide, etc.) and therefore its hardness matches to the pure, usually electrodeposited, nickel.

All of the aqueous hard nickel baths contain addition agents or hardening agents which are incorporated into the deposits and cause failures in certain applications. In this bath there are no addition agents present and even hydrogen consequences are hardly realized thus eliminating this source of failure.

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Formation of Copper Phthalocyanine Thin Films by Electrolysis of Surfactants with Ferrocenyl Moiety

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Thin films of phthalocyanine compounds continue to be the subject of numerous research studies (1). In particular, the preparation of copper phthalocyanine (CuPc) films and their derivatives are important for a number of reasons: (i) they are most stable in phthalocyanine compounds; (ii) they show many interesting physical and chemical properties; (iii) a variety of halogenated derivatives are commercially available; (iv) they strongly absorb light; (v) they exist in many polymorphic forms (α , β , γ . . .).

The optical and electronic properties of CuPc are dependent on their crystallography (2-6). The technique for

the preparation of copper phthalocyanine thin films is limited to vacuum sublimation because of their insolubility in most of organic solvents. The crystalline structure of CuPc thin films has been controlled by temperature, pressure, and rate at sublimation, and the thermal and organic solvent treatments of sublimed films (2-6). However, sometimes these conditions are rather critical making it difficult to obtain the desired crystal form.

Recently, we have presented a novel technique for electrochemical formation of an organic thin film by disruption of micellar aggregates formed by cationic surfactants having a ferrocenyl moiety (MD method) (7). Furthermore, we reported the preparation of metal-free

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