Electrodeposition of Nickel on Polycrystalline Nickel and Copper in Presence of Sulphur Compounds

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ADDITION agents are added in electroplating baths to give enhanced physical properties viz., brightness, smoothness, etc. of the deposits. The mode of action of addition agents in modifying the form of electrodeposits on several metals and electrochemical effects have been reported [1, 2]. But no systematic attemps have been made to identify the compounds present in order to elucidate the exact function of addition agents. In the present study, electrodeposition of nickel on polycrystalline nickel from nickel ammonium sulphate bath at various current densities have been carried out in presence of known quantities of sulfanilamide, sulfaguanidine and sulfadiazine in the bath. With the help of IR spectra, the change in the topography of the Nickel deposits has been attributed to the formation of Nickel complex with the above sulphur compounds. Attempts have been made to correlate the morphology of the Nickel deposits and the electro-chemical parameters. The morphology of Nickel electrodeposits deposited on copper single crystal (100), (110) and (111) planes also has been studied from Nickel ammonium sulphate bath at several current densities, with the view to study the breakdown of epitaxial growth.

EXPERIMENTAL

A pure polycrystalline surface of Nickel was electropolished in an aqueous bath containing 15.6% H_2SO_4 + 15.8% H_3PO_4 in water under potential 1.1 – 1.2 V and a current 5-10 mA for 12-13 minutes. An electrolytic bath containing 0.25 M Nickel Sulphate and 0.25 M Ammonium Sulphate was prepared and the addition agent (Sulfanilamide, Sulfaguanidine or Sulfadiazine) of suitable concentration was added. The deposition of Nickel was carried out at various current densities to an average thickness of 10 C/cm^2. The Cathodic overpotential was recorded using a digital pH meter with reference to freshly prepared nickel electrode with an accuracy of ±5 mV. The deposit on the substrate surface was examined under a metallurgical microscope and photomicrographs were taken at a magnification 625X.

For the deposition of Nickel on Copper single crystal (100), (110) and (111) planes, the single crystal faces were prepared by electropolishing in a phosphoric acid bath[4]. Deposition of Nickel on these planes was carried out from pure Nickel Ammonium Sulphate bath at various current densities. The substrate surface was photographed at a magnification 625X.

The solution containing Nickel Ammonium sulphate and 10^{-5} mol/l sulfanilamide, or sulfaguanidine (10^{-6} mol/l of sulfadiazine) was refluxed in a water bath for 36 hours. It was evaporated in vacuum and IR spectra of the solid obtained was taken.

RESULTS

Electrodeposition of Nickel on Polycrystalline Nickel Surface

Surface Morphology at low current densities : When Nickel was deposited on a polycrystalline nickel surface from pure Nickel Ammonium sulphate bath at 2, 5 and 10 mA/cm^2, fine grain deposits were observed (Fig. 1). In presence of



FIG. 1. Fine grain deposit obtained when Nickel deposited from pure Nickel Aluminium Sulphate bath on a polycrystalline Nickel surface at 5 mA/cm^2 (Magnification 625X)

10^{-5} mol/l of sulfanilamide or sulfaguanidine (10^{-6} mol/l of sulfadiazine) in the bath the deposit consisted of refined grains and a bright deposit was observed (Fig. 2).

Surface Morphology at higher current densities : At 15 and 20 mA/cm^2, the electrodeposit



FIG. 2. Refined fine grains obtained when Nickel is deposited on a polycrystalline nickel surface from nickel ammonium sulphate bath in presence of 10^{-6} mol/l sulfadiazine (Magnification 625X)

contained larger or coarse grains. In presence of 10^{-5} mol/l of sulfanilamide or sulfaguanidine (10^{-6} mol/l of sulfadiazine) in the bath, grain size of the electrodeposit was reduced and a fine grain deposit was observed with fairly bright appearance

Overpotentials : At all current densities, during the deposition of nickel from pure Nickel Ammonium Sulphate bath, the overpotential decreased with time and attained a steady value. In presence of the addition agent in the bath, the over potential value was less than that of the pure solution at the corresponding current density. The Tafel relation holds good in pure solution and in presence of addition agent at low concentrations (Fig. 6). At higher concentration of the addition agent, it is no longer valid.

Electrodeposition of Nickel on Copper Single Crystal Planes

Surface Morphology on Copper (100) Plane : When Nickel was deposited on Copper (100) face from Nickel Ammonium Sulphate bath, a polycrystalline deposit was noticed at 1 and 2 mA/cm^2. At 5 mA/cm^2 a uniform, bright, polycrystalline deposit was observed. Hydrogen evolution was observed at all current densities.

Surface Morphology on Copper (110) Plane : At 1 mA/cm^2, deformed ridges with occasional pitting were seen (Fig. 3). At 2 mA/cm^2 the deposit was polycrystalline with pitting (Fig. 4). At 5 mA/cm^2, broken ridges along with pitting were observed.

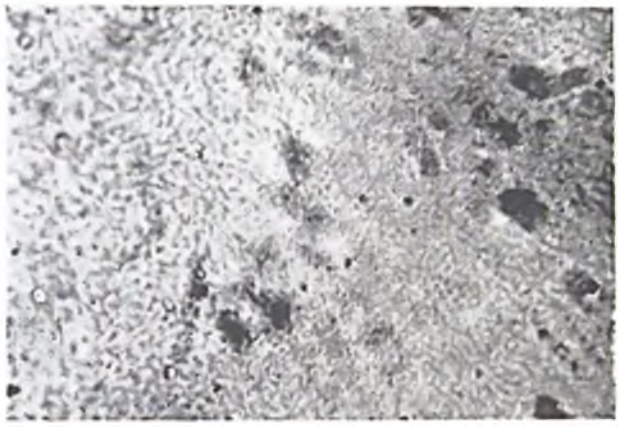


FIG. 4 Polycrystalline type of deposit with pitting obtained when nickel is deposited on a copper single crystal (110) face from nickel ammonium sulphate bath at mA/cm^2 (Magnification 625X)

Surface Morphology on Copper (111) Plane : When Nickel was deposited from a Nickel Ammonium Sulphate bath on copper (111) plane, at 1 mA/cm^2 the deposit consisted of very small broken layers with occasional protrusions on the surface (Fig. 5). At 2 mA/cm^2, polycrystalline



FIG. 3 Deformed ridges with occasional pitting obtained on a copper single crystal (110) face when nickel is deposited from nickel ammonium sulphate bath at 2 mA/cm^2 (Magnification 625P)



FIG. 5 Very small broken layers with occasional protrusions on the surface when nickel is deposited on a copper single crystal (111) face from nickel Ammonium sulphate bath at 1 mA/cm^2 (Magnification 625X)

type of deposit with pitting was observed. There was epitaxial breaking of pyramids and a uniform polycrystalline deposit was observed.

Overpotentials : The value of overpotentials when Nickel was deposited on copper single cystal planes at various current densities from Nickel Ammonium Sulphate bath are given in the following Table :

TABLE : *Electrodeposition of Nickel on Copper Single crystal (100), (110) and (111) faces from Nickel Ammonium Sulphate bath*

Plane	Current Density mA/cm^2	Overprotential mV
(100)	1	160—415
(100)	2	715—600
(110)	1	65—400
(110)	2	445—465
(111)	1	75—455
(111)	2	460—380

DISCUSSION

The Tafel relation holds good at lower concentrations of these sulfa compounds, (Fig. 6)

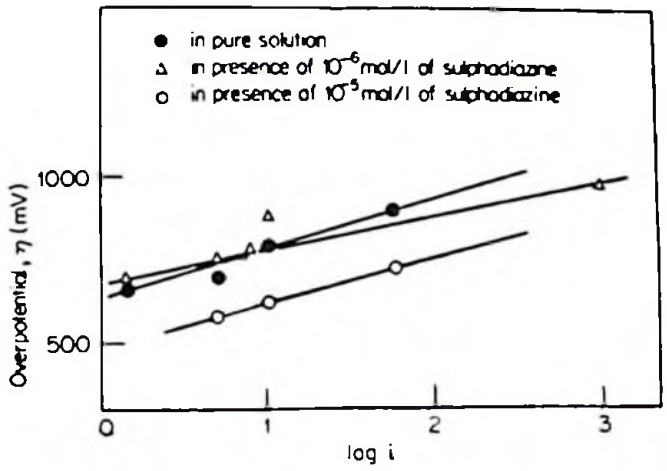


FIG. 6

indicating that charge transfer is the rate determining step. The overpotential in presence of the addition agent was lower than that of pure

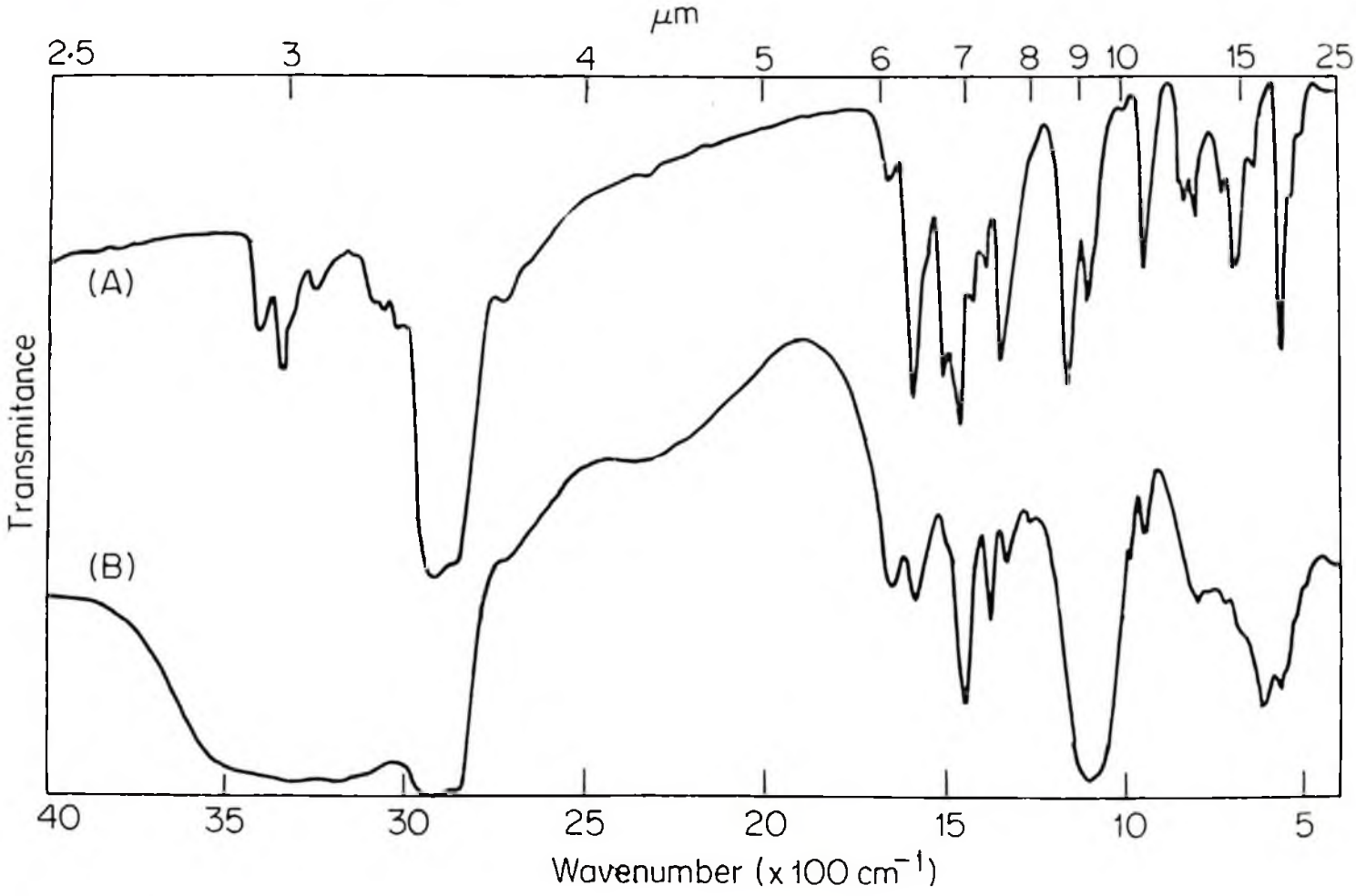


FIG. 7. INFRARED SPECTRA OF (A) SULPHADIAZINE (B) NICKEL COMPLEX WITH SULPHADIAZINE

solution at all current densities studied. Thus diffusion and incorporation of adions are favoured.

Further, it has been noticed that at higher concentration of the addition agent used, the Tafel relation does not hold good. Thus indicates that the rate determing step may not be charge transfer at higher concentration of the addition agent.

It therefore, appears that the morphological changes of the deposit are due to complexation effects. The effect of these Sulfa compounds can be explained with the help of absorption and complexation theory[5, 6, 7, 8]. It could be assumed that sulfaguanidine may form a complex which gets absorbed on the Nickel surface. There will be random nucleation resulting in a polycrystalline deposit.

The IR studies of the compounds obtained by treating the Nickel salt solution with the addition agents are in conformity with the complexation mechanism. The spectra of the complexes are compared with those of Sulphur compounds used (Fig. 7). Sulfanilamide shows an absorption at 3410 cm^{-1} characteristic of the primary amino group directly bonded to the ring. Sulfaguandine and sulfadiazine show these characteristic absorptions at 3400 cm^{-1} and 3390 cm^{-1} respectively. In the spectra of the complexes, these bands are absent and there is a broadening of the spectral peak indicating that the complex is formed in each case by the coordination between Nickel ion and the primary amino group.

In the case of the deposition of Nickel on copper, the epitaxial growth ceases after certain thickness due to the random nucleation.

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