EFFECT OF DIELECTRIC CONSTANT AND BASICITY ON THE ELECTRODEPOSITION OF NICKEL FROM AMIDE SOLVENTS

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Amide solvents have been used frequently for electrodeposition studies. Deposition of copper, lead, tin and zinc [1], chromium and uranium [2] and manganese [3] from formamide bath, copper and nickel fron trifluoro acetate/farmamide bath [4] have been reported. Deposition of Nickel and Copper has been reported from their trifluoro acetate in dimethyl formamide also [5]. Copper, cadmium, zinc and cobalt have been deposited from their perchlorates also from dimethyl formamide bath, [6]. Aluminium chloride from formamide - nitrobenzene - benzoyl chloride mixture is reported to give bright aluminium deposits [7]. N-methylacetamide has been patented for the deposition of oxide layers on p- or n- type silicon semiconductors or on n- type germanium bodies [8]. The only report of the deposition of metals from solution of their salts in molten acetamide is that ot Yntema and Audrieth [9]. However N-methylformamide and other amides have not been studied [14,17] in detail for electrodeposition of metals.

The present work is intended to study the physical characteristics of nickel electrodeposited from $NiCl_2.6H_2O$ dissolved in pure formamide, N-methylformamide and N,N-Dimethylformamide seperately.

EXPERIMENTAL

Formamide [10], N-methylformamide [11] and N,N-dimethylformamide [12] were purified as given in literature. Copper strip cathodes (15x10x1 mm) were subjected to the usual operations of grinding, polishing, degreasing and pickling. The copper strips were weighed at this stage and then electrocleaned cathodically using sodium carbonate for about 3 min as recommended by Lainer [13]. The electrocleaning solution was maintained at a temperature around 50°C. Finally, the electrocleaned plate was pickled with 10% H_2SO_4 solution. In between different operations, the cathode was carefully washed with doubly distilled water. High purity nickel sheets were used as anodes. A copper coulometer was employed to measure the current. The rest of experimental set up was the same as described earlier [14]. Microhardness of the as-plated nickel plates was measured on a Tukon Wilson microhardness tester using Knoop indenter applying a load of 25 gl.

RESULTS AND DISSCUSSION

The bath composition and operating conditions are given in Table 1. The nature of deposit, cathode current efficiency and microhardness of the nickel electrodeposited are summarised in Table 2.

Electrolysis of $NiCl_2$ /formamide or $NiCl_2$ /NMF leads to electrodeposition; but no deposition occurs with $NiCl_2$ /DMF electrolyte, unless a little HCl is added.

Loaded with two electron releasing methyl groups, the electron density of oxygen in N,N-dimethylformamide (DMF) is enormously enhanced

TABLE 1

BATH COMPOSITION AND CONDITION OF ELECTROLYSIS

Parameters	Values
Nickel chloride (M) $NiCl_2.6H_2O$	0.2
Boric acid (M) H_3BO_3	0.2
Current density (A/dm^2)	0.5
Temperature (°C)	40
Duration of electrolysis (min)	60
Inter-electrode distance (mm)	20
Agitation	Nil

TABLE 2

CHARACTERISTICS OF NICKEL ELECTRODEPOSITED FROM FORMAMIDE AND ITS N-METHYL DERIVATIVES

Solvent	Dielectric constant (25°C)	Boric acid conc.	Nature of deposit	Cathode current efficiency (%)	Hardness* $(KHN)_{25}$
$HCONH_2$	109.5	0.00	Bright**	99.5	130
		0.20	Hazy-bright	92.5	260
$HCONH(CH_3)$	182.5	0.00	Bright	76.3	78
		0.20	Bright"	70.0	101
$HCON(CH_3)_2$	36.7	0.00	Bright	99.8	157
		0.20	Bright	99.8	340

* $(KHN)_{25}$ for Cu basis metal = 68

** Grayish at edges; " Mild peeling at edges

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as compared to N-methylformamide (NMF) or formamide. As such, the formation of $NiCl_2$ X DMF complex is highly probable [15]. Little probability exists for the formation of such complexes in case of formamide or N-methylformamide.

Probably DMF of the complex $NiCl_2$ X DMF is released on addition of HCl; 1:1 complex of HCl:DMF has already been reported [16]. In this way, a little $NiCl_2$ is freed for ionisation. $NiCl_2.6H_2O$ (0.2 M)/DMF, HCl (sp.gr.1.18) electrolyte (pH = 4.7) led to satisfactory deposition [17]. The slow release of nickel ions minimize concentration polarisation around cathode leading to high cathode current efficiency and thus provide favourable condition for the formation of basic colloidal hydroxide in presence of boric acid [18] resulting in hard deposits. A high dielectric constant in case of NMF (Dipole moment 4 D) causes heavy concentration of metal ions in the catholyte resulting in low cathode current efficiency and soft deposits. Presence of an amido hydrogen renders NMF so basic that a little addition of boric acid leads to formation of a ponderous concentration of basic colloidal hydroxide that peeling starts at edges. It was observed that the electrolysis of $NiCl_2$ /NMF at 60°C in presence of 0.1M boric acid resulted in a greenish hydroxide, soluble in acids and giving tests with dimethylglyoxime. This was a positive evidence for the formation of basic colloidal hydroxide in the catholyte.

The pK values determined in acetic acid medium by Huisgen and Brade [19] revealed that large positive increase in pK from formamide to its N-methyl derivative while a much smaller increase occurred when second methyl group was added. The effect was due to the ability of a methyl group to release electron donating oxygen more susceptible to protonation. This shows the least basic character of formamide in the series. It seems that due to this reason, adhesive smooth deposition without peeling effect are obtained using $NiCl_2$ /formamide, H_3BO_3 bath.

The difference in basicity and dielectric constant even affects the microstructure of the deposited nickel. In absence of boric acid, under similar operating conditions, crackfree smooth dposits were obtained in case of N-methylformaide (Fig.1), grained but with mild cracks in case of formamide (Fig.2), but a fine structure with some extra deposits over the base nickel deposition was marked in case of dimethylformamide (Fig. 3). Large protonation ability of NMF ad DMF led to protonation and deprotonation of oxygen of NMF and DMF linked to adions so vigorously that mild peeling at edges occurred in NMF media & mild cracks at edges appeared in DMF. Moreover the adsorption and suosequent diffusion of hydrogen in widened lattice spacings (rifts) resulted in pit formation in case of DMF (Fig.4). Both these effects reduced to neglegible extent when temperature was raised to 50° C. Further, it was observed that peeling effect did not occur in case of DMF, probably due to the formation of solvate species which render DMF molecules less available to link with addions. It is also speculated that due to least availability of lone pair of oxygen for protonation in case of formamide, the frequency of protonation and deprotonation is minimum resulting in structure with less cracks.

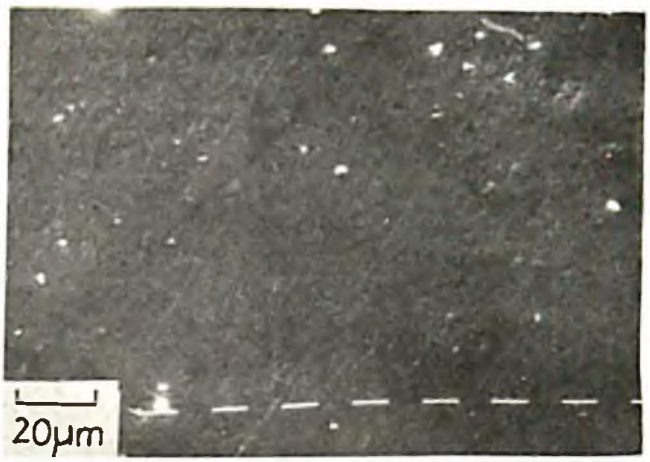


Fig.1 SEM of as-plated nickel from $NiCl_2$/NMF bath at c.d. 0.5 A/dm at 40°C

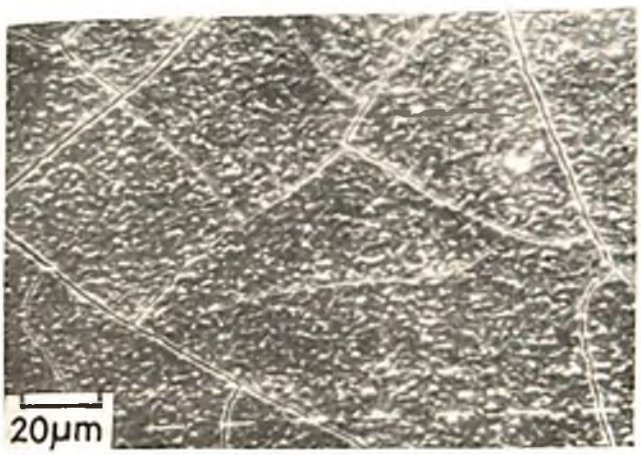


Fig.2 SEM of as-plated nickel from $NiCl_2$/F bath at c.d. 0.5 A/dm^2 at 40°C



Fig.3 SEM of as-plated nickel from $NiCl_2$/N,N DMF bath at c.d. 0.5 A/dm at 40°C.

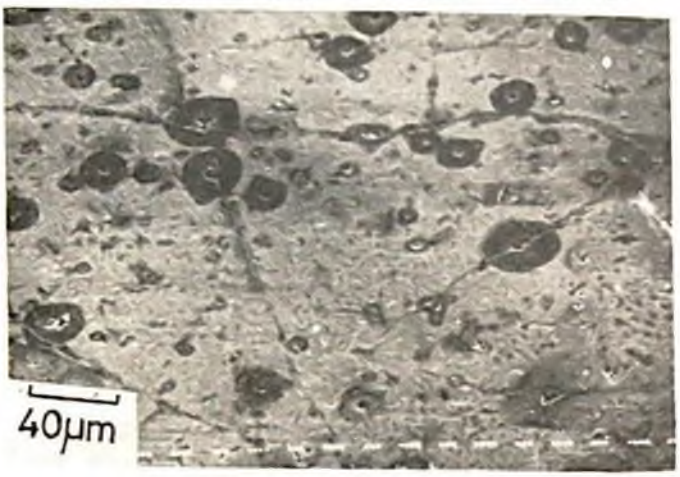


Fig.4 SEM of as-p'ated nickel from $NiCl_2$/N,N DMF bath in presence of 0.2 M boric acid at c.d. 0.5 A/dm^5 at 40°C near the edge.

CONCLUSION

* N,N-dimethylformamide is most suitable solvent as compared to N-methylformamide or formamide for deposition of nickel using nickel chloride electrolyte.

* Boric acid (0.2M) enhances the hardness more in case of N<N-dimethylformamide.

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