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PULSE PLATED NICKEL ELECTRODEPOSITS

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ABSTRACT

Amide-water mixtures with sulfate and acetate have been employed for nickel electrodeposition. Improved physicomechanical properties were related to the presence of amide as cosolvent. Bright, though in some cases highly stressed, deposits were obtained under direct current. Pulse current applications reduced stress and in some cases bright nickel electrodeposits having low stress were obtained. In particular, pulse reverse waveform in millisecond range was found effective. Effects of cathodic or anodic current density, duration of pulse waveform, frequency and temperature on the quality of deposits have been reported. Auger spectra and thermogravimetric analyses of bright nickel deposits revealed pure nickel without inclusion. Support to the brightening theory, where layer of colloidal particles formed near the cathode is captured by a catalytically generated hydrogen film, is thus obtained. A bright nickel foil obtained by dissolving the substrate (brass) proved to be of high strength. This foil was electrodeposited from dimethylformamide-water bath under pulse reverse current waveform.

Key Words: Pulse Plating, Nickel, Amide-water, stress, bright deposit.

INTRODUCTION

Organic solvents as such or mixed with water has been utilized for electrodepositing metals and alloys. Nickel[1, 2] or Chromium alloys of iron[3] and nickel[4, 5] have been deposited from mixed organic-water baths. Effect of nonaqueous solvent and nonaqueous solvent mixture on Cu deposition from acidified sulfate electrolyte was studied[6]. Particular series of amide solvents, namely, Formamide (F), N-methylformamide (NMF) and N, N-dimethylformamide (DMF) have been useful in electrodeposition studies because of change in their physicochemical properties in relation to methyl group substitution. Variation in viscosity, dielectric constant, solvent structure, solubility properties, etc., affects the electrochemical reaction to a great extent. Further, change in operating condition, e.g., temperature, agitation, concentration, etc., for a particular solvent system affects the electrodeposition process by way of change in physicochemical properties. Increase in temperature was observed to increase the rate of mass transfer in case of copper electrodepostion from nonaqueous and nonaqueous-water solvents[6]. Though dielectric constant decreases with temperature, increasing the forces among ions, rate of mass transfer increases because of decreased solvent viscosity.

Electrodeposition study in amide-water solvents showed significant effect of methyl group substitution in amides. Enhancement in physicomechanical properties of nickel deposits were observed from some mixed amide-water solvents. In particular DMF, because of its aprotic nature, proved to be a good solvent in combination with water. Bright though cracked nickel deposits were obtained from NMF-water[2]. Sulfamate bath in DMF-water was investigated for nickel electrodeposition[1]. Pits and black spots observed for deposits from aqueous bath were quite suppressed by the addition of DMF. However, 50 mol% DMF-water bath produced nickel deposits having microcracks. Direct current was used for all investigations. It would be of interest to select

optimum solvent composition and effect rate of mass transfer by using pulse current wave form. Pulse current in different wave forms affect the process of electrodeposition in a number of ways. Interruption in the mass transfer process may reduce the cumulative build up of stress particularly in nickel deposits. Nucleation and growth of crystals is also effected when electrodeposition process is not continuous. Different pulse wave forms may be applied as to suit a particular electrodepostion process. While peak current density, on time, off time or reverse pulse time may all be varied, it is not possible to exceed the average current density in pulsed current deposition[7].

Present investigation is to study the effect of different pulse current parameters on the quality of nickel electrodeposits, in particular, improvement of stressed nickel electrodeposits obtained under direct current were tried by the application of pulsed current.

EXPERIMENTAL

Constant hydrodynamic flow condition was maintained by using a rotating disc electrode[8]. One litre solution was used in a thermostatic double walled cylindrical cell for all electrodeposition experiments. Substrate was electropolished brass (Cu-37 Zn) disc encapsulated in PTFE cylindrical mantle. The exposed electropolished area of well lacquered disc was 7 cm^2. Counter electrode was a platinum spiral. Cathodic current density, cathodic on time, anodic current density and anodic time has been denoted as i_c, t_c, i_a and t_a respectively. Electrodeposits were more than 1 mil thick. The current efficiency in case of Pulse reverse current electrodeposition was obtained by dividing the experimental rate of deposition by the theoretical one. The theoretical rate of electrodeposition ($mg.cm^{-2}.min^{-1}$) was calculated as follows:

$$Rate = (W_{dep.} - W_{diss.}).\ N$$

Where $W_{dep.}$= weight (µg) of coating deposited on 1 cm^2 in one cathodic pulse at 100% current efficiency. $W_{diss.}$= weight of coating dissolved on 1 cm^2 in one anodic pulse at 100% current efficiency.
N= number of cycles per min.

Organic solvents N, N-Dimethyl-formamide, N-methylformamide and formamide were of high purity and were mixed with distilled water in order to use as solvents.

PAR 173 Potentio/galvanostat with digital coulometer 179 and universal programmer PAR 175 were used for direct and pulse current deposition. X-ray diffraction analysis was carried out for residual stress measurement. (220) plane was selected using a chromium radiation at eleven angles ranging between 0 and ±45 °.

RESULTS AND DISCUSSION

Characteristics of nickel electrodeposits obtained from different amide-water baths under both direct and pulse reverse current has been shown in tables. The effect of various electrodeposition parameters on the current efficiency, deposition rate, residual stress and appearance of electrodeposits have been elucidated in these tables. Results for nickel electrodeposition are discussed for different amide-water baths separately.

Formamide-water bath

Formamide (5 mol%)-water bath was investigated for nickel electrodeposition under direct as well as pulse reverse current wave forms. 3.1.1 Direct Current.

Tables 1 and 2 give the results for electrodeposition under varying current density and temperature of bath, respectively. Current efficiency shows a maximum (95%) at 5 A/dm^2 but an increase beyond this current density resulted in increase of tensile stress to such an extent that bright nickel deposits developed stressed lines (Table 1). Increase in temperature to 50° C produced bright deposits without stressed lines or cracks but further increase resulted in deposits having milky films (Table 2). Increase of current density changed the texture from (200) to (311) while increase of temperature has the opposite effect. Bright nickel electrodeposits without stressed lines having (200) texture were obtained at higher temperature.

Pulse reverse current

Tables 3 and 4 show the effect of pulse

Table - 1: Electrodeposits obtained from formamide (5 mol%) water bath at different current densities (direct). bath composition: 0.5 m Nickel sulfate ($NiSO_4.6H_2O$) + 0.1 m boric acid; pH: 4.9; temp: 40°C; RDE: 500 r.p.m; texture: (200) to (311)

S. No.	C.D. A/dm²	Current Efficiency %	Rate ofDeposit mm/min	Stress N/mm²	Appearance
1.	1	71	0.14	758	Bright
2.	2	82	0.33	-	Bright
3.	3	88	0.54	574	Bright
4.	5	95	0.97	603	Bright, stressed lines (periphery)
5.	6	87	1.08	915	Bright, stressed lines
6.	10	81	1.67	791	Bright, stressed lines throughout

Table - 2: Electrodeposits obtained from formamide (5 mol%)-water bath at different temperatures. bath composition: 0.5 m nickel sulfate ($NiSO_4.6H_2O$) + 0.1 m boric acid; pH: 4.9; current density (direct): 5 a/dm²; rde: 500 r.p.m; texture: (311) to (200)

S.No.	Temp. ° C	Current Efficiency %	Rate ofDeposit mm/min	Appearance
1.	30	80	0.83	Bright, broad spaced cracks
2.	40	95	0.97	Bright, stressed line (periphery)
3.	50	82	0.84	Bright
4.	60	83	0.85	Bright with milky film

frequency and anodic on time on the electrodeposits. Extremely high frequency in the range of 1 KHz does not have much effect but good deposits having (200) preferred orientation could be obtained at a frequency of 62.5 Hz when the cathodic current density was 9.2 A/dm² (Table 3). Increase in anodic pulse time decreased the tensile stress and semibright deposits without cracks were obtained above 4 msec duration.

N-methylformamide-water bath

Increase in bath temperature was studied for the quality and residual stress of nickel electrodeposits. Tables 5 and 6 give the results for two set of pulse reverse current parameters at the same frequency of 7 Hz. Both current wave forms showed the same effect of temperature on nickel electrodeposits, namely, decrease in stress with grayish deposits at higher temperatures from NMF (5 mol%)-water baths.

Table - 3 Electrodeposits obtained from formamide (5 mol%)-water bath at different frequencies. bath composition: 0.5 m nickel sulfate ($NiSO_4.6H_2O$) + 0.1 m boric acid; pH: 4.9; current: pulse reverse (i_c= 9.2 a/dm²; i_a= 2 a/dm²) temp: 40° C; rde: 500 r.p.m; texture: (311) [(200) at 62.5 Hz]

S. No.	Freq. Hz	Current Efficiency %	Rate ofDeposit mm/min	Stress N/mm²	Appearance
1.	6.25	62	0.63	704	Grey, bright at periphery (cracks)
2.	12.2	68	0.70	603	Bright at periphery (cracks)
3.	62.5	70	0.71	647	Semibright, uniform
4.	625	67	0.69	866	Bright, highly stressed

Table - 4: Electrodeposits obtained from formamide (5 mol%)-water bath at different anodic pulse duration (t_a). bath composition: 0.5 m nickel sulfate ($NiSO_4.6H_2O$) + 0.1 m boric acid; pH: 4.9; current: pulse reverse (i_c= 5 a/dm^2; i_a= 2 a/dm^2, t_c= 10 msec) temp: 40° C; rde: 500 r.p.m; texture: (311)

S. No.	t_a msec	Current Efficiency %	Rate ofDeposit mm/min	Stress N/mm^2	Appearance
1.	6	57	0.27	529	Semibright, uniform
2.	4	61	0.37	637	Bright periphery
3.	2	66	0.52	758	Bright, few cracks
4.	1	67	0.60	676	Broad spaced cracks

Table - 5: Electrodeposits obtained from nmf (5 mol%)-water bath at different temperatures. bath composition: 0.5 m nickel acetate + 0.1 m boric acid; pH: 6.4; current: pulse reverse (i_c= 3 a/dm^2; i_a= 2 a/dm^2, t_c= 0.1s, t_a= 0.04s) rde: 300 r.p.m; texture: (311) to (311) + (111)

S. No.	Temp. ° C	Current Efficiency %	Rate ofDeposit mm/min	Stress N/mm^2	Appearance
1.	22	81	0.26	-	Bright with cracks
2.	30	85	0.27	427	Milky, nodular with crack at periphery
3.	40	87	0.28	876	Bright to milky
4.	50	98	0.30	289	Grayish
5.	67	99	0.32	146	Grey

Table - 6: Electrodeposits obtained from nmf (5 mol%)-water bath at different temperatures. bath composition: 0.5 m nickel acetate + 0.1 m boric acid; pH: 6.4; current: pulse reverse (i_c= 1.5 a/dm^2; i_a= 2 a/dm^2, t_c= 0.1s, t_a= 0.04s) rde: 300 r.p.m; texture: (111), (311)

S. No.	Temp. ° C	Current Efficiency %	Rate ofDeposit mm/min	Stress N/mm^2	Appearance
1.	22	76	0.07	-	Ash coloured
2.	30	104	0.10	469	Ash coloured
3.	40	110	0.12	608	Dull, uniform
4.	50	109	0.10	278	Dull, bright (only periphery)
5.	67	99	0.12	220	Blackish grey

N, N-dimethylformamide-water

Tables 7 to 10 depict the result of electrodeposits from DMF (5 mol%)-water bath under pulse reverse current. Effect of pulse frequency, bath temperature, rotation speed, etc., on the quality of deposits and residual stress has been shown in tables. Increased pulse frequency resulted in reduction of stress (Table 7). Effect of high rotation speed (1000 r.p.m) with high temperature (65° C) on residual stress is significant as is clear from Table 9. High cathodic current density of 11 A/dm^2 could be applied at a frequency of 625 Hz but the deposits showed increased stress with cracks at periphery. Lower temperature (35° C) and lower rotation speed (300 r.p.m) could allow the use of cathodic current density only up to

Table - 7: Electrodeposits obtained from dmf (5 mol%)-water bath at different frequencies. bath composition: 0.5 m nickel acetate + 0.1 m boric acid; pH: 6.6; current: pulse reverse (i_c= 3 a/dm^2; i_a= 2 a/dm^2) temp: 35° c; rde: 300 r.p.m; texture: (200) to (220), (311)

S. No.	Freq. Hz	Current Efficiency %	Rate of Deposit mm/min	Stress N/mm^2	Appearance
1.	6.25	85	0.19	431	Bright
2.	62.5	87	0.20	-	Bright
3.	625	90	0.20	140	Semibright

Table - 8: Electrodeposits obtained from dmf (5 mol%)-water bath at different cathodic current densities. bath composition: 0.5 m nickel acetate + 0.1 m boric acid; pH: 6.6; current: pulse reverse (i_c= 3 a/dm^2; i_a= 2 a/dm^2, t_c= 1 msec, t_a= 0.6 msec) temp: 35° C; rde: 300 r.p.m; texture: (220), (331) to (311), (220)

S. No.	C.D. A/dm^2	Current Efficiency %	Rate ofDeposit mm/min	Stress N/mm^2	Appearance
1.	3	90	0.20	254	Semibright
2.	5	93	0.45	326	Semibright
3.	7	98	0.70	333	Semibright, stressed lines

Table - 9: Electrodeposits obtained from dmf (5 mol%)-water bath at different cathodic current densities. bath composition: 0.5 m nickel acetate + 0.1 m boric acid; ph: 6.6; current: pulse reverse (i_c= 3 a/dm^2; i_a= 2 a/dm^2, t_c= 1 msec, t_a= 0.6 msec) temp: 65°C; rde: 1000 r.p.m; texture: (331), (220)

S. No.	C.D. A/dm^2	Current Efficiency %	Rate ofDeposit mm/min	Stress N/mm^2	Appearance
1.	7	96	0.69	143	Semibright
2.	9	85	0.82	170	Semibright
3.	11	91	1.12	218	Semibright, cracks (periphery)

7 A/dm^2. Residual stress increased significantly with cathodic current density at this lower temperature and rotation speed (Table 8). Similar anodic current density (2 A/dm^2) at a frequency of 83 Hz resulted in grayish deposits with low stress as is shown in Table 10.

Thermogravimetry and Auger Electron Spectroscopy

Thermogravimetric analysis of electrodeposits obtained from all amide-water baths under pulse current wave forms revealed only purity of electrodeposits. In all cases a little weight loss observed was only after a temperature of 450° C. Percentage weight loss was little more (2.2%) in case of deposits obtained from NMF-water baths while it was only 1.5% in case of electrodeposits obtained from F-water and DMF-water baths.

Auger electron spectroscopy of electrodeposits obtained from amide-water baths under different operating bath parameters showed

Table - 10: Electrodeposits obtained from dmf (5 mol%)-water bath at different cathodic current densities. bath composition: 0.5 m nickel acetate + 0.1 m boric acid; ph: 6.6; current: pulse reverse (i_c= 3 a/dm^2; i_a= 2 a/dm^2, t_c= 10 msec, t_a= 2 msec) temp: 65° C; rde: 1000 r.p.m; texture: (220), (331)

S. No.	C.D. A/dm^2	Current Efficiency %	Rate ofDeposit mm/min	Stress N/mm^2	Appearance
1.	2	87	0.23	87	Slight grayish
2.	3	90	0.40	107	Grayish
3.	7	94	1.06	101	Slight grayish, cracks (periphery)

little peaks for carbon and oxygen on surface of electrodeposits but no peak for nitrogen even at high sensitivity. Sputtering just a few Angstroms (Å) revealed pure nickel in all the electrodeposits.

Results of thermogravimetric analyses and Auger electron spectra of these nickel electrodeposits rule out the incorporation of organic matter. Therefore, brightening of electrodeposits may be explained on the basis of theory proposed by Kaikaris (1967), According to this theory, a bright coating is said to be produced when a layer of colloidal particles formed near the cathode is captured by a catalytically generated hydrogen film.

Bright nickel foil

Figures 1a and 1b show the nickel foil obtained by dissolving the substrate in chromic acid. These 4-6 mils foils were deposited from DMF (5 mol%)-water bath under pulse reverse current. Strength of the foil can be gauged from figure 1b which shows a nickel foil bent at 180.

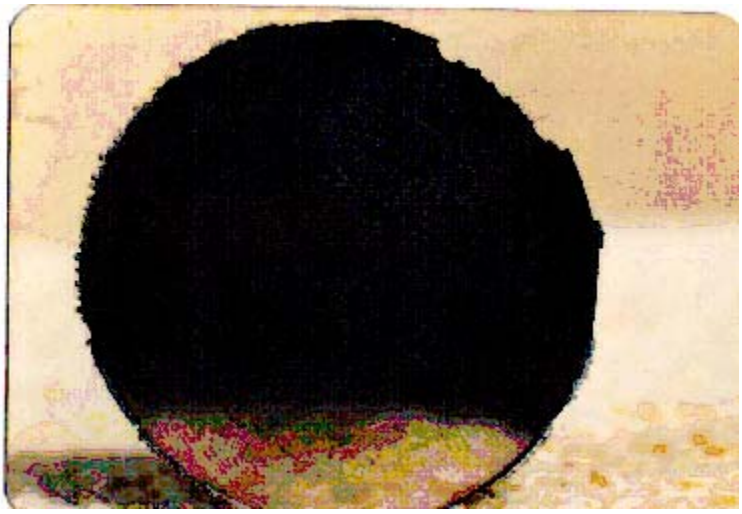

Fig. - 1a: Bright nickel foil electrodeposited from DMF (5 mol%)-water bath under pulse reverse current

Figure 1b Nickel foil bent at 180°

Conclusion

Formamide, a protic solvent, is similar to water and therefore pulse reverse current application was more effective in dissolution of the deposited nickel as compared to other amide-water baths. Optimum condition of pulse reverse produces a smooth, semibright, crack free deposit.

Application of suitable pulse reverse wave forms in case of amide-water baths may be utilized for producing good bright nickel electrodeposits. In all the amide-water baths electrodeposited nickel was pure. The brightening of electrodeposits is therefore not due to incorporation of organic molecules in part or as a whole. The small loss in weight at higher temperature (@450° C) indicates probable hydroxide inclusion. Slightly greater loss in weight (2.2%) in case of electrodeposits obtained from NMF-water bath may be explained as due to greater adsorption of the linear form of NMF on electrode surface facilitating hydroxide incorporation.

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