Effect of NH_4^+ and Co^{++} Ions on the Hardening of Electrodeposited Nickel from Nickel Acetate in Amide Solvents

By H. K. Srivastava* and P. K. Tikoo*

Addition of 0.2 kmol/m^3 ammonium acetate, along with 0.1 kmol/m^3 boric acid, to nickel acetate/formamide, nickel acetate/N-methylformamide and nickel acetate/N, N-dimethylformamide baths resulted in nickel electrodeposits having a high degree of hardness. Further, the addition of a small amount of cobalt acetate was found to be highly effective in enhancing the hardness as well as improving the surface appearance of nickel deposits. The presence of ammonium and cobalt ions was highly influential in improving the hardness. Nevertheless, the basicity and dielectrical properties of amide solvents were highly instrumental in deciding the grain refinement of electrodeposited nickel. Peeling due to the internal stress of the electroplates obtained from a nickel acetate/formamide bath disappeared totally when they were annealed at 473 K. Scanning electron micrography revealed refinement in grain size with successive inclusion of methyl group in formamide.

(Received May 6, 1987)

Keywords: electrodeposition, non-aqueous baths, ammonium ion, cobalt ion, hardness of deposits

I. Introduction

The hardness and mechanical strength of electrodeposited metals essentially depend on the plating conditions, but selection of a non-aqueous bath becomes sometimes highly significant. Hardness is an essential factor in wear resistance. Stress in nickel deposits is connected with their structure, which in turn affects the hardness, porosity, electrical conductivity and other properties. In the case of very hard deposits, when the tensile strength reaches values close to the strength of metal, cracking and peeling may occur. Annealing, quenching and tempering operations are sometimes very helpful in relieving the internal stress of electrodeposited metals. In the recovery range of annealing, the hardness and strength are little affected but stresses are at least partially removed. Thus, the susceptibility to peel with the lag of time, due to internal stress, is diminished or eliminated. The recrystallization range is a range of rapid changes of properties from a strained structure to a strain-free one. Thus although the hard-

ness and strength are reduced depending on the annealing temperature, the ductility increases.

Cobalt is being used as a hardening agent for nickel deposits⁽¹⁾; but its use is restricted due to certain limitations. Even traces of cobalt contained in nickel deposits restrict its use for nuclear application because of a large neutron absorption cross-section of cobalt and the long half-life of the resulting radioactive isotope. Sulfur bearing hardening agents have also been used successfully but codeposition of sulfur causes embrittlement⁽²⁾ especially if the deposit is elevated to a high temperature⁽³⁾. Further, sulfur-free organic compounds have also been investigated. Dill⁽⁴⁾ suggested benzamides and its derivatives to be good hardening agents for nickel electrodeposits and as substituents in those baths which could not tolerate cobalt or sulfur in their deposits. But the rapid development of organic addition agents during recent years, especially for hard and bright plating, has for the time being complicated rather than clarified the picture. One difficulty is that for bright and hard nickel deposits, more than one type of additive has to be added and this may affect the behaviour of the products. Selection of a non-aqueous bath sometimes overcomes this difficulty and leads to bright as well as hard deposits. Takei deposited hard nickel

* Department of Chemistry, Banaras Hindu University, Varanasi-221005, India.

from methanol bath⁽⁵⁾. NH_4^+ ion plays a vital role in electrodeposition of nickel having no internal stress from the dimethylsulfoxide (DMSO) bath⁽⁶⁾. Bright chromium electrodeposits were obtained from the chromium (III) chloride hexahydrate/methanol bath at 50% cathode current efficiency⁽⁷⁾. Satisfactory deposits of lead were obtained from PbCl_2 or PbNO_3 dissolved in pure dimethylformamide (DMF)⁽⁸⁾. Study of mechanism of chromium electrodeposited from DMF and DMSO baths revealed interesting results⁽⁹⁾. High quality electrodeposits of aluminium were obtained using the AlCl_3 - LiAlH_4 /tetrahydrofuran (THF)-benzene bath⁽¹⁰⁾. Bright electroplates of nickel with 100% cathode current efficiency were obtained using the nickel chloride/DMF bath⁽¹¹⁾; addition of boric acid led to a high degree of hardness⁽¹²⁾.

The present work is intended to study the effect of ammonium and cobalt ions in electrodeposition of nickel from nickel acetate dissolved in pure formamide, N-methylformamide and N, N-dimethylformamide, with the aim to get hard and ductile deposits.

II. Experimental

Copper strips of area 1.5 cm^2 ($1.5 \text{ cm} \times 1.0 \text{ cm}$) and thickness 1 mm were used as cathode. These strips were first ground to get a smooth surface. Stains were removed using different emery papers (1/0 to 4/0); bright image surface followed by disc polishing. For degreasing, hot soap solution (Idipol) cleaning, electrolyte cleaning using sodium carbonate (pH 12.0) and solvent cleaning (acetone) operations were performed. After pickling with 10% sulfuric acid, and degreasing adequately, the specimen was cleaned with cold and hot double distilled water. High purity nickel sheets were used as anodes. A copper strip cathode was placed in between two parallel anodes and inter-electrode distance of 2 cm was maintained throughout the experiment. Current was measured by a copper coulometer. The bath composition and condition of electrolysis are given in Table 1. Formamide⁽¹³⁾, N-methylformamide⁽¹⁴⁾ and N, N-dimethylformamide⁽¹⁵⁾ were distilled as suggested. 0.2 kmol/m^3

Table 1 Bath compositions and electrolytic conditions

Parameter	
Nickel acetate	0.2 kmol/m^3
Ammonium acetate	$0.1\text{--}0.8 \text{ kmol/m}^3$
Cobalt acetate	$0.005\text{--}0.05 \text{ kmol/m}^3$
Boric acid	$0.1\text{--}0.2 \text{ kmol/m}^3$
Current density	$50\text{--}100 \text{ A/m}^2$
Temperature	303–323 K
Annealing temperature	473–673 K
Duration of electrolysis	3600 s
Duration of annealing	3600 s
Agitation	nil

$(\text{CH}_3\text{COO})_2\text{Ni} \cdot 6\text{H}_2\text{O}$ salt was dissolved separately in these purified solvents. Nickel acetate/formamide bath required a little concentration of boric acid to avoid precipitation, probably of nickel hydroxide; in absence of boric acid the bath turned colloidal after 86.4 ks (24 h).

Hardness was measured on a Tukon Wilson hardness tester using diamond pyramid indenter, applying a load of 10 gf (0.098 N). Magnitude of load applied to the indenter is very important from the viewpoint of depth of penetration of the diamond in the testing material. The depth of indentation is one-seventh the diagonal length in accordance with ASTM E standard⁽¹⁶⁾; the thickness of the testing material should be ten times the depth of indentation. Anvil effect leads to erroneous results.

III. Results and Discussion

1. Effect of NH_4^+ ion

Ammonium ions played a vital role in enhancing the hardness of the electrodeposited nickel to a sufficiently high degree; nevertheless, the basicity and dielectric behavior of the solvents had their own influence.

0.2 kmol/m^3 nickel acetate dissolved in pure formamide (FA) offered a high resistance to the passage of electricity. An appropriate concentration of ammonium acetate enhanced the conductivity of the bath along with cathode current efficiency, quality and hardness of the electrodeposited nickel. 0.2 kmol/m^3 ammonium acetate appeared to be the optimum concentration at which hard deposits with high

cathode current efficiency could be obtained (Table 2). Nickel acetate in conjunction with 0.2 kmol/m^3 ammonium acetate and 0.2 kmol/m^3 boric acid probably produced an optimum concentration of basic colloidal salt in the catholyte⁽¹⁷⁾ resulting in hard deposits.

In case of nickel acetate/N-methylformamide (NMF) electrolyte a higher concentration of ammonium acetate (0.4 kmol/m^3) was found to be necessary to produce a high degree of hardness, although it led to a low cathode efficiency. N-methylformamide having a high dielectric constant and thereby high polarity⁽¹⁸⁾ allows a greater number of nickel ions to concentrate around the cathode which is proportionate to a ponderous concentration of ammonium acetate in the catholyte. This results in higher buffering action leading to a high degree of hardness (Table 3).

Hardness exhibited a declining trend after 0.2 kmol/m^3 concentration of ammonium acetate in case of nickel acetate/N, N-dimethylformamide (DMF) bath, probably due to the lowest dielectric constant of this solvent in the amide series (Table 4).

The above experiments were performed under such operating conditions of temperature and current density, at which pure baths without any additive (except nickel acetate/formamide) exhibited their maximum values of cathode current efficiency. Hence operating temperature and current density were different in three cases. For comparison, bath of similar composition, operated under similar experimental conditions (Table 5) led to the con-

Table 2 Effect of ammonium acetate on the electro-deposition of nickel from formamide bath.

System: nickel acetate/formamide, boric acid (0.2 kmol/m^3), 313 K and 50 A/m^2 .

Ammonium acetate concentration (kmol/m^3)	Nature of electro-deposit	Cathode current efficiency (%)	Vickers hardness number DPH_{10}
0.0	Bright*	87.2	490
0.1	Bright	89.9	585
0.2	Mirror-image	93.6	670
0.3	Mirror-image	80.1	640
0.4	Mirror-image*	76.5	610
0.5	Bright*	70.2	528

*Peeling

Table 3 Effect of ammonium acetate on the electro-deposition of nickel from N-methylformamide bath.

System: nickel acetate/N-methylformamide, 305 K and 100 A/m^2 .

Ammonium acetate concentration (kmol/m^3)	Nature of electro-deposit	Cathode current efficiency (%)	Vickers hardness number DPH_{10}
0.0	Bright	14.0	—
0.1	Bright	66.8	795
0.2	Milky	80.4	845
0.3	Whiteness reduces	78.0	925
0.4	Light grayish	77.1	1003
0.5	Light grayish	69.0	911
0.6	Light grayish	67.1	867
0.8	Light grayish, white streaks at edges.	55.2	750

Table 4 Effect of ammonium acetate on the electro-deposition of nickel from N, N-dimethylformamide.

System: nickel acetate/N, N-dimethylformamide, 313 K and 50 A/m^2 .

Ammonium acetate concentration (kmol/m^3)	Nature of electro-deposit	Cathode current efficiency (%)	Vickers hardness number DPH_{10}
0.1	Grayish*	60.3	590
0.2	Light grayish	80.1	712
0.3	Shining grayish	72.0	642
0.4	Shining grayish	69.5	568
0.5	Shining light-grayish	66.7	545

*Mild peeling at edges

clusion that although surface appearance of the electrodeposits deteriorated with the successive inclusion of methyl group in formamide, yet hardness showed a steep rising trend. Dimethylformamide was found to be a most appropriate solvent in producing hard deposits.

Loaded with two electron releasing methyl groups, the electron density of oxygen in N, N-dimethylformamide is enormously enhanced, followed by N-methylformamide which contains one methyl group. Under such circumstances, the formation of $(\text{CH}_3\text{COO})_2\text{Ni}:\text{xDMF}$ and $(\text{CH}_3\text{COO})_2\text{Ni}:\text{xNMF}$ complexes⁽¹⁹⁾ are highly probable as compared to $(\text{CH}_3\text{COO})_2\text{Ni}:\text{FA}$ complex. The slow release

Table 5 Physical characteristics of nickel electrodeposited from amide solvents.

Operating conditions: AmAc (0.2 kmol/m^3), boric acid (0.1 kmol/m^3), 323 K and 50 A/m^2 .

Systems	Nature of electrodeposit	Cathode current efficiency (%)	Vickers hardness number DPH_{10}
NiAc/FA	Semi-bright	87.2	670
NiAc/NMF	Milky	80.2	820
NiAc/DMF	Light grayish	72.5	1012

NiAc: nickel acetate, AmAc: ammonium acetate, FA: formamide, NMF: N-methylformamide, DMF: N, N-dimethylformamide

of nickel ions in the catholyte due to dissociation of dimethylformamide and methylformamide complexes result in sound deposition leading to a high degree of hardness. Association of formamide molecules among themselves⁽²⁰⁾ and the least probability of complexation, causes heavy concentration polarization of free nickel ions around cathode leading to high efficiency but comparatively less hard deposits. A low peeling tendency of the electrodeposits from formamide bath is due to the protic nature of the solvent. The released hydrogen is thought to be contained as hydride in the initially deposited layer which tends to diffuse to certain favored sites and form gas pockets. The high pressure in such a pocket results in expansion of the deposited layer leading to cracked structure⁽²¹⁾.

Using acetic acid as a solvent, the pK values determined by Huisgen and Brade for formamide and its N-methyl derivatives⁽²²⁾ revealed that a large positive increase in pK accompanied, by the addition of a single methyl group while a much smaller increase occurred when a second methyl group was added. This effect was due to the ability of a methyl group to release electron, making oxygen more susceptible to protonation. This shows the least basic character of formamide in the series. The difference in basicity is responsible for the bright deposition of nickel in the case of formamide and deterioration in the quality with increasing basicity in the case of N-methylformamide and N, N-dimethylformamide.

X-ray analysis of the electrodeposits, from N, N-dimethylformamide (DMF) bath, revealed that the values of lattice parameter, 'a', was $3.5297 \times 10^{-10} \text{ m}$ which was in close agreement with the literature value of $3.523 \times 10^{-10} \text{ m}$. This confirmed the deposition of nickel in its purest form having face-centred cubic lattice. That the amide solvents were not embodied in the electrodeposits and were simply adsorbed (exhibiting surface phenomena) was confirmed by the fact that even the darkest plate turned mirror-image when polished on buffing wheels for a few seconds.

Well-defined cracked structure in case of formamide (Fig. 1) turned fine-grained with the successive replacement of hydrogen by methyl group in formamide (Figs. 2 and 3). It is, however, well known that foreign substances, if present in plating bath, are frequently codeposited. These foreign substances may be addition agents; they could be hydroxides formed because the pH is much higher near the cathode than in the bulk of plating solution⁽²³⁾. These foreign atoms or molecules can attach themselves to a kink site and thereby block further growth⁽²⁴⁾. This causes overpotential for crystal growth to enhance, resulting in fine-grained deposits. It appears that favourable chances exist for the formation of basic nickel, hydroxide in the catholyte in case of N, N-dimethylformamide (DMF) and N-methylformamide (NMF) due to their higher pH values. These basic salts are absorbed and subsequently included in the deposit checking

Fig. 1 Scanning electron micrograph (SEM) of as-plated nickel from NiAc/FA bath in presence of 0.2 kmol/m^3 AmAc and 0.1 kmol/m^3 boric acid at 50 A/m^2 and 323 K.

Fig. 2 SEM of as-plated nickel from NiAc/NMF bath in presence of 0.2 kmol/m^3 AmAc and 0.1 kmol/m^3 boric acid at 50 A/m^2 and 323 K .

Fig. 4 SEM of as-plated nickel from NiAc/NMF bath containing 0.2 kmol/m^3 AmAc and 0.1 kmol/m^3 boric acid at 305 K and 50 A/m^2 .

Fig. 3 SEM of as-plated nickel from NiAc/DMF bath in presence of 0.2 kmol/m^3 AmAc and 0.1 kmol/m^3 boric acid at 50 A/m^2 and 323 K .

Fig. 5 SEM of as-plated nickel from NiAc/NMF bath in presence of 0.2 kmol/m^3 AmAc and 0.1 kmol/m^2 boric acid at 305 K and annealed to 323 K passing current of 50 A/m^2 .

the outgrowth of the crystal leading to fine-grained hard deposits.

2. Effect of annealing

Nickel deposits were found to be highly susceptible to heat treatment. Cracks, developed at a lower temperature, were found to diminish when the operating temperature was raised. The cracks developed during electrodeposition of nickel from N-methylformamide bath operated at 305 K were markedly reduced when the operating temperature was raised to 323 K (Fig. 4), but cracks were found to disappear totally when instead of raising the operating temperature, the electroplate was simply heated to 323 K for 3.6 ks (1 h) applying a current density of 50 A/m^2 and allowed

to cool in air under atmospheric pressure (Fig. 5). However this simple operation was not sufficient for reducing the internal stress in case of electroplates obtained from formamide bath. These plates needed annealing for 3.6 ks at 473 K and cooling slowly in furnace to room temperature, for getting stress-free hard deposits. The tendency to peel due to internal stress was found to nullify by these annealing operations. Further, annealing of as-plated nickel caused slow recovery of defect structures. One of the important functions, indeed the most important one, of heat treatment is to alter the microstructure of metals and alloys which govern the mechanical properties too⁽²⁵⁾. At 673 K a definite change in microstructure

occurred. Although cracks persisted yet the hidden fine cells grew to well shaped subgrains (Fig. 6). Effect of annealing is summarized in Table 6.

3. Effect of Co^{++} ion

The hardness of nickel electrodeposited from NiAc/FA, AmAc (0.2 kmol/m^3), boric acid (0.1 kmol/m^3), 50 A/m^2 , 323 K bath exhibiting $\text{DPH}_{10}=670$, further enhanced gradually with the addition of cobalt acetate upto 0.01 kmol/m^3 whereat it exhibited its maximum value of 950 and thereafter hardness as well as reflectivity showed a declining trend (Table 7). The effectiveness of cobalt as a brightener was well marked in case of N-methylformamide (NMF) and N, N-dimethylformamide (DMF) (Tables 8 and 9). A bit higher concentration of cobalt acetate (0.02 kmol/m^3) was needed in the case of N-methylformamide to produce hard deposits of the order of $\text{DPH}_{10}=1013$. But its effectiveness as a brightener was marked upto 0.05 kmol/m^3 . Mirror-image bright deposits in the presence of a higher concentration of cobalt acetate exhibited fine-grained structure but mild cracks, at edges, persisted (Fig. 7). Fedot'ev⁽²⁶⁾ has reported that adsorption of brightener on the active centres of crystal, though leads to grain refinement, causes hardness as well as tensile strength to enhance. But once the adsorbed material is entrapped, it

Fig. 6 SEM of as-plated nickel from NiAc/FA bath containing 0.2 kmol/m^3 AmAc and 0.2 kmol/m^3 boric acid at 313 K and annealed to 673 K .

shows a cleaving action which lowers the tendency of the deposit to decrease its volume resulting in cracked structure. Dimethylformamide (DMF) appears to be best solvent for getting hard deposits of highest degree as compared to methylformamide (NMF) or formamide (FA). Cobalt acetate acts well as a brightener and as a hardener. Hardest deposits resulted in presence of 0.02 kmol/m^3 cobalt acetate but even a slight amount of it was highly effective in enhancing the hardness enormously. A remarkable aspect of these deposits from dimethylformamide bath was that all electroplates were fine-grained and devoid of cracks (Fig. 8).

Table 6 Effect of annealing temperature on microhardness and microstructure of electrodeposited nickel from amide solvents. Current density: 50 A/m^2

Systems	Operating temperature (K)	Annealing temperature (K)	Vickers hardness number (DPH_{10})	Microstructure
NiAc/NMF, AmAc (0.2 kmol/m^3) boric acid (0.1 kmol/m^3).	303	—	895	Mild cracks
	323	—	1016	No crack at Cp, mild cracks at Ed.
	303	323^*	878	No crack anywhere
NiAc/FA, AmAc (0.2 kmol/m^3), boric acid (0.1 kmol/m^3).	313^{**}	—	670	Cracks throughout
	333	—	820	Cracks reduced
	313	473	658	Peeling diminishes
	313	673	649	Grain size reformed

Cp: Central portion, Ed: Edges

*Passing current while heating (50 A/m^2)

**Peeling at edges after 86.4 ks of electrolysis

Table 7 Effect of cobalt acetate on the electrodeposition of nickel.

System: NiAc/FA, AmAc (0.2 kmol/m³), boric acid (0.1 kmol/m³), 323 K and 50 A/m².

Concentration of CoAc (kmol/m ³)	Nature of deposit	CCE (%)	DPH ₁₀
0.000	Semi-bright	87.2	670
0.005	Bright	86.0	680
0.010	Bright	94.4	720
0.015	Bright	82.3	950
0.020	Semi-bright	77.1	896
0.030	Hazy-bright	76.7	802
0.045	Hazy-bright	71.4	777

Table 8 Effect of cobalt acetate on the electrodeposition of nickel.

System: NiAc/NMF, AmAc (0.2 kmol/m³), boric acid (1.0 kmol/m³), 323 K and 50 A/m².

Concentration of CoAc (kmol/m ³)	Nature of deposit	CCE(%)	DPH ₁₀
0.000	Milky	80.2	820
0.005	Hazy-bright	53.6	865
0.010	Semi-bright	56.2	883
0.015	Bright	85.1	995
0.020	Bright	71.5	1013
0.030	Bright, mirror-image	54.6	783
0.050	Bright, mirror-image	50.1	760

Table 9 Effect of cobalt acetate on the electrodeposition of nickel.

System: NiAc/DMF, AmAc (0.2 kmol/m³), boric acid (1.0 kmol/m³), 323 K and 50 A/m².

Concentration of CoAc (kmol/m ³)	Nature of deposit	CCE (%)	DPH ₁₀
0.000	Light grayish	72.7	1012
0.005	Semi-bright	51.6	1010
0.010	Semi-bright	47.7	1028
0.015	Shining semi-bright	75.3	1032
0.020	Bright	40.2	1058
0.030	Bright, mirror-image	37.0	1008
0.045	Bright, mirror-image	31.6	870

CoAc: Cobalt acetate hexahydrate

CCE: Cathode current efficiency

Fig. 7 SEM of as-plated nickel from NiAc/NMF bath containing 0.2 kmol/m³ AmAc, 0.1 kmol/m³ boric acid and 0.02 kmol/m³ CoAc at 50 A/m² and 323K.

Under similar operating conditions, the cathode current efficiency was found to decrease with increasing number of methyl group in formamide. This may be due to the fact that loading of the methyl group successively causes a greater electrophoretic effect resulting in low cathode current efficiency.

High degree hardness of nickel electro-deposited from amide solvents in presence of a little concentration of cobalt acetate may be attributed to the following facts:

(1) Although the traces of cobalt ions present have no significant influence on viscosity or conductivity, yet it has a marked influence on anode potential⁽²⁷⁾.

(2) The presence of a little cobalt acetate facilitates the dissociation of nickel acetate/amide complexes especially in case of dimethylformamide as the rate constant for solvent exchange of Co⁺⁺ ion⁽²⁸⁾ is much higher

Fig. 8 SEM of as-plated nickel from NiAc/DMF bath containing 0.2 kmol/m^3 AmAc, 0.1 kmol/m^3 boric acid and 0.02 kmol/m^3 CoAc at 50 A/m^2 and 323 K .

than Ni^{++} ion⁽²⁹⁾ in N, N-dimethylformamide (DMF).

The presence of very small concentrations of cobalt ion in the bath will not markedly effect the composition of electrodeposit due to the fact that polarographic half wave potential for reduction of Co^{++} ions is much lower than of Ni^{++} ions in amide solvents⁽³⁰⁾.

IV. Conclusions

(1) Ammonium ions act as a hardener during electrodeposition of nickel from amide/nickel acetate baths.

(2) Cobalt acetate in conjunction with 0.2 kmol/m^3 ammonium acetate and 0.1 kmol/m^3 boric acid acts as a perfect hardener for nickel electrodeposited from formamide, N-methylformamide and N, N-dimethylformamide containing nickel acetate.

(3) N, N-dimethylformamide (DMF) is better than N-methylformamide (NMF) or formamide (FA) in producing hard and fine-grained deposits.

(4) Cobalt acetate acts perfectly as a brightener.

(5) Peeling at edges due to internal stress in case of nickel deposits from nickel acetate / formamide bath is totally checked on annealing the plates to 473 K .

Acknowledgements

Thanks are due to Prof. I. S. Ahuja, Head,

Department of Chemistry for providing necessary facilities. Messrs. S. N. Lal and Prakash Singh of Metallurgical Engineering College, B. H. U. are also thanked for helping in preparing scanning electron micrograph; Mr. Rameshwar Singh for annealing experiments. One of us (HKS) gratefully acknowledges the award of teaching research fellowship sponsored by University Grants Commission, Government of India and academic leave sanctioned by the management of Post-Graduate College, Ghazipur, Uttar Pradesh, India.

REFERENCES

- (1) K. C. Belt, J. A. Crossley and S. A. Watson: *Trans. Inst. Met. Fin.*, **48** (1970), 133.
- (2) N. P. Fedot'ev and Yu. M. Pozin: *Zhur. Priklad. Khim.*, **31**(1958), 419.
- (3) W. H. Safranek: *Plating*, **53** (1966), 1211.
- (4) A. J. Dill: *Plating*, **62** (1975), 770.
- (5) T. Takei: *Electrochim. Acta*, **23** (1978), 1325.
- (6) H. K. Srivastava and P. K. Tikoo: *Plat. Surf. Fin.*, **74** (1987), 67.
- (7) T. Tsuru and I. Takenaka: *Kinzoku Hyomen Gijutsu*, **28** (1977), 85.
- (8) T. Tsuru, S. Kobayashi, T. Kimura and T. Inui: *Kinzoku Hyomen Gijutsu*, **27** (1976), 230.
- (9) T. Tsuru, S. Kobayashi and K. Kusuhara: *Kyushu-sangyo Daigaku Kogakubu Kenkyu Hokoku*, **21** (1984), 41.
- (10) V. A. Kazakov, N. Nakamura and M. Ioshio: *Elektrokhimiya*, **21** (1985), 1331.
- (11) H. K. Srivastava and P. K. Tikoo: *Bull. Electrochem.*, **2** (1986), 227.
- (12) H. K. Srivastava and P. K. Tikoo: *Trans. Ind. Inst. Met.*, (In press).
- (13) L. R. Dawson, T. M. Newell and W. J. McCreary: *J. Amer. Chem. Soc.*, **76** (1954), 6024.
- (14) L. A. La Plache and M. T. Rogers: *J. Amer. Chem. Soc.*, **86** (1964), 337.
- (15) P. G. Sears, E. F. Wilhoit and L. R. Dawson: *J. Phys. Chem.*, **59** (1955), 373.
- (16) E 384, *Annual Book of ASTM Standards*, ASTM, Philadelphia, (1984), 497.
- (17) V. Gluck: *Plat. Surf. Fin.*, **62** (1975), 865.
- (18) G. R. Leader and J. F. Gormley: *J. Amer. Chem. Soc.*, **73** (1951), 5731.
- (19) B. Anilin and A-G Soda Fabrik: *British Patent*, (1957), 774, 956.
- (20) T. Ishikawa: *Bull. Chem. Soc. Japan*, **31** (1958), 524.
- (21) D. R. Gabe and J. M. West: *Trans. Inst. Met. Fin.*, **40** (1963), 197.
- (22) R. Huisgen and H. Brade: *Chem. Ber.*, **90** (1957), 1432.
- (23) A. Knodler and K. W. Neugeboren: *Metalloberfläche*, **24** (1970), 78.

- (24) R. Weil: *Plating*, **61** (1974), 654.
(25) B. E. Jacobson and J. W. Silwa: *Plat. Surf. Fin.*, **66** (1979) Sept, 42.
(26) N. P. Fedot'ev: *Plating*, **53**(1966), 309.
(27) J. A. Friend and F. Gutamamm: *Electrochemistry*, Eds. Proc. First Austr. Conf. Electrochemistry, p. 894.
(28) N. A. Matwiyoff: *Inorg. Chem.*, **5** (1966), 788.
(29) L. S. Frankel: *Chem. Commu.*, (1969), 1254.
(30) O. Duschek and F. Gutamann: *Anorg. Alloy Chem.*, **394** (1972), 243.
-