Effect of Temperature on Physical Characteristics of Nickel Electrodeposited from Nickel Salts in Presence 1,4-Dioxane-aqueous Bath

H.K. SRIVASTAV* and AARTI PANDEY
Department of Chemistry, Postgraduate College, Ghazipur-233 001, India
E-mail: vinay_dwivedi@rediffmail.com

Electrodeposition of metal or its alloy not only protects the base metal but also provide decorative appeal. Nickel is one of the most important metals employed for electrodeposition on various base metals. There are various parameters, which affect the physical characteristics of nickel electrodeposited from different salt solutions. Temperature is one such parameter whose effect on physical characteristics (cathode current efficiency and thickness) of the nickel electrodeposited from nickel acetate alone or in combination with nickel formate and nickel sulphamete in presence of 0, 10 and 20 mol % 1,4-dioxane has been observed. It has been found out that variation in temperature affects the values of cathode current efficiency and thickness.

Key Words: Nickel, Electrodeposition, Cathode current efficiency.

INTRODUCTION

The electrodeposition of metal[1] or its alloy protect the base metal as well as provide decorative appeal. Metallic coatings are used in industries, particularly where the requirements involve high chemical resistance, good electrical conductivity and low contact resistance as well as high hardness and melting points with a pleasing appearance[2].

There are 70 metals mentioned in the long form of periodic table and less than half (about 30) of these can be electrodeposited from their aqueous solution. The ease of deposition depends on the ease of reducibility of the metal ions in solution by the electrons supplied at cathode by the passage of direct current. How easily this charge neutralization takes place is characteristics of the M/M^{z+} system concerned and is approximately determined by the position of the system in a series called the Electrochemical series. The Electrochemical series is an increasing or decreasing order of thermodynamic potentials assigned to metals in contact with aqueous solutions of their ions at unit activity with reference to that for the standard hydrogen electrode, which is taken as zero[3].

Nickel is one of the most important metals employed for electro deposition[4]. There are various parameters that influences the electrodeposition of nickel. Temperature is one such parameters whose variation influences the electrodeposition[5].

EXPERIMENTAL

Initially copper strips of dimension 2 cm × 5 cm × 0.1 cm were used as substrate for nickel electrodeposition studies, but in most of the subsequent experiment the copper strips of dimensions 2 cm × 1 cm × 0.1 cm were used.

The experimental copper strips were first grinded to obtain smooth surfaces and polishing consecutively with emery polishing papers 1/0 finished the scratches of grinding, 2/0, 3/0 and 4/0 finished the scratches of grinding.

Smooth reflective surfaces which were free of stains and pits were made by disc polishing using aluminium powder. Final disc polishing was performed using fine quality polishing silver cloth. Copper strips, thus prepared were washed with distilled water and after that with methanol[6].

The mechanically polished strip were degreased in hot soap (Edipol) solution for some period, washed thoroughly under running water and washed repeatedly with double distilled hot and cold water. Solvent degreasing was done by dipping the copper strip in acetone for minute and thereafter washing thoroughly the strip with double distilled water[7]. The copper strip was electrocleaned cathodically without NaOH for a minute as suggested by Lainer[8]. The electrocleaning solution was maintain at a temperature around 50-55 ºC as in hotter solution the drag out dried on the part resulting in inferior quality of deposites[9].

The electrocleaning of the strips pickled in a light pickling solution for 4 min. Thus the obtained copper strip was weight at this final stage and then made the cathode in the experimental cell.

Cleanliness of a copper strip was evaluated by the Water break test. The capacity of a copper strip surface to hold an unbroken film of clean water was seen, after cleaning and rinsing and finally dipping the part in clean, cool water. This process is very essential for electrodeposition.

The cleaned sample strips was then used as cathode for nickel placing it between two parallel pieces of nickel anodes. The interelectrode distance in all experiment was maintained at 2 cm. The current measured with the help of a copper coulometer in series with the all studies. The coulometer contained recrystallized copper sulfate (150 g), dissolved in 1 L of double distilled water having 50 g sulfuric acid and 50 g ethyl alcohol, as recommended by Ottel. Ethyl alcohol added to prevent the dissolution of deposited copper by oxidation. The cathode current efficiency was computed as the ratio of the weight of nickel actually deposited to the maximum that could be deposited by that quantity of current in accordance with Faraday's law. The different solution, which is used for the electrodeposition of nickel, were purified by electrolysis at low current density[10]. All experiments were carried out without agitation.

A glass container (150 mL capacity) was used as the electrolysis cell for nickel plating. It was covered with a wooden block that did not seal airtight and contained holes for connecting rods to the electrodes. The electrolysis cell was placed in a thermostat to maintain a uniform temperature inside the cell.

Effect of temperature on electrodeposition was observed in both conditions, firstly when nickel acetate was used alone and secondly when it was used in combination with nickel formate and nickel sulphamate. Different molar concentrations of boric acid which is used as a buffer was taken to get better electrodeposition. Few drops of concentrated HCl also added for better dissolution of salts since there was no agitation.

The parameters used in the current study are given in Table-1.

TABLE-1

1	Nickel salts (M)	$Ni(CH_3COO)_2.4H_2O$ (0.2 M) $Ni(HCOO)_2.4H_2O$ (0.2 M) $Ni(SO_3NH_2)_2.4H_2O$ (0.2 M)
2	Duration of electrolysis	45 min
3	Temperature	30-70 ºC
4	Agitation	Nil
5	Area of Cu strips used as subs.	2.0 × 1.0 (cm)
6	Inter-electrode distance	2.0 (cm)

RESULTS AND DISCUSSION

Thickness of electodeposits were measured by using a digital microthicknometer in terms of micrometers (μm).

Cathode current efficiency (CCE) was computed as the ratio of the weight of the nickel actually electrodeposited to the maximum that could be electrodeposited by that quantity of the current in accordance with Faraday's law. The cathode current efficiency of the electrodeposited nickel was calculated using the formula:

$$\text{CCE} = \frac{\text{Wt. of Nickel deposited on cathode in electrlytic cell}}{\text{Wt. of copper deposited on the cathode Cu Coulometer}}$$

TABLE-2
SHOWING EFFECT OF TEMPERATURE ON PHYSICAL CHARACTERISTICS [CATHODE CURRENT EFFICIENCY (CCE) (%) & THICKNESS (µm)] OF NICKEL ELECTRODEPOSITED FROM NICKEL SALTS IN PRESENCE OF AQUEOUS (0 mol %) 1,4-DIOXANE-AQUEOUS BATH

Temp. (ºC)	System: NiAc (0.2 M), boric acid (0.2 M)- aqueous bath, 0.5 A/dm^2		System: NiAc (0.2 M), NiFMT (0.2 M), boric acid (0.2M)-aqueous bath, 0.5 A/dm^2		System: NiAc (0.2 M), NiSMT (0.2 M), boric acid (0.2 M)-aqueous bath, 0.5 A/dm^2		System: NiAc (0.2 M), NiFMT (0.2 M), NiSMT (0.2 M), Boric acid (0.2 M) / aqueous bath, 0.5 A/dm^2	
	CCE	Thickness	CCE	Thickness	CCE	Thickness	CCE	Thickness
30	96.4	2.09	99.8	2.80	58.0	1.87	95.4	3.40
40	82.4	1.63	99.0	3.74	56.0	1.87	98.3	2.80
50	51.8	1.40	59.6	2.87	64.0	1.94	90.6	2.99
60	55.5	1.82	54.3	2.85	70.3	1.93	89.4	1.87
70	57.2	1.60	60.4	2.74	80.4	1.91	86.3	1.05

TABLE-3
SHOWING EFFECT OF TEMPERATURE ON PHYSICAL CHARACTERISTICS [CATHODE CURRENT EFFICIENCY (CCE) (%) & THICKNESS (µm)] OF NICKEL ELECTRODEPOSITED FROM NICKEL SALTS IN PRESENCE OF (10 mol %) 1,4-DIOXANE – AQUEOUS BATH

Temp. (ºC)	System: NiAc (0.2 M), boric acid (1.0 M), (10 mol %) dioxane-aqueous bath, 0.5 A/dm^2		System: NiAc (0.2 M), NiFMT (0.2 M), boric acid (1.0 M), (10 mol %) dioxane-aqueous bath, 0.5 A/dm^2		System: NiAc (0.2 M), NiSMT (0.2 M), boric acid (1.0 M), (10 mol %) dioxane-aqueous bath, 0.5 A/dm^2		System: NiAc (0.2 M), NiFMT (0.2 M), NiSMT (0.2 M), Boric acid (1.0 M), (10 mole) dioxane-aqueous bath, 0.5 A/dm^2	
	CCE	Thickness	CCE	Thickness	CCE	Thickness	CCE	Thickness
30	50.0	1.98	86.4	2.94	69.7	2.54	60.7	3.65
40	50.0	1.76	72.0	3.00	98.4	5.09	95.6	2.32
50	63.2	1.12	73.2	3.74	99.3	5.54	94.2	1.04
60	30.4	1.87	86.7	4.79	88.6	4.68	95.6	3.74
70	22.5	2.04	90.4	5.50	87.3	5.16	93.9	5.06

Tables 2-4 reveals the effect of temperature on physical characteristics of nickel when aqueous (0 mol %), (10 mol %)1,4-dioxane-aqueous bath and (20 mol %) 1,4-dioxane-aqueous bath were used, respectively on single salt nickel acetate or in combination with nickel formate and nickel sulphamate. Bright deposits resulted only at the lower temperature range whether it was aqueous or dioxane/aqueous mixture. Cathode current efficiency was better in case of aqueous as compared to (20 mol %) 1,4-dioxane-aqueous bath but it was comparable with (10 mol %) 1,4-dioxane-aqueous bath. Thick deposits were obtained at lower temperature which decreased with increasing temperature in case of aqueous as well as in case of 10 mol % and 20 mol % 1,4-dioxane-aqueous bath.

TABLE-4
SHOWING EFFECT OF TEMPERATURE ON PHYSICAL CHARACTERISTICS [CATHODE CURRENT EFFICIENCY (%) & THICKNESS (μm)] OF NICKEL ELECTRODEPOSITED FROM NICKEL SALTS IN PRESENCE OF (20 mol %) 1,4-DIOXANE-AQUEOUS BATH

Temp. (ºC)	System: NiAc (0.2 M), boric acid (0.8 M), (20 mol %) dioxane-water bath, 0.5 A/dm^2		System: NiAc (0.2 M), NiFMT (0.2 M), boric acid (0.8 M), (20 mol %) dioxane-water bath, 0.5 A/dm^2	
	CCE	Thickness	CCE	Thickness
30	86.4	2.99	90.3	3.57
40	80.4	2.87	85.2	3.07
50	82.3	1.57	73.4	2.70
60	80.3	1.49	80.2	2.87
70	79.2	1.74	71.2	2.49
Temp. (ºC)	System: NiAc (0.2 M), NiSMT (0.2 M), boric acid (0.8 M), (20 mol %) dioxane-water bath, 0.5A/dm^2		System: NiAc (0.2 M), NiSMT (0.2 M), NiFMT (0.2 M), boric acid (0.8 M), (20 mol %) Dioxane-water bath, 0.5 A/dm^2	
	CCE	Thickness	CCE	Thickness
30	80.7	4.23	70.4	3.94
40	70.2	4.94	64.3	4.76
50	55.9	3.23	56.4	4.74
60	50.4	2.43	43.2	4.79
70	50.1	2.41	21.4	4.78

When a single salt is replaced by salt combination, at 0 mol % dioxane-aqueous bath, there is no major change in the nature of electrodeposits. Cathode current efficiency is quite high at early temperature range when salt combination is used. Same is the case with thickness of electrodeposits. But both cathode current efficiency and thickness decreases with increase in temperature above 50 ºC.

At (10 mol %) 1,4-dioxane-aqueous bath combination, there is drastic change in both cathode current efficiency and thickness when salt combinations were used. Both increases with increase in temperature.

At (20 mol %) 1,4-dioxane-aqueous bath combination, there is change in both cathode current efficiency and thickness when salt combinations were used. Both decreases with increase in temperature.

From these results it can be concluded that temperature plays great role in electrodeposition of nickel and its variation can cause significant effect on electrodeposition.

REFERENCES

1. Metal Industry Hand Book Directory (1971).
2. J.W. Dim, *Proc. Electrochem. Soc.*, **57**, 639 (1987).
3. J.M. Deuber, *Proc. Electrochem. Soc.*, **87**, 7 (1987).
4. W.L. Pinner, B.B. Kuepp and M.B. Diggin, in ed.: P.A. Lowessheim, Nickel in Modern Electroplating, John Wiely & Sons, NewYork, Ch. 12, (1963).
5. D. Dubperhell, *Plating*, **46**, 599 (1959).
6. O.P. Watts and P.L. Deverter, *Trans. Am. Electrochem. Soc.*, **30**, 145 (1916).
7. K. Boto, *Electrodep. Surf. Treat.*, **3**, 77 (1975).
8. V.I. Lainer, Modern Electroplating Israel Program for Scientific Translations, Jerusalem (1976).
9. W.H. Wade, *Plating*, **55**, 740 (1968).
10. L.R. Dawson, T.M. Newell and W.J. McCreary, *J. Am. Chem. Soc.*, **76**, 6024 (1954).

(*Received*: 30 June 2006; *Accepted*: 31 July 2007) AJC-5782