

ELECTRODEPOSITED TIN-NICKEL ALLOY FOR DECORATIVE AND PROTECTIVE APPLICATIONS

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Electrodeposited tin-nickel (Sn-Ni) alloy is a hard, wear and tarnish resistant coating that can replace the conventional nickel-chromium coatings in many applications. In the present study, an electrolyte based on ammonium fluoride and sulphate of tin and nickel has been developed for depositing the Sn-Ni alloy. Deposition parameters have been optimized using Hull Cell experiments. The current efficiency and throwing power of the solution are measured. Hardness, wear resistance, corrosion resistance and structure of the deposited alloy have also been found.

Key words: Tin-nickel alloy, sulphate bath, deposit characteristics, structure

INTRODUCTION

Electrodeposited tin-nickel (Sn-Ni) alloy is an inter-metallic compound of approximately 65% tin and 35% nickel by weight, with a variation of 2-5% over a wide range of operating conditions and solution variables. They have been used for decorative and protective applications. When plated on a polished substrate, the alloy is fully bright and requires little or no buffing. Sn-Ni alloy is highly resistant to tarnish and corrosion in humid atmospheres. It also possesses good contact resistance and excellent frictional resistance. Because of these properties, the alloy is almost a substitute for decorative chromium in a vast number of industries such as metal furnitures, hardware, domestic and light engineering electrical appliances and other equipments that are strongly resistant to corrosive chemicals [1].

The alloy was first deposited from an alkaline bath containing sodium stannate and potassium nickel cyanide [2]. The present commercially successful chloride-fluoride plating process was reported by Parkinson [3] and modified by the Tin Research Institute [4]. Electrodeposits of Sn-Ni alloy have also been reported from acid, alkaline and cyanide based solutions [5-6]. Although these baths are commonly used, they are proprietary in nature and are electroplated in

presence of additives. Moreover, cyanide based solutions evolve corrosive and toxic vapors during operation apart from pollution. In the present investigation, deposition parameters for the chloride electrolyte are optimized systematically using Hull Cell studies and the current efficiency and throwing power of the solution are determined. Hardness, wear resistance and corrosion resistance of the alloy have also been measured.

EXPERIMENTAL

Laboratory grade nickel chloride 300 g and stannous chloride 50 g were dissolved in 600 ml distilled water containing 55 g ammonium-bifluoride. About 2 g activated charcoal was added to the solution and digested thoroughly. After 8 hours settling, it was decanted and pre-electrolysed at 0.3 Adm^{-2} for 24 hours. The solution was then filtered and the filtrate was made upto 1 litre. The pH was adjusted with dilute hydrochloric acid or aqueous ammonia. Before plating, the copper or steel specimens were degreased with trichloroethylene, cathodically cleaned and etched.

Hull Cell experiments

To judge the quality and nature of the alloy deposits at various cell currents (0.5, 1 and 2 amps), pH (1.5, 2.5 and 3.5) and temperature (308 to 338 K), plating was carried out

on polished and cleaned copper sheets (7.5 x 10 cm) using a standard 267 ml Hull Cell for 5 minutes. From the results, the optimum current density, pH and temperature for deposition were obtained.

Effect of current density on current efficiency and alloy composition

For current efficiency determination the alloy was plated on polished copper sheets (2.5 x 2.5 cm) so as to pass 1000 coulombs at 1 to 4 Adm^{-2} current densities. From the weight of the deposits, current efficiency was calculated using the relation,

$$\text{Current efficiency (\%)} = \frac{W}{Z \times C} \times 100$$

where W is the weight of the alloy, in milligrams; Z is the electrochemical equivalent of the alloy, in mg/coulomb and C is the coulombs passed for deposition

For determination of alloy composition, the Sn-Ni alloy was plated on copper specimens (2.5 x 2.5 cm) at 1 to 4 Adm^{-2} using a combined nickel and tin anode to thickness of 50 μm . The plated panel was weighed and the deposit was stripped off anodically in 10% hydrochloric acid. The resulting solution was made up to 100 ml and the amount of nickel was determined volumetrically by titrating the made up solution against 0.01 M EDTA. The tin content of the alloy could thus be deduced from the difference between the weight of the Sn-Ni alloy and the nickel therein. Triplicate analyses were made in each case and the average values reported.

Throwing power

Haring-Blum cell was employed to determine the throwing power of the sulphate bath. Deposition was made on copper cathodes positioned at both ends of a rectangular cell at a distance of 1:5 from the perforated nickel anode. The plating was carried out for 30 minutes at 1 to 5 Adm^{-2} . From the weight of the deposits obtained at the near (W_n) and far (W_f) cathodes, the throwing-power was calculated using Fields formula

$$\text{Throwing power (\%)} = \frac{L - M}{L + M - 2} \times 100$$

where L is the primary current distribution ratio and M is the metal distribution ratio, W_n/W_f

Hardness

The hardness of Sn-Ni alloy with varying percentages of nickel content was determined by an indentation technique

with a micro hardness tester at 50 g load. A minimum of 6 indentations were made on each sample and the average value of the diagonal (d) was obtained. The Vickers hardness number (VHN) was calculated using the relation,

$$\text{VHN} \left(\frac{\text{Kg}}{\text{mm}^2} \right) = \frac{1854 \times \text{load (g)}}{d^2}$$

Wear resistance

The wear resistance of Sn-Ni alloy was found with a Taber abraser using CS-18 Calibrase wheel at 1000 g load. The test sample (10 x 10 cm) was weighed before and after abrasion of each cycle consisting of 1000 revolutions. The wear rate was expressed in terms of Taber Wear Index (TWI) which is the weight loss in milligrams per cycle of abrasion for a test performed under a specific set of conditions. An average TWI value of three consecutive cycles was reported.

Corrosion resistance

The corrosion behavior of Sn-Ni alloy deposited to a thickness of 5, 10 and 15 μm on polished mild steel sheets was studied in 1 M HCl medium using galvanostatic polarization technique. A three-electrode cell assembly was used. A platinum foil was used as counter electrode and a saturated calomel electrode as reference electrode (SCE). 1 cm^2 of the alloy was immersed in the test solution and the rest potential (OCP) was recorded after attaining a steady state. The working electrode (WE) was polarized from -200 mV to +200 mV to the OCP. The current (I) was increased from zero in steps and the potential (E) between the WE and the SCE was measured at a steady state. E vs log I was plotted and the polarization curves were obtained. Using Tafel extrapolation technique, the corrosion potential (E_{corr}) and the corrosion current (I_{corr}) were obtained for each sample. A duplicate test was made in each case and every time the test solution was changed.

RESULTS AND DISCUSSION

Hull Cell studies

The codes employed for recording the Hull Cell patterns and the effect of cell currents on the nature of Sn-Ni alloy deposits from the chloride bath are shown in Figs. 1 and 2 respectively. As is seen from Fig. 2, a dull grey, semi-bright and bright pattern was obtained at 0.5 amp cell current. With increase of cell current, the bright pattern range was widened and extended up to 8 Adm^{-2} . Above this limit, a semi-bright deposit was obtained.

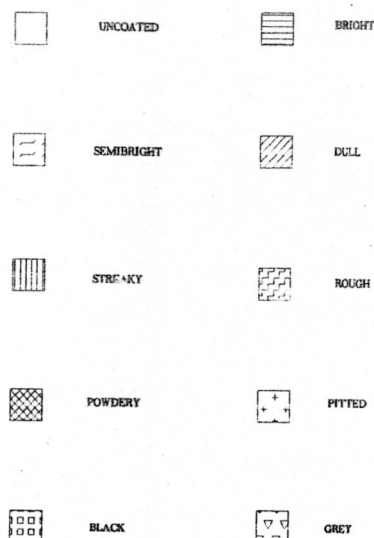


Fig. 1: Codes for recording hull cell pattern

igs. 3 and 4 show the deposit patterns obtained with 2 amp cell current at various temperatures and pH of the bath respectively. The deposits were found to be uniform and bright at pH 2.5 and at 338 K. Above and below pH 2.5, a rough, burnt or grey deposit was observed at high current densities. A powdery and semi-bright deposit was found at 0.8- 3.28 K.

From the Hull Cell studies, the optimum conditions for obtaining a smooth bright deposit from the chloride bath were found to be about 2-8 Adm^{-2} at pH 2.5 and at temperature 338 K.

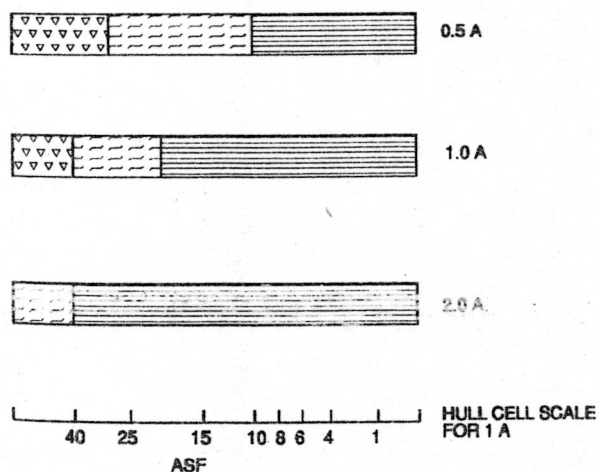


Fig. 2: Effect of cell current in tin-nickel alloy plating
Temp: 338 K pH: 2.5
Time: 5 min Bath: Chloride-fluoride

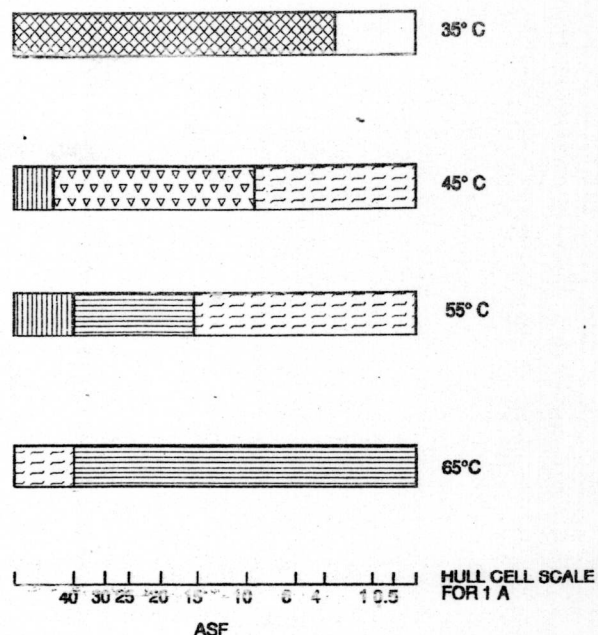


Fig. 3: Effect of temperature in tin-nickel alloy plating
Cell current: 2A pH: 2.5
Time: 5 min Bath: Chloride-fluoride

Effect of current density on current efficiency and alloy composition

The effect of current density on current efficiency and alloy composition is significant and the weight percentages of tin in the Sn-Ni alloy at various current densities are shown in Table I. The current efficiency was seen to increase with increase in current density and at 3-4 Adm^{-2} , it remained at $95 \pm 1\%$. It was also observed that with an increase in

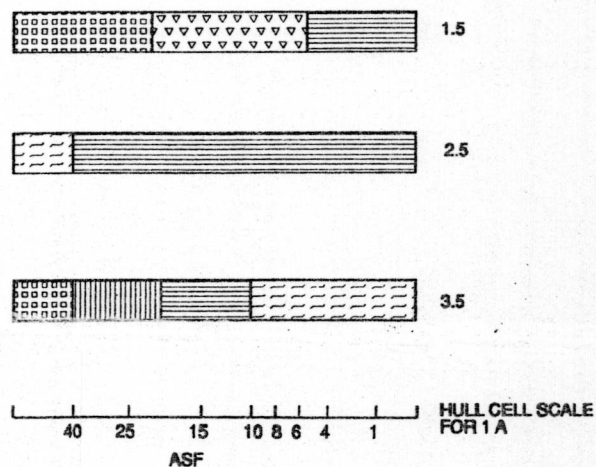


Fig. 4: Effect of pH in tin-nickel alloy plating
Temp: 338 K Cell current: 2A
Time: 5 min Bath: Chloride-fluoride

TABLE I: Effect of current density on current efficiency and alloy composition

Current density (A.dm ⁻²)	Current efficiency (%)	% of tin	% of Ni
1.0	59.6	73.6	26.4
1.5	65.5	69.8	31.2
2.0	69.9	65.2	34.8
2.5	80.3	65.2	34.8
3.0	94.8	63.6	36.4
4.0	95.0	62.7	37.3

TABLE II: Throwing power data

Current density (A.dm ⁻²)	Throwing power (%)
2	29
3	32
4	30
5	25

current density, the tin content of the alloy had decreased from 74 to 63%. A bright alloy containing $35 \pm 1\%$ nickel was obtained over a wide current density range between 2-3 Adm⁻².

Throwing power

The throwing power of the chloride bath measured at various current densities is given in Table II. The solution had about 30% throwing power and varied with current density between 25 and 30%.

TABLE III: Hardness and taber wear resistance data

Sample	Hardness, VHN ₅₀	TWI, (load 1000g)
Nickel	190	21.1
Sn-Ni (30%)	625	25.2
Sn-Ni(35%)	662	23.7
Sn-Ni(40%)	685	23.5
Chromium	920	12.8

Hardness

The hardness of Sn-Ni alloy with varying nickel content is given in Table III and a comparison made with that of nickel and chromium deposits. There appears to be a close relationship between the structure and the hardness of the deposit, the harder deposits being fine-grained, brighter and smoother. In this study, the electrodeposited Sn-Ni (30%) alloy had a hardness of about 620 VIIN and increased significantly with nickel content. The hardness is found to be in between those reported [7] for nickel and chromium deposits.

Wear resistance

In general, hardness is not necessarily a reliable criterion for the wear behaviour of an electrolytic coating. The growth habit of ad-atoms during electrocrystallisation is important for the wear behaviour. The TWI of the alloy is given in Table III and compared with that of nickel and chromium deposits. The alloy had a TWI of about 25, which found to decrease with increase in nickel content of the alloy but possess poor wear resistance compared with nickel and chromium deposits [7]. Stress and brittleness of the Sn-Ni alloy and the soft tin coatings may cause a considerable

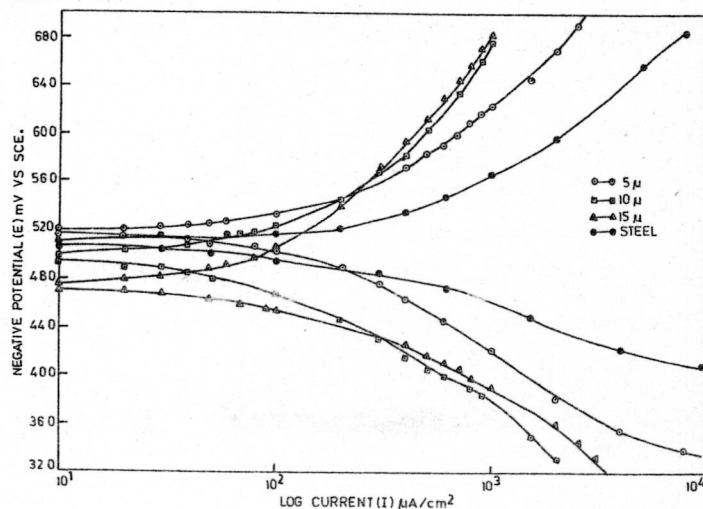


Fig. 5: Galvanostatic polarisation curves of Sn-35% Ni alloy in 1 M HCl solution

TABLE IV: Corrosion data of
Sn-Ni alloy in 1 M HCl solution

sample	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (mV vs SCE)
Mild steel	120	-515
Sn-Ni(35%) 5 μm	26	-516
Sn-Ni(35%) 10 μm	24	-496
Sn-Ni(35%) 15 μm	18	-474

reduction in the wear-resistance, because under the influence of applied load, the soft deposits are abraded easily thereby increasing the wear loss. This accounts for the excessive wear of Sn-Ni alloy as compared with nickel and chromium.

Corrosion resistance

Electroplated Sn-Ni alloy is resistant to corrosion at ordinary temperature by alkalis, neutral solutions and nitric acid and by other non-oxidising acids at pH values greater than 1.2 [8]. The typical galvanostatic polarisation behaviour of the Sn-Ni (35%) alloy in 1 M HCl solution is shown in Fig. 5. For comparison, the curve for mild steel is also shown and the corrosion data are given in Table IV. It could be seen that the I_{corr} values of the alloy decreased with increase in thickness of the alloy. Compared with steel, the alloy had shown about 6 to 7 times more resistance to corrosion in chloride environments under identical experimental conditions.

CONCLUSION

Smooth, uniform and bright Sn-Ni alloy deposit was obtained using a sulphate solution at 338 K at pH 2.5 and at 2-8 Adm^{-2} . The plating solution had about 30% throwing power and 95% current efficiency. The hardness of the alloy was found to be in between those of nickel and chromium deposits and was fine grained in nature. It had a poor wear resistance as compared with nickel and chromium deposits and possess more corrosion resistance than steel in chloride solutions. The high corrosion resistance of the alloy suggests it as a suitable alternative to decorative chromium protective coatings.

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