A Study on Electrolytic Tin-Nickel Alloy Plating from Fluoride Bath

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A study of the tin-nickel alloy plating from chloride-fluoride bath has been carried out and the effect of complexing the stannous ions with fluoride ions on polarization behaviour has been studied. Complexation of Sn(II) ions has been found to increase the extent of polarization and to shift the deposition potential of tin to a more negative value. Gradual addition of nickel chloride further shifted the cathode potential of the electrolyte indicating alloy deposition. Present observations indicated that for bright and smooth plating of alloy of equiatomic composition higher temperatures were needed. The best results were obtained at 65°C while below 45°C codeposition was not possible except at very low current densities.

1 Introduction

Since the introduction of bright tin-nickel electroplate from chloride-fluoride bath by Parkinson¹⁾, important advances have been made in the understanding and control of the deposition process. Cuthbertson and Parkinson²⁾ worked out the conditions of codeposition of tin-nickel electroplate in detail and obtained bright alloy plating from a solution containing tin (II) and nickel (II) chloride along with sodium fluoride and ammonium bifluoride. Davies³⁾ modified the bath by replacing sodium fluoride by ammonium fluoride to avoid the continuous slow precipitation of sodium hexafluoro-stannate (VI) formed by aerial oxidation. Lowenheim and Gore⁴⁾ introduced fluoride as ammonium bifluoride in the electrolyte to obtain excellent solderable deposits. Conditions of codeposition of tin and nickel were studied by Serravalle⁵⁾ from conductometric and potentiometric titrations. The process of electroplating tin-nickel alloy from fluoride bath and the properties of the deposit have been further studied by Kudryavtsev *et al.*⁶⁾⁻¹¹⁾ and Dunkic^{12), 13)}.

Deposits obtained from chloride-fluoride bath containing 65-68% tin were shown to be a single phase, intermetallic compounds, with hexa-

gonal nickel arsenide unit cell by Rooksby¹⁴⁾. The intermetallic compound was shown to decompose in expected stable phases, viz., Ni_3Sn_2 and Ni_3Sn_4 above 350°C . Further studies on the structure of the deposit carried by Smart and Robins¹⁵⁾ and Clarke¹⁶⁾ have confirmed the deposition of the alloy in equiatomic proportion to produce metastable phase of the intermetallic compound NiSn .

Electrodeposited tin-nickel alloy film is known to be highly corrosion resistant over a wide range of pH^{17), 18)}.

The present work describes a systematic investigation of the process of codeposition of tin-nickel alloy from a chloride-fluoride bath. The effect of such parameters as polarization, temperature and current density, has been undertaken to obtain a suitable bath for the codeposition of the alloy in equiatomic proportions.

2 Experimental

The electrolysis was accomplished in a rectangular cell made of 0.30 cm thick perspex sheet. The interelectrode distance was maintained at 15 cm. A copper strip (2×10 cm) was pasted on a perspex plate with the help of an acid proof, heat resistant (to the extent of 100°C and non-conducting) adhesive, so as to make it cathode. The free surface of the copper strip

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was cleaned with nitric acid, washed with distilled water before using as cathode. Only 10 cm² area of the cathode was immersed in the electrolyte. The rest of the surface of cathode above the meniscus of the electrolyte was covered with the adhesive. The copper cathode was electroplated at the desired current density until the whole of the surface of copper cathode was covered with the desired electrodeposit and a stationary cathode potential was reached. Cathode potentials at constant current densities were measured using Luggin's capillary with fine tip placed in contact with the cathode and other end immersed in a saturated KCl solution of the calomel half cell. The electrolytic cell was immersed in a thermostat to provide temperature control. Current and potential measurements were made as outlined¹⁹⁾ previously. The anodes used were of material depending on the electrolyte concerned and are mentioned with the results of the appropriate experiments. All chemicals used were Analar (B.D.H. grade).

In order to determine the composition of the deposit the electroplate was made on a smooth and bright stainless steel cathode. The deposit was peeled off and a known weight of it was dissolved in concentrated HCl. Tin was precipitated by concentrated HNO₃ as metastannic acid which was strongly heated to give tin dioxide. Tin was thus analysed. Nickel in the filtrate was analysed gravimetrically by the dimethylglyoxime method.

Table 1 Variation of cathode potential with the addition of ammonium fluoride in Tin(II) chloride

Plating current density A/dm ²	0.52	1.05	2.15	3.12	4.28	5.16	6.18
Amount of ammonium fluoride g/l	Cathode potential on saturated calomel scale, volts						
0	-0.522	-0.532	-0.540	-0.552	-0.564	-0.568	-0.576
10	-0.538	-0.554	-0.572	-0.584	-0.592	-0.602	-0.614
20	-0.596	-0.616	-0.658	-0.670	-0.706	-0.712	-0.906
30	-0.680	-0.708	-0.746	-0.772	-0.826	-0.895	-1.005
40	-0.726	-0.748	-0.806	-0.875	-0.918	-0.956	-1.010
50	-0.752	-0.770	-0.858	-0.932	-0.948	-0.992	-1.014
60	-0.759	-0.782	-0.874	-0.940	-0.960	-0.994	-1.016
70	-0.774	-0.794	-0.892	-0.942	-0.966	-0.996	-1.018
80	-0.780	-0.798	-0.901	-0.944	-0.968	-0.998	-1.020

Electrolyte : 50 g/l SnCl₂·2H₂O Anode used : Tin, Temp. : 65°C

3 Results and Discussion

Standard potentials of the processes $\text{Ni}^{2+} + 2e^- = \text{Ni}$, and $\text{Sn}^{2+} + 2e^- = \text{Sn}$ are -0.25 V and -0.136 V respectively. Although the difference in the discharge potentials of tin and nickel ions was very small, a satisfactory deposit consisting of a single phase bright plate could not be obtained from a simple mixture of tin and nickel chloride. Addition of fluoride ions to the electrolyte helped to bring the discharge potentials of the two ions closer together to enable the codeposition of the alloy.

The variation of cathode potential with addition of fluoride ions in the form of ammonium fluoride in the electrolyte containing 50 g/l of SnCl₂·2H₂O has been summarized in Table 1 and shown in Fig. 1. The gradual addition of

Fig. 1 Variation of cathode potential with the addition of NH₄F in SnCl₂·2H₂O electrolyte

ammonium fluoride to the solution of tin(II) chloride at a constant temperature of 65°C, shifted the cathode potential towards a more negative value for each value of current densities from 0.52 to 6.18 A/dm². The change in cathode potential was slow up to 16 g/l of ammonium fluoride followed by a rapid shift up to 33 g/l and finally a practically constant value of cathode potential was attained after addition of more than 50 g/l of ammonium fluoride. It can thus be inferred from the above observations that at a given current density Sn²⁺ ions are at first converted into ionic compound SnF₂, and on further addition of fluoride ions, complex ions Sn₂F₅⁻, SnF₃⁻ and SnF₄²⁻ are formed. The amount of ammonium fluoride required for complete conversion of Sn²⁺ into SnF₄²⁻ ions in a solution containing 50 g/l of SnCl₂ · 2 H₂O has been calculated to be 32.75 g. As practically all the Sn²⁺ ions are converted into complex ions their equilibrium concentration in the electrolyte is diminished so as to give a rapid shift in cathode potential towards a more electronegative value. This behaviour became more appreciable as the current density increased (c.f. the curve at c.d. 6.18 A/dm²).

Further addition of ammonium fluoride beyond 33 g/l resulted in a slow increase in potential which can be due to slow aerial oxidation of Sn(II) to Sn(IV) resulting in the formation of the complex ions SnF₆²⁻³⁾. As the formation of hexafluoro-stannate from tetrafluoro-stannite ions does not result in further decrease in free Sn²⁺, the change in cathode potential to a more ne-

gative value possibly appears to be due to much lower value of the dissociation constant of SnF₆²⁻ ions. Further addition of ammonium fluoride beyond 50 g/l resulted in giving a practically constant value of cathode potential. This indicated that the equilibrium of the reaction $\text{SnF}_4^{2-} + 2\text{F}^- = \text{SnF}_6^{2-} + 2\text{e}^-$ has been attained.

Schaap²⁰⁾ has shown the existence of SnF₃⁻ ions in acidic or neutral solution of Sn²⁺ electrolyte from polarographic studies. According to them extremely lower values of dissociation constant of the latter ion was responsible for further shift in cathode potential when all the Sn²⁺ were completely complexed.

Variation of cathode potential during codeposition of the tin and nickel from a solution

Fig. 2 Variation of cathode potential with the addition of NiCl₂ · 6 H₂O in the electrolyte containing 50 g/l of SnCl₂ · 2 H₂O

Table 2 Variation of cathode potential with the addition of nickel chloride

Plating current density A/dm ²	0.52	1.05	2.15	3.12	4.28	5.16	6.18
Amount of NiCl ₂ · 6 H ₂ O added, g/l	Cathode potential on saturated calomel scale, volts.						
0	-0.752	-0.770	-0.858	-0.922	-0.948	-0.992	-1.014
50	-0.656	-0.671	-0.773	-0.825	-0.859	-0.895	-0.933
100	-0.621	-0.634	-0.716	-0.754	-0.787	-0.820	-0.852
150	-0.606	-0.617	-0.674	-0.706	-0.730	-0.752	-0.772
200	-0.598	-0.606	-0.639	-0.666	-0.686	-0.698	-0.714
250	-0.595	-0.603	-0.625	-0.642	-0.651	-0.663	-0.672
300	-0.593	-0.601	-0.618	-0.633	-0.642	-0.652	-0.663
350	-0.590	-0.598	-0.614	-0.625	-0.637	-0.644	-0.652

Electrolyte : 50 g/l SnCl₂ · 2 H₂O + 50 g/l NH₄F, Anode : tin-nickel alloy, Temp. : 65°C

Table 3 Effect of nickel concentration on the percentage of electrodeposit

Plating current density A/dm ²	0.50	1.50	2.50	4.00
Amount of NiCl ₂ ·6 H ₂ O added, g/l	Nickel percentage in the alloy			
100	31.1	27.5	24.7	24.3
150	33.2	29.9	27.9	27.7
200	34.2	33.4	31.5	30.8
250	36.2	34.8	32.8	31.8
300	36.7	35.2	34.3	33.7
350	36.9	35.3	36.2	34.9
400	37.2	35.3	36.2	36.5

Electrolyte : 50 g/l SnCl₂·2 H₂O+50 g/l NH₄F containing 50 g/l of SnCl₂·2 H₂O and 50 g/l of NH₄F with the gradual addition of NiCl₂·6 H₂O has been recorded in Table 2 and depicted in Fig. 2. The shift towards less negative values of cathode potential was observed at constant current densities. The decrease in polarization became more pronounced at low current densities in comparison at high current densities.

The analysis of the electrodeposits obtained on a stainless steel plate from a bath containing 50 g/l SnCl₂·2 H₂O, 50 g/l NH₄F with varying amount of NiCl₂·6 H₂O at various current densities revealed that bright deposits containing tin and nickel in approximately equiatomic ratio were obtained with bath containing 200-300 g/l of NiCl₂·6 H₂O (Table 3). The nickel content, however, was found to increase with:

- (1) increasing the current density,
- (2) increasing the bath temperature,
- (3) increasing the ratio Ni²⁺/Sn²⁺ and F⁻/

Table 4 Variation of cathode potential with temperature in tin-nickel alloy plating solution

Plating current density A/dm ²	0.50	1.03	2.05	3.04	4.06	5.02
Plating solution Temperature °C	Cathode potential on saturated calomel scale, volts.					
20	-0.712	-0.722	-0.761	-0.777	-0.792	-0.803
30	-0.633	-0.684	-0.734	-0.746	-0.771	-0.788
40	-0.633	-0.647	-0.696	-0.723	-0.748	-0.769
50	-0.603	-0.614	-0.652	-0.677	-0.686	-0.704
60	-0.598	-0.608	-0.633	-0.652	-0.662	-0.678
70	-0.592	-0.598	-0.616	-0.633	-0.640	-0.646
80	-0.588	-0.592	-0.598	-0.611	-0.615	-0.620

Electrolyte : 50 g/l SnCl₂·2 H₂O+250 g/l NiCl₂·6 H₂O+50 g/l NH₄F, pH=2.5

Sn²⁺,

- (4) decreasing the bath pH by adding HF or HCl,

and

- (5) increasing the chloride concentration by adding HCl.

Deposits obtained from a bath containing NH₄F were found to be bright, brittle and porous while those with NaF were matt but elastic. When fluoride was added as NH₄HF₂, matt, porous and brittle deposits were obtained. With KF matt deposits were obtained. When fluoride of both the ions NH₄⁺ and Na⁺ were present in the electrolyte the deposits obtained were quite bright, smooth, without cracks and less porous. This indicated that Na⁺ ions play an important role in bright tin-nickel alloy plating which may be introduced either as sodium fluoride or sodium chloride.

As a result of the investigations made so far the following baths are recommended for the most satisfactory tin-nickel alloy electroplate :

A		B	
SnCl ₂ ·2 H ₂	50 g/l	SnCl ₂ ·2 H ₂ O	50 g/l
NiCl ₂ ·6 H ₂ O	250 g/l	NiCl ₂ ·6 H ₂ O	250 g/l
NH ₄ F	50 g/l	NH ₄ F	35 g/l
NaCl	40 g/l	NaF	30 g/l
c.d.	0.5-4.0 A/dm ²	c.d.	0.5-4.0 A/dm ²
Temperature	65°C	Temperature	65°C
Sufficient HCl to make pH	2.5	Sufficient HCl to make pH	2.5

These baths were found to be stable for a pretty long time and may be successfully employed for commercial tin-nickel alloy plating on copper or brass materials. Stirring of the bath

Fig. 3 Variation of cathode potential with temperature in tin-nickel alloy plating solution

was found to give the best results in so far as the brightness of the coatings were concerned, as it inhibited the deposition of some black material on the electrodeplate.

The effect of temperature on cathode potential of Ni-Sn electrolyte at constant current density has been recorded in Table 4 and shown in Fig. 3. It has been observed that the increase in temperature decreased the extent of polarization linearly up to a temperature of 40°C followed by a remarkable fall in the temperature range of 40–50°C. After 50°C the decrease in polarization was again linear but was not marked. From the analysis of the electrodeposited alloys it has been observed that codeposition was only possible at temperatures above 50°C and the best results were obtained at 65°C. At lower temperature tin alone was found to deposit except at very low current densities when the deposits were dull in appearance.

4 Summary

A study of the tin nickel alloy plating from chloridfluoride bath has been carried out and the effect of complexing the Sn^{2+} ions with fluoride ions on polarization behaviour has been studied. Complexation of Sn^{2+} ions has been found to increase the extent of polarization and

to shift the deposition potential of tin to a more negative value. Gradual addition of nickel chloride further shifted the cathode potential of the electrolyte indicating alloy deposition. Present observations indicated that for bright and smooth plating of Sn-Ni alloy of equiatomic composition higher temperatures were needed. The best results were obtained at 65°C while below 45°C codeposition was not possible except at very low current densities.

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