ELECTROCHEMICAL PREPARATION OF TIN FLUOBORATE FOR TIN PLATING

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Tin plating is finding increasing importance in electronic, canning and automobile industries. The sulphate and chloride formulations have many limitations. Fluoborate bath is more favourable because of its high solubility, ease of deposition etc. However, the preparation of tin fluoborate is still carried out by a time consuming chemical process which yields product containing impurities much higher than the recommended standards. An electrochemical method described in this paper offers a simple, easier and quicker method for the preparation of $Sn(BF_4)_2$ with negligible impurity levels, thereby quality electrodeposits can be obtained.

Keywords: Tin plating, tin fluoborate, membrane cell.

INTRODUCTION

Electrodeposition of tin is mainly preferred by the electronic, can manufacturing and automobile industries due to its exceptional solderability, lubricity and nontoxicity and corrosion resistance in many environments. The fluoborate bath is preferred very much in view of the limited solubility of other tin salts. The high solubility of tin fluoborate permits deposition at higher current densities than the normally used current density as required in high speed plating bath. The bath is highly stable, negligible sludge formation and almost 100% efficiency. The anodic dissolution is very smooth even at very high current densities. Because of high solubility of tin fluoborate, it is difficult to produce it in the solid form and is available in commerce as a concentrate. Stannous fluoborate is produced by chemical and electrochemical route. In the former, it is prepared by dissolving stannous oxide in fluoboric acid [1-5]. The preparation of pure stannous oxide is a difficult process and the fluoborate thus prepared always containing Sn(IV) and traces of copper, silica, sulphate and chloride which create problems during deposition.

Electrochemically, stannous fluoborate is produced by dissolution of tin in fluoboric acid using either mercury cathode [6] or graphite cathode using ion exchange membrane [7-11]. However, the exact operating conditions for the above preparation still remain undiscussed and the experimental conditions recommended often lead to Sn(IV) formation.

This paper described the preparation of Sn(II) fluoborate by electrochemical process. The kinetics of dissolution and the viability of the electrolyte thus prepared for the commercial tin plating are included.

EXPERIMENTAL

Hull cell studies were carried out to determine the current density at which dissolution of tin was uniform using various fluoboric acid concentrations. A 267 ml Hull cell was used with pure tin anode and stainless steel cathode and a current of 2A was passed.

Preparation of tin fluoborate

Laboratory scale experiment — Cell

The cell used for the preparation of tin fluoborate on Laboratory scale consist of a PVC rectangular container (9(l) x 8(b) x 8(h) cm) fitted with a PVC cover to hold the separator membrane at the center. The base of the anode compartment alone was perforated and a PVC cone with a stopcock was fitted to the base of the cell for draining the anolyte.

Membrane

Four different membranes are (a) PVC, (b) Micro porous rubber mat, (c) Permutit A-20 anion selective membrane and (d) Anion selective membrane of Central Salt and Marine Chemical Research Institute (CSMCRI), Bhavnagar, India, were tried. The selectively of the membrane was one as used by its permeability to cation viz., Sn^{2+} and calculated using the formula.

$$S_{Sn}^{++} = \frac{A}{B} \qquad (1)$$

where A is equivalents of cations passing through the membrane and B is the number of Faradays and the selectivity of the anion i.e. BF_4^- is $S_{BF^-} = 1 - S_{Sn^{++}}$.

Electrodes

Pure tin sheet (8(l) x 6(b) x 0.5(t) cm) with immersion depth of 7 cm and fitted to a copper busbar was used as the anode. Stainless steel sheet of the same dimensions and immersion depth that of anode and fitted to a copper busbar was used as the cathode.

The inter-electrode distance was 2 cm with the membrane positioned at the center. The whole assembly was positioned on a tripod stand to enable easy draining of the anolyte.

Electrolyte

Fluoboric acid was prepared by adding boric acid (Analar) in small increment with constant stirring to chemically pure hydrofluoric acid (40 wt%) in the stoichiometric ratio. The presence of unreacted HF was tested by the formation of a white precipitate with a sample of lead nitrate solution. The strength of fluoboric acid prepared by the above method was around 5 M.

Process optimisation

Fluoboric acid of different concentrations (1-5 M) were transferred to the cell and the anodic dissolution of tin was conducted at different current densities viz., 2, 2.5, 3, 4 and 5 A.dm^{-2} to achieve optimum concentration and current density. Each experiment was carried out by passing 6 ampere hours of electricity after which the anolyte was drained and estimated for tin content.

Bench scale experiments

The cell was rectangular type (18(l) x 15(b) x 16(h) cm) with the same anode and cathode materials as described earlier with the dimension (12.2(l) x 15(b) x 0.5(t) cm) and an immersion depth of 13.5 cm. In addition to the experiments conducted for 6 Ah longer duration experiments were also carried out to find the selectivity of the membrane and formation efficiency of tin fluoborate. The anode efficiency and energy consumption of the process were also calculated.

Analysis of the product

Trace metallic impurities in the electrochemically prepared tin fluoborate and the commercial tin fluoborate were analyzed using an Atomic Absorption Spectrophotometer (Perkin Elmer 350). The total and free fluoboric acid was estimated by acidimetric method [12] and tin content was estimated by iodimetric method [13].

Cyclic voltammetry

Cyclic voltammetry for the dissolution of tin in various concentration of fluoboric acid (5 x 10^{-2} M to 5 x 10^{-4} M) and in tin fluoborate containing 5 x 10^{-1} M fluoboric acid with various amounts of Sn^{2+} (1.7 x 10^2 M to 1.3 x 10^{-1} M) using Bioanalytical system and a glass cell lined with araldite were employed. Tin rod (99.9% pure and 0.28 cm^2 area) embedded in Teflon was used as the working electrode. Platinum and saturated calomel were used as counter and reference electrodes respectively.

The working electrode was perturbed with triangular potential sweep from -600 mV to +600 mV at a sweep rate of 1 mVs^{-1}.

Corrosion current estimation

Potentiodynamic polarization studies on the dissolution behaviour of tin were carried out under the above conditions. The anodic and cathodic polarization curves were obtained on both 50 mV cathodic and 200 mV anodic directions from the open circuit potential. The intercept of the Tafel region gives the corrosion current.

Weight loss experiments

Weight loss experiments were carried out to estimate the corrosion rate for tin in fluoboric acid. The electrodes of 10 cm^2 area were exposed for seven days in fluoboric acid of different concentration and the loss in weight was noted and converted into corrosion current.

Properties of electroplated tin
Porosity

Porosity of the electroplated tin, coated over steel was detected by the following tests (a) Ferroxyl test, (b) Hot water test, (c) Electrographic test. Tin was plated from the tin bath prepared by electrochemical method (bath A) and commercial (bath B) one of the following composition.

Tin fluoborate 80 g/l (as tin)

Free fluoboric acid   125 g/l

Gelatin 6 g/l

β naphthol   1 g/l

(a) Special test papers were prepared (15) by the impregnation in a solution containing 50 g/l NaCl and 50 g/l gelatin and drying. They were rewetted in 50 g/l NaCl solution again just before the test, then pressed against the electrodeposited panel and left for 10 min, the papers were immersed in 10 g/l solution of potassium ferricyanide. Blue marks, developed in the region where steel was exposed through discontinuities in the coating, were counted by examining the surface in a microscope at 10X magnification. The porosity of the coating was expressed as the percentage defective area.

(b) The coated specimens were immersed in hot water at 368 K for 6 hrs the pores in the deposit were examined by metallurgical microscope. Special paper prepared was sandwiched between the anode (i.e. the test specimen) and an aluminium foil cathode. A current density of 5 mA.dm^{-2} was applied for 3 min. The paper was then developed with potassium ferricyanide. The percentage defective area was calculated. Panels with coating thicknesses of 2.5, 3.5 and 5 μm were used for testing porosity.

Corrosion resistance studies

The corrosion resistance of coatings 2.5, 3.5, 5 and 10 μm in thickness were estimated by potentio-dynamic method, using a bioanalytical system. The potentials were scanned over 150 mV in both the cathodic and anodic directions from the open circuit potentials with suitable IR corrections. The intercepts of the linear portions of the two polarization curves give i_{corr} and f_{corr} values.

The corrosion resistance of deposits with thickness of 5 and 10 μm were also assessed by conducting salt spray experiments in 5% sodium chloride solution, with 8 hrs spraying followed by 16 hrs rest. The total hours of spraying as well as total hours spent in the cabinet until the onset of failure of the sample as indicated by red rust formation were recorded. The corrosion resistance of the panels was evaluated according to ASTM standards [16].

RESULTS AND DISCUSSION

Hull Cell experiments

The patterns (Fig. 1) obtained with increasing HBF_4 concentration indicates the minimum current density for smooth dissolution of tin is around 0.5 A.dm^{-2}. This type of dissolution occurred upto 3.75 A.dm^{-2} to 5 A.dm^{-2} with increase of fluoboric acid solution from 1.5 M to 5 M. Above this region, film formation with grey colour occurred.

Membrane selection

PVC separator and the microporous rubber matt separator being porous membranes selectively exchanged neither the cations nor the anions as expected. The amount of tin deposited on the cathode is proportional to the quantity of current passed. Permutit A20 membrane selectively exchanged the anions and gave 80% yield for the tin fluoborate. However, as the electrolysis proceeded the membrane was attacked by fluoboric acid as seen by the floating pieces of the attacked membrane on the electrode surface. The anion exchange membrane obtained from CSMCRI withstood all the experimental conditions and exhibited high chemical and mechanical stability, low IR drop etc., the permeability of the membrane was found to be 0.02 for Sn(II) and 0.98 for BF_4 during its maximum life time.
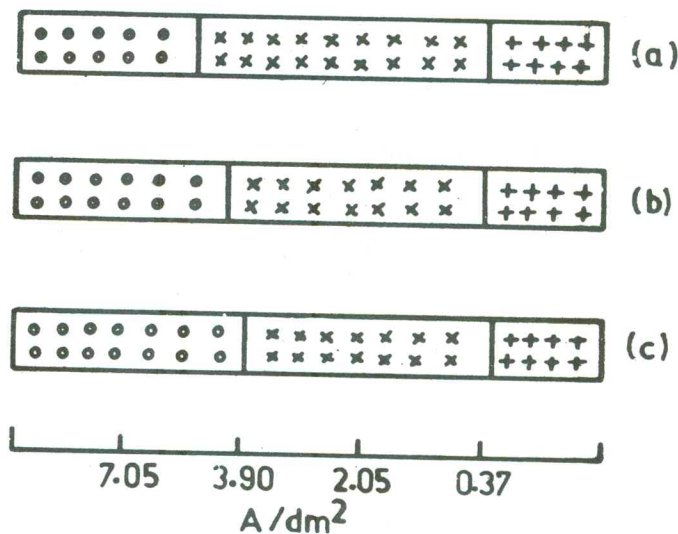

Fig. 1: Hull Cell patterns showing the dissolution of tin in fluoboric acid
(a) 5 M   (b) 3 M   (c) 1.5 M
(0000) Powdery dissolution   (xxx) Smooth uniform dissolution
(++++) Non uniform dissolution

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Effect of fluoboric acid concentration

Generally the product efficiency increased with increasing fluoboric acid concentration both in the laboratory scale and bench scale experiments as shown in Table I. Likewise a reduction in the energy consumption was observed due to increase in electrolyte conductivity.

Effect of anode current density

From Table II it can be inferred that the formation efficiency is maximum at 3 A.dm^{-2}, whereas the energy consumption remained almost constant upto 3 A.dm^{-2} and thereafter tended to increase.

Formation efficiency for longer duration

From Fig. 2, it is observed that the formation efficiency decreases gradually upto 100 Ah and thereafter attains a steady value. This can be attributed to the formation of thin porous film on the anode which has been observed and is responsible for hindering the easy dissolution of tin. This is further confirmed by potentiodynamic study [14].

Cyclic voltammetry

Both positive and negative scans did not reveal any peaks. Addition of Sn(II) ions did not modify the electrochemical spectrum (Fig. 3). In order to determine the mechanism of dissolution of tin fluoboric acid solutions, the dissolution current at various anodic potentials were calculated. The dependencies of dissolution currents on various solution parameters were also obtained.

If M is the metal (Sn) undergoing dissolution then,

TABLE I: Effect of fluoboric acid concentration in the preparation of tin fluoborate

Anode current density	:	3 A.dm^{-2}
Area of the anode (lab scale) (L)	:	6.5 cm (b) x 7 cm (h)
Area of the anode (bench scale) (B)	:	12.2 cm (b) x 13.5 (h)
Quantity of electricity passed	:	6 Ah
Temperature	:	300 ± 3 K

Concn (M)	Tin fluoborate formation efficiency (%)		Energy consumption for Sn(BF$_4$)$_2$ (KWh/Kg)	
	(L)	(B)	(L)	(B)
1	84.0	83.0	2.7	3.1
2	87.3	86.3	2.5	2.8
3	89.6	89.2	2.3	2.6
4	92.8	92.1	2.0	2.3
5	95.1	94.6	1.6	2.1

TABLE II: Effect of anode current density for the preparation of tin fluoborate

Concentration of fluoboric acid	:	5 M
Area of the anode (lab scale) (L)	:	6.5 cm (b) x 7 cm (h)
Area of the anode (bench scale) (B)	:	12.2 cm (b) x 13.5 (h)
Quantity of electricity passed	:	6 Ah
Temperature	:	300 ± 3 K

Current density (A.dm^{-2})	Tin fluoborate formation efficiency (%)		Energy consumption for Sn(BF$_4$)$_2$ (KWh/Kg)	
	(L)	(B)	(L)	(B)
2.0	81.8	81.6	1.9	2.0
2.5	88.4	88.2	1.9	2.1
3.0	95.1	94.6	1.9	2.1
4.0	87.4	87.2	2.2	2.3
5.0	82.6	82.0	2.3	2.4

$$M \longrightarrow M^+ + e \qquad (1)$$

$$M^+ + BF_4 \longrightarrow MBF_4 \qquad (2)$$

$$MBF_4 + BF_4^- \longrightarrow M(BF_4)_2 + e \qquad (3)$$

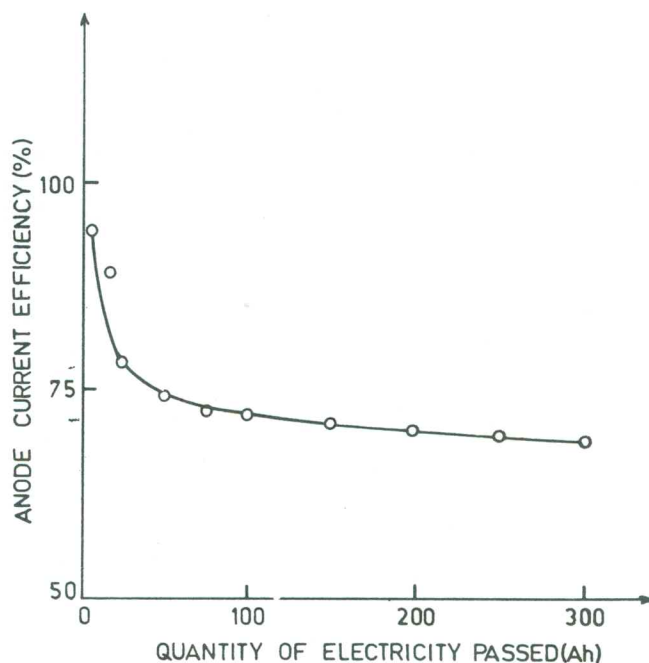If (2) is the rate determining step

Fig. 2: Tin fluoborate formation efficiency at different stages of electrolysis

$$I_a = K_a (M) (BF_4) \exp^{a F \Delta \varphi RT} \qquad (4)$$

where $\Delta\varphi$ is the interfacial potential difference. In fluoboric acid solutions the dissolution of tin is found to involve the chemical step proceeding the second electro transfer as the rate determining step.

$$\frac{d \log i_a}{d \log (BF_4)^-} = 0.4 \qquad (5)$$

A fractional dependence of 0.4 for tin dissolution in presence of BF_4^- ions suggests that the formation of soluble fluoborate species would have been hindered by the partial coverage of the surface by passivation.

Corrosion current

The corrosion current values showed a linear dependence with concentration of HBF_4 both in potentiodynamic studies and weight loss method. However, the values obtained by weight loss method are much less compared to the former (Fig. 4).

Analysis of trace metal impurities

Analysis of trace metal impurities present in the commercial as well as the electrochemically prepared tin fluoborate is shown in Table III. Zinc, nickel and iron are present in the
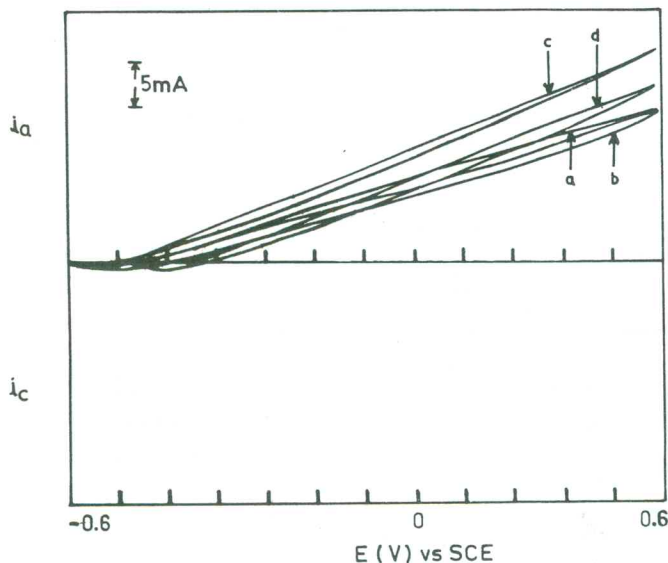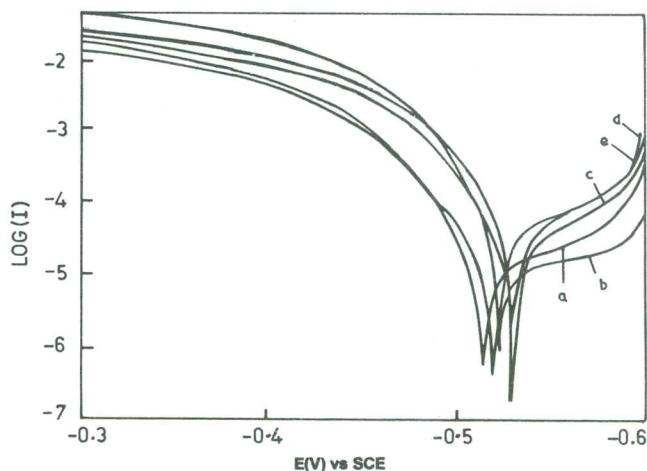

Fig. 4: Corrosion of tin in various concentrations of fluoboric acid
(a) 1.7×10^{-2} M (b) 4.2×10^{-2} M
(c) 8.5×10^{-2} M (d) 1.3×10^{-1} M (e) 2×10^{-1} M

commercial solution above the specified level, which can lead to problems during tin deposition.

Porosity

The results of all three tests listed in Table IV indicate that the porosity of the deposits decreases as the thickness is increased from 2.5 to 5 μm. The results of the hot water test are slightly on the higher side compared to the other tests, which may be a result of the higher temperature and extended duration of the test. The deposit obtained from Bath B is more porous than that from Bath A.

Corrosion tests — Potentiodynamic polarization

The results of potentiodynamic polarization are summarized in Table V. As the coating thickness is increased from 2.5 to 10 μm, the corrosion current decreases by as much as 5 μm, thereafter it remains constant in both cases. These numbers

Fig. 3: Cyclic voltammogram for tin in different concentration of Sn^{++} in fluoboric acid (0.5 M)
(a) 1.7×10^{-2} M (b) 4.2×10^{-2} M
(c) 8.5×10^{-2} M (d) 1.3×10^{-1} M

TABLE III: Metal impurities present in the tin fluoborate solution

Metals present	Standard specification level (%)	Electrochemically prepared solution(%)	Commercial soluion (%)
Lead	0.005	0.0020	0.002
Copper	0.005	—	—
Iron	0.010	0.0081	0.120
Nickel	0.001	—	0.040
Zinc	0.001	0.0010	1.200

TABLE IV: Porosity at different coating thickness

| Solution | Coating thickness μm | % Defective area | | Hot water |
		Chemical method	Electrographic method	
*				
1	2.5	10	14	16
2	3.5	8	8	10
3	5.0	2	3	5
**				
1	2.5	24	29	33
2	3.5	14	20	25
3	5.0	6	9	13

* Deposit from Bath A   ** Deposit from Bath B

TABLE V: Polarisation behaviour of tin coating

Bath	Coating thickness (μm)	E_{corr} (mV)	i_{corr} (mA)
A			
1	2.5	-575	4.59×10^{-3}
2	3.5	-545	1.59×10^{-3}
3	5.0	-539	7.33×10^{-4}
4	10.0	-538	7.24×10^{-4}
B			
1	2.5	-582	1.46×10^{-2}
2	3.5	-566	9.07×10^{-3}
3	5.0	-558	1.23×10^{-3}
4	10.0	-560	1.20×10^{-3}

support the porosity results. The corrosion current for the deposits from Bath B is always higher.

Salt spray

The results of the salt spray test conducted for 1680 hr are shown in Table VI. The appearance rating of the deposit obtained from Bath B at thickness of 5 μm is 4, while the deposit obtained

TABLE VI: Salt spray results

Sl No	Deposit thickness (μm)	Protective rating (No)	Appearance rating (No)
Bath A			
1	5	5.6	4.4
2	10	7.1	6.1
Bath B			
3	5	4.5	4.0
4	10	6.7	5.6

from bath A is 4.4. For a thickness of 10 μm, the recommended ASTM rating to pass the test is 4. The deposit obtained from Bath A meets this requirement, even at a thickness of 5 μm. A similar result is obtained with thickness of 10 μm also, indicating that the deposits obtained from Bath A are superior to those from Bath B. Eventhough the appearance rating in both cases is around 4, for a thickness of 5 μm, the protective is poor for the deposit from bath B, these results confirm the results obtained by porosity tests [17-20].

CONCLUSION

The electrochemical method of preparing tin fluoborate is much easier and the quicker process yielding purer product compared to that obtained with chemically prepared tin fluoborate and it give better performance in electroplating.

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