

CORROSION RESISTANT TIN ELECTRO DEPOSIT

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A neutral gluconate plating bath was developed which offered a silvery white, compact deposit. The deposits were evaluated for the corrosion resistance by non electrochemical and electrochemical methods. The corrosion resistance behaviour was compared with the deposits obtained by conventional plating baths. A correlation between corrosion potential, porosity and corrosion resistance was attempted. Detailed discussion is presented.

Keywords: Corrosion resistance, electrodeposit, tin plating

INTRODUCTION

Tin coatings occupy an unparalleled position in electronic industry and for bearing applications. The conventional acidic baths are addition agent dependent and involve corrosive acids. The acidic baths have low throwing power. The alkaline stannate formulations have low conductivity, high operating voltages and lower cathode current efficiencies. To meet out the present demand of electronic industry and eliminate inherent problems associated with the conventional acid and alkaline plating baths, a neutral pH gluconate bath was developed [1-5]. The corrosion resistance behaviour of the tin plated specimens is discussed in this paper.

TABLE I: Bath composition and operating conditions

| Bath | Ingredients | Conc g/l | pH | CD A/dm ² | Temp K |
|----------------------|-----------------------|-------------|----|-------------------------|-----------|
| Acid | Stannous sulphate | 10.0 | 1 | 2 | 303 |
| | Sulphuric acid | 20.0 | | | |
| | Phenol sulphonic acid | 16.2 | | | |
| | Beta-naphthol | 0.2 | | | |
| | Gelatin | 0.4 | | | |
| Alkaline | Sodium stannte | 100.0 | 10 | 2 | 343 |
| | Potassium hydroxide | 10.0 | | | |
| Neutral gloconate | Stannous sulphate | 50.0 | 7 | 2 | 343 |
| | Sodium gluconate | 120.0 | | | |
| | Sodium acetate | 10.0 | | | |
| | Peptone | 1.0 | | | |

EXPERIMENTAL

Table I presents the plating bath compositions and operating conditions. The solutions were prepared using laboratory grade chemicals. The pH of the plating bath was measured electrometrically and the temperature of the solution was controlled using a thermostat.

Mild steel panels of 2 x 4 cm area were polished, degreased, electrocleaned, acid dipped and then introduced into the plating bath. For salt spray experiments, specimens of 10 x 5 cm area were used while maintaining the effective plating area as 7.5 x 5 cm.

Soluble, cold rolled plating grade tin anodes were used in acid and alkaline tin plating baths. In neutral gluconate bath platinised titanium insoluble anode [6] was used.

Porosity of the tin plated specimens of 6 μm and 12 μm thicknesses were measured by the electrographic test using a mixture of potassium ferricyanide and sodium chloride solutions [7]. The deposits after the above test were examined at 100 x magnification and the porosity detected was expressed as percentage defective area.

Potentiodynamic polarisation studies were carried out to calculate corrosion currents for various electrodeposits. A conventional three electrode system was used with a platinum counter electrode and saturated calomel reference electrode. Plated specimens of 1 cm² area suitably masked at the unwanted portions were used as the working electrode. Analytical grade sodium chloride (5%) was used as the corrosive medium. The experiments were carried out using

Electrochemical Analyser 100A, Bio Analytical Systems, USA.

Salt spray testing was carried out in 5% sodium chloride solution at a rate of 8 hours spray and 18 hours rest. The experiment was run for 1648 hours and the results are expressed as per the ASTM standard (B 537 - 70) indicating both protection and appearance rating [8].

RESULTS AND DISCUSSION

The corrosion resistance of noble coatings is primarily decided by the porosity. The 3 μm thick electrodeposit obtained from the acid bath was found to contain numerous pores compared to that obtained from alkaline bath in spite of the presence of various addition agents. The 3 μm thick deposit, usually recommended for flow melting operations, obtained from neutral gluconate bath exhibited least porosity (Table I). Variation of corrosion potential of electrodeposits with porosity is understood as follows [9].

If the anodic reaction (steel dissolution) is activation controlled and cathodic reaction (oxygen reduction) activation controlled,

$$E_{\text{corr}} = \frac{E_{\text{corr}}^A b_a^A + E_{\text{corr}}^C b_c^C + b_a^A b_c^C \log \frac{i_{\text{corr}}^C}{i_{\text{corr}}^A}}{b_a^A + b_c^C}$$

$$\frac{b_a^A b_c^C}{b_a^A + b_c^C} \log \left(\frac{A^A}{A^C} \right)$$

and for a diffusion controlled cathodic reaction,

$$E_{\text{corr}} = \frac{E_{\text{corr}}^C}{b_c^C} + E_{\text{corr}}^a + b_a^A \log \frac{i_{\text{corr}}^C}{i_{\text{corr}}^A} + b_a^A \log \left(\frac{A^A}{A^C} \right)$$

where

E_{corr}^C = Corrosion potential for the uncoupled metal, C [Tin]

E_{corr}^A = Corrosion potential for the uncoupled metal, A [iron]

b_c^C = Cathodic Tafel slope for tin

b_a^A = Anodic Tafel slope for iron

E_c^C = Potential of Tin at an overpotential c_c

E_a^A = Potential of iron at an overpotential, a_a

i_{cC} = Current densities of tin at E_{cC}

i_{aA} = Current densities of steel at E_{aA}

i_{corr}^C = Corrosion current densities of tin at E_{corr}^C

i_{corr}^A = Corrosion current densities of steel at E_{corr}^A

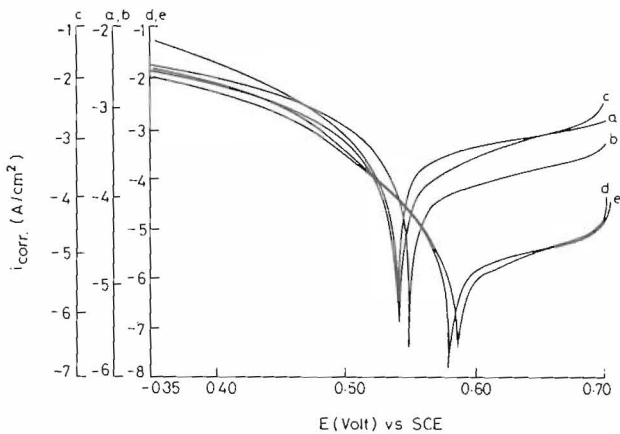


Fig. 1: Typical potentiodynamic polarisation curves for various tin electrodeposits obtained from acid bath in 5% NaCl solution at 303 K (5 mV⁻¹) (a) 0.5 μm (b) 2.5 μm (c) 5.0 μm (d) 7.5 μm (e) 10 μm

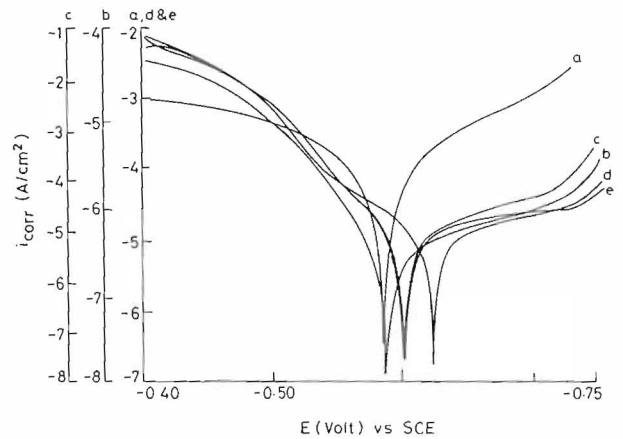


Fig. 2: Typical potentiodynamic polarisation curves for the corrosion of various electrodeposits obtained from alkaline bath in 5% NaCl solutions at 303 K (5 mVs⁻¹) (a) 0.5 μm (b) 2.5 μm (c) 5.0 μm (d) 7.5 μm (e) 10 μm

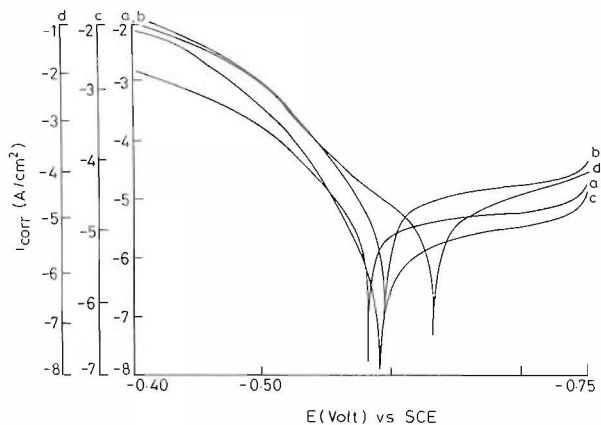


Fig. 3: Typical potentiodynamic polarisation curves for the corrosion of various tin deposits obtained from neutral gluconate bath in 5% NaCl solution at 303 K (5 mVs^{-1}) (a) $0.5 \mu\text{m}$ (b) $1.0 \mu\text{m}$ (c) $5.0 \mu\text{m}$ (d) $7.5 \mu\text{m}$

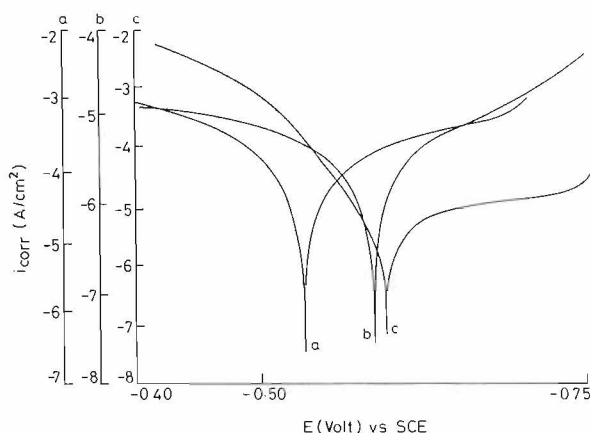


Fig. 4: Typical polarisation curves for tin deposits obtained from various bath of $1.0 \mu\text{m}$ thickness in 5% NaCl solution at 303 K (5 mVs^{-1}) (a) acid bath (b) alkaline bath and (c) neutral sodium gluconate bath

It may be seen that for an oxygen starved condition, the corrosion potential would become more active with decrease in porosity. For $3 \mu\text{m}$ thickness of all electrodeposits a decrease of porosity caused the corrosion potentials to become active. The electrodeposits from gluconate bath offered active corrosion potentials with decrease in porosity. For various thicknesses of electrodeposits obtained from acid, alkaline and neutral gluconate baths, potentiodynamic polarisation curves are shown in Figs. 1-3. The corrosion currents obtained for deposits obtained from the acid baths are higher by one order of magnitude than that of those obtained from other two baths. The deposits obtained from alkaline and gluconate baths exhibit similar behaviour (Table II).

The corrosion currents obtained for the various deposits of $1 \mu\text{m}$ thickness were compared (Fig. 4). On tin electrodeposited steel, the steel substrate exposed through the pores will act as anodic areas and the deposit itself will be the cathode, porosity would decrease with thickness. A reduction in corrosion current with thickness is due to the

TABLE II: Porosity values for various electrodeposits

| Deposit | Thickness μm | Corrosion potential* mV vs SCE | Percentage defective area |
|-------------------|-------------------------|--------------------------------|---------------------------|
| Acid bath | 3.0 | -542 | 35 |
| Alkaline bath | 3.0 | -586 | 15 |
| Neutral gluconate | 1.5 | -580 | 35 |
| | 3.0 | -590 | 10 |
| | 6.0 | -600 | 5 |
| | 12.0 | -628 | 2 |

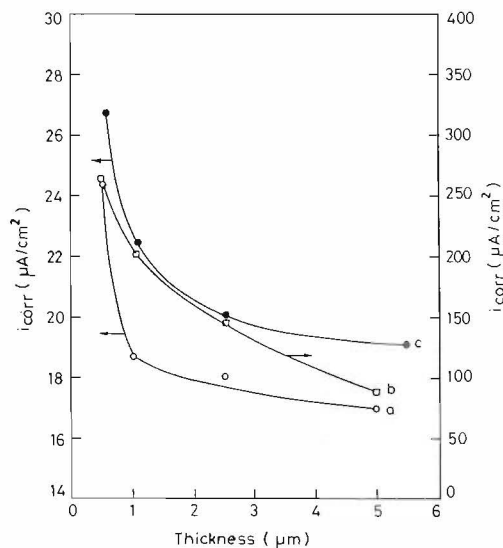


Fig. 5: Variation of corrosion current density with thickness of tin electrodeposits obtained from various baths (a) neutral gluconate bath (b) alkaline bath & (c) acid bath

TABLE III: Variation of corrosion current densities with thickness - Effect of plating baths

| Thickness μm | Corrosion current density (μA/cm ²) | | |
|-----------------|---|---------------|------------------------|
| | Acid bath | Alkaline bath | Neutral gluconate bath |
| 0.5 | 261 | 26.8 | 24.4 |
| 1.0 | 200 | 22.4 | 18.6 |
| 2.5 | 150 | 20.0 | 18.0 |
| 5.0 | 93 | 19.0 | 17.0 |

reduction in porosity. The galvanic current flowing between steel and tin would decrease with reduction in anodic areas [3].

Variation of corrosion current with thickness is shown in Fig. 5. Above 2.5 μm thickness, the electrodeposit obtained from an alkaline bath reached steady corrosion while for the electrodeposit obtained from neutral gluconate bath it was 1 μm. But even at 5 μm thickness, the electrodeposits obtained from acid baths are not pore free (Table III).

The salt spray experiments were carried out for a period of 1648 hours. A high rating value shows best corrosion resistance. The electrodeposit obtained from acid bath exhibited poor appearance and protection (Table IV). The other two electrodeposits offered nearly same protection.

CONCLUSIONS

The electrodeposits obtained from neutral gluconate bath offered identical corrosion resistance to the deposit from alkaline bath and superior to that of acid bath.

TABLE IV: Salt spray testing of tin electrodeposits

| Bath | Thickness μm | ASTM rating number | |
|-----------|-----------------|--------------------|------------|
| | | Protection | Appearance |
| Gluconate | 6 | 9.2 | 7.3 |
| | 12 | 9.8 | 8.2 |
| Alkaline | 6 | 9.4 | 7.5 |
| | 12 | 9.8 | 8.2 |
| Acid | 6 | 9.0 | 6.0 |
| | 12 | 9.8 | 6.8 |

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