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Leaching behaviour of tin with oxygen in recycled phenolsulfonic acid tin plating solutions

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Abstract

The dissolution characteristics of metallic tin with oxygen in recycled phenolsulfonic acid (PSA) tin plating bath to compensate tin consumed during the previous plating operation were investigated using electrochemical methods and leaching experiments at 30 °C. Electrochemical polarization data indicate that the diffusion of dissolved oxygen is the rate determining step and this is confirmed by leaching experiments. The sludge formed due to further oxidation of stannous ions during leaching in PSA tin plating solutions contains approximately 40 wt % Sn.

1. Introduction

Electrolytic tin plating on steel substrate has been widely used in the food and beverage industries due to its nontoxic nature [1]. Recently, it also has been applied in the semiconductor industry because of its strong resistance to corrosion and tarnishing of the component leads, solderability and ductility. Commercial tin plating processes are basically of two types: acid and alkaline [2]. The major acidic tin plating electrolytes are those based on phenolsulfonic acid, hydrofluoric acid or fluoboric acid. Alkaline plating baths are based on sodium or potassium stannate and their respective hydroxide.

In tin plating, the method using tin metal as an anode can automatically compensate tin ion by anodic dissolution. Side reactions occur, however, like hydrogen evolution at the cathode which causes asymmetry of current efficiency between the anode and the cathode. To maintain the tin layer quality, it is important to maintain a constant concentration of tin during plating.

A process using insoluble, instead of soluble, anodes has been developed by Nippon Steel Co. [3], Hoogovens [4], and LeaRonal [5]. This process has prestage operation which involves the dissolution of tin metal to make up the tin consumed in the plating solution. But it is relatively difficult to dissolve tin metal in acidic sulfate solution and it also produces sludge consisting of tin oxide or tin hydroxide due to a further oxidation of stannous ion into stannic ion. This phenomenon can induce approximately 13% loss of tin metal and also requires more electric power for plating [6].

The purpose of present study was to investigate the dissolution characteristics of tin metal in recycled tin plating solution by electrochemical methods and direct leaching experiments in the presence of oxygen.

2. Experimental details

Tin metal and Pt discs of 1 cm diameter were mounted in epoxy resin for the rotating disc experiments. Immediately prior to each experiment, the disc surface was polished with silicon carbide emery paper with a final polish using a 1200 grit. Distilled water and reagent grade chemicals were used to prepare the solution and the chemical composition of typical PSA tin plating solution is shown in Table 1. Purified nitrogen, air or oxygen was purged through the solutions to maintain the dissolved oxygen concentration constant. All experiments were carried out at 30 °C and a typical three-electrode system (tin or Pt working electrode, graphite counter electrode and standard calomel reference electrode) was employed for electrochemical measurements. Anodic (or cathodic) polarizations and cyclic voltammetry (CV) experiments were carried out at scan rates of 1 and 100 mV s^{-1}, respectively, using a potentiostat/galvanostat (EG&G 273A). All the potentials reported are referred to the saturated calomel electrode (SCE).

For leaching experiments, spherical tin granules of 4 mm diameter (Cerac Inc.) were dissolved with controlled oxygen partial pressure in the absence or presence of tin ions at 30 °C in a stirred reactor equipped with baffles. 5 cm^3 of solution was withdrawn

Table 1. Chemical composition of a typical PSA tin plating solution

Concentration/g l^{-1}		
$SnSO_4$	PSA*	ENSA†
56	75.8	6.7
Sn^{2+}	Sn^{4+}	Total Sn
28.11	1.20	29.32

* Phenolsulfonic acid.

† Ethoxylated alpha-naphthol sulfonic acid.

periodically and analysed for total Sn, Sn^{2+} and Sn^{4+} ion concentration by titration [7]. The titration was carried out immediately after sampling for accurate analysis since Sn^{2+} can oxidize to Sn^{4+} during storage. Dissolved oxygen concentration was measured with DO meter (Istech, 225D).

3. Results and discussion

3.1. *Characteristics of polarization curves*

The leaching of tin in recycled PSA solutions with oxygen is electrochemical in nature, involving the oxidation of metallic tin to Sn^{2+} and reduction of oxygen. Some of the Sn^{2+} produced can be oxidized further to Sn^{4+}, which can be expressed as follows,

$$Sn^0 = Sn^{2+} + 2\,e^- \quad E^o = -0.38\,V \tag{1}$$

$$Sn^{2+} = Sn^{4+} + 2\,e^- \quad E^o = -0.09\,V \tag{2}$$

$$O_2 + 4\,H^+ + 4\,e^- = 2\,H_2O \quad E^o = 0.99\,V \tag{3}$$

Here E^o is the standard potential of each reaction.

Figure 1 illustrates the cyclic voltammogram of Sn^{2+} at a Pt electrode surface between −1.0 and 1.25 V. The scan was initiated cathodically from the rest potential. The cathodic part of the curve shows a crossover between cathodic and anodic scans, which indicates typical nucleation and growth [8–10]. During the anodic scan, tin began to dissolve and the total charge passed during oxidation (0.0214 C) is less than that (0.0240 C) of the previous reduction process. In other words, approximately 10% of cathodic current is consumed by hydrogen evolution causing asymmetry of current efficiencies as mentioned previously. The current decreases almost to zero near 0.0 V since the tin deposited during the cathodic scan is dissolved completely, and there is no indication of the oxidation of stannous ions into stannic ions.

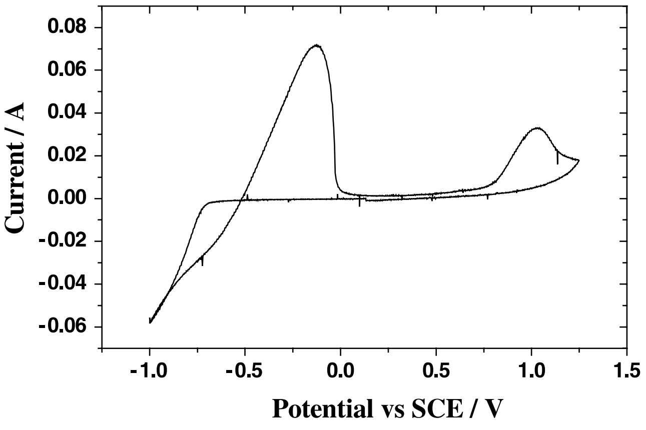

Fig. 1. Cyclic voltammogram in PSA tin plating solutions with Pt electrode with a scan rate of 0.1 V s^{-1}(total Sn 25 g l^{-1}, 30 °C).

Figure 2 shows the CV data at a Pt electrode between −0.2 and 0.7 V. Without additives, current increases steadily showing the oxidation of stannous ions. But stannous ions are relatively stable up to 0.5 V in the presence of PSA as Homp mentioned [6] since no other characteristics of oxidation of stannous ions are visible.

Potentiodynamic polarization curves for each half-cell reaction are shown in Figure 3. Cathodic reduction of oxygen in terms of various rotating speeds on Pt was carried out in the presence of additives only (no stannous ions). It shows a well developed limiting current region and hydrogen evolution occurs at approximately −0.55 V. The diffusivity of oxygen was obtained using the Levich equation [11] and was found to be 6.86×10^{-6} cm^2 s^{-1}. This value is expected to be lowered in PSA tin plating solution, similar to the manner in which the diffusivity of oxygen falls with increasing KOH concentration [12]. Also, in case of the anodic polarization curve, current density increases rapidly with potential from the equilibrium potential.

A mixed potential is formed at approximately −0.42 V, where the curve for the anodic dissolution of tin metal and that for the cathodic discharge of oxygen on Pt cross each other. The anodic polarization curve intersects the limiting current region of the cathodic polarization curve, which suggests that the leaching reaction would be controlled by diffusion of dissolved

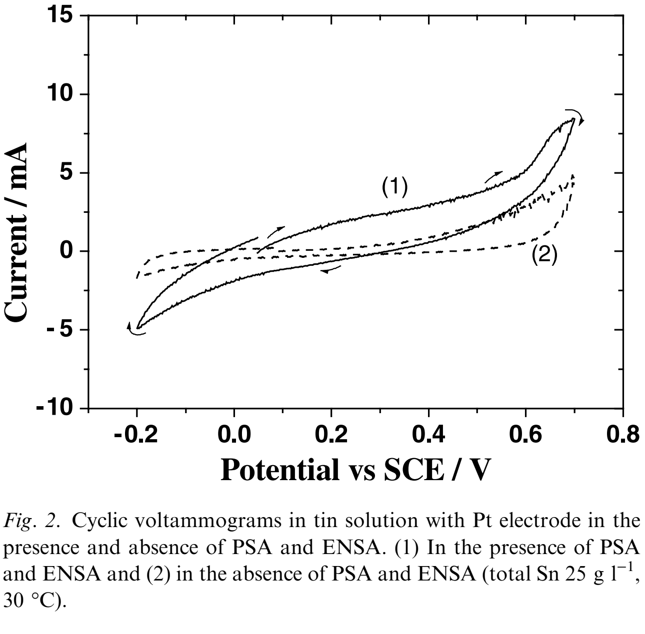

Fig. 2. Cyclic voltammograms in tin solution with Pt electrode in the presence and absence of PSA and ENSA. (1) In the presence of PSA and ENSA and (2) in the absence of PSA and ENSA (total Sn 25 g l^{-1}, 30 °C).

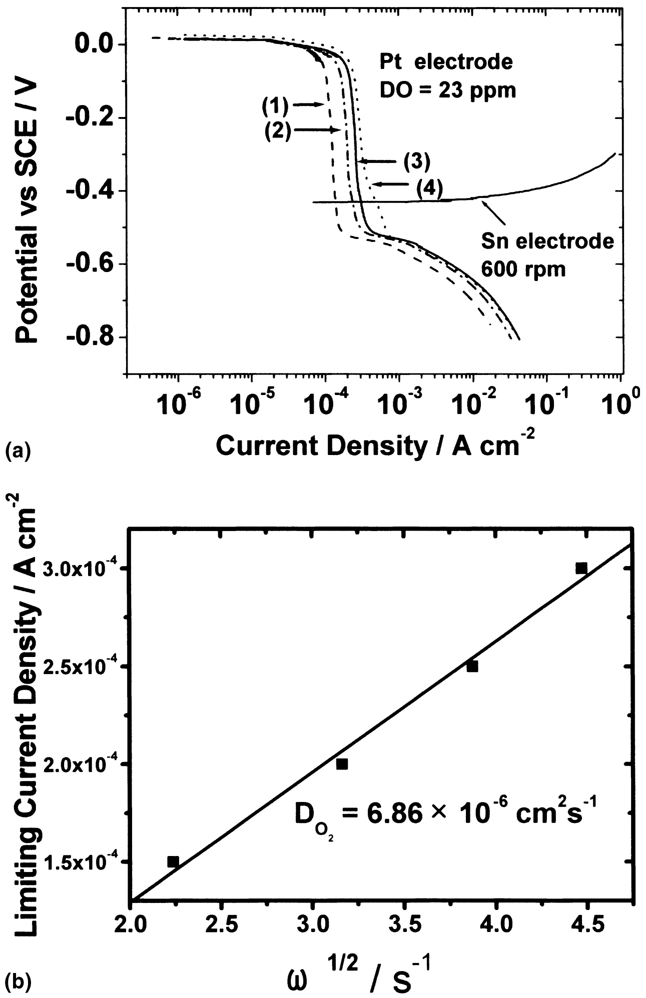

Fig. 3. (a) Polarization curves of tin and Pt electrode in PSA solution with a variation of rotation speed, ω: (1) 300, (2) 600, (3) 900 and (4) 1200 rpm (Anodic polarization case: total Sn 25 g l^{-1}, 30 °C, Cathodic polarization case: total Sn 0 g l^{-1}, 30 °C). (b) A plot of limiting current as a function of rotation speed.

oxygen in solution, which is similar to many cementation systems [13].

3.2. *Leaching reactions*

3.2.1. *Leaching kinetics of tin*

The dissolution rate of metallic tin was measured in recycled PSA tin plating solution and Figure 4 shows the variation of concentration of Sn^{2+} with time for different oxygen partial pressures. The dissolution of metallic tin increases with oxygen partial pressure. As mentioned previously, the reaction kinetics for dissolution of spherical tin granules with oxygen can be expressed as follows if the diffusion of oxygen is rate limiting [14]:

$$1-(1-\alpha)^{1/3}=\frac{[O_2]D_{O_2}v}{2r_o\delta}t \qquad (4)$$

where α is the fraction reacted, $[O_2]$ is the concentration of dissolved oxygen, D_{O_2} is the diffusion coefficient of

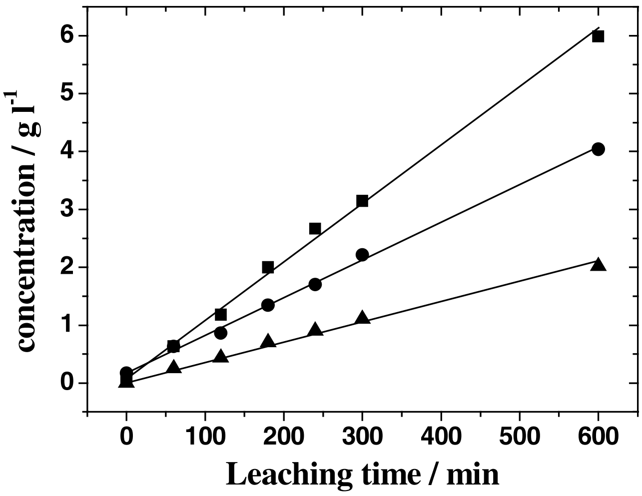

Fig. 4. Variation of Sn^{2+} concentration with time for different oxygen partial pressure. Key: (■) 1.0, (●) 0.5 and (▲) 0.2 atm. (Initial concentration of Sn^{2+} 24.3 g l^{-1}, 30 °C).

oxygen, v is molar volume of tin, r_o is radius of a tin granule at $t = 0$, and δ is the diffusion boundary layer thickness. The concentrations of dissolved oxygen were 0.72×10^{-6}, 0.43×10^{-6} and 0.23×10^{-6} mol cm^{-3} while the partial pressure of oxygen was 1, 0.5 and 0.2 atm, respectively. Figure 5 shows an excellent fit based on Equation 4 for various partial pressures of oxygen. Also the slope in Equation 4 is a linear function of oxygen concentration, and a good linearity can be obtained between the slopes obtained from Figure 5 and the oxygen concentration.

From these results, it is obvious that the rate determining step for dissolution of tin granules is the oxygen diffusion through the liquid film boundary layer. Using the values of $[O_2]$, v, r_o and D_{O_2} (0.72×10^{-6} mol cm^{-3} ($P_{O_2} = 1$ atm), 16.26 cm^3 mol^{-1}, 0.2 cm and 6.86×10^{-6} cm^2 s^{-1}, respectively), the diffusion boundary layer thickness, δ, obtained is 1.1×10^{-4} cm, which is an order of magnitude thinner than the

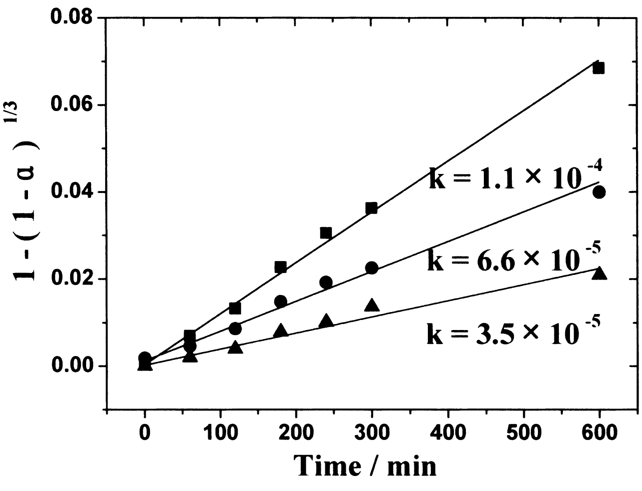

Fig. 5. A plot of $1-(1-\alpha)^{1/3}$ against time for different oxygen partial pressure. Key: (■) 1.0, (●) 0.5 and (▲) 0.2 atm.

conventional value with vigorous stirring. Also the leaching rate obtained from Figure 4 is approximately ten times larger than that obtained from the electrochemical data in Figure 3. This discrepancy can be explained qualitatively as follows. The polarization data using the rotating disc electrode was obtained under laminar flow conditions (Reynolds number is approximately 3530 at 1200 rpm). In contrast, leaching was carried out using metallic tin particles of 4 mm diameter under vigorous agitation with a turbine type impeller (1000 rpm), but the tin particles were not suspended. Since the impeller was rotated just above the rolling particles at the bottom of the reactor, it would provide the turbulent hydrodynamic condition which makes the diffusion boundary layer thickness very thin.

3.2.2. *Sludge formation in solution*

Table 1 shows the concentrations of various species which exist in typical PSA tin plating solution and shows that most of the tin ions exist as a form of Sn^{2+}. The amount of sludge produced during solution preparation is approximately 1.64 g. Some of the Sn^{4+} formed due to the oxidation of Sn^{2+}, combines with ENSA (ethoxylated alpha-naphthol sulfonic acid) to form sludge; it consists of approximately 40% tin, which agrees with reported data [6, 15]. After blowing oxygen through the filtered solution for 30 h, followed by filtering off the sludge again, the concentration of Sn^{4+} was measured and this procedure was repeated up to seven times. The concentration of Sn^{4+} in solution remains constant with an average value of 0.385 g l^{-1}, while the concentration of Sn^{2+} decreases continuously due to oxidation. The amount of sludge formed was approximately 1.914 g during each step.

4. Conclusions

The dissolution characteristics of metallic tin in recycled PSA tin plating solution to make-up the tin consumed during plating were investigated using potentiodynamic polarization methods and leaching experiments. The leaching rate of tin with oxygen in recycled PSA tin solution was found to be controlled by the diffusion of oxygen in solution. The discrepancy between the leaching rate and the corrosion current at the mixed potential was explained in terms of turbulence provided during leaching. The sludge formed in PSA tin plating solutions consisted of approximately 40 wt % tin.

Acknowledgments

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