JOURNAL OF APPLIED ELECTROCHEMISTRY **24** (1994) 404–410

Synergistic effects of benzalacetone and benzophenone on the electrocrystallization of tin from acid stannous sulphate solutions

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Received 2 June 1993; revised 28 July 1993

The synergistic effects of two kinds of aromatic ketones (benzalacetone (BA), benzophenone(BP)) and N,N-bis(polyoxyethylene)octadecylamines (POOA) on the surface morphology and the crystal orientation of electrodeposited tin from acid stannous sulphate solutions have been studied by electrochemical methods, scanning electron microscopy and X-ray diffractometry. BA itself had no effect on the reduction of tin (II) ions, but the reduction product of BA had a strong inhibitory effect on the reduction of tin (II) ions. However, the inhibitory effect of BP was stronger than that of the reduction product of BP. POOA induced a uniform deposition of tin over the whole surface, but the crystal grain size and the surface roughness of electrodeposited tin were relatively large. On the other hand, fine-grained and smooth electrodeposited tin, which had a preferred orientation with the (1 0 0) plane parallel to the surface, were obtained from acid stannous sulphate solutions containing POOA, BA and BP due to the synergistic effects of the three kinds of adsorbed species. It was found that BA has a levelling action and BP has a grain refinement action.

1. Introduction

Electrodeposited tin obtained from acid stannous sulphate solutions in the absence of organic additives was dendritic, needle-like or columnar, but compact electrodeposits could not be obtained. To obtain compact, smooth and fine-grained electrodeposits of tin, it has been found that appropriate organic additives such as various surface active agents [1–4], aromatic carbonyl compounds [1, 2, 5] and amine-aldehyde reaction products [1, 2, 6–8] are required. The authors have already reported the electrochemical characteristics of N,N-bis(polyoxyethylene)octadecylamines (POOA) [9], aromatic carbonyl compounds [10, 11] and diphenylamine–crotonaldehyde reaction product [12], and the effects of such organic additives on the electrocrystallization of tin [13–15]. As a result, it became apparent that POOA induce a uniform deposition of tin over the whole surface and that smooth and compact electrodeposits can be obtained by adding both POOA and one or two appropriate adsorbed species. The purpose of this investigation was to study the synergistic effects of the adsorbed species (benzalacetone (BA), benzophenone (BP) and POOA) on the surface morphology, as well as the crystal orientation, of electrodeposited tin from acid stannous sulphate solutions.

2. Experimental details

2.1. *Apparatus and procedure*

D.c. polarograms were recorded using a Yanagimoto Model P-1100 polarograph. Electrocapillary curves were obtained by plotting the drop time of mercury instead of the surface tension against the applied potential. The dropping mercury electrode had the following characteristics: a mercury height of 65 cm, a mercury flow rate, m, of 1.40 mg s^{-1}, and a mercury drop time, t, of 4.50 s (in 1 M potassium chloride solution, open circuit). Potentiostatic electrolyses and galvanostatic electrolyses were carried out using a Hokuto Denko Model HA-310 potentiostat–galvanostat. Current/potential curves under potentiostatic conditions were obtained by plotting the steady state current after 30 s from the beginning of electrolysis against the applied potential. The surface morphology of the electrodeposited tin was observed using a Nihon Denshi Model JSM-T20 scanning electron microscope. X-ray diffraction patterns were obtained using a Rigaku Denki Model RAD-IA X-ray diffractometer with CuK_α radiation of 0.154 nm wavelength.

Sulphuric acid solution (0.5 M) containing 10 vol % ethylalcohol was used as the base solution because of the low solubility of aromatic ketones in water. A cell having a volume of 100 cm^3 was employed. The temperature was maintained constant at 25 ± 1 °C. All potentials were referred to a saturated calomel electrode (SCE).

2.2. *Chemicals and electrode materials*

Sulphuric acid (H_2SO_4), stannous sulphate ($SnSO_4$), ethylalcohol (EtOH; C_2H_5OH) and benzophenone (BP; $C_6H_5{-}CO{-}C_6H_5$) were guaranteed reagents (Wako Pure Chemical Industries, Ltd). Benzalacetone (BA; $C_6H_5{-}CH{=}CHCOCH_3$) was of guaranteed reagent grade (Tokyo Kasei Kogyo Co., Ltd). Three kinds of N,N-bis(polyoxyethylene) octadecylamines (N,N-bis(monooxyethylene)octadecylamine (POOA–1; $C_{18}H_{37}N[CH_2CH_2OH]_2$), N,N-bis(tetraoxyethylene)octadecylamine (POOA–4; $C_{18}H_{37}N[(CH_2CH_2O)_4H]_2$) and N,N-bis(decaoxyethylene)octadecylamine (POOA–10; $C_{18}H_{37}N{-}[(CH_2CH_2O)_{10}H]_2$)) were also of guaranteed reagent grade (Kao Co.). All chemicals were used without further purification. Solutions were prepared in redistilled water.

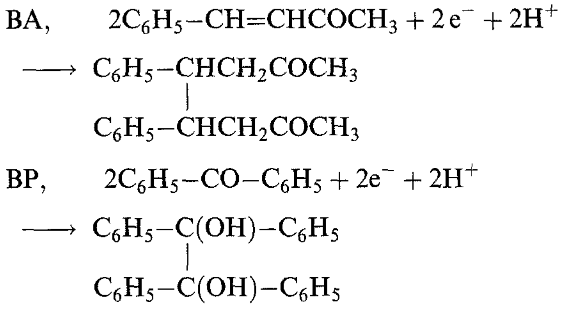
Low carbon steel plate (Nisshin Steel Co.) of 10 cm^2 surface area was used as the cathode. The precleaning procedure was as follows [16]. The low carbon steel plate was degreased in alkaline solution (Dipsol Chemical Co., Ltd, No. 44-S, 40 g dm^{-3}) at 50 ~ 60 °C for 30 min. It was then electropolished in alkaline solution (Dispol Chemical Co., Ltd, NC–10, 100 g dm^{-3}) at 10 A dm^{-2} for 1 min. Tin metal plate (Yoneyama Chemical Industries, Ltd, 99.9%) of approximately 10 cm^2 surface area was used as the anode.

3. Results and discussion

3.1. *Electrochemical characteristics of BA and BP on the dropping mercury electrode*

As described previously [9, 14], POOA is not subject to either oxidation or reduction, but POOA, to which a proton is added in sulphuric acid solution, is adsorbed on the electrode as a quaternary ammonium ion in the potential range 0 to −1.50 V. Further, POOA adsorbed on the electrode converts the polarographic reduction of tin (II) ion from a reversible process to an irreversible process [9].

Figure 1 shows d.c. polarograms and electrocapillary curves for BA and BP. As shown in the polarograms, two kinds of aromatic ketones exhibited one reduction wave with halfwave potentials ($E_{1/2}$) of −0.65 V for BA and −0.78 V for BP, respectively. It has already been reported that the reduction of BA and BP in acidic solution are one-electron processes as follows [17, 18]:



$$\text{BA,}\quad 2C_6H_5{-}CH{=}CHCOCH_3 + 2e^- + 2H^+ \longrightarrow \begin{array}{l} C_6H_5{-}CHCH_2COCH_3 \\ \quad\;\; | \\ C_6H_5{-}CHCH_2COCH_3 \end{array}$$

$$\text{BP,}\quad 2C_6H_5{-}CO{-}C_6H_5 + 2e^- + 2H^+ \longrightarrow \begin{array}{l} C_6H_5{-}C(OH){-}C_6H_5 \\ \quad\;\; | \\ C_6H_5{-}C(OH){-}C_6H_5 \end{array}$$

As for the electrocapillary curves in Fig. 1, when BA or BP was added, decreases in the drop time of mercury from the curve of the base solution were observed. These decreases in the drop time mean that aromatic ketones are adsorbed on the dropping mercury electrode. In the electrocapillary curves for two kinds of aromatic ketones, intersection points of two curves were observed at −0.65 V for BA and −0.78 V for BP, respectively. Furthermore, the potentials of the intersection points coincided with $E_{1/2}$ of the reduction waves for each aromatic ketone. These results imply that BA or BP is adsorbed as the oxidant at a potential more positive than the intersection point and is adsorbed as the reduction product at a potential more negative than the intersection point, respectively [10, 11].

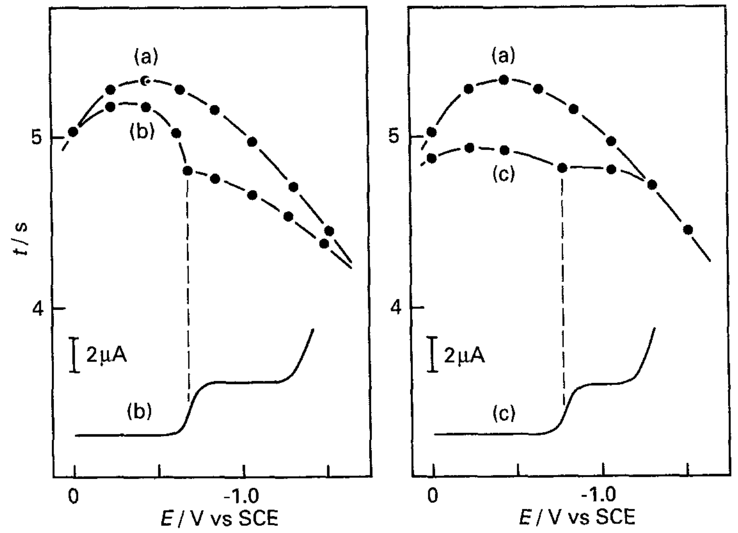


Fig. 1. D.c. polarograms and electrocapillary curves of BA and BP: (a) 0.5 M H_2SO_4 + 10% EtOH; (b) (a) + 1 mM BA; (c) (a) + 1 mM BP.

Figure 2 shows d.c. polarograms for acid stannous sulphate solutions (0.5 M H_2SO_4 + 5 mM $SnSO_4$ + 10% EtOH) in the absence or presence of aromatic ketones. As shown in Fig. 2, curve (a), the tin (II) ion exhibited one reduction wave with $E_{1/2}$ of −0.46 V in 0.5 M sulphuric acid solution. When BA was added, $E_{1/2}$ of the reduction wave for the tin (II) ion was unchanged (Fig. 2, curve (b)). However, the reduction current of the tin (II) ion decreased at potentials more negative than −0.55 V which corresponds to the ascending potential of the reduction wave for BA (Fig. 1, curve (b)), and was strongly inhibited in the potential range −0.60 to −0.80 V. The above inhibitory effect on the reduction of the tin (II) ion may be ascribed to the reduction product of BA which is produced by the reduction of BA at potentials more negative than −0.55 V [10, 11]. It became apparent that BA itself has no effect on the reduction of tin (II) ions, but the reduction product of BA has a strong inhibitory effect on the reduction of the tin (II) ion.

On the other hand, when BP was added (Fig. 2, curve (c)), the reduction current of tin (II) ions largely decreased in the potential range −0.40 to −0.70 V and $E_{1/2}$ of the reduction wave for the tin (II) ion shifted to a more negative potential by about 0.3 V. This potential range corresponds to the potential range of adsorption of BP as the oxidant (Fig. 1, curve (c)). The above inhibitory effect of BP on the reduction of tin (II) ion may, therefore, be ascribed to BP itself, which has stronger adsorbability on the electrode than the reduction product of BP.

3.2. *Current/potential curves of tin (II) ion on the solid electrode under potentiostatic conditions*

To study the synergistic effects of POOA and aromatic ketones, POOA-4 was used because it has an intermediate character in regard to electrochemical behaviour among the three kinds of POOA [14]. Figure 3 shows current/potential curves for acid stannous sulphate solutions (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH) in the absence or presence of organic additives using low carbon steel as the cathode under potentiostatic conditions. These curves were obtained by plotting the steady state current against the applied potential. In the absence of organic additives the current increased abruptly at a potential of −0.45 V due to the reduction of the tin (II) ion (Fig. 3, curve (a)). When POOA-4 was added, the limiting current (2.5 A dm^{-2}) was observed in the potential range −0.50 to −0.90 V (Fig. 3, curve (b)). As reported by Tobias *et al.* [19], when mass transfer from the bulk of solution to the cathode surface is limited by diffusion control with natural convection, the value of the limiting current is proportional to the 1.25 power of the bulk concentration of metal ion. In our experiments, it was found that the value of the limiting current is proportional to the 1.26 power of the bulk concentration of the tin (II) ion [14]. Further, when the acid stannous sulphate solution containing POOA-4 was stirred, the limiting current disappeared and the current increased abruptly at a potential of −0.45 V [14]. These facts suggest that the limiting current appearing on the current/potential curve in the presence of POOA-4 is mainly caused by the convective diffusion of tin (II) ions.

As for the current/potential curve in the presence of both POOA-4 and BA (Fig. 3, curve (c)), the reduction current of the tin (II) ion decreased at potentials more negative than −0.50 V and was strongly inhibited in the potential range −0.60 to

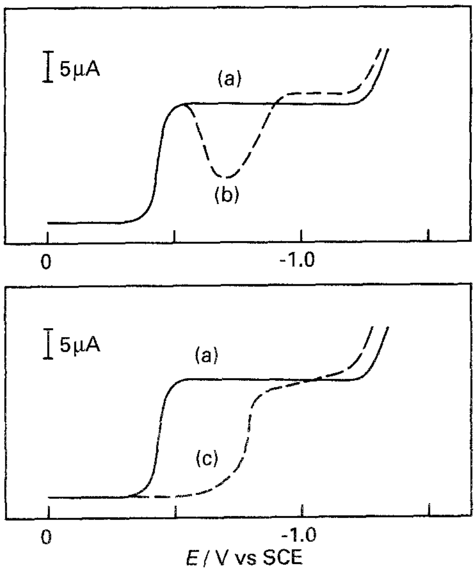


Fig. 2. Effects of BA and BP on the polarographic reduction of tin (II) ion: (a) 0.5 M H_2SO_4 + 5 mM $SnSO_4$ + 10% EtOH: (b) (a) + 1 mM BA; (c) (a) + 1 mM BP.

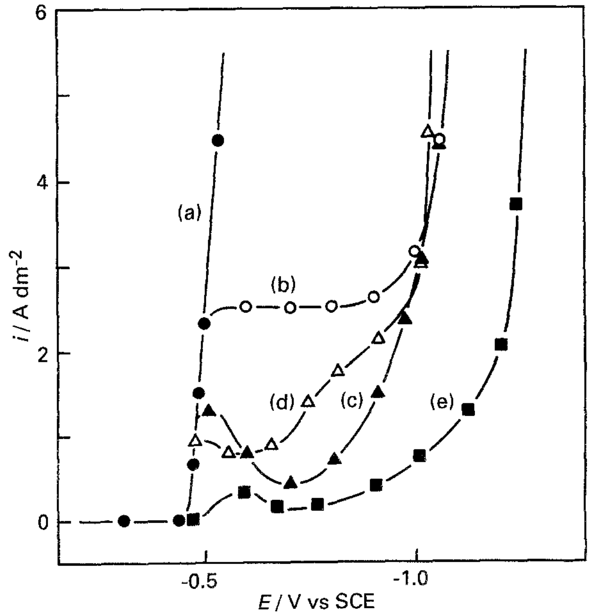


Fig. 3. Current/potential curves of tin (II) ion in the presence of organic additives under potentiostatic conditions: (a) 0.5M H_2SO_4 + 0.25M $SnSO_4$ + 10% EtOH; (b) (a) + 1 mM POOA-4; (c) (b) + 1 mM BA; (d) (b) + 1 mM BP; (e) (b) + 1 mM BA + 1 mM BP.

−0.80 V. Taking into account the results for the dropping mercury electrode (Figs 1 and 2), this decrease in the reduction current of the tin (II) ion in the presence of POOA–4 and BA may be ascribed to the inhibitory effect of the reduction product of BA. On the other hand, when POOA–4 and BP were added, the limiting current (0.9 A dm^{-2}) was observed in the potential range −0.45 to −0.70 V (Fig. 3, curve (d)). Subsequently, the reduction current of the tin (II) ion increased gradually, and then increased abruptly at a potential of −1.0 V. This decrease in the reduction current of the tin (II) ion in the range −0.45 to −0.70 V may be ascribed to the fact that the inhibitory effect of BP is stronger than that of the reduction product of BP (Figs 1 and 2). On the basis of the results for the dropping mercury electrode (Figs 1 and 2) and the solid electrode (Fig. 3), it became apparent that the inhibitory effects on the reduction of the tin (II) ion becomes stronger in the order of BA and BP in the case of oxidant, and in the order of BP and BA in the case of reduction product.

When POOA–4, BA and BP were added, the reduction current of the tin (II) ion was strongly inhibited over a wide potential range of −0.45 to −1.2 V due to the synergistic effects [19, 20] of the three kinds of adsorbed species (Fig. 3, curve (e)).

3.3. *Surface morphology of electrodeposited tin*

Scanning electron micrographs (SEMs) of electrodeposited tin, which were obtained from acid stannous sulphate solutions (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH) in the presence of 1 mM POOA–1, –4 or –10 under galvanostatic condition (3.0 A dm^{-2}), are shown in Fig. 4. As described in previous papers [13, 14], columnar or block-like electrodeposits of tin were obtained in the absence of organic additives, and the surface of the low carbon steel used as the substrate were also observed. However, as can be seen from Fig. 4, block-like crystals (7–10 μm) were observed on the whole surface and the low carbon steel was not observed by adding POOA alone. Further, the crystal grain size and the surface roughness of the electrodeposited tin became smaller in the order POOA–1, –4 and –10. It can be considered from the above results that the three kinds of POOA induce a uniform deposition of tin over the whole surface.

Figure 5 shows SEMs of electrodeposited tin obtained in the presence of both POOA–4 and BA under galvanostatic conditions (1.0, 3.0 and 5.0 A dm^{-2}). When electrolysis was carried out at 1.0 A dm^{-2}, the potential was kept constant at −0.49 V at which BA is adsorbed as the oxidant (Fig. 1). In this case, block-like and needle-like crystals were observed on the surface, but a smooth electrodeposit of tin could not be obtained (Fig. 5(a)). When electrolyses were carried out at 3.0 or 5.0 A dm^{-2}, the deposition potentials of tin were shifted from −0.49 V which is the deposition potential at 1.0 A dm^{-2} to more negative potentials (−1.06 V at 3.0 or 5.0 A dm^{-2}) at which BA is adsorbed as the reduction product (Fig. 1). In these cases reticular crystals (network structure) were observed on the surface and the surface roughness of electrodeposited tin was relatively small (Fig. 5(b) and (c)). It seems that the reduction product of BA which has a strong inhibitory effect on the reduction of the tin (II) ion (Fig. 2, curve (b) and Fig. 3, curve (c)) inhibits the outward growth of tin but allows the lateral growth. As a result, the surface roughness becomes small and relatively smooth electrodeposits are obtained. It can be concluded

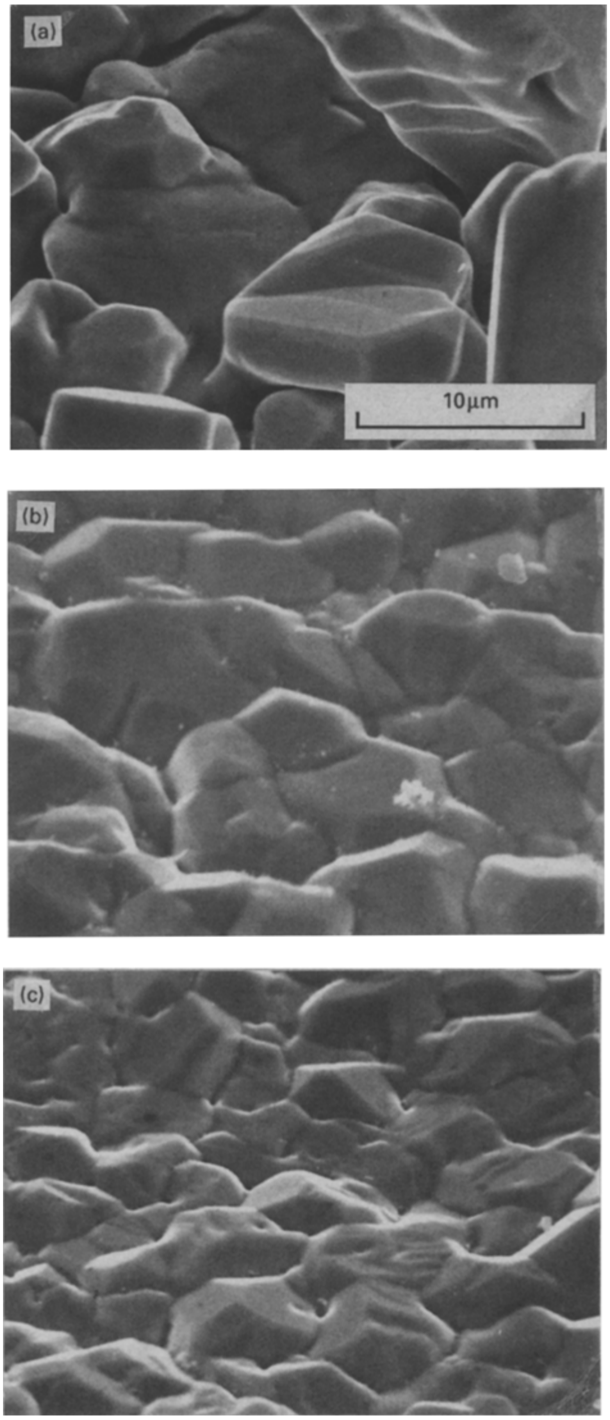


Fig. 4. Scanning electron micrographs of electrodeposited tin in the presence of POOA (3.0 A dm^{-2}, 5 min): (A), 0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH; (a) (A) + 1 mM POOA–1; (b) (A) + 1 mM POOA–4; (c) (A) + 1 mM POOA–10.

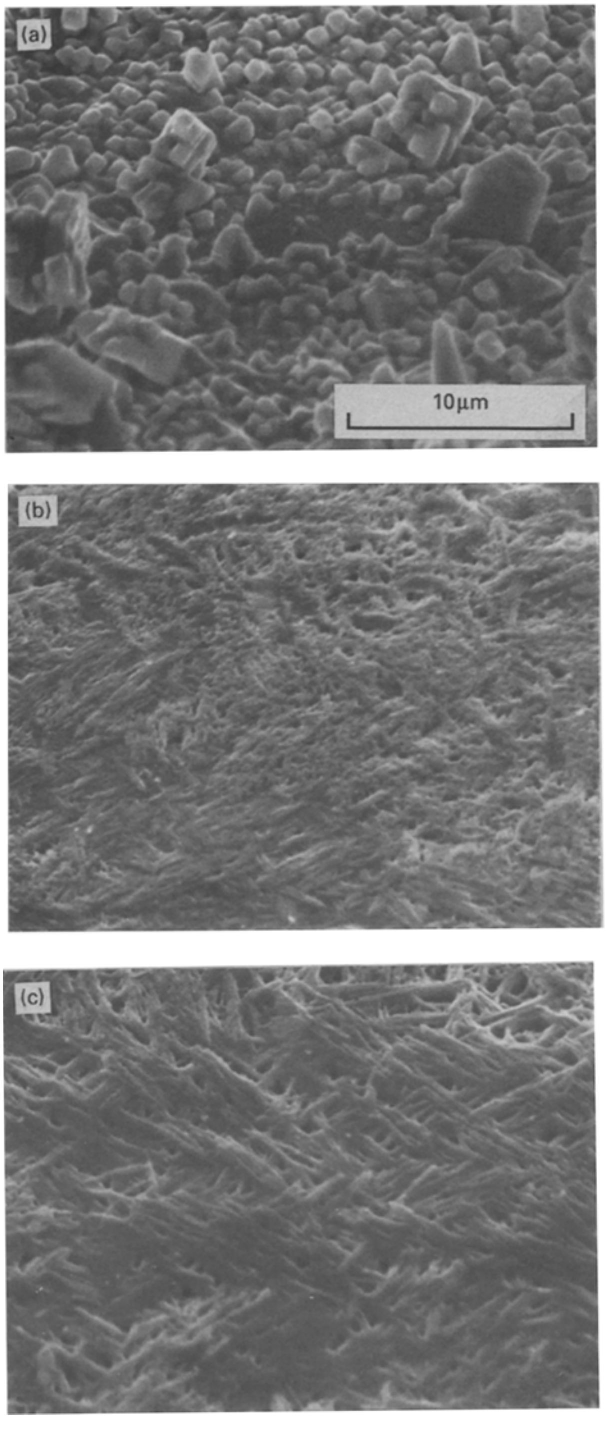


Fig. 5. Scanning electron micrographs of electrodeposited tin in the presence of POOA–4 and BA (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 1 mM POOA–4 + 1 mM BA + 10% EtOH, 5 min): (a) 1.0 A dm^{-2}; (b) 3.0 A dm^{-2}; (c) 5.0 A dm^{-2}.

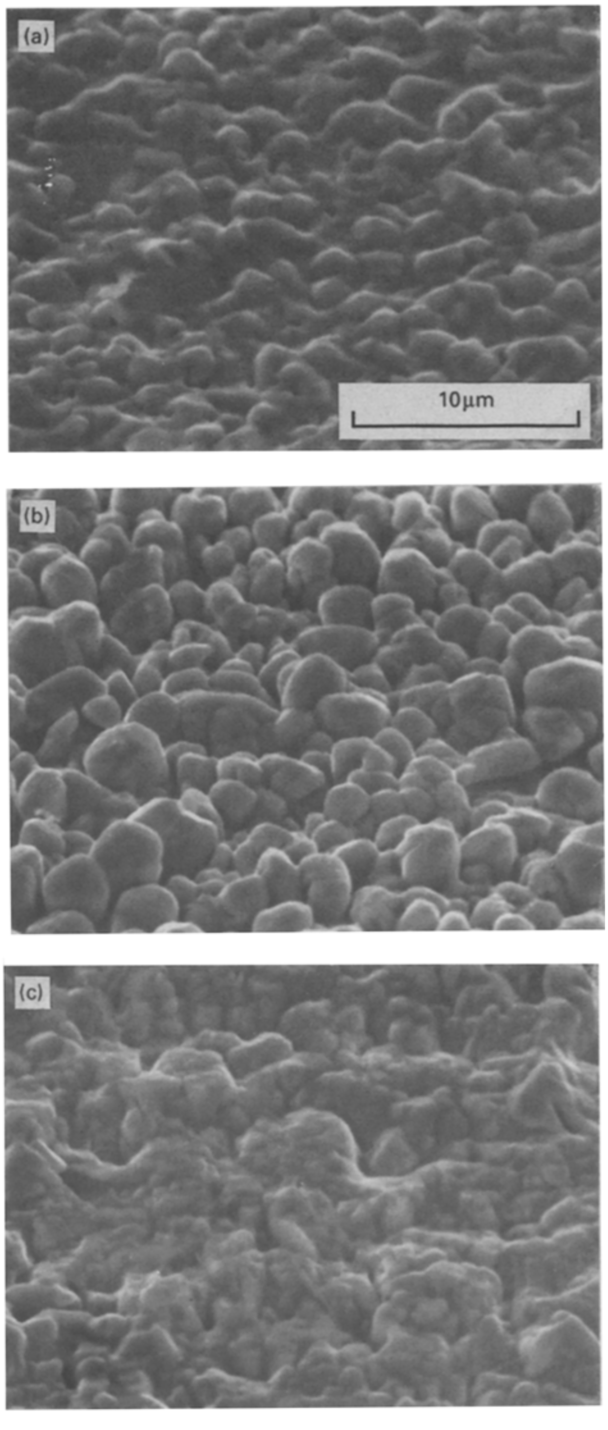


Fig. 6. Scanning electron micrographs of electrodeposited tin in the presence of POOA–4 and BP (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 1 mM POOA–4 + 1 mM BP + 10% EtOH, 5 min): (a) 1.0 A dm^{-2}; (b) 3.0 A dm^{-2}; (c) 5.0 A dm^{-2}.

that BA (the reduction product of which has a strong inhibitory effect on the reduction of the tin (II) ion) has a levelling action.

Figure 6 shows SEMs of electrodeposited tin obtained in the presence of both POOA–4 and BP under galvanostatic conditions (1.0, 3.0 and 5.0 A dm^{-2}). When electrolysis was carried out at 1.0 A dm^{-2}, relatively small block-like crystals (2–3 μm) were observed on the whole surface (Fig. 6(a)). The crystal grain size was smaller in contrast to those obtained by adding POOA–4 alone (Fig. 4(b)). In this case, the deposition potential of tin was kept at −0.69 V at which BP is adsorbed as the oxidant and has a strong inhibitory effect on the reduction of the tin (II) ion (Fig. 1, curve (c) and Fig. 2, curve (c)). When electrolysis was carried out at 3.0 A dm^{-2}, the crystal grain size became slightly larger (Fig. 6(b)). Further, as can be seen from Fig. 6(c), at 5.0 A dm^{-2}, the surface roughness was analogous to that obtained in the presence of POOA–4 alone (Fig. 4(b)). In these cases, the deposition potentials of tin were shifted from −0.69 V to more negative values (−0.96 V at 3.0 A dm^{-2} and −1.02 V at 5.0 A dm^{-2}) at which BP is adsorbed as the reduction product (Fig. 1). Consequently, BP itself has the action of grain refinement but the reduction product of BP has a relatively weak effect on the electrocrystallization of tin.

Figure 7 shows SEMs of electrodeposited tin obtained in the presence of POOA–4, BA and BP under galvanostatic conditions (1.0, 3.0 and $5.0\,\mathrm{A\,dm^{-2}}$). When electrolysis was carried out at $1.0\,\mathrm{A\,dm^{-2}}$, at which the deposition potential of tin was more positive than the reduction potential of BA, small block-like or needle-like crystals were observed, but a smooth and compact electrodeposit of tin could not be obtained (Fig. 7(a)). However, when electrolyses were carried out at 3.0 or $5.0\,\mathrm{A\,dm^{-2}}$, at which the deposition potentials of tin were more negative than the reduction potential of BA, fine-grained and smooth electrodeposits of tin were obtained due to the synergistic effects [19, 20] of the three kinds of adsorbed species (Fig. 7(b) and (c)).

3.4. *Crystal orientation of electrodeposited tin*

X-ray diffraction patterns of electrodeposited tin from acid stannous sulphate solutions ($0.5\,\mathrm{M}$ $H_2SO_4 + 0.25\,\mathrm{M}$ $SnSO_4$ + 10% EtOH) containing organic additives under galvanostatic conditions ($3.0\,\mathrm{A\,dm^{-2}}$) are shown in Fig. 8. Electrodeposited tin obtained in the presence of POOA–4 alone exhibited (1 0 1) and (1 1 2) diffraction peaks with weak intensities (Fig. 8(a)). Consequently, when POOA–4 was added alone, tin with a preferred orientation could not be obtained. Figure 8(b) and (c) shows X-ray diffraction patterns of electrodeposited tin obtained in the presence of both POOA–4 and BA or POOA–4 and BP. When POOA–4 and BA were added, a (2 0 0) peak with strong intensity was observed (Fig. 8(b)). This result suggests a preferred orientation with the (1 0 0) plane

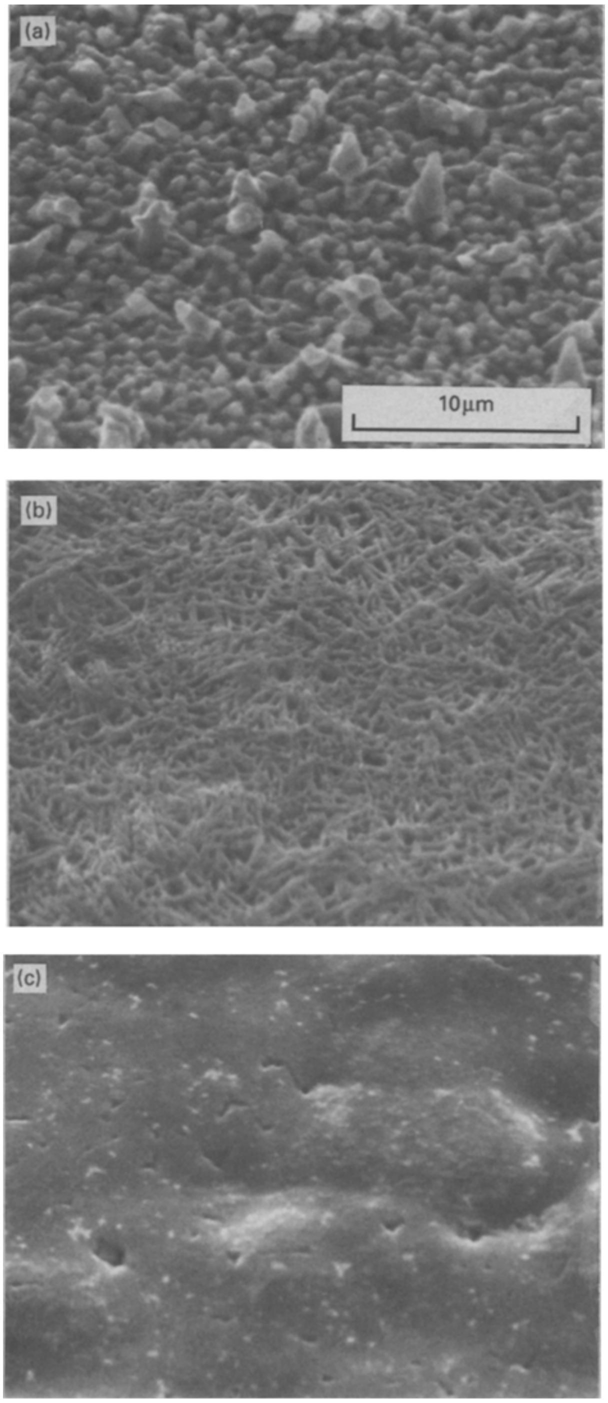


Fig. 7. Scanning electron micrographs of electrodeposited tin in the presence of POOA–4, BA and BP ($0.5\,\mathrm{M}$ $H_2SO_4 + 0.25\,\mathrm{M}$ $SnSO_4 + 1\,\mathrm{mM}$ POOA–4 + 0.5 mM BA + 0.5 mM BP + 10% EtOH, 5 min): (a) $1.0\,\mathrm{A\,dm^{-2}}$; (b) $3.0\,\mathrm{A\,dm^{-2}}$; (c) $5.0\,\mathrm{A\,dm^{-2}}$.

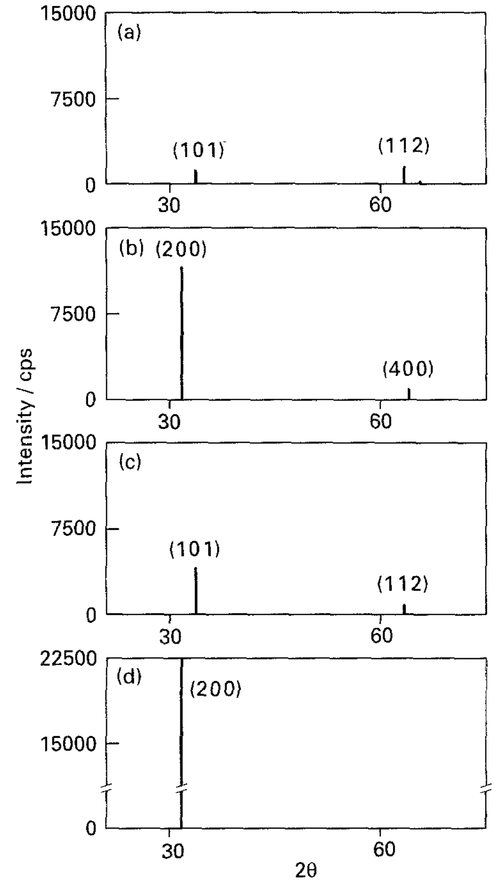


Fig. 8. X-ray diffraction patterns of electrodeposited tin in the presence of POOA–4, BA and BP ($3.0\,\mathrm{A\,dm^{-2}}$, 5 min): (a) $0.5\,\mathrm{M}$ $H_2SO_4 + 0.25\,\mathrm{M}$ $SnSO_4 + 1\,\mathrm{mM}$ POOA–4 + 10% EtOH; (b) (a) + 1 mM BA; (c) (a) + 1 mM BP; (d) (a) + 0.5 mM BA + 0.5 mM BP.

parallel to the surface. When POOA–4 and BP were added, the X-ray diffraction pattern was analogous to those obtained in the presence of POOA–4 alone (Fig. 8(a) and (c)). Figure 8(d) shows an X-ray diffraction pattern obtained in the presence of POOA–4, BA and BP. In this case, an intense (2 0 0) peak was observed and the diffraction pattern was similar to those of electrodeposits obtained by adding POOA–4 and BA (Fig. 8(b)). That is to say, the effect of BA may preferentially appear on the crystal orientation of electrodeposited tin. Consequently, when POOA–4, BA and BP were added, electrodeposited tin exhibiting a preferred orientation with the (1 0 0) plane parallel to the surface was obtained.

4. Conclusions

In the present work, the effects of two kinds of aromatic ketones (BA and BP) and POOA on the electrocrystallization of tin from acid stannous sulphate solutions were studied. The conclusions can be summarized as follows.

(a) The inhibitory effects on the reduction of the tin (II) ion becomes stronger in the order of BA and BP in the case of oxidant, and in the order of BP and BA in the case of reduction product.

(b) Three kinds of POOA induce a uniform deposition of tin over the whole surface.

(c) When both POOA–4 and BA or POOA–4 and BP are added, BA (reduction product of which has a strong inhibitory effect on the reduction of tin (II) ion) has a levelling action, and BP (oxidant, that is, BP itself has a strong inhibitory effect on the reduction of tin (II) ion) acts as a grain refiner.

(d) In the presence of POOA–4, BA and BP, fine-grained and smooth electrodeposits of tin, which exhibit a preferred orientation with the (1 0 0) plane parallel to the surface, can be obtained due to the synergistic effects of the three kinds of adsorbed species.

Acknowledgement

The authors gratefully acknowledge the Kao Co. for supplying the N,N-bis(polyoxyethylene)-octadecylamines.

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