Synergistic effects of adsorbed species on the surface morphology and crystal orientation of electrodeposited tin

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The synergistic effects of adsorbed species (polyoxyethylenealkylamine (POAA), diphenylamine–crotonaldehyde reaction product (RP) and benzalacetone (BA)) on the surface morphology and crystal orientation of electrodeposited tin from acid stannous sulfate solutions have been studied by means of various electrochemical methods, scanning electron microscopic observation and measurements of X-ray diffraction patterns. Needle-like or columnar electrodeposits of tin were obtained from acid stannous sulfate solution in the absence of adsorbed species. On the other hand, fine-grained, smooth and compact electrodeposits of tin, which had a preferred orientation with the (200) plane parallel to the surface, were obtained from acid stannous sulfate solutions containing POAA, RP and BA due to the synergistic effect of the three kinds of adsorbed species. It was found that POAA acts to produce a uniform tin deposition over the whole surface, RP acts as a grain refiner and BA has a leveling action.

1. Introduction

Dendritic, needle-like or columnar electrodeposits of tin were obtained from acid stannous sulfate solutions in the absence of organic species while compact electrodeposits of tin were not obtained. Appropriate organic species such as surface active agents [1-4], amine–aldehyde reaction products [1, 2, 5-8] and aromatic carbonyl compounds [1, 2, 9, 10] have been found to be required in order to obtain fine-grained, smooth and compact electrodeposits. But, the systematic research of electrochemical characteristics of organic species has not been studied electrochemically.

The authors have already reported the adsorption behaviors of polyoxyethylenealkylamine (POAA), diphenylamine–crotonaldehyde reaction product (RP) and benzalacetone (BA), and the inhibitory effects of POAA, RP and BA on the electrochemical reduction of tin(II) ion [11-13]. The purpose of the present investigation has been the fundamental study of the synergistic effect of the adsorbed species on the surface morphology and crystal orientation of electrodeposited tin from acidic solutions containing stannous sulfate and organic species.

2. Experimental details

2.1. Apparatus and procedure

D.c. polarograms were recorded using a Yanagimoto Model P8-A polarograph. Electrocapillary curves were obtained by plotting the mercury drop time instead of the surface tension against the applied potential. The dropping mercury electrode had a mercury head of 60 cm, a flow rate of mercury, $m = 1.71 \, \text{mg s}^{-1}$ and a drop time of mercury, $t = 4.3 \, \text{s}$ (in 1 M potassium chloride, open circuit). Potentiostatic electrolyses and galvanostatic electrolyses were carried out using a Hokuto Denko Model HA-310 potentiostat–galvanostat. The surface morphology of electrodeposited tin was observed using a Nihon Denshi Model JSM-T20 scanning electron microscope. X-ray diffraction patterns of electrodeposited tin were obtained using a Rigaku Denki Model RAD-IA X-ray diffractometer with CuKα radiation of 1.54 Å wavelength.

0.5 M sulfuric acid solution containing 10 vol % ethylalcohol was used as the base solution because of the low solubility of diphenylamine–crotonaldehyde reaction product and benzalacetone in water. The temperature was maintained constant at $25 \pm 1°\text{C}$. All potentials were referred to a saturated calomel electrode (SCE).

2.2. Chemicals and electrode materials

Sulfuric acid (H_2SO_4), ethylalcohol (EtOH; C_2H_5OH), diphenylamine (DPA; C_6H_5–NH–C_6H_5), crotonaldehyde (CA; $CH_3CH=CHCHO$) and benzalacetone (BA; C_6H_5–CH$=$CHCOCH$_3$) were of guaranteed reagents (Wako Pure Chemical Industries Ltd), and stannous sulfate (SnSO$_4$) was of a practical grade reagent (Wako Pure Chemical Industries Ltd). Polyoxyethylenealkylamine (POAA; $C_{18}H_{37}N$ [(CH$_2$CH$_2$O)$_4$H]$_2$) was of a guaranteed reagent
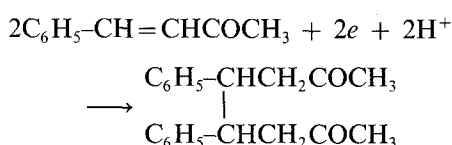
(Kao-Atlas Co. Ltd). Sodium tetraphenylborate (TPB; Na[B(C$_6$H$_5$)$_4$]) was of a guaranteed reagent (Nakarai Chemicals Ltd). All chemicals were used without further purification. Solutions were prepared in redistilled water. The DPA–CA reaction product (RP) was prepared by mixing 40 mmol DPA and 20 mmol CA in 1 l because it has already been found that DPA reacts with CA in a 2 : 1 mole ratio [12].

Low carbon steel plate (Nisshin Steel Co. Ltd) of 10 cm^2 surface area was used as the cathode, which was precleaned by a procedure described in a previous paper [14]. Tin metal plate (Yoneyama Chemical Industries Ltd, 99.9%) of approximate 10 cm^2 surface area was used as the anode.

3. Results and discussion

3.1. Electrochemical characteristics of POAA, RP and BA

D.c. polarograms and electrocapillary curves for POAA, RP and BA are shown in Fig. 1. As shown in the polarograms, POAA and RP were not subject to oxidation or reduction in the range of potentials from 0.00 to − 1.30 V, which is the reduction potential of the hydrogen ion (Fig. 1, curves 2 and 3). On the other hand, BA exhibited one reduction wave with a half-wave potential ($E_{1/2}$) of − 0.65 V (Fig. 1, curve 4). Zuman et al. had already reported that the reduction of BA to 4,5-diphenyl-2, 7-octanedione in acidic solution is a one-electron process as follows [15]:

$$2C_6H_5\text{-}CH=CHCOCH_3 + 2e + 2H^+$$

$$\longrightarrow \begin{array}{c} C_6H_5\text{-}CHCH_2COCH_3 \\ | \\ C_6H_5\text{-}CHCH_2COCH_3 \end{array}$$

As for the electrocapillary curves, a decrease in the mercury drop time in the range of potentials from 0.00 to − 1.40 V was observed in the presence of POAA, RP and BA (Fig. 1, curves 2–4). The decrease in the drop time means that POAA, RP and BA are adsorbed on the electrode in the range of potentials from 0.00 to − 1.40 V. In the electrocapillary curve for POAA (Fig. 1, curve 2), the mercury drop time

decreased more markedly at the negative potential than the potential of zero charge (p.z.c.) and the p.z.c. shifted to more positive potential. Further, when sodium tetraphenylborate solution, which is the precipitant of quaternary ammonium ions, was added to sulfuric acid solution containing POAA, a white precipitate was formed. These facts suggest that POAA, to which a proton is added in sulfuric acid solution, is adsorbed on the electrode as a quaternary ammonium ion [11].

On the other hand, in the electrocapillary curve for RP (Fig. 1, curve 3), a decrease in the mercury drop time was observed on both sides of the p.z.c. From the shape of the electrocapillary curve for RP, it is concluded that RP is adsorbed on the electrode as a neutral species. In the electrocapillary curve for BA (Fig. 1, curve 4), an intersection point of two curves was observed at − 0.65 V and the potential of the intersection point coincided with $E_{1/2}$ of the reduction wave for BA. This intersection point implies that BA is adsorbed as the oxidant at a potential more positive than − 0.65 V and is adsorbed as the reductant at a potential more negative than − 0.65 V, respectively [13, 16].

Figure 2 shows d.c. polarograms for acid stannous sulfate solutions (0.5 M H$_2$SO$_4$ + 5 mM SnSO$_4$ + 10% EtOH) containing POAA, RP and BA. As shown in Fig. 2, curve 1, the tin (II) ion exhibited one reduction wave with $E_{1/2}$ of − 0.46 V in the absence of adsorbed species. When POAA was added, the onset of the reduction wave for the tin ion was unchanged but the slope of the ascending portion of the current decreased (Fig. 2, curve 2). $E_{1/2}$ of the reduction wave for the tin ion shifted to a more negative potential by 0.1 V. Furthermore, the transfer coefficient (α) of the tin ion varied from 0.70 to 0.19 due to the presence of POAA [11]. From the above results, POAA adsorbed on the electrode as a quaternary ammonium ion shifts the reduction of the tin ion from a reversible process to an irreversible one.

In the d.c. polarogram of the tin ion in the presence of RP (Fig. 2, curve 3), the reduction current of the tin ion decreased considerably in the range of potentials from − 0.45 to − 0.70 V, indicating that
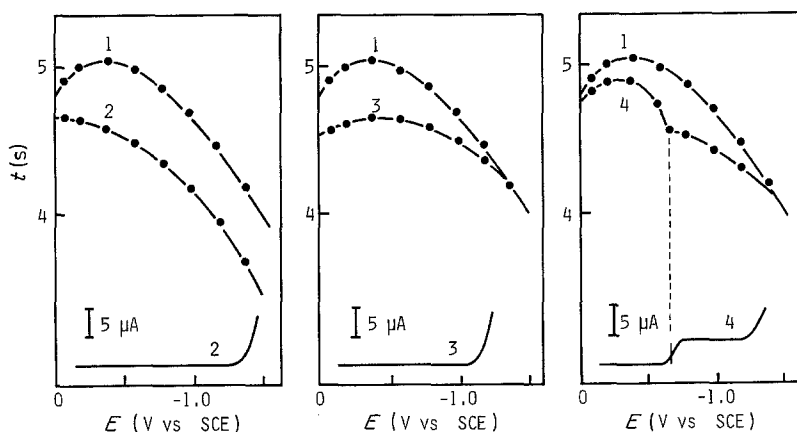

Fig. 1. D.c. polarograms and electrocapillary curves of POAA, RP and BA: (1) 0.5 M H$_2$SO$_4$ + 10% EtOH; (2) (1) + 1 mM POAA; (3) (1) + 1 mM RP; (4) (1) + 1 mM BA.
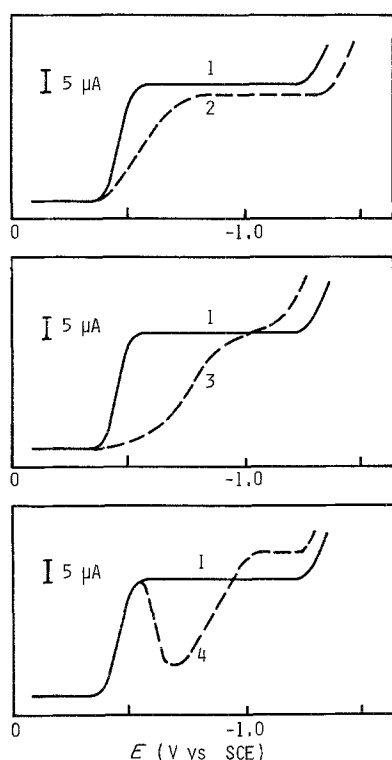
Fig. 2. Effects of POAA, RP and BA on the polarographic reduction of tin (II) ion: (1) 0.5 M H_2SO_4 + 5 mM $SnSO_4$ + 10% EtOH; (2) (1) + 1 mM POAA; (3) (1) + 1 mM RP; (4) (1) + 1 mM BA.

Fig. 3. Current–potential curves of tin (II) ion in the presence of POAA, RP and BA under potentiostatic conditions: (1) 0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH; (2) (1) + 5 mM POAA; (3) (1) + 1.5 mM RP; (4) (1) + 1 mM BA; (5) (1) + 5 mM POAA + 1.5 mM RP + 1 mM BA.

RP, adsorbed on the electrode as a neutral species, has a strong inhibitory effect on the reduction of the tin ion. On the other hand, when BA was added, $E_{1/2}$ of the reduction wave for the tin ion was unchanged (Fig. 2, curve 4). However, the reduction current of the tin 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 4) and was inhibited in the range of potentials from − 0.60 to − 0.80 V. The above inhibitory effect on the reduction of the tin ion may be attributed to the reductant of BA which is produced by the reduction of BA at potentials more negative than − 0.55 V [13].

3.2. Current–potential curves under potentiostatic conditions

Current–potential curves for acid stannous sulfate solutions (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH) containing POAA, RP and BA using low carbon steel as the cathode under potentiostatic conditions are shown in Fig. 3. These curves were obtained by plotting the steady state current against the applied potential. In the absence of adsorbed species the current increased abruptly at the negative potential of − 0.45 V due to the reduction of the tin (II) ion (Fig. 3, curve 1).

The curve in the presence of POAA showed limiting current (2.0 A dm^{-2}) in the range of potentials from − 0.50 to − 0.90 V (Fig. 3, curve 2). Tobias et al. reported that when mass transfer is limited by the diffusion control with natural convection, the value of limiting current is proportional to the 1.25 power of
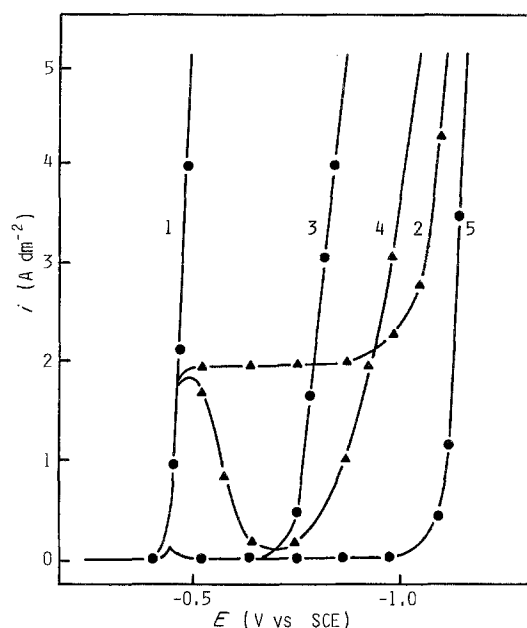
the concentration of metal ion [17]. In our experiments, it was found that the value of limiting current is proportional to the 1.25 power of the concentration of the tin ion [18]. Further, the limiting current disappeared and current increased abruptly at − 0.45 V by stirring the solution. These facts indicate that the limiting current appearing on the current–potential curve (Fig. 3, curve 2) in the presence of POAA is due to the diffusion control of the tin ion with natural convection.

When RP was added, the reduction current of the tin ion was entirely inhibited in the range of potentials from − 0.5 to − 0.7 V and the current increased abruptly at potentials more negative than − 0.75 V (Fig. 3, curve 3). On the basis of the electrocapillary curve results (Fig. 1, curve 3) and the d.c. polarogram results (Fig. 2, curve 3), it is suggested that RP adsorbed on the electrode has a strong inhibitory effect on the reduction of the tin ion. On the other hand, the current–potential curve in the presence of BA (Fig. 3, curve 4) was similar in shape to the d.c. polarogram of the tin ion in the presence of BA (Fig. 2, curve 4). That is to say, the reduction current of the tin ion decreased at potentials more negative than − 0.55 V and was inhibited in the range of potentials from − 0.60 V to − 0.80 V. Taking into account the results for the dropping mercury electrode (Fig. 1, curve 4 and Fig. 2, curve 4), the decrease in the reduction current of the tin ion may be attributed to the inhibitory effect of the reductant of BA.

When POAA, RP and BA were added, the reduction current of the tin ion was completely inhibited over a wide range of potentials from − 0.5 to − 1.00 V due to the synergistic effect [19, 20] of the three kinds of adsorbed species and the current increased abruptly at the negative potential of − 1.10 V (Fig. 3, curve 5).
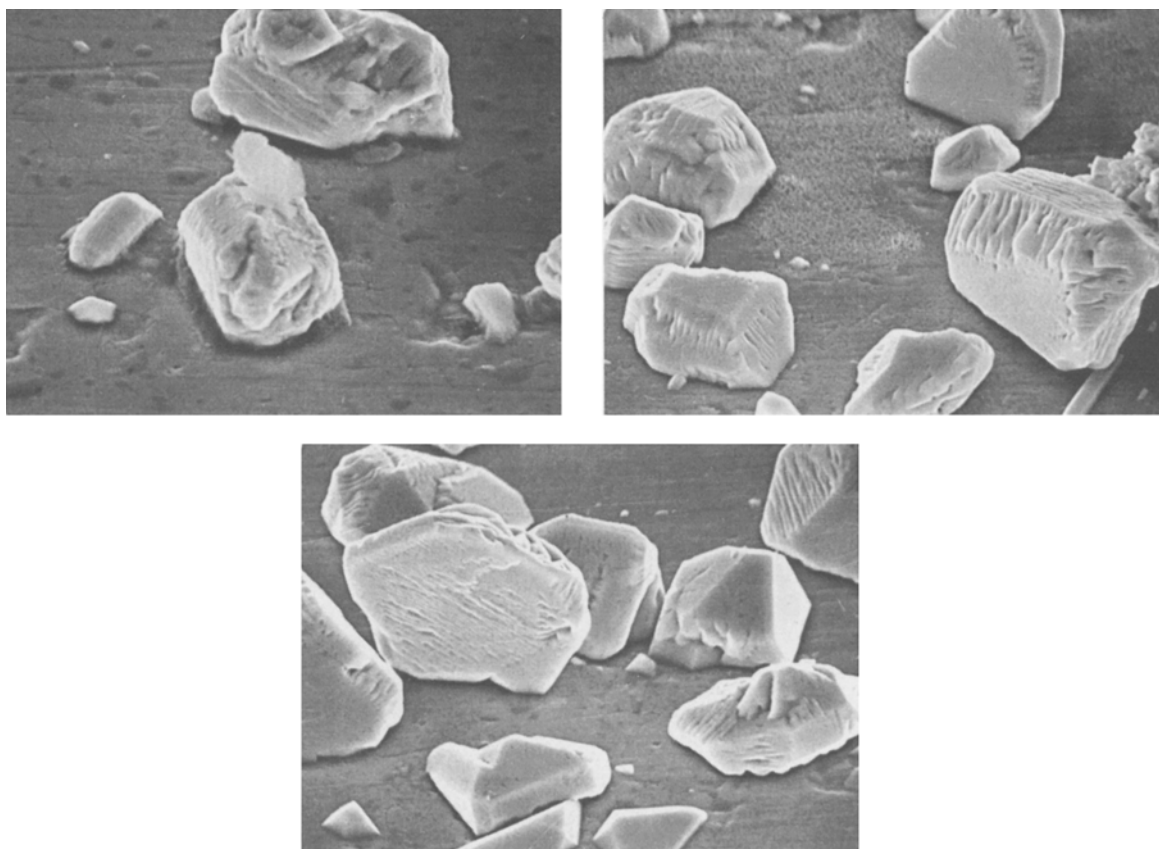
Fig. 4. Scanning electron micrographs of electrodeposited tin in the absence of adsorbed species (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH, 1 min): (a) 1.0 A dm^{-2}; (b). 2.0 A dm^{-2}; (c) 3.0 A dm^{-2}.
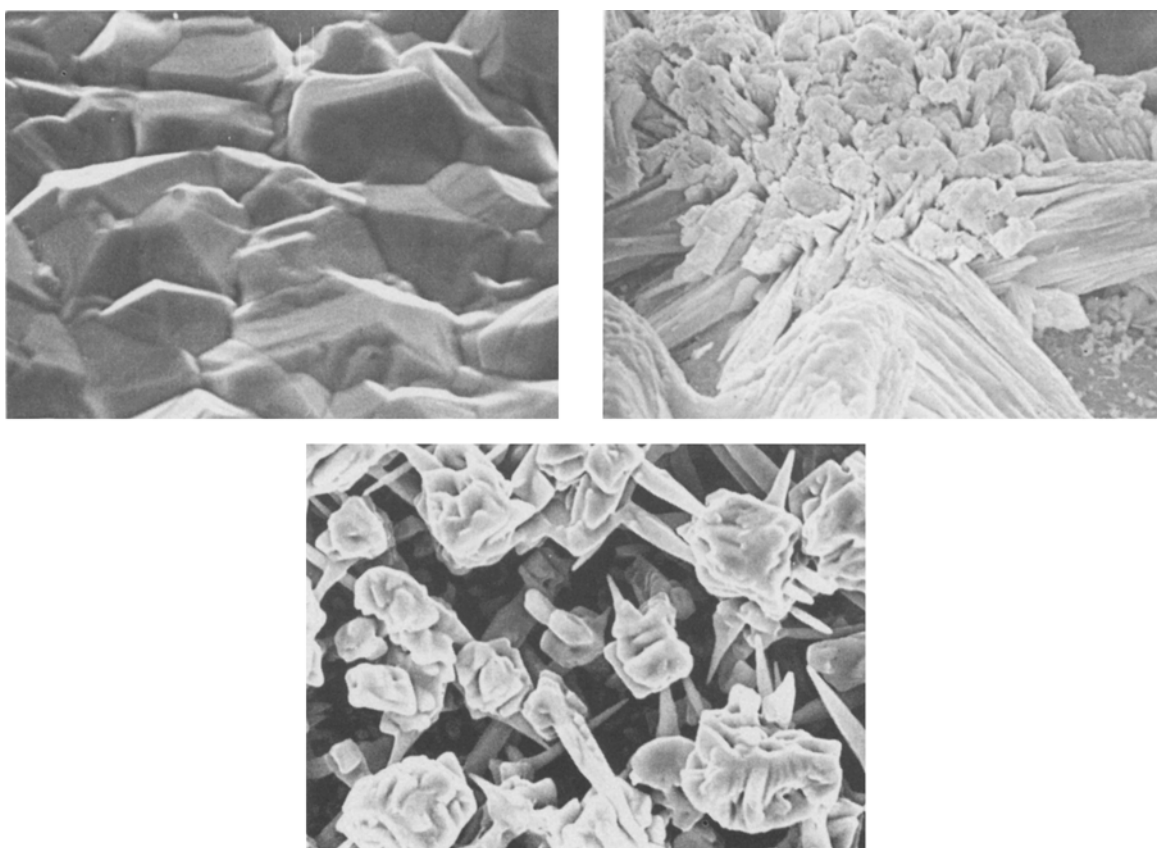

Fig. 5. Scanning electron micrographs of electrodeposited tin in the presence of POAA, RP and BA (2.0 A dm^{-2}, 5 min): (A) 0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH; (a) (A) + 5 mM POAA; (b) (A) + 1.5 mM RP; (c) (A) + 1 mM BA.

3.3. Surface morphology of electrodeposited tin

Scanning electron micrographs of electrodeposited tin, which were obtained from acid stannous sulfate solution (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH) in the absence of adsorbed species under practical conditions (1.0, 2.0 and 3.0 A dm^{-2}), are shown in Fig. 4. In all cases, large block crystals (their sides were 3–10 μm) were observed and the number of crystals increased gradually with increasing current density. Furthermore, the surface of low carbon steel used as the cathode was also observed (Fig. 4 a–c). Consequently, it became apparent that compact electrodeposits of tin are not obtained in the case where adsorbed species are not present.

Figure 5 shows scanning electron micrographs of electrodeposited tin which were obtained from acid stannous sulfate solutions containing POAA, RP or BA alone under galvanostatic conditions (2.0 A dm^{-2}). When POAA was added, surface roughness of the electrodeposited tin was found but the surface of the low carbon steel was not observed (Fig. 5a). Block crystals (their sides were 3 to 5 μm) were observed on the whole surface. It can be considered from the above results that POAA acts to produce a uniform deposition of tin over the whole surface. On the other hand, large massive tin crystals were observed on the surface by adding RP alone (Fig. 5b) and large needle-like or columnar tin crystals were observed with BA alone (Fig. 5c). Thus, compact electrodeposits of tin could not be obtained in the case where RP or BA were added alone.

Figure 6 shows scanning electron micrographs of electrodeposited tin which were obtained in the presence of both POAA and RP or POAA and BA at 2.0 A dm^{-2}. When POAA and RP were added, fine-grained crystals (their diameters were smaller than 1 μm) were observed over the whole surface (Fig. 6a). In this case both POAA, as cationic species, and RP, as neutral species, which have a strong inhibitory effect on the reduction of the tin ion, are adsorbed on the electrode. Consequently, the deposition potential of tin is largely shifted from a positive potential (−0.46 V) to a negative one (−0.94 V) due to the inhibitory effect of POAA and RP, and nucleation-

dependent growth of tin may occur. As a result, the crystal grain size may be smaller. On the other hand, when POAA and BA were added, reticular crystals were observed and the surface roughness was relatively small (Fig. 6b). In view of the X-ray diffraction results (Fig. 9b), it seems that the reductant of BA preferentially adsorbs on the (200) plane of tin, inhibiting outward growth, but allowing lateral growth. As a result, the surface roughness of electrodeposited tin becomes small and a relatively smooth electrodeposit is obtained in the case where POAA and BA are present together.

Figure 7 shows scanning electron micrographs of electrodeposited tin which were obtained in the presence of POAA, RP and BA at 2.0 A dm^{-2}. As shown from the surface micrographs (Fig. 7a and b), when POAA, RP and BA were added, fine-grained, smooth and compact electrodeposits of tin could be obtained due to the synergistic effect [19, 20] of the three kinds of adsorbed species. Further, it can be seen from the micrograph of the cross section (Fig. 7c) that compact and fibrous electrodeposits of tin, which grow parallel to the direction of current, are observed.

Taking into account the electrochemical characteristics and the surface morphology as mentioned above, it can be concluded that three kinds of adsorbed species have the following effects on the crystal growth of tin. (1) POAA, which shifts the reduction of the tin ion from a reversible process to an irreversible one (Fig. 2, curve 2) and which gives the limiting current on the current–potential curve (Fig. 3, curve 2), has the action of causing a uniform deposition of tin over the whole surface. (2) RP, which has a strong inhibitory effect on the reduction of the tin ion (Fig. 2, curve 3 and Fig. 3, curve 3), has the action of grain refinement. (3) BA, which is reducible (Fig. 1, curve 4) (the oxidant has no effect on the reduction of the tin ion and the reductant has an inhibitory effect on the reduction of the tin ion (Fig. 2, curve 4 and Fig. 3, curve 4)), has a leveling action.

3.4. Crystal orientation of electrodeposited tin

X-ray diffraction patterns of electrodeposited tin obtained from acid stannous sulfate solutions (0.5 M
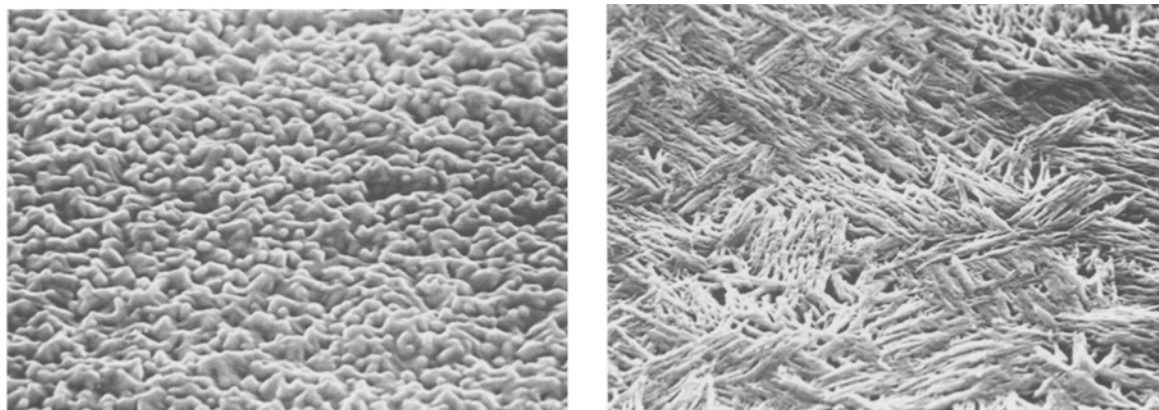

Fig. 6. Scanning electron micrographs of electrodeposited tin in the presence of POAA, RP and BA (2.0 A dm^{-2}, 5 min): (A) 0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH; (a) (A) + 5 mM POAA + 1.5 mM RP; (b) (A) + 5 mM POAA + 1 mM BA.
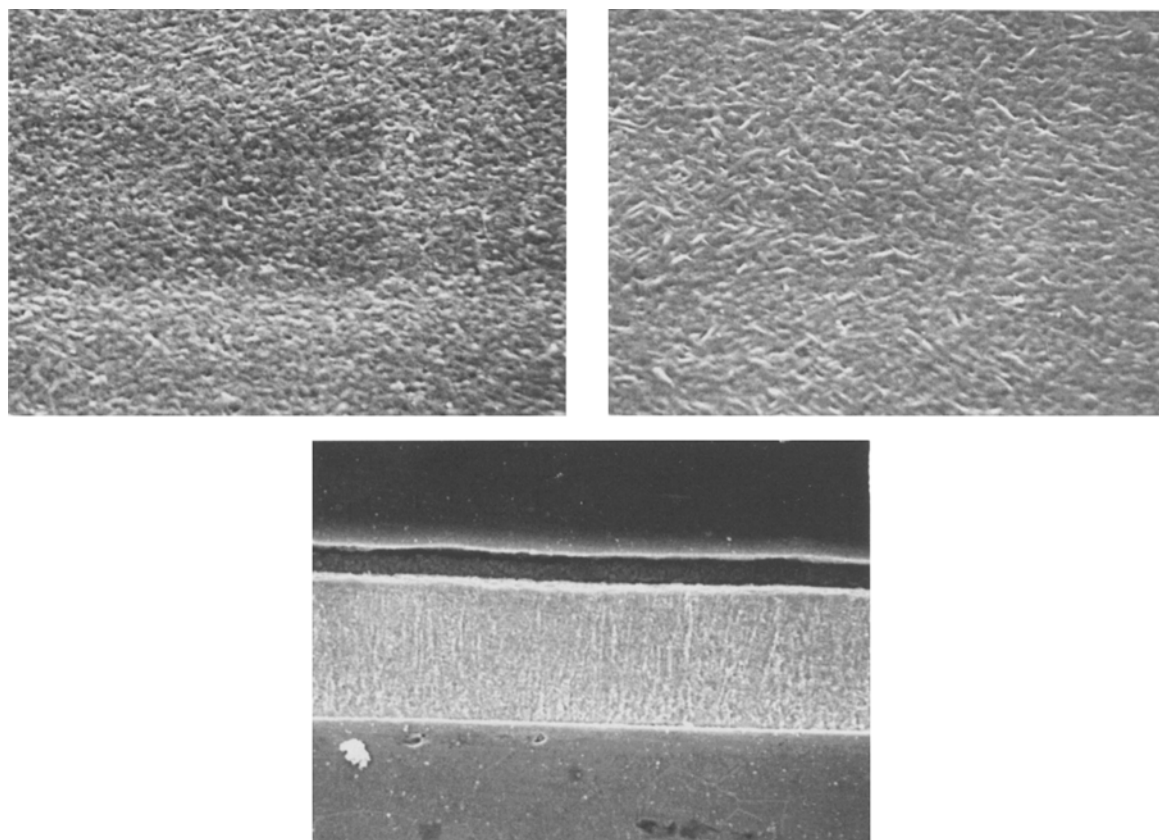
Fig. 7. Scanning electron micrographs of electrodeposited tin in the presence of POAA, RP and BA (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH + 5 mM POAA + 1.5 mM RP + 1 mM BA, 2.0 A dm^{-2}): (a) 1 min; (b) 5 min; (c) 30 min (cross section).

H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH) containing POAA, RP or BA alone under galvanostatic condition (2.0 A dm^{-2}) are shown in Fig. 8. Electrodeposited tin obtained by adding POAA, RP or BA alone exhibited (200), (101), (211) and (400) planes

with weak intensities. Consequently, when POAA, RP or BA were added alone it became apparent that electrodeposited tin, which exhibits a preferred orientation, cannot be obtained. However, the (200) plane was observed in all cases (Fig. 8a–c).
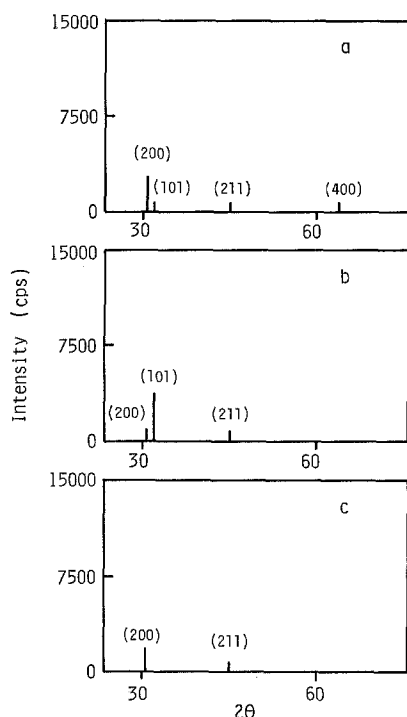

Fig. 8. X-ray diffraction patterns of electrodeposited tin in the presence of POAA, RP and BA (2.0 A dm^{-2}, 5 min): (A) 0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH; (a) (A) + 5 mM POAA; (b) (A) + 1.5 mM RP; (c) (A) + 1 mM BA.
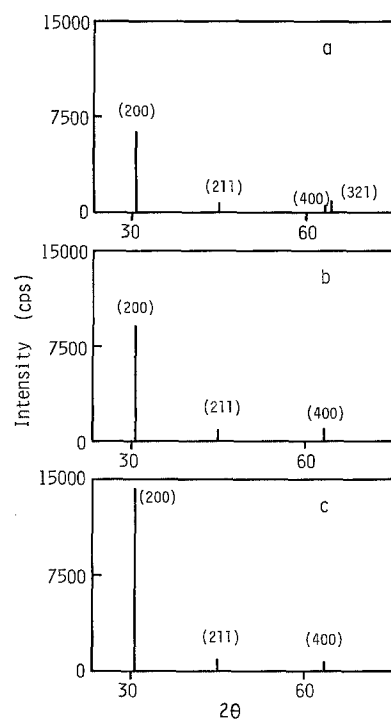

Fig. 9. X-ray diffraction patterns of electrodeposited tin in the presence of POAA, RP and BA (2.0 A dm^{-2}, 5 min): (A) 0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH; (a) (A) + 5 mM POAA + 1.5 mM RP; (b) (A) + 5 mM POAA + 1 mM BA; (c) (A) + 5 mM POAA + 1.5 mM RP + 1 mM BA.

Figures 9a and b show X-ray diffraction patterns of electrodeposited tin which were obtained in the presence of both POAA and RP or POAA and BA at $2.0\,A\,dm^{-2}$. In these cases, the (200) plane with relatively strong intensity was observed. On the other hand, Fig. 9c shows an X-ray diffraction pattern which was obtained in the presence of POAA, RP, and BA at $2.0\,A\,dm^{-2}$. In this case, the (200) plane with strong intensity was observed. When POAA, RP and BA were added, tin, which exhibited a preferred orientation with the (200) plane parallel to the surface, could be obtained due to the synergistic effect [19, 20] of the three kinds of adsorbed species.

References

[1] R. M. MacIntosh, in 'Modern Electroplating', 3rd ed (edited by F. A. Lowenheim), John Wiley, New York (1974) p. 401.

[2] N. Dohi, Kinzoku Hyomen Gijutsu 21 (1970) 248.

[3] S. Meibuhr, E. Yeager, A. Kozawa and F. Hovorka, J. Electrochem. Soc. 110 (1963) 190.

[4] B. Nagaraj and C. K. Mital, Metal Finishing 73 (1975) 76.

[5] M. Clarke and S. C. Britton, Trans. Inst. Metal Finishing 39 (1962) 5.

[6] M. Clarke and J. A. Bernie, Electrochim. Acta 12 (1967) 205.

[7] N. Dohi and S. Takashima, Kinzoku Hyomen Gijutsu 13 (1962) 515.

[8] N. Dohi, Kinzoku Hyomen Gijutsu 14 (1963) 406.

[9] Y. Matsuda, F. Koyama, Y. Hanada and Y. Tanaka, Kinzoku Hyomen Gijutsu 29 (1978) 185.

[10] Y. Matsuda, J. Itami, Y. Hanada and Y. Tanaka, Kinzoku Hyomen Gijutsu 32 (1981) 253.

[11] N. Kaneko, H. Nezu and N. Shinohara, Denki Kagaku 50 (1982) 959.

[12] N. Kaneko, H. Nezu, N. Shinohara and T. Aoyama, Denki Kagaku 53 (1985) 834.

[13] N. Kaneko and H. Nezu, Denki Kagaku 52 (1984) 774.

[14] H. Nezu, N. Kaneko and N. Shinohara, Kinzoku Hyomen Gijutsu 31 (1980) 244.

[15] P. Zuman, D. Barnes and A. Ryvolová-Kejharová, Discuss. Faraday Soc. 45 (1968) 202.

[16] H. Nezu, N. Kaneko and S. Wakabayashi, Denki Kagaku 47 (1979) 553.

[17] C. W. Tobias, M. Eisenberg and C. R. Wilke, J. Electrochem. Soc. 99 (1952) 359C.

[18] H. Nezu, N. Kaneko and N. Shinohara, Denki Kagaku 54 (1986) 173.

[19] O. Kardos and D. G.Foulke, in 'Advances in Electrochemistry and Electrochemical Engineering', Vol 2 (edited by C. W. Tobias), Interscience Publishers, New York (1962) p. 145.

[20] K. Boto, Electrodep. Surf. Treat. 3 (1975) 77.