Surface morphology and crystal orientation of electrodeposited tin from acid stannous sulphate solutions containing various additives

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The changes in surface morphology and crystal orientation of electrodeposited tin from acid stannous sulphate solutions containing 1 mM N,N-bis(tetraoxyethylene)octadecylamine (TOOA) and various concentration (0.2–2 mM) of benzalacetone (BA) have been studied as functions of electrolysis time or BA concentration by electrochemical methods, scanning electron microscopy and X-ray diffractometry. The inhibitory effect on the reduction of the tin (II) ion became stronger with increasing concentration of BA. In the presence of both TOOA and BA, when electrolyses were carried out at the more negative potentials than the reduction potential of BA, the reduction product of BA induced reticular crystals (network structure) of tin over the whole surface. This structure appeared in the early stage of electrolysis and exhibited an intense (200) diffraction peak. On the other hand, the crystal grain size and the surface roughness of electrodeposited tin became smaller with increasing concentration of BA from 0.2 to 2 mM. Further, fine-grained and smooth electrodeposits of tin were obtained from acid stannous sulphate solutions containing TOOA and high concentration of BA due to the synergistic effect of these adsorbed species.

1. Introduction

Dendritic, needle-like or columnar electrodeposits of tin were obtained from acid stannous sulphate solutions in the absence of organic additives, but compact electrodeposits could not be obtained. In order to obtain compact, smooth and fine-grained electrodeposits of tin, it has been found that various organic additives such as 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 behaviour of N,N-bis(polyoxyethylene)octadecylamines (POOA) [9], aromatic carbonyl compounds [10, 11] and diphenylamine-crotonaldehyde reaction product [12]; and the effects of the above organic additives on the electrocrystallization of tin [13–16]. 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 changes in the surface morphology and the crystal orientation of electrodeposited tin from acid stannous sulphate solutions containing the adsorbed species [N,N-bis(tetraoxyethylene)octadecylamine (TOOA) and benzalacetone (BA)] as functions of electrolysis time or BA concentration.

2. Experimental details

2.1. Apparatus and procedure

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 BA in water. A cell having a volume of 100 cm^3 was employed. The temperature was maintained constant at $25 \pm 1°$ C. All potentials were referred to a saturated calomel electrode (SCE).

2.2. Chemicals and electrode materials

Sulphuric acid (H_2SO_4), stannous sulphate ($SnSO_4$) and ethylalcohol (EtOH; C_2H_5OH) 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). N,N-bis(tetraoxyethylene)octadecylamine (TOOA; $C_{18}H_{37}N[(CH_2CH_2O)_4H]_2$) was 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 [17]. The low carbon steel plate was degreased in alkaline solution (Dipsol Chemical Co., Ltd, No. 44-S, 40 g dm^{-3}) at 50 $\sim$ 60° C for 30 min. It was then electropolished in alkaline solution (Dipsol 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 TOOA and BA

As described in previous papers [9, 14], TOOA, to which a proton is added in sulphuric acid solution, is strongly adsorbed on the electrode as a quaternary ammonium ion in the potential range 0 to −1.50 V. Further, TOOA adsorbed on the electrode inhibits the polarographic reduction of the tin (II) ion and converts the reduction of the tin (II) ion from a reversible to an irreversible process [9]. On the other hand, BA exhibits one reduction wave in the d.c. polarogram with a half-wave potential $(E_{1/2})$ of −0.65 V [13, 15]. It has already been reported that the reduction of BA to 4,5-diphenyl-2,7-octanedione in acidic solution is a one-electron process as follows [18]:

$$2C_6H_5\text{-CH=CHCOCH}_3 + 2e^- + 2H^+$$

$$\longrightarrow C_6H_5\text{-CHCH}_2\text{COCH}_3$$
$$|$$
$$C_6H_5\text{-CHCH}_2\text{COCH}_3$$

As described previously [13, 15, 16], BA is adsorbed as the oxidant at a potential more positive than the reduction potential of BA and is adsorbed as the reduction product at a potential more negative than the reduction potential; and BA itself has no effect on the reduction of the tin (II) ion, but the reduction product of BA has a strong inhibitory effect on the reduction of the tin (II) ion.

Figure 1 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. 1, curve (a)). When TOOA was added

Fig. 1. Current/potential curves of tin (II) ion in the presence of organic additives under potentiostatic conditions. (a): 0.5 M H_2SO_4 + 0.25 M SnSO$_4$ + 10% EtOH; (b): (a) +1 mM TOOA; (c): (b) +0.2 mM BA; (d): (b) +0.5 mM BA; (e): (b) +1 mM BA; (f): (b) +1.5 mM BA; (g): (b) +2 mM BA.

alone, the limiting current (2.2 A dm^{-2}) was observed in the potential range −0.50 to −0.90 V (Fig. 1, curve (b)). Tobias et al. reported that when mass transfer is limited by diffusion control with natural convection, the value of the limiting current is proportional to the 1.25 power of the concentration of metal ion [19]. In our experiments, it was found that the value of the limiting current is proportional to the 1.26 power of the concentration of the tin (II) ion [14]. Further, the limiting current disappeared and the current increased abruptly at a −0.45 V by stirring the solution [14]. These facts indicate that the limiting current appearing on the current/potential curve in the presence of TOOA (Fig. 1, curve (b)) is mainly due to the convective diffusion of the tin (II) ion.

As for the current/potential curves in the presence of both 1 mM TOOA and various concentration of BA (Fig. 1, curves (c)-(g)), the reduction current of the tin (II) ion decreased at potentials more negative than −0.50 V. The limiting current caused by addition of TOOA became smaller with increasing concentration of BA from 0.2 to 0.5 mM (Fig. 1, curves (c) and (d)). When the BA concentration became higher, the reduction current of the tin (II) ion was strongly inhibited in the potential range −0.60 to −0.80 V for 1 mM BA (Fig. 1, curve (e)) and, further, was completely inhibited in the potential range −0.7 to −0.8 V for 1.5 mM BA and −0.7 to −1.1 V for 2 mM BA, respectively (Fig. 1, curves (f) and (g)). Taking into account the results for the dropping mercury electrode discussed in previous papers [13, 15, 16], this decrease in the reduction current of the tin (II) ion in the presence of TOOA and BA may be ascribed to the inhibitory effect of the reduction product of BA.

3.2. Surface morphology and crystal orientation of electrodeposited tin

Scanning electron micrographs (SEMs) of electrodeposited tin, which were obtained from acid stannous sulphate solution (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH) in the presence of both 1 mM TOOA and 1 mM BA under galvanostatic conditions (1.0 and 3.0 A dm^{-2}), are shown in Fig. 2. As described previously [13–16], columnar or block-like electrodeposits of tin were obtained in the absence of organic additives, and the surfaces of the low carbon steel used as the substrate were also observed. However, by adding TOOA alone, block-like or granular crystals were observed on the whole surface [14, 16]. Therefore, it became apparent that TOOA induce a uniform deposition of tin over the whole surface [14, 16]. 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. 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. 2(a)). When electrolysis was carried out at 3.0 A dm^{-2}, the deposition potential of tin was shifted from −0.49 V to more negative value (−1.06 V) at which BA is adsorbed as
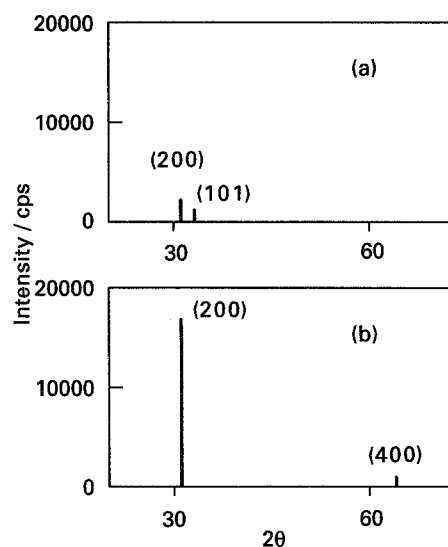
Fig. 3. X-ray diffraction patterns of electrodeposited tin in the presence of TOOA and BA under galvanostatic conditions (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 1 mM TOOA + 1 mM BA + 10% EtOH, 5 min). (a) 1.0 A dm^{-2} and (b) 3.0 A dm^{-2}.

the reduction product. In this case reticular crystals (network structure) were observed on the surface and the surface roughness of electrodeposited tin was relatively small (Fig. 2(b)). It seems that the
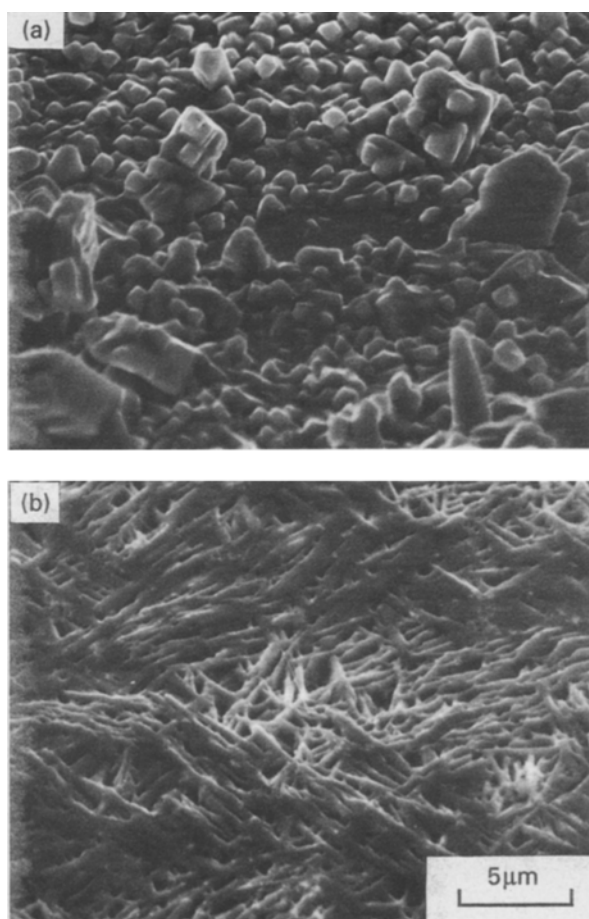
Fig. 2. Scanning electron micrographs of electrodeposited tin in the presence of TOOA and BA under galvanostatic conditions (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 1 mM TOOA + 1 mM BA + 10% EtOH, 5 min). (a) 1.0 A dm^{-2} and (b) 3.0 A dm^{-2}.
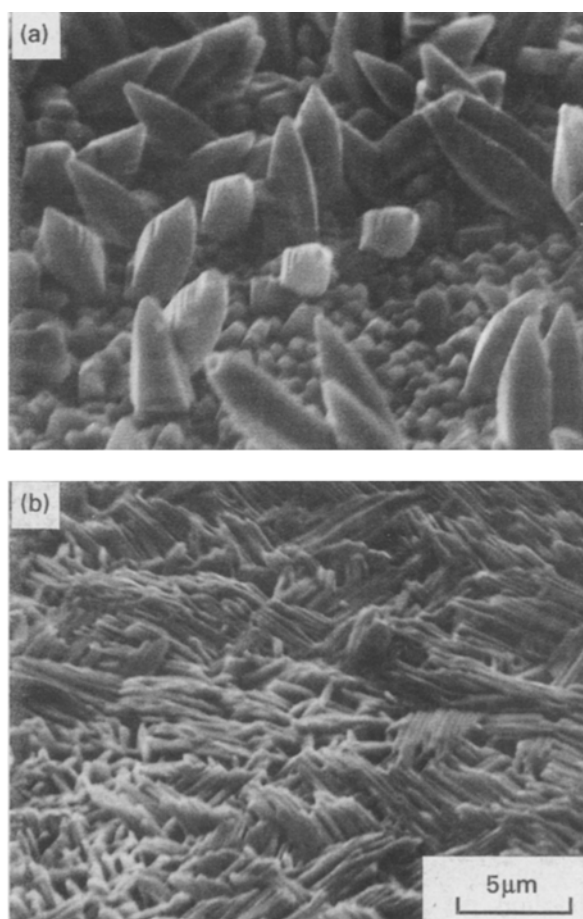
Fig. 4. Scanning electron micrographs of electrodeposited tin in the presence of TOOA and BA under potentiostatic conditions (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 1 mM TOOA + 1 mM BA + 10% EtOH, 5 min). (a) −0.5 V and (b) −0.9 V.
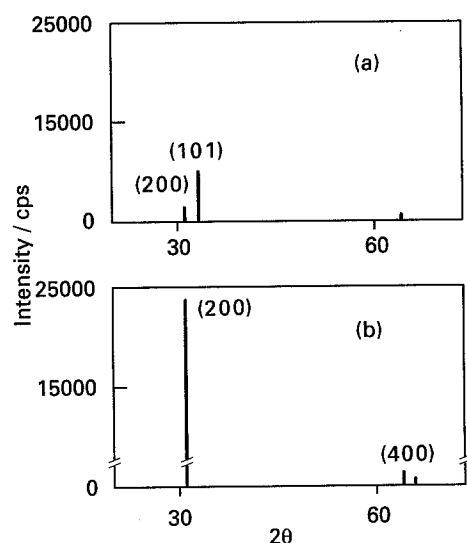
Fig. 5. X-ray diffraction patterns of electrodeposited tin in the presence of TOOA and BA under potentiostatic conditions (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 1 mM TOOA + 1 mM BA + 10% EtOH, 5 min). (a) −0.5 V and (b) −0.9V.

reduction product of BA, which has a strong inhibitory effect on the reduction of the tin (II) ion (Fig. 1, curve (e)), inhibits the outward growth of tin but allows lateral growth. As a result, the surface roughness becomes small and a relatively smooth electrodeposit is obtained. It can be concluded from these results that BA (the reduction product of which has a strong inhibitory effect on the reduction of the tin (II) ion) has a leveling action.

Figure 3 shows X-ray diffraction patterns of electrodeposited tin corresponding to Fig. 2. Electrodeposited tin obtained at 1.0 A dm^{-2} exhibited (2 0 0) and (1 0 1) diffraction peaks with weak intensities (Fig. 3(a)). Consequently, when electrolysis was carried out at 1.0 A dm^{-2}, tin with a preferred orientation could not be obtained. Figure 3(b) shows X-ray diffraction pattern of electrodeposited tin obtained at 3.0 A dm^{-2}. In this case a (2 0 0) peak with strong intensity was observed. This result suggests a preferred orientation with the (1 0 0) plane parallel to the surface.

Figure 4 shows SEMs of electrodeposited tin obtained in the presence of both 1 mM TOOA and 1 mM BA under potentiostatic conditions (−0.5 and −0.9 V). When electrolysis was carried out at −0.5 V which is a potential more positive than the reduction potential of BA, block-like and large columnar crystals were observed on the surface (Fig. 4(a)). On the other hand, when electrolysis was carried out at −0.9 V which is a potential more negative than the reduction potential of BA, reticular crystals similar to those obtained under galvanostatic condition at 3.0 A dm^{-2} were observed (Fig. 4(b) and 2(b)). X-ray diffraction patterns of electrodeposited tin corresponding to Fig. 4 are shown in Fig. 5. These patterns were also similar to those obtained under galvanostatic conditions (Fig. 3). Therefore, these results from Figs 4 and 5 support the idea that the reduction
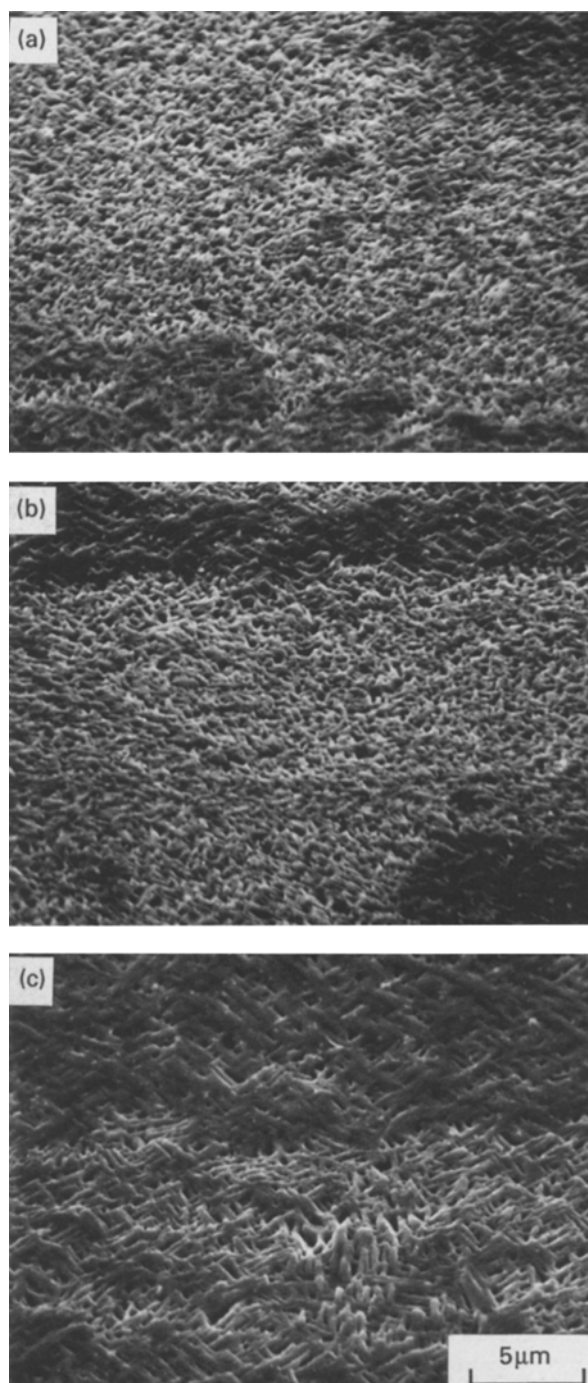
Fig. 6. Scanning electron micrographs of electrodeposited tin as a function of electrolysis time (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 1 mM TOOA + 1 mM BA + 10% EtOH, 3.0 A dm^{-2}). (a) 15 s, (b) 30 s and (c) 1 min.

product of BA induces reticular crystals of tin with a preferred orientation of the (1 0 0) plane.

3.3. Changes in surface morphology and crystal orientation of electrodeposited tin as a function of electrolysis time

Figure 6 shows SEMs of electrodeposited tin obtained from acid stannous sulphate solution (0.5 M H_2SO_4+ 0.25 M $SnSO_4$ + 10% EtOH) in the presence of 1 mM TOOA and 1 mM BA under galvanostatic condition
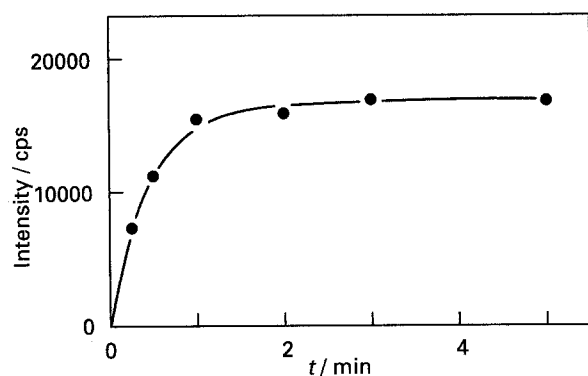
Fig. 7. Plots of intensity of (2 0 0) X-ray diffraction peak against electrolysis time (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 1 mM TOOA + 1 mM BA + 10% EtOH, 3.0 A dm^{-2}).

is formed in the early stage of electrolysis and the growth of crystals proceeds maintaining this feature.

The time dependence of the intensity of (2 0 0) X-ray diffraction peak for electrodeposited tin in the presence of 1 mM TOOA and 1 mM BA under galvanostatic condition (3.0 A dm^{-2}) is shown in Fig. 7. The intensity of the (2 0 0) peak increased abruptly in the early stage of electrolysis and became constant at a strong intensity after about 1 min. This suggests that a preferred orientation with the (1 0 0) plane parallel to the surface appears in the early stage. Further, it becomes apparent from the above results (Figs 6 and 7) that the intensity of the (2 0 0) peak becomes constant after the reticular crystals deposit over the whole surface.

(3.0 A dm^{-2}) as a function of electrolysis time (15, 30 s and 1 min). In the early stage of electrolysis, e.g. 15 s (Fig. 6(a)), fine-grained crystals were observed and reticular crystals were also observed partially. On the other hand, reticular crystals (network structure) were observed on the whole surface after 1 min from the beginning of electrolysis (Fig. 6(c)). As can be seen from Fig. 6 and Fig. 2(b) (SEM after 5 min), this structure of the reticulation became more clear and large with increasing electrolysis time. As a result, a morphological feature of network structure

3.4. Changes in surface morphology and crystal orientation of electrodeposited tin as a function of BA concentration

Figure 8 shows SEMs of electrodeposited tin obtained from acid stannous sulphate solutions (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 10% EtOH) in the presence of both 1 mM TOOA and various concentration of BA (0.2, 0.5, 1 and 2 mM) under galvanostatic condition (3.0 A dm^{-2}, 5 min). It can be seen from Fig. 8 that
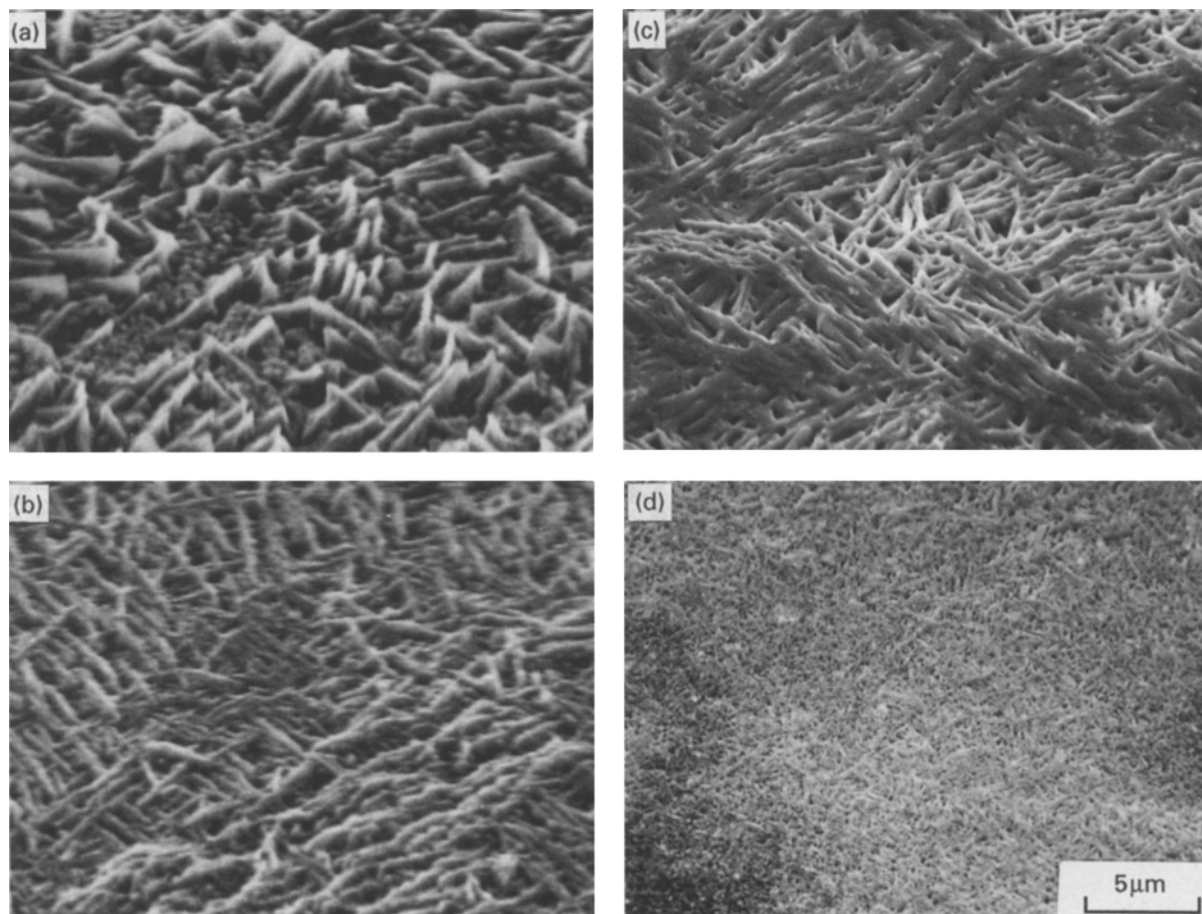

Fig. 8. Scanning electron micrographs of electrodeposited tin in the presence of TOOA and various concentration of BA (3.0 A dm^{-2}, 5 min). (A) 0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 1 mM TOOA + 10% EtOH. (a) (A) + 0.2 mM BA, (b) (A) + 0.5 mM BA, (c) (A) + 1 mM BA and (d) (A) + 2 mM BA.
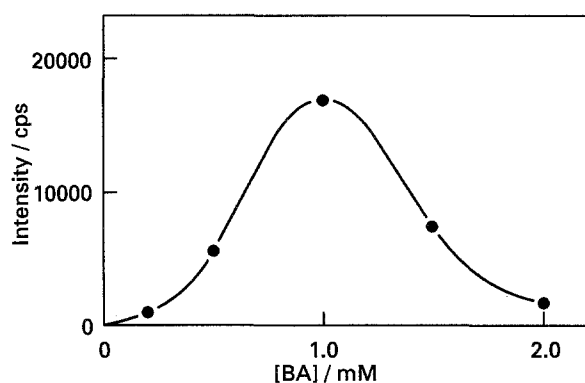
Fig. 9. Plots of intensity of (2 0 0) X-ray diffraction peak against BA concentration (0.5 M H_2SO_4 + 0.25 M $SnSO_4$ + 1 mM TOOA + [BA] + 10% EtOH, 3.0 A dm^{-2}, 5 min).

the crystal grain size and the surface roughness of the tin become smaller with increasing concentration of BA from 0.2 to 2 mM. When 1 mM TOOA and 0.2 mM BA were added, relatively large plate-like crystals were observed over the whole surface (Fig. 8(a)). However, reticular crystals (network structure) were observed by adding 1 mM TOOA and 0.5 mM BA (Fig. 8(b)), and this structure of the reticulation became more clear with increasing concentration of BA from 0.5 to 1 mM (Fig. 8(c)). In contrast fine-grained granular crystals were observed over the whole surface by adding 1 mM TOOA and 2 mM BA (Fig. 8(d)). When the concentration of BA was higher than 1 mM, the deposition potentials of tin at 3 A dm^{-2} were largely shifted in the negative direction (Fig. 1, curves (f) and (g)), and the nucleation-dependent growth of tin occurred preferentially. As a result, the crystal grain size was smaller (Fig. 8(d)). Thus, fine-grained and smooth electrodeposits of tin can be obtained by adding both 1 mM TOOA and 2 mM BA due to the synergistic effect [19, 20] of these adsorbed species.

The variation in the intensity of the (2 0 0) diffraction peak of tin as a function of BA concentration under the given condition is shown in Fig. 9. The intensity of the (2 0 0) peak increased with increasing BA concentration from 0.2 to 1 mM, and then decreased with increasing concentration beyond 1 mM. It can be concluded from above results (Figs 8 and 9) that the intensity of the (2 0 0) peak increases during the transformation of the surface structure from plate-like crystals to reticular crystals and decreases from reticular crystals to fine-grained granular crystals. These results also support the fact that the reticular crystals (network structure) exhibit an intense (2 0 0) diffraction peak.

4. Conclusions

The conclusions can be summarized as follows.

(i) The inhibitory effect on the reduction of the tin (II) ion becomes stronger with increasing concentration of BA.

(ii) When electrolyses are carried out at more negative potentials than the reduction potential of BA, the reduction product of BA induces reticular crystals of tin with a preferred orientation with the (1 0 0) plane parallel to the surface.

(iii) The reticular structure of electrodeposited tin appears in the early stage of electrolysis and exhibits a (2 0 0) diffraction peak with strong intensity.

(iv) The crystal grain size and the surface roughness become smaller with increasing the BA concentration.

(v) In the presence of both 1 mM TOOA and 2 mM BA, fine-grained and smooth electrodeposits can be obtained due to the synergistic effect of these adsorbed species.

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