Grain size effect of electro-plated tin coatings on whisker growth

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Tin and tin–lead coatings electro-plated in various solutions have been observed by means of high voltage electron microscopy, and the grain size effect of the coatings on whisker growth has been examined. As a result, it was found that the tin and tin–lead coatings from which whiskers hardly grew consisted of well-polygonized grains which were a few micrometre in size, and that the tin coatings from which whiskers easily grew consisted of irregular-shaped grains which were a few tenths of a micrometre in size. The irregular-shaped grains contained dislocation rings which might be formed by clustering of vacancies or interstitial atoms upon electro-plating.

1. Introduction

Metallic tin has unique properties, such as ease of soldering, high resistance to corrosion and good electrical conductivity, and it has been used extensively as a coating material for metal finishing in the electronic industries. An electro-plating technique has been developed as an economical method for fabricating tin coatings. However, tin whiskers have been observed to grow on the electro-plated tin coatings, and the whisker growth has caused a practical problem of short circuit error. Thus, many studies have been made to search for some method of preventing the whisker growth as well as the growth mechanism. It has been shown that the whisker growth is influenced by tinning brightener [1, 2], metallic substrate [3, 4], atmosphere [5], internal stress of coating [6–8], thickness of coating [9], addition of lead atoms [10] and so on [11].

On the other hand, tin whisker itself has also been studied, and is known to be a single crystal which is a few microns in diameter and 0.1 to 5 mm in length [12, 13]. Moreover, the tin whisker has been observed to grow only at the base [12], and to have a kinked shape and an irregular shape of intersection [14]. Based on this knowledge, many models have previously been proposed for the mechanism of whisker growth, and these have now been reduced to two models. One is the dislocation model [15–18], in which it is thought that an edge dislocation rotates around the corresponding screw component and new atomic planes are successively created in every rotation, forming a rise and finally becoming a whisker on an electro-plated tin coating. The other is the recrystallization model [19, 20], in which a strained tin plate is assumed to be recrystallized with the help of internal stress and one of the recrystallized grains grows upwards to form a whisker. However, no conclusive experimental evidence has been obtained for the two models.

Crystal grains and internal defects of electro-plated tin coatings have not been fully examined, except in one work [21], in spite of the fact that

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TABLE I Specimens and electrolytic solutions

Sample	Kind of coating	Electrolytic solution
A	Tin	*
B	Tin–20 wt % lead	Plutin LA†
C	Tin–5 wt % lead	‡
D	Tin	Stanosta
E	Tin	Tinglocoulmo
F	Tin	Stanosta §

* 150 g dm^{-3} H_2SO_4, 50 g dm^{-3} $SnSO_4$, 10 g dm^{-3} β-naphthol, 10 g dm^{-3} gelatin, 5 cm^3 dm^{-3} formaldehyde, 5 cm^3 dm^{-3} surface active-agent.
† 120 g dm^{-3} HBF_4, 12 g dm^{-3} $Sn(BF_4)_2$, 4 g dm^{-3} $Pb(BF_4)_2$, 10 g dm^{-3} conductive salt, 40 cm^3 dm^{-3} starter.
‡ 150 g dm^{-3} Hydroxybenzenesulphuric acid, 12 g dm^{-3} tin hydroxybenzenesulphate, 2 g dm^{-3} lead hydrobenzene-sulphate, 20 g dm^{-3} UTB. No. 1., 20 cm^3 dm^{-3} UTB. No. 2, 5 cm^3 dm^{-3} acetaldehyde.
§ One-third of the usual quantity of tinning brightener was used.

they could be important factors in tin whisker growth. Thus, the present work has been carried out in order to observe the grains and internal defects in variously prepared electro-plated tin and tin–lead coatings, and to learn about some of their effects on whisker growth.

2. Experimental methods

First, copper substrate (thickness 0.5 μm) was prepared by an electro-plating technique on a non-annealed Kovar alloy, and then tin (specimens A, D, E and F) and tin–lead (specimens B and C) coatings were electro-plated on to the copper substrate with various kinds of electrolytic solutions, as shown in Table I. The thickness of the coatings was adjusted to 0.5 μm under a current density of 1 A dm^{-2}.

The electro-plated tin and tin–lead coatings were strongly scratched with a knife edge into 2 mm × 2 mm squares and to the depth of the Kovar alloy. Then the coatings were immersed in a 10% KCN solution for 24 to 48 h together with the copper substrate and Kovar base, and then they were detached from the Kovar base by dissolving the copper substrate. The detached tin and tin–lead coatings were well washed and mounted on double grids for high voltage electron microscopy (HVEM). The HVEM used was a Hitachi HU-650 operated at 500 kV.

The easiness of whisker growth has also been examined for all the coatings, and the results are shown in Table II together with the results of electron microscope observations.

3. Experimental results

Fig. 1a to c are typical examples of the HVEM photographs taken from specimens A, B and C, respectively. Fig. 1a is of a tin coating on which whiskers find it difficult to grow. Crystalline grains are seen to be well polygonized having a size of a few microns. This means that the grains are already recrystallized. Fig. 1b and c are of tin–lead coatings on which whiskers find it very difficult to grow, although strictly speaking a little difference can be found between specimens B and C, as will be mentioned later. Well-polygonized grains are observed as in Fig. 1a, and the grains appear also to be recrystallized. Fig. 1d is an electron diffraction pattern of the encircled area in Fig. 1a. This pattern surely indicates that the grain is a tin crystal as indexed, although thermal diffusion streaks can be seen. According to the phase diagram of the tin–lead alloy system, no lead atoms dissolve in tin at room temperature, and so lead crystals should be separated from tin crystals. The little dark grains in Fig. 1b and c may be such lead crystals separated from tin crystals. Apart from this, there is little difference between the tin and tin–lead coatings, both of which exhibit a difficulty in whisker growth. Table II seems to show that the lead atom is useful in the formation of recrystallized grains in electro-plated coatings, as has been reported.

Fig. 2a, b and c are the HVEM photographs taken from tin coatings D, E and F, respectively, on which whiskers easily grow. Crystalline grains

TABLE II Ease of whisker growth and electron microscopy results

Sample	Grain size	Grain shape	Ease of whisker growth	Figure
A	1–8 μm	Well-polygonized	Difficult	1(a)
B	1–3 μm	Well-polygonized	Very difficult	1(b)
C	1–3 μm	Well-polygonized	Very difficult	1(c)
D	0.2–0.8 μm	Not polygonized	Easy	2(a)
E	0.2–0.5 μm	Not polygonized	Easy	2(b)
F	0.2–0.8 μm	Not polygonized	Easy	2(c)

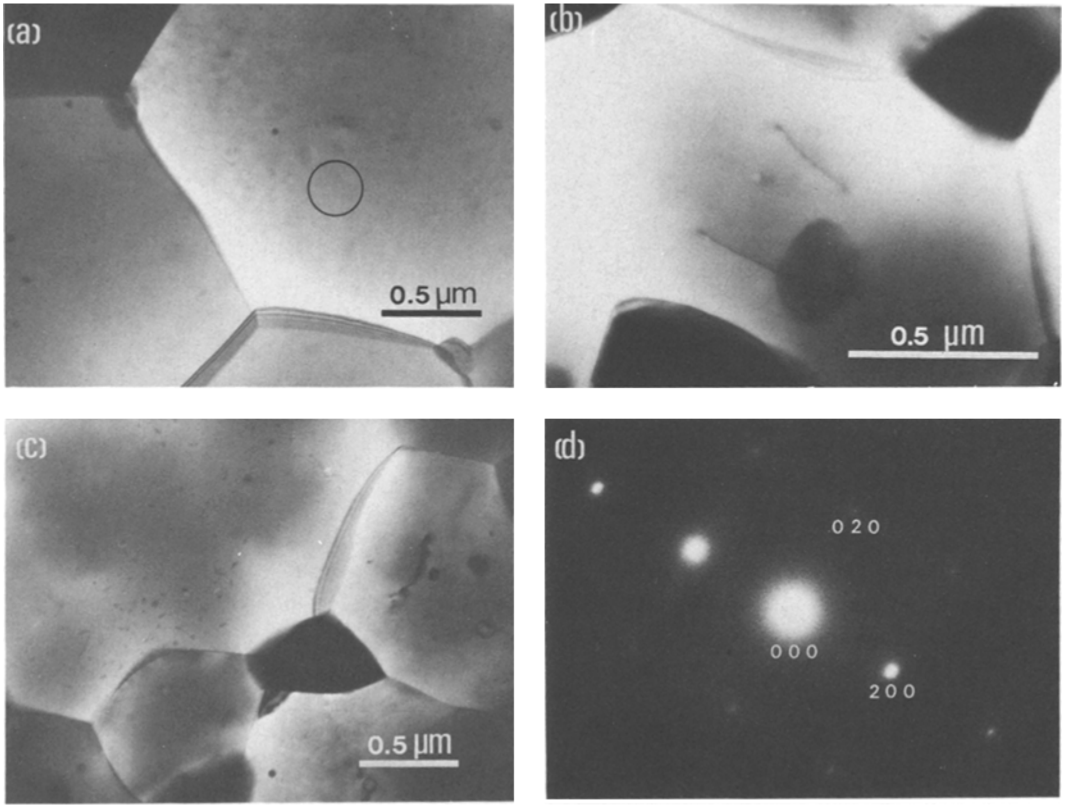

Figure 1 HVEM photographs taken from (a) specimens A, (b) B, and (c) C, showing well-polygonized grains, and (d) an electron diffraction pattern taken from the encircled area of (a).

are also seen, but the grains are surrounded by irregular-shaped boundaries and their size is much smaller than that in Fig. 1a to c, being a few tenths of a micrometre. In comparison to those in Fig. 1a to c, the grains in Fig. 2a to c appear not yet to be recrystallized, although they are crystallized as shown in Fig. 2d which is an electron diffraction pattern taken from the encircled area in Fig. 2a. Therefore, the above electron microscopy suggests that the size and shape of crystalline grains may play an important role in the ease of whisker growth on electro-plated tin coatings, and the addition of tinning brightners seems to play a role in supressing the formation of coatings with recrystallized grains and therefore to make whisker growth easier.

Fig. 3a and b give HVEM photographs showing internal defects in a grain of specimens A and D, respectively. In Fig. 3a only dislocation lines are seen, and such a structure is common to specimens A, B and C on which whiskers were hardly observed and in which well-polygonized grains were observed. On the other hand, in Fig. 3b many small loop-like contrasts are seen, and this structure is common to specimens D, E and F on which whickers were easily found and in which irregular-shaped grains were observed, although the loop contrasts were also observed in specimen C with well-polygonized grains. In order to learn about the nature of the small loops, a specimen (D) exhibiting the loop contrasts was tilted in the microscope, and a change of the contrasts was examined. Fig. 4 is a series of HVEM photographs taken at various tilt angles, and a contrast change is clearly recognized depending on the angles, sometimes showing dot-like contrasts. This means that the loops exist inside the specimen but not on the surface and have an orientation dependence. Therefore, the loops are crystallographic objects and may be dislocation rings which might be formed by clustering and collapsing of vacancies or by clustering of interstitial atoms, although Lindborg *et al.* [21] explained their dot-like contrasts by stating that they were due to an organic brightener. Such dislocation rings may be formed by electron irradiation during the HVEM. However, such loop contrasts are not observed in Figs. 1a and b, and therefore they might be formed in coatings

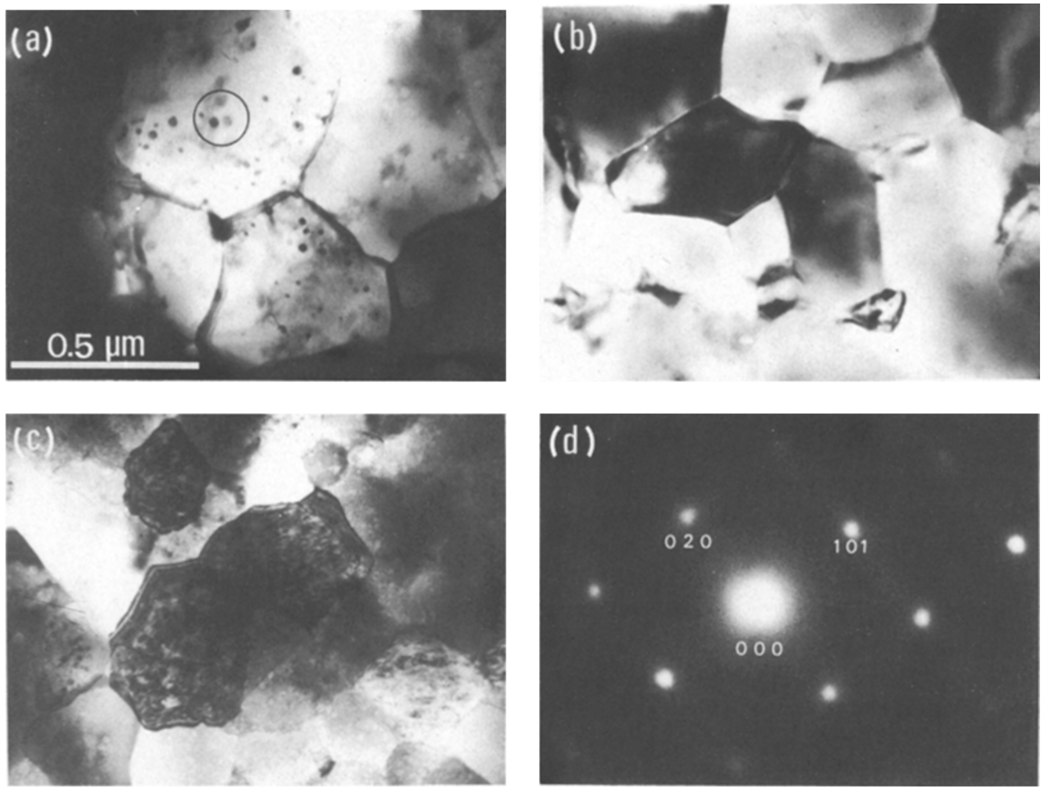

Figure 2 HVEM photographs (same magnification) taken from (a) specimens D, (b) E and (c) E, showing irregular-shaped grains, and (d) an electron diffraction pattern taken from the encircled area of (a).

upon electro-plating. As shown in Table I, the dislocation rings are observed in the coatings electro-plated in solutions with a tinning brightener (more aldehyde for specimens C, D and F and more ketone for specimen E). As mentioned before, a little difference is found between specimens B and C, that is, extrusions are sometimes observed on specimen C but not on specimen B. Such a difference may originate in the existence of dislocation rings and a smaller grain size which may come from the addition of an organic brightener. Therefore, it may be concluded that whisker growth is affected not only by the grain size and shape of the coatings but also by the kind of internal defects.

4. Discussion

It has been shown above that whiskers grow easily on electro-plated coatings with irregular-shaped grains and moreover on internal dislocation rings,

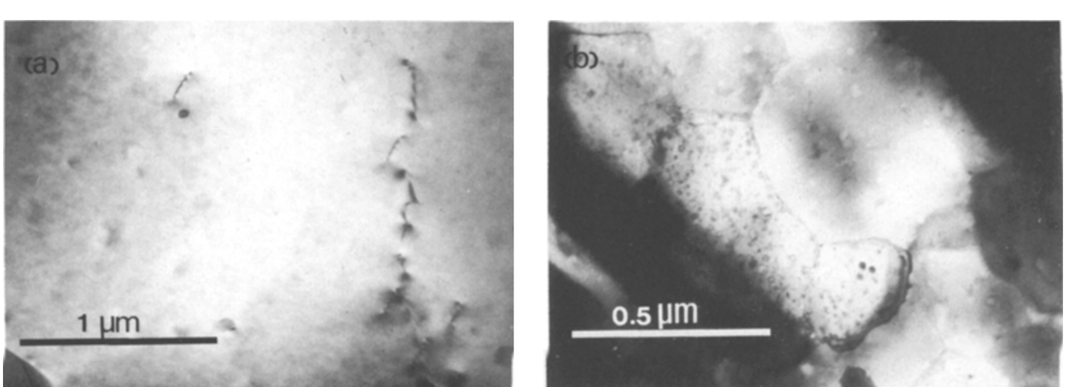

Figure 3 HVEM photographs showing dislocation lines in (a) specimen A and loop-like contrasts in (b) specimen D.

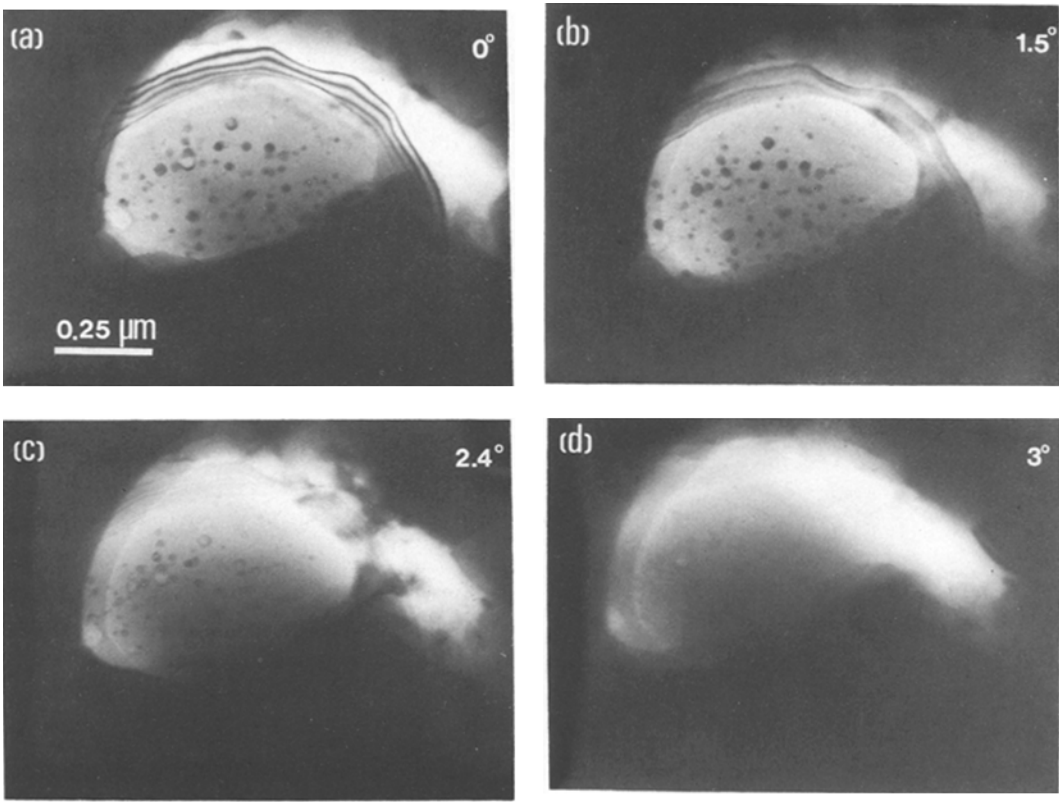

Figure 4 A series of HVEM photographs showing a contrast change of dislocation rings upon tilting a specimen (D).

but not on coatings with well-polygonized grains. The diameter of the whiskers is known to be 1 to 3 μm [12], and it is nearly the same as that of well-polygonized grains in the present work. Using this knowledge, a discussion will follow below on the mechanism of whisker growth.

First, it should be noted that whiskers cannot grow on coatings such as specimens D, E and F as they are, because the whiskers are single crystals, a few micrometres in diameter, while the grain size of the coatings is a few tenths of a micrometre. Whiskers should grow on crystalline grains whose size is a few microns, and this grain size is nearly the same as that of the well-polygonized grains observed in specimens A, B and C. Therefore, whiskers are considered to grow on recrystallized grains, and in fact it has been shown by scanning electron microscopy [22] that a tin whisker

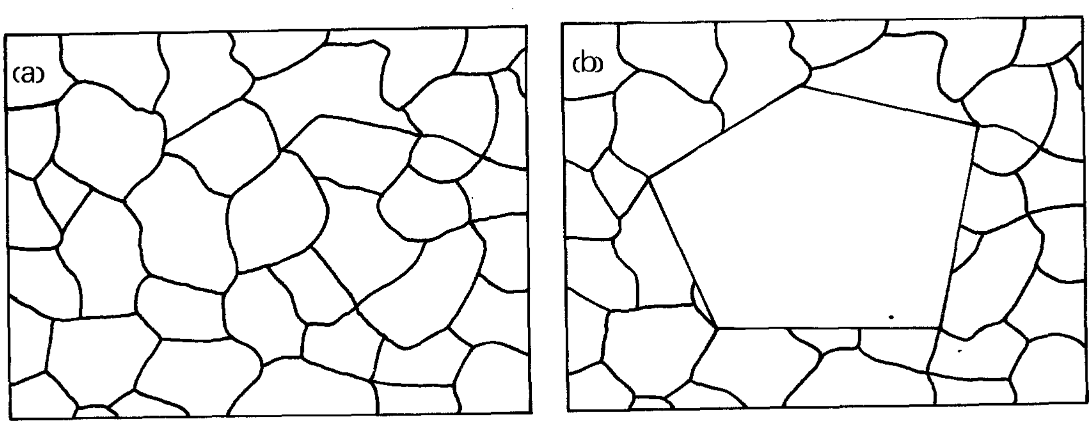

Figure 5 Schematic illustration of the growth mechanism of a whisker from a coating with irregular-shaped grains.

grows on a well-polygonized grain. Thus, the mechanism of whisker growth may be explained as follows.

Let us now imagine an electro-plated coating and assume that the coating contains small and irregular-shaped grains as in specimens D, E and F, as schematically illustrated in Fig. 5a. If such a coating is aged at room temperature, a recrystallized grain may appear and grow at the expense of the original irregular-shaped grains, as in Fig. 5b. Growth may be continued until the grain size becomes a few microns, and then stopped, presumably because some barrier is formed along the recrystallized grain boundary due to an accumulation of lattice defects or formation of tarnish film. At this stage, a whisker may start to grow upwards on the recrystallized grain with the help of internal stress which is possibly caused by the barrier formed along the bounary or by formation of intermetallic compounds (Cu_6Sn_5 and Cu_3Sn) [23, 24] between the tin coating and copper substrate. Such an internal stress may gradually be relieved as the whisker growth advances, and the stress relief may bring about a further recrystallization in the surroundings still consisting of irregular-shaped grains. After the advance of whisker growth and recrystallization, the surrounding irregular-shaped grains may finally be well-polygonized, as actually observed [22]. Therefore, this mechanism may be said to be a modification of the recrystallization model previously proposed.

According to the above mechanism, the origin of whisker occurrence is in the existence of irregular-shaped or heavily distorted grains, and the origin of whisker growth is in the existence of an internal stress. That is, the existence of both distorted grains and internal stress is necessary for whisker appearance. Therefore, whiskers may hardly appear if one of the two origins does not exist; for example, if an electro-plated coating is well-polygonized from the beginning for some reason as in specimen A, B and C. Such a scarcity of whisker occurrence and growth may also be observed if a coating is polygonized or recrystallized by annealing at a temperature higher than room temperature. In fact, annealing at 423 K for 3 h is adopted as a commercial method for preventing whisker appearance, although annealing may also be useful for relieving an internal stress.

It has been reported that an external stress promotes whisker occurrence and growth [6–8]. However, according to the above mechanism, the external stress should be such a localized one that distorted or deformed grains are formed, but not a homogeneous one. In fact, whiskers were rarely observed when a well-annealed tin metal was homogeneously stressed by pressing, but were easily observed when the same tin metal was locally stressed by scratching [25]. In this way, the present mechanism for whisker occurrence and growth is consistent with other experimental results. It can thus be concluded that grain size and shape of electro-plated coatings as well as internal defects are important factors in whisker occurrence and growth.

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