ELECTRON MICROSCPY STUDY OF DEFORMATION AND RECRYSTALLIZATION BEHAVIOR OF PURE TIN FOR MITIGATION OF WHISKERS

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ABSTRACT

The clarification of whisker growth mechanism is a key to the mitigation of tin-whiskers. In order to confirm the growth model the present authors had proposed, the process of recrystallization of tin was investigated. A single crystal of tin was prepared by using a slow-cooling method and plate samples were prepared by using a spark-cutter and electro-polishing. Deformation was applied to the plate samples by scratching. The microstructural changes with time at room temperature after scratching were observed by scanning electron microscopy (SEM) and electron back-scatter diffraction (EBSD). The experimental results showed clearly that recrystallization can proceed even at room temperature. A tensile test was also performed in order to investigate its ordinary deformation behavior. The present results have supported the model for tin whisker growth mechanism, suggesting that if the recrystallization phenomenon can be controlled to proceed homogenously in tin solder and plating, the whisker growth will be mitigated.

Keywords— tin-whisker, SEM, EBSD, recrystallization, mitigation

1. INTRODUCTION

Tin-Lead (Sn-Pb) alloys have been used for a long time as basic materials for solders and platings. Alloying Pb with Sn gives notable improvements in mechanical properties of tin-base solder and plating materials such as; (1) lower melting point, (2) higher toughness and (3) mitigation of whiskers. However, these alloys containing Pb are not used further due to restriction of hazardous substances for environmental concerns [1]. Then whiskers grow up again from Sn-materials, and the whisker formation became a revived issue. Lindoborg [2] proposed a model for the whisker formation mechanism that an expansion of dislocation loop by climb-up results in the growth of a whisker. Nakadaira et al. [3] pointed out that contribution of atomic vacancies are required for a continuous growth of whiskers. However, an experimental evidence that proves directly the mechanism has not be obtained yet. On the other hand, the whisker formation has been understood to result from internal pressure in a solder/plating. Actually tin-whiskers are categolized into 4 types according to their formation process; (1) External stress type, (2) Internal stress type (3) Surface oxidation/corrosion type and (4) Welding type. [4] All these types of whiskers are formed after applying stress. Therefore, it is clear that stress is a key factor of whisker formation. [5, 6] But the formaion mechanism is not yet clarified. The surface of solder/plating is usually covered with a thin and tough tin-oxide layer that is naturally formed. If there are holes or cracks on the oxide layer, the body of tin is spouted out through the hole or crack by the internal pressure to be a whisker, just like "*cream on a cake*". This model is thought instinctively to be very plausible, but actually there are several experimental results that cannot be explained by the model. For example, there are occasionally formed voids or valleys below the whisker. This reflects the existance of tensile stress instead of compressive one, being against the model of *cream on a cake*. Smetana [7] reported the process of whisker formation in an article entitled "End Game". He intorduced the most believed model that a whisker is curled by insertion of edge dislocations. But the present authors [8] confirmed that actually the crystallographic orientation is not tilted in the whole region of whisker even when the whisker is curled or jogged. The game has not ended yet.

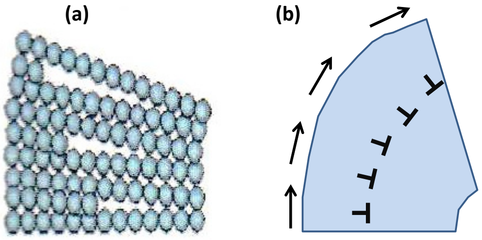

Fig. 1 Growth model for a curling whisker
(a) Model adopted by Smetana [7]
Partial layers are inserted.
(b) Morphology of a curling whisker expected from (a).

The present authors [9] have proposed a new model for growth of whiskers: There are highly-stressed regions and stress-relieved ones in a layer of tin, and tin atoms have a high and low potential energy in these regions, respectively. Therefore tin atoms diffuse from the highly-stressed regions to the stress-relieved ones. Tin atoms coming to the stress-relieved region are spouted out from the surface of tin layer to become a whisker. The high stress is produced by a pressure that is applied internally or externally depending on the case of the type of whiskers. The issue is how the stress-relieved region is formed. The present authors has suggested that recrystallization is strongly related with the formation of stress-relieved regions.

The recrystallization temperature depends upon the degree of deformation, and it is sometimes near room temperature in case of pure tin. Therefore, there is a possibility that recystallization proceeds during deformation at the same time at room temperature. This issue is very important in order in order to understand correctly the deformation behavior. However, such characteristics have not been taken into account well so far. In the present work, the microstructure was analyzed with taking into account the behavior after deformation in order to examine if recrystallization proceeds at room temperature. Finally, the mechanism of tin whisker formaion is discussed for mitigation of whiskers.

2. METHODOLOGY

2.1. Experimental Methods

2.1.1. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is one of the most popular technique for characterization. A basic structure of SEM is composed of electron beam illumination part and electron detectors. When an electron beam hits a specimen, two types of electrons come back from the specimen. One is secondary electrons (SE) with a low energy about a few 10 V or less, and the second is back-scatter elecrons (BSE) with higher energy up to that of incident electrons. If the SE are collected with an electron detector positioned aside, the intensity of them corresponds roughly to the orientation of the specimen surface. Therefore SE images are used for observation of an external morphology of specimen. On the other hand, the BSE intensity depends upon the chemical composition and the direction of BSE is almost perpendicular to the specimen surface. Therefore BSE are used for observing the distribution of chemical compositon as well as observation of the external morphology of specimen. Therefore a conventional SEM has usually two elecron detectors aside the specimen and below the objective lens for SE and BSE, respectively. An advanced model of SEM has 4 electron detectors or more; two detectors are those mentioned above, and other two detectors are positioned inside the column of objective lens, being for SE and BSE, respectively. Fig. 2 shows a typical example of the positions of electron detectors in an advanced SEM.

It was thought conventionally that SEM is a tool to observe an external morphology of specimen and a disribution of chemical composition. But it is not the case. When the incident beam has a high coherecy the intensity of BSE, as well as SE sometimes, depends considerably on the crystallographic orientation of specimen. Such image contrast are called “channeling contrast”. Then the information on crystallographic characters can be analyzed by using channeling contrast. [10, 11] . Therefore, SEM is a strong tool with which a variety of information can be obtained provided the observation is conducted and analyzed properly.

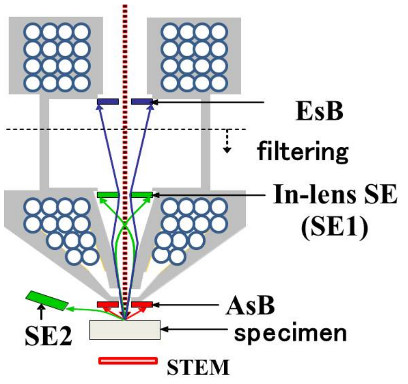

Fig. 2. Positions of electron detectors in an advanced SEM (Ultra 55, Carl Zeiss)
SE1, SE2: Detectors for secondary electrons
AsB: Angular-selective back-scatter electron detector
EsB: Energy-selective Back-scatter elctron detector
STEM: Scanning transmission electron microscopy detector

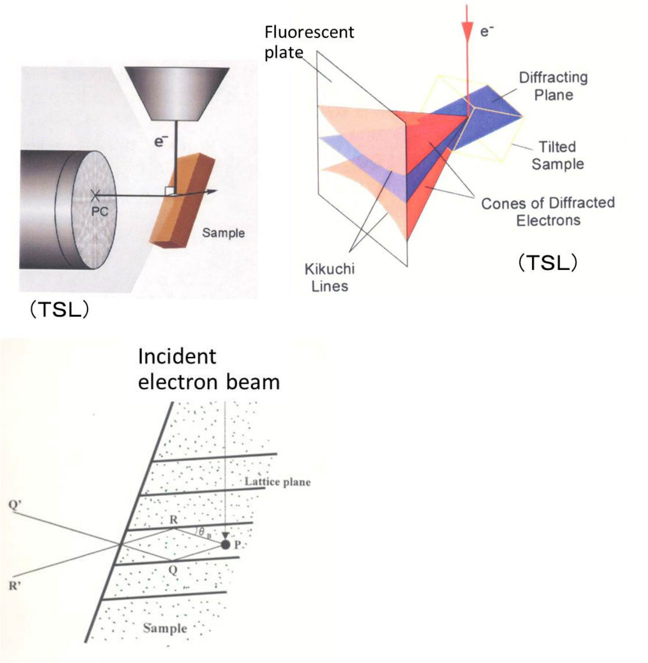

Fig. 3 Configuration in SEM for EBSD pattern and basics of geometry for Kikuchi lines.(Courtesy of TSL Solutions, Co. Ltd.) and the explanation for a pair of Kikuchi lines

2.1.2. Electron back-scatter diffraction (EBSD)

As explained in the previous subsection, the intensity of BSE depends on the crystallographic orientation. The intensity of BSE emitted from a single point on the specimen surface also has an angular distribution. Basically electron beam is an electron wave, so that diffraction phenomenon occurs. When an inelastic scattering occurs inside a specimen, the scattered electron waves run in every direction. Then some of them are diffracted by a certain set of crystal lattice planes, modifying the intensity distribution of inelastically scattered electrons or BSE. Then the intensity distribution contains the information on the orientations of crystal lattice planes. Usually the intensity of BSE changes quickly at the diffraction condition, and then sets of two lines, or Kikuchi lines, are observed in the angular distribution of BSE. These are called “Kikuchi pattern”. By analysing such a Kikuchi pattern, the crystallographic orientation can be determined for the position of the incident beam on the specimen. By accumulating the data, a map of crystallographic orientation can be obtained. It is very important to recognize that a center line between a pair of Kikuchi lines corresponds to a trace of a set of the planes that contribute to the diffraction for the Kikuchi lines. Therefore the Kikuchi pattern is formed by the diffraction phenomenon, but the geometry of Kikuchi pattern is of the direct space.

The crystallographic orientations of each position in the specimen are represented in two dimension, or inverse pole figure (IPF) for three orthogonal directions; ND (normal direction to the specimen surface), RD (rolling direction; horizontal) and TD (transverse direction; vertical). The sharpness of Kikuchi pattern corresponds to the crystallinity, so that the distribution of crystallinity can be also shown as “quality map”.

2.2. Experimental Procedure

2.2.1. Preparation of single crystal specimens

Rods of pure tin (Sn) were prepared by using a quartz crucible. Single crystals of pure tin were grown by melting the rod in a soft mould of fine alumina powder, followed by one-dimentional slow-cooling [12]. A rod of single crystal was cut out into slabs with a spark-cutting machine. Damaged layers on a surface of the slab formed by spark-cutting were removed by electro-polishing in a solution of 20% perchloric acid and 80% acetic acid at 20^{o}C with a direct current at 10V.

2.2.2. Scratching test

Scratching test was performed with a diamond pen (a glass-cutter) under a force of 1kgf on a plate specimen of pure tin single crystal afer electropolishing. After scratching, the specimen was put into a specimen chamber of a SEM (Ultra 55, Carl Zeiss) and observed after certain durations.

2.2.3. Tensile test

Tensite tests were performed with a tensile test devise (TSL Solutions, Japan) in SEM of Ultra 55, Carl Zeiss. Stress-strain curves were measured. SEM images and EBSD data were also collected under loading at a certain position of strain with fixing the elongation or strain.

3. EXPERIMENTAL RESULTS

3.1. Scratching test

Fig. 4 shows the results of EBSD experiments after scratching. It is confirmed that small crystal grains are formed very quickly after scratching, This phenomenon can be explained by either of twinning deformation or spontaneous recrystallization. Actually, characteristic lammelar structure is observed in part. But most parts of the scratched region is composed with round-shape crystal grains. As proposed previously [12], regions with a different crystallographic orientation from the undeformed matrix are formed without changes in morphology of external surface. It is clearly seen that a new crystal grain of a round shape (indicated with an arrow in Fig. 4) appears and grows with time. It is witnessed that recrystallization and crystal growth proceed even at room temperature.

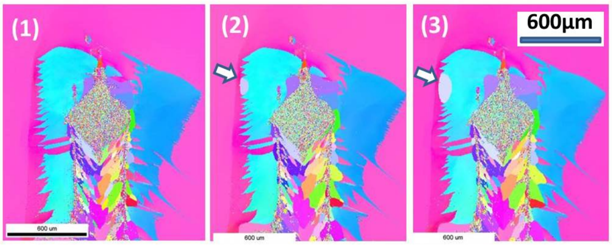

Fig. 4 Changes in EBSD IPF (ND) image with the durtion of room temperature annealing
(1) 1 hr, (2) 3 hr, (3) 5 hr

3.2 Tensile test

A preliminary experiment of tensile test was carried out for a single crystal specimen of pure tin. A stress strain curve is shown in Fig. 5. During application of strain, the elongation was kept constant for a while at particular strains in order to observe SEM images and to collect EBSD data. Short lines running from the stress-strain curve shows the stress is reduced during the constant elongation. This suggests that some rearrangement in defecs occurs. By loading again, stress exceeds the value for the moment of keeping the strain constant, indicating the existence of work hardening.

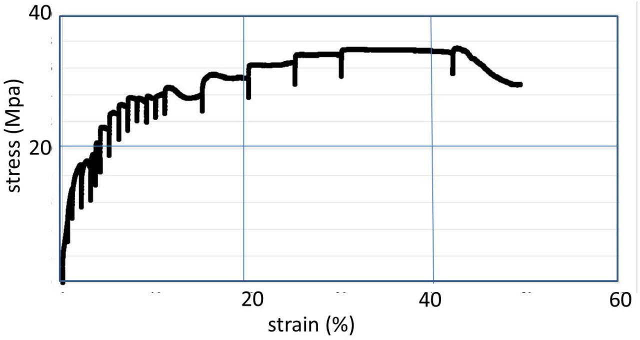

Fig. 5 Stress-strain curve experimentally obtained for a single crystal specimen of pure tin

At each position of keeping constant strains, the morphology was observed in SEM. Some results were shown in Fig. 6. Parallel striations run across the specimen. In the region where the striations are concentrated, the surface of spcimen has many steps so that the specimen is bent. These striations seem to resemble the deformation morphology due to slide deformation. As tin is one of presentative materials that present twinning deformation, these striations can be also due to twinning deformation in part at least. More detail analysis is needed to characterize the deformation process.

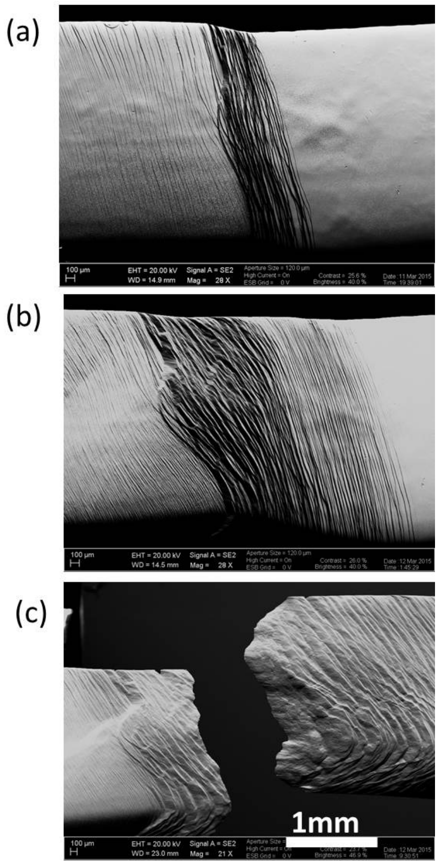

Fig. 6 SEM SE-images of a tin single crystal during tensile test

(a) Elongation = 701 μm, Load = 46.22 N

(b) Elongation = 2002μm, Load = 56.21 N

(c) after rupture

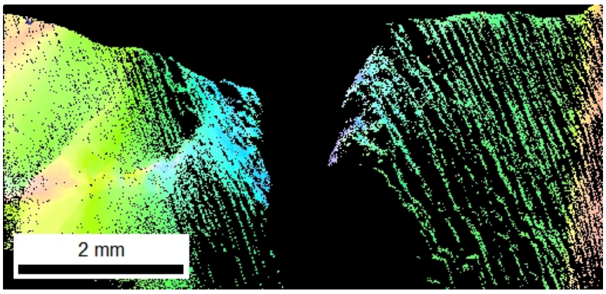

Fig. 7. EBSD result for a single crystal of tin after rupture IPF image (ND)

After rupture, the regions where strains are concentrated are made of plate-like plates piled up in morphology. The morphology is quite different from that obtained after scratching. We need to examine the morphology of crystal grains inside of the ruptured specimen. If recrystallization does not proceed after the rupture, deformation structure containg dislocations piled up and/or twinning plates would be observed, in correpondence with the external morphology. If recrystallization has already proceeded, a lot of small crystal grains with a round shape appear inside the specimen irrespective with the strucrure with striations. Fig. 7 shows an example of EBSD data for the tin specimen of a single crystal after rupture. It is confirmed that large crystal grains have been formed irrespective of the lammelar morphology formed by deformation. this result indicates that recrystallization and grain-growth proceed almost spontaneously also in this case. EBSD data for each stage have been already collected from this specimen. The results of analysis will be presented elsewhere.

4. DISCUSSION

4.1 Deformation and recrystallizaion behavior

From the experimental results, it is be concluded that the deformation of single crystal seems to proceed in a way of sliding deformation or twinning deformation up to rupture. Large crystal grains are formed after the rupture. When a severe deformation like skratchng is applied, small round crystal grains without strains are formed almost spontaneously. These results indicate that recrystallization and grain-growth process proceeds almost spontaneously during the deformation at room temperature.

4.2 Growth mechanism of tin whiskers

The mechanism of whisker growth has been discussed extensively, and it should be a conclusive result that the stress is a key for whisker formation. That is; compressive pressure is a driving force for whisker formation. However, there are some experimental results that cannot be explained by a conventional understanding. The present authors [9] proposed a new theory of whisker formation. As explained already in Introduction, there should be regions of high stress and a “point” where stress is almost relieved. Tin atoms have a high potential energy in the matrix of high stress, and a low potential energy at a low stress. Then tin atoms flow toward the point of stress-free. If the atoms coming up to the point can go out of the matrix by spouting out, tin atoms flow continously. That is, it is not compressive pressure that make tin atoms flow, but the point of stress-free draws up tin atoms and spouts them out to form a whisker. The point of stress-free works as a pump. This model can explain the voids and cracks that are frequeatly observed near whiskers. Recrystallization process should proceed at room temperature in order to realize a point of stress-free. Concerning the formation of a curled whisker without grain boundary inside, it can be explained by taking it into account that the rotation in crystallographic orientation of whisker occurs spontaneously at the boundary between the whisker and the grains below it The detail of the formation mechanism will be discussed separately elsewhere.

If a point of stress-free does not appear but recrystallization occurs in a wide region, whiskers will not be formed. Even if whiskers appear, they will not be elongated much. Controlling the recrystallization is a key for mitigation of whisker formation.

5. CONCLUSION

Behavior of deformation and recrystallization was investigated by means of electron mcroscopy, and the following conclusions were drawn:

(1) It has been confirmed that in a pure tin, recrystallization and grain growth occur almost spontaneously during the deformation and proceed even at room temperature.
(2) Deformation behavior during a tensile test was successfully observed in a way of in-situ. Preliminary analysis indicated that recrystallization and grain growth occur almost spontaneously during the deformation.
(3) The experimental results that indicate the occurrance of recrystallization at room temperature support the model for whisker formation proposed by the present authors.

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