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C. C. Wei, P. C. Liu, Chih Chen, Jeffrey C.B. Lee, and I Ping Wang

Citation: [Journal of Applied Physics](#) **102**, 043521 (2007); doi: 10.1063/1.2770832

View online: <http://dx.doi.org/10.1063/1.2770832>

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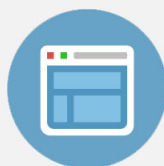
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Relieving Sn whisker growth driven by oxidation on Cu leadframe by annealing and reflowing treatments

C. C. Wei, P. C. Liu, and Chih Chen^{a)}

Department of Materials Science and Engineering, National Chiao Tung University, Hsin-chu 30010, Taiwan, Republic of China

Jeffrey C.B. Lee and I Ping Wang

Integrated Service Technology, Hsin-chu 30072, Taiwan, Republic of China

(Received 26 December 2006; accepted 10 July 2007; published online 28 August 2007)

Owing to environmental concern, Pb-free solders are replacing eutectic tin lead in electronic packaging industry. Thus, whisker growth becomes a serious reliability issue for Sn finishes. In this study, the mechanism of whisker growth from Sn finish on Cu leadframe was investigated under the temperature/humidity storage test. It is found that oxidation of the Sn finish was the driving force behind the whisker growth. Thermal treatments including annealing at 220 °C and reflowing at 260 °C were employed to mitigate the whisker growth. It is found that both heat treatments can significantly reduce the whisker growth rate. It is speculated that the heat treatments can relieve the residual stress in the Sn finishes and can modify their grain structure, resulting in a slower oxidation rate. Thus, they can slow down the grow rate of Sn whiskers. In addition, reflowing treatment can change the columnar grain structure of the Sn film to the equiaxed grain structure in some of its regions, resulting in a lower grain boundary diffusion rate of Sn. Therefore, the reflowed sample had the lowest growth rate of Sn whiskers. © 2007 American Institute of Physics.

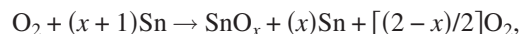
[DOI: [10.1063/1.2770832](https://doi.org/10.1063/1.2770832)]

I. INTRODUCTION

Sn whisker growth in Sn film has been a serious reliability issue in the electronic packaging industry over the last 50 years.¹⁻⁵ Spontaneous growth of Sn whiskers occurs in Sn-based finishes on Cu leadframes. The length of the whiskers may be as long as tens of millimeters, which could shorten the neighboring legs of a lead frame.⁶ This may result in the failure of devices in satellites.⁷⁻⁹ Eutectic tin-lead alloy has been widely used in the microelectronic industry, which exhibits low cost, low melting temperature, and excellent mechanical properties. However, environmental concern and the ban on use of lead in the electronic industry have given rise to the pressure of removing lead from the electronic industry. It is reported that the addition of Pb may mitigate the growth of Sn whiskers.¹⁰ Pb-free finishes will replace the eutectic SnPb ones, and most of the Pb-free finishes are rich in Sn. The whisker issue has become more serious with the implementation of Pb-free solders, and has thus attracted a lot of attention recently.¹¹⁻¹⁷ Spontaneous whisker growth indicates that compressive stress gradient exists in the Sn finishes. There are three indispensable conditions for spontaneous whisker growth; they are (1) the room-temperature grain boundary diffusion of Sn, (2) the room-temperature reaction between Sn and Cu to form Cu₆Sn₅ intermetallic compound (IMC), which provides the compressive stress, and (3) the stable and protective surface Sn oxide. In principle, there will be no whisker growth if any one of them is removed. The National Electronics Manufacturing Initiative (NEMI) has recommended a solution for removing condition (2) by

preventing Cu from reacting with Sn. Arnold *et al.* found that the addition of Pb can form fine grains, which can remove condition (1) by slowing down grain boundary diffusion.¹⁰ However, owing to the environmental concern, the use of Pb will be banned. How to relieve Sn whisker growth is an urgent issue.

It has recently been reported that Sn whiskers grow in humid ambient environment when Sn oxides are formed.¹⁸ This oxidation occurs due to condensation of moisture on the base material. The oxidation reaction could be expressed by the following equation:



where $x=1$ or 2 . In general, tin oxide formation could drive whisker growth due to the volume expansion. The molar volume of tin is 16.2 cc/mole, and that of tin oxide is 21.7 cc/mole. Thus, the volume increases about 33% after formation of Sn oxide. Barsoum *et al.* proposed that the formation of tin oxide could provide another kind of driving force for whisker growth.¹⁸ As oxygen atoms diffuse into the Sn film and form an oxide layer, the relative volume change, $\Delta V/V_0$, would form a stress field. However, only a few studies have addressed this issue.¹⁹⁻²¹ The microstructure of the Sn film near the Sn whiskers is not clear. In addition, how to relieve Sn whisker growth due to formation of Sn oxide has not been studied yet.

In this study, annealing and reflowing treatments were employed to mitigate the growth of Sn whiskers. Accelerated test under 60 °C/90% RH was adopted to investigate whisker growth. The mechanism of how the annealing and reflowing treatments can relieve the whisker growth is pro-

^{a)}Author to whom correspondence should be addressed. Electronic mail: chih@faculty.nctu.edu.tw

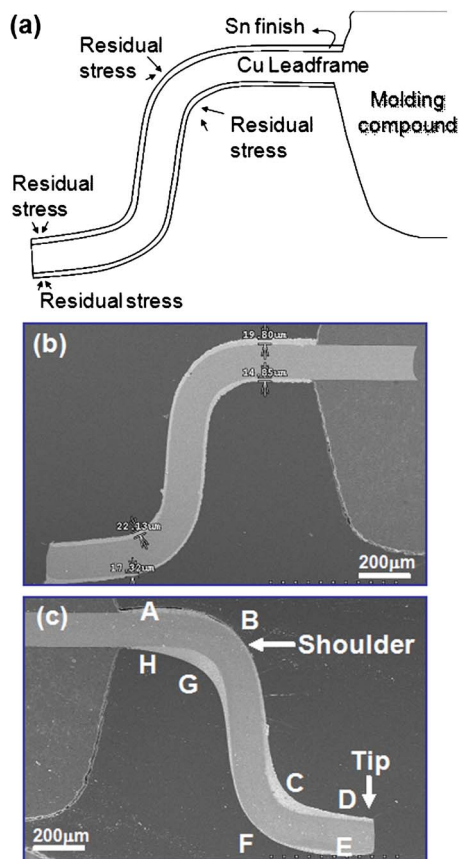


FIG. 1. (a) Cross-section schematic diagram for the leadframe used in this study. SEM images showing the cross-section view of the (b) as-fabricated, and (c) reflowed sample before the temperature/humidity test.

posed. This study offers a deeper understanding on the effect of annealing and reflowing on Sn whisker growth from the Sn finish on Cu leadframes.

II. EXPERIMENT

The samples used in this study were Cu-based leadframe of a low-profile quad flat package (LQFP) with the dimensions of 28 mm × 28 mm and a pitch of 0.5 mm. Figure 1(a) shows the schematic drawing for one of the legs of the Cu leadframes. Because the leg needs to be bent and cut to be mounted on a substrate, four locations may have large residual stress, as indicated in the figure. Figure 1(b) shows the scanning electron microscope (SEM) image of a leg mounted on a print circuit board (PCB) substrate. The average thickness of the matte tin was about 10–12 μm, which was electroplated on the Cu-based leadframe. The Sn layer had a uniform thickness and no whiskers were observed before the temperature/humidity storage test.

To investigate how to relieve Sn whisker growth, one of the leadframes was treated by an annealing process while the other one underwent a reflowing process. For the former, LQFP packages on PCB substrates were annealed in a furnace and the peak temperature was 220 °C with the total process time of 498 s. After being annealed, the packages were cooled at a rate of 3 °C/s. For the latter, the packages were preheated at 175 °C for 50 s, held at 230 °C for 25 s, and then reflowed at 268 °C. The total time for the reflowing

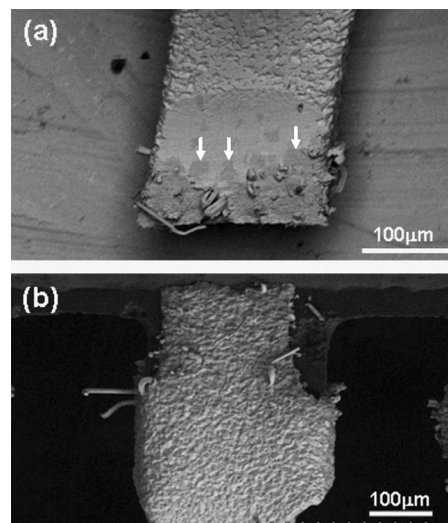


FIG. 2. SEM images showing the surface morphology of the as-fabricated sample (a) at lead tip, and (b) at top region after the 3000-h storage at 60 °C/90% RH ambient. Tin whiskers grew in both regions.

process was 410 s. Finally, the packages were cooled at a rate of 3.8 °C/s. Since the melting point of Sn is 232 °C, the Sn finish melted during the reflowing process and solidified during the cooling step. For the accelerated test on whisker growth, three sets of packages, including as-fabricated, annealed, and reflowed ones, were stored in a furnace for temperature and humidity test (THT), in which the temperature and humidity were kept at 60 °C and 90% RH, respectively. The samples were taken out and examined after 1000 and 3000 h.

The surface morphology and the microstructural changes were examined by SEM, focus ion beam (FIB), transmission electron microscope (TEM), and optical microscopy (OM). Energy dispersive spectrum (EDS) was employed to analyze the composition of the surface of the Sn finish. In order to observe the grain boundary, some of the legs were polished and then etched by a mixture of hydrochloric acid (98%) and glycerol (2%). The morphology of the Sn layer changed after the reflowing process. Figure 1(c) shows the cross-sectional SEM image for one of the reflowed legs. Eight distinguished regions were labeled on the leg, as seen in the Fig. 1(c). Owing to gravity and surface tension effects, the Sn film on Regions C and G grew thicker, while the Sn film in Regions B and F became thinner. Before the reflow treatment, the matte tin had uniform thickness of about 10–12 μm. After the heat treatment, the Sn layer may become as thick as 60 μm in Region C and 34 μm in Region G. On the contrary, the Sn layer was depleted slightly at Regions B and F, and its thickness may reduce down to about 10 μm.

III. RESULTS

Humidity was found to have significant influence on whisker growth. Whiskers were found at many locations of the lead surface after the THT. Figures 2(a) and 2(b) show the surface morphology near the tip (Region D) and the top (Region A) of the leg after the 3000-h THT for the as-fabricated samples. In the tip area, several darker regions were observed near the roots of whiskers, as indicated by the

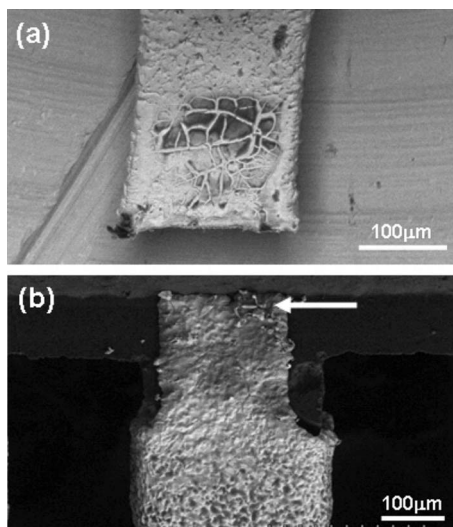


FIG. 3. SEM images showing the surface morphology of the annealed sample (a) at lead tip, and (b) at top region after the 3000-h storage at 60 °C/90% RH ambient. Less tin whiskers grew in both regions.

arrows in Fig. 2(a). The Sn film in these regions may be corroded. This point will be discussed later. Whiskers were found to grow intensively in the tip and top regions, while much less whiskers grew in the remaining regions of the legs. In this study, the whisker growth was evaluated by its maximum length, since the length of whiskers is the critical concern for shortening neighboring legs. The maximum length of whiskers was measured to be 95 μm for the samples without thermal treatment after the 3000-h THT, and it was 21 μm after the 1000-h THT.

Tin whisker growth was relieved to some extent after the annealing at 220 °C. Figures 3(a) and 3(b) show the surface morphology for the tip and top regions, respectively, for the 220 °C-annealed sample after the THT for 3000 h. The surface morphology is quite different from that of the as-fabricated sample in Fig. 2. Some patterns were formed on the Sn film near the tip of the leg, as shown in Fig. 3(a), which did not trigger whisker growth. Fewer whiskers grew on the Sn finish, while some whiskers were observed near the junction of the leg and molding compound (Region A), as indicated by the arrow in Fig. 3(b). In addition, the length of the longest whisker decreased to 26 μm after the 3000-h THT, and it was 13 μm after 1000-h THT.

Tin whisker growth can be further suppressed by the reflowing process at 260 °C. Figures 4(a) and 4(b) show the surface morphology of the tip and the top regions, respectively, for the reflowed sample after the THT for 3000 h. Only few whiskers grew on the surface of the leg. The longest whisker that could be found was only 10 μm after 3000-h THT, and no whiskers were observed after 1000-h THT. The above results are listed in Table I.

To investigate the driving force for whisker growth during the THT, FIB was employed to examine the microstructure of the Sn film after THT. Figure 5(a) shows the FIB image of the corroded area in the tip region for the as-fabricated sample after the 3000-h THT. Part of the Sn finish near the whisker was etched by Ga ions, and the cross sections of the Sn and the IMC layers can be observed clearly. It

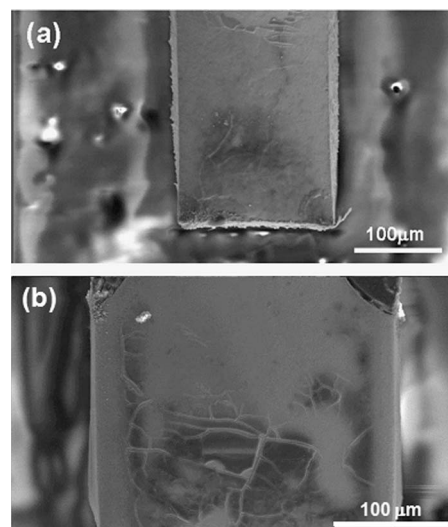


FIG. 4. SEM images showing the surface morphology of the reflowed sample (a) at lead tip, and (b) at top region after the 3000-h storage at 60 °C/90% RH ambient. Tin whisker growth was further suppressed.

is found that the whole Sn layer becomes oxidized. The EDS results indicate that it becomes Sn oxide. For the annealed sample, oxidation was not serious, as shown in Fig. 5(b). The EDS analysis shows that only the surface of the Sn layer became oxidized. As for the reflowed sample, most of the area was not oxidized, as shown in Fig. 5(c). The interfacial IMC grew thicker after the reflowing process. To examine the microstructure of the Sn film near the root of a whisker, FIB cross-sectional etching was performed in the vicinity of a whisker. Figure 5(d) shows the tilted FIB image near a whisker grown from uncorroded area in region A for the as-fabricated sample after the 3000-h THT. The whisker is labeled in the Fig. 5(d). In addition, the Sn grains appear to be columnar. It is found that there was no growth or formation of Cu_6Sn_5 in the Sn grain boundary, indicating that the IMC formation was not the driving force for whisker growth in this testing condition. Instead, a white patch appeared near the root of the whisker, and it extended to the interface of the Sn and the IMC layer. This region was identified to constitute of Sn and oxygen by SEM EDS.

To further verify the microstructure of near the root of the whisker in Fig. 5(d), a TEM sample was prepared by FIB. The dotted square in Fig. 5(d) indicates from where the TEM sample was cut. Figure 6(a) illustrates the TEM image for that region, and the corresponding diffraction patterns for the left and right regions are shown in Fig. 6(b) and 6(c), respectively. The left region appears to be a Sn grain; while the white patch in Fig. 5(d) is identified to be polycrystalline SnO_2 . The results indicate that oxygen may diffuse faster along the grain boundaries of the Sn finish, causing the whole Sn film near the grain boundary to be oxidized. Therefore, the oxidation of the Sn film during the THT may produce compressive stress, resulting in whisker growth in the neighboring grains.

To investigate the mechanism of how the annealing and reflowing treatments can suppress whisker growth, the microstructure of the Sn film and the IMC layer for the above three samples were examined. Figures 7(a)–7(c) illustrate the

TABLE I. The longest whisker that can be observed after the 1000-h and 3000-h THTs for the three sets of samples in this study.

THT storage time (h)	As-fabricated		Annealed at 220 °C		Reflowed at 268 °C	
	1000	3000	1000	3000	1000	3000
Longest whisker length	21 μm	95 μm	13 μm	26 μm	0 μm	10 μm

cross-sectional SEM images for the as-fabricated, annealed, and reflowed samples before the THT, respectively. The IMC thickness was 1.3, 1.3, and 5.0 μm for the as-fabricated, annealed, and reflowed samples, respectively. In addition, the IMC did not form in the grain boundaries of Sn grains. Although thicker Cu_6Sn_5 IMCs may produce more compressive stress in the Sn film, the reflowed sample had the shortest whiskers among the three samples, indicating that the IMC growth is not the driving force for the Sn whisker growth in the present study. As mentioned above, the driving force for whisker growth during THT was the compressive stress induced by tin oxide formation. Therefore, the annealed and reflowed samples must gain some advantage to resist the formation of Sn oxide, and thus had slower whisker growth rate. Figure 8(a) shows an OM photograph for the grain structure of the Sn film before thermal treatments. Columnar

grains exist for the Sn film, which is consistent with the FIB results in Fig. 5(d). After the annealing treatment, the grain structure did not change much, and it remained columnar, as shown in Fig. 8(b). However, the grain size (width) in Fig. 8(b) may increase to 54 μm . Thus, the annealing treatment reduces the total area of the grain boundary, causing the Sn film to become more resistive to the oxidation, since oxygen may diffuse more easily through the grain boundaries of the Sn film. For the reflowed sample, the grain structure varies with the thickness of Sn film. For the thicker area at Regions A and C, the grain structure became equiaxed, as shown in

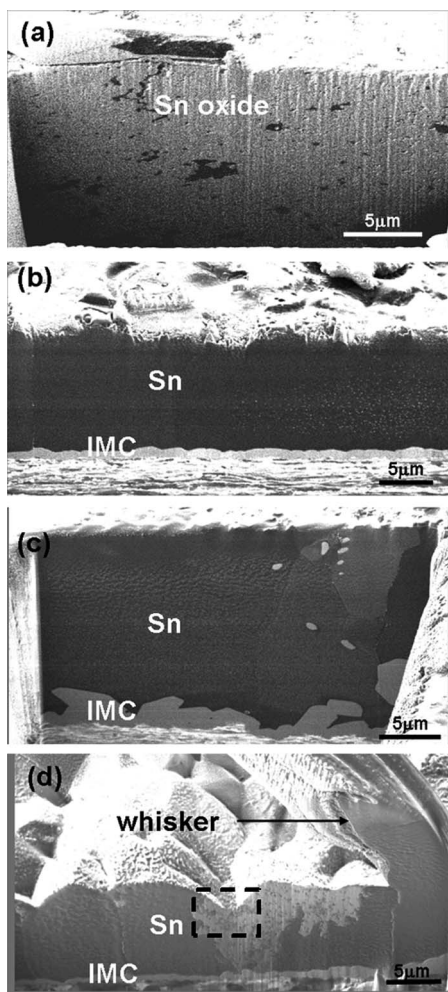


FIG. 5. Cross-sectional FIB images for (a) as-fabricated, (b) annealed, and (c) reflowed sample after the 3000-h THT. Extensive Sn oxide was formed at the corroded region in the as-fabricated sample. (d) FIB image showing the root of a whisker and its neighboring grains. Serious oxidation was found near the root of the whisker.

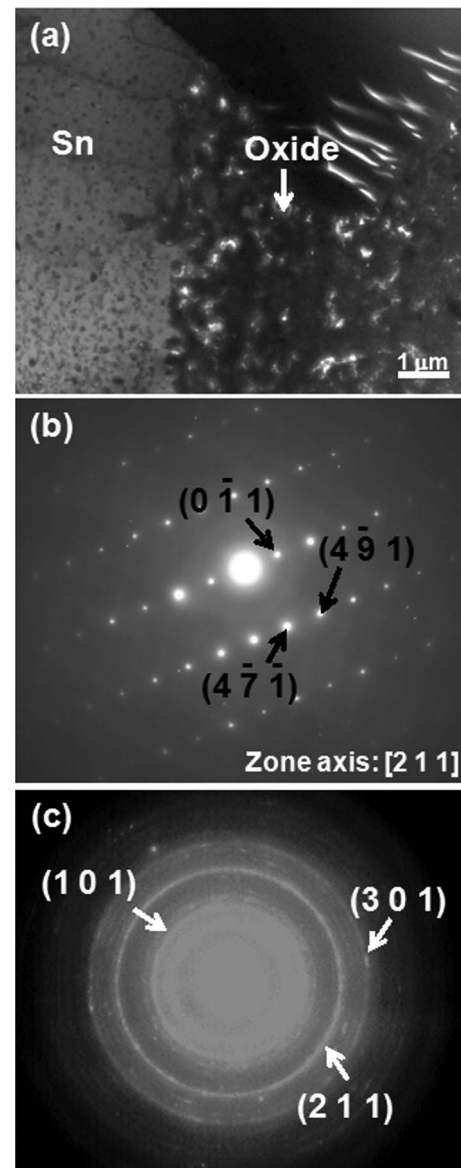


FIG. 6. (a) TEM image for the dotted-square region in Fig. 5(d). Very thick tin oxide was found in the Sn film near the root of a whisker. (b) The diffraction pattern for the Sn film. (c) The diffraction pattern for the oxide and the oxide layer is identified as SnO_2 .

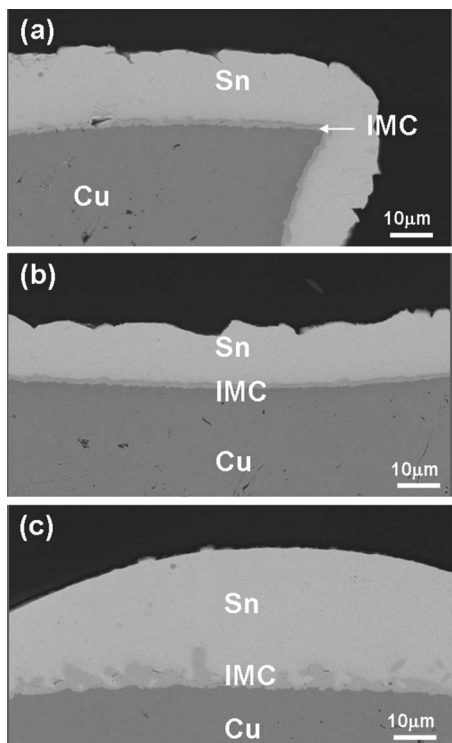


FIG. 7. Cross-sectional SEM images of the leadframe after the 3000-h THT for (a) as-fabricated sample, (b) the sample annealed at 220 °C, and (c) the sample reflowed at 268 °C.

Fig. 9(a). This is because the Sn film melted and solidified during the reflowing treatment, and the film thickness in these regions was over 50 μm. Such grain structure may hinder the grain boundary diffusion of Sn, as proposed by Boettinger *et al.*¹² Therefore, the reflowed sample not only has a reduced grain boundary area, but also possesses a lower supply rate of Sn atoms, resulting in a significantly slower growth rate of the Sn whiskers.

IV. DISCUSSION

The oxidation of the Sn film provides the driving force for Sn whisker growth. It is known that a dense SnO or SnO₂

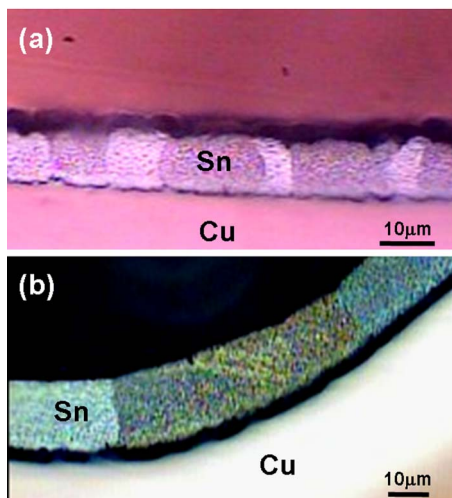


FIG. 8. Cross-sectional OM images of the grain boundary structure for (a) as-fabricated, and (b) annealed samples. The Sn grain size increased after the annealing treatment.

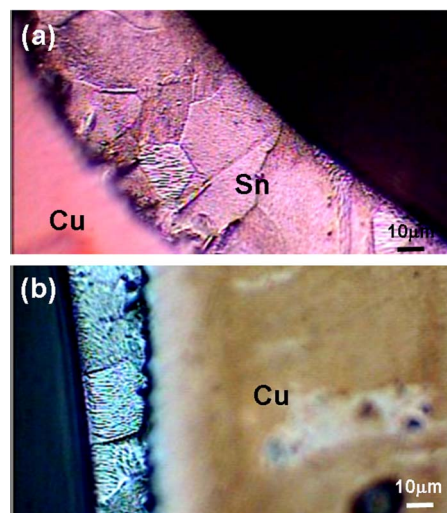
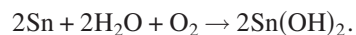
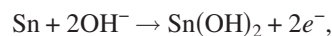
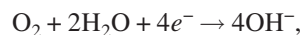


FIG. 9. (a) Cross-sectional OM images showing the formation of equi-axed grains in the thicker region of Sn film for the reflowed sample. (b) Cross-sectional OM image showing the columnar grain structure in the thinner region of Sn film after reflowing treatment.

film may form during the oxidation of the Sn film, and the increase in volume induced by the oxidation produces compressive stress. In this study, it is found that SnO₂ formed along the grain boundary of the Sn finishes and extended to the neighboring region after the THT. This process produces the driving force for the growth of the Sn whiskers under humid ambient environment. It is noteworthy to mention that corrosion of the Sn film also took place sometimes near the tip and the top regions, which formed fragile rust of Sn(OH)_x, as indicated by the arrows in Fig. 2(a). To investigate this issue, cross-sectional observation by OM was performed. Figures 10(a)–10(c) show the cross-sectional OM photographs near the tips of the legs after the 3000-h THT for the as-fabricated, annealed, and reflowed samples, respectively. It is found that corrosion happened at the tip region for all three samples. In addition, corrosion also happened at the top region for the as-fabricated sample, as shown in the cross-sectional OM photograph in Fig. 11(a). Yet, no corrosion was found for the annealed and reflowed samples, as illustrated in Figs. 11(b) and 11(c). The reason why the corrosion could happen in the leadframe during the THT may be attributed to the galvanic couple of Sn and Cu. At the tip region where the lead was cut, the Cu was exposed to water vapor, corrosion may occur due to water condensation. The Sn layer and the Cu base may form a galvanic couple with Sn layer being the anode and the Cu base being the cathode. The following reactions may take place:



In general, this aqueous corrosion occurs in a large area of the cathode and a small area of the anode. This reaction also may happen in the leadframe near the tip region when the tip was cut, since the cross section of the Cu (cathode) was approximately 2.4 times larger than that of the Sn film

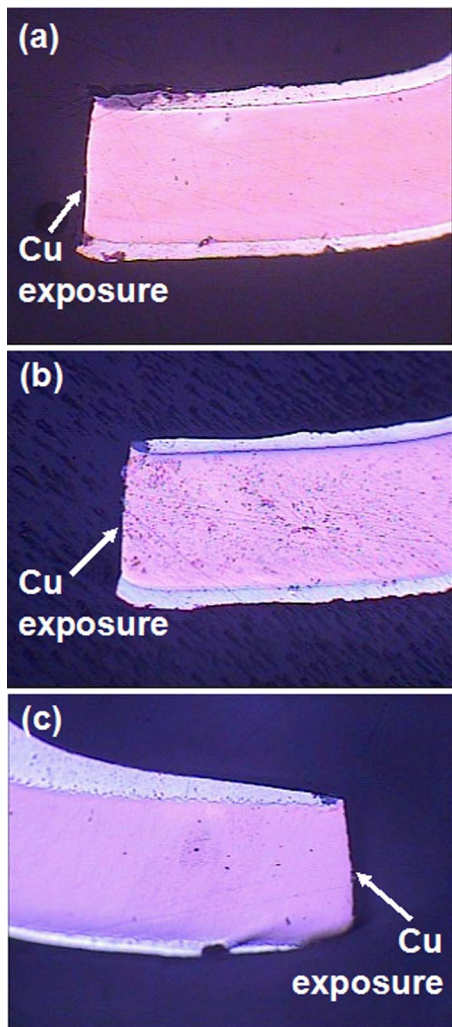


FIG. 10. Cross-sectional OM images of the leadframe leg near the top region for (a) as-fabricated sample, (b) the annealed sample, and (c) the reflowed sample. Corrosion was also observed in the Sn film close to the exposed Cu base after THT.

(anode). For the top region, some of the Cu base near the molding compound was also exposed to the humid ambient, as indicated in Fig. 11(a). Thus, corrosion may also occur in the top region. The residual stress seems to enhance the formation of corrosion. For the as-fabricated sample, the legs were bent and cut, causing high residual stress in the tip and in the top regions. Hence, the corrosion occurred seriously in those two regions. For the annealed sample, recrystallization and grain growth occurred during the annealing treatment, and thus the residual stress and the total area of grain boundary were reduced, resulting in a much slower corrosion rate, as shown in Figs. 10(b) and 11(b). As for the reflowed sample, the Sn layer melted and solidified. As a result, no residual stress existed in the solidified Sn film. In addition, the quality of the Sn film may also become better after reflow, and thus corrosion was almost eliminated for the reflowed samples.

Since this rust is quite loose, it may not be able to modify the stress in the neighboring Sn film. Thus, there should be no whiskers grown in the corroded regions. However, whiskers grew sometimes in the vicinity of the cor-

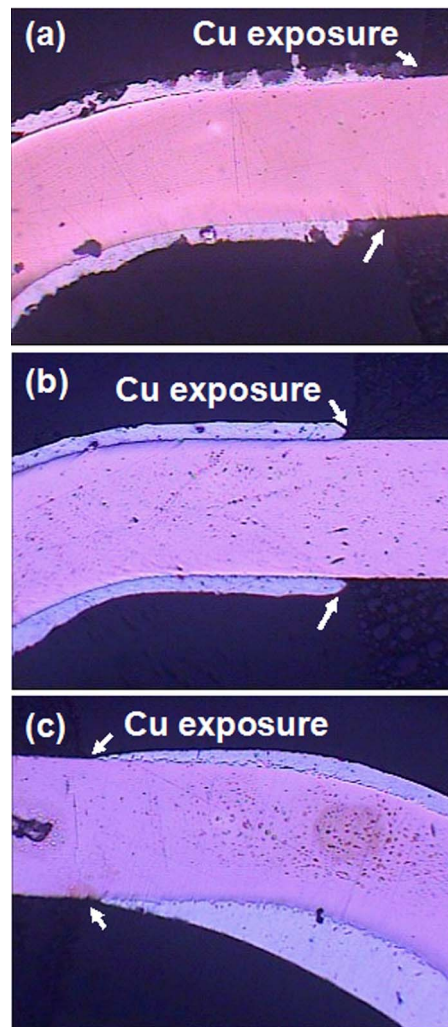


FIG. 11. Cross-sectional OM images of the leadframe leg near the top region for (a) as-fabricated sample, (b) the annealed sample, and (c) the reflowed sample. Corrosion was also observed in the Sn film close to the exposed Cu base near the molding compound after THT for the as-fabricated sample.

roded regions, as shown in Fig. 2(a). This phenomena is also observed by other researchers.^{19,20} How the corrosion of the Sn film affects the whisker growth is not clear, and more studies need to be done to clarify this issue.

V. CONCLUSIONS

The effects of annealing and reflowing on Sn whisker growth have been studied using THT. It is found that both annealing and reflowing treatments after assembly can retard the growth rate of the whiskers. The heat treatments were effective in reduction of the grain boundary area of the Sn finish, resulting in a slower rate of oxidation. Since oxidation provides the compressive stress needed for the Sn whisker growth under THT, the heat treatments could mitigate the Sn whisker growth. In addition, the reflowing treatment produced an equiaxed grain structure after solidification, which had slower grain boundary diffusion of Sn than the columnar structure. Therefore, the reflowing process is an excellent way for relieving Sn whisker growth in the Sn finish on the Cu leadframes.

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