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Rapid whisker growth on the surface of Sn–3Ag–0.5Cu–1.0Ce solder joints

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In spite of the many beneficial effects obtained from the addition of rare earth elements to solder alloys, rapid growth of tin-whiskers has been found in Sn–3Ag–0.5Cu–1.0Ce solder joints. The morphology of the whiskers changes from fiber-shaped to hillock-shaped when the storage temperature increases from 25 to 150 °C. The driving force for the whisker growth is the compressive stress resulting from the volume expansion of the oxidized $CeSn_3$ phase, which is constrained by the surrounding solder matrix.
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The eutectic Sn–Ag–Cu alloy system has been considered to be the most promising candidate on environmental grounds to replace traditional Sn–37Pb solder. Many studies have shown that Sn–Ag–Cu solders possess superior mechanical properties such as high strength, good ductility and long fatigue life [1]. To gain further improvement of its creep resistance, Chen et al. added rare earth elements to this solder [2]. They found that the creep rupture life of a Sn–3.8Ag–0.7Cu alloy with 0.2 wt.% mixed metal (Ce, La) addition is 7-fold higher than that of undoped Sn–3.8Ag–0.7Cu [2]. Another study from Chen et al. indicated that the addition of 0.1 wt.% mixed metal into Sn–3.8Ag–0.7Cu solder resulted in the increase of its creep stress exponents [3]. Recently, Dudek et al. have presented evidence that the strain to failure of a Sn–3.8Ag–0.7Cu solder containing 0.5 wt.% La is increased by nearly 150% over that of undoped alloy [4]. In fact, rare earth elements have also been reported to be beneficial for the wettability, tensile strength and creep resistance of many other Pb-free solder alloys such as Sn–3.5Ag [5], Sn–0.7Cu [6] and Sn–9Zn [7].

In the development of Pb-free solders, whisker growth is an important issue for the reliability of electronic devices. It is known that the whiskers on solder joints can grow to lengths of a few hundred microns, and that these whiskers possess a chemical composition near to that pure tin, with good electrical conductivity. This may result in short circuiting or interference with other devices. For the mechanism behind tin whisker formation, many researchers have proposed that the growth is related to oxidation of the solder surface and compressive stress in the solder interior. For a Cu/Sn thin film specimen, Tu reported that a compressive stress induced by the formation of Cu_6Sn_5 intermetallic compounds at the Cu/Sn interface extruded the tin atoms out of the outer oxide layer of Sn film [8]. Sheng et al. suggested that tin whiskers are squeezed by an internal compressive stress to sprout from the weaker spots in the oxide layer on the outer surface of the solder [9]. Boettinger et al. proposed another mechanism for the formation of hillocks and whiskers on the electroplated Sn and Sn–Cu films on Cu substrates, based on localized creep of columnar grain structures to relieve the intrinsic compressive stresses in plated thin films [10].

In most cases, the growth of tin whiskers in solder joints occurs very slowly, with a typical rate of 0.01–0.1 Å/s, as summarized in the literature [11]. Since rare earth elements are notable for their high chemical activity, they can much more easily react with the oxygen in the air and accelerate tin whisker growth in a rare earth element-containing solder alloy. Evidence validating this suspicion has been found in this study on Sn–3Ag–0.5Cu–1.0Ce solder joints after room temperature storage in air. A whisker growth rate of 1.2 Å/s has been observed in this case. If the specimens are heated to 150 °C, tin whiskers appear as early as after 15 min, and their morphology is different from that observed during room temperature storage.

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For the experiments, Sn–3Ag–0.5Cu–1.0Ce solder was prepared by melting a Sn–6.6 wt.% Ce master alloy at 1000 °C in 10^{-5} Torr vacuum and then remelting it under the same conditions, adding the Sn, Ag and Cu elements. The ingot was rolled into a 180 μm thick plate and punched into a disk with a diameter of 400 μm. The solder disks were dipped in rosin mildly activated (RMA) flux and then placed on the Cu pads of a printed circuit board, which had been surface-finished with immersion Ag. The specimens were reflowed in a hot-air furnace with a soaking temperature and a peak temperature of 190 and 240 °C, respectively. The surface tension of Sn–3Ag–0.5Cu–1.0Ce alloy causes the solder disks to become spherical solder balls after solidification.

The reflowed solder joints were cut through the cross-section of a row of solder balls and polished with 0.3 μm Al_2O_3 powder. The cross-sectioned specimens were stored at room temperature and at 150 °C in air. After various storage periods, the whiskers that appeared on the surface of the solder balls and cross-sectioned specimens were observed via scanning electron microscopy (SEM), and their chemical compositions were analyzed using an electron probe microanalyzer (EPMA).

Figure 1(a) and (b) reveals that whiskers appear on the surface of Sn–3Ag–0.5Cu–1.0Ce solder balls after storage at room temperature for 10 days. The morphology of these whiskers can be curly (Fig. 1(a)) or linear (Fig. 1(b)). The maximum growth rate in this case is about 1.2 Å/s, which is much higher than rates reported in the literature [11].

The cross-section of as-reflowed Sn–3Ag–0.5Cu–1.0Ce solder joint contains needle-like Ag_3Sn and cluster-shaped $CeSn_3$ precipitates, as shown in Figure 2(a). In addition, scallop-shaped Cu_6Sn_5 intermetallic compounds appear in the solder matrix and at the solder/pad interface. After storage at room temperature for 3 days, the surface of the cluster-shaped $CeSn_3$ phase becomes dark in color (Fig. 2(b)). EPMA analysis shows that its chemical composition changes to Ce:Sn:O = 25.6:18.3:56.1. However, the composition of the solder matrix remains unchanged. This demonstrates that the $CeSn_3$ precipitate oxidizes much more easily than the Sn–3Ag–0.5Cu–1.0Ce solder matrix. The oxide layer of the $CeSn_3$ precipitates was analyzed via transmission electron microscopy (TEM). Figure 3(a) shows that its grain size is about 0.1–0.2 μm, and the diffraction pattern in Figure 3(b) shows that the oxide layer is a CeO_2 phase. The TEM results, in combination with

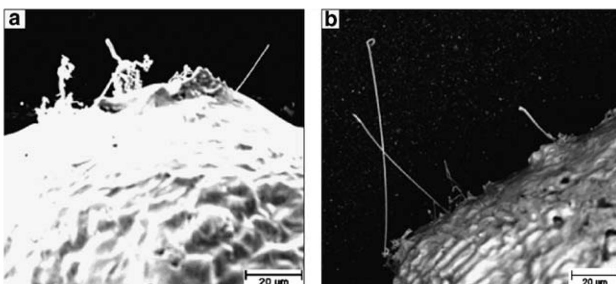

Figure 1. Whiskers formed on the surface of a Sn–3Ag–0.5Cu–1.0Ce solder joint after storage at room temperature for 10 days.

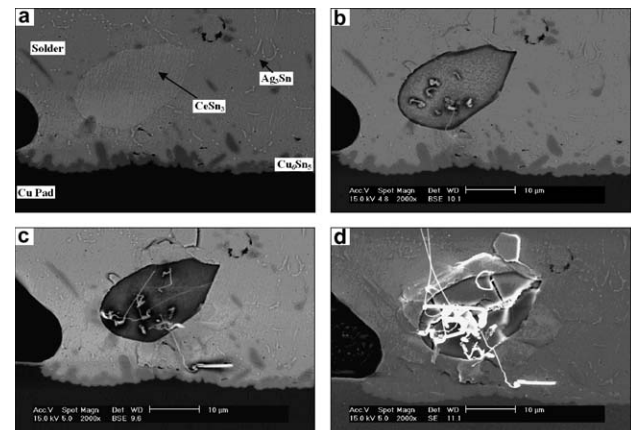

Figure 2. Thread-type whisker growth in Sn–3Ag–0.5Cu–1.0Ce after storage at room temperature for various time periods: (a) as reflow, (b) 3 days, (c) 7 days, (d) 14 days.

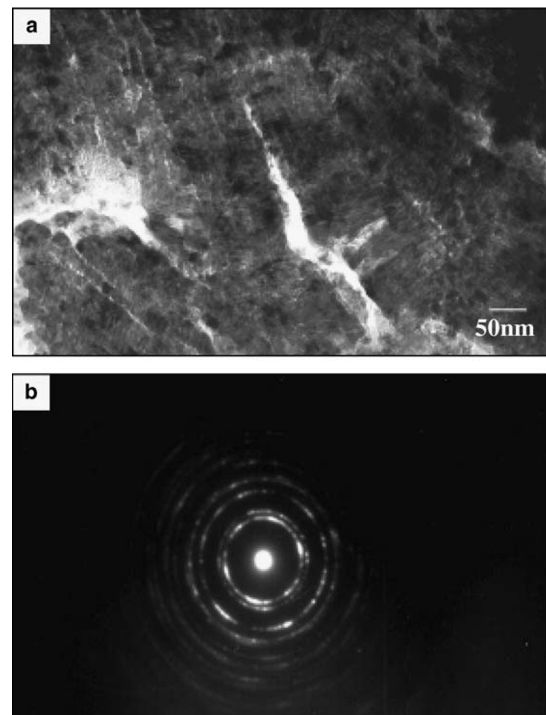

Figure 3. TEM analysis of the oxide layer on the outer surface of $CeSn_3$ precipitates formed in the Sn–3Ag–0.5Cu–1.0Ce solder alloy.

the existence of tin content (18.3 at.%) in the EPMA analysis, imply that the pure tin contained in the oxide layer of $CeSn_3$ precipitate is inserted in the CeO_2 phase.

Figure 2(b) also shows that during the oxidization of the $CeSn_3$ phase, many tin sprouts appear on the oxide layer, growing to long whiskers as storage durations increase (Fig. 2(c) and (d)). Figure 2(d) reveals that after long storage periods, the oxide layer of $CeSn_3$ phase has cracked, and the solder matrix adjacent to the $CeSn_3$ phase has been pushed outward to become a convex surface around the $CeSn_3$ phase. This phenomenon implies that the oxide layer of $CeSn_3$ has expanded in volume. The volume expansion of oxidized $CeSn_3$ phase is attrib-

uted to the diffusion of oxygen into the $CeSn_3$ lattice during oxidation, which is constrained by the surrounding solder matrix and results in a compressive stress that squeezes the unoxidized tin atoms in the oxide layer of $CeSn_3$ phase, thus forming tin whiskers.

When the storage temperature is raised to 150 °C, whiskers appear as early as the 15 min mark, and their morphology changes to hillock-shaped with a large size of 3–5 μm in diameter (Fig. 4(b)). The maximum growth rate for the hillock-length in this initial stage reaches 5.5 Å/s. However, further increases in the storage time do not cause these hillocks to grow (Fig. 4(c) and (d)). Figure 4 shows that the hillocks are extruded from the solder matrix around the oxidized $CeSn_3$ phase, rather than from the interior of the oxidized $CeSn_3$, as in the case of long whisker growth during room temperature storage. Furthermore, EPMA analysis indicates that the hillocks contain a certain amount of Ag, confirming the morphological observations. In addition to these hillocks, Figure 4 also reveals that a few sprouts are squeezed out of the oxide layer on the $CeSn_3$ phase, which, in contrast to the surrounding hillocks, has been determined to possess a chemical composition approximating that of pure tin.

In order to clarify the mechanism for the growth of whiskers and hillocks in this study, a specimen that had been stored at 150 °C for 1 h was cut across the $CeSn_3$ phase (Fig. 5(a)). This cross-section, as demonstrated in Figure 5(b), reveals very thick oxide layers on the outer surface of the $CeSn_3$ precipitates. The micrograph in Figure 5(c), taken at a larger magnification, indicates that a thin layer of pure tin is inserted into the cerium oxide layer. This tin layer might have originated from the unoxidized tin atoms released from the $CeSn_3$ phase after the reaction of cerium with oxygen. It is proposed that the volume expansion caused by the formation of the thick oxide layer on $CeSn_3$ induces a large compressive stress, which squeezes the Sn–3Ag–0.5Cu–1.0Ce solder matrix around the oxidized $CeSn_3$ phase to form the hillocks during storage at 150 °C. On the other hand, the pure tin layer inserted into the cerium oxide is also squeezed out through the inherent defects in the oxide layer, which results in

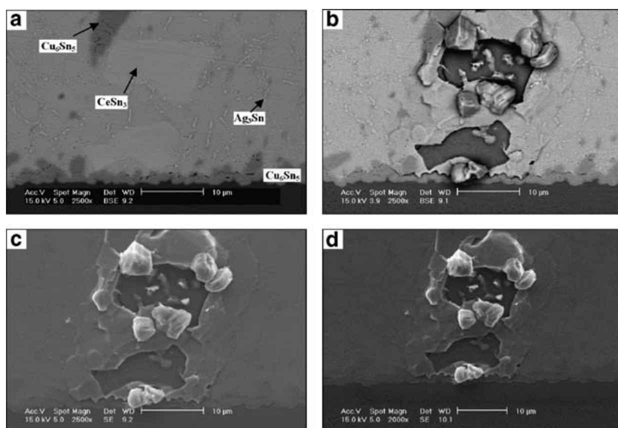

Figure 4. Hillock-type whisker growth in Sn–3Ag–0.5Cu–1.0Ce after storage at 150 °C for various time periods: (a) as reflow, (b) 15 min, (c) 30 min, (d) 45 min.

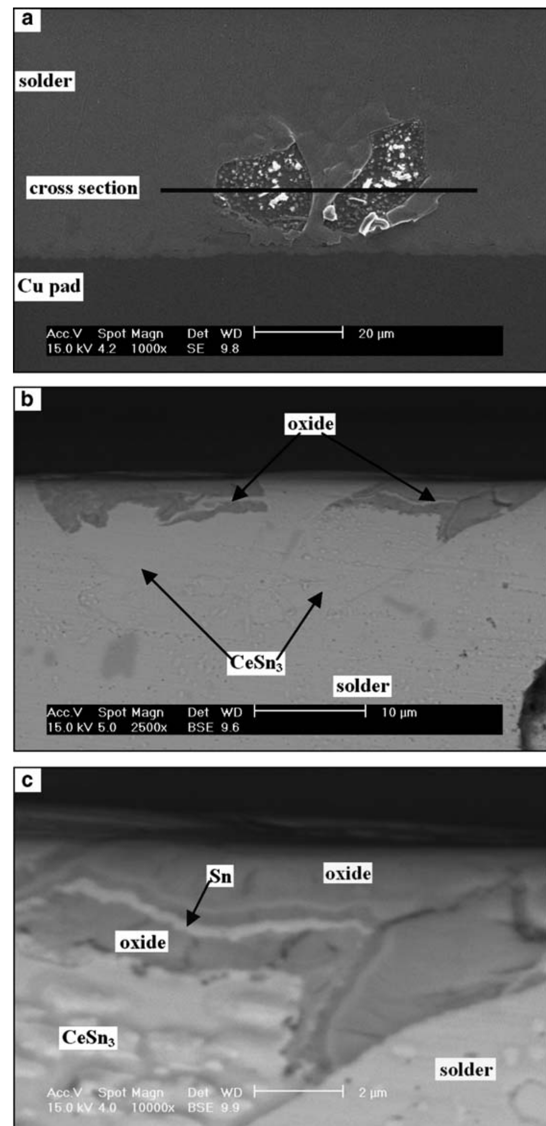

Figure 5. Three-dimensional cross-section of an oxidized $CeSn_3$ phase with whiskers grown on its surface oxide, in a Sn–3Ag–0.5Cu–1.0Ce joint after storage at 150 °C for 1 h.

the tin sprouts in the inner region of the oxidized $CeSn_3$ phase. Since the driving force (compressive stress) has been exhausted by the hillock formation, these tin sprouts do not lengthen further. In storage at room temperature, the compressive stress is insufficient to cause the extrusion of large-volume hillocks. Instead, the slow oxidation reaction creates a milder compressive stress, which leads to a continuous growth of tin sprouts on the oxidized $CeSn_3$ phase to form long whiskers. It is obvious that the origin of compressive stress as the driving force for the whisker growth is quite different from whisker growth mechanisms reported by Tu [8], Sheng et al. [9] and Boettinger et al. [10]. In addition, Boettinger et al. suggested that the formation of whiskers on electroplated Sn and Sn–Cu films resulted from the flowing of Sn atoms vertically toward the specimen surfaces through the columnar grain boundaries. The appearance of Sn channels parallel to the specimen surfaces in Figure 5(b) and (c) indicate that the mechanism of

whisker growth in this study is different from that found by Boettinger et al. [10].

In conclusion, the cluster-shaped $CeSn_3$ precipitates in a rare earth element-containing Sn–3Ag–0.5Cu–1.0Ce solder oxidize significantly more than the solder matrix. The oxide layer has been analyzed as CeO_2 phase with pure Sn inserted into it. Along with the oxidization reaction during storage at room temperature, many tin sprouts on the oxidized $CeSn_3$ surface grow rapidly to long whiskers, with a maximum growth rate of 1.2 Å/s. Raising the storage temperature to 150 °C causes many large hillocks to be extruded from the adjacent Sn–3Ag–0.5Cu–1.0Ce solder matrix surrounding the oxidized $CeSn_3$ phase. A certain number of tin sprouts can also be found in the inner region of oxidized $CeSn_3$, where they cannot grow to long whiskers. The formation of fiber-shaped whiskers during room temperature storage and of short tin sprouts at 150 °C is attributed to the volume expansion accompanying the oxidization of $CeSn_3$ precipitates in this solder, which leads to a compressive stress that extrudes the unoxidized pure Sn layer inserted into the CeO_2 oxide out of the $CeSn_3$ surface. However, the rapid formation of a thick oxide layer during storage at 150 °C drastically induces a large compressive stress, which squeezes the Sn–3Ag–0.5Cu–1.0Ce solder alloy around the oxidized $CeSn_3$ phase outward to form coarse hillocks. From the viewpoint of the electronics industry, in spite of the many beneficial effects obtained from the addition of rare earth elements to solder alloys, the formation of whiskers and hillocks can cause short circuits in solder joints, which is clearly undesirable in electronic devices.

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