Rapid growth of tin whiskers on the surface of Sn–6.6Lu alloy

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During the storage of a Sn–6.6Lu alloy in air for several days, large amounts of thread-like tin whiskers appear on the oxidized surface of Lu_4Sn_5 precipitates in this alloy. Storage at 150 °C for 30 min causes hillock-type whiskers to form. The driving force for whisker growth in this Sn–6.6Lu alloy is the compressive stress resulting from the diffusion of oxygen into the lattice of the Lu_4Sn_5 precipitates.

The formation of tin whiskers on electrodeposited Sn and Sn-alloys has been acknowledged for over 50 years [1]. Tin whiskers were found to be single crystals with a typical length of a few hundred micrometers which sprout from the Sn matrix and can get kinked during the growth process. Typical growth rates of tin whiskers in a bulk material are about 0.01–0.1 Å s^{-1} [2]. However, some cases with more rapid growth rates have been reported. Tin whiskers were observed by Furuta and Hamaura to grow in a rapidly cooled Al–50%Sn film at rates of about 0.5–5 Å s^{-1} [3]. Higher whisker growth rates of about 2–4 Å s^{-1} were found in electroplated Sn–Mn films [4]. Liu et al. reported that tin whisker growth can be accelerated to 3 Å s^{-1} with an electrical current density of $1.5 \times 10^5 \text{ A cm}^{-2}$ [5]. They also found that the whisker growth rates increase with rising temperature.

Several models for the growth mechanism of tin whiskers, including dislocation theory [6] and recrystallization theory [3], have been proposed. However, other researchers have reported that tin whisker growth is related to the outer oxide layer on the Sn surface and the internal compressive stress in the Sn matrix. Tu studied the tin whiskers on a bimetallic Cu–Sn thin-film specimen and proposed the existence of a biaxial compressive stress produced in Sn film accompanying Cu_6Sn_5 formation, which drives the extrusion of the whiskers from the outer oxide layer [7]. Sheng et al. further suggested that whiskers sprout from weaker spots of the oxide layer on

the Sn surface and that the roots of whiskers become localized stress relief centers [8].

It is known that rare-earth elements exhibit high chemical activity. Sn alloys containing rare-earth elements should readily form an oxide layer that can give rise to the growth of tin whiskers. This study presents the effect of rare-earth elements on tin whisker growth in a Sn–6.6Lu solder alloy.

For the preparation of the Sn–6.6Lu alloy, pure Sn (99.9%) and pure Lu (99.9%) were melted at 1000 °C under a 10^{-5} Torr vacuum. The as-cast specimens were cut with a diamond saw, and their cross sections were ground with 2000 grit SiC paper and polished with 0.3 μm Al_2O_3 powder. Some specimens were stored at room temperature in air, while others were aged at 150 °C in an air furnace. After various storage periods, the morphology of the tin whiskers that formed on the surface was observed by scanning electron microscopy (SEM). The chemical composition of the specimens was analyzed using an electron probe microanalyzer (EPMA).

The microstructure of the as-cast Sn–6.6Lu alloy contains many large precipitates, as shown in Figure 1(a). EPMA analysis indicates that the composition (at.%) of these precipitates is Lu:Sn = 44.4:55.6, which corresponds to the Lu_4Sn_5 phase. Figure 1(b) reveals that after storage at room temperature in air for 4 h, the surface of the Lu_4Sn_5 is covered with many bright particles, and its chemical composition (at.%) changes to Lu:Sn:O = 37.2:29.3:33.5. This result indicates that the Lu_4Sn_5 precipitates have oxidized much more rapidly than the matrix of the Sn–6.6Lu alloy. The bright
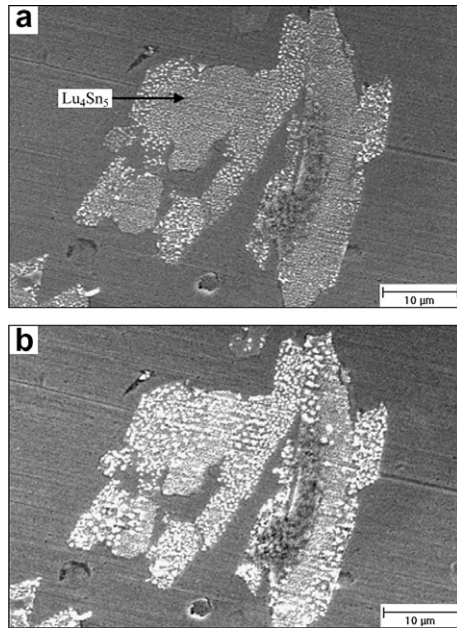
Figure 1. Morphology of Lu_4Sn_5 precipitates with tin particles distributed in Sn–6.6Lu alloy after air storage at room temperature for short periods: (a) 10 min, (b) 240 min.

particles are composed of nearly pure Sn, which implies that they are the sprouts of tin whiskers. With a further increase of the storage time to over 2 days, many thread-like whiskers appear in the oxidized Lu_4Sn_5 precipitation region, as shown in Figure 2(a). Some whiskers grow very quickly to a length of over 45 μm with an increase of storage time, as can be seen in Figure 2(b). The maximal growth rate of tin whiskers for the case of room-temperature storage in air is about 1 Å s^{-1}.

When the storage temperature is raised to 150 °C, tin whiskers form much earlier, as compared to the samples stored at room temperature. Figure 3(a) shows that some whiskers grew to a length of about 30 μm in the sample that was stored at 150 °C for only 10 min. The whisker growth rate in this case reaches about 500 Å s^{-1}. Such rapid and early growth of tin whiskers has never been reported previously in the literature. When the storage time is increased, a few hillock-type whiskers coexist with the thread-like whiskers in the oxidized Lu_4Sn_5 region, as shown in Figure 3(b). A long period of storage at 150 °C in air causes further growth of both the thread-like and hillock-type whiskers in the oxidized Lu_4Sn_5 region (Fig. 4). It can be seen in Figure 4(a) that more than 500 μm^3 of tin has been extruded out of the Lu_4Sn_5 precipitate in the micrograph after storage at 150 °C for 112 h through the growth process of hillock-type whiskers. In contrast, whisker growth was obviously reduced when the specimens were stored at room temperature for 3 days and at 150 °C for 2 h in a vacuum furnace of 10^{-3} Torr as illustrated in Figure 5(a) and (b), respectively. The results imply that the formation of tin whiskers in this Sn–6.6Lu alloy is closely related to the oxidation of Lu_4Sn_5 precipitates.

In order to clarify the mechanism for whisker growth in this rare-earth–Sn alloy, specimens were cut across the Lu_4Sn_5 precipitates. The three-dimensional cross section in Figure 6(a) reveals a continuous oxide layer with a thickness of about 2 μm on the outer surface of a Lu_4Sn_5 precipitate in the Sn–6.6Lu stored at room temperature for 4 h. The diffusion rate of oxygen, as estimated from the thickness of the oxide layer, is about 1.4 Å s^{-1}. The chemical composition (at.%) of the outer oxide layer is Lu:Sn:O = 30.9:35.1:34.0, which is similar to that analyzed for the surfaces of Lu_4Sn_5 phase in Figure 1(b), However, Figure 6(b) shows that in the specimen stored at 150 °C for 90 min, the oxygen
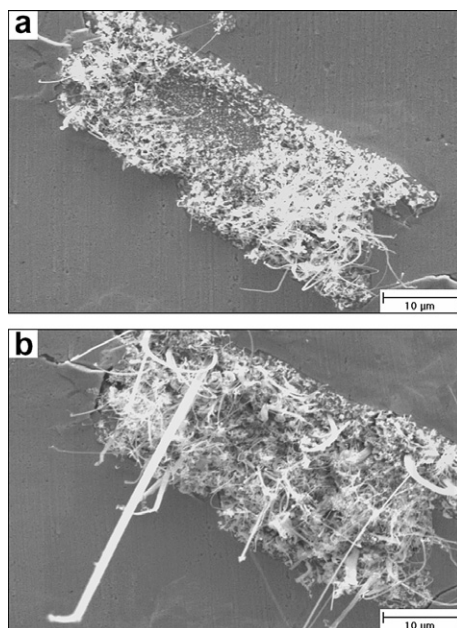

Figure 2. Thread-like tin whiskers formed on the surface of Lu_4Sn_5 precipitates in Sn–6.6Lu alloy after air storage at room temperature for long periods: (a) 48 h, (b) 240 h.

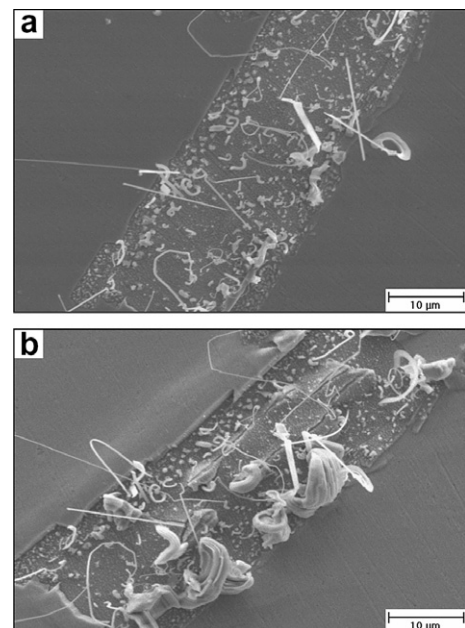**Figure 3.** Hillock-type tin whiskers formed on the surface of Lu_4Sn_5 precipitates in Sn–6.6Lu alloy after air storage at 150 °C for short periods: (a) 10 min, (b) 90 min.
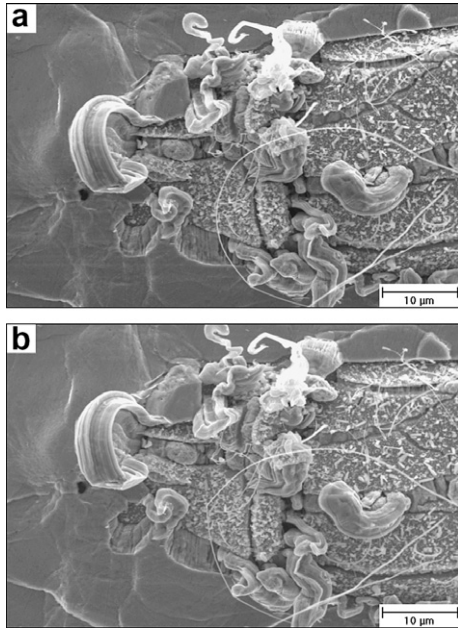
Figure 4. Hillock-type tin whiskers formed on the surface of Lu_4Sn_5 precipitates in Sn–6.6Lu alloy after air storage at 150 °C for long periods: (a) 112 h, (b) 224 h.
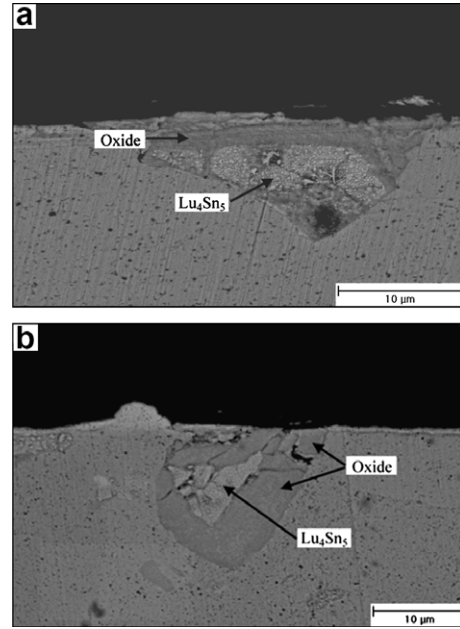

Figure 6. Three-dimensional cross section of Lu_4Sn_5 precipitates in Sn–6.6Lu alloy after storage in air: (a) at room temperature for 4 h, (b) at 150 °C for 90 min.
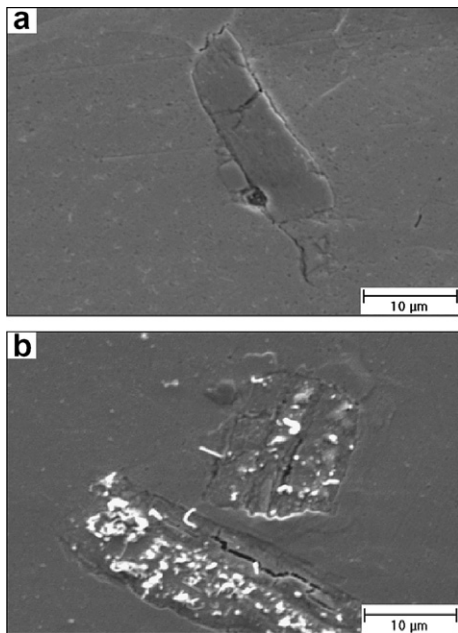

Figure 5. Morphology of Lu_4Sn_5 precipitates in Sn–6.6Lu alloy after storage in a vacuum furnace of 10^{-3} Torr: (a) at room temperature for 3 days, (b) at 150 °C for 120 min.

penetrated through the Lu_4Sn_5/Sn–6.6Lu interface to form a thick oxide layer of about 5 µm thickness on the outer surface and around the Lu_4Sn_5 phase in the interior of the specimen, which corresponds to a diffusion rate of about $10 \, \text{Å s}^{-1}$ for the oxygen into the Lu_4Sn_5 phase. EPMA analysis indicates that the enveloped oxide layer possesses a composition (at.%) of Lu:Sn:O = 51.3:5.9:42.8. The results imply that the Lu_4Sn_5 precipitates react predominantly with oxygen to form an

LuO layer due to the high activity of the Lu element: $2Lu_4Sn_5 + O_2 \rightarrow 8LuO + 10Sn$. The diffusion of oxygen into the crystal lattice of the Lu_4Sn_5 phase leads to lattice expansion, which is constrained by the surrounding matrix. A compressive stress can be created, which extrudes the resulting Sn atoms after oxidation out of the surface of the Lu_4Sn_5 phase. During storage at room temperature, Sn atoms in smaller quantities are extruded from the weak spots of the LuO layer to form thread-like whiskers that are uniformly distributed over the whole surface of the Lu_4Sn_5 phase. In this case, a higher Sn concentration of above 30 at.% was detected in the outer oxide layer. In contrast, large amounts of Sn atoms in the LuO around the Lu_4Sn_5 phase have been extruded to form hillock-type whiskers, and the Sn concentration in the enveloped LuO layer drops to a minor value of 5.9 at.%.

In conclusion, after storage at room temperature in air for several days, thread-like whiskers appear on the surface of Lu_4Sn_5 precipitates in Sn–6.6Lu solder alloy. The maximal growth rate of tin whiskers in this case is about $1 \, \text{Å s}^{-1}$. In contrast, no whiskers can be found in the Sn–6.6Lu matrix. During air storage at 150 °C, the thread-like whiskers grow to a length of about 30 µm in 10 min, which corresponds to an amazingly high growth rate of $500 \, \text{Å s}^{-1}$. After 30 min, hillock-type whiskers coexist with the thread-like whiskers in the Lu_4Sn_5 region of Sn–6.6Lu alloy. The rapid growth of tin whiskers in this rare-earth-element-containing alloy is attributed to the predominant oxidation of Lu atoms, which possess high chemical activity. The oxidation reaction results in the release of Sn atoms, which are inserted in the LuO layer. The diffusion of oxygen into the Lu_4Sn_5 phase leads to a compressive stress, which extrudes the resulting tin atoms out of the LuO layer.

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