Tin whisker growth on bulk Sn–Pb eutectic doping with Nd

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Abstract

Tin whisker growth is a serious reliability concern for electronics using high-density packaging. Whisker growth behavior of tin lead eutectic solders doped with different neodymium concentration (5–0.1 wt.%) was studied in present work. Results indicate that the Nd in the all of the Sn–Pb–Nd alloys mainly exists in NdSn₃ intermetallic compound, and that the distribution of the NdSn₃ phase is very non-uniform in the alloy with low Nd concentration. Tin whiskers growth was observed on all samples doped with Nd. All of these whiskers were seen to originate from the NdSn₃ phase, it appears that the Pb does not suppress whisker growth in these alloy because it does not influence the formation of the tin–rare earth intermetallic compound. These results suggest that the addition of rare earth elements into tin alloy systems renders whisker formation nearly inevitable. Therefore, any suggestion to dope tin-based solders with rare earth elements for application in high-density electronic packaging should be carefully reconsidered.

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1. Introduction

Tin whisker growth is a serious problem in the reliability of electronic devices with high-density electronic packaging. Since tin whisker is an excellent metal conductor, that is capable of inducing an electrical short in an electronic device, and sometimes, resulting in some calamitous accidents [1–3]. Therefore, both the whisker growth behavior and the growth mechanism have been paid attention to by both materials engineers and scientists for a long time [4–6]. With the advent of lead free soldering, many researches were focused on the whisker propensity and growth rate in deferent conditions, such as exposure to room ambience [7], stress [8,9], electrical current [8] and chemical composition [10,11]. Recently, Boettinger et al. [10] reported a interesting observation, in which they found that Cu had a significant effect on whisker formation and growth from Sn-plating. In the conclusion of the paper, they suggested that some impurities in a Sn-plating such as copper should be avoided in order to mitigate whisker growth.

Traditionally, tin whisker mainly occurred in the tin or tin alloy plating [12–14], and lead was an important element to mitigate the whisker growth. In 1959, Arnold [15] suggested that it was effective to mitigate the whisker growth by adding at least 3 wt.% Pb. This suggestion has been extensively applied in electronic industy, although the mechanism of whisker suppression is not clear yet. On the other hand, in looking for the new lead free solders, some research reports showed that rare earth element (RE)-doping (mainly Ce, La, Nd [16]) in the lead free solders was beneficial to improve their properties such as to increase strength, wetting ability, etc. [16–18]. Similar research has also been done early on the Sn–Pb solder [19]. However, recently, Chuang [20–22], Jiang and Xian [23,24] observed heavy whisker growth from the bulk tin and tin alloys by adding rare earth (RE) elements (Ce [20,22] and Nd [23,24]). Since tin–lead eutectic solders are now applied in some significant cases [1–3,25] in order to avoid the troubles resulted from the whisker growth, it raises the question: can Pb repress the whisker occurrence on the bulk RE-bearing tin–lead alloys? And whether there is a side effect when one chooses RE to add into Sn–Pb solder to improve its properties? This is a challenging question, at the same time it will also supply a new opportunity to observe and study the phenomenon of tin whisker growth.

2. Experiment

The composition design in present work was the eutectic Sn–Pb alloy (63% Sn and 37% Pb) doping with varying amounts of Nd (5.0%, 0.5%, 0.25% and 0.1%). An intermediate alloy of Sn–Pb eutectic–5.0%Nd was first prepared by melting. The raw materials, Sn (99.9%, wt.% as following), Pb (99.9%) and Nd (99.6% Nd and 0.4% Co), weighing about 20 g in all were melted in a graphite crucible in a resistance furnace at 800 ℃ for 20 min under a protective atmosphere, and then were rapidly cooled to room temperature to avoid a segregation of RE in the bulk alloys (when using a slow cooling rate, the Sn–RE intermetallic compound can float on the top of the ingot). The other compositions of alloys were prepared by the Sn–Pb eutectic alloy and the intermediate alloy of Sn–Pb eutectic–5.0%Nd using just the same process as described above. The Sn–Pb eutectic alloy without Nd was also prepared to compare with the Sn–Pb eutectic–Nd alloys.
The cast ingots were sectioned mechanically to prepare a polished surface, in order to observe the whisker growth. The surface of the samples were gradually ground by SiC paper up to 3000 grit, and then were mechanically polished with 0.5 µm Al₂O₃ powder to remove the surface scrapes during grinding. The polished surface of the Sn–Pb alloy was etched (90 vol.% C₂H₅OH and 10 vol.% HNO₃) for just a few seconds to observe the eutectic microstructure, while the alloys doped with rare earth were not etched, since the Sn–RE intermetallic compound in the microstructure was already apparent without etching. Finally the samples were exposed to ambient conditions (about 298 K, 35%RH, RH means relative humidity) to observe the whisker growth from the polished surfaces. All samples (including a Sn–Pb sample) used for whisker observation were not etched to prevent the influence of surface corrosion on the whisker growth.

The microstructure of the alloys was observed by both an optical microscope and a scanning electron microscopy (SEM). The whisker growth on the surface of the samples was first observed by the optical microscope periodically, in which only a whisker to be more than 10 µm in length can be observed by OM; then the details of the whiskers morphology were showed by SEM, since SEM has an excellent depth of focus to obtain a good sharpness. An Energy Dispersive X-ray Spectroscopy (EDS) attached to the SEM was used to measure the chemical compositions of the intermetallic compounds (IMCs) at the selected areas. The surface of the alloys were measured by the X-ray diffractometer (Rigaku D/MAX-2400, Cu Kα radiation λ = 0.15418 nm), in order to distinguish the possible chemical reaction before and after whisker growth.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the microstructures of the Sn–Pb and the Sn–Pb–RE solder alloys with Nd contents of 0%, 0.1%, 0.25%, 0.5% and 5.0%, respectively. The microstructure of the Sn–Pb eutectic alloy consisted of 100% eutectic structure, in which the eutectic interval between the tin slice and lead slice was in the range of 1–3 µm. The microstructure of the Sn–Pb–RE solder alloys consisted of both the Sn–Pb eutectic and the Sn–RE intermetallic compounds. As a comparison, the eutectic microstructure of the Sn–Pb–RE alloy was finer than that of Sn–Pb eutectic alloy. The morphology of the Sn–Nd intermetallic compounds was nearly round for Sn–Pb–5%Nd, and

![Fig. 1. Microstructure of the Sn–Pb eutectic–Nd alloys (right after polishing). (a) 63%Sn–37%Pb eutectic (etched); (b) Sn–Pb eutectic–5.0%wt.Nd; (c) Sn–Pb eutectic–0.5wt.%Nd; (e) Sn–Pb eutectic–0.25wt.%Nd; (e) Sn–Pb–0.1wt.%Nd.](image-url)
their size was about 15–20 μm in diameter. It is worth noting that, with the decreasing Nd concentration, the morphologies of the Sn–Nd intermetallic compounds gradually changed to fragments with irregular shapes, which was similar to the behavior of the Sn–Nd alloy reported earlier [23]. The amount of the Sn–Nd intermetallic compounds increased with Nd concentration, while the distribution of the Sn–Nd compounds became very non-uniform in the case of low Nd concentration. In some regions, no Sn–Nd compound was observed. Also the size of the Sn–Nd compound decreased with the reduction of Nd concentration. After polishing, compositional analysis of the Sn–Nd intermetallics was carried out by EDS, which showed that the Sn–Nd intermetallics was consisted of 75.8 at.% Sn and 24.2 at.% Nd. Based on the Sn–Nd binary phase diagram [26], the Sn–Nd intermetallics was NdSn3.

After exposure to air for 20 days, the composition of the Sn–Nd intermetallic was measured by EDS again, and was found to be 12.7 at.% Sn, 21.8 at.% Nd and 65.5 at.% O. In other words, there was a significant change from the original composition (75.8 at.% Sn and 24.2 at.% Nd), which implies strong oxidation of the NdSn3 surface under ambient conditions. Fig. 2 shows the color change of the NdSn3 compounds when it was exposed to the ambient conditions for 5 days. As shown in Fig. 2, the surface color of the NdSn3 was rapidly darkened, since oxygen is a light element, the darker color shows the existence of light elements for BSE image. This implies the formation of the oxidation product. In chemistry, the reason is that Nd in the NdSn3 is active in the ambient conditions. However, we were unable to distinguish the RE oxide on the surface by X-ray diffraction (XRD). The likely reason is that the amount of the RE oxide on the surface was too small to be measured by XRD.

3.2. Tin whisker growth

After oxidation of the NdSn3 surface, tin whiskers started to grow from the oxidized surface of NdSn3 under ambient conditions. Fig. 3 is a set of the SEM pictures of the whiskers grown from the Sn–Pb–Nd alloys (after 33 days). It was clear that the whiskers existed in all cases of different Nd-concentration alloys. The whis-

![Fig. 2. The oxidization of the NdSn3 intermetallic compound in Sn–Pb eutectic–0.1%Nd (a) right after polished; (b) 5 days after exposure in ambient condition.](image1)

![Fig. 3. Tin whiskers observed on the surface of the Sn–Pb–Nd alloys with different Nd concentration (298 K/35%RH, 33 days). (a) Sn–Pb–5.0%Nd; (b) Sn–Pb–0.5%Nd; (c) Sn–Pb–0.25%Nd; (d) Sn–Pb–0.1Nd.](image2)
kers were observed to originate exclusively from the area of the NdSn$_3$ compounds in the Sn–Pb–Nd alloys, and no whisker growth was observed on any Sn–Pb eutectic area. As a comparison, there was no whisker growth on the surface of the non-doped Sn–Pb eutectic alloy under the same conditions. This phenomenon shows that, once the NdSn$_3$ compounds exist, whether the size of the NdSn$_3$ compounds is big or small, whisker growth is observed on all samples of the Sn–Pb–Nd solders, even if the Nd concentration in the alloy is very low (such as only 0.1%). This represents a potential problem for the reliability of electronics, if a RE-bearing Sn–Pb solder is used in the electronic packaging.

The incubation time for the whisker growth, as observed by optical microscopy (OM), from the NdSn$_3$ compounds was about 5–7 days after polishing. After exposure to ambient conditions for 12 days, the longest whisker for Sn–Pb–5.0%Nd alloy observed by OM was about 200 μm, by which the average growth rate of the whisker was calculated at about 3.3 Å/s. Compared to the average growth rate (about 0.01–0.3 Å/s) of the whiskers on tin plating reported by Fang et al. [7], Tu [5], Ellis et al. [27], Choi [28] and Kedesh [29], this growth rate was very high. Recently, Chen and Wilcox [30] reported an example of high speed growth of whisker on electrodeposits of Sn doped with Mn, the whisker growth rate was about 2–6 Å/s; moreover, Panashchenko et al. [31] observed a more high growth rate (about 15 nm/s) of whisker on Sn–Cu finish. It is interesting that all of the observation was done on Sn with impurities.

As shown in Fig. 3a–c, both the long whiskers and short whiskers coexisted at the same area, which is consistent with other observation [32]. Moreover, as shown in Fig. 4a, some long whiskers and nodules coexisted at the same NdSn$_3$ block, in which the nodules may be the nucleation of the whisker for future growth. Also, the whisker growth behavior was scattered on the surface of the NdSn$_3$ compound, as shown in Fig. 3, there have been several long whiskers on some NdSn$_3$ blocks, but there also were no whiskers on other NdSn$_3$ blocks. These observations reflect the variability of the whisker growth behavior, which can not currently be explained.

Fig. 4. Morphology of tin whiskers on the surface of Sn–Pb–0.15%Nd exposed on ambient condition (293–298 K/35%RH) for different time: (a) coexistence of the long and short tin whisker (33 days), (b) straight flute whisker with stripe on the surface (22 days), (c) crooked flute whisker (22 days), (d) coexistence of big and fine whisker, one whisker with several kinks (22 days), (e) coexistence of big and fine whisker, fine whisker with a branch (33 days).
As shown in Fig. 4, there were mainly two kinds of whiskers on the NdSn3 surface. The first is fluted whisker with 1 μm or more in diameter (Fig. 4b), and the size of the whisker was relatively big, which was similar to the typical size (1–5 μm) of the whiskers in the case of tin plating [23,33]. There were obvious striations on the surface of majority of the whisker. The whisker was straight (Fig. 4b) or crooked (Fig. 4c), and the latter looked like a worm. There were also fine whisker with about 0.1–0.3 μm in diameter (Fig. 4.c–e), which is much less than the normal size of the tin whisker reported before [34]. It is interesting that there was a big root (as shown in Fig. 4c and Fig. 4e) for the fine whisker. This phenomenon implies that there may be secondary nucleation of the fine whisker on the original nodule. The whiskers on the surface of the Sn–RE alloys can grow relatively longer, Fig. 5 shows two long whiskers, in which one of them was measured as 200 μm in length. In the case of high-density electronic packaging, of cause, a long whisker such as this could be very harmful to the reliability.

Pb is such an element that can effectively prevent whisker growth from tin plating [15], however, present work shows that it is ineffective to mitigate the whisker growth from the Sn–Pb–Nd alloys, although the Pb concentration in the alloy has been up to 37%. Since Nd in the Sn–Pb–Nd alloys exists as the NdSn3 compound, and the tin whiskers only originated from the NdSn3 compound, it is a reasonable inference that Pb does not exert an influence on the mechanism of the whisker growth in this case. The reason and mechanism of the tin whiskers growth from the Sn–RE compound is interesting but is presently unclear. A basic observation on the phenomenon implies that it is related to the oxidation reaction between the Sn–RE compound and oxygen or water in air. Since the rare earth element is active in air, the oxidation reaction between the Sn–RE compound and oxygen is interesting but is presently unclear. A basic observation on the phenomenon implies that it is related to the oxidation reaction between the Sn–RE compound and oxygen or water in air. Since the rare earth element is active in air, the oxidation of NdSn3 surface will be inevitable, which would result in a decomposition of the NdSn3, and the fresh tin atoms would be released by this process. As a result, the nucleation and growth of the whisker will take place by the fresh tin atoms [23]. In this explanation, the influence of the environment on the whisker growth is significant, because it is a key factor for both the oxidation and decomposition of the Sn–RE compound. Obviously, this would be a further research project in the future. Also, if the oxidation mechanism does control the whisker growth and supplies the resource of the fresh tin atoms, it would explain why the whisker grows fast and inevitably on the NdSn3 surface.

4. Summary

The whisker growth behavior of the Sn–Pb eutectic solder doped with different Nd concentrations (5.0%, 0.5%, 0.25% and 0.1%) was studied in present work. Results show that Nd in the Sn–Pb–Nd alloys mainly exists as the NdSn3 compound in all alloys with different Nd concentrations, while the distribution of the Sn–Nd compounds was very non-uniform in the case of low Nd concentration. It was observed that whiskers grew on all samples doped with Nd, while they originated exclusively from the NdSn3 compound. Pb presence is ineffective in mitigating the whisker growth from the RE-bearing Sn solders, since Pb does not influence the formation of the Sn–RE compound. Present work reveals that the whisker growth is possible on the surface of the solders doped with RE, even if the Nd concentration in the alloy is very low (such as only 0.1%). Therefore, in the case of high-density electronic packaging, the application of the Sn–Pb eutectic solder doped with RE is not appropriate.

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