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Letter

Sn whisker growth in Sn–9Zn–0.5Ga–0.7Pr lead-free solder

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ABSTRACT

The spontaneous growth of Sn whisker in Sn–Zn series solder is newly reported in this work. It is found that during the exposure of Sn–9Zn–0.5Ga–0.7Pr bulk solder to ambient conditions for a few hours, many different lengths of needle-like Sn whiskers originate spontaneously from the Sn–Pr intermetallic compounds of the solder and grow rapidly at a rate of about 3.5 Å/s. It is proposed that the driving force for whisker formation is the compressive stress resulting from the oxidation of Sn–Pr compounds, and that the free Sn atoms released from oxidation reaction feed the whisker growth during exposure.

1. Introduction

Sn whisker growth is a serious reliability concern for electronic devices with high-density packaging since Sn whisker is a conductive metal wire, that is capable of causing many potential risks such as short circuiting, metal vapor arcing and interference with other components and finally results in the failure of devices [1,2]. Reports from the electronic industry indicate that whisker-inducing failures have resulted in many enormous losses including failures of satellites and military and medical devices [3]. Therefore, increasing attention has been paid to studying the details of whisker growth for sake of enhancing the reliability of electronic assemblies.

Traditionally, Sn whisker growth has been occurred mainly on tin-based thin films such as on tin electroplating and Sn–Cu finish [4,7]. Research from Nychka et al. [5] discuss that the thin-film geometry is required for whisker formation as it can provide a back stress for the growth, and that Sn whisker cannot be initiated in a bulk solder, even in the presence of mechanical stress or oxidation. However, recently, some new reports show that there is a potential risk of whisker growth in bulk lead-free solders. Liu and Xian [6] have reported that large amounts of Sn whiskers are present in Sn–0.7 wt.% Cu–Nd bulk solder, and lately they have found that whiskers can directly grow from the bulk $NdSn_3$ compounds [7]. Dudek and Chawla [8] have shown that varying-type whiskers take place on the surface of many Sn–3.9Ag–0.7Cu (wt.%, as following) based solders. Similar observations have also been found in Sn–6.6Lu and Sn–3Ag–0.5Cu–Ce bulk alloys [9,10]. Moreover, a further study by Chuang and Lin [11] showed that Sn whisker growth can be inhibited by element Zn, even the addition of 0.5 wt.% Zn into Sn–3Ag–0.5Cu–0.5Ce alloy could effectively diminish the rapid whisker growth in the solder.

In a series of our investigations on the microstructure and reliability of Sn–Zn based lead-free solders, an amazing phenomenon of Sn whisker growth was observed and discovered in Sn–9Zn–0.5Ga–0.7Pr bulk solder. It is worth noting that these whiskers originate spontaneously from the alloy and grow rapidly just under ambient air conditions. In addition, the element Zn contained in Sn–9Zn–0.5Ga–0.7Pr alloy seems to show no inhibition effect on the whisker growth. This result is quite different from the discussions previously reported. Since the application of lead-free solders in electronic manufacturing is inevitable [12–15], the potential risk of whisker growth in lead-free solders should cause more concerns. Our new findings would be helpful in re-understanding this issue.

2. Experimental

For the experiments, as-cast plates of Sn–9Zn–0.5Ga–0.7Pr solder were remelted with a peak temperature of 235 °C to simulate the reflow operations. The obtained specimens were tested by inductively coupled plasma auger electron spectroscopy (ICP-AES) to confirm the compositions, and then were mechanically polished with emery papers and diamond paste (0.5 μm) to remove the surface scratches. For the observation of microstructures, the polished specimens were etched with a solution of 5% HNO_3–alcohol and then dried. Finally, the specimens were kept under ambient conditions (at room temperature and in air) for half a day. The microstructures of the

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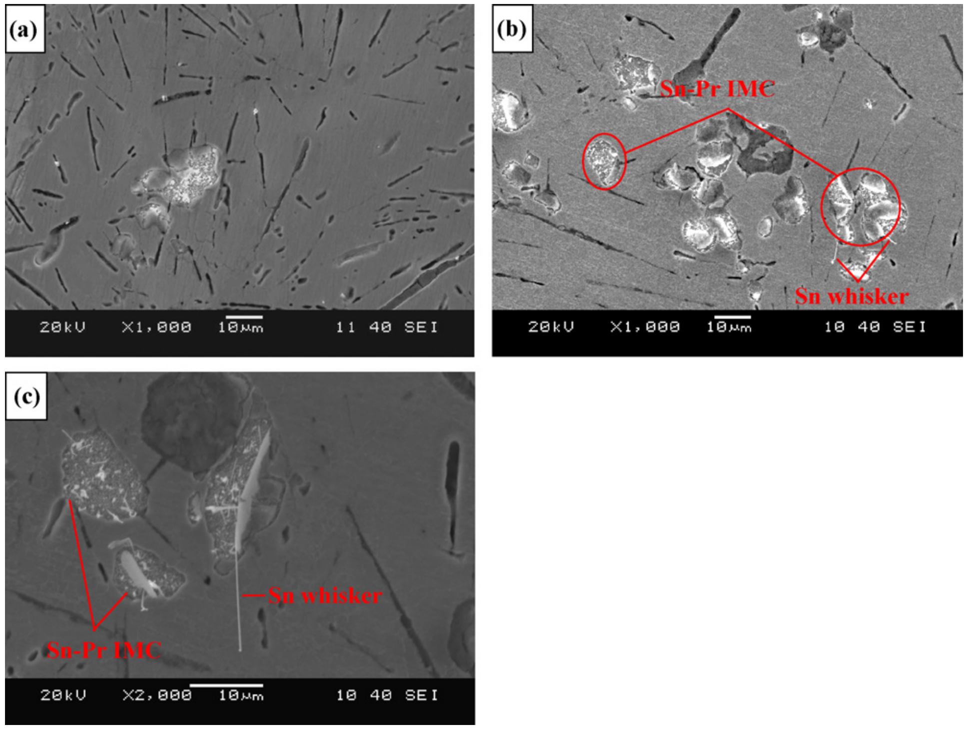

Fig. 1. SEM images of Sn–9Zn–0.5Ga–0.7Pr solders: (a) image of Sn–9Zn–0.5Ga–0.7Pr initial solder, (b) image of Sn–9Zn–0.5Ga–0.7Pr solder after exposure, and (c) image of Sn–9Zn–0.5Ga–0.7Pr solder after exposure with high magnification.

alloy were observed by optical microscopy (OM) and scanning electron microscopy (SEM). Energy dispersive spectroscopy (EDS) analysis was also used to determine the element compositions at selected areas.

3. Results and discussion

Fig. 1 shows the SEM images of Sn–9Zn–0.5Ga–0.7Pr quaternary alloy (the testing composition is Sn–8.8 wt.% Zn–0.5 wt.% Ga–0.68 wt.% Pr). Fig. 1(a) is the microstructure of the initial alloy. Fig. 1(b) and (c) is the images of the solder after exposure to ambient conditions for 12 h. It could be found that both alloys consist of gray-colored β-Sn matrix phase and dark needle-like Zn-rich phase, which are the typical features of Sn–Zn based solder. Besides these, some island-like (Fig. 1(a) and (c)) and petal-like (Fig. 1(b)) intermetallic compounds (IMC) were found apparently in the solder matrix. The EDS analysis with these compounds reveals that they are composed of Sn and Pr and the atomic ratio between them is approximately 3:1, as seen in Fig. 2(b). Combined the result with Sn–Pr phase diagram, it could be predict that these compounds are $PrSn_3$ phases.

Accompanying the appearance of Sn–Pr IMC, varying lengths of needle-like whiskers, which are proved to be pure Sn by EDS analysis (Fig. 2(c)), were observed to originate exclusively from the areas of $PrSn_3$ compounds in the exposed Sn–9Zn–0.5Ga–0.7Pr solder compared with the initial alloy. This growth is quite distinct from previously reported whisker growth on electroplated tin as it has an extremely short incubation period of 12 h only, followed by a spectacularly rapid growth. As seen in Fig. 1(b), the longest whisker for the bulk solder observed by SEM is about 15 μm, by which it could be calculated that the maximum whisker growth rate in this case is about 3.5 Å/s. The growth rate is approximately 40 times higher than the typical whisker growth rate of 0.01–0.1 Å/s on electroplated tin [16,17] and reach the level that reported by Chuang et al. [10] in the case of Sn–3Ag–0.5Cu–0.5Ce solder (about 2.9 Å/s). In addition, it is worth noting that many researches [11,18] have discussed that Zn is such a useful element that can effectively prevent whisker growth from solder alloy. However, present work shows that it is ineffective to mitigate the whisker growth from the Sn–Zn–Ga–Pr alloy, although the Zn concentration in the alloy is up to 9 wt.%. Apparently, the suggestion of Zn addition for inhibiting the whisker growth in lead-free solders should be seriously re-considered. And a deep research should be conducted on the effect mechanism of alloying elements.

Figs. 2(a) and 3(a) are the magnification morphologies of the interesting areas around the intermetallic compounds. Several interesting features can be seen around the $PrSn_3$ particles. First, both the long whiskers and short whiskers coexist on the surface, namely, the lengths of Sn whisker growth on $PrSn_3$ phases are varied. This feature indicates that the whisker growth in the solder is non-uniform. After growth competition, only a few whiskers can grow long. Secondly, the phenomenon of grain relief is visible around the $PrSn_3$ compounds, which reveals that there are volume expansions around the $PrSn_3$ phases. Meanwhile, the fact that some dark parts seeing apparently on the surface of $PrSn_3$, as shown in Figs. 3 and 4, reveals that the Sn–Pr compounds are oxidizing during whisker growth. It is known that the reason and mechanism of whisker growth is presently still unclear, but the above basic observations suggest that maybe there is a positive correlation between whisker growth and the oxidation of Sn–Pr compound. RE elements are known as reactive metals, Sn–RE compounds could have the same characteristics according to the theory of Dudek and Chawla [8,19]. In the case of RE-containing Sn–9Zn–0.5Ga–0.7Pr solders, the Sn–Pr compounds contained in the matrix are easy to oxide, even under ambient conditions. Once $PrSn_3$ particles are exposed on the polished surface of the solder, the immediate oxidation is likely inevitable, the possible oxidation reaction may take place as follow:

$$4PrSn_3 + 3O_2 \rightarrow 2Pr_2O_3 + 12Sn$$

During the exposure, $PrSn_3$ compounds are reacted rapidly with oxygen to form Pr_2O_3 according to above equation and result in the volume expansion because of the diffusion of oxygen into the $PrSn_3$

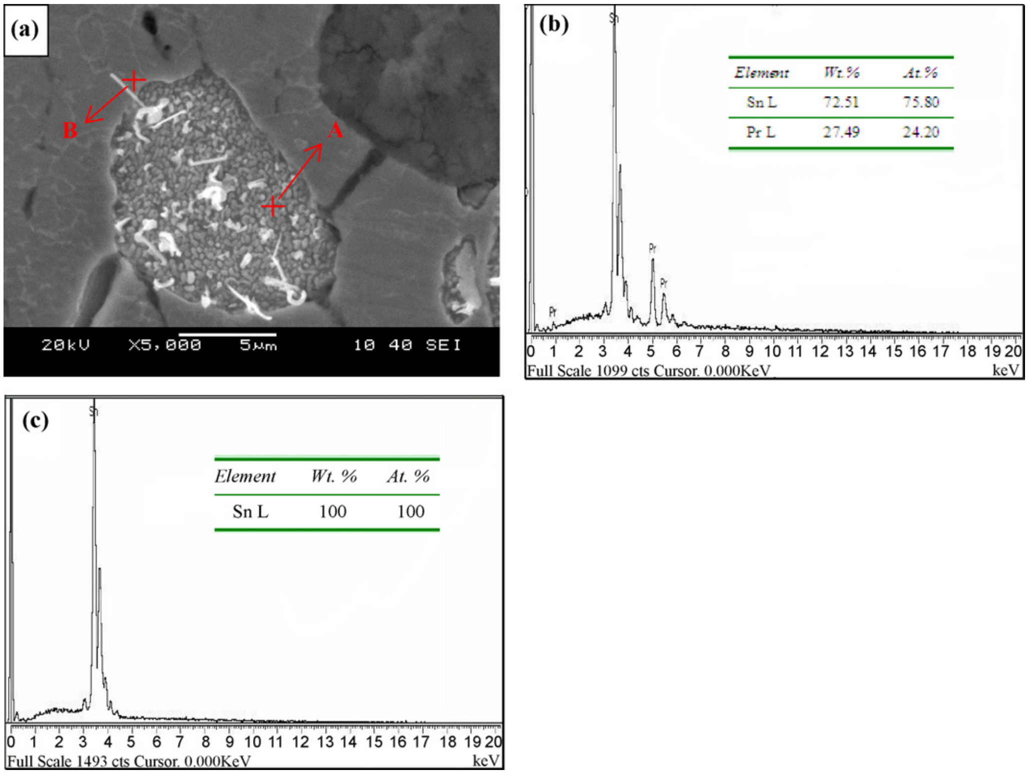

Fig. 2. EDS analysis with selected areas in the solder: (a) SEM image of selected area, (b) EDS analysis with spot A, and (c) EDS analysis with spot B.

lattice. The cell volume of $PrSn_3$, Pr_2O_3 and Sn is 105.8, 480.4 and 54.1 $Å^3$ [20], respectively. Based on above data, it could be calculated that the oxidation of $PrSn_3$ would results in volume increase of about 14.6% if no constraints were applied. However, the volume expansion is constrained due to the surrounding Sn matrix. As a result, the compressive stress would be produced within $PrSn_3$ phase. When the content of Pr in the solder is high enough, many $PrSn_3$ compounds form. Following an inevitable rapid oxidation, a high stress would be accumulated within $PrSn_3$ phases. It is proposed that the relief of this high compressive stress would be served

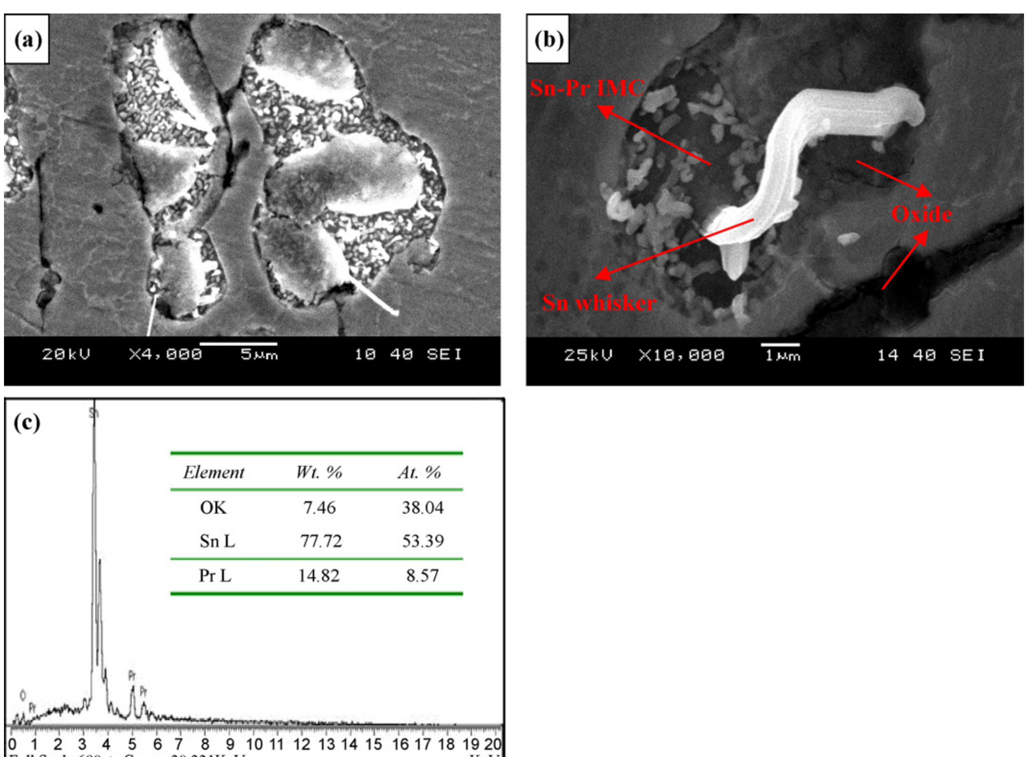

Fig. 3. SEM images of Sn–Pr compounds: (a) SEM image of selected areas, (b) SEM image of Sn–Pr compounds, and (c) EDS analysis of the oxide.

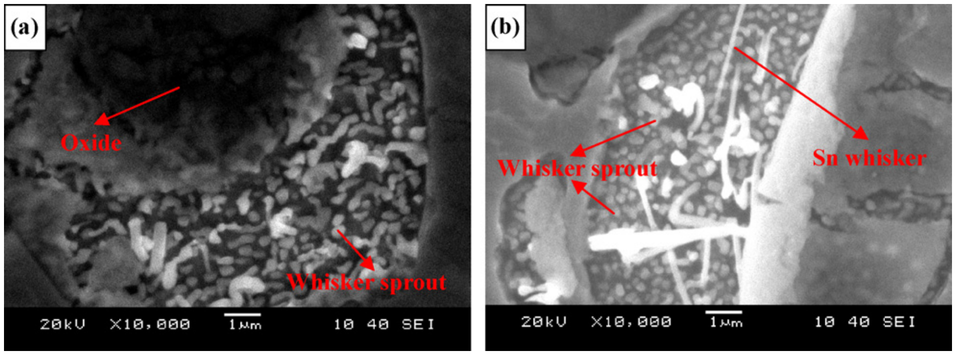

Fig. 4. Morphology of whisker sprouts within Sn–Pr phases.

as driving force to induce the whisker nucleation and growth [8,9], which results in many rice-shape nodules and sprouts formed in the inner regions of Sn–Pr compounds, as it is seen apparently from Fig. 4. Another result of the oxidation reaction is that a number of fresh tin atoms would be released, which would act as Sn source for the whisker growth. However, Sn matrix around the IMC also has the possibility of providing Sn atoms. The fact that all the whiskers only originate from Sn–Pr compounds rather than Sn matrix, which is quite different from the growth phenomenon reported in literature [16], indicates that the real source for whisker nucleation and growth would be the fresh Sn released from the oxidation, or else similar phenomenon also could be found on the matrix. Based on above discussions, the mechanism for whisker growth in the bulk solder could be assumed that the high compressive stress and the Sn atoms resulting from the oxidation of $PrSn_3$ compounds are served as driving force and growth source respectively, the driving force squeezes the new released Sn to sprout from the weaker spots in the oxidized $PrSn_3$ compounds to form nucleation, which would grow subsequently and develop into whiskers until the compressive stress and the Sn source are exhausted. Further studies of the details of whisker growth behavior and growth mechanism, in addition to the method for inhibiting whisker growth, need to be carried out in the future research project.

4. Conclusions

Sn–Zn series alloys have been expected to be one of the best alternative choices for Sn–Pb eutectic solder. In our work, the microstructure of Sn–9Zn–0.5Ga–0.7Pr quaternionic alloy was studied. In the microstructure of the alloy, some petal-like and island-like Sn–Pr intermetallic compounds form in the solder matrix. During the exposure of the solder to ambient conditions for some hours, varying lengths of needle-like Sn whiskers grow spontaneously on the surface of Sn–Pr compounds at a rate of about 3.5 Å/s. It is noting that the growth has an extremely short incubation period of a few hours only (12 h), followed by such a spectacularly rapid growth. The cause of whisker growth was discussed. It is proposed that the driving force for whisker formation in the bulk solder is related to the compressive stress due to the oxidation of Sn–Pr phases, and that the free Sn atoms released from the oxidation reaction feed the growth of Sn whisker during exposure. This new finding that Sn whisker growth in Sn–Zn–Ga–Pr solder, combined with previous studies reported that Sn whiskers growth in Sn–Ag–Cu and Sn–Cu series bulk solders, indicates that there is an increased potential risk of whisker growth in lead-free solders. More efforts should be made on further study of the microstructure and reliability of lead-free solders for the future practical application of these alloys.

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