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Abstract

The changes in microstructure and microhardness of Sn-0.5%Ag, Sn-1.0%Ag, and Sn-0.7%Cu Pb-free solders were investigated during high temperature aging at 200°C for 2 h. As-solidified microstructures, revealed by cross-polarized light microscopy, consist of relatively large grains of β-Sn phase with twinned microstructure in both Sn-Ag and Sn-Cu solders. The bright-field light microscopy displays Sn-dendrite cellular structure in Sn-Ag, and a mixture of Sn-dendrite cells and the eutectic microstructure in Sn-Cu. Upon aging at 200°C, 2 h, Sn grains become smaller compared to the as-solidified ones. In addition, the microhardness of Sn-Ag solders surprisingly increases after the aging, while that of Sn-Cu solder decreases. Detailed inspection of the redistribution and coarsening of intermetallic particles in each system further explains this unusual response of mechanical properties during high temperature aging. In this study, it is demonstrated that the microhardness of Sn-Ag and Sn-Cu solders is better correlated with the characteristics of their intermetallics, such as particle size, density and distribution, rather than Sn grain size.

Key Words: Grain, hardness, Sn-rich solders, microstructure

Pb-free solders have been extensively developed to replace Pb-containing solders in microelectronic packaging applications. The majority of Pb-free solders is Sn-based, containing minor alloying elements [1, 2]. The most popular Pb-free solders include near eutectic Sn-Ag-Cu, Sn-Ag and Sn-Cu alloys. Although the near-ternary eutectic Sn-Ag-Cu solder is the leading candidate in printed circuit board assembly, the reliability of the solder system has been challenged by several technical issues, particularly in chip-level interconnect applications, namely, flip-chip solder joints. Difficulty of electroplating a ternary solder composition, formation of large intermetallic phases during reflow, high modulus or stiff solder joints are just a few of the concerns. To mitigate these concerns, Sn-Ag or Sn-Cu binary systems, especially with a low Ag and/or Cu content are proposed to produce low modulus or more ductile flip-chip interconnections [3, 4]. However, reducing the alloying content in the binary and ternary Sn-based solders would significantly affect their microstructure and, consequently, their mechanical behavior when the solder joints are subjected to thermomechanical stress conditions or high temperature, high current density electromigration tests. In this study, the high temperature stability of microstructure and mechanical properties of Sn-low Ag (0.5 and 1.0 wt %) and Sn-0.7Cu (wt %) alloys is reported during the aging at 200 °C for 2 h.

Sn-0.5Ag, Sn-1.0Ag, and Sn-0.7Cu solder balls (380 μm in diameter) used in this study were commercially produced. Solders were reflowed at 250 °C for 10 min in a vacuum oven and cooled in air (1~5 °C/sec). Because the melting temperature of the solder alloys is about 230 °C, all solders were melted at 250 °C. Subsequently, the reflowed solder balls were annealed at 200 °C for 2 h.

Finely polished cross-sections of solder balls were examined with an optical microscope under both bright-field and cross-polarized imaging conditions. Cross-polarized images revealed β-Sn dendrites and grain structures, while bright field images exhibited the presence of intermetallic particles and their network structure. Different polishing process was employed for the different imaging conditions; a mostly flat surface is preferred for cross-polarizing images, while a slightly etched surface for bright-field images to detect the intermetallic phases. Although cross-polarized images could not give the information about grain orientation like electron backscatter diffraction (EBSD) technique, it was well demonstrated as a useful tool to identify Sn grain size, in agreement with the results from EBSD work [5].

Microhardness tests were performed using 5 g force and 5 s dwell-time on a cross-section of solder balls. The Vickers hardness number (VHN) was reported as an average value of 12 indentations or more.

Fig.1 shows typical cross-polarized light images of Sn-0.5Ag, Sn-1.0Ag and Sn-0.7Cu both as-solidified and aged at 200 °C, 2 h. Different color contrasts mean the different orientations of Sn grains. As shown in Fig. 1(a), (b) and (c), a few large Sn grains (1 to 5) are observed in as-solidified samples. This observation is in good agreement with the previous work on pure Sn of a BGA size solder ball, but is not consistent with the case of a high Ag (3.0 wt%) alloy of Sn-Ag, where many Sn grains below 10 μm size were reported, independent of cooling rate after reflow [6, 7].

After aging at 200 °C, 2 h, the large grains changed to many small grains (80 to 150) as shown in Fig. 1(d), (e) and (f). And Sn grains in Sn-Ag solders are smaller than in Sn-Cu after the aging. The grain size reduction observed here after high temperature aging was initially difficult to explain. Grain size reduction is often observed during a recrystallization process of heavily deformed metals and alloys to release their stored energy during thermal treatment or aging at an elevated temperature. It is difficult to expect the as-solidified solders, which is free of stored energy, to initiate a recrystallization process to form a finer grain structure. To find a possible mechanism of the microstructure changes during the high temperature aging, the microstructure of the solders was further investigated in bright-field light images, especially focusing on the intermetallic particles and their network.

Fig.2 exhibits the corresponding bright-field images at a higher magnification from the same samples of Sn-0.5Ag, Sn-1.0Ag and Sn-0.7Cu shown in Fig. 1. Gray color contrast is Sn matrix and light-colored features are the Ag_3Sn or Cu_6Sn_5 intermetallic particles or networks in each corresponding solder. In as-solidified Sn-Ag solders, Figures 2(a) and 2(b), the bright-field images reveal a well-developed cellular structure of β-Sn. The cell boundary forms a network of Ag-rich regions in Sn-Ag, occasionally decorated with very small Ag-Sn intermetallic particles. The Sn dendrite size is found to be larger in Sn-0.5Ag than in Sn-1.0Ag, because the Ag content is smaller in Sn-0.5Ag. In as-solidified Sn-Cu, Figure 2(c) a mixture of Sn dendrite cells and the eutectic microstructure is noted, and the cell boundaries consist of fine Cu-Sn intermetallic particles. It is noted that the Sn dendrite cell size is quite smaller than the grain size in as-reflowed conditions, but similar to the grain size in the aged-conditions. As shown in the cross-polarized images, a group of Sn dendrite cells can have a common crystallographic orientation, such as <110>, a well-known dendrite growth direction of Sn [8], to yield a few large grains or even single crystal orientation in the as-solidified conditions.

After the aging of Sn-Ag solders at 200 °C, 2h, small Ag-Sn intermetallic particles at the cell boundaries become coarsened and redistributed to form a smaller cell structure compared to the as-solidified. In the case of Sn-0.7Cu, a mixture of Sn dendrite and the eutectic structure is totally broken, and Cu-Sn intermetallic particles significantly coarsened and redistributed during the aging. In the process, it appears that the coarsening and re-distribution of intermetallic particles during the aging have apparently broken up the large grain structure into a finer grain structure as shown in the aged solders.

Fig.3 shows Vickers hardness values of Sn-0.5Ag, Sn-1.0Ag and Sn-0.7Cu in as-solidified and aged conditions. After the aging at 200 °C, 2 h, the hardness of Sn-0.5Ag and Sn-1.0Ag solders surprisingly increases, while the hardness of Sn-0.7Cu decreases upon the aging. This result would be difficult to understand based on the Hall-Petch type relationship, which predicts a higher yield strength or hardness for metals or alloys with a smaller grain size [9, 10]. In this study, the microhardness changes during the aging at 200 °C were understood by noting the changes in the redistribution and coarsening of the intermetallic phases, not with the changes of grain size. In Sn-Ag solders, the Sn cell structure or intermetallic network became smaller upon aging, while the initial solidified microstructure of Sn-Cu was mostly broken during the aging to produce a larger intermetallic network in addition to coarsening of the individual intermetallic particles. Hence, the hardness increase in Sn-Ag and the decrease in Sn-Cu solders were better accounted for by the changes in the intermetallic characteristics rather than the grain size of the solders.

In summary, the high temperature aging at 200 °C, 2 h has caused a reduction in Sn grain size in Sn-rich, Sn-Ag and Sn-Cu solders. But the aging has produced different changes in the intermetallic structure of Sn-Ag versus Sn-Cu; a reduction of Sn dendrite cell structure or intermetallic network in Sn-Ag, while a destruction of Sn dendrite cell and the eutectic microstructure, effectively causing an increase in the intermetallic network size in Sn-Cu in addition to coarsening of the Cu-Sn intermetallics. Hence, the microhardness or mechanical properties of Sn-rich solders is better represented by the intermetallic characteristics, such as particle size, density and distribution, rather than Sn grain size.

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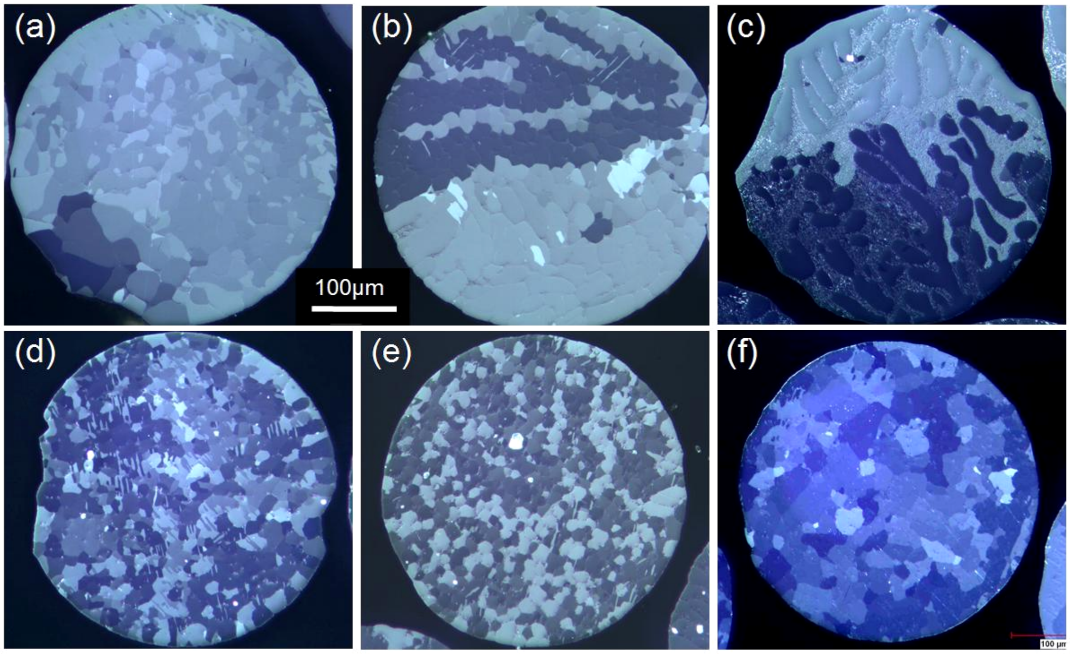

Figure 1. Cross-polarized light images: (a) Sn-0.5Ag, (b) Sn-1.0Ag and (c) Sn-0.7Cu are as-solidified after reflow and (d) Sn-0.5Ag, (e) Sn-1.0Ag and (f) Sn-0.7Cu are aged at 200 °C for 2 h after reflow.

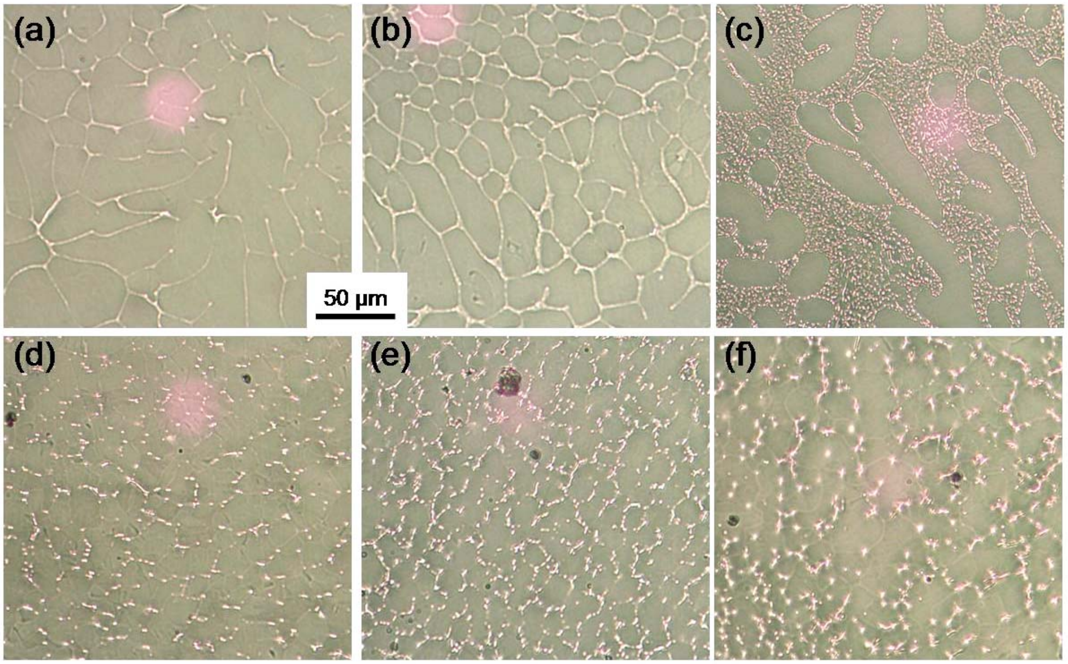

Figure 2. Bright-field light images: (a) Sn-0.5Ag, (b) Sn-1.0Ag and (c) Sn-0.7Cu are as-solidified after reflow and (d) Sn-0.5Ag, (e) Sn-1.0Ag and (f) Sn-0.7Cu are aged at 200°C for 2h after reflow.

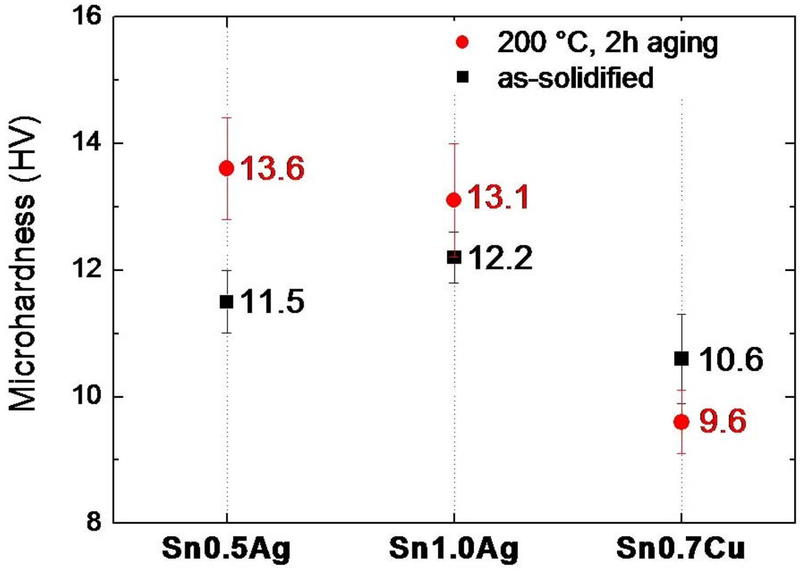

Figure 3. Microhardness (5 g force, 5 sec dwell-time) of Sn-0.5Ag, Sn-1.0Ag, and Sn-0.7Cu solders as-solidified and aged at 200 °C for 2h.