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Effect of small amount of rare earth addition on electromigration in eutectic SnBi solder reaction couple

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Abstract Effect of small amount of rare earth (RE) addition on electromigration behavior of Cu/SnBi/Cu solder reaction couple (SRC) was investigated with current density of 5×10^3 A/cm^2 at room temperature and 100 °C, respectively. Results indicate that tiny RE addition to eutectic SnBi solder alloy can make the energy of interfaces and grain boundaries decrease, restrain the movement of dislocations and grain boundary sliding. Therefore, phase segregation and IMC growth will be effectively suppressed which enhances the electromigration resistance.

Introduction

Electromigration (EM) which occurs in the solder joints and results in the failure is becoming a crucial reliability issue with the dimension of solder joints decreasing. It is normally defined as the atomic diffusion and migration driven by current stressing. The diffusivity of metal atoms can be altered through either material microstructure or texture in-homogeneity, resulting in the atomic flux divergence and hence the appearance of some defects such as cracks/voids and hillocks formation [1–3]. Recently, a number of investigations have been addressed about EM behavior on lead-free solder.

Eutectic SnBi solder alloy has been considered as one of the most promising lead-free products as a substitute for conventional SnPb solders in the recent years. Its low melting point make it widely used in some special situation for soldering [4–6]. Similar to SnPb solder alloy, phase segregation and redistribution will occur during the EM process [7, 8]. Several predecessors as Chih-ming Chen et al. had referred the EM behavior of eutectic SnBi alloy and investigated the effect of Cu or Ag addition on EM. However, EM character of RE addition to eutectic SnBi solder alloy has never been reported before. It is well-known that RE is often applied to improve the microstructures and properties of various alloys. It has also been proved that tiny RE addition to SnAgCu solder alloy can effectively enhance its mechanical properties and its static creep-rupture life seven times as well as ultimate strength and elongation trait is distinctly improved. In addition, significant microstructure refinement is obtained due to RE addition, which leads to further strengthening [9, 10]. Therefore, in this study, a small amount of RE is recommended to add into eutectic SnBi alloy to understand the effective mechanism on EM at room temperature and under high temperature.

Experimental

Sample preparation

The Cu/SnBi/Cu SRC was fabricated in this study which could eliminate the current crowding effect due to its one dimensional structure. Pure Sn and Bi metal particles with purity of 99.9 wt% were used as raw materials. It should be noted that the composition of the RE mixture mainly concluded (40–50%) Ce, (20–30%) La, 15% Nd, and 8%Pr. First of all, Sn and Bi metal particles were weighed accurately according to the mix percentage and then put into some ceramic crucibles. In the mean while, eutectic salt (KCl + LiCl) with weight ratio of 1.3:1 was used to

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cover the surface of the particles to prevent oxidation during smelting. The crucibles were placed in an induction furnace at 550 °C for about 20 min. With the help of a cast-iron bell with holes on the sidewall, 0.1 wt% RE was pushed into the molten solder. When the RE melted, the molten alloy was then held on for about 40 min and mechanically stirred for every 10 min with a glass rod to promote uniformity of the solder alloy. The molten solder was finally chill cast onto a rod ingot in a mold [9, 10].

Solder balls with average size of 300 μm in diameter were made of solder alloy using uniform droplet spraying equipment in our laboratory. Differential Scanning Calorimetry (DSC) test was conducted to inquire the melting and solidification behavior which found out that the melting point of RE-doped solder alloy was similar with that of eutectic SnBi solder alloy. Consequently, the same reflowing temperature would be applied. Solder balls were placed between two copper wires with 500 μm in diameter and placed on a hot plate fixed in the soldering platform designed and built by ourselves. The specific soldering procedure was described in detail in our previous study [11, 12].

In order to observe the interior microstructural evolution of the solder matrix, SRCs were mounted with epoxy resin. Grinding machine was applied to reduce the dimension of the samples, followed by grid sandpapers, and finely polished with Al_2O_3 suspension. Microstructural and compositional analysis was examined by an S-3400N scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX) system.

Current stressing

Two samples, Cu/Sn-58 wt%Bi/Cu named SRC1 and Cu/Sn-58 wt%Bi-0.1 wt%RE/Cu named SRC2, were connected in series with a DC power supply to provide a constant current flow. A thermocouple was attached on the surface of the SRCs to detect the temperature fluctuation. The current density was about 5×10^3 A/cm^2, calculated by dividing the current value by the virtual cross-sectional area through which the electrons passed. The two samples were stressed at room temperature and under high temperature, respectively. The cross-sectional surfaces of the solder matrixes were polished again to observe the interior microstructural evolution.

Results and discussion

Microstructural evolution in SRC1 and SRC2 after current stressing at room temperature

Comparison of microstructural evolution between SRC1 and SRC2 after current stressing for 254 h and 465 h at room temperature are shown in Figs. 1 and 2. Figure 1 shows the SEM images of SRC1 after current stressing for 0–465 h, where Fig. 1a, c, and e show the cathode side and Fig. 1b, d, and f show the anode side. A clear two-phase microstructure, the bright white Bi-rich phase, and the dark gray Sn-rich phase, is uniformly distributed in the solder matrix as shown in Fig. 1a and b. EDX analysis revealed that a continuous Cu_6Sn_5 layer with average thickness of 1 μm was rapidly formed at the solder/substrate interface during the reflow process. The direction of the current flow was from the anode to the cathode but the direction of the electrons was on the contrary. With the stressing time increasing, obvious different microstructural evolution occurred both at the cathode and the anode. A few sporadic voids and cracks were found at the cathode interface when the stressing time reached 254 h. These voids and cracks propagated along the interface to become a continuous crack when the stressing time increased to 465 h as seen in Fig. 1c and e. In the mean time at the anode interface, Bi atoms were extruded out of the surface which formed a successive row of Bi hillocks as shown in Fig. 1d and f. The appearance of cracks and Bi hillocks indicated that electromigration occured in the eutectic SnBi solder matrix with current density of 5×10^3 A/cm^2 at room temperature. Bi phases at both sides coarsened due to the Joule heating induced by current stressing and many of them were migrated from the cathode to the anode because of the electron wind force. Under this experimental condition we can conclude that Bi atoms diffuses faster than Sn atoms do, therefore they are the main diffusion species during the EM process. With continuous Bi atoms departing from the cathode region, a tensile stress is formed at the solder/substrate interface resulting in the void and crack formation. In addition, when more and more Bi atoms accumulate at the anode, some Bi atoms are extruded out of the surface because of the compressive stress.

Figure 2 shows the SEM images of SRC2 after current stressing for 0–465 h, where Fig. 2a, c, and e show the cathode side and Fig. 2b, d, and f show the anode side. Compared with Fig. 1a and b, we could find out that microstructure in Fig. 2a and b was more uniform and finer, which indicated that small amount of RE addition refined the grain size. It should be noted that no RE phases were detected in the RE-doped solder matrix because the quantity of additional RE was particularly minute. Similar microstructural changes were observed in SRC2 as that of in SRC1, in which cracks and hillocks were formed at the cathode and the anode interfaces, respectively. However, it was not as significant as that in SRC1 which illustrated that minor RE addition could suppress the movement of Bi and Sn atoms effectively.

To contrast the coarsening rate of Bi-rich phases in the eutectic SnBi solder matrix and the RE-doped SnBi solder

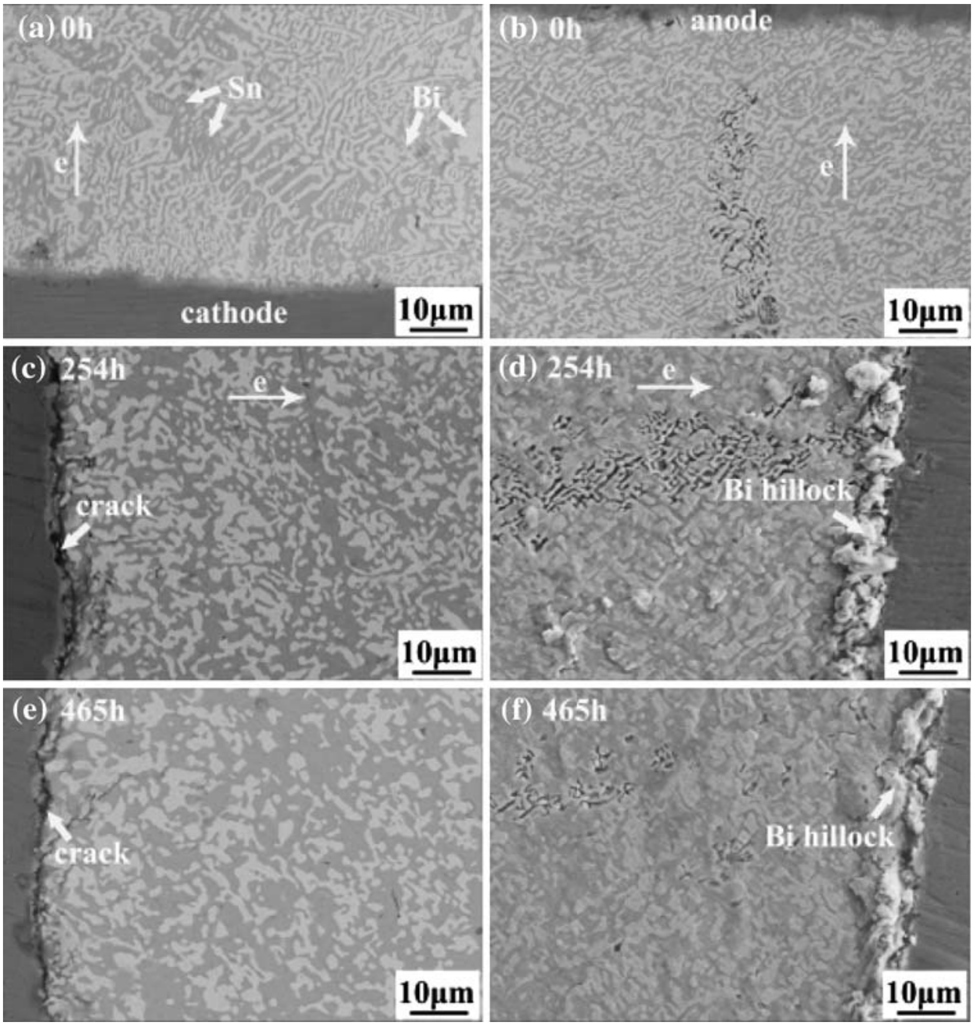


Fig. 1 SEM images of SRC1 with current density of 5×10^3 A/cm^2 at room temperature (**a**, **c**, and **e**) at the cathode, (**b**, **d**, and **f**) at the anode

matrix, a method of calculating 'average grain area' of the Bi-rich phases is introduced in this paper which has been widely used in temperature aging experiment. We define the average grain area (A) as a quantitative value to illustrate the coarsening rate of Bi-rich phases in different stressing time at room temperature. The general expression of average grain area is $A = A_s/N_s$, where A_s is the sum area of the Bi-rich phases in selected dimensional area, and N_s is the number of Bi-rich phases in selected dimensional area. The whole analytical process is conducted with the help of Image J software. The average grain area of the Bi-rich phases in both solder matrixes as a function of various stressing time at room temperature is listed in Table 1 and Fig. 3. The original average grain areas of the eutectic SnBi and the RE-doped SnBi are 8.92 μm^2 and 5.29 μm^2, respectively. When the stressing time increases to 465 h, they become 12.55 μm^2 and 9.77 μm^2, respectively. This result further demonstrates that 0.1 wt% RE addition can refine the grain size and restrain coarsening rate of the Bi-rich phase.

Microstructural evolution in SRC1 and SRC2 after current stressing at 100 °C

When SRC1 and SRC2 were stressed at 100 °C for 115 h, the current circuit was broken off. An ohmer was used to detect the two samples to confirm which one was failed. The result proved that there was something wrong with SRC1. Figure 4 shows the SEM images of SRC1 after current stressing for 67 h and 115 h, where Fig. 4a, c, and e shows the cathode side and Fig. 4b, d, and f shows the anode side. Severe cracks were observed at the cathode interface when the stressing time was 67 h as shown in Fig. 4a. Much more Bi atoms were extruded out of the surface at the anode as shown in Fig. 4b. Figure 4c and d show the SEM images of SRC1 after current stressing for 115 h. We found out from the images that the morphology of the solder matrix was completely changed due to the combined effect of high temperature and electromigration. It seemed that the solder matrix was completely melted during the EM test. Solder depletion was observed at the

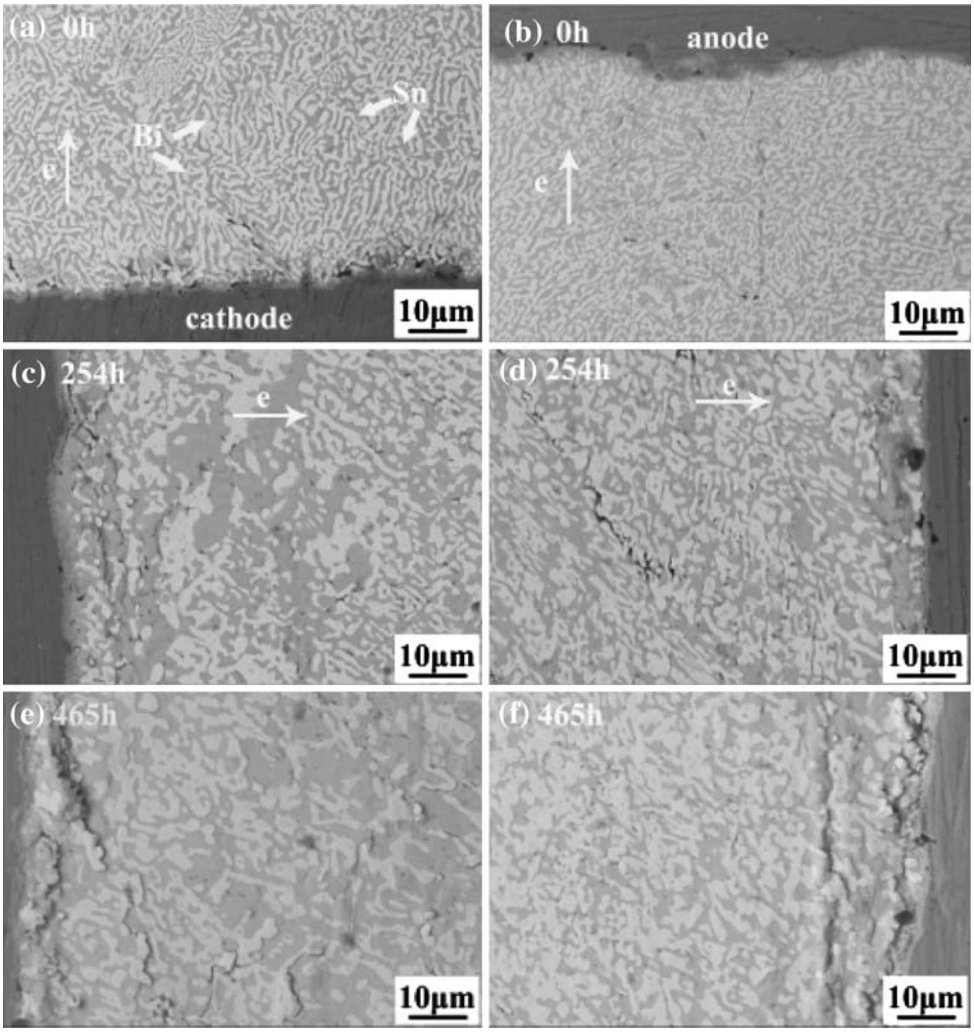


Fig. 2 SEM images of SRC2 with current density of 5×10^3A/cm^2 at room temperature (**a**, **c**, and **e**) at the cathode, (**b**, **d**, and **f**) at the anode

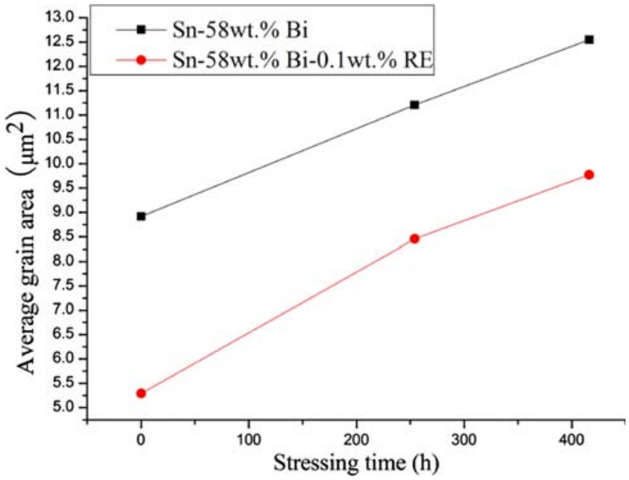


Fig. 3 Average grain area of the Bi-rich grain as a function of stressing time at room temperature

Table 1 Average grain area of the Bi-rich phase versus stressing time at room temperature

	Stressing time (h)		
Average grain area	0	254	465
Sn-58 wt%Bi (μm^2)	8.92	11.21	12.55
Sn-58 wt%Bi-0.1 wt%RE (μm^2)	5.29	8.46	9.77

upper-left corner of the solder matrix leading to a deep valley there and a thick “Bi stripe” was formed at the anode. Figure 4e and f show the interior microstructure of SRC1 after polishing. As could be seen from the images that almost all the Bi atoms accumulated at the anode and most of the Sn atoms were missing. Besides, it was worth mentioning that many Cu_6Sn_5 bumps with different sizes were found in the solder matrix, and few Sn and Bi atoms were still remained among these IMCs. What was important to note was that an IMC layer was formed at the anode interface, which consisted of a Cu_6Sn_5 layer with average thickness of 47.7 μm and a Cu_3Sn layer with average thickness of 3.3 μm. From the left to the right, Bi layer, Cu_6Sn_5 layer, Cu_3Sn layer and Cu substrate were in sequence in the horizontal line as shown in Fig. 4f.

As the stressing time increased under high temperature, migration and diffusion of Bi atoms towards the anode was accelerated, resulting in larger tensile stress at the cathode. Therefore, crack formation or solder depletion occurred, leading to much higher current density because of the reduction of the current contact area. On the other hand, Joule heating might increase the temperature of the solder joint, and the amount of temperature increase depended on many factors such as the joint geometry, materials, and applied current and so on. Continuous Bi migration in accordance with the movement direction of electrons from the cathode to the anode formed the Bi layer. In order to take room for the arrival of the Bi atoms, Sn atoms were pushed back towards the cathode. The diffusion path included three channels: Bi grain boundaries, Sn grain boundaries, and Bi/Sn grain boundaries. In the molten state, Cu atoms from the anode substrate were migrated and diffused faster into the solder matrix reacting with Sn atoms to form the Cu_6Sn_5 bumps as shown in Fig. 4e [13]. However, we could not confirm if these Cu_6Sn_5 bumps were formed there or migrated from the anode. Little information about the EM character of the Cu_6Sn_5 had been reported before. Ying-Chao Hsu et al. had pointed out that the Cu_6Sn_5 IMC exhibited a better EM resistance than the Sn3.8Ag0.7Cu solder, because the IMC remained intact after EM test. Whereas, for some specimens stressed at

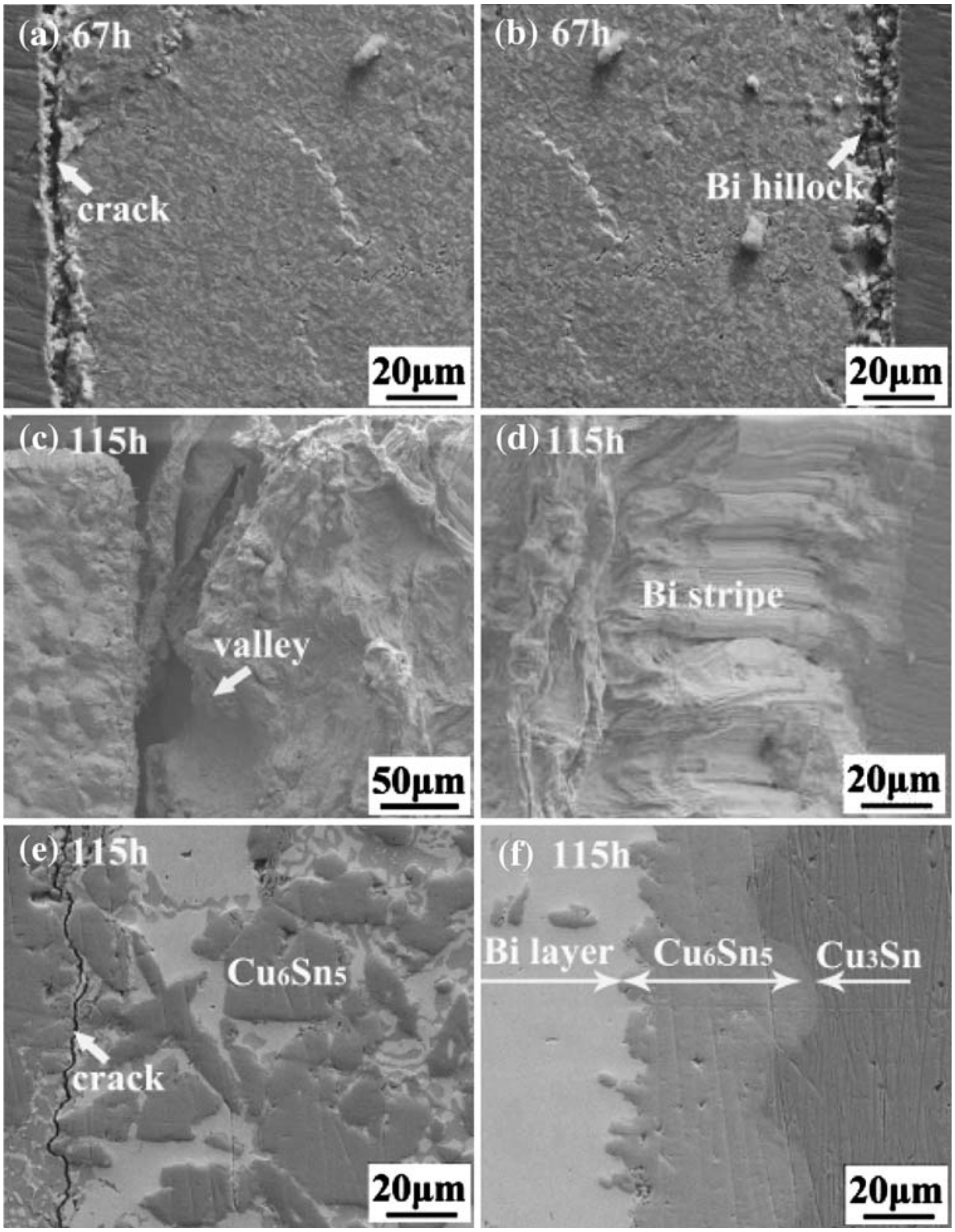
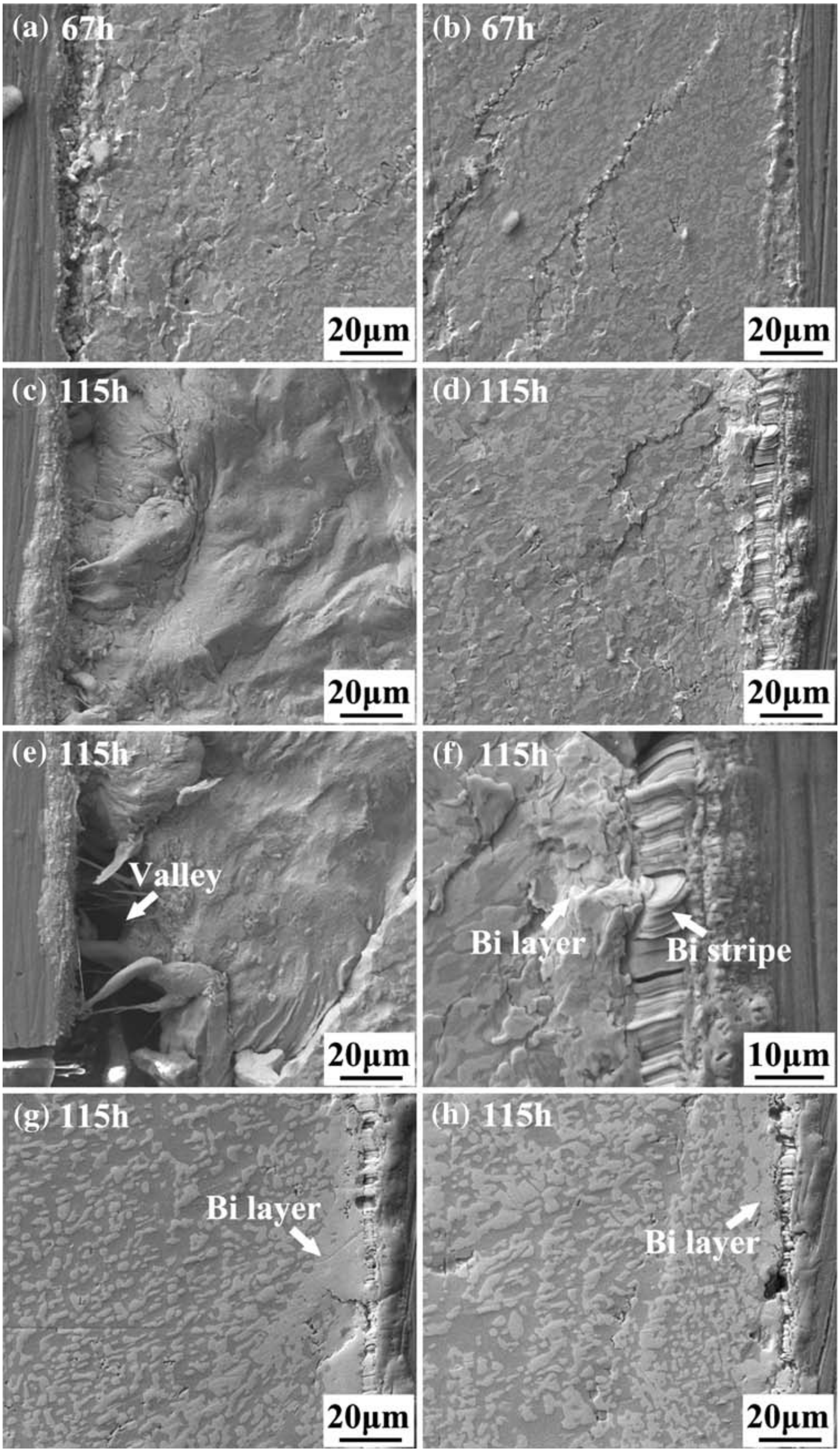


Fig. 4 SEM images of SRC1 with current density of 5×10^3 A/cm^2 under high temperature of 100 °C (**a**, **c**, and **e**) at the cathode, (**b**, **d**, and **f**) at the anode

Fig. 5 SEM images of SRC2 with current density of 5×10^3 A/cm^2 under high temperature of 100 °C (**a**, **c**, and **e**) at the cathode, (**b**, **d**, **f**, **g** and **h**) at the anode



more severe condition, the IMC at the cathode was also found to migrate away after the depletion of the solder. Therefore, the migration of the Cu_6Sn_5 from the interface into the matrix indicates that high temperature and 'electron wind force' have important effect. This may be related to an increased interfacial energy due to the formation of the Cu_6Sn_5, but further investigation should be conducted for confirmation. The formation of two IMC layers, Cu_6Sn_5 and Cu_3Sn, is observed at the anode interface between Bi layer and Cu substrate. This can be explained that the thickening process of Cu_3Sn appear to be diffusion controlled as in the solid-state interfacial reactions where such two-layer structures are very common. The formation of Cu_3Sn occurs because diffusion-controlled growth implies that all IMCs of the phase diagram should appear along the diffusion profile in accordance with the local composition.

Compared with SRC1, there was no significant solder melting/depletion, phase segregation, coarsening and IMC bumps formation/migration in SRC2 at 100 °C as shown in Fig. 5. Figure 5a, c, and e shows the cathode side and Fig. 5b, d, f, g, and h shows the anode side. When the stressing time increased to 115 h, partial matrix melted and solder depletion occurred at the cathode interface which resulted in a deep valley there as shown in Fig. 5c and e. A Bi stripe layer with average thickness of 5 μm was arranged between IMCs layer and Bi layer at the anode interface as shown in Fig. 5d and f. The structure and arrangement is very regular as if the Bi plates are ranked one by one in the vertical direction. However, its thickness is far less than that in SRC1 with the same stressing time. We can see that many grooves appear on the surface of the Bi stripe layer. It should be noted that the thickness of the Bi layer is not uniform as shown in Fig. 5g and h. The eutectic SnBi structure is still observed in the solder matrix.

Discussion

Based on the above experimental results, we tried to bring forward some explanations for the fundamental mechanism of how Bi-rich phase and Sn-rich phase migrated. The paths where Bi atoms migrated merely with three modes: Bi-rich phase, Sn-rich phase, and their boundaries. Because the boundaries have the relative low compact structure, Bi atoms may migrate easily through them. When a number of Bi atoms reached the anode but there were not enough Sn atoms leaving away, thus Bi atoms would be extruded out of the surface in succession due to the compressive stress and voids or cracks will be developed at the cathode due to the tensile stress. Therefore, we can say that during the initial EM test, Bi atoms migrate faster than Sn atoms do. When the stressing time increased, these disadvantages became more serious. The Sn/Bi segregation and voids/cracks formation resulted in the strength reduction and more Joule heating at the interface because of higher brittleness and resistivity of Bi atoms [4, 5]. When the solder matrix was depleted by the electron flow and Joule heat crowding, the current density flowing through the Cu_6Sn_5 became much higher. For the above stressing condition, it was estimated that the current density in the IMC bumps after the depletion of the solder matrix increased high enough to drive them away. Therefore, the Cu_6Sn_5 bumps coarsened and migrated into the solder matrix with the dual effect of a high current density and a high temperature.

According to the microstructural evolution in SRC1 and SRC2 after EM test whatever at room temperature or under high temperature, it is proved that RE addition to the eutectic SnBi solder alloy can effectively restrain the Sn/Bi segregation as indicated in Figs. 4 and 5. As active elements, RE will accumulate at the grain boundaries and interfaces of the Sn/Bi atoms. The adsorption phenomenon plays an important role during solidification processes of alloys and might greatly affect the microstructure of Bi and Sn atoms. The RE addition can make the energy of interfaces and grain boundaries decrease. Thus the movement of dislocations and grain boundary sliding may be suppressed leading to difficult migration of Sn and Bi atoms [14, 15]. The driving force for RE to aggregate at the boundaries is the difference of the lattice-aberration energy between the interior and the boundaries of Sn/Bi atoms, which is caused by a solution of RE atoms. As ever reported that the size of RE and Sn/Bi differs greatly. The radius of Sn is 0.141 nm and that of Ce and La are 0.183 nm and 0.187 nm, respectively [9, 10]. The radius of the RE atom is larger than that of Sn. Therefore, it is difficult for RE atoms to exist as replacement atoms in the lattice of Sn. In the RE-doped solder matrix, the RE solid solution is enriched at the boundaries to form the web. This kind of structure can effectively limit the migration of Sn and Bi atoms. Consequently, RE addition can enhance the EM resistance. As we all know that RE is recognized as a surface-active agent because it will accumulate at the boundaries resulting in lowering the surface/interface tension and boundary energy. This can stabilize the boundaries and restrain the moving or sliding of the boundaries. It will be helpful to investigate the form of the presence of RE in the lead-free solder to find out the present characteristics of RE in the boundary and effect of RE on the state of the boundary.

Conclusion

In this paper, effect of small amount of rare earth (0.1 wt%) addition on EM behavior of eutectic SnBi SRC was investigated with current density of 5×10^3 A/cm^2 at room temperature and 100 °C. The conclusions were as follows:

(1) Cracks were formed at the cathode interface and hillocks were extruded out of the surface at the anode interface in SRC1, however, no distinct microstructural evolution was observed in SRC2. Furthermore, no obvious Sn/Bi segregation took place in both solder matrixes at room temperature.

(2) The solder matrix of SRC1 exhibited severe transformation under high temperature. It seemed that it had been melted during EM process. Solder depletion happened at the cathode and a thick Bi stripe was formed at the anode. To analyze the interior evolution, SRC1 was polished again. Almost all the Bi atoms accumulated at the anode and most of the Sn atoms were depleted to form a quantity of Cu_6Sn_5 bumps in the solder matrix. A Cu_6Sn_5 layer with average thickness of 47.7 μm and a Cu_3Sn layer with average thickness of 3.3 μm were arranged between Bi layer and Cu substrate. Nevertheless, there was no significant solder matrix melting/depletion, phase segregation/coarsening and IMC bumps formation in the RE-doped solder matrix no matter at room temperature or under high temperature.

(3) The addition of RE can make the energy of interfaces and grain boundaries decrease. Hence, the movement of dislocations and grain boundary sliding may be suppressed. It becomes very difficult for Sn and Bi atoms to migrate away. Therefore, addition of RE can restrain the movement of atoms and enhance the EM resistance.

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