

Eliminating interfacial segregation and embrittlement of bismuth in SnBi/Cu joint by alloying Cu substrate

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The segregation of Bi at the Cu/Cu₃Sn interfaces of the SnBi/Cu couple dramatically decreases this couple's mechanical properties. Here, we deliberately add Ag, Al, Sn and Zn elements into the Cu substrate to eliminate the interfacial segregation and embrittlement of the SnBi/Cu couple. Experimental results confirmed that there is always a perfect Cu₃Sn/Cu alloy interface without Bi segregation, and excellent mechanical properties are thus maintained. The most important finding is that the interfacial embrittlement of SnBi/Cu alloy joints was successfully eliminated even after prolonged aging.

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Soldering is a very important procedure in the electronic packaging field [1]. Lead-free solders, though promising, present two serious defects: (i) their melting points are much higher than those of traditional SnPb solders [1]; (ii) Bi segregation at the Cu/Cu₃Sn interface always occurs with the SnBi/Cu couple [2]. The segregation of impurities always seriously deteriorates the physical and mechanical properties of the material [3,4], as does Bi segregation. This is why, in the electronic packaging field, use of lead-free solders is still not widespread even though legislation to limit the use of SnPb has been extant in many countries for many years [1].

In order to extend the application of lead-free solder, one must: (i) decrease its melting point; or (ii) restrict the Bi segregation at the SnBi/Cu interface. Research results concerning the former are not promising [1,5]. About the latter, Liu and Shang [6] and Zhu et al. [7] have tried to employ electrodeposition of Ag or Ni thin films onto the Cu substrate to successfully prevent the interfacial embrittlement of SnBi/Cu interconnects even after long aging times. But this approach cannot be used on certain interfaces where it is difficult or impossible to electrically deposit thin films on the interfaces. Historically, the poor ductility of polycrystalline Ni₃Al has been successfully improved by adding B [8], and this approach has infused

new life into the research and application of intermetallics in the past two decades [9–12]. In this context, therefore, the deliberate addition of Ag, Al, Sn, Zn elements into Cu substrate was expected to restrain interfacial Bi segregation. Ample experimental evidence has indicated that alloying Cu substrate can successfully eliminate Bi segregation at the SnBi/Cu interface, leading to the improvement of interfacial mechanical properties. Therefore, in the electronic packaging field, this strategy might enable SnBi solder to be widely used and in the future replace SnPb solder. More importantly, the method provides a new visualization to understand and eliminate other interfacial segregation (such as P, S or Sb in steels and Bi in poly-Cu).

In this study, pure Cu and Cu alloys (Cu–2.3Al, Cu–2.5Ag, Cu–18.7Ag, Cu–10Zn and Cu–3Sn) were used as substrates. Eutectic Sn–58 wt.% Bi alloy was employed as solder. Cu, Cu alloys and SnBi alloy were cut and ground with 800#, 1000#, 2000# SiC paper and then carefully polished with the 2.5 and 1.5 μm polishing pastes. All the prepared samples were kept in an oven at a constant temperature of 200 °C for 6 min. One group of samples was isothermally aged at 120 °C for different times to reveal the interfacial microstructure of the SnBi couples. Some tensile samples of SnBi/Cu and SnBi/Cu–X joints (X = Al, Ag, Zn and Sn) were isothermally aged at 120 °C for different numbers of days in order to investigate the interfacial mechanical properties of the joints. Tensile tests were

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performed with an Instron 8871 testing machine at an average strain rate of about $5 \times 10^{-5} \text{ s}^{-1}$ at room temperature in air. The fracture surfaces were observed by scanning electron microscopy (SEM) to reveal their deformation and fracture morphologies.

Figure 1 shows the close-up backscattered electron SEM images of the interfaces in the SnBi/Cu and SnBi/Cu–X (X = Ag, Al, Sn and Zn) couples at 120 °C for different periods. Discontinuous Bi particles could be easily observed at the SnBi/Cu interface when the sample was aged at 120 °C for 12.5 days, as indicated by the red circles in Figure 1a. This implies that Bi segregation would take place at the SnBi/Cu interface after prolonged aging, as has been detected in previous studies [2,6,7]. Liu and Shang [6], however, considered that the Bi atoms would mainly appear in the form of a monolayer at the Cu/Cu₃Sn interface, which is different from the current experimental results. Furthermore, some voids can be observed near the Bi particles, as displayed by the white arrow in Figure 1a.

Since the Bi segregation at the Cu/Cu₃Sn interface can affect the nucleation and growth of Kirkendall voids simultaneously, the free energy barrier for the void nucleation can be expressed as [13]:

$$\Delta G = \frac{4\gamma^3 f_V}{\sigma^2}, \quad (1)$$

where σ , γ , f_V are the local stress, interface energy and a geometrical factor of the void, respectively. Obviously, σ includes the thermal stress and other residual stress formed during the aging procedure. According to the Gibbs isotherm, the interfacial energy would reduce because of the Bi segregation at the Cu/Cu₃Sn interface. In

addition, the thermal stress would increase with aging time. Based on Eq. (1), the ΔG would decrease as the value of γ reduces, and increase the local stress σ . Therefore, a steady-state nucleation rate of voids would occur during the aging procedure. The growth of voids would accelerate because the atoms on the void surface diffuse to the solder. As a result, a high concentration of voids would form near the interface and further support the growth of voids due to the Kirkendall effect [13,14]. In contrast, Bi particles and voids were not observed at the SnBi/CuSn interface when the couple was aged at 120 °C even for 17 days, as displayed in Figure 1b. This indicated that Bi segregation would be restrained at the SnBi/CuSn interfaces even after a longer aging time.

Based on these experimental results, the interfaces of SnBi/CuAg couples were investigated. A fine Cu₃Sn/CuAg interface was observed irrespective of whether the Ag concentration was high (18.7%) or low (2.5%) for the CuAg substrate, as illustrated by the black arrows in Figure 1c and d. The current experimental results further confirm that Bi segregation was also inhibited in the SnBi/CuAg couples. In addition, Cu–2.3Al and Cu–10Zn alloys were used to reveal whether these can inhibit Bi segregation. These results demonstrate that Bi segregation did not occur at the interfaces of the SnBi/CuAl and SnBi/CuZn couples, as illustrated by the black arrows in Figure 1e and f.

A very important question, however, needs to be considered: where are the Bi atoms for these SnBi/Cu–X couples? It is assumed that the Bi atoms from the SnBi solder should diffuse into the Cu alloy to form a more stable alloy system compared with the Bi segregation at the Cu/Cu₃Sn interface. In order to confirm such assumption, an accelerated experiment was designed. The Cu–18.7Ag alloy was completely saturated in liquid Bi at 500 °C for 6 h. It is clearly seen that some Ag in the Cu–18.7Ag alloy was almost replaced by Bi, as illustrated in Figure 2. This indicates that the replacement of Ag atoms by Bi atoms makes the Cu–Ag system more stable compared with the binary Cu–Ag alloy. It has been proved previously that the Ag–Cu–Bi alloy forms the Ag₅Cu_{0.5}Bi_{94.5} (at.%) eutectic phase [15]. Thus, the existence of Ag in Cu–Ag alloy assists the diffusion of Bi atoms into Cu–Ag alloy, forming a more stable ternary CuAgBi alloy during aging. However, the diffusion of Bi atoms into the

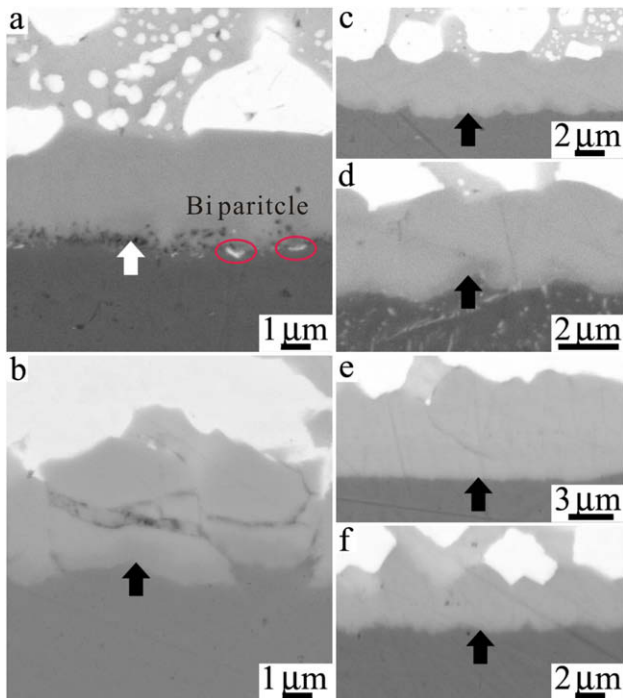


Figure 1. Interfacial microstructures of samples aged at 120 °C: (a) SnBi/Cu for 12.5 days; (b) SnBi/Cu–3Sn for 17 days; (c) SnBi/Cu–2.5Ag for 12.5 days; (d) SnBi/Cu–18.7Ag for 12.5 days; (e) SnBi/Cu–2.3Al for 17 days; and (f) SnBi/Cu–10Zn for 17 days.

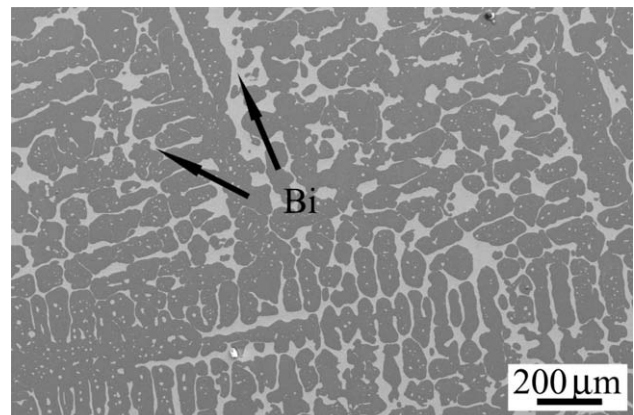


Figure 2. Microstructure of Cu–18.7Ag alloy after saturating in liquid Bi for 6 h.

pure Cu substrate is very difficult because the Cu–Bi system is completely immiscible [16–18].

Since Bi segregation has been eliminated, it is necessary to measure the mechanical properties of the SnBi/Cu–X joints after aging for different periods. Figure 3a shows the tensile stress–strain curves of the SnBi/Cu and SnBi/Cu–18.7Ag joints. These results demonstrate that different mechanical properties are observed for the SnBi/Cu and SnBi/CuAg joints. The tensile strength of the SnBi/Cu is strongly affected by the aging time (see curves A and C). Figure 3b shows that the tensile strength of SnBi/Cu dramatically decreases from about 155 MPa for as-reflowed to 31 MPa after aging at 120 °C for 8.25 days. When the SnBi/Cu joints were aged at 120 °C for 13.5 days, the joints were very easy to break even during grinding, so its tensile strength is deemed to be approximately zero.

However, the tensile stress–strain curve of the SnBi/Cu–18.7Ag joint shows no obvious change (see curves B and D in Fig. 3a). The decrease in the tensile strength is only about 10 MPa when the SnBi/Cu–18.7Ag joint samples were aged at 120 °C for 11 days. Since alloying Cu substrate can significantly improve the joint strength, other SnBi/Cu–X joints were also investigated in our experiment. Figure 3b shows the dependence of tensile strength on aging time for all the SnBi/Cu–X (X = Al, Ag, Sn and Zn) joints. It can be seen that the tensile strength decreases only slightly with increasing aging time for all the joints, which is significantly different from the SnBi/Cu joints, as illustrated by the panel in Figure 3b. If only the mechanical properties are considered, the Cu–Ag alloys are the best substrate. However, the growth kinetics of intermetallic compounds (IMCs) and the cost of the product need to be considered. Experimental results have confirmed that the Cu₃Sn would not form at the interface and the growth rate of IMC is the slowest for the Cu–Zn alloy (H.F. Zou, unpublished). In addition, the price of Zn is the lowest among these metals [1]; therefore, the Cu–Zn alloy can be recommended as a potential substrate for the application of the SnBi/Cu–X couple joints.

Figure 4 shows the fracture morphologies of the joints. Many solders and IMCs were observed on the fracture surfaces of the as-reflowed SnBi/Cu joints, which is similar to other lead-free solder joints [19], as

displayed in Figure 4a. The inset picture of Figure 4a indicates, based on the cross-section of fracture morphology, that the IMC layer adhered to Cu substrate. Compared with the as-reflowed SnBi/Cu joint, the fracture morphology of the SnBi/Cu joint aged for 8.25 days is remarkably different from that of the as-reflowed samples, as displayed in Figure 4b. Most of the Cu substrate was exposed on the fracture morphology, as illustrated by the left inset diagram of Figure 4b. The Cu–Sn IMC layers adhere at the SnBi solder, but not at the Cu substrate, as demonstrated by the right inset diagram of Figure 4b. These results indicate that the fracture occurs along the Cu/Cu–Sn IMC interface rather than along the Cu–Sn IMC/solder interface, leading to the interfacial embrittlement.

Concerning the fracture mode of the SnBi/Cu joint aged at 120 °C over 8.25 days, Liu and Shang postulated that the difference in size between Cu and Bi atoms plays a significant role in the embrittlement as in the case of Bi–Cu alloy because the Bi atom is larger than the Sn and Cu atoms [2]. The previous results reported that the size effect causes Bi precipitation and void formation in the Cu matrix for the Cu–Bi alloy. Bi particles and voids were found on the fracture surface of the Cu–Bi alloy because of the different thermal expansion coefficients and the weak adhesion between the Cu matrix and Bi precipitates [20]. This is completely different from the situation found in SnBi/Cu joints. Thus, the embrittlement mechanism of SnBi/Cu joints should be different from that of the Cu–Bi alloy system. As mentioned above, Bi segregation accelerates the formation of voids in SnBi/Cu joints. Furthermore, the voids would isolate the Cu/Cu₃Sn interface and then dramatically decrease the interfacial bonding strength of the SnBi/Cu joint, as confirmed in Figure 1a and the left inset diagram in Figure 4b.

However, the tensile strengths of all SnBi/Cu–X joints decrease only slightly with increasing aging time, as illustrated by the panel in Figure 3b. All joints broke along the SnBi/Cu₆Sn₅ interface, and some SnBi solder was observed to adhere on the fracture surface for the as-reflowed SnBi/Cu–18.7Ag couples, as displayed in Figure 4c. The fracture morphologies of the SnBi/Cu–18.7Ag couple show no obvious change although the aging time increases up to 11 days, as shown by

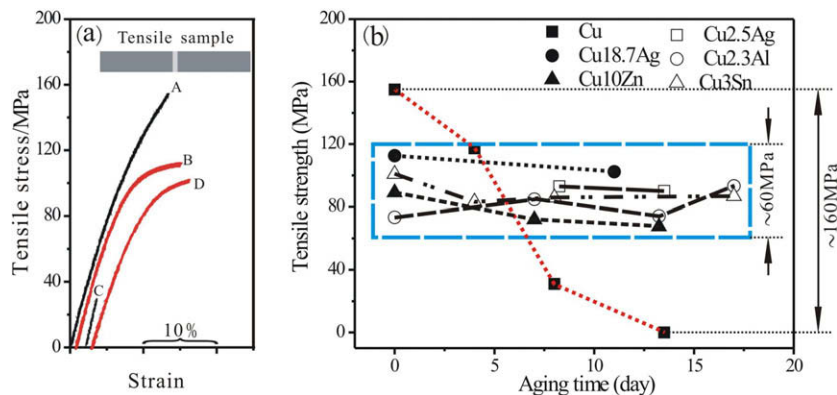


Figure 3. (a) Tensile stress–strain curves for SnBi joints. A and C represented the tensile curves of SnBi/Cu joints aged at 120 °C for 0, 8.25 days, respectively; B and D represented the tensile curves of SnBi/Cu–18.7Ag joints aged at 120 °C for 0, 11 days, respectively. (b) The dependence of tensile strength on aging time for all the SnBi/Cu and SnBi/Cu–X joints.

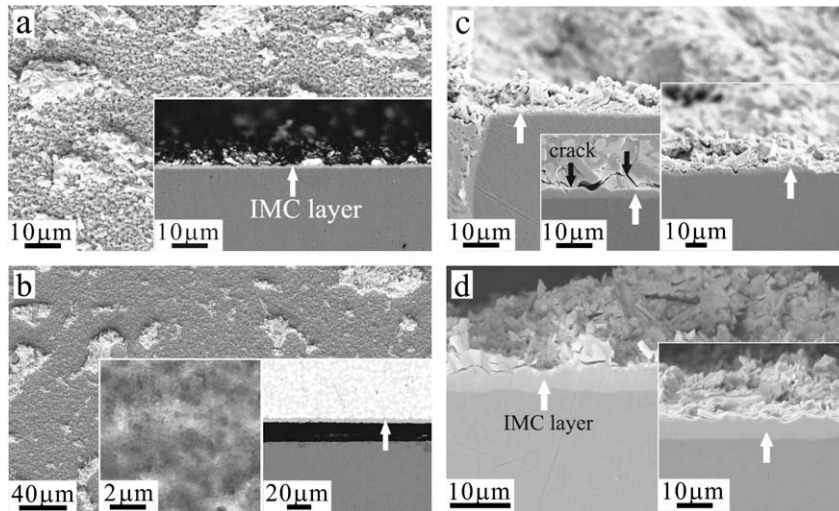


Figure 4. Fracture surfaces of SnBi/Cu, SnBi/Cu–18.7Ag and Cu–2.3Al/SnBi joints. (a) SnBi/Cu joint as-reflowed; (b) aged at 120 °C for 8.25 days—the left inset displays a magnified morphology, the right inset displays the cross-section morphology; (c) as-reflowed SnBi/Cu–18.7Ag joint and the joint aged for 11 days; and (d) as-reflowed SnBi/Cu–2.3Al joint and the joint aged for 17 days.

the right inset diagram in Figure 4c. The main reason is that the void would not form at the SnBi/Cu–X interface without Bi segregation. The left inset diagram in Figure 4c demonstrates that the crack first nucleated along the SnBi/Cu–Sn IMC interface. Irrespective of whether the SnBi/Cu–2.3Al joints were as-reflowed or aged, some SnBi solder still clung to the substrate, as displayed by the white arrows in Figure 4d. For other Cu alloy substrates, the fracture mode was unchanged for both as-reflowed and aged states. These results further confirm the elimination of Bi segregation and the interfacial embrittlement in SnBi/Cu–X joints on the micro-scale.

In summary, alloying Cu substrate can essentially eliminate the interfacial embrittlement and dramatically improve the mechanical properties of the SnBi/Cu system after prolonged aging. This strategy not only paves the new way for the widescale future use of SnBi solder in the electronic packaging field in the future, but also provides a new method to analyze interfacial segregation in systems such as Bi-doped Cu.

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