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Diffusion reaction-induced microstructure and strength evolution of Cu joints bonded with Sn-based solder containing Ni-foam

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Abstract

Sn based composite solder, reinforced with low porosity Ni-foam, was used to fabricate high melting point Cu interconnects by soldering at 260 °C. The effects of soldering time on the microstructure and mechanical properties of the joints were investigated. The Sn matrix was rapidly consumed by the formation of $(Cu,Ni)_6Sn_5$ and $(Ni,Cu)_3Sn_4$ phases in under 10 min. With increasing soldering time, the $(Cu,Ni)_6Sn_5$ phase was largely transformed into the $(Ni,Cu)_3Sn_4$ phase, accompanied by the refinement in the size of the phases. The average shear strength of the joint soldered for 60 min was up to 76.9 MPa, which is significantly stronger than commonly reported for Cu joints soldered with Sn based alloys.

Key word: Ni foam/Sn composite solder, Cu joint, solid state reaction, intermetallic compounds

1. Introduction

Miniaturization of electronic devices has led to the requirement for Cu interconnections at small scales. Where they are formed by Sn-based solders, these interconnects can be completely composed of high melting point Cu-Sn based intermetallic compounds (IMCs) which arise from consumption of the solder as a result of interdiffusion between solid and liquid phases during the bonding process [1]. However, the Cu-Sn IMC interlayers in Cu interconnects formed by this Sn/Cu interfacial reaction are brittle in nature [2]. Moreover, a relatively long soldering time (up to several hours) is necessary for complete removal of the Sn, which may lead to extra thermal stress in the bonded components and affect the reliability of the packaging system [3]. In previous studies [4, 5], addition of Ni particles to the solder was confirmed to be helpful in accelerating the Sn/Cu liquid/solid interfacial reaction rate and refining the $(Cu,Ni)_6Sn_5$ phase, though the resulting strength improvement of the Sn/Cu joint is limited because of the brittle nature of the IMC phases. Therefore, the development of a new solder material that can form reliable IMC joints using a short bonding time is highly desirable. It may be possible for the problem to be solved by using a low porosity and small pore size Ni foam or sponge as a strengthening phase permeating the Sn-based solder. Owing to the large specific surface area of the Ni foam, and its distribution throughout the solder, the rate of consumption of the molten Sn solder as a result of the Ni/Sn interfacial reaction should be increased. Besides, the unique 3D continuous structure of the Ni foam can provide a percolating network of ductile strengthening phase, which persists after the joining process [6], and may be helpful to improve the structural reliability of the brittle IMC layer. Thus, in this study, low porosity Ni-foam strengthened Sn-based composite solder was used to bond Cu interconnects. The research was focused on characterizing the isothermal diffusion reaction-induced microstructure and the mechanical properties of the resulting joints.

2. Experimental procedure

Commercial T2-Cu alloy cylinders with dimensions of Ø 5×3 mm were used as substrates. Open-cell Ni-foam foil with purity, thickness, porosity and average pore diameter of 99.99 wt%, 0.5 mm, 60 % and 50 μm respectively was used as the reinforcement phase for a Sn-based solder. The composite solder was fabricated by immersing Ni-foam into a molten Sn bath at 260 °C for 10 s, then pulling out the infiltrated foam, and rolling in a series of passes to a thickness of 60 μm in an electric rolling machine. The Cu substrates and composite solder foil were assembled in a sandwich structure and were soldered in a vacuum furnace at 260 °C with a pressure of 0.1 MPa, for various times. The cross-sectional microstructure of the joints produced was analyzed by scanning electron microscope (SEM, Zeiss Auriga40) equipped with an electron backscatter diffraction (EBSD, JSM-7001F) detector. Shearing tests on the joints were performed on an electron tensile testing machine (Instron-5569) at a crosshead speed of 0.5 mm/min. The shear strength was obtained by averaging the results for five tested samples.

3. Results and discussion

Fig. 1a-c show the cross-section SEM images of Cu joints soldered for 10, 60 and 120 min, respectively. The Sn matrix is completely consumed in the joint soldered for 10 min, and no longer observed in isolation (Fig. 1a). This is accompanied by the formation of a new phase around the Ni skeleton and another layernear the Cu substrate surface. It is known from previous work that the interaction of Sn/Ni and Su/Cu couples (with the Sn in the liquid state) leads to the formation of polycrystalline $(Ni,Cu)_3Sn_4$ (between Sn and Ni) and $(Cu,Ni)_6Sn_5$ (between Sn and Cu) [7, 8]. The high specific surface area presented by the Ni foam allows the reaction to proceed rapidly, and the molten Sn matrix is completely consumed, resulting in the formation of composite joint consisting of IMCs and a residual Ni skeleton distributed randomly through the joint. On increasing the soldering time to 60 and 120 min, the amount of residual Ni skeleton in the solder seam decreases gradually (Fig. 1b and 1c). A thin layer, identified as Cu_3Sn IMC, with a thickness of approximately 1~2 μm is formed on the Cu substrate surface in the joints soldered for 10 and 60 min (Fig. 1d and 1e), but this becomes the $(Cu,Ni)_3Sn$ phase with an increased thickness of about 4 μm in the joint soldered for 120 min (Fig. 1f). It should be noted that after 10 minutes, the only remaining phases have a high melting point, and so changes after this time must be occurring in the solid state. These changes therefore indicate that extensive solid diffusion and resulting reactions have occurred between the residual Ni skeleton and the reaction phases.

To observe the phase distribution of reaction phases more clearly in the above joints, EBSD mapping was performed, with images shown in Fig. 2a-c. This technique confirms the preliminary phase identification made earlier. The $(Cu,Ni)_6Sn_5$ phase mainly accumulates near the Cu substrate surface, with some isolated (at least in a planar view, they may connect out of plane) $(Cu,Ni)_6Sn_5$ islands dispersed inside the $(Ni,Cu)_3Sn_4$ phase in the joint soldered for 10 min (Fig. 2a). With increasing soldering time, the amount of $(Cu,Ni)_6Sn_5$ IMC (both in the layer and the islands) gradually decreases, accompanied by an increase in the $(Ni,Cu)_3Sn_4$ phase (Fig. 2b and 2c). Fig. 2d-f show grain mapping images of the corresponding joints. The joint exhibits a decreasing grain size with increasing soldering time. In particualr, a very refined microstructure is obtained in the joint soldered for 120 min. The measured grain sizes of the reaction phases are shown in Fig. 2g. It can be seen that the average grain size of the $(Cu,Ni)_6Sn_5$ phase is 7.9 μm at 10 min and this decreases to 3.6 μm at 120 min; meanwhile, the $(Ni,Cu)_3Sn_4$ grain size dramatically refines from 4.5 μm to 0.8 μm in the same soldering time range.

As discussed above, when prolonging the soldering time from 10 min to 60 min and 120 min, the metallurgical reaction of the solder seam will occur through a solid-state diffusion process. During this stage, elemental Ni tends to segregate at the $Cu_3Sn/(Cu,Ni)_6Sn_5$ interface and inhibit the diffusion of Cu from the Cu substrate into the solder seam [9]. This means that the supply of Cu into the soldering seam can be restricted, whilst Ni can keep diffusing into the solder seam by ongoing Ni-Sn interfacial reaction. Since the solubility of Cu in the $(Ni,Cu)_3Sn_4$ phase can reach 10 at. %, by replacing Ni atoms in the structure [10], a massive concentration gradient of elemental Cu would be formed between the $(Cu,Ni)_6Sn_5$ phase and the newly formed Ni/Sn reaction phase. Meanwhile, Sn is suggested to be the dominant species diffusing as part of the solid-state Sn/Ni interfacial reaction [11]. Hence, the rate of growth of the $(Ni,Cu)_3Sn_4$ phase is principally governed by the diffusion of Sn and Cu, through grain boundary diffusion. These processes may result in the decomposition of the $(Cu,Ni)_6Sn_5$ phase to accommodate the Cu and Sn shortages near the Ni skeleton surface, resulting in reduction in the fraction of $(Cu,Ni)_6Sn_5$ phase, as well as refining its size. As elemental Cu arrives, it can induce extensive nucleation of the $(Ni,Cu)_3Sn_4$ phase near the Ni skeleton surface [12]. Thus, due to the high rate of nucleation, the newly-formed $(Ni,Cu)_3Sn_4$ grains around the Ni skeleton surface exhibit a much refined grain size, and continued nucleation of new grains (outweighing grain growth) results in a decreased averaged grain size of the $(Ni,Cu)_3Sn_4$ phase. A simplified depiction of the phase transformation and refining process of the $(Cu,Ni)_6Sn_5$ and $(Ni,Cu)_3Sn_4$ phases is schematically shown in Fig. 2h.

The measured shear strength of the joints first increases, then sharply decreases, with prolonging soldering time (Fig. 3a). The joints soldered for 60 min exhibit the highest shear strength of 76.9 MPa. This value is much larger than that of more conventional Cu joints consisting of completely Cu_3Sn phase and $(Cu,Ni)_6Sn_5$ phase [4]. The joints soldered for 10 min and 60 min mainly fail in the solder interlayer (Fig. 3b and 3c), while the joint soldered for 120 min completely breaks near the $(Cu,Ni)_3Sn$ IMC layer (Fig. 3d). It can be deduced that the refinement of the size of the grains in the IMCs and the strengthening effect of the continuous Ni skeletons are most probably behind the strength improvement of the joint soldered for 60 min. On the other hand, for longer times, the excessive phase transition from the $(Cu,Ni)_6Sn_5$ phase to the $(Ni,Cu)_3Sn_4$ phase may induce volume shrinkage of the solder seam [13], which results in the formation of cracks in the joint soldered for 120 min (Fig. 1f) and thus decreases the shear strength the joint.

4. Conclusion

In summary, Cu interconnects that have potential to serve at high temperature were soldered using a Sn-based composite solder strengthened with Ni foam. The molten Sn matrix was consumed in under 10 min, as a result of the rapid metallurgical reaction with both the high surface area of the Ni skeletons and also with the Cu substrates. This is accompanied by the formation of the high melting point $(Cu,Ni)_6Sn_5$ and $(Ni,Cu)_3Sn_4$ phases. Further solid-state diffusion reactions, allowed by prolonging the soldering time, can induce the massive decomposition of $(Cu,Ni)_6Sn_5$ phase and the increase of $(Ni,Cu)_3Sn_4$ phase. This was confirmed to be beneficial to decrease the grain sizes of $(Cu,Ni)_6Sn_5$ and $(Ni,Cu)_3Sn_4$ phases and thus, in combination with the residual Ni skeleton, improved the shear strength of joint.

Acknowledgments

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Conflict of interest

No.

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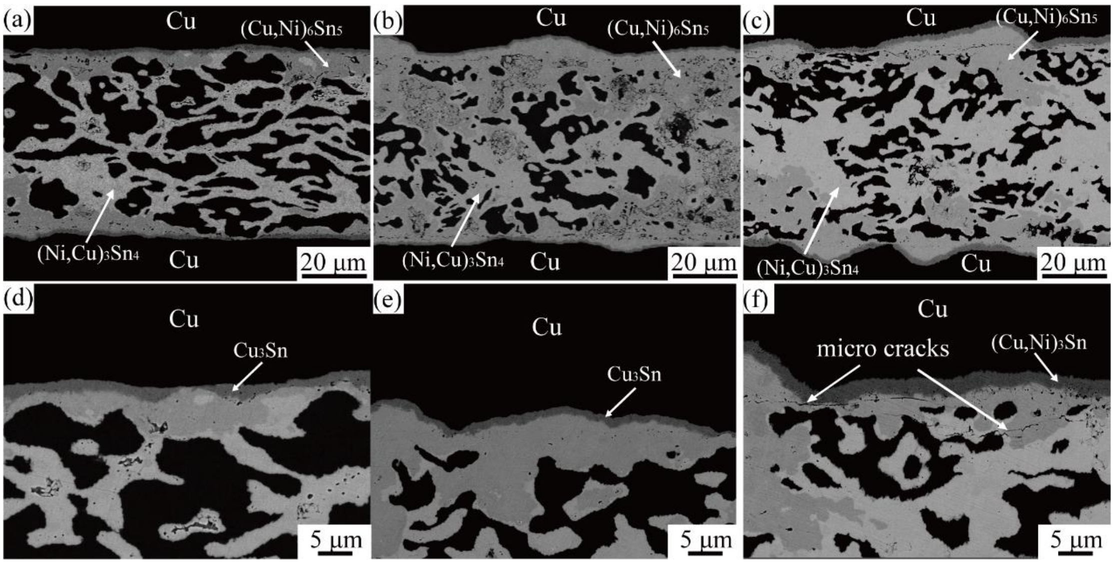
Figures:

Fig. 1. SEM images of Cu joints soldered for (a, d) 10 min, (b, e) 60 min and (c, f) 120 min.

Fig. 2. EBSD images of (a-c) phase mapping and (d-f) grain mapping of Cu/Ni-Sn/Cu joints soldered for (a, d) 10 min, (b, e) 60 min and (c, f) 120 min, (g) average grain size of reaction phases and (h) schematic diagram of phase transforming and grain refining process.

Fig. 3. (a) Shear strength of Cu joints and SEM images of shearing failed Cu joints soldered for (b) 10 min, (c) 60 min and (d) 120 min.



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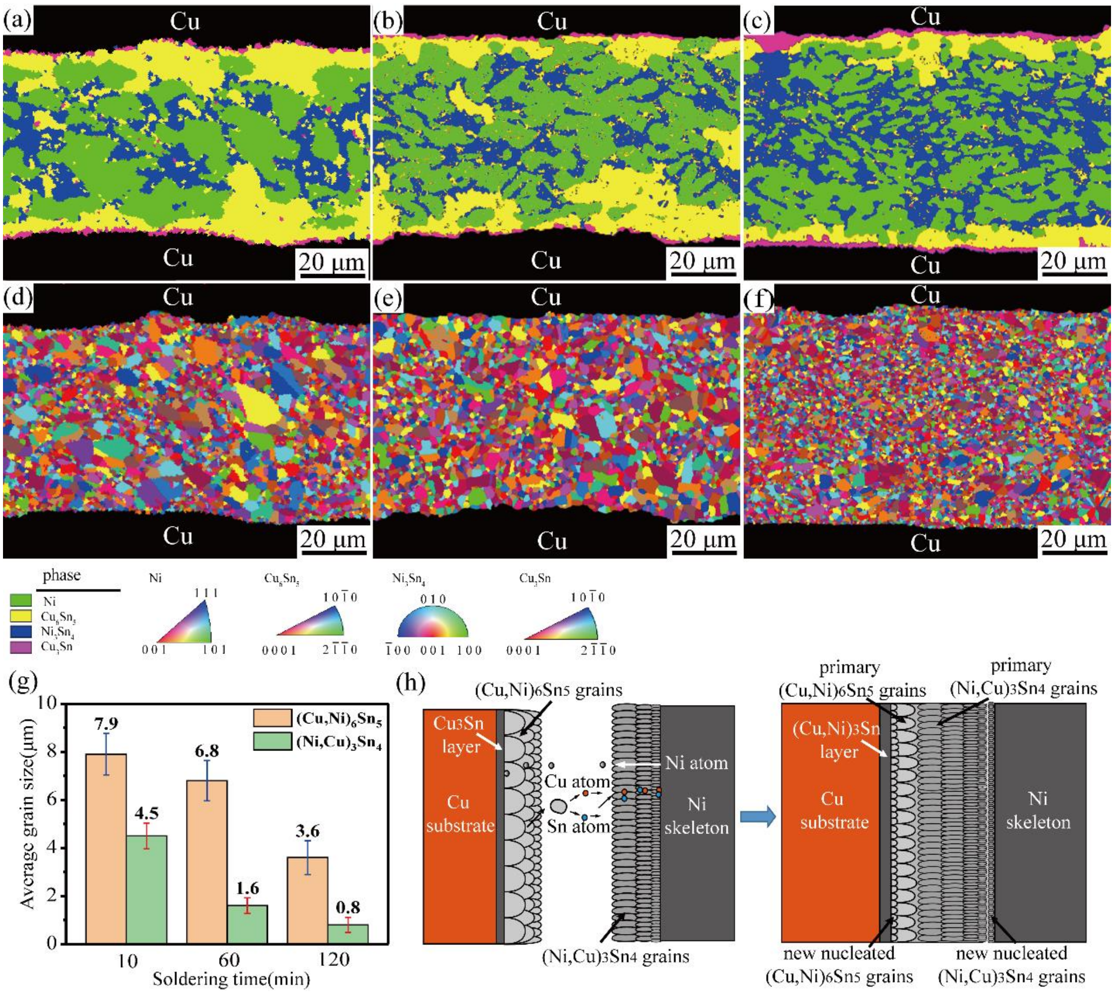

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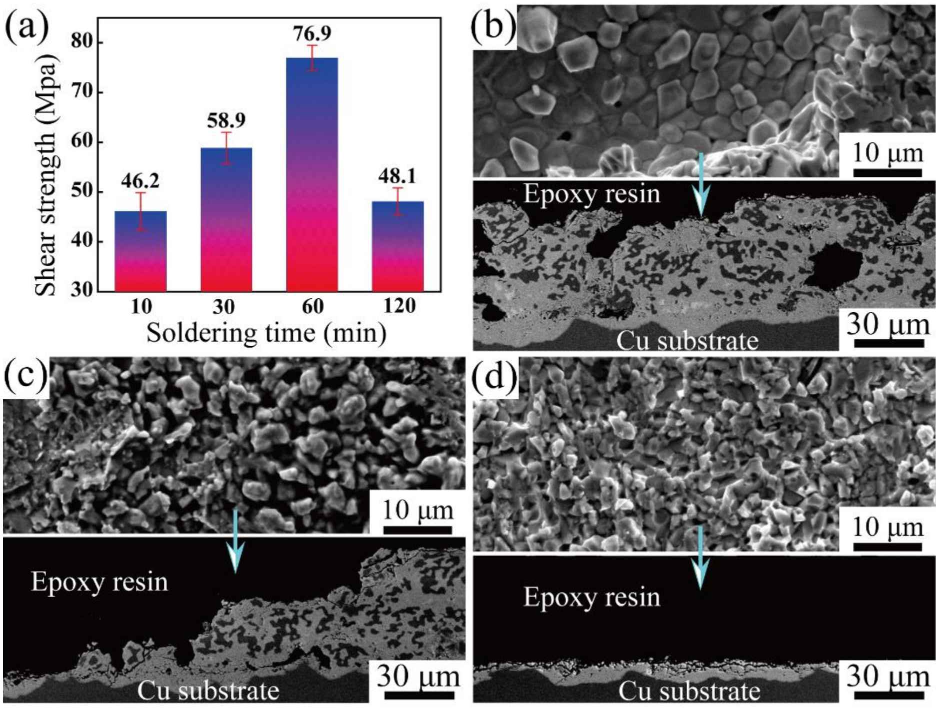

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