**Article:**

He, H., Huang, S., Ye, Y. et al. (4 more authors) (2020) Microstructure and mechanical properties of Cu joints soldered with a Sn-based composite solder, reinforced by metal foam. Journal of Alloys and Compounds, 845. 156240. ISSN 0925-8388

https://doi.org/10.1016/j.jallcom.2020.156240

# Microstructure and mechanical properties of Cu joints soldered with a Sn-based composite solder, reinforced by metal foam

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## Abstract

In this study, Ni foam, Cu coated Ni foam and Cu-Ni alloy foams were used as strengthening phases for pure Sn solder. Cu-Cu joints were fabricated by soldering with these Sn-based composite solders at 260 °C for different times. The tensile strength of pure Sn solder was improved significantly by the addition of metal foams, and the Cu-Ni alloy/Sn composite solder exhibited the highest tensile strength of 50.32 MPa. The skeleton networks of the foams were gradually dissolved into the soldering seam with increasing soldering time, accompanied by the massive formation of $(Cu,Ni)_6Sn_5$ phase in the joint. The dissolution rates of Ni foam, Cu coated Ni foam and Cu-Ni alloy foams into the Sn matrix increased successively during soldering. An increased dissolution rate of the metal foam leads to an increase in the Ni content in the soldering seam, which was found to be beneficial in refining the $(Cu,Ni)_6Sn_5$ phase and inhibiting the formation of the $Cu_3Sn$ IMC layer on the Cu substrate surface. The average shear strength of the Cu joints was improved with increasing soldering time, and a shear strength of

61.2 MPa was obtained for Cu joints soldered with Cu-Ni alloy/Sn composite solder for 60 min.

Keywords: Cu interconnects, metal foams, Sn-based solder, microstructure, mechanical properties

## 1. Introduction

With the rapid development of function integration and volume miniaturization in electronic products, better mechanical properties for Sn-based solder bonded interconnects are required to guarantee the reliability of electronic devices [1,2]. Adding appropriate alloying elements into Sn-based solder through the solid solution mechanism is the usual approach to improve the reliability of solder alloys [3]. Although some merits such as melting point reduction, wettability increase and oxidation resistance enhancement can be obtained by alloying in this way, the strengthening effect of common additions is limited [4,5]. An alternative way to improve the strength of a joint is adding micro- or nano-sized ceramic particles [6,7] or carbon nanotubes [8] into a Sn-based solder. Generally, the strength of these Sn-based solders can be substantially improved by dispersing strengthening [9]. However, the added second phases tend to aggregate during the soldering process, and cracks and cavities are easily created in the solder seam because of the poor interfacial bonding between Sn-based solder and the strengthening phases. Thus, more suitable strengthening materials should be selected to improve the soldering reliability of Sn-based solders and enhance the strength of the joint.

As a type of porous material, potentially integrating both structural and functional roles, metal-foams have been widely applied in fields including alloy strengthening [10], noise control [11], catalytic reaction [12], energy absorption [13] and so on. Huang et al. [14] reported that adding high melting point metal foam into a low melting point alloy can effectively improve the mechanical properties of that alloy, due to the unique three-dimensional (3D) continuous structure of metal foam providing a percolating network of strengthening phase. Open-cell Ni foam, which exhibits high strength and toughness and good metallurgical reactivity with Sn-based solder, has been considered as a promising strengthening phase to Sn-based solders. In our previous study [15], Ni foam reinforced Sn-based composite solder was used to bond Cu substrates with an ultrasonic-assisted soldering method. Interfacial reactants, including $(Ni,Cu)_3Sn_4$ and $(Cu,Ni)_6Sn_5$ intermetallic compounds (IMCs), were formed in large quantity, homogeneously dispersed in the solder seam, and excellent bonding strength was obtained with the combined strengthening effects of the Ni skeletons and these IMC particles. However, the ultrasonic bonding technology is known to be unable to connect devices which require high precision and which are made from materials with brittle characteristics. The strength of Ni foam/Sn composite solder bonded Cu joints is largely correlated with the number and morphology of the Sn/Ni interfacial reaction phases [15]. When the soldering process is performed without the assistance of ultrasonic vibration, dense interfacial IMC layers are formed on the solid substrate surface [16, 17], which may inhibit the interfacial reaction and thus deteriorate the strengthening effects of the metal foams. For example, Shao et al. [2] utilized a porous Cu interlayer to produce a high heat-resistant Cu joint via soldering process, the gap of the Cu foam was filled with dense $Cu_3Sn$ phase and the highest shear strength of joint was only 32.9 MPa. Numerous previous studies [16,18,19] have reported that the presence of Cu can affect the reaction behavior of the Ni/Sn interface, inducing both the phase and polycrystalline transformation of the Ni/Sn interfacial IMC layer, and accelerating the Ni/Sn interfacial reaction rate. This implies that by adjusting the composition of the Ni foam, the microstructure and properties of Cu joints bonded with alloy foam reinforced Sn-based composite solder may be optimized.

In this study, three types of metal foams, including Ni foam, Cu coated Ni foam and Cu-Ni alloy foam, were used to reinforce pure Sn solder. Comparable studies of the microstructure and mechanical properties of Sn-based composite solders as well as Cu joints bonded with these composite solders were performed, with an emphasis on correlating the metal foam type with the metallurgical reaction behavior of joints. The information found in this study may be beneficial to fabricate highly reliable Cu alloy joints at low temperature by using a new type Sn-based composite solder.

## 2. Experimental materials and methods

Pure Ni foam foils with thicknesses, purities and porosities of 0.5 mm, 99.9 % and 98 %

respectively were used in this study. The Cu coated Ni and Cu-Ni alloy foams were fabricated based on the pure Ni foam foil, with processing routes which are shown schematically in Fig. 1. The Cu coated Ni foam was fabricated by depositing a pure Cu metal layer (approximately 6 μm in thickness) on the Ni skeleton surface with an ultrasonic electroplating method. A pyrophosphate plating solution was used with a plating current density of 8 A/dm$^2$ and a plating time of 30 minutes. The Cu-Ni alloy foam was made by sintering the Cu coated Ni foam in a vacuum furnace at 900 °C for 2 h. The Sn-based composite solder foils were made by first immersing metal foams into a molten pure Sn bath kept at 260 °C. After the metal foams were completely infiltrated with pure Sn solder, the composite solder slices were taken out of the Sn bath and cold rolled in a series of passes to a thickness of 60 μm in an electric rolling machine (Kejing Co., Ltd, MSK-2150).

The base metal used in this study was commercial T2-Cu alloy cylinders with dimensions of Ø 5×3 mm. Prior to the soldering process, the surfaces of Cu substrates and composite solder foils were polished and ultrasonically cleaned in ethanol. Then the Cu substrates and composite solder foil were assembled in a sandwich structure and fixed in a stainless steel clamp, as shown in Fig. 1. Rosin flux was used during soldering. The soldering process was performed in a vacuum furnace, which was heated from room temperature to a soldering temperature of 260 °C with a heating rate of 10 °C/min. The as-soldered samples were kept at the soldering temperature for 10, 30, 60 and 120 min, respectively, and then taken out of the furnace and cooled in air to room temperature.

Cross-sections of the as-soldered joints were prepared for metallographic observation. The microstructure and elemental compositions of the joints were observed with a scanning electron microscope (SEM/EDS, Zeiss Auriga40). An electron back scatter diffraction analyzer (SEM/EBSD, JSM-7001F) was used to characterize the phase distribution and grain mapping of the soldering seam. The tensile strength of metal foams and composite solder foils, as well as the shear strength of the Cu joints were tested in an electronic universal mechanical testing machine (MTS-E44.104) with a crosshead speed of 0.5 mm/min. Prior to the tensile test, the metal foams and composite solder foils with a thickness of 0.5 mm were cut into a dumbbell shape, the sizes of which is shown in Fig. 2. During shearing test, the as-soldered Cu joint was fixed in a special fixture, the schematic diagram of which can be seen in previous studies [20]. Five samples were tested for each parameter to obtain an average value.

## 3. Results and discussion

### 3.1 Microstructure and mechanical properties of metal foams

The micrographs of Ni foam, Cu coated Ni foam and Cu-Ni alloy foam are shown in Fig. 3. The initial Ni foam is gray with a pore size of about 200 μm (Fig. 3a). After the electroplating process, the Ni skeleton surface is completely covered with (on the scale of the pores) smooth Cu metal (Fig. 3b). As for the Cu-Ni alloy foam, the skeleton exhibits a rough surface morphology (Fig. 3c), which may be helpful for the molten Sn solder to infiltrate the Cu-Ni alloy foam since increasing the surface roughness of wettable substrates can improve the wettability of molten Sn solder on them. The EDS mapping results of the Cu-Ni alloy skeleton are shown in figure 3d-f. The cross section through one of the skeleton struts shows a triangular shape with a wall thickness of about 20 μm. Cu and Ni are distributed homogeneously in the skeleton, and the measured content of Ni and Cu elements are 36.4% and 63.6%, respectively.

Fig. 4 shows the cross-section images of composite solder foils. Metal skeletons are randomly distributed in the Sn matrix (Fig. 4a-c), and the Cu coated Ni skeleton and Cu-Ni alloy skeleton occupy a larger volume fraction of the composite solder than the Ni skeleton because of the addition of Cu. It is difficult to find the reaction layer at the Ni/Sn interface (Fig. 4d), while a thin reaction layer can be found on the Cu coated Ni skeleton surface (Fig. 4e). Some cracks are formed in the Cu deposit layer and at the interface between the Cu deposit layer and the Ni skeleton, which may be created during the cold rolling process due to the difference in strength of these two phases. In the case of the Cu-Ni alloy foam/Sn composite solder, a gray contrast IMC layer with a thickness of about 2.5 μm is formed on the skeleton surface, and part of the reaction layer has been stripped into the soldering seam (Fig. 4f). This demonstrates that the Cu-Ni alloy foam exhibits higher reaction rate with Sn matrix than Ni foam and Cu coated Ni foam.

The tensile strengths of pure Sn solder, metal foams and metal foam reinforced composite solder foils are shown in Fig. 5. The measured tensile strengths of Ni foam, Cu coated Ni foam and Cu-Ni alloy foam are 3.81 MPa, 4.23 MPa and 4.79 MPa, respectively. While the tensile strengths of Sn-based composite solder foils strengthened with these metal foams are 39.29 MPa, 45.19 MPa and 50.32 MPa, respectively, which are 20.42 MPa, 25.91 MPa and 30.48 MPa higher than the sum of pure Sn solder (15.05 MPa) and the corresponding metal foams added to form a composite in each case. Compared with the measured tensile strength of pure Sn solder, the strength of Ni/Sn, Cu coated Ni/Sn and Cu-Ni alloy/Sn composite solder is improved by 161.1 %, 200.2 % and 234 .4 %, respectively. This demonstrates that the strength of Sn matrix can be significantly improved by the addition of metal foams.

In the metal foam/Sn composite solder, the 3D continuous network structure of metal foam can provide Sn matrix with interpenetrating strengthening structure. Such an interpenetrating microstructure keeps continuous distribution of Sn matrix and reinforcement phase, which enables the metal skeletons to bear and transmit load and the plastic Sn matrix to blunt or deflect the cracks. Increasing the strength of the metal foam is beneficial to improve the mechanical properties of metal foam/Sn composite solder. Furthermore, the enhanced interfacial reaction activity between metal foam and Sn matrix is another key issue for the strengthening of the Sn-based composite solder. Thus, the strength of Sn matrix can be significantly improved by the addition of metal foams, and the Cu-Ni alloy/Sn composite solder exhibits the highest tensile strength.

### 3.2 Microstructure of Cu joints

Fig. 6 shows the cross-section images of Cu joints soldered with Ni/Sn, Cu coated Ni/Sn and Cu-Ni alloy/Sn composite solders for different times. Some gray reaction phases are formed around the metal foam skeletons and on the Cu substrate surfaces, the amount of which increases noticeably with prolonging soldering time in Cu joints soldered with each of the three kinds of composite solders. The reaction phase exhibits different growth rates in joints soldered with different solders. The joints soldered with Cu coated Ni/Sn and Cu-Ni alloy/Sn composite solders show faster metallurgical reaction rates than those soldered with Ni/Sn composite solder.

Fig. 7 shows magnified images of the composite solder/Cu interfaces. In the joint soldered with Ni/Sn composite solder for 10 min (Fig. 7$a_1$), continuous IMC layers are formed on the Ni skeleton and Cu substrate surfaces, which are inferred to be $(Cu,Ni)_6Sn_5$ phase according to the EDS analysis results shown in Table 1. The formation of $(Cu,Ni)_6Sn_5$ phase on the Ni skeleton surface can be attributed to the high diffusion rate of Cu in the Sn matrix [21]. Increasing the soldering time to 60 min (Fig.7$a_2$), the $(Cu,Ni)_6Sn_5$ phase grows rapidly, parts of which is stripped off and distributed in large, block-like forms in the soldering seam. Further increasing the soldering time to 120 min (Fig. 7$a_3$), the joint is mainly composed of the $(Cu,Ni)_6Sn_5$ phase and Ni skeleton, with only a small amount of Sn matrix identifiable in the soldering seam. A $Cu_3Sn$ IMC layer with a thickness of about 3.9 μm is formed on the Cu substrate surface. For the Cu joint soldered with Cu coated Ni/Sn composite solder for 10 min (Fig. 7$b_1$), a large number of loose $(Cu,Ni)_6Sn_5$ IMCs are identified in the solder seam. This indicates that the Cu electroplating layer on the Ni skeleton surface has been partially or completely consumed, and the Ni skeleton is involved in the interfacial reaction. Increasing the soldering time to 60 min and 120 min (Fig. 7$b_2$ and 7$b_3$), the Sn matrix is gradually substituted by the $(Cu,Ni)_6Sn_5$ phase, and a large number of micro cavities are formed in the $(Cu,Ni)_6Sn_5$ phase near the Ni skeleton. Similar to the joint soldered with Ni/Sn composite solder, a $Cu_3Sn$ IMC layer with a thickness of approximately 3.1 μm is formed in the joint soldered for 120 min (Fig. 7$b_3$). In the case of the Cu joint soldered with Cu-Ni alloy/Sn composite solder for 10 min (Fig. 7$c_1$), the $(Cu,Ni)_6Sn_5$ IMC layer near the Cu-Ni alloy skeleton is denser than that near the Cu coated Ni skeleton shown in Fig. 7$b_1$. With increasing soldering time (Fig. 7$c_2$ and 7$c_3$), the Sn matrix is almost completely transformed to dense $(Cu,Ni)_6Sn_5$ phase accompanied by extensive dissolution of the Cu-Ni alloy skeleton. A thin $Cu_3Sn$ IMC layer with a thickness of only 1.8 μm is formed in the joint soldered for 120 min (Fig. 7$c_3$), which is much thinner than that observed in Fig. 7$a_3$ and Fig. 7$b_3$.

To further analyze the phase distribution and grain morphology of Cu joints, EBSD characterization was performed. Fig. 8a-c show the phase distribution images of Cu joints soldered with Ni/Sn composite solder for different times. The Sn matrix is almost completely transformed to the $(Cu,Ni)_6Sn_5$ phase with increasing soldering time, and a thick $Cu_3Sn$ IMC layer is formed on the Cu substrate surface in the joint soldered for 120 min. These results are consistent with those obtained in the SEM investigation above. The grain mapping images of Cu joints are shown in Fig. 8d-f. The joint soldered for 10 min is mainly composed of blocky β-Sn phase (Fig. 8d). Increasing the soldering time to 60 and 120 min (Fig. 8e and Fig. 8f), the $(Cu,Ni)_6Sn_5$ phase shows a homogeneous structure with an average grain size of about 6.8 μm.

Fig. 9a-c show the EBSD images for phase distribution of Cu joints soldered with three kinds of composite solders for 60 min. The solder seams are mainly composed of $(Cu,Ni)_6Sn_5$ phase with some Ni skeletons and residual Sn matrix dispersed in it. The metal skeletons remaining in the solder seam are decreased gradually in the three kinds of joints, indicating increasing dissolution rate of the metal skeletons. Fig. 9d-f show the grain mapping images of the corresponding solder seams. The average grain sizes of the $(Cu,Ni)_6Sn_5$ phase and residual Sn matrix in joints soldered with Ni/Sn, Cu coated Ni/Sn and Cu-Ni alloy/Sn composite solders are 6.8 μm, 6.3 μm and 4.8 μm, respectively. Compared with the relatively uniform grains formed in the joint soldered with Ni/Sn composite solder, the grains are significantly refined in the center of soldering seam but grow bigger near the Cu substrates in joints soldered with Cu coated Ni and Cu-Ni alloy composite solders. Thus, Cu joints soldered with three kinds of composite solders exhibit different microstructure and grain size.

### 3.3 Metallurgic reaction mechanism of Cu joints

It is known that a dense $Ni_3Sn_4$ IMCs layer always forms at a Sn/Ni interface [22]. Previous studies demonstrated that the $Ni_3Sn_4$ IMC layer was an excellent elemental diffusion barrier layer, which could inhibit the mutual diffusion of Ni and Sn [22,23]. The $Ni_3Sn_4$ phase is few found in the joint soldered with Ni/Sn composite solder (Fig. 8a-c). This may be affected by the Cu present in the joint from dissolution of the substrates. The diffusion rate and solubility of Cu in molten Sn matrix is much higher than that of Ni [16]. Elemental Cu can diffuse rapidly from the Cu substrate to the Sn/Ni interface. When Cu diffuses into the $Ni_3Sn_4$ IMC layer, the $(Ni,Cu)_3Sn_4$ phase can be changed to the $(Cu,Ni)_6Sn_5$ phase under the driving force due to the increase of entropy [24], and the morphology of the dense $Ni_3Sn_4$ IMC layer can be broken into a loose porous structure under the mechanical stress created by the phase transformation [25,26].

Moreover, the presence of elemental Ni in molten Sn matrix can dramatically reduce the solubility of Cu, which can result in the massive and dispersive precipitation of Cu and Ni atoms in the form of $(Cu,Ni)_6Sn_5$ particles, and thus induce the refining of the $(Cu,Ni)_6Sn_5$ phase [27,28]. The fine scale polycrystalline structure may further improve the diffusion rate of Ni through the material by increasing the number of available grain boundary diffusion paths [29]. Thus the elemental Ni can diffuse rapidly into the Sn matrix accompanied by the rapid growth of the $(Cu,Ni)_6Sn_5$ IMC layer.

For the joint soldered with Ni foam/Sn composite solder, the elemental Cu required for tailoring the Sn/Ni interfacial reaction comes from the Cu substrate. The interfacial reaction is limited by the long diffusion distance from the Cu substrate to the Ni skeleton surface. By depositing a Cu metal layer on the Ni skeleton surface, a $Cu_6Sn_5$ IMC layer can be formed there first. Since there are cracks present in the Cu deposition layer, Ni from the skeleton can diffuse to the $(Cu,Ni)_6Sn_5$ phase, and thus induce the breaking up and rapid growth of the $(Cu,Ni)_6Sn_5$ IMC layer [30,31]. After the Cu deposit layer is consumed, Cu atoms can diffuse from the nearby $(Cu,Ni)_6Sn_5$ particles to the Ni skeleton surface, resulting in the rapid growth of the $(Cu,Ni)_6Sn_5$ phase on the Ni skeleton surface [25]. Thus, the dissolution rate of Cu coated Ni foam in the Sn matrix is higher than that of uncoated Ni foam. The extensive diffusion of Cu which occurs from the initially formed $(Cu,Ni)_6Sn_5$ phase to the Sn/Ni interface may induce the formation of Kirkendall cavities, which can be found in Fig. 7$b_2$ and 7$b_3$. These cavities may be detrimental to the reliability of the joint. As to the Cu-Ni alloy foam, interaction reactions of Sn/Ni and Su/Cu couples occur at the initial stage, which can decrease the formation energy of the $(Cu,Ni)_6Sn_5$ phase and induce the rapid growth of the interfacial IMC layer [27,32]. Moreover, the Cu-Ni alloy has a lower melting point than that of pure Ni, which means a higher dissolution rate of Cu-Ni alloy into the molten Sn matrix would be expected. Thus, the Ni-Cu alloy foam exhibits the highest dissolution rate in the Sn matrix seen among the three kinds of metal foams examined here.

A faster dissolution rate of metal skeletons implies a much higher Ni content in the Sn matrix after bonding. The Ni content of the solder seams in joints soldered with the three kinds of composite solders for 120 min are shown in Table 1. The Ni content increases gradually in joints soldered with Ni/Sn, Cu coated Ni/Sn and Cu-Ni alloy/Sn composite solders. The large dissolution of Ni in the Sn matrix can accelerate the non-interfacial precipitation of Cu and thus increase the nucleation rate of the $(Cu,Ni)_6Sn_5$ phase [27,33]. In joints soldered with Cu coated Ni/Sn and Cu-Ni alloy/Sn composite solders, the dissolution of Cu and Ni atoms can occur almost simultaneous near the metal foams, which means that massive and dispersive $(Cu,Ni)_6Sn_5$ particles can be formed near the metal skeletons. The overgrowth of $(Cu,Ni)_6Sn_5$ grain can be restricted, resulting in the formation of significantly refined grains near the metal foams. Thus, in joints soldered with Cu coated Ni/Sn and Cu-Ni alloy/Sn composite solders, the grain size of $(Cu,Ni)_6Sn_5$ phase around the metal foams is smaller than those formed near the Cu substrate surface. Furthermore, because of it having the highest Ni content in soldering seam, the joint soldered with Cu-Ni alloy/Sn composite solder exhibits the smallest grain size among joints soldered with the three types of composite solders.

The increase of Ni content in the solder seam may also be beneficial to inhibit the growth of the $Cu_3Sn$ IMC layer on the Cu substrate surface. Zeng et al. [34] found that the elemental Ni tended to segregate at the $(Cu,Ni)_6Sn_5/Cu$ interface in the Sn-0.7Cu-0.05Ni/Cu joints, which was ascribed to significant difference in mobility of the Cu and Ni atoms in the $(Cu,Ni)_6Sn_5$ phase during the interfacial reaction process. The segregation of Ni can block the reaction between Cu and Sn, and thus inhibit the formation of $Cu_3Sn$ IMC layer as well as the dissolution of Cu substrate. The inhibition effect is inferred to be associated with the low diffusion rate of Sn in the Ni-rich layer. Increasing the Ni content in the solder seam can enhance the segregation of Ni between $(Cu,Ni)_6Sn_5$ IMC layer and Cu substrate, and thus further retarding the growth of the $Cu_3Sn$ IMC layer [35]. As a result, the $Cu_3Sn$ IMC layer formed on the Cu substrate surfaces in the joint soldered with Cu-Ni alloy/Sn composite solder is thinner than that soldered with Cu coated Ni/Sn composite solder and especially so in comparison with the case when soldered with Ni/Sn composite solder.

### 3.4 Shear strength of failure mechanism of Cu joints

To evaluate the effect of microstructure on the mechanical properties of Cu joints, shear strength tests were performed. Fig. 10 shows the shear strength of Cu joints soldered with three kinds of composite solders for different times. When soldering for 10 min, the average shear strength of joints soldered with Ni/Sn, Cu coated Ni/Sn and Cu-Ni alloy/Sn composite solder is 16.3 MPa, 31.9 MPa and 38.6 MPa, respectively. This demonstrates that the strength of Cu joints soldered with Cu-Ni alloy/Sn composite solder is approximately 137 % higher than that soldered with Ni/Sn composite solder. With increasing soldering time, the shear strengths of joints soldered with different composite solders all initially increase, and then decrease. All the joints exhibit the highest shear strength when soldering for 60 min; 61.2 MPa, 56.7 MPa and 52.7 MPa for joints soldered with Cu-Ni alloy/Sn, Cu coated Ni/Sn and Ni/Sn composite solders, respectively. Moreover, when soldering for the same time, the shear strength of joints soldered with Cu-Ni alloy/Sn composite solder is higher than those soldered with Cu coated Ni/Sn composite solder, and the joints soldered with Ni/Sn composite solder exhibit the lowest shear strength.

Fig. 11 shows the cross-section images after failure in shear of Cu joints soldered with the three types of composite solders for different times. For joints soldered for 10 min and 60 min, cracking mainly happens in the solder seam for all the joints. This implies that the shear strength of joints is closely related to the solder seam interlayer. The tensile strength of Cu-Ni alloy/Sn composite solder is much higher than that of Cu coated Ni/Sn and Ni/Sn composite solders. Moreover, $(Cu,Ni)_6Sn_5$ particles are formed in large amounts and exhibit smallest grain size in joints soldered with Cu-Ni alloy/Sn composite solders. Thus, the strength of joints soldered with Cu-Ni alloy/Sn composite solder is higher than those soldered with Cu coated Ni/Sn and Ni/Sn composite solder. Increasing the soldering time to 120 min, cracking is seen in the $Cu_3Sn$ IMC layer for joints soldered with Ni/Sn and Cu coated Ni/Sn composite solders, while it mainly happens in the solder seam for the joint soldered with Cu-Ni alloy/Sn composite solder. Previous studies demonstrated that poor adhesion could be created between thick $Cu_3Sn$ and $Cu_6Sn_5$ IMC layers [17]. Moreover, many Kirkendall cavities are formed in the joint soldered with Cu coated Ni/Sn composite solder. Thus, the shear strengths of joints soldered with Ni/Sn and Cu coated Ni/Sn composite solders rapidly decrease when prolonging the soldering time from 60 min to 120 min. As to the joint soldered with Cu-Ni alloy/Sn solder, it seems that the strength decrease can be ascribed to the excessive dissolution of Cu-Ni alloy skeletons, leading to the breakup of this phase. The disappearance of the 3D continuous network structure of ductile Ni-Cu alloy skeletons makes it easier for cracks to propagate in the brittle $(Cu,Ni)_6Sn_5$ IMC, resulting in a decreased reliability of joint.

## 4 Conclusion

In this study, Cu joints were soldered with metal foams reinforced Sn-based composite solders, and the effects of metal foam composition and soldering time on the microstructure and mechanical properties of joints were investigated. The main conclusions are as follows:

(1) The tensile strength of pure Sn solder could be significantly improved by adding Ni foam, Cu coated Ni foam and Cu-Ni alloy foam into it. The Cu-Ni alloy/Sn composite solder exhibited the highest tensile strength of 50.32 MPa, which could be attributed to the high strength and strong reactivity of Cu-Ni alloy foam.

(2) During soldering, $(Cu,Ni)_6Sn_5$ IMC was formed on the metal skeletons and Cu substrates surfaces, the amount of which was increased with prolonging soldering time. For joints soldered for 120 min, the soldering seam was mainly composed of metal skeletons and $(Cu,Ni)_6Sn_5$ phase.

(3) The dissolution rate of the Ni foam in the Sn matrix was lower than Cu coated Ni foam, while that of Cu coated Ni foam was lower than Cu-Ni alloy foam. Extensive dissolution of metal foam could increase the Ni content in the soldering seam, which could in turn decrease the grain size of the $(Cu,Ni)_6Sn_5$ phase and inhibit the formation of $Cu_3Sn$ IMC layer on the Cu substrate surface.

(4) The average shear strengths of joints soldered with three types of composite solders were all first increased and then decreased with increasing soldering time. Cu joints soldered with Cu-Ni alloy/Sn composite solder exhibited the highest shear strength, while those soldered with Ni foam had the lowest. The highest shear strength of 61.2 MPa was obtained for the Cu joint soldered with Cu-Ni alloy/Sn composite solder at 260 °C for 60 min.

## Acknowledgments

This work was supported by National Nature Science Foundation of China (No. 51605357). Dr. Yong Xiao is grateful to the Sir SY Chung Fellowship in the University of Sheffield.

**References**

[1] D.K. Mu, S.D. McDonald, J. Read, H. Huang, K. Nogita, Critical properties of $Cu_6Sn_5$ in electronic devices: Recent progress and a review, Curr. Opin. Solid State Mater. Sci. 20(2) (2016) 55-76.

[2] H. Shao, A. Wu, Y. Bao, Y. Zhao, G. Zou, L. Liu, Novel transient liquid phase bonding through capillary action for high-temperature power devices packaging, Mater. Sci. Eng., A 724 (2018) 231-238.

[3] T. Laurila, V. Vuorinen, M. Paulasto-Kröckel, Impurity and alloying effects on interfacial reaction layers in Pb-free soldering, Mater. Sci. Eng., R 68(1-2) (2010) 1-38.

[4] H. Pan, J. Huang, H. Ji, M. Li, Enhancing the solid/liquid interfacial metallurgical reaction of Sn+Cu composite solder by ultrasonic-assisted chip attachment, J. Alloys Compd. 784 (2019) 603-610.

[5] A.H. Nobari, M. Maalekian, K. Seelig, M. Pekguleryuz, Effect of Ag, Ni and Bi Additions on Solderability of Lead-Free Solders, J. Electron. Mater. 46(7) (2017) 4076-4084.

[6] G. Chen, H. Peng, V.V. Silberschmidt, Y.C. Chan, C. Liu, F. Wu, Performance of Sn-3.0Ag-0.5Cu composite solder with TiC reinforcement: Physical properties, solderability and microstructural evolution under isothermal ageing, J. Alloys Compd. 685 (2016) 680-689.

[7] A. Yakymovych, Y. Plevachuk, P.S. Švec, P. Švec, D. Janičkovič, P. Šebo, N. Beronská, A. Roshanghias, H. Ipser, Morphology and shear strength of lead-free solder joints with $Sn_{3.0}Ag_{0.5}Cu$ solder paste reinforced with ceramic nanoparticles, J. Electron. Mater. 45(12) (2016) 6143-6149.

[8] C.M. Tan, C. Baudot, Y. Han, H. Jing, Applications of multi-walled carbon nanotube in electronic packaging, Nanoscale Res. Lett. 7 (2012) 183.

[9] Y. Zhong, R. An, H.W. Ma, C.Q. Wang, Low-temperature-solderable intermetallic nanoparticles for 3D printable flexible electronics, Acta Mater. 162 (2019) 163-175.

[10] L.Z. Zhao, M.J. Zhao, L. Na, Y. Hong, J.S. Zhang, Microstructure of nickel foam/Mg double interpenetrating composites, Trans. Nonferrous Met. Soc. China 20 (2010) s463-s466.

[11] P.S. Liu, H.B. Qing, H.L. Hou, Primary investigation on sound absorption performance of highly porous titanium foams, Mater. Des. 85 (2015) 275-281.

[12] M.C. Tucker, Progress in metal-supported solid oxide fuel cells: A review, J. Power Sources 195(15) (2010) 4570-4582.

[13] N. Michailidis, F. Stergioudi, A. Tsouknidas, Deformation and energy absorption properties of powder-metallurgy produced Al foams, Mater. Sci. Eng., A 528(24) (2011) 7222-7227.

[14] L. Huang, L. Geng, H. Peng, Microstructurally inhomogeneous composites: is a homogeneous reinforcement distribution optimal?, Prog. Mater Sci. 71 (2015) 93-168.

[15] Y. Xiao, Q. Wang, L. Wang, X. Zeng, M. Li, Z. Wang, X. Zhang, X. Zhu, Ultrasonic soldering of Cu alloy using Ni-foam/Sn composite interlayer, Ultrason. Sonochem. 45 (2018) 223-230.

[16] H.J. Dong, Z.L. Li, X.G. Song, H.Y. Zhao, H. Tian, J.H. Liu, J.C. Yan, Grain morphology evolution and mechanical strength change of intermetallic joints formed in Ni/Sn/Cu system with variety of transient liquid phase soldering temperatures, Mater. Sci. Eng., A 705 (2017) 360-365.

[17] K. Chu, Y. Sohn, C. Moon, A comparative study of Cn/Sn/Cu and Ni/Sn/Ni solder joints for low temperature stable transient liquid phase bonding, Scr. Mater. 109 (2015) 113-117.

[18] Y.S. Huang, H.Y. Hsiao, C. Chen, K.N. Tu, The effect of a concentration gradient on interfacial reactions in microbumps of Ni/SnAg/Cu during liquid-state soldering, Scr. Mater. 66(10) (2012) 741-744.

[19] S.J. Wang, C.Y. Liu, Asymmetrical solder microstructure in Ni/Sn/Cu solder joint, Scr. Mater. 55(4) (2006) 347-350.

[20] Y. Xiao, S. Li, Z. Wang, Y. Xiao, Z. Song, Y. Mao, M. Li, Microstructure and mechanical properties of 7075-Al alloy joint ultrasonically soldered with Ni-foam/Sn composite solder, Mater. Sci. Eng., A 729 (2018) 241-248.

[21] R. Tian, C. Hang, Y. Tian, L. Zhao, Growth behavior of intermetallic compounds and early formation of cracks in Sn-3Ag-0.5Cu solder joints under extreme temperature thermal shock, Mater. Sci. Eng., A 709 (2018) 125-133.

[22] J. Görlich, D. Baither, G. Schmitz, Reaction kinetics of Ni/Sn soldering reaction, Acta Mater. 58(9) (2010) 3187-3197.

[23] A. Lis, C. Kenel, C. Leinenbach, Characteristics of reactive $Ni_3Sn_4$ formation and growth in Ni-Sn interlayer systems, Metall. Mater. Trans. A 47(6) (2016) 2596-2608.

[24] G. Zeng, S.D. McDonald, Q. Gu, Y. Terada, K. Uesugi, H. Yasuda, K. Nogita, The influence of Ni and Zn additions on microstructure and phase transformations in Sn–0.7Cu/Cu solder joints, Acta Mater. 83 (2015) 357-371.

[25] S.C. Yang, C.C. Chang, M.H. Tsai, C.R. Kao, Effect of Cu concentration, solder volume, and temperature on the reaction between SnAgCu solders and Ni, J. Alloys Compd. 499(2) (2010) 149-153.

[26] J.W. Ronnie Teo, Y.F. Sun, Spalling behavior of interfacial intermetallic compounds in Pb-free solder joints subjected to temperature cycling loading, Acta Mater. 56(2) (2008) 242-249.

[27] X.J. Guo, Z.L. Li, X.G. Song, H. Tian, H.J. Dong, H.Y. Zhao, Influence of Ni particle addition on grain refinement of Cu-Sn intermetallic compound joints bonded at various temperatures, J. Alloys Compd. 774 (2019) 721-726.

[28] M.A.A. Salleh, S.D. McDonald, C.M. Gourlay, S.A. Belyakov, H. Yasuda, K. Nogita, Effect of Ni on the formation and growth of primary $Cu_6Sn_5$ intermetallics in Sn-0.7 wt.%Cu solder pastes on Cu substrates during the soldering process, J. Electron. Mater. 45(1) (2015) 154-163.

[29] J.W. Xian, M.A.A. Mohd Salleh, S.A. Belyakov, T.C. Su, G. Zeng, K. Nogita, H. Yasuda, C.M. Gourlay, Influence of Ni on the refinement and twinning of primary $Cu_6Sn_5$ in Sn-0.7Cu-0.05Ni, Intermetallics 102 (2018) 34-45.

[30] Z. Li, H. Tian, H. Dong, X. Guo, X. Song, H. Zhao, J. Feng, The nucleation-controlled intermetallic grain refinement of Cu-Sn solid-liquid interdiffusion wafer bonding joints induced by addition of Ni particles, Scr. Mater. 156 (2018) 1-5.

[31] J.W. Yoon, B.I. Noh, B.K. Kim, C.-C. Shur, S.-B. Jung, Wettability and interfacial reactions of Sn-Ag-Cu/Cu and Sn-Ag-Ni/Cu solder joints, J. Alloys Compd. 486(1-2) (2009) 142-147.

[32] V. Vuorinen, H. Yu, T. Laurila, J.K. Kivilahti, Formation of intermetallic compounds between liquid Sn and various $CuNi_X$ metallizations, J. Electron. Mater. 37(6) (2008) 792-805.

[33] X. Zhang, X. Hu, X. Jiang, Y. Li, Effect of Ni addition to the Cu substrate on the interfacial reaction and IMC growth with $Sn_{3.0}Ag_{0.5}Cu$ solder, Appl. Phys. A 124(4) (2018) 315.

[34] G. Zeng, S.D. McDonald, D. Mu, Y. Terada, H. Yasuda, Q. Gu, K. Nogita, Ni segregation in the interfacial $(Cu,Ni)_6Sn_5$ intermetallic layer of Sn-0.7Cu-0.05Ni/Cu ball grid array (BGA) joints, Intermetallics 54 (2014) 20-27.

[35] T. Maeshima, H. Ikehata, K. Terui, Y. Sakamoto, Effect of Ni to the Cu substrate on the interfacial reaction with Sn-Cu solder, Mater. Des. 103 (2016) 106-113.