Advances in Engineering Research (AER), volume 137
2018 Joint International Advanced Engineering and Technology Research Conference (JIAET 2018)

Research on preparation and properties of isothermal solidification Cu-Sn high temperature solder paste

Manmen Liu[1,2,3,a], Jialin Chen[3,b], Hao Cui[3,c], Xudong Sun[1,2,4,d], Shaohong Liu[1,2,e], Ming Xie[3,f *], Xiaoli Zhu[1,2,g]

[1] Key Laboratory for Anisotropy and Texture of Materials (Ministry of Education), Northeastern University, Shenyang, 110819, China
[2] Institute of Ceramics and Powder Metallurgy, School of Materials Science and Engineering, Northeastern University, Shenyang, 110819, China
[3] State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals, Kunming Institute of Precious Metals, Kunming, 650106, China
[4] Liaoning Engineering Laboratory of Special Optical Functional Crystals, College of Environment and Chemical Engineering, Dalian University, Dalian, 116622, China

[a]lmm@ipm.com.cn, [b]cjl@ipm.com.cn, [c]cuihao@ipm.com.cn, [d]xdsun@mail.neu.edu.cn, [e]liush@smm.neu.edu.cn, [f]powder@ipm.com.cn, [g]zhuxl@hglaser.com

Keywords: Pb-free solder; Isothermal solidification; Diffusion; Shear strength

Abstract: A novel environmental-friendly Cu-Sn high temperature solder paste was fabricated by mixing Cu powder, Sn powder and commercial purchased flux. Different type and content of the flux may significantly affect the thermal properties of the solder paste. The bonding layer was composed of compact Cu_3Sn and loose Cu_6Sn_5. The thickness of the Cu_3Sn layer increased with the extension of the bonding time. The high temperature (at 300℃) shear strength of the bonding layer bonded under pressure of 10MPa was 23 MPa.

1. Introduction

The development of information technology and the rapidly expanding of their application area motivate the micromation and multi-functionalization of electronic devices. Advanced packaging technique and higher temperature tolerance solders were requested [1]. For example, flip chip(FC) technique usually needs high temperature solders, and it is essential to use a higher temperature bond for the first bonding step and progressively lower temperature bonds for the subsequent assembly steps in the multi-step welding of multi-chip module(MCM) packaging technique. However, the application of currently common high temperature solders Sn-95Pb (with melting point of 300℃) and Sn-80Au (with melting point of 280℃) encounters limitation because of their toxicity or expensiveness. Elevating the tolerance temperature of the Pb-free solder or developing new high temperature solder becomes an urgent problem to be solved[2]. Isothermal solidification(IS) technology, which was originally defined as Solid-liquid interdiffusion (SLID) technology by Bernstein and Bartholomew, was described as “a process whereby high-temperature phases are formed by diffusion in the presence of liquid”, and also “a technique which utilizes these phenomena in producing high-temperature-stable bonds which have been fabricated at low temperatures” by Bernstein[3,4]. On the isothermal solidification process, at least one low-melting metal and one high-melting metal are involved. Generally, isothermal solidification bonding consists of four stages: melting, dissolution, isothermal solidification, and homogenization. Once the bonding temperature is above the eutectic point of the system in question, a liquid phase appears. Then, the low-melting-point metal begins to react with the high-melting-point metal or the base metals. Intermetallic compounds (IMCs) with much higher melting temperature than the operation temperature were generated [5]. Because of the high melting temperature (over approximately 400℃) of the IMCs, the bonding technology is anticipated to satisfy the need for both high temperature reliability and repeatable multi-sided bonding [6]. In the present study, an isothermal solidification solder paste was prepared by mixing atomized copper powder and atomized tin powder with commercial purchased flux. Bonding can be achieved at temperatures above 231℃(the melting point of tin). The shear strength of the bonding layer at 300℃ is up to more than 20 MPa. The influence of type and content of flux on the performance of the solder paste was investigated. The effect of bonding pressure and time on microstructure of the bonding layer was analyzed.

2. Experiment procedure

The metal filler (atomic percentage N_{Cu}:N_{Sn}=55:45) and flux was mixed at a speed of 1800r/min, for 10 minutes, in an AR-100 CONDITIONING MIXER to gain the homogeneous solder paste. The calcination of the solder paste was performed in an tube furnace at 300℃ for 4 hours in flowing ultra-high purity Argon. The thermal property of the calcinate was analyzed by differential scanning calorimeter (DSC, DSC-131, NETZSCH, GER). The composition of the calcinate was analyzed by X-Ray Diffractometry (XRD, XPert, PANlytical, NED). Two pickling cleaned electrolytic copper sheets were glued by solder paste. Then the glued sample was naturally dried. A customized loading fixture of rectangular alumina plates with one hole at each corner along with appropriate alumina screws and bolts was prepared to hold the samples during bonding at joining temperatures. At room temperature, the whole fixture with samples between them was compressed to a uniaxial pressure of 1 or 10 MPa in an MTS Insight electromechanical test frame. The fixture was then placed in an alumina boat in the tube furnace (HF-Kejing, GSL-1100X-11-S2, CHN) to carry out bonding experiments at 300℃ for 4 hours. The vacuum level in the tube furnace was held at 2×10^{-2} Pa for 5 min followed by purging with ultra-high purity Argon. The purging process was repeated once again before heating the samples to the desired temperatures in flowing argon environment. Heating/cooling rate of 5℃/min was used during the joining experiments in the tube furnace. The shear strength of the joining layer at 300℃ was tested on an electronic universal testing machine (AG-X, SHIMADZU, JPN). Microstructure and fracture morphology of the cross-section of the joining layer were observed using scanning electron microscopy (SEM, JEM-IT001, JEOL, JPN). Composition analysis was carried out with an Energy dispersive spectrometer (EDS, JED-2300, JEOL, JPN).

3. Results and discussion

3.1 The morphology of the metal filler

Fig. 1 showed the morphology of the metal filler. The atomized copper powder (Fig. 1a) is spherical sub-micrometer particulates with a relatively wide size distribution. The atomized tin powder (Fig.1b) is roughly spherical micrometer particulates. A fine combination of particulates is beneficial to the densification of the joining seam and then to improve the shear strength of the soldered joint.

3.2 The influence of flux type on thermal properties of the soldering paste

Flux is usually composed of solvent, activation agent, filmogen, antioxidant, inhibiter and so on. Flux has non-ignorable influence on the thermal properties of the solder paste. The four solder pastes and corresponding fluxes are shown in Table 1. The thermal properties of the solder pastes

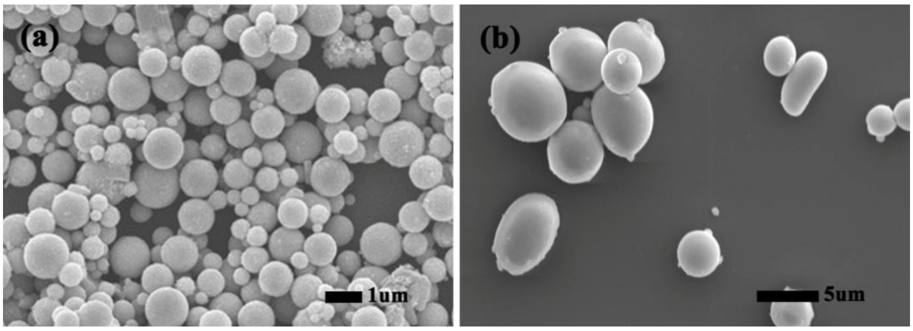

Figure 1. The morphology of the metal filler: (a) copper powder; (b) tin powder

were investigated by DSC analysis (shown in Fig. 2). The compositions of calcinates of the solder pastes were characterized by XRD analysis (shown in Fig. 3). The DSC curves show that the endothermic peak at 231℃ (the melting point of Sn) of calcinate of the solder pastes B1 is lowest. This result indicates that the residual tin in the calcinate of solder paste B1 is least. The XRD pattern shows that the calcinates are composed of Cu_6Sn_5, Cu_3Sn and Sn. The calcinate of solder paste B1 contain the least content of Sn and the most content of Cu_3Sn, as indicated by the strongest diffraction peak of Cu_3Sn and the weakest diffraction peak of Sn. This result indicated that Sn was consumed to the greatest extent by means of the reaction $Cu_6Sn_5+9Cu \rightarrow 5Cu_3Sn$.

Table 1. The names solder pastes and corresponding fluxes

Solder paste	Flux	Content of flux
A1	L-F3A(Tianjin Qinghe science and technology development co. , ltd)	15%
A2	L-3A(Tianjin Qinghe science and technology development co. , ltd)	15%
B1	JS-E-15X(KOKI co., ltd. JPN)	15%
B2	JS-EU-31(KOKI co., ltd. JPN)	15%

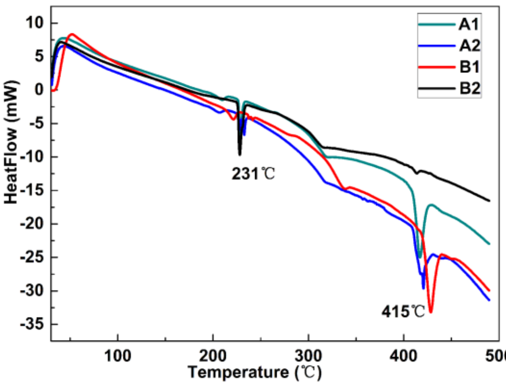

Figure 2. The DSC curves of the calcinates of the four solder pastes

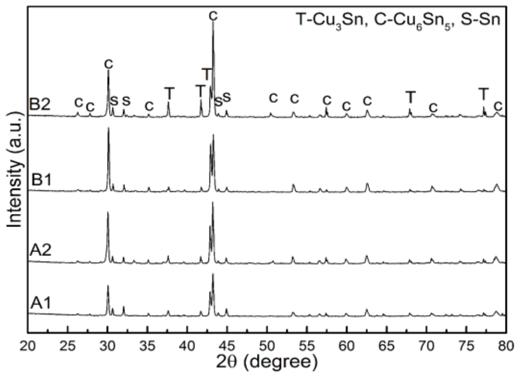

Figure 3. The XRD patterns of the calcinates of the four solder pastes

3.3 The influence of flux content on the thermal properties of the soldering paste

It can be seen from DSC curve of the calcinate of the solder pastes (Fig. 4) that the intensity of the endothermic peak at 231℃ increases with increasing flux content. There is no obvious endothermic peak at 231℃ in the DSC curve of the calcinate of solder paste with 13 wt.% flux. The results show that an excess of flux will lead to residual Sn in the calcinates. The possible reason for this phenomenon is that with an excess of flux, reduction of viscosity of the solder paste and enhancement of fluidity of the metal particulate accelerated the separation of the homogeneously mixed Sn and Cu particulates because of their significantly difference in density. Therefore, the interdiffusion path was elongated and the reaction is difficult to perform.

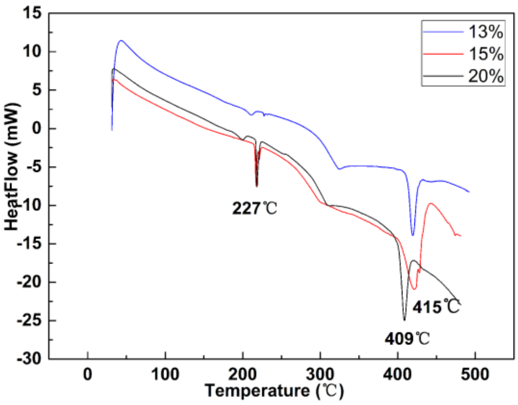

Figure 4. The DSC curves of the calcinates of solder pastes with different flux content.

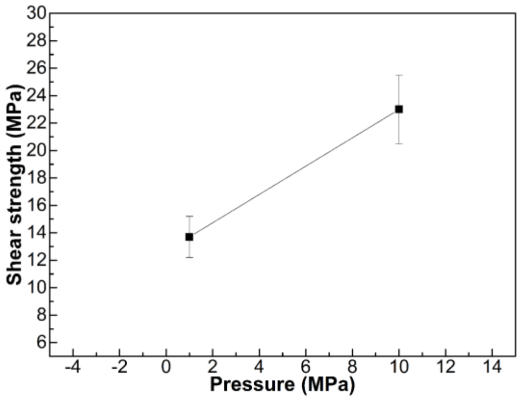

Figure 5. The shear strength of bonding layer bonded under 1MPa and 10MPa.

3.4 The influence of pressure on shear strength and microstructure of the bonding layer

Using solder paste B1, two pieces of electrolytic copper sheets were bonded according to the experimental procedure mentioned above. The shear strength was tested at 300℃ and the results are shown in Fig. 5. The shear strength of the bonding layer increases from 13.7±1.5 MPa to 23.0±2.5 MPa when the load pressure increases from 1 MPa to 10 MPa. Fig. 6 shows microstructure of the cross section of the bonding layer. The elemental compositions on the labeled positions are shown in Tab. 2. As shown in Fig. 6(a), fracture occurred under the action of low shear stress in the loose interlayer composed of intermetallic compound Cu_6Sn_5. By contrast, the formation of the compact interlayer composed of Cu_3Sn improved the shear strength of the bonding layer bonded under 10 MPa (as shown in Fig.6b).

Table 2. Elemental composition of the labeled position in Fig. 6.

position	Cu(at.%)	Sn(at.%)	phase	position	Cu(at.%)	Sn(at.%)	phase
001	55.15	44.85	Cu_6Sn_5	004	74.28	25.72	Cu_3Sn
002	76.12	24.88	Cu_3Sn	005	75.76	24.24	Cu_3Sn
003	100	0	Cu	006	100	0	Cu

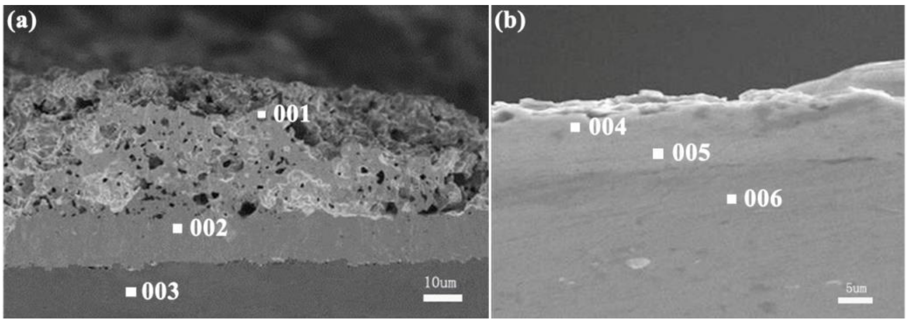

Figure 6. Microstructures of cross section of bonding layers: (a) bonded under 1MPa, (b) bonded under 10MPa.

3.4 The influence of bonding time on the microstructure of the bonding layer.

Using solder paste B1, five groups of samples were bonded at 300℃ under 1MPa for different duration time (1h, 8h, 16h, 24h and 32h, respectively), according to the experiment procedure mentioned above. The microstructure of cross section of the bonding layers and the Cu_3Sn thickness varies with increasing bonding time, as shown as Fig. 7. The compact Cu_3Sn layer adjoining to the copper sheet was formed by means of Cu_6Sn_5+9Cu=5Cu_3Sn. The Cu was provided *via* diffusion from the copper sheets. The Cu_3Sn thickness increases with increasing bonding time. However, the thickening rate gradually decreases with the extension of heating time. The reason for this may be due to the blocking of the diffusion of Cu from metal substrate to Cu_6Sn_5 layer by the formed compact Cu_3Sn layer.

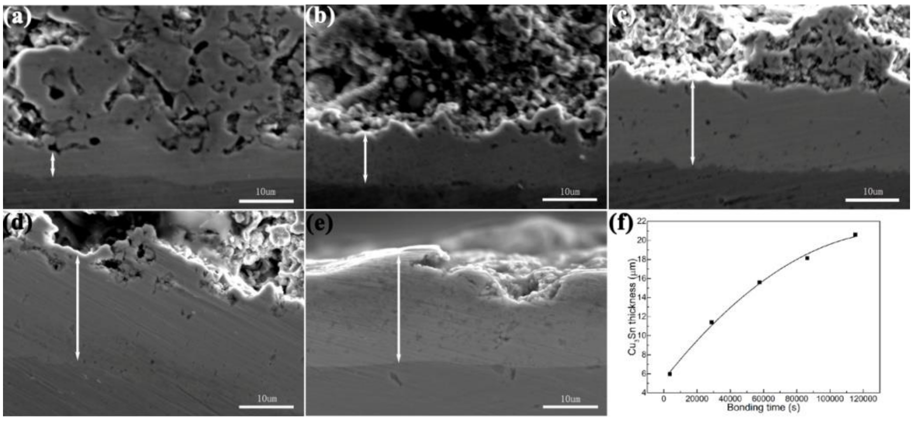

Figure 7. Microstructure of cross section of the bonding layer bonded for (a) 1h, (b) 8h, (c) 16h, (d) 24h, and (e) 32h; (f) The fitted curve of variation of thickness of Cu_3Sn with bonding time.

4. Conclusions

An isothermal solidification Cu-Sn high temperature solder paste was successfully fabricated by adding commercially purchased flux. The formation of intermetallic compounds (Cu_3Sn and Cu_6Sn_5) with high melting point in the bonding layer significantly improved the service temperature of the solder paste. Extension bonding time and increase bonding pressure is beneficial to form a compact Cu_3Sn layer and improve the shear strength of the bonding layer.

Acknowledgements

This work was financially supported by the National Key R&D Program of China (2017YFB0305700).

References

[1] W. Zhong, J. C. Zhao, First experimental measurement of calcium diffusion in magnesium using novel liquid-solid diffusion couples and forward-simulation analysis, Scripta Mater. 127 (2017) 92-96.

[2] S.W. Park, S. Nagao and Y. Kato，Quasi-transient liquid-phase bonding by eutectic reaction of Sn-plated Zn on Cu substrate for high-temperature die attachment, J. Alloys Comd. 637 (2015) 143-148.

[3] L. Bernstein, Semiconductor Joining by the Solid-Liquid-Interdiffusion (SLID) Process I. The Systems Ag-In, Au-In, and Cu-In, J. Electrochem. Soc. 113 (1966) 1282-1288.

[4] L. Bernstein, H. Bartholomew, Applications of solld-liquid interdiffnsion (SLID) bonding in integrated-circuit fabrication, Trans. Metall. Soc. AIME 236 (1966) 405-409.

[5] A. Sharif, C. L. Gan, Z. Chen, Transient liquid phase Ag-based solder technology for high-temperature packaging applications , J. Alloys Comd. 587 (2014) 365-368.