J Mater Sci: Mater Electron (2015) 26:9164–9170
DOI 10.1007/s10854-015-3606-y

Reliability study of industry Sn3.0Ag0.5Cu/Cu lead-free soldered joints in electronic packaging

Lei Sun[1] · **Liang Zhang**[1] · **Su-juan Zhong**[2] · **Jia Ma**[2] · **Li Bao**[2]

Received: 8 May 2015 / Accepted: 6 August 2015 / Published online: 13 August 2015
© Springer Science+Business Media New York 2015

Abstract The wettability of Sn3.0Ag0.5Cu on copper substrate with different reflow temperature was studied. The growth mechanism of intermetallic compound (IMC) and mechanical properties were also investigated under isothermal aging condition at 125, 150 and 175 °C with different aging time. The results showed that, with the reflow temperature increasing, the spreading area of Sn3.0Ag0.5Cu lead-free solder increased. The morphology of IMC formed at Sn3.0Ag0.5Cu/Cu interface was gradually changed from scallop-type to planar-type, and the thickness of IMC was increased with the aging temperature and aging time. Meanwhile, the IMC growth rate increased with aging temperature but decreased with aging time. In addition, the mechanical properties of solder joints with different isothermal aging decreased with increasing aging time. In the initial stage of isothermal aging, the mechanical properties of solder joints decreased rapidly, then the rate of decline became stabilized.

1 Introduction

SnPb solders have been widely used in electronic packaging. Due to the increasing environmental and human health concerns over the toxicity of lead, the development of highly reliable solder has become an important problem for electronic packaging industries [1]. Among several candidate alloys, Sn–Ag–Cu solder has been proposed as the most promising lead-free solder for replacement of traditional tin–lead solder owing to its relatively low melting temperature, good wettability, and excellent mechanical properties [2–4]. However, there are still some demerits need to be solved, such as higher soldering temperature and large undercooling. In addition, the formation of large brittle intermetallic compound (IMC) and large primary Sn dendrite may lead to serious problems in the actual series for printed circuit boards (PCB).

Interfacial reaction in solder/substrate systems is particular important to the manufacturability and reliability of electronic products [5]. During soldering, the solder will react with the substrate to form IMCs at the interface [6], such as Cu_6Sn_5, Cu_3Sn and other IMCs. It is known to all that a thin IMC layer is desirable to achieve a good metallurgical bound at the interface. However, an excessive IMC growth may degrade the reliability of solder joints owing to the brittle nature of IMC and their tendency to generate structural defects [7, 8]. Hence, the study on the growth kinetics and morphology of IMC is very important to understand of the reliability of the solder interconnection.

The Sn3.0Ag0.5Cu/Cu interfacial intermetallic compound layer and mechanical properties of solder joints after reflow and during isothermal aging were studied, respectively. An attempt has been made to understand how the morphology and growth of the interfacial IMC.

2 Experimental

2.1 Preparation of samples

Sn3.0Ag0.5Cu solder paste (a particle size of less than 34 μm) was employed in this study. Spreading area test

---

✉ Liang Zhang
zhangliang@jsnu.edu.cn

[1] School of Mechanical and Electrical Engineering, Jiangsu Normal University, Xuzhou 221116, China

[2] State Key Laboratory of Advanced Brazing Filler Metals and Technology, Zhengzhou Research Institute of Mechanical Engineering, Zhengzhou 450001, China

schematic of solder joint was shown in Fig. 1a. Before putting the solder paste, the Cu substrates were cleaned in alcohol. Then, the solder pastes were placed on the Cu substrate using a glass rod and putted in a reflow oven with temperatures of 250, 260 and 270 °C for soldering. After the reflow, the samples were taken out from the oven and cooled to room temperature in the air ambient. Subsequently, each sample was cut into half and embedded in epoxy resin as shown in Fig. 1b. They were ground with different grit sized sandpapers, and then polished with 2.5 μm diamond suspensions.

2.2 Isothermal aging

Isothermal aging can be used to simulate alteration of microstructure and properties of solder joints under working environment [9]. Therefore, isothermal aging was used for investigating solid-state IMC growth. The samples were aged in a furnace where temperatures were set to 125, 150 and 175 °C, the dwell times were 100, 200, 300 and 400 h.

2.3 Microstructure and thickness measurement of IMC

A Quanta 250 scanning electron microscopes (SEM) equipped with a thermo-electron X-ray energy dispersion spectrometry (EDS) was used to examine the microstructure and determine the phases in the interfacial region. In order to observe clearly the cross-section microstructures and the morphology of IMC at the interface, the samples were etched with a solution of $5HNO_3 + 95CH_3OH$ for several seconds. Considering the irregular shape of the IMC layer as shown in Fig. 2, the thickness of the interface layer was measured by using Image-J software. While, the average thickness of the interface layer (x) was calculated through dividing the integrated area (A) by the length of the interface layer (L), as shown in the following equation:

$$x = A/L \tag{1}$$

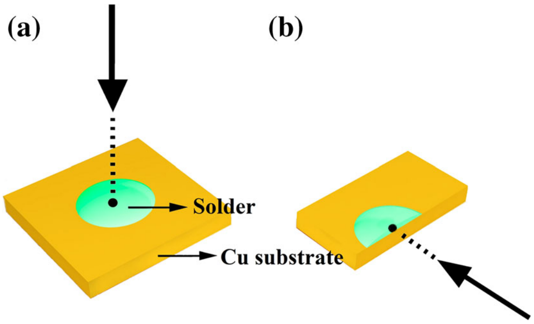

Fig. 1 Schematic drawing of **a** spreading area test, **b** the cross sectional view for SEM analysis

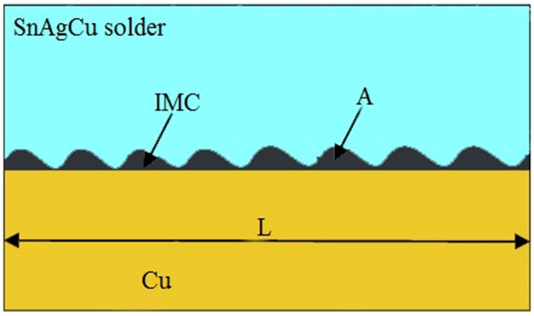

Fig. 2 The model of IMC

2.4 Mechanical properties testing

In order to reflect the practical application of electronic industry, the quad flat packages (QFP256) devices and resistors were selected as test carrier, which were soldered with SnAgCu solders, respectively. The package meets the Electronic Industry Association of Japan (EIAJ) package specifications, the dimensions of this QFP256 are 28 mm × 28 mm × 1.4 mm and the body is made of plastic. The QFP256 devices and resistors were soldered with Sn3.0Ag0.5Cu solder on the PCB substrate in an industrial reflow oven, then the samples were aged in a furnace where temperature was set to 150 °C, the dwell times were 100, 200, 300 and 400 h. Subsequently, the pull test and shear test were adopted to evaluate the mechanical properties of Sn3.0Ag0.5Cu solder by STR-1000 micro-joints strength tester (as shown in Figs. 3, 4).

3 Result and discussion

3.1 Wettability

The wettability is an importance index of solder. In the electronic industry, electronic devices with metal substrates

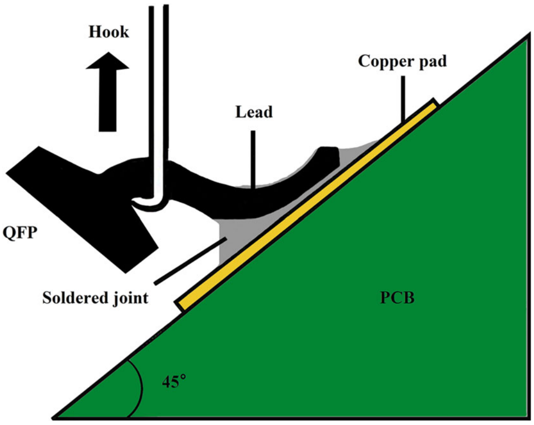

Fig. 3 Schematic of pull tester

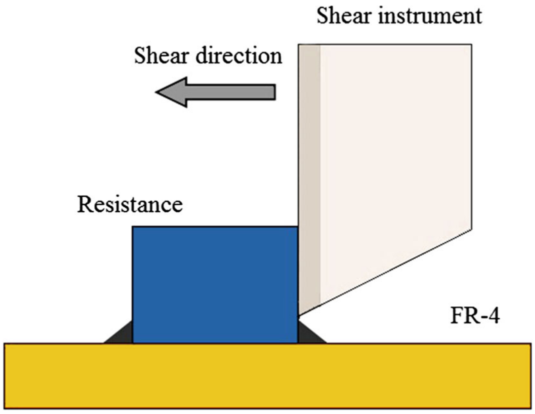

Fig. 4 Schematic of shear tester

are soldered with lead-free solders by reflow soldering. The wettability directly determines the ability of lead-free solder wetting the substrate under certain temperature conditions. Spreading area can be used to assess the wettability of SnAgCu solder.

Figure 5 shows the spreading areas of SnAgCu solder at different temperatures. With the reflow temperature increasing, the spreading area of SnAgCu lead-free solder increases. Due to the increase of temperature, the atomic diffusion movement between liquid solder and substrate surface becomes acute. Therefore, the solder spreading area increases.

3.2 Microstructure of solders

The microstructures of Sn3.0Ag0.5Cu/Cu solder joints aged at 150 °C for different aging times, are shown in Fig. 6. It is found that the typical microstructures of SnAgCu solder alloys consist of primary β-Sn grains, needle-like Ag_3Sn and scallop-type Cu_6Sn_5. After aging time, the second-phase particles of Ag_3Sn and Cu_6Sn_5 in the eutectic structure become coarse. We also find that, with the increase of aging temperature, the speed of coarsening is faster. In order to precisely determine the influence of isothermal aging on the needle-like IMC, the average length of needle-like IMC in the matrix was 20 μm with calculation in the microstructure. Figure 7 shows average length of needle-like IMCs in solder matrix with different aging time. Before aging, the average length of needle-like IMCs was about 13 μm. After aging 300 h, the length of needle-like IMCs increased remarkably. The coarsening mechanism of Ag_3Sn particles can be attributed to the reaction of residual Ag and Sn elements and small Ag_3Sn particles disappeared during isothermal aging.

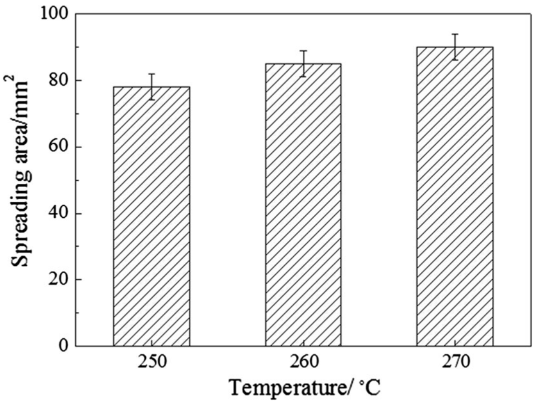

Fig. 5 Spreading areas of Sn3.0Ag0.5Cu solder at different temperatures

3.3 Microstructure of the interface

Figure 8 shows SEM micrographs of Sn3.0Ag0.5Cu solder joint depending on the aging times of 100, 200, 300 and 400 h at 150 °C on copper substrate. It can be seen that average thickness of scallop-type IMC layer was 2.3 μm at the Sn3.0Ag0.5Cu/Cu interface after soldering reaction. Moreover, the interfacial IMC layer was uneven. Some IMC grains were significantly larger than others, even appeared with prism-type morphology. When the aging time was 400 h, the morphology of interfacial IMC was changed from scallop-type to planar-type. A possible explanation was that the diffusion and reaction between Sn and Cu elements in the interfacial IMC layer during isothermal aging. According to Gibbs–Thomson theory [10], Fig. 9 shows a schematic diagram of the diffusion paths and growth process of the IMC layer. In solid-state aging, Cu atom has two main different paths that were the sources of the further IMC growth. Path 1 from the peak of scallop-type Cu_6Sn_5 to the bottom was driven by the curvature effect. Path 2 from copper substrate to the lead-free solder was driven by the interfacial reaction between copper substrate and solder to form the IMC. Hence, the morphology of interfacial IMC was changed from scallop-type to planar-type.

3.4 Growth behavior of IMC

Figure 10 shows the changes in the average thickness of the initial IMC layer during isothermal aging. It was found that the IMC layer thickness increased with aging time, and higher IMC growth rate was closely connected with higher aging temperature. Moreover, in the initial stage of isothermal aging, the IMC grew rapidly, and then the growth rate gradually slowed. In general, the IMC growth kinetic with isothermal aging time is controlled by diffusion process, and its thickness as a function of the time can be described as [11]:

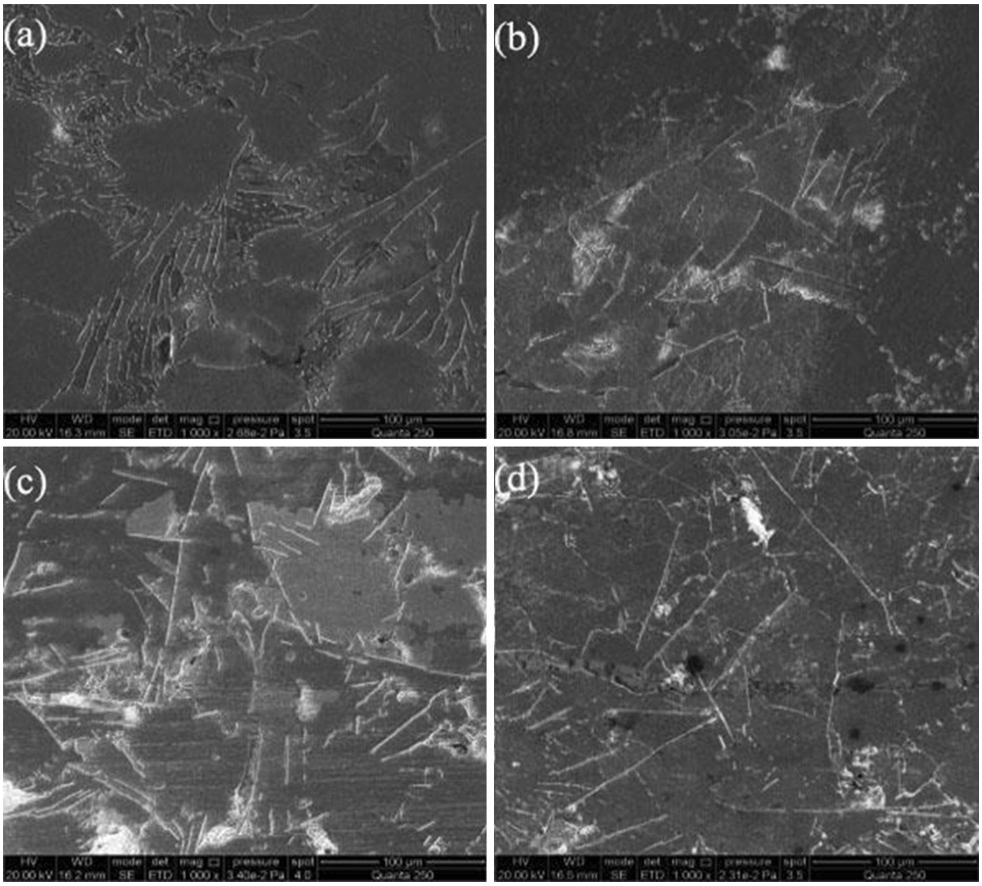

Fig. 6 Microstructure of solders with different aging times; **a** 100 h, **b** 200 h, **c** 300 h, **d** 400 h

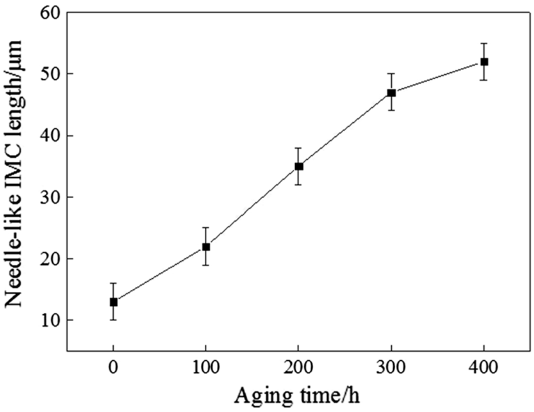

Fig. 7 Average IMC lengths in the solder matrix

$$x = x_0 + \sqrt{Dt} \tag{2}$$

where x is the IMC layer thickness at time t, x_0 is the initial IMC layer thickness after reflow, D is the diffusion coefficient as a function of temperature. The interfacial IMC growth is a diffusion dominant process. Thus, the Arrhenius equation is applicable. The activation energy of IMC growth is calculated using the Arrhenius equation, as follows [12]:

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \tag{3}$$

where D_0 is the diffusion constant, Q is the activation energy, R is the gas constant (8.314 J/mol), and T is the absolute temperature.

According to the measured IMC thickness data, D can be confirmed for each experimental temperature. Using Eq. (3), the activation energy Q can be confirmed from the slope of the straight line obtained by plotting ln(D) against 1/T. Equation (3) could then be expressed as follows [13].

$$\ln(D) = \ln(D_0) - \left(\frac{Q}{RT}\right) \tag{4}$$

Figure 11 plots the variation of interfacial IMC layer thickness of SnAgCu solder joint as a function of the aging time depending on aging temperature of at 125, 150 and 175 °C on copper substrates. It is obvious that the thickness of IMC increases linearly with the square root of aging time. The growth rate constant of IMC growth can be

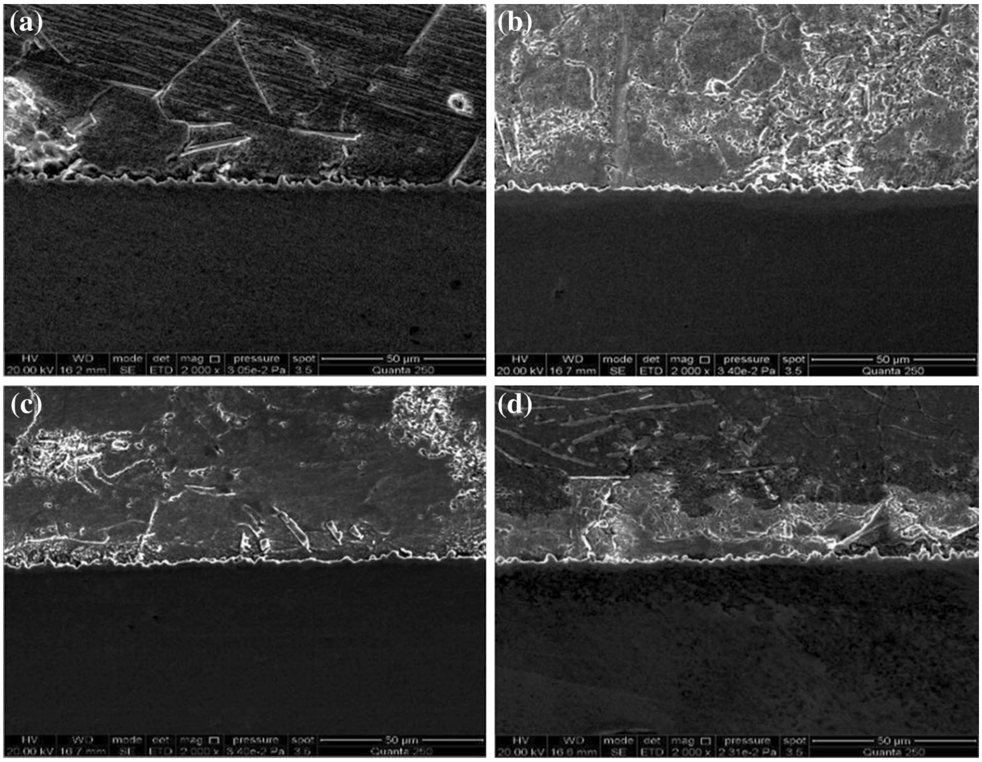

Fig. 8 SEM micrographs of Sn3.0Ag0.5Cu solder joint depending on aging time; **a** 100 h, **b** 200 h, **c** 300 h, **d** 400 h

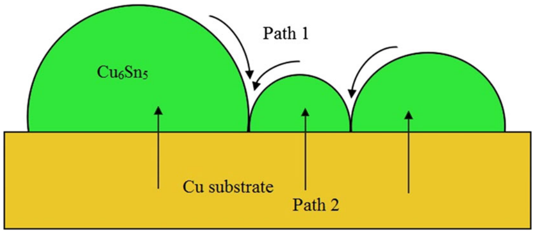

Fig. 9 The model of IMC growth during solid-state aging

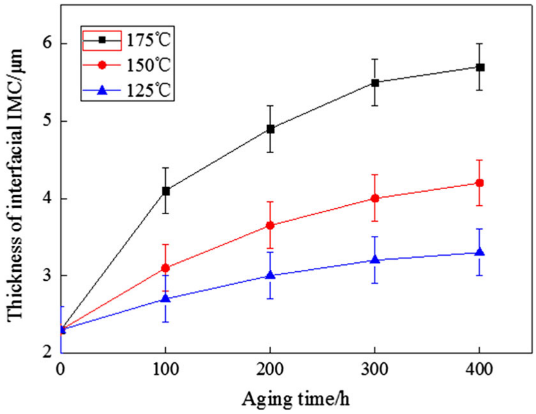

Fig. 10 The thickness of IMC layer versus aging time

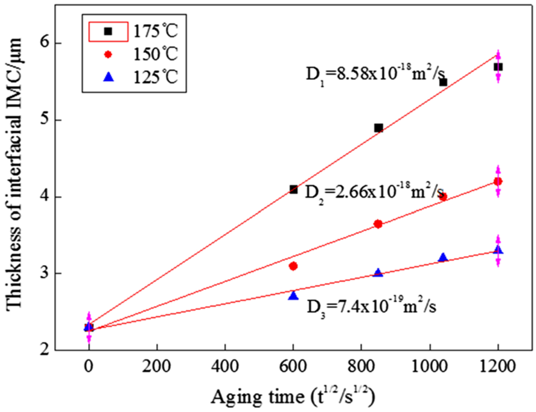

Fig. 11 The thickness of IMC layer versus square root of aging time

measured from the slope of the line with different temperatures.

Figure 12 shows the Arrhenius plot for the growth of IMC at Sn3.0Ag0.5Cu/Cu interface, and the activation energy Q is determined from the slope of the Arrhenius plot using a linear fitting model. The calculated result, activation energy for the IMC growth was estimated to be 72.7 kJ/mol.

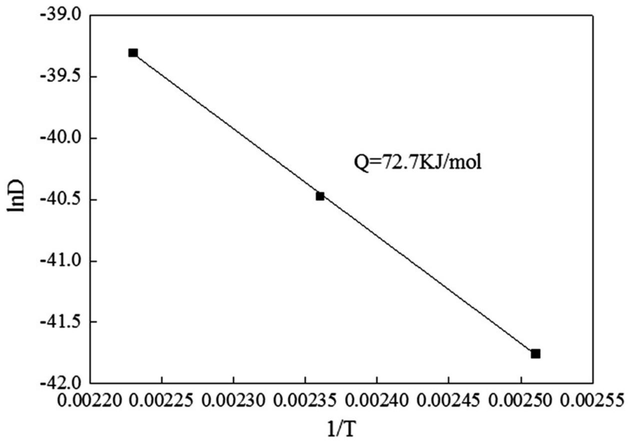

Fig. 12 Arrhenius plot of interfacial IMC growth

Our result is smaller than previously reported, such as the result of Kim [14] obtained was 79.79 kJ/mol. The discrepancies between the activation energies calculated in our experiment and in the references result from differences in the solder materials, aging condition, diffusion couple methods and relative analytical method used.

3.5 Mechanical properties

In the electronic devices, the solder joints can provide both the electrical connection and mechanical support in the modules [15]. So the mechanical properties of Sn3.0Ag0.5Cu solder joints were tested to evaluate the effect of the interfacial reactions on the reliability of the solder joints as a function of the aging treatment in this study. Figure 13 shows the pull force values of SnAgCu solder joints with different aging treatment. It was found that the pull force changed obviously as a function of aging time. Before aging, the pull force of Sn3.0Ag0.5Cu solder joint was 6.9 N. However, after aging 400 h, the pull force was decreased to 5.2 N. Moreover, in the initial stage of isothermal aging, the pull force of solder joints decreased rapidly, then the rate of decline became stabilized. Figure 14 shows the shear force values of SnAgCu solder joints with different aging treatment. It was found that the shear force of solder joints decreased markedly when the aging time was 100 h, and then gradually slowed. The reason could be attributed to: (1) the increase in thickness of IMC layer (as shown in Fig. 8), and (2) the coarsening of the second-phase particles of Ag_3Sn and Cu_6Sn_5 in the solder matrix during isothermal aging.

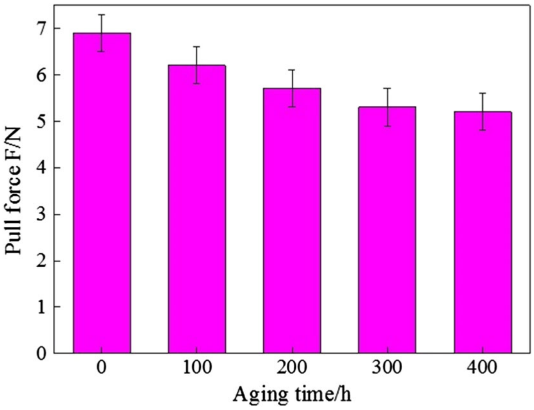

Fig. 13 The pull force of Sn3.0Ag0.5Cu solder joints with different aging time

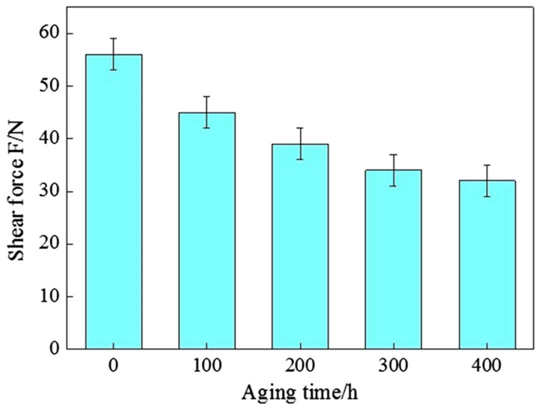

Fig. 14 The shear force of Sn3.0Ag0.5Cu solder joints with different aging time

4 Conclusions

The reliability of Sn3.0Ag0.5Cu/Cu lead-free soldered joint in electronic packaging was investigated. With the reflow temperature increasing, the spreading area of Sn3.0Ag0.5Cu lead-free solder increases. The morphology of IMC formed at Sn3.0Ag0.5Cu/Cu interface was gradually changed from scallop-type to planar-type, and the thickness of IMC was increased with the aging temperature and aging time. The IMC thickness was linearly proportional to the square root of aging time, which revealed a diffusion-controlled mechanism during aging. During isothermal aging, the growth rate of interfacial IMC grew faster. When the temperatures were 125, 150 and 175 °C, the diffusion coefficient were 7.4×10^{-19}, 2.66×10^{-18} and 8.58×10^{-18} m^2/s. Meanwhile, the activation energy of the IMC growth was estimated to be 72.7 kJ/mol for Sn3.0Ag0.5Cu/Cu during isothermal aging. In addition, the mechanical properties of solder joints during isothermal aging decreased with aging time increasing. In the initial stage of isothermal aging, the mechanical properties of solder joints decreased rapidly, and then the rate of decline became stabilized.

Acknowledgments This work was supported by the National Natural Science Foundation of China (No. 51475220), the Natural Science Foundation of Jiangsu Province (BK2012144), and the State Key Laboratory of Advanced Brazing Filler Metals and Technology (Zhengzhou Research Institute of Mechanical Engineering) (SKLABFMT-2015-03).

References

1. W.P. Zhang, B.G. Zhao, C.D. Zou, Q.J. Zhai, Y.L. Gao, Role of reactant concentration in size control of SnAgCu nanoparticles. Trans. Nonferrous Metals Soc. China **23**(6), 1668–1673 (2013)
2. S. Xu, A.H. Habib, A.D. Pickel, M.E. McHenry, Magnetic nanoparticle-based solder composites for electronic packaging application. Prog. Mater. Sci. **67**, 95–160 (2015)
3. L. Zhang, K.N. Tu, Structure and properties of lead-free solders bearing micro and nanoparties. Mater. Sci. Eng. R **82**, 1–32 (2014)
4. J. Keller, D. Baither, U. Wilke, G. Schmitz, Mechanical properties of Pb-free Sn–Ag solder joints. Acta Mater. **59**(7), 2731–2741 (2011)
5. P.T. Vianco, K.L. Erickson, P.L. Hopkins, Solid state intermetallic compound growth between copper and high temperature, tin-rich solders—part I: experimental analysis. J. Electron. Mater. **23**(8), 721–727 (1994)
6. G. Zeng, S.B. Xue, L. Zhang, L.L. Gao, W. Dai, J.D. Luo, A review on the interfacial intermetallic compounds between Sn–Ag–Cu based solders and substrates. J. Mater. Sci.: Mater. Electron. **21**(5), 421–440 (2010)
7. A.A. El-Daly, A.E. Hammad, G.S. Ganainy, M. Ragab, Properties enhancement of low Ag-content Sn–Ag–Cu lead-free solders containing small amount of Zn. J. Alloy. Compd. **614**, 20–28 (2014)
8. G.Y. Li, X.Q. Shi, Effects of bismuth on growth of intermetallic compounds in Sn–Ag–Cu Pb-free solder joints. Trans. Nonferrous Metals Soc. China **16**(s2), s739–s743 (2006)
9. K. Kanlayasiri, T. Ariga, Influence of thermal aging on microhardness and microstructure of Sn–0.3Ag–0.7Cu–xIn lead-free solders. J. Alloy. Compd. **504**, L5–L9 (2010)
10. H.K. Kim, K.N. Tu, Kinetic analysis of the soldering reaction between eutectic SnPb alloy and Cu accompanied by ripening. Phys. Rev. B **53**(23), 16027–16034 (1996)
11. L. Zhang, S.B. Xue, G. Zeng, L.L. Gao, H. Ye, Interface reaction between SnAgCu/SnAgCuCe solders and Cu substrate subjected to thermal cycling and isothermal aging. J. Alloy. Compd. **510**(1), 38–45 (2012)
12. H. Xiao, X.Y. Li, Y.X. Zhu, J.L. Yang, J. Chen, F. Guo, Intermetallic growth study on SnAgCu/Cu solder joint interface during thermal aging. J. Mater. Sci.: Mater. Electron. **24**(7), 2527–2536 (2013)
13. W.Q. Peng, E. Monlevade, M.E. Marques, Effect of thermal aging on the interfacial structure of SnAgCu solder joints on Cu. Microelectron. Reliab. **47**(12), 2161–2168 (2007)
14. Y.M. Kim, H.R. Roh, S. Kim, Y.H. Kim, Kinetics of intermetallic compound formation at the interface between Sn–3.0Ag–0.5Cu solder and Cu–Zn alloy substrates. J. Electron. Mater. **39**(12), 2504–2512 (2010)
15. L. Zhang, J.G. Han, Y.H. Guo, L. Sun, Properties and microstructures of SnAgCu–xEu alloys for concentrator silicon solar cells solder layer. Sol. Energy Mater. Sol. Cells **130**, 397–400 (2014)