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International Journal of Minerals, Metallurgy and Materials
Volume 16, Number 6, December 2009, Page 677

Materials

Effects of nano-sized Ag reinforcing particulates on the microstructure of Sn-0.7Cu solder joints

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(Received 2008-12-10)

Abstract: Composite solders were prepared by mechanically dispersing different volumes of nano-sized Ag particles into the Sn-0.7Cu eutectic solder. The effects of Ag particle addition on the microstructure of Sn-0.7Cu solder joints were investigated. Besides, the effects of isothermal aging on the microstructural evolution in the interfacial intermetallic compound (IMC) layer of the Sn-0.7Cu solder and the composite solder reinforced with 1vol% Ag particles were analyzed, respectively. Experimental results indicate that the growth rate of the interfacial IMC layer in the Ag particles reinforced composite solder joint is much lower than that in the Sn-0.7Cu solder joint during isothermal aging. The Ag particles reinforced composite solder joint exhibits much lower layer-growth coefficient for the growth of the IMC layer than the corresponding solder joint.

Key words: lead-free solder; composite solder; intermetallic compounds; microstructure; isothermal aging

[*This work was financially supported by the New Star Project of Beijing Science and Technology Commission, China (No.2004B03).*]

1. Introduction

The reliability of solder joints in electronic industries has become a great concern with the miniaturization of modern electronic products as well as the transition from the Pb-bearing solders to the Pb-free solders. One of the most important reliability issues is the microstructural evolution of the solder joint during service, in which the formation and growth of the interfacial intermetallic compound (IMC) between the solder and substrate has been considered to be an essential one [1-2]. Since the mechanical performance of the solder, such as tensile properties, creep properties, and thermomechanical fatigue behavior, is directly related to its microstructure, its evolution might have detrimental effects on the integrity of solder joints, especially at elevated temperatures [3]. The microstructural study of different solders either in bulk or joint configuration has been reported in the past decade [4-11]. Most of the studies which focused on the formation and growth of IMC during soldering and long-term service [4-11], confirmed that the deterioration of the solder joint was due to the growth of IMC. Furthermore, with the extensive application of lead-free solders, the formation and growth of the IMC layer in lead-free solders/joints have been paid special attentions [8-11], even at high service temperatures [9-10]. Generally, with the growth of brittle IMC layers, thermal fatigue life, tensile strength, and creep properties of the solder joint are significantly reduced [5-7, 11].

Sn-0.7Cu eutectic solder is currently considered as one of the most promising Pb-free solder candidates, especially in the wave soldering applications. Ag particles, though relatively expensive, were considered as good reinforcements for their non-coarsening nature in the solder [12]. Besides, Ag particles have low inter-diffusion characteristics with Sn at service temperatures [12]. Our earlier study has shown that adding small amount of nano-sized Ag reinforcement particles into the Sn-0.7Cu solder improved its solderability, shear strength, and creep rupture life of the solder joint [13]. The shear strength of the composite solder reinforced with 1vol% Ag particles is about 60% higher than that of the Sn-0.7Cu solder joint. The creep rupture life of the composite solder joint is 13 times to the Sn-0.7Cu solder joint at 75°C and 16 MPa

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[13]. According to those research data, nano-sized Ag can be considered as an effective reinforcement. In this research, the microstructure of the Sn-0.7Cu solder joint was expected to be stabilized using the same composite approach, in an ultimate goal to improve the service reliability of Sn-0.7Cu solder joints. Therefore, to explore the effects of nano-sized Ag reinforcing particles on the growth of the interfacial IMC layer, the current investigation was focused on the microstructural evolution of the Sn-0.7Cu solder joints with and without Ag particle additions, through a series of isothermal aging studies.

2. Experimental procedure

Sn-0.7Cu solder paste was mechanically mixed with nano-sized Ag particles to form the composite solder. The purity of Ag particles was 99.9% with a nominal size distribution of 20-60 nm. The morphology and size of the as-received Ag particles were reported in our earlier TEM analysis [14]. The volume fractions of Ag reinforcing particles ranged from 0.5vol% to 2vol%. Based on the earlier study, the composite solder reinforced with 1vol% Ag particles exhibited the best comprehensive properties in terms of solderability, shear strength, and creep rupture life at different temperatures [13]. Thus, 1vol% of Ag particle addition was used in this study for extensive microstructural characterization purposes. The Ag particles were subjected to a pickling process to achieve oxide-free surfaces before they were mechanically added into the Sn-0.7Cu solder paste in an Al_2O_3 ceramic crucible. The composite solder paste was blended for at least 15 min to ensure the uniform distribution of reinforcements.

The single shear lap solder joint specimen used in this study was prepared by melting and solidifying small amounts of the composite or non-composite solder paste between two dog-bone shaped copper substrates at 280°C [15]. Isothermal aging studies were conducted at 150°C using the solder joint specimens for up to 1000 h. Microstructural characterization was carried out after 100, 200, 500, and 1000 h. The thickness of the IMC layer was measured and other microstructural features were observed and analyzed using a FEI-Quanta 200 scanning electron microscope equipped with the backscattered electron detector and an energy-dispersive analysis of X-ray (EDAX).

3. Results and discussion

3.1. Microstructures of solder joint specimens

The typical microstructures of the as-prepared Sn-0.7Cu solder and composite solder joints containing different Ag additions are shown in Fig. 1. As can be seen in Fig. 1(a), the microstructure of the Sn-0.7Cu solder matrix is characterized by Sn grains and Cu_6Sn_5 IMCs around Sn grains. The bright area is Sn-rich phase, while the dark areas are grain boundaries. The microstructures of corresponding composite solders are similar to the Sn-0.7Cu solder. Comparing Figs. 1(a)-(d), with the increase of Ag particle addition, the

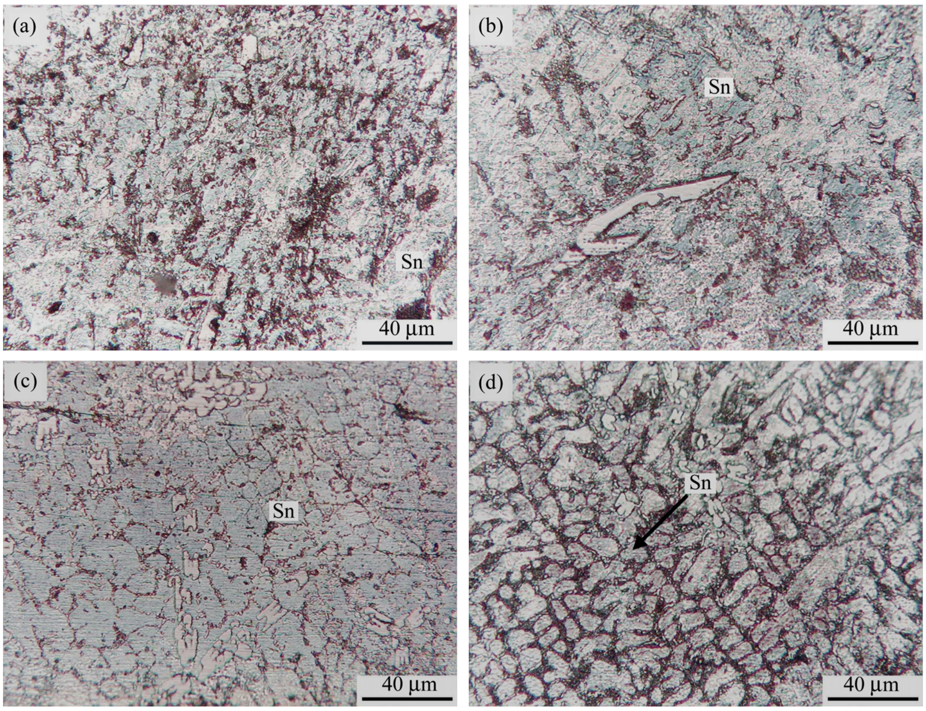

Fig. 1. Microstructures of the Sn-0.7Cu solder with different Ag additions: (a) Sn-0.7Cu; (b) Sn-0.7Cu+0.5vol% Ag; (c) Sn-0.7Cu+1vol% Ag; (d) Sn-0.7Cu+2vol% Ag.

grain size tends to become smaller and more uniform. The volume fraction of Cu-Sn IMCs in the solder also increases with the increase of Ag particles. Most of the Cu-Sn IMCs are located either at or near the grain boundaries. Such microstructure generally enhances the mechanical properties of the solder joints due to the refined size of grains.

A closer observation of the formation of IMCs in the bulk region and at the Cu substrate/solder interface of the as-prepared Sn-0.7Cu solder joint is illustrated in Fig. 2. Fig. 2(a) exhibits the distribution of Cu_6Sn_5 IMCs in the bulk region. Some thin strip Cu_6Sn_5 IMCs appear in the solder matrix. The morphology of the Cu_6Sn_5 IMC layer at the Cu substrate/solder interface is scallop shape, as shown in Fig. 2(b).

The microstructure of the composite solder reinforced with 1vol% Ag particles is shown in Fig. 3. Two types of IMCs, Ag_3Sn and Cu_6Sn_5, are observed in the solder matrix. The sizes of Cu_6Sn_5 IMC particles are generally much bigger than those of Ag_3Sn IMCs, as indicated by arrows in Fig. 3(a). In addition, Ag_3Sn or Cu_6Sn_5 precipitates with different sizes and shapes are dispersed in or at primary β-Sn grains in the solder matrix. It is obvious that Ag_3Sn observed in the composite solder joint is the reaction product between incorporated Ag particles and the solder matrix. As shown in Fig. 3(b), a layer of Cu_6Sn_5 IMCs forms at the Cu substrate/solder interface. However, the morphology of this layer is somewhat different from the scalloped shape as observed in the Sn-0.7Cu solder joint without Ag additions. Fewer scallop shapes are observed at the interfacial IMC layer in the composite solder joint reinforced with 1vol% Ag particles. It is possible that such morphology is due to the addition of Ag particles which block the original diffusion path of Cu atoms into the bulk solder. Fig. 4 illustrates the existence of Cu_6Sn_5 and Ag_3Sn IMCs in the solder matrix by composition analysis through energy dispersive X-ray spectroscopy.

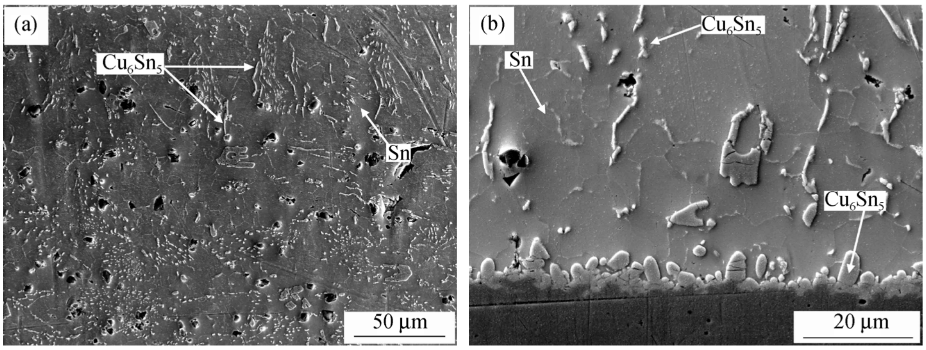

Fig. 2. SEM images of the microstructure of the as-prepared Sn-0.7Cu solder joint: (a) IMCs in the bulk; (b) IMCs at the Cu substrate/solder interface.

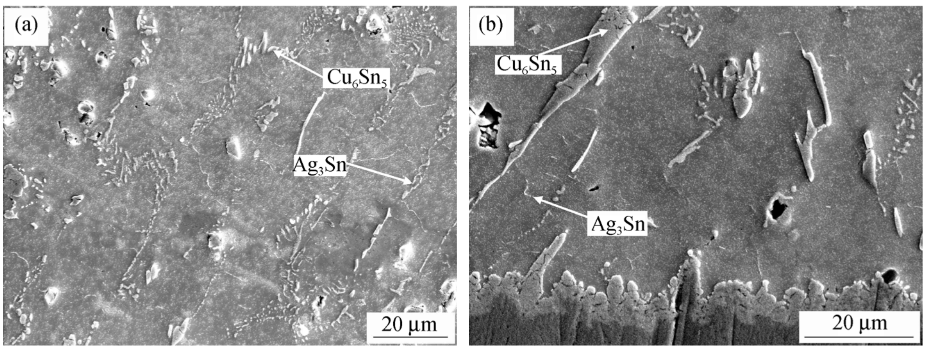

Fig. 3. SEM images of the microstructure of the as-prepared composite solder reinforced with 1vol% Ag particles: (a) IMCs in the bulk; (b) IMCs at the Cu substrate/solder interface.

It is very interesting to note that in the microstructure of the composite solder joint reinforced with 1vol% Ag particles, different morphologies of Cu_6Sn_5 IMCs are observed as shown in Fig. 5. Some Cu_6Sn_5 IMCs exhibit solid rod-like morphology (Fig. 5(a)), while most of the IMCs exhibit different shaped cross sections with a hollow center (Fig. 5(b)-(f)). Such hollow center may be circular, oval, or even as irregular as open shapes. It is suggested [16] that long Cu_6Sn_5 solid forms at the interface near Cu substrate by a screw dislocation mechanism, while the irregular hollow type Cu_6Sn_5 results when the core of rod dissolves away due to its higher energy, and fills with molten solder. The outer edge of the hollow Cu_6Sn_5 IMCs exhibits mostly faceted morphology, showing different letter-like shapes, such as U, E, and H (Figs. 5(b), (c), and (d), respectively). In general, it is more likely to form some irregular IMCs in solder joints with nano-sized Ag addition than that without Ag.

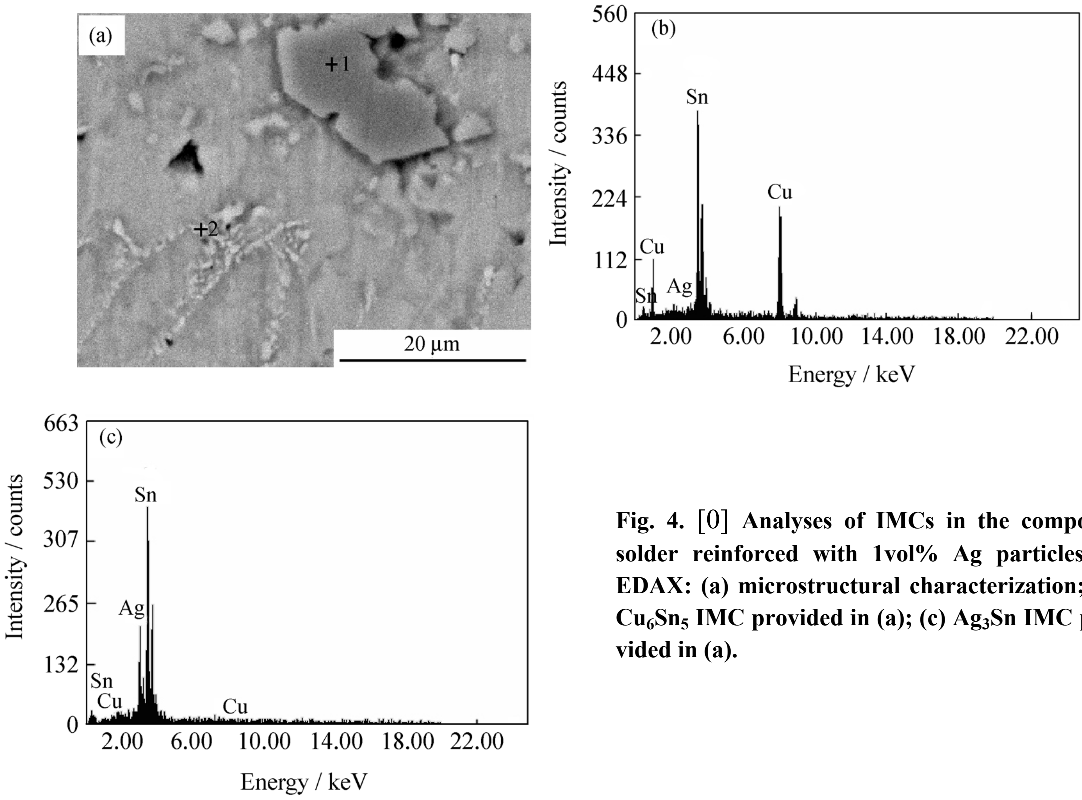

Fig. 4. [0] Analyses of IMCs in the composite solder reinforced with 1vol% Ag particles by EDAX: (a) microstructural characterization; (b) Cu_6Sn_5 IMC provided in (a); (c) Ag_3Sn IMC provided in (a).

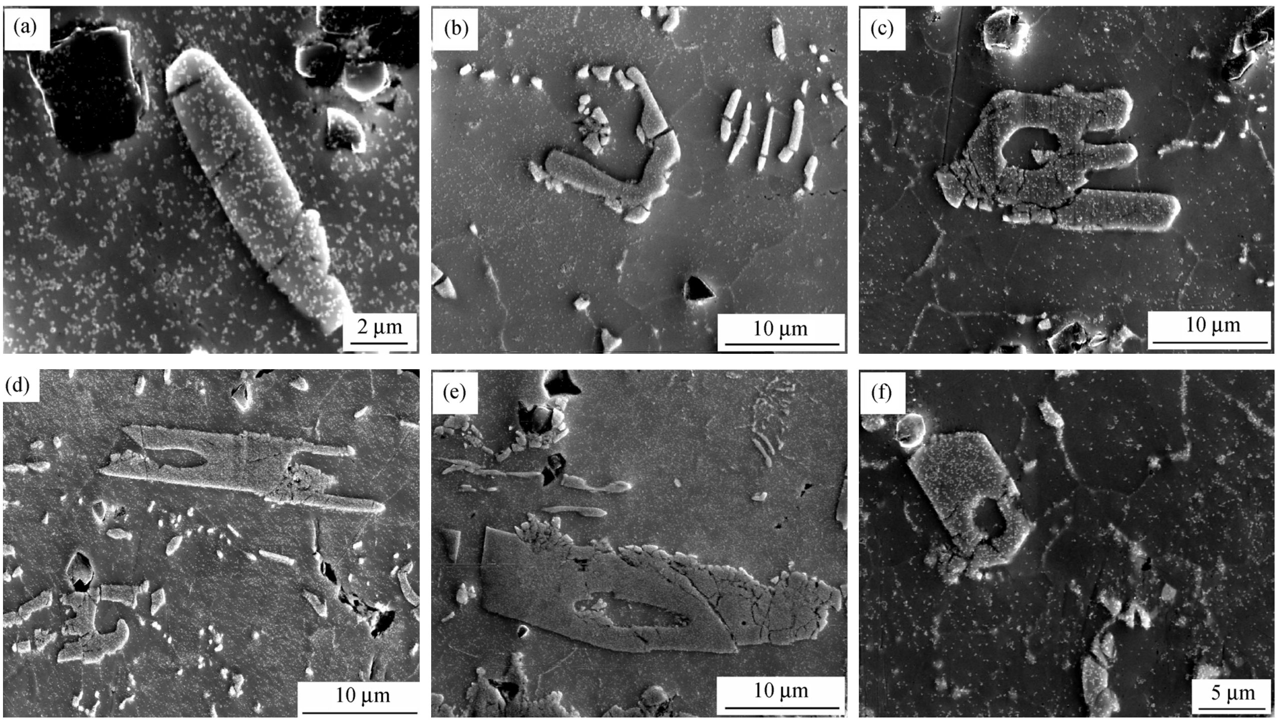

Fig. 5. Various morphologies of Cu_6Sn_5 IMCs in the as-prepared composite solder reinforced with 1vol% Ag particles: (a) solid rod-like shape; (b) U shape; (c) E shape; (d) H shape; (e) irregular hollow shape; (f) circular hollow shape.

The distribution of Ag containing phases is of great importance in the microstructure evolution and the mechanical properties of the composite solder joint. To further investigate the distribution of Ag_3Sn in the solder matrix, both secondary electron and backscattered electron images are made, as shown in Figs. 6(a)-(b). Cu_6Sn_5 and Ag_3Sn IMCs are not easily distinguished from secondary electron images because the contrast difference is not significant, as shown in Fig. 6(a), though some of the Ag_3Sn appears to be smaller. However, the contrast of Ag_3Sn IMCs appears to be much brighter than the Cu_6Sn_5 IMCs, which appears to be dark, in the backscattered electron images, as shown in Fig. 6(b). X-ray dot mapping of the same field is shown in Fig. 6(c). The result confirms the existence and distribution of Ag_3Sn IMCs as predicted from the contrast difference in the backscattered electron image of Fig. 6(b). The Ag_3Sn IMCs tends to segregate locally, as shown in Fig. 6(b). However, the Ag_3Sn IMCs disperse homogeneously in the solder matrix generally.

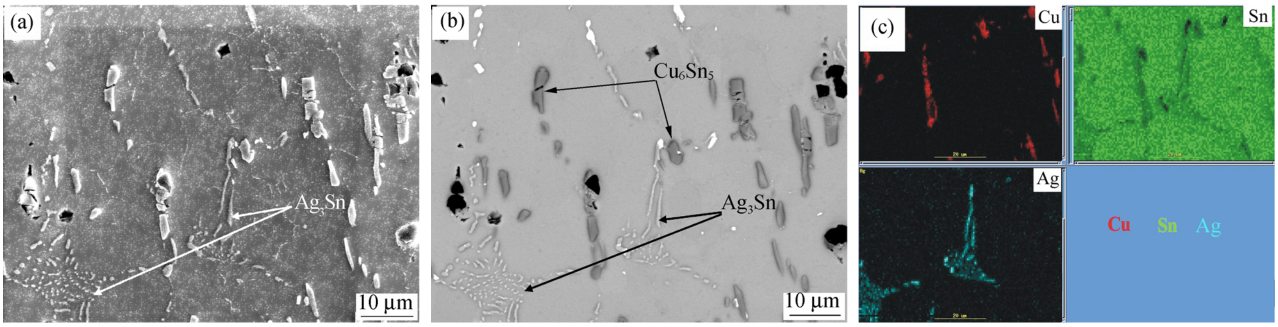

Fig. 6. Microstructures of the composite solder joint reinforced with 1vol% Ag particles: (a) secondary electron images; (b) backscattered images; (c) element analysis of X-ray dot mapping.

3.2. Effects of isothermal aging on the IMC layer at the Cu substrate/solder interface

Both Sn-0.7Cu non-composite and composite solder joints are subjected to solid-state isothermal aging at 150°C for up to 1000 h to investigate the effects of thermal annealing on the growth of the interfacial IMC layer and how such growth is affected by Ag additions. The effects of such isothermal aging on the growth of the interfacial IMC layer in the Sn-0.7Cu non-composite and composite solder joints are shown in Figs. 7 and 8, respectively. Note that these two figures were focused on the same locations in the solder joint after different aging times.

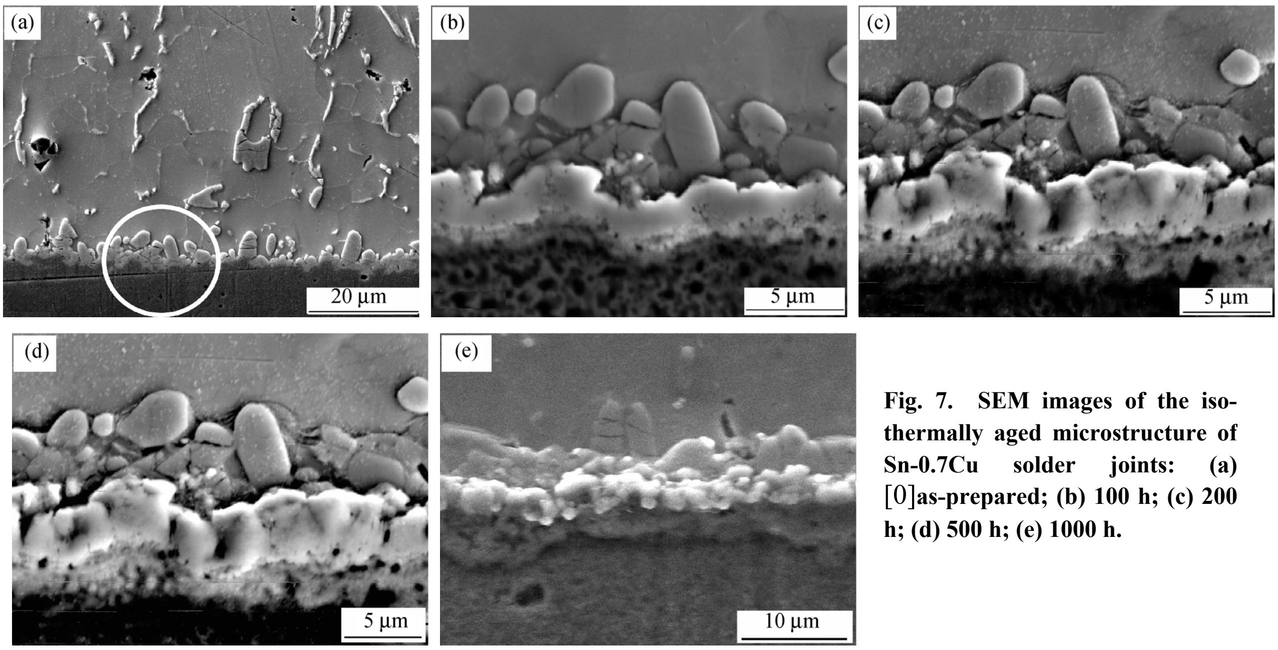

Fig. 7. SEM images of the isothermally aged microstructure of Sn-0.7Cu solder joints: (a) [0]as-prepared; (b) 100 h; (c) 200 h; (d) 500 h; (e) 1000 h.

In terms of microstructure features, isothermal aging at 150°C causes significant IMC evolution at the Cu substrate/solder interface. A layer of Cu_3Sn is clearly observed after the first 100 h aging (Fig. 7(b)). Comparing the micrographs, it is not difficult to notice that the growth of the Cu_3Sn layer adjacent to Cu substrate contributes to the continuous growth of the IMC layer at the interface. The Cu_6Sn_5 IMC layer between the solder and Cu_3Sn layer does not exhibit obvious growth as compared with Cu_3Sn layer. Kirkendall voids are also observed at the interface of Cu_3Sn layer/Cu substrate. The amount of such voids tends to increase with aging, which causes the formation of bigger voids and cracks in the interfacial IMC layer (Figs. 7(b)-(d)). From Fig. 8, it can be find that less scalloped interfacial IMC forms in the composite solder joint though the microstructural characteristics of IMC at the Cu substrate/composite solder interface in the 1vol% Ag reinforced solder joint are quite similar to that in the Sn-0.7Cu solder joint. However, the growth rate of the interfacial IMC layer is significantly suppressed by the 1vol% Ag addition, though no Ag is detected at the interface.

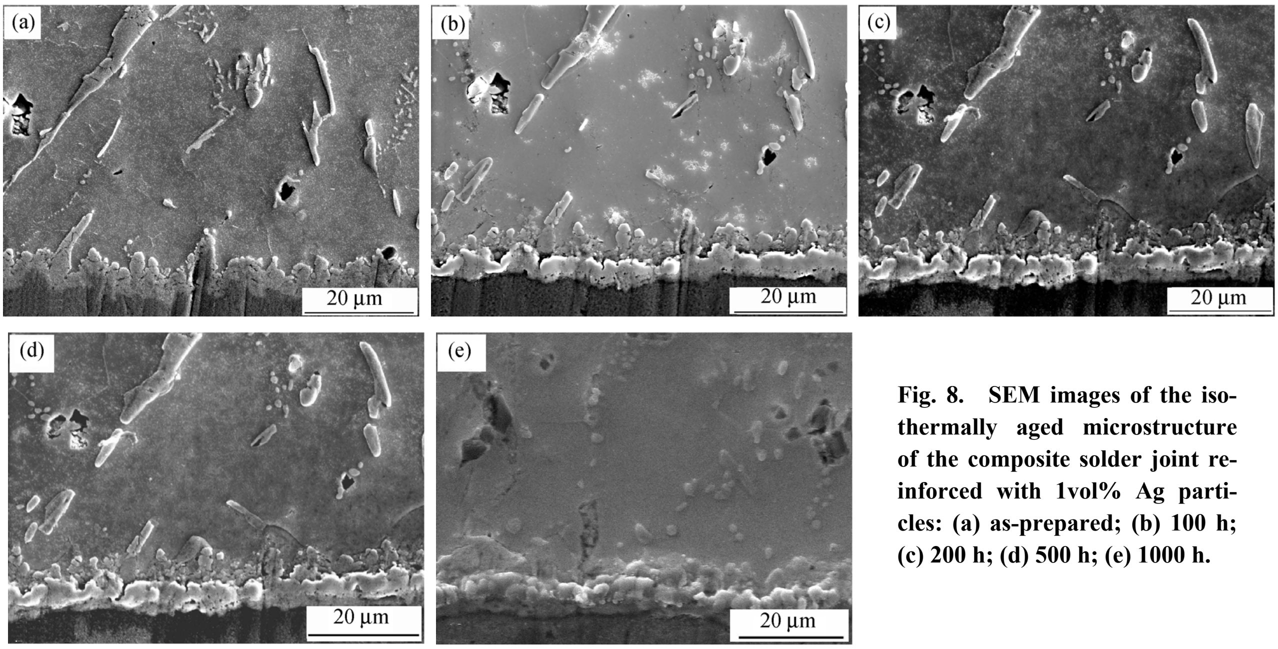

Fig. 8. SEM images of the isothermally aged microstructure of the composite solder joint reinforced with 1vol% Ag particles: (a) as-prepared; (b) 100 h; (c) 200 h; (d) 500 h; (e) 1000 h.

Interfacial IMC layers in both the composite and non-composite solder joints grew with aging time, however, significant difference in the growth rate was observed. A comparison of aging effect on the growth of the interfacial IMC layer between the Sn-0.7Cu solder and composite solder joint is illustrated in Fig. 9. As can be seen in Fig. 9, in the Sn-0.7Cu solder joint, the thickness of the IMC layer grows from 2.67 μm to 11.36 μm after 1000 h, while in the 1vol% Ag reinforced composite solder joint, the thickness of the IMC layer grows from 4.69 μm up to 10.46 μm after 1000 h. The growth rate of the interfacial IMC layer in the Ag particles reinforced composite solder is much lower than that in the Sn-0.7Cu solder joint. However, the general growth rate of the interfacial IMC layers decreases with the increase of aging time for both the composite and non-composite solder joint. Such growth kinetics has been observed in most of the Sn based solder joints under solid-state isothermal aging conditions [12].

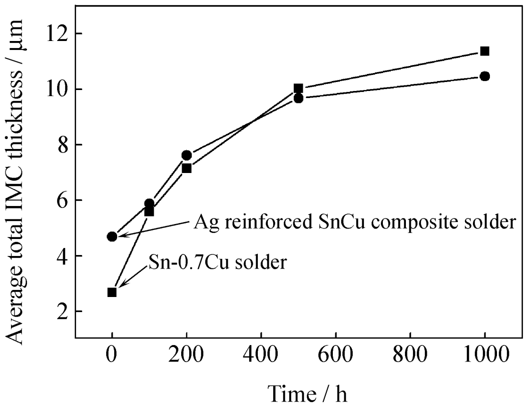

Fig. 9. Comparison of the growth of the interfacial layer between Sn-0.7Cu solder and composite solder reinforced with 1vol% Ag particles.

The most frequently used model for layer growth was employed in this study to determine the layer-growth coefficients K for the total Cu-Sn IMC layer, which is illustrated as follows [17]:

$$d = d_0 + \sqrt{Kt} \quad (1)$$

where d is the thickness of the IMC layer at time t, μm; d_0 the initial thickness of the IMC layer, μm; K the layer-growth coefficient, cm^2/s; and t the aging time, s.

The layer-growth coefficients are obtained from a linear regression analysis of d *vs*. $t^{1/2}$, where the slope of the linear curve is $k^{-1/2}$ (Fig. 10). In Fig. 10, the values of layer-growth coefficient for the IMC layer growth are determined from plotting the thickness of IMC layer *vs*. square root of aging time at 150°C. The linear correlation coefficients of the Sn-0.7Cu solder and its composite solder joint are more than 0.9, and the Sn-0.7Cu composite solder joint shows a much lower layer-growth coefficient for the growth of the IMC layer than the corresponding non-composite solder joint. The lower layer-growth coefficient value of the composite solder joint suggests that the addition of Ag reinforcing particles restrains the growth of IMC layers under isothermal aging conditions. The diffusion of Sn toward IMC layers in composite solder joints is reduced compared with that in eutectic Sn-0.7Cu solder joints. It was considered that the existence of Ag in the bulk solder might be able to change the diffusion path of Cu atoms through the interface into the bulk region. In the non-composite solder joint, Cu atoms contributed to the formation and growth of Cu-Sn IMCs in the bulk and at the interface. However, in the Ag reinforced Sn-0.7Cu composite solder joint, microstructural features (Figs. 7 and 8) suggest that Ag particles maybe block the filling of channels between Cu_6Sn_5 scallops. As consequence, fewer amounts of Cu elements contributed to the IMC layer growth, resulting in a reduced growth rate.

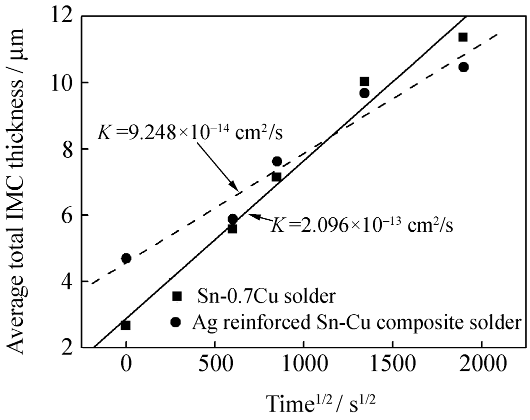

Fig. 10. Thickness of the IMC layer *vs*. square root of aging time at 150°C for solder joints.

4. Conclusions

(1) The morphology of the Cu_6Sn_5 IMC layer at the solder/Cu substrate interface in non-composite Sn-0.7Cu solder is scallop shape. However, the interfacial IMC layer formed at the 1vol% Ag reinforced composite solder/Cu is less scalloped.

(2) Different morphologies of Cu_6Sn_5 IMCs are observed in Sn-0.7Cu composite solder joints. Some Cu_6Sn_5 IMCs exhibit solid rod-like morphology, while most of the IMCs exhibit hollow-centered rods with different cross-sectional shapes.

(3) During isothermal aging, the growth rate of the interfacial IMC layer in the Ag particles reinforced composite solder is much lower than that in the Sn-0.7Cu solder joint. It is believed that the Cu_3Sn layer, observed after aging for the first 100 h, contributes primarily to the total layer growth, while the Cu_6Sn_5 IMC layer between the solder and Cu_3Sn layer does not exhibit active growth as compared with the Cu_3Sn layer during aging.

(4) The Sn-0.7Cu composite solder joint shows a much lower layer-growth coefficient for the growth of the IMC layer than the corresponding non-composite solder joint. The lower layer-growth coefficient value observed for the composite solder joint suggests that the addition of Ag reinforcement particles maybe restrain the growth of IMC layers under isothermal aging conditions.

References

[1] A.W. Gibson, S. Choi, K.N. Subramanian, *et al*., Issues regarding microstructural coarsening due to aging of eutectic tin-silver solder, [in] R.K. Mahidhara, ed., *Reliability of Solders and Solder Joints*, TMS, Orlando, USA, 1997, p.97.

[2] D.R. Frear, Trends and issues in Pb-free soldering for electronic packaging, *Electron. Inf. Technol*., 118(2001), No.2, p.81.

[3] J.W. Morris Jr., J.L. Freer Goldstein, and Z. Mei, Microstructure and mechanical properties of Sn-In and Sn-Bi solders, *JOM*, 45(1993), No.7, p.25.

[4] D.Q. Yu, C.M.L. Wu, C.M.T. Law, *et al*., Intermetallic compounds growth between Sn-3.5Ag lead-free solder and Cu substrate by dipping method, *J. Alloys Compd*., 392(2005), p.192.

[5] K.S. Kim, K.W. Ryu, C.H. Yu, *et al*., The formation and growth of intermetallic compounds and shear strength at Sn-Zn solder/Au-Ni-Cu interfaces, *Microelecton. Reliab*., 45(2005), No.3, p.647.

[6] P.L. Tu, Y.C. Chan, and J.K.L. Lai, Effects of intermetallic compounds on the thermal fatigue of surface mount solder joints, *IEEE Trans. Compon. Packag. Manuf. Technol. Part B*, 20(1997), No.1, p.87.

[7] R.E. Pratt, E.I. Stromswold, and D.J. Quesnel, Effect of solid state intermetallic growth on the fracture toughness of Cu/63Sn37Pb solder joints, *IEEE Trans. Compon. Packag. Manuf. Technol. Part A*, 19(1996), p.134.

[8] M.C. Wang, S.P. Yu, T.C. Chang, *et al*., Formation and morphology of the intermetallic compounds formed at the 91Sn-8.55Zn-0.45Al lead-free solder alloy/Cu interface, *J. Alloys Compd*., 389(2005), p.133.

[9] H.L. Pang, T.H. Low, B.S. Xiong, *et al*., Thermal cycling aging effects on Sn-Ag-Cu solder joint microstructure, IMC and strength, *Thin Solid Films*, 462-463(2004), p.370.

[10] Y.H. Xia and X.M. Xie, Intermetallic compounds evolution between lead-free solder and Cu-based lead frame alloys during isothermal aging, *J. Mater. Sci*., 41(2006), No.8, p.2359.

[11] J.M. Song, G.F. Lan, T.S. Lui, *et al*., Microstructure and tensile properties of Sn-9Zn-*x*Ag lead-free solder alloys, *Scripta Mater*., 48(2003), No.8, p.1047.

[12] F. Guo, S. Choi, J.P. Lucas, *et al*., Microstructural characterisation of reflowed and isothermal-aged Cu and Ag particulate reinforced Sn-3.5Ag composite solders, *Soldering Surf. Mount Technol*., 13(2001), No.1, p.7.

[13] F. Tai, F. Guo, Z.D. Xia, *et al*., Processing and creep properties of Sn-Cu composite solders with small amounts of nanosized Ag reinforcement additions, *J. Electron. Mater*., 34(2005), No.11, p.1357.

[14] J.P. Liu, F. Guo, Y.F. Yan, *et al*., Development of creep resistant, nanosized Ag particles-reinforced Sn-Pb composite solders, *J. Electron. Mater*., 33(2004), No.9, p.958.

[15] F. Guo, J.P. Lucas, and K.N. Subramanian, Creep behavior in Cu and Ag particle-reinforced composite and eutectic Sn-3.5Ag and Sn-4.0Ag-0.5Cu non-composite solder joints, *J. Mater. Sci. Mater. Electron*., 12(2001), No.1,

p.27.

[16] D. Frear, D. Grivas, and J.W. Morris Jr., The effect of Cu_6Sn_5 whisker precipitates in bulk 60Sn-40Pb Solder, *J. Electron. Mater.*, 16(1987), No.3, p.181.

[17] S. Choi, T.R. Bieler, J.P. Lucas, *et al.*, Characterization of the growth of intermetallic interfacial layers of Sn-Ag and Sn-Pb eutectic solders and their composite solders on Cu substrate during isothermal long-term aging, *J. Electron. Mater.*, 28(1999), No.11, p.1209.