Effect of Addition Cobalt Nanoparticles on Sn-Ag-Cu Lead-free Solder

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Abstract

Nowadays, nanoelectroctronic, electro-nanotechnologies environmental friendly products become the roadmap in industry. Hence, nanoscale of reinforcement into lead-free solder becomes more popular rather than the micro size of reinforcement. In this paper, Cobalt nanoparticles-reinforced Sn-Ag-Cu composite solders were prepared by thoroughly blending 0.75 wt% of cobalt nanoparticles with near eutectic cement tended to suppress the growth of Cu_3Sn intermetallic layer. However, upon addition of Co nanoparticles, the growth of Cu_6Sn_5 was enhanced. The distribution of the Co nanoparticles was observed by the elemental mapping which was carried out by using electron micro probe analysis (EPMA) and transmission electron microscopy which equipped together with electron-dispersive X-ray spectroscopy (TEM-EDX). There was no Co detected in the Cu_3Sn, it only presented in Cu_6Sn_5. The interdiffusion coefficient was increased with the ageing temperature. Upon additionof Co nanoparticles, the interdiffusion coefficient for the formation of Cu_3Sn intermetallic layer was reduced, but the interdiffusion coefficient for the formation of Cu_6Sn_5 layer was increased. The activation energy for the formation of Cu_3Sn was also increased with the Co addition.

Keywords: Lead-free solder, intermetallic layer, nanoparticles, cobalt nanoparticles

Introduction

Solder materials play an important role in electronic packaging for interconnection and as a surface coating for component leads and PCB surface finishes. In recent years, the usage of Pb, which can be harmful to the human body, has attracted much global attention. Due to the environmental concern, it has prompted intense research activities on lead-free solder.

Among the numerous lead-free solder options, SnAgCu (SAC) is the most prevailing alloy family for electronic soldering. [1] However, the properties of Sn-Ag-Cu alloys are not adequate enough to meet severe board level reliability requirements. [2] To improve the properties of the lead-free solder, various elements were suggested added into common lead-free solder either by alloying or reinforcing particles.

Co has been attracting a great deal for recent of its benefit such as improve the ductility [3], reduce the brittle failure mode in BGA solder joint [4], improve thermal fatigue, creep resistance [5] and etc. As the development of nano technology has become active lately, various nano-sized particles were SAC387 solder paste. Soldered samples were then subjected to high temperature ageing at 125, 150 and175°C for up to 1008 hours. In the solder joint, Cu_6Sn_5 intermetallic was observed on Cu substrate, followed by Cu_3Sn intermetallic formation between Cu_6Sn_5 and Cu after prolonged ageing. The thickness of both IMC increased with the ageing time and ageing temperature. The Co nanoparticle reinfor chosen as reinforcements in producing composite lead-free solders. The nano-sized particles were added in the hope that they could possible more effective compared to the micron-sized reinforcements. [6]

Research effort the effect of nanoparticle reinforced composite is in an early stage. Study of the Co nanoparticles addition is even scarce. Amagai [7] studied the effect of addition Co nanoparticles into Sn-3.5Ag solder after multiple reflow cycles on the interfacial structure and drop performance. However, the performance of solder joint at high temperature and the kinetic analysis is important to determine the reliability joint. In this paper focuses on the effect of Co nanoparticle additions to Sn-3.8Ag-0.7Cu solder paste on the interfacial reaction between the nanocomposite solder and Cu substrate during high temperature ageing. The activation energy of the diffusion for each IMC growth is also determined.

Experimental Procedures

Nanocomposite solder (Sn-3.8Ag-0.7Cu+0.75 n-Co) was prepared by mixing Sn-3.8Ag-0.7Cu (SAC) solder paste (Indium Corporation of America, Singapore) with commercial Co nanoparticles (~28 nm, Accument Materials, Co., USA). The solder paste was manually blended with Co nanoparticles approximately for 30 minutes. Solders were prepared on commercial polycrystalline copper sheets (30 mm x 30 mm x 0.3 mm). Prior to soldering, the sheets were cleaned and dipped in 50 vol% HNO_3 to remove oxide and then rinsed thoroughly in distilled water followed by cleaning with acetone. After the surface preparation the composite solder paste was placed on the copper substrate through a mask having an opening diameter of 6.5 mm and 1.24 mm thickness (JIS Z3198-3, 2003). Then the composite solder paste was reflowed on a hot plate at 250ºC for 45 s. After the reflow, the solder joint was cleaned to remove the flux residue. The reflowed samples were subjected to aging at 3 different temperatures at 125, 150 and 175 ºC up to 1008 h. After the aging tests, the samples were cross sectioned and polished to a 0.02 μm finish employing the standard metallographic techniques. The microstructure was examined by an optical microscope and a scanning electron microscope (SEM). The

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average thickness of the IMCs was calculated by dividng the area of IMC by its length with the aided Olympus Analysis Five Software. The elemental analysis of the phases was carried out using energy-dispersive X-ray spectroscopy (EDX) and electron probe microanalysis (EPMA, JEOL-8500F). For a better resolution, selected samples were also investigated by using a Philips CM200 transmission electron microscope attached together with energy-dispersive X-ray spectroscopy (TEM-EDX). The TEM specimens were prepared by using XT Nova NanoLab 200 which was combining a dual beam high resolution focussed ion beam (Ga FIB) and a high resolution scanning electron microscope. The milled sample was liftout by using ex-situ liftout microscope and then put on the Cu grid. The activation energy for the formation of each IMCs was calcaluted via Arrhenius eauation.

Results and Discussion

Fig.1 shows the cross sectional micrographs of SAC and SAC+0.75 n-Co after reflow and ageing at 150 °C for 504 h. A scallop shaped intermetallic layer (lighter layer) was formed in the SAC sample after reflow. Upon the addition of Co nanoparticles, the morphology of IMC changes substantially. The IMC layer appears to have a relative flat morphology with the addition of Co nanoparticles. After prolonged aging another intermetallic layer (darker layer) with a planer shape formed in between the first intermetallic layer and Cu substrate in the both SAC and nanocomposites. The morphology of inner darker layer is seen to be similar in both SAC and nanocomposites. The thickness of this dark IMC layer is thicker in the SAC samples compared with Co nanoparticles added SAC solder. Energy dispersive spectroscopy was used to determine the composition of each layer. By comparing the ratio of Cu:Sn, it is inferred that the outer layer is Cu_6Sn_5 and the inner layer is Cu_3Sn. Co was found in Cu_6Sn_5 IMC in the nanocomposite solder in the ratio of $(Cu,Co)_6Sn_5$. However, within the resolution of EDX, there was no Cobalt detected in Cu_3Sn.

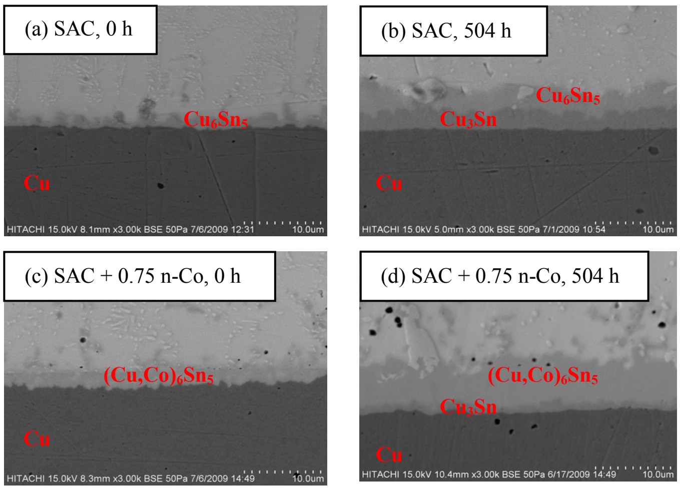
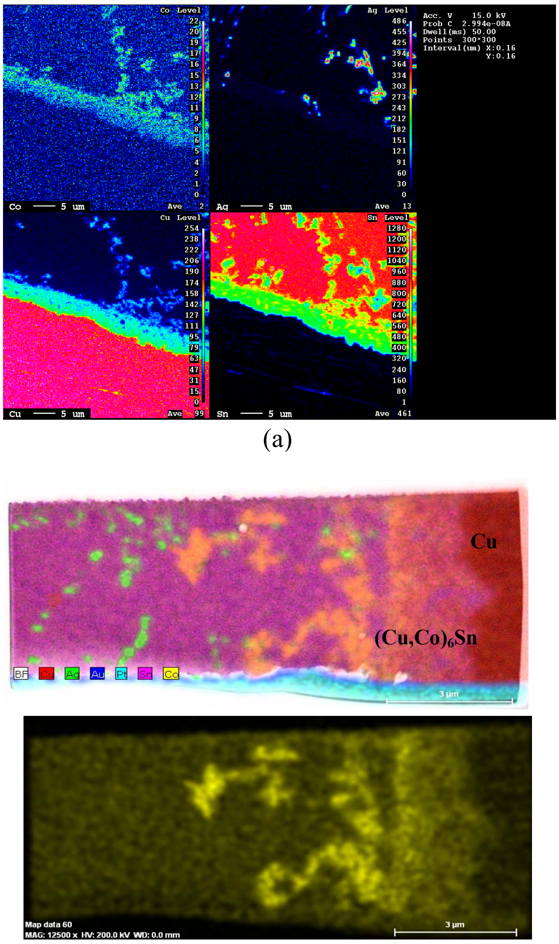


Fig. 1. SEM micrographs of solder-substrate interface after ageing at 150°C for 0 h and 504 h.

Fig. 2 shows the elemental mapping of SAC+0.75 n-Co nanocomposite after as- reflowed by using electron probe microanalyser (EPMA) and transmission electron microscope which is equipped together with elemental dispersive spectrometer (TEM-EDX). Result show that the concentration of Co nanoparticles in the $(Cu,Co)_6Sn_5$ layer was higher on the top IMC layer compared to the bottom IMC layer. This result is similar with other researchers who found out the outer region of Cu_6Sn_5 contained higher concentration of Co or Ni than the inner region for the Sn-3.5Ag solder alloy dope with Co or Ni as additives. [8, 9]



(a)

(b)

Fig. 2. Elemental mapping of SAC+0.75 n-Co nanocomposite after as- reflowed by using (a) EPMA, (b) TEM-EDX.

Table 1 shows the interdiffusion coefficient of total, Cu_6Sn_5 and Cu_3Sn intermetallic layer for the SAC solder and SAC doped with Co nanoparticles. It is assumed that the diffusion controlled is the main growth mechanism for the intermetallic formation. The interdiffusion coefficient (D_{eff}) of the each IMC layer can be determined by the following equation (1):

$$x_t - x_0 = \left(D_{eff}\right)^{1/2} \qquad (1)$$

where x_t is the thickness of IMCs at time *t*, x_0 is the thickness after reflow, D_{eff} is the interdiffusion coefficient in the IMC layer. For the Cu_3Sn layer, $x_0 \approx 0$, due to only a few tens nm can form after reflow and it is usually not resolvable under an SEM. [10,11]

The interdiffusion coefficient is tended to increase with the temperatures for all the IMC layers. Upon addition of Co nanoparticles, the interdiffusion coefficient for Cu_3Sn is much smaller in the (SAC+0.75 n-Co) composite compare to SAC solder. The addition of Co nanoparticles therefore has a significant influence on the growth kinetics of Cu_3Sn. On the other hand, the interdiffusion coefficient for the growth of Cu_6Sn_5 is tended to decrease. This finding might be related to the IMC thickness. The IMC of Cu_6Sn_5 is enhanced but the IMC of Cu_3Sn is suppressed with the presence of Co. With the higher IMC thickness, the interdiffusion coefficient also increases. Gao *et. al.* [12] studied the studied the effect of Co as an alloying addition to Sn–3.5Ag. The thickness of Cu_6Sn_5 and the total IMC thickness were found to be higher for Co alloyed solder at all aging time. The growth of Cu_3Sn, however, was suppressed by Co alloy addition. It has been observed that during IMC formation, Co atoms enter the Cu sublattice of Cu_6Sn_5 and substitutes some of the Cu atoms. [13] Theoretical calculation revealed that the presence of Co in the IMC causes a greater reduction in the heat of formation and hence makes Cu_6Sn_5 more stable. Furthermore, the driving force for the diffusion of Sn through $(Cu,Co)_6Sn_5$ increases in Co nanoparticle added solder resulting in its faster growth. [14]

Table 1. Effective interdiffusion coefficient of each IMC layers at the interface.

Solder	IMC	Effective Interdiffusion Coefficient, (m^2s^{-1})		
		125°C	150°C	175°C
SAC	Total	5.38×10^{-18}	8.48×10^{-18}	3.68×10^{-17}
	Cu_6Sn_5	1.40×10^{-18}	2.35×10^{-18}	8.01×10^{-18}
	Cu_3Sn	5.35×10^{-19}	2.98×10^{-18}	1.01×10^{-17}
SAC+ 0.75 n-Co	Total	2.24×10^{-18}	8.81×10^{-17}	6.73×10^{-17}
	Cu_6Sn_5	1.19×10^{-18}	5.93×10^{-18}	4.14×10^{-17}
	Cu_3Sn	1.25×10^{-19}	3.73×10^{-19}	3.12×10^{-18}

The activation of energies for the diffusion of each IMC layer maybe calculated via the Arrhenius relation:

$$D_{eff} = D_o e^{(-Q/RT)} \qquad (2)$$

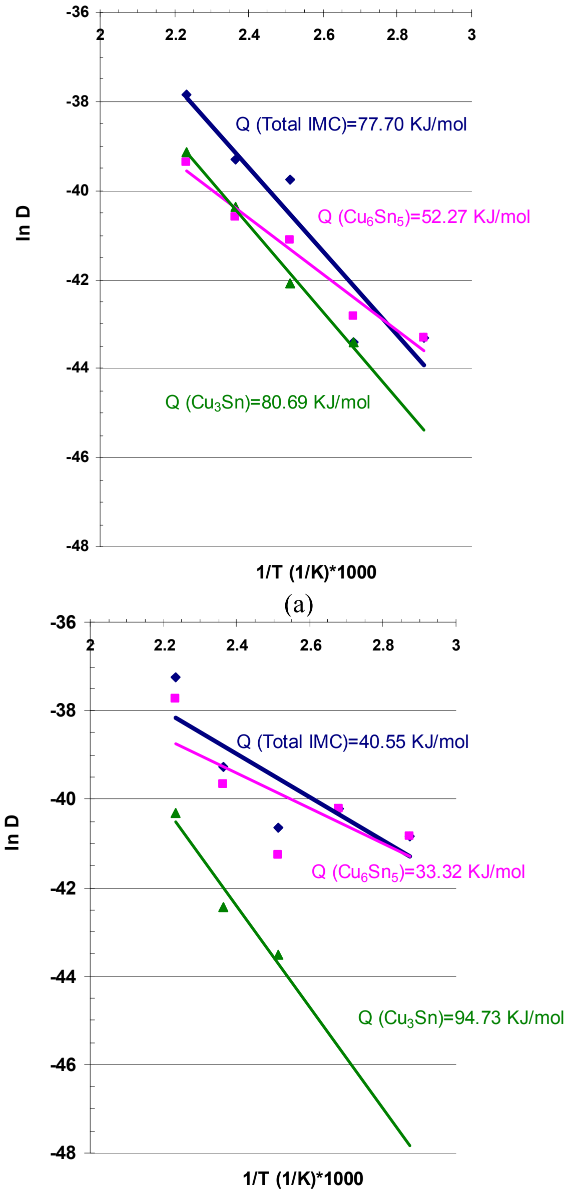
and can written as

$$\ln D_{eff} = \frac{-Q}{RT} + \ln Q_o \qquad (3)$$

where D_{eff} is the interdiffusion coefficient, D_o is the interdiffusion constant, Q is the activation energy, R is the ideal gas constant (8.314 J/mol) and T is the absolute temperature. The activation energy for the layer growth was obtained from the slope of ln D (where D is D_{eff}) versus 1/T plot multiplied by the ideal gas constant as shown in Fig. 3.

Results show that the activation energy for Cu_3Sn is higher compared to the activation energy for the formation of total IMC or Cu_6Sn_5 in both SAC and SAC+0.75 n-Co composite solder. This result is similar with other researchers. [15-17] Upon addition Co nanoparticles, the activation energy for the formation of Cu_3Sn increases. However, this finding was contrats to Vianco *et al.* (2004) [18] who found that the activation energy for Cu_3Sn (38 KJ/mol) was much lower than the total IMC (58 KJ/mol) for the Sn-0.5Ag-4.0Cu solder. It was also reported that the activation energy for both Cu_3Sn and total IMC was similar (50 KJ/mol) for the Sn-3.9Ag-0.6Cu solder.

Due to the higher activation energy needed for the formation of Cu_3Sn, the layer of Cu_3Sn might be retarded. The higher activation energy could reduce the atomic diffusion rate and thus inhibit the excessive of IMC. [19].



(a)

(b)

Fig. 3. Arrhenius plot of the IMC growth for (a) SAC387; (b) SAC387+0.75 n-Co solder joint.

Conclusions

Cu_6Sn_5 is the first intermetallic layer formed in the interaction between solder and copper substrate. Upon the aging, another Cu rich intermetallic layer, Cu_3Sn is formed in between the Cu_6Sn_5 intermetallic layer and Cu substrate. The thicknesses of both intermetallic layers are increasing with aging time and aging temperatures. The morphology on Cu_6Sn_5 after reflow changes from a scallop to a planner type upon addition of Co nanoparticles. Co is only present in the Cu_6Sn_5 intermetallic layer and there is no cobalt detected in Cu_3Sn. Co has higher concentration on the top region in Cu_6Sn_5 compare to the bottom region.

Upon addition of Co nanoparticles, the Cu_3Sn is tended to be suppressed. The interdiffusion coefficient for the growth of Cu_3Sn is also reduced with the addition of Co nanoparticles. The interdiffusion coefficients are increasing with the increasing of ageing temperature. The activation for the formation of the Cu_3Sn is higher compared to the activation for the formation of total and Cu_6Sn_5 IMCs in both SAC solder and SAC-doped with Co nanoparticles.

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