Effect of Nickel Addition into Sn-3Ag-0.5Cu on Intermetallic Compound Formation during Soldering on copper

A. Ourdjini[1], I. Siti Rabiatull Aisha[2], Y.T. Chin[3]
[1]Universiti Teknologi Malaysia, 81300 Skudai, Johor, Malaysia
[2]Universiti Malaysia Pahang, Kuantan, Pahang
[3]Intel Technology Malaysia, Penang
Corresponding author: ourdjini@fkm.utm.my

Abstract

Doping lead-free solders with minor additions of alloying and impurity elements such as Ni, Bi or Zn appears to have major effects on the growth of intermetallics (IMC) in solder joints during reflow soldering between the Sn-Ag-Cu lead-free solders and the surface finish metallurgy. In this paper, the results of the effect of small Nickel additions (0.05 and 0.1 wt%) on intermetallic formation during soldering with Sn-3Ag-0.5Cu (SAC305) are presented. The Ø500µm solder alloys of Sn-3Ag-0.5Cu, Sn-3Ag-0.5Cu-0.05Ni and Sn-3Ag-0.5Cu-0.1Ni were investigated in detail after reflow soldering at 250°C on copper finish and isothermally aged at 150°C for up to 2000 hours. The results show that after reflow soldering, scallop-type Cu_6Sn_5/ $(Cu, Ni)_6Sn_5$ was the only reaction product formed. A strong influence of Ni addition on the growth rate and thickness of the Cu_3Sn layer was also observed. Addition of as little as 0.05wt% Ni to SAC305 solder effectively slows down the growth of this Cu_3Sn phase while growth of the Cu_6Sn_5 continued to increase with increasing in aging time.

1. Introduction

In recent years, the Sn-Ag-Cu family of alloys has been considered as the best candidates to replace the conventional Sn-Pb solders in the electronic industry. Solder joint reliability is strongly influenced by the type and size of intermetallics formed at the solder/substrate metal interface. Thus, it is important to understand how changes to the properties of these intermetallics be induced in order to increase the reliability of solder interconnections. One frequently used method to influence the interfacial reactions and improve the mechanical properties of intermetallic layers is to alloy either the metallization or solders with small amounts of additional elements, [1]. Recent work revealed that additions of small amounts of Ni to Sn–Cu or Sn–Ag–Cu solders could improve the wettability, mechanical strength and growth of intermetallics in solders [2-5].

The addition of Ni is particularly notable because it hinders the Cu_3Sn growth during the reaction with Cu substrates [3]. The growth of Cu_3Sn had been linked to the formation of microvoids within the Cu_3Sn layer [6], which increases the tendency for brittle interfacial fracture. Accordingly, the Ni addition to solders offers the potential benefit of raising solder joint strength through decreasing the amount of the microvoids. The purpose of the present paper is to examine further the effect of Ni on intermetallics formed during reflow soldering and also the effect of solid state ageing on their growth.

2. Experimental Methods

The substrate used is an FR4 (epoxy glass) material sandwiched between two electroplated copper layers with dimensions: width x length x thickness of 25 x 40 x 1 mm. the substrates were first ground with fine silicon carbide paper to remove oxides, grease and oil. Prior to reflow soldering, the substrates were first laminated with a layer of dry solder mask to restrict the molten solder from flat spreading during reflow. The solder mask and the printed negative film were then exposed to ultraviolet (UV) light for 40 seconds in the UV unit. After removing the film, the substrates were soaked in the developer which contains potassium carbonate mixed with water at a ratio of 25:1 to form a layer of solder mask with small pad openings of desired diameter for the solder bump size investigated. After that, the substrates were populated with Sn-Ag-Cu solder balls with 500µm in diameter arranged in several rows and bonding to form the solder joints was made by reflowing in a furnace with the peak reflow temperature set at 250°C.

To investigate the effect of ageing the solder joints were subjected to solid state ageing at 150°C for up to 2000 hours. Cross sections from the samples were then prepared and examined by means of optical and scanning electron microscopy. The average thickness of intermetallics was measured by image analysis and their compositions were identified using EDX spot analysis across the intermetallic layer.

3. Results and discussion

The results of the present work indicate that the interfacial characteristics of solder joints are affected by the addition of Ni in the solder. Figure 1 shows the IMC for Sn–3Ag–0.5Cu, Sn–3Ag–0.5Cu-0.05Ni and Sn–3Ag–0.5Cu-0.1Ni solders on Cu substrates after reflow respectively. The results clearly show that there is a significant difference between Ni-containing (SAC-Ni) and Ni-free (SAC) solders. Addition of Ni to the SAC solder refined the grain size of the intermetallic formed during reflow, confirming previous observations [7]. EDX analysis of the intermetallics for Sn–3Ag–0.5Cu-0.05Ni and Sn–3Ag–0.5Cu-0.1Ni showed that Ni has dissolved in Cu_6Sn_5, albeit in small concentrations up to 2.4wt% and thus the intermetallic layer should be labeled as $(Cu, Ni)_6Sn_5$. Similar results were reported by Amagai [8] and Laurila *et al.* [1] who argued that the IMC layer formed should be labeled as $(Cu, Ni)_6Sn_5$ even though elemental analysis clearly showed that the ratio of Ni: Cu: Sn (in wt%) was 1.3–2.9:43–53:45–54. In the present work the amount of Ni dissolved in Cu_6Sn_5 was found to be 1.4wt%.

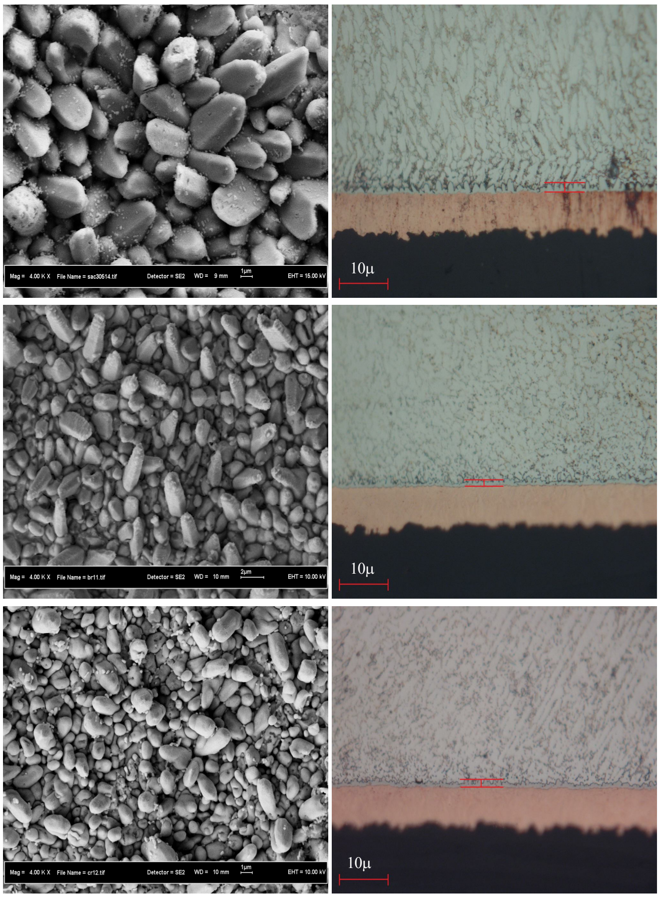

Fig. 1: Top view morphologies of intermetallics after reflow (a), Sn-3Ag-0.5Cu/Cu; (b) Sn-3Ag-0.5Cu-0.05Ni/Cu, (c) Sn-3Ag-0.5Cu-0.1Ni/Cu.

Figure 2 shows the electron micrographs of the SAC/ Cu and SAC-Ni/Cu after reflow. Only Cu_6Sn_5 in SAC solder and $(Cu, Ni)_6Sn_5$ in SAC-Ni solder are clearly visible in both cases as at this stage, the Cu_3Sn is not observed. The Cu_6Sn_5 in SAC solder exhibits the scallop-type morphology, consistent with what had been reported by previous researchers [9-12]. However, the classical scallop-type morphology appears to have been lost when Ni was added to solder as shown in Figure 2b. Wang *et al.* [13] showed that $(Cu, Ni)_6Sn_5$ has a block-like structure when Ni was doped into the solder and argued that such change in the morphology may be due to the amount of Ni dissolved in the $(Cu, Ni)_6Sn_5$.

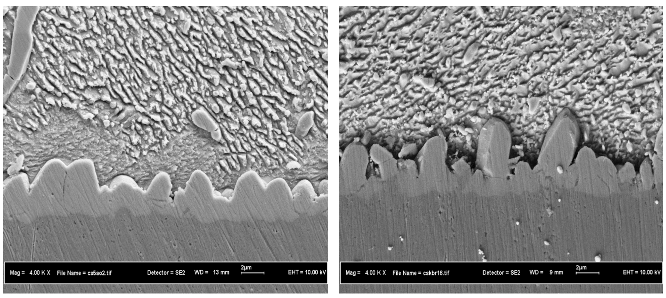

Fig. 2: SEM cross-sectional images of the interfacial intermetallics at (a) SAC/ Cu and (b) SAC-0.05Ni/ Cu.

After reflow it was observed that addition of Ni, and in particular 0.05wt% Ni, to the Sn–3Ag-0.5Cu solder was very effective in reducing the thickness of intermetallic as the amount of the Cu_6Sn_5 at the interface was measured as 2.81µm, 1.51µm and 2.13µm for SAC, SAC-0.05Ni and SAC-0.1Ni solder respectively. These results contradict what has been reported in the literature which reported that addition of Ni accelerated the growth of Cu_6Sn_5 but hindered the growth of Cu_3Sn intermetallics during isothermal ageing.

After the solder joints were subjected to solid state ageing, the addition of Ni into the solder was found to slow down the growth of Cu_3Sn IMC layer and lower its thickness at the same time (Figure 3).

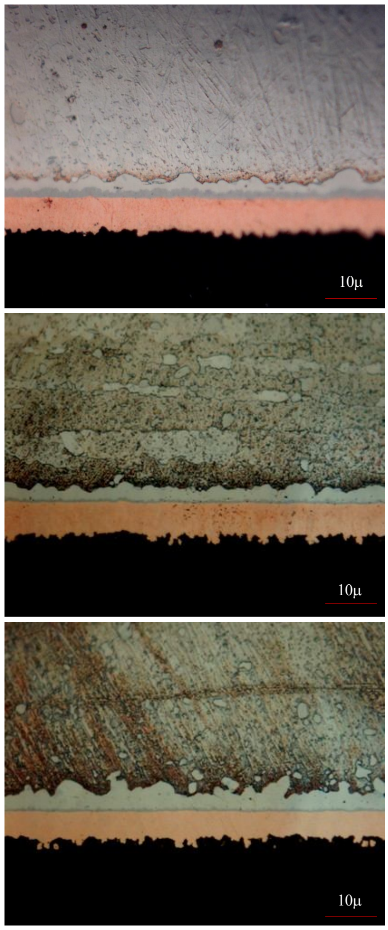

Fig. 3: Cross sections of intermetallics for; (a) Sn-3Ag-0.5Cu, (b) Sn-3Ag-0.5Cu-0.05Ni/Cu and (c) Sn-3Ag-0.5Cu-0.1Ni/Cu after aging at 150^{o}C for 1000 hours.

After ageing at 150^{o}C for 250 hours the thickness of Cu_3Sn layer was measured as 2.15µm, 0.53µm and 1.29µm for SAC, SAC-0.05Ni and SAC-0.1Ni solder respectively. Increasing the ageing time to 2000 hours, increased the Cu_3Sn thickness to 3.4µm, 1.95µm and 1.86µm for SAC-0.05Ni and SAC-0.1Ni solder respectively. The thickness of Cu_3Sn intermetallics is plotted in Figure 4 for SAC and SAC-Ni solders. It is seen in all cases that Cu_3Sn grew thicker with aging and its growth shows a linear relationship with ageing time in accordance with previous findings [11]. On the other hand, the thickness of $(Cu, Ni)_6Sn_5$ layer increases with ageing time with the addition of Ni to SAC solder but the overall thickness of the total intermetallic (Cu_6Sn_5 + Cu_3Sn) was found to be lower in the solder with Ni addition compared with the solder without Ni.

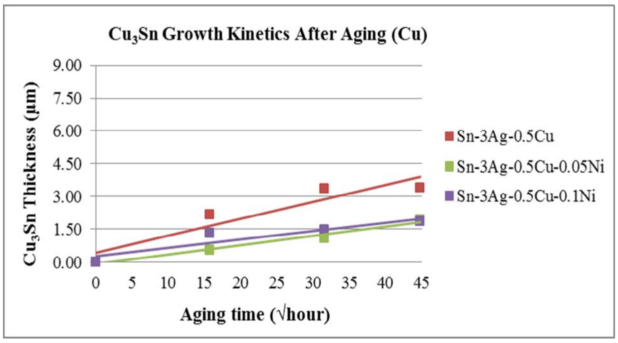

Fig. 4: Thickness of Cu_3Sn as function of aging time

The important observation made in the current study is that by adding 0.05wt% Ni into the solder was able to reduce the growth rate of Cu_3Sn compared with the solder without Ni but when more Ni (0.1wt%) was added into the solder, the Cu_3Sn layer grew faster again. This is because, when 0.05wt% of Ni was added to the solder, an optimum thickness of intermetallic was formed. While for solder with 0.1wt% of Ni, more (Cu, $Ni)_6Sn_5$ were formed due to more Ni dissolving into Cu_6Sn_5 and producing as a result thicker overall intermetallics. These results are in good agreement with Nogita and Nishimura (2008), who reported that the intermetallic thickness will increase when the percentage of Ni added to the solder is more than 0.05wt%.

The exact mechanism responsible for reducing the growth rate of the Cu_3Sn layer is yet to be resolved. Possible theories to explain this phenomenon have been proposed based on both thermodynamics and kinetics [1]. Recently, Wang *et al.* [13] suggested that Ni retards the growth of Cu_3Sn layer either directly or through the Cu_6Sn_5 layer. By investigation the effect of Ni addition in two high lead solders, 10Sn-90Pb and 5Sn-95Pb they showed that with Ni addition was not effective in retarding the growth of Cu_3Sn because there was no Cu_6Sn_5 layer. However, when soldering with lead-free alloys such as the SAC investigated in the present work, the (Cu, $Ni)_6Sn_5$ layer grew much thicker after reflow and subsequent solid state ageing as shown in Figure 3. The fact that this (Cu, $Ni)_6Sn_5$ layer has growth much thicker it may act as a diffusion barrier between Cu_6Sn_5 and Cu_3Sn.

4. Conclusions

The interfacial reactions of Sn-3wt%Ag-0.5wt%Cu solder added with two different Ni contents of 0.05 wt%, and 0.1 wt% Ni in reaction with a Cu substrate were examined during reflow and solid state ageing. It was found that after reflow only Cu_6Sn_5 and (Cu, $Ni)_6Sn_5$ formed in Ni-free and Ni-containing solders respectively. After solid-state aging both Cu_6Sn_5/ (Cu, $Ni)_6Sn_5$ and Cu_3Sn formed. However, addition of Ni to the solder produced a much thinner Cu_3Sn layer. The lower Ni concentration of 0.05wt% was found to be more effective in reducing the thickness of Cu_3Sn layer.

Acknowledgements

The authors would like to acknowledge the financial support provided by INTEL (Malaysia) Research Grant (vot 3C037) and Universiti Teknologi Malaysia for providing research facilities.

References

1. Laurila, T. *et al*, “Impurity and alloying effects on interfacial reaction layers in Pb-free soldering”, Materials Science and Engineering R 68 (2010) pp1–38
2. Nishikawa H, *et al*, “Interfacial reactions between Sn–0.7Cu (–Ni) solder and Cu substrate”, Journal of Electronic Materials Vol. 35 (2006), pp1127–1132.
3. Tsai, J. Y. *et al*, “A study on the reaction between Cu and Sn3.5Ag solder doped with small amounts of Ni”, Journal of Electronic Materials, Vol. 32 (2003), pp1203–1208.
4. Yao, P. *et al*, “Interfacial reaction and shear strength of SnAgCu–xNi/Ni solder joints during aging at 150°C”, Microelectronic Engineering, Vol. 86 (2009), pp1969–1974.
5. Chuang, T. H., *et al*, “Intermetallic reactions in Sn3Ag0.5Cu and Sn3Ag0.5Cu0.06Ni0.01Ge solder BGA packages with Au/Ni surface finishes”. Journal of Electronic Materials, Vol. 35 (2006), pp302–309
6. Zeng, K. *et al*, “Kirkendall void formation in eutectic SnPb solder joints on bare Cu and its effect on joint reliability”, Journal of Appled Physics, Vol. 97 No. 2 (2005), p4508
7. Gao, F. *et al*, Materials Science and Engineering A Vol. A420 (2006), p39
8. Amagai, M., “A study of nanoparticles in Sn–Ag based lead free solders”, Microelectronic Reliability. Vol. 48 (2008) p1-16
9. Chen, S. W. *et al*, Journal of Electronic Materials, Vol. 28 (1999), pp1203.
10. Choi, W. K. *et al*, Journal of Electronic Materials Vol. 29 (2000), pp1207.
11. Chi, Y. Y., *et al*, “Effects of Minor Ni Doping on Microstructural Variations and Interfacial Reactions in Cu/Sn-3.0Ag-0.5Cu-xNi/Au/Ni Sandwich Structures”, Journal of Electronic Materials, Vol. 39, No. 12, 2010, pp2544-2552
12. Wang, Y. W. *et al*, “Effects of minor Fe, Co, and Ni additions on the reaction between SnAgCu solder and Cu”, Journal of Alloys and Compounds, Vol. 478 (2009), pp121–127
13. Wang, C. H. *et al*, “Effects of Ni addition on the interfacial reactions between Sn–Cu solders and Ni substrate”, Intermetallics, Vol. 18 (2010), pp616–622