

EFFECT OF SURFACE FINISH ON INTERMETALLIC COMPOUND FORMATION DURING SOLDERING WITH Ni-DOPED SOLDERS

I. Siti Rabiattull Aisha ^{1,*}, A. Ourdjini ¹, A. Astuty ¹ and O. Saliza ²

¹*Materials Department, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia*

²*Faculty of Mechanical Engineering, Universiti Tun Hussien Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia*

**Corresponding author: aisha_hideaki@yahoo.com*

ABSTRACT

Solder joint reliability is dependent on both thickness and morphology of the intermetallics that form and grow at the solder joint interface during soldering and subsequent thermal ageing and examining the morphology of these intermetallics is of great importance. The focus of this paper is to present experimental results of a comprehensive study of the interfacial reactions during soldering of Sn-Ag-Cu-Ni lead-free solders on copper (Cu), immersion silver (ImAg), and electroless nickel/ immersion gold (ENIG) surface finishes. Using scanning electron microscopy detailed a study of the 3-D morphology and grain size of the intermetallics was conducted. The results showed that when soldering on ENIG surface finish, several morphologies of intermetallics with different grain sizes form at the solder joint interface compared to a single intermetallic morphology that forms when soldering on copper and immersion silver. An attempt was made to discuss the effect of several factors that may have an influence on the type of morphology the intermetallics may grow into. The results obtained in the present investigation also revealed that the technique of removing the solder by deep etching to examine the morphology of intermetallics is a convenient and efficient method to investigate the intermetallics formed at the solder joints.

Keywords: lead-free solder; surface finish; intermetallics; solder joint;

INTRODUCTION

Many researchers have tried to add minor elements to improve the properties of Sn-Ag solder [1-6]. They investigated the use of alloying elements such as Cu, Ni, Co, Sb, Bi, and so on, as a means of reducing the melting temperature of Sn-Ag solder, while simultaneously improving its mechanical properties. Among these alloying elements, Cu and/or Ni have primarily been chosen, owing to the formation of additional intermetallic phases that could improve the mechanical properties of the solder. The addition of small amounts of Cu was found to decrease the melting temperature and improve the wetting properties of the Sn-Ag solder [1, 5]. In addition, Ni is commonly used to provide a diffusion barrier between Cu and Sn-based solder alloys, in order to

prevent, or at least suppress, the formation of Cu_6Sn_5 and Cu_3Sn intermetallic compounds (IMCs). Ni is an effective additive, since the stable phases, which it forms in the Ni-Sn binary system, grow more slowly than the Cu-Sn IMCs.

In addition, the selection of an appropriate surface finish plays an important role in developing a reliable packaging technology. Cu is widely used in the under bump metallurgy and substrate metallization for flip-chip and ball-grid-array (BGA) applications. It is known that, at the solder/Cu interface, Sn reacts rapidly with Cu to form Cu-Sn IMC, which weakens the solder joints due to its brittle nature [7]. Therefore, electroless Ni plating has been used as a diffusion barrier layer on the Cu bond pad for flip-chip and BGA packages, because of its low cost and simple process [3, 8]. Generally, solder joints provide both electrical conductivity and mechanical strength and, consequently, play an important role in the connection of electronic components to printed circuit boards. In the development of package material systems, the joint reliability should be considered as one of the most critical criteria [9,10]. Since the joining process is a direct consequence of the interfacial reaction between the solder and substrate, understanding the interaction between such materials is an integral part of developing a reliable joining system. Many studies have been performed on the joint reliability and interfacial reaction between Pb-free solders and various surface finishes, such as Cu, immersion silver (ImAg) and electroless nickel-immersion gold (ENIG), during reflow or aging [6-10]. Therefore, in this study, we investigated the effect of different types of surface finishes using Ni-doped solders. In addition, we evaluated the effects of different percentage of Ni addition into Sn-Ag-Cu solder on the interfacial reactions of the Sn-Ag- Cu (or xNi)/ENIG, Sn-Ag- Cu (or xNi)/ImAg and Sn-Ag- Cu (or xNi)/Cu joints. The formation and growth of interfacial IMCs between the Ni containing Sn-Ag-Cu-xNi solder and ENIG as well as ImAg surface finish were studied and the results were compared to those obtained from the Sn-Ag-Cu/Cu joint. The effect of the surface finish on the growth kinetics of the interfacial IMCs of the Sn-Ag-Cu/Cu or ENIG as well as ImAg joints is also discussed.

EXPERIMENTAL DETAILS

Three different surface finish metallurgies were selected for this study: bare copper (Cu), immersion silver (ImAg) and electroless nickel/immersion gold (ENIG). The ImAg and ENIG surface finishes were deposited on FR4 substrate with the dimensions (width x length x thickness) of 45 x 50 x 1 mm. The copper substrate was first subjected to a pretreatment process to remove the oxide and activate the copper surface before the desired finish layers are deposited. Prior to soldering, a dry solder mask was laminated onto the plated substrates using a laminated machine. Then, the solder mask was exposed to the ultraviolet (UV) light through a patterned film. The exposure is to ensure an array of pads is made onto the solder mask upon the subsequent development stage in the developing solution. The substrates were then populated with Sn-3Ag-0.5Cu (SAC305), Sn-3Ag-0.5Cu-0.1Ni (SAC305-0.1Ni) and Sn-3Ag-0.5Cu-0.05Ni (SAC305-0.05Ni) solder spheres. The solder spheres were arranged in several rows and bonding to form the solder joints was made by reflow in a furnace with the peak reflow

temperature set at 250 °C. Before soldering, all substrates were treated with a no clean flux to remove surface oxide. In order to reveal the morphology of intermetallics formed during the soldering process a useful method of selective chemical etching of the top surface was employed and examination of the intermetallics was made by means of scanning electron microscopy. Energy dispersive x-ray (EDX) was used to identify the type and composition of intermetallics formed.

RESULTS AND DISCUSSION

Thermodynamics is usually used to describe the intermetallics which form at the interface between metal pads in the surface finish and liquid Sn-based solders and thus phase diagrams are important to explain why such an intermetallic can form or not. The type of intermetallic formed depends on the surface metallurgy used. It is well established that when soldering on bare Cu and ImAg, Cu₆Sn₅ IMC is formed during reflow, while Ni₃Sn₄ and (Ni,Cu)₃Sn₄ formed when soldering on ENIG.

For ImAg surface finish, the topmost Ag layer was dissolved completely into the molten Sn–Ag–Cu solder after initial reflow soldering, leaving the Cu layer exposed to the molten solder. Such complete consumption of the Ag layer was also observed in other studies on the rapid dissolution of Ag in liquid solder and was explained based on thermodynamics and kinetics [11]. Once the Ag layer was consumed, some part of Cu layer was also dissolved into the molten solder during reflow allowing the IMC grows at the interface between solders and Cu pad. Figure 1 shows the backscattered electron micrographs for samples with different levels of Ni additions that were aged up to 1000 hours. In all reaction couples, only scallop-type Cu₆Sn₅ is detected between the solders and Cu layer and no Cu₃Sn IMC was observed at this stage, but it appeared after the solid-state ageing. The formation of Cu₃Sn is affected by the phase stability of Cu₆Sn₅ according to the following reaction:



In addition, the morphology of the interfacial Cu–Sn IMC gradually changed from scallop-type to layer-type. These two IMC layers, Cu₆Sn₅ and Cu₃Sn grew thicker with increasing aging time. The interfacial reaction and IMC growth in this solder system are well-known and have been reported in previous studies [12, 13]. As can be seen in figure 1, the amount of Cu₆Sn₅ IMC becomes increased when the Ni concentration increased or in other words, the IMC thickness increased with the increasing of Ni addition. An explanation for this dependency had been presented elsewhere [14].

As can be seen in Figure 1, when Ni doped solder being used, Cu₆Sn₅ exhibited a needle-like microstructure. However, some part of the IMC still exhibited features of the scallop-type microstructure. This needle-like microstructure had also been described as the columnar microstructure [6, 15-16] or the aggregate-type microstructure [17]. Most obvious features of this microstructure were the size of the IMC itself, where it

became smaller when the percentage of Ni addition increased. Apart from that, the addition of Ni into SAC solder able to substantially hinder the Cu_3Sn growth in the reaction between these solders and the Cu substrate especially after isothermal ageing (Figure 2). The growth of Cu_3Sn often accompanies the formation of Kirkendall voids, which has been linked to the weakening of the solders joints. Accordingly, Ni has been proposed as a useful alloying additive to these solders [19]. To sum up, the addition of Ni did not change the Cu_6Sn_5 microstructure too much, and also did not thicken this phase substantially.

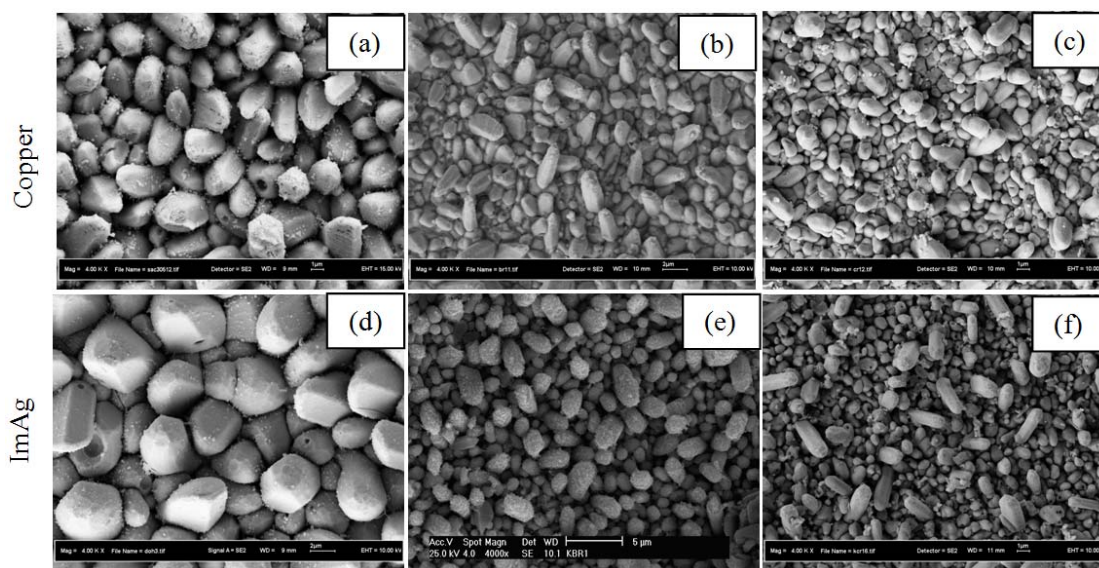


Figure 1: Top view micrograph of Cu_6Sn_5 IMCs formed between ImAg, Cu surface finish and; (a,d) SAC305, (b,e) SAC305-0.05Ni, (c,f) SAC305-0.1Ni after reflow soldering

In the case of electrolytic Ni/Au finished Cu pad, topmost Au layer dissolves readily into the molten solder during the initial reflow, leaving the Ni layer exposed to the molten solder. The reaction between the molten solder and Ni plating layer resulted in the formation of IMC containing the element of Cu, Ni, and Sn at the interface, which indicated the ternary IMC had a lower Gibbs free energy than a binary compound of the same structure from the entropy argument. Only one continuous IMC layer was detected at the interface for all solders. As can be seen in Figure 3, SEM-EDX analysis indicated that this IMC is needle-like Ni_3Sn_4 when using SAC305 and SAC305-0.05Ni, while $(\text{Ni,Cu})_3\text{Sn}_4$ formed when using SAC305-0.1Ni. These observations of the reaction products are in good agreement with the previous reports [19–21]. The Ni-barrier at the interface between solder and Cu pads prevents diffusion of Cu atoms from the pads into the interface, and thus producing Ni_3Sn_4 . When Ni-doped solder being used, especially with the higher percentage, the IMCs changed from Ni_3Sn_4 to $(\text{Ni,Cu})_3\text{Sn}_4$. The Ni content in $(\text{Ni,Cu})_3\text{Sn}_4$ layer is mainly originated from the SAC solder alloy. However, we could not find this IMC in SAC305-0.05Ni solder since that

the percentage is too low.

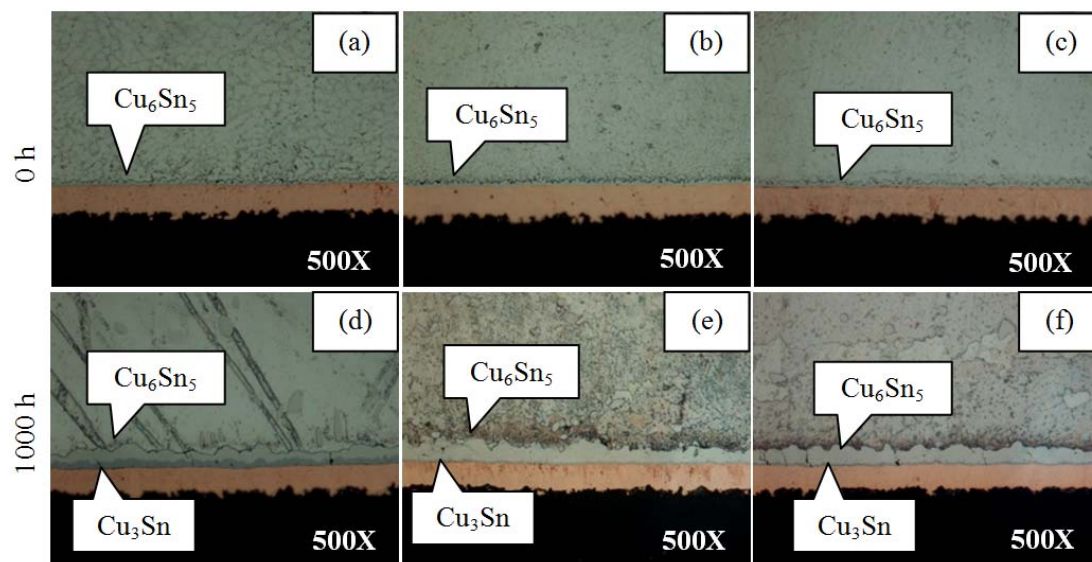


Figure 2: Cross sectional view of IMCs formed between 0h, 1000h of ageing and; (a,d) SAC305, (b,e) SAC305-0.05Ni, (c,f) SAC305-0.1Ni.

Nevertheless, the $(\text{Ni,Cu})_3\text{Sn}_4$ can be seen after prolonged isothermal ageing. Basically, the formation and growth of the $(\text{Ni,Cu})_3\text{Sn}_4$ IMC are partially caused by a decrease of Cu atom diffusing into the interface during ageing. With the increased addition of Ni particles, the increasing amount of Cu atoms will be pinned and prevented from moving to the interface. The same type of IMC formed for SAC305-0.1Ni after ageing. While for SAC305, the IMC changed from Ni_3Sn_4 to $(\text{Cu,Ni})_6\text{Sn}_5$. This layer also thickened gradually both with the increased presence of Ni particles as well as solid state ageing. The IMC growth is ascribed to an interfacial diffusion during ageing. As shown in Figure 4, the thickness of IMC at the interface of SAC305 and SAC-0.05Ni grows more slowly than that of SAC-0.1Ni. In addition, the interfaces of SAC305-0.05Ni and SAC305-0.1Ni joints show thinner IMC layers, which had formed slower than that of SAC305 joints. Apart from that, the solders of SAC305-0.05Ni and SAC305-0.1Ni contain bulk IMCs particles which may contribute to the reaction between solder and added Ni. During the ageing process, these bulk IMCs have a tendency to migrate to the interface and combine with the interfacial IMCs.

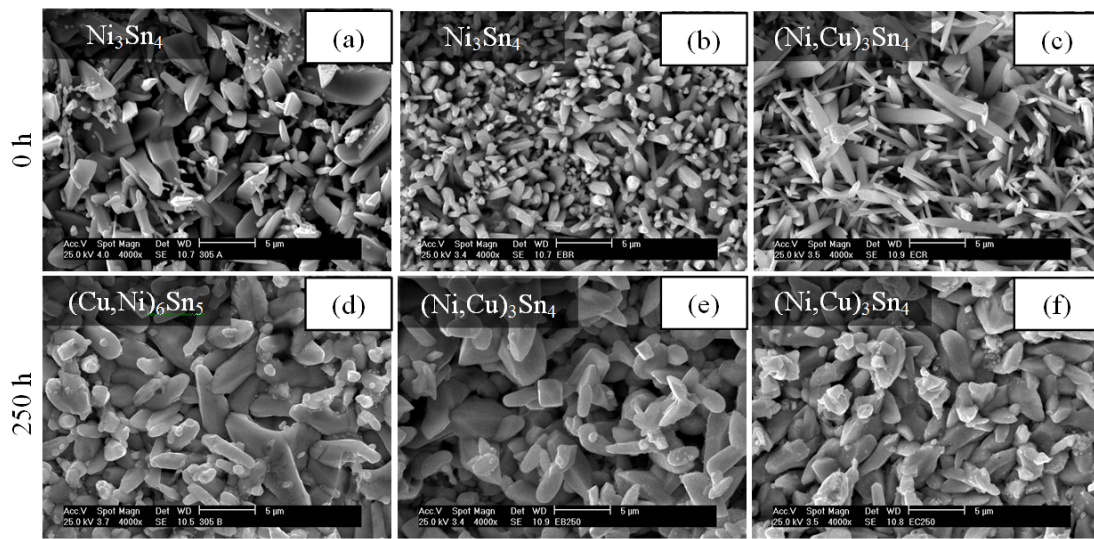


Figure 3: Top view micrograph of IMCs formed between ENIG and; (a,d) SAC305, (b,e) SAC305-0.05Ni, (c,f) SAC305-0.1Ni after reflow soldering

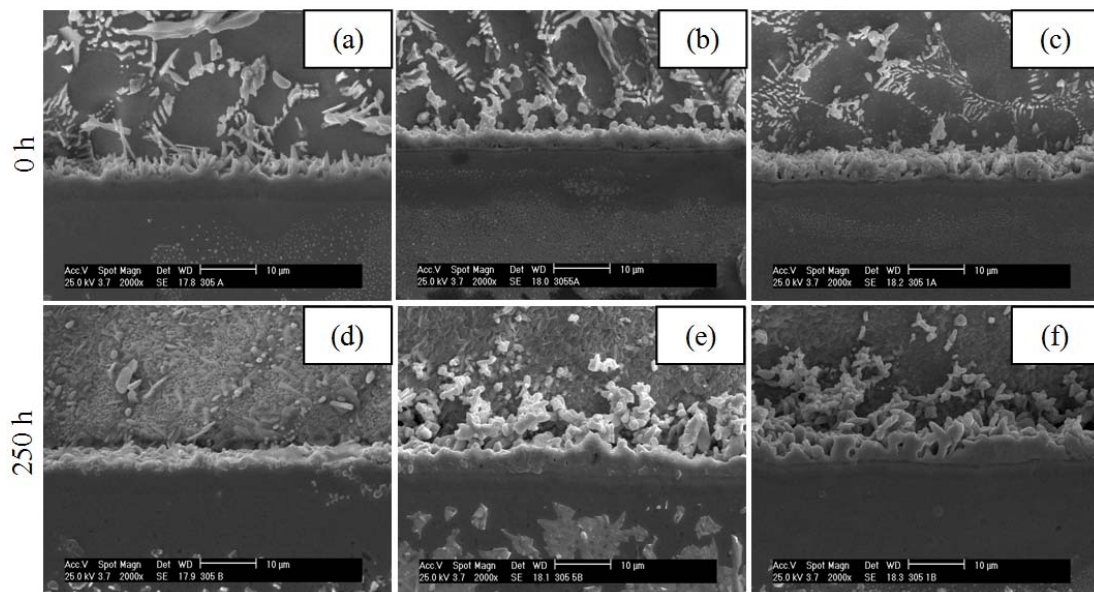


Figure 4: Cross sectional view of IMCs formed between 0h, 250h of ageing and; (a,d) SAC305, (b,e) SAC305-0.05Ni, (c,f) SAC305-0.1Ni

As mentioned before, the IMCs are basically affected by isothermal ageing. In the case of ImAg and Copper surface finish, Cu_6Sn_5 and Cu_3Sn are the two phases of the reaction products at the interface of SAC- $x\text{Ni}$ /ImAg and SAC- $x\text{Ni}$ /Cu after ageing. This, Cu_3Sn will form through a solid-state reaction between Cu and Cu_6Sn_5 during

ageing process. After prolonged ageing, the Cu_3Sn layer becomes thicker (shown in Figure 2). It has been reported [24,25] the growth kinetic of the interfacial IMC layer follows the square root time law expressed in the equation below:

$$\delta_t = \delta_0 + kt^{1/2} \quad (2)$$

where δ_t is the average thickness of the IMC layer at ageing time t , δ_0 is the initial thickness before ageing, k is the growth rate constant, and t is the ageing time. Figure 5 shows the thickness of the IMC layer as a function of the square root of time for each solder after aging at 150 °C for up to 1000 h. For all the diffusion couples, the mean thickness of the interfacial IMC layers increases linearly with the square root of the ageing time. Therefore, the atomic diffusion is the main controlling process for the IMCs growth during ageing process. In comparing the three types of surface finishes used in this study, the most interesting aspect of the aged SAC305-0.05Ni/Cu and SAC305-0.1Ni/Cu joints was that the growth of the Cu_3Sn IMC, where it was significantly retarded by the formation of the thick Cu_6Sn_5 IMC layer, due to the presence of Ni in the solder, in comparison with the SAC/Cu system (shown in Figure 6). It is found that for ImAg and Cu surface finishes, the Cu_3Sn IMC growth rate decreased with the increasing of Ni addition into the solder while Cu_6Sn_5 IMC become increased. However, overall, the IMCs thickness ($\text{Cu}_6\text{Sn}_5 + \text{Cu}_3\text{Sn}$) for both ImAg and Cu surface finishes getting increased when the percentage of Ni addition into the solder increased and it grew thicker during ageing (Figure 5). This suggests that the addition of more Ni into the SAC solder effectively suppresses the growth of the Cu_3Sn IMC, while substantially increasing the amount of Cu_6Sn_5 IMC at the interface. However, some researchers mentioned that there is a limit to the Ni addition into the solder and we should know the minimum Ni concentration that is effective in retarding the Cu_3Sn growth and at the same time not inducing an excessive Cu_6Sn_5 formation [24]. The reason why Ni addition is effective in reducing the Cu_3Sn thickness is unclear at this moment. Several theories have been proposed, including thermodynamic arguments [6] and kinetic arguments [22, 25]. It was likely that the Ni addition somehow increased the ratio of interdiffusion flux through the Cu_6Sn_5 layer and the Cu_3Sn layer [22]. It is widely known that a phase with a higher interdiffusion coefficient will grow faster at the expense of its neighboring phase that has a lower interdiffusion coefficient [22]. Nevertheless, the mechanism explaining how the Ni addition can change the ratio of interdiffusion flux is still lacking. More studies are needed to elucidate this point.

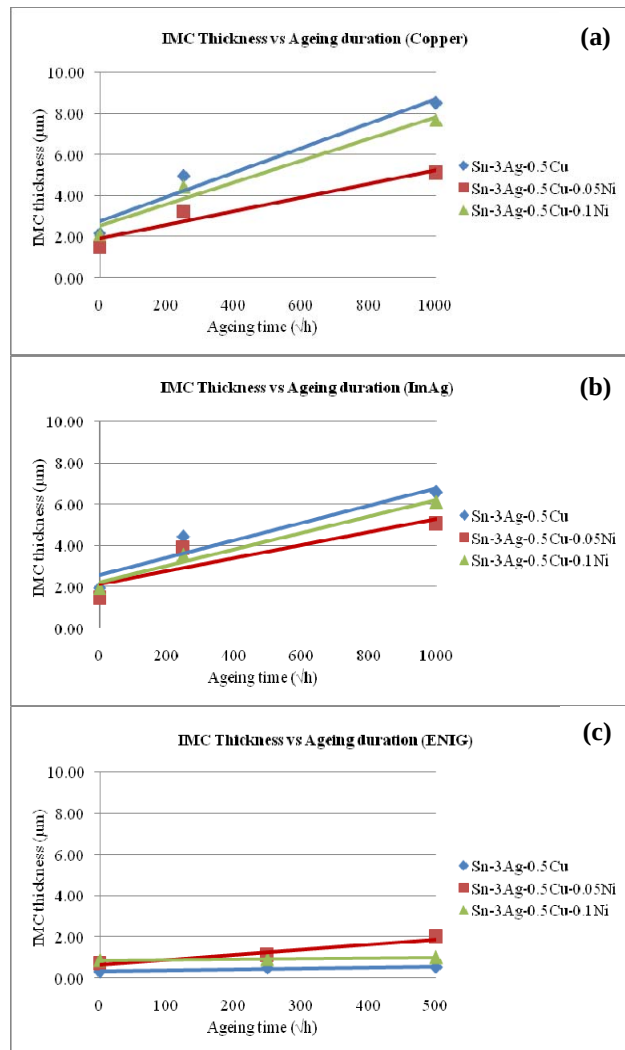


Figure 5: Thickness of the total IMC layer as a function of the square root of time for each solder after aging at 150 °C

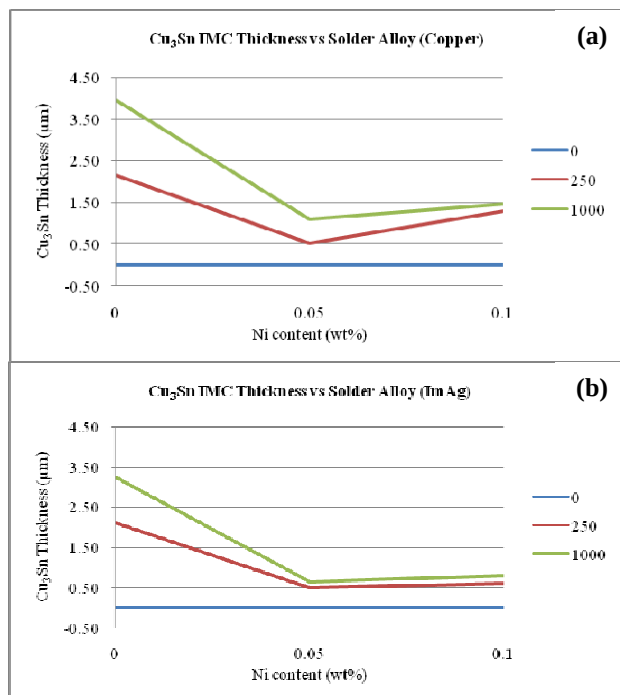


Figure 6: Thickness of the Cu_3Sn IMC layer as a function of the square root of time for each solder after aging at 150°C

CONCLUSION

In this study, the microstructure of the IMCs has been studied when SAC305, SAC305-0.05Ni and SA305-0.1Ni react with different surface finishes. When soldering on ImAg and Cu, only Cu_6Sn_5 IMCs formed at the interface after reflow, but with ageing at 150°C , Cu_3Sn formed between the Cu_6Sn_5 and Cu substrate. The Cu_3Sn grew due to the slow diffusion rate of Cu_6Sn_5 after ageing treatment. The addition of Ni into SAC305 solders alloy causes reduction in Cu_6Sn_5 grain size and also hindered the growth of Cu_3Sn IMCs, thus producing lower thickness than solder without Ni addition. Apart from that, in terms of effect of Ni addition to surface finish, ENIG (Boron) gives better result than ImAg and Cu surface finish, where IMCs thickness for ENIG (Boron) is thinner than ImAg and Cu which also means that Boron somehow slows down the diffusion rate of Cu into Sn. In addition, we also found that 0.05 wt% Ni addition is better than 0.1 wt% Ni addition to retard the Cu_3Sn growth. Finally ageing resulted in the growth of the IMC in terms of overall thickness, coarsening of intermetallic compounds and also changes in morphology of intermetallic compounds to more spherical shape.

ACKNOWLEDGEMENT

The authors would like to acknowledge the financial support provided by INTEL (Malaysia) Research Student Fellowship (vot 73724) and UTM for providing the research facilities.

REFERENCES

- [1] J.G. Lee, F. Guo, K.N. Subramanian and J.P. Lucas, *Soldering and Surface Mount Technology*, **14** (2) (2002) 11–17
- [2] F. Guo, S. Choi, J.P. Lucas and K.N. Subramanian, *Soldering and Surface Mount Technology*, **13** (1) (2001) 7–18
- [3] J.W. Yoon, C.B. Lee and S.B. Jung, *Journal of Electronic Materials*, **32** (11) (2003) 1195-1202
- [4] F. Guo, J. Lee, S. Choi, J.P. Lucas and K.N. Subramanian, *Journal of Electronic Materials*, **30** (9) (2001) 1073–1082
- [5] K.S. Kim, S.H. Huh and K. Suganuma, *Microelectronics Reliability*, **43** (2) (2003) 259–267
- [6] F. Gao, T. Takemoto and H. Nishikawa, *Materials Science and Engineering A*, **420** (1-2) (2006) 39-46
- [7] C.B. Lee, I.Y. Lee, S.B. Jung and C.C. Shur, *Materials Transactions*, **43** (4) (2002) 751-756
- [8] A. Kumar, Z. Chen, S.G. Mhaisalkar, C.C. Wong, P.S. Teo and V. Kripesh, *Thin Solid Films*, **504** (2006) 410-415
- [9] J.W. Yoon, S.W. Kim and S.B. Jung, *Materials Transactions*, **45** (3) (2004) 727-733
- [10] W.M. Chen, M. McCloskey and S.C. O’Mathuna, *Microelectronics Reliability*, **46** (5-6) (2006) 896-904
- [11] G. Ghosh, *Acta Materialia*, **49** (14) (2001) 2609–2624
- [12] J.W. Yoon, J.H. Lim, W.C. Moon, H.J. Lee, J. Joo and S.B. Jung, *Journal of Materials Research*, **21** (2006) 3196-3204
- [13] J.W. Yoon and S.B. Jung, *Journal of Alloys and Compounds*, **359** (1-2) (2003) 202-208
- [14] C. W. Chang, S. C. YANG, C. T. TU and C. R. Kao, *Journal of Electronic Materials*, **36(11)** (2007) 1455-1461
- [15] H. Nishikawa, J.Y. Piao and T. Takemoto, *Journal of Electronic Materials*, **35(5)** (2006) 1127-1132
- [16] F. Gao, T. Takemoto, H. Nishikawa and A. Komatsu, *Journal of Electronic Materials*, **35** (5) (2006) 905-911
- [17] J.Y. Tsai, Y.C. Hu, C.M. Tsai and C.R. Kao, *Journal of Electronic Materials*, **32(11)** (2003) 1203-1208
- [18] C. E. Ho, S. C. Yang and C. R. Kao, *Journal of Materials Science: Materials in Electronics*, **18** (1-3) (2006) 155-174

- [19] J.P. Liu, F. Guo, Y.F. Yan, W.B. Wang and Y.W. Shi, *Journal of Electronic Materials*, **33** (9) (2004) 958–963
- [20] P. Liu, P. Yao and J. Liu, *Journal of Electronic Materials*, **37**(6) (2008) 874–879
- [21] S.M.L. Nai, J. Wei and M. Gupta, *Thin Solid Films*, **504**, (2006) 401–404
- [22] T. Lauril, V. Vuorinen and J.K. Kivilahti, *Materials Science and Engineering Research*, **49** (2005) 1–60
- [23] X. Deng, R.S. Sidhu, P. Johnson and N. Chawla, *Metallurgical and Materials Transactions, A* **36** (2005) 55-64
- [24] Y.W.Wang, C.C. Chang, C.R. Kao, *Journal of Alloys and Compound*, **478** (2009) L1-L4
- [25] L. Garner, S. Sane, D. Suh, T. Byrne, A. Dani, T. Martin, M. Mello, M. Patel and R. Williams, (1993). “Finding Solutions to the Challenges in Package Interconnect Reliability, Intel Technology Journal, issue 4, pp 297-308, November 9 2005W.-K. Chen, *Linear Networks and Systems* (Book style). Belmont, CA: Wadsworth, pp. 123–135.