Loughborough University

This item was submitted to Loughborough's Institutional Repository (https://dspace.lboro.ac.uk/) by the author and is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/

Interactions Between Liquid Sn-Bi Based Solders and Contact Metals
for High Temperature Applications

J.F. Li, S.H. Mannan, M.P. Clode, H.M. Lobato
Department of Mechanical Engineering, King's College London, Strand, London WC2R 2LS, UK
Email: jianfeng.li@kcl.ac.uk, Tel: +44 (0)20 7848 1862, Fax: +44 (0)20 7848 2932

C. Liu, D.C. Whalley
Wolfson School of Mechanical and Manufacturing Engineering, Loughborough University, Loughborough LE11 3TU, UK

F.T. Lawrence, G. Jackson, H. Steen
Henkel Technologies, Kelsey House, Wood Lane End, Hemel Hempstead HP2 4RQ, UK

Abstract

Liquid solder interconnects are promising as an alternative approach to conventional high melting point solder interconnects for applications where the operating temperature is likely to exceed 125°C. In order to ensure that a liquid solder interconnect remains in contact with the terminations on the component and the substrate, and that electrical contact between them remains unbroken, there must be some growth of an intermetallic compound (IMC) at the interfaces between the solder and the contact metallizations. However, given that IMC growth is generally much faster when the solder is liquid, the growing IMC must act as a strong diffusion barrier to suppress further IMC growth. This paper presents preliminary studies of liquid-phase Sn-Bi based solders that result in stable interfaces between the solders and three common contact metallizations, consisting of electroless Ni(P)/Au, of Cu and of Ti-W. Small quantities (1 or 2 %) of an additional element, including Cr, Si, Zn, Ag, Au, Al and Cu, have been alloyed with the eutectic Sn-Bi composition to find an effective inhibitor additive that can achieve a strong IMC diffusion barrier. IMCs and their growth rates, as well as the consumption rates of the three contact metallizations in contact with the molten solders, were investigated. Storage temperatures of 200°C and 240°C were used, with storage times ranging between two hours and one month. Results to date show that suitable additives can significantly reduce IMC growth rates for both the Ni(P)-Au and Cu contact metallizations, while no appreciable IMC growth is observed for Ti-W in contact with both the original and the various alloyed Sn-Bi based solders. Based on the current results, criteria to further assist the design of feasible molten liquid solder – contact metallization systems have been deduced.

Introduction

Solder interconnects for applications where the operating temperature is likely to exceed 125°C are generally composed of high melting point solders (e.g. 90Pb/10Sn or 96Sn/4Cu) [1]. However, they can still be prone to low cycle fatigue and eventual crack formation resulting in loss of electrical continuity. An alternative approach is to allow the solder interconnects to melt, releasing the stresses on the joint completely. The component must then be mechanically attached to the substrate by other means, such as an underfill or glob-top. Such applications rely on surface tension to ensure that the liquid solder interconnect remains in contact with the terminations on the component and the substrate, and that electrical contact between them remains unbroken.

In order for mechanical adhesion to develop between the solder and the contact metallizations, there must be growth of an Intermetallic Compound (IMC) at the interface. Otherwise, the joint will fail at low temperatures when the solder is solid. However, given that IMC growth is generally much faster when the solder is liquid, the growing IMC must act as a strong diffusion barrier to suppress further IMC growth. In previous work [1] it has been demonstrated that the combination of Nb as the contact metallization and eutectic In-Sn as the solder results in just such a diffusion barrier. However Nb requires sputtering or evaporation methods for deposition and hence is only suitable for niche applications.

This paper considers the reactions of molten Sn-Bi based solders with contact metallizations consisting of electroless Ni(P)/Au, of Cu, and of Ti-W. Eutectic 42Sn-58Bi, with a eutectic point of 138 °C, is chosen as the basic solder alloy because it is cheaper than In-Sn solder, while the volume change on melting is negative; use of an off-eutectic composition can reduce this change to zero [2]. Of the three contact metallizations, Ni(P)/Au was chosen because Cu/Ni/Au is a common metallization used for both substrates, and flip-chips, Cu was chosen for study as it is also common for both substrate and flip-chip metallizations, while 10Ti-90W was chosen as it is frequently used as the Under Bump Metallization (UBM) for flip chip applications, and may come into contact with the solder after the original contact metallization is consumed by the solder.

The IMCs are believed to have a great effect on the mechanical properties of conventional solder interconnects. There is a wealth of studies on the kinetics of IMC growth between solid Sn-based solders and various contact metallizations, such as electroless Ni(P) and various types of Cu, under thermal ageing [3-5]. The IMCs formed during the soldering process also play an important role in the wettability of solders. Thus there are some studies of the IMC formation between the molten solders, including An-Ag-Cu, Sn-Pb, Sn-Ag, Sn-Sb, Sn-Zn, Sn-Bi and pure Sn, and the various contact metallizations containing Ni(P) or Cu [6-9]. In a few cases, the reaction times were up to several hours. However, corresponding to the soldering process, the majority of the studies was carried out for short-term periods, from several seconds to dozens of minutes. Nonetheless, results from these

studies show that the consumption rates of the common Ni(P) and Cu contact metallizations in contact with the molten solders are extremely high.

The motivation of this study is to examine the possibility of limiting IMC growth between the alloyed Sn-Bi based solders and the contact metallizations, by means of adding suitable additives to act as effective inhibitor within the solders. Therefore, in the present study, small quantities (1 or 2%) of an additional element, including Cr, Si, Zn, Ag, Au, Al and Cu, have been alloyed with the eutectic Sn-Bi composition.

Experimental Procedure

The electroless Ni(P)/Au substrate (ENIG), used in this study consisted of 3mm □ metal pads, on polyimide PCB boards. The metal structure consists of a top layer of Au(~0.9μm), then Ni(P)(4.1μm), then Cu(25μm). The Cu and Ti-W substrates were formed by sputtering a layer of Ti-W (0.25μm) onto a Si wafer followed by a sputtered layer of ~6 μm of Cu, both through a mask containing circular apertures 5 mm in diameter. These 5mm ϕ pads were used as both the Cu and Ti-W substrates in this study as during high-temperature storage, once the Cu layer was consumed, interactions between the molten solders and the Ti-W substrate could be studied.

The alloyed solders with 2wt% of Al, Si and Cr, here referred to as BiSn41.2Al2, BiSn41.2Si2 and BiSn41.2Cr2, were custom prepared by a supplier, while the other alloyed solders with 1wt% of Au, Ag, Cu and Zn, here named as BiSn41.6Au1, BiSn41.6Ag1, BiSn41.6Cu1 and BiSn41.6Zn1, were fabricated in-house by dissolving the corresponding metallic wires or foils temperatures from 240 to 540 °C for 10 to 30 min in the basic eutectic Sn-Bi solder.

Before application of the solder, all substrate pads were cleaned using isopropyl alcohol (IPA), acetone and finally distilled water. The basic eutectic Sn-Bi solder paste was deposited onto the surfaces of both types of the pads by printing through a 0.20mm thick stencil. The resulting samples had a maximum solder thickness of 0.3 mm at the top of the solder dome. The solder paste was also deposited onto the surfaces of some Cu/Ti-W/Si pads using a syringe to produce the samples with BiSn42 solder about 1 mm in maximum thickness. For all the alloyed Sn-Bi based solders, 0.022 to 0.024 g of diced solder pieces were placed on each of the Au/Ni(P)/Cu/polyimide pads, while 0.099 to 0.101 g of solder pieces was placed on each of the Cu/Ti-W/Si pads to prepare the samples with a solder layer approximately 1 mm in maximum thickness. The solder was then covered by a thin layer of flux and then reflowed in air at 220°C for 300s. These were finally cleaned using IPA, acetone and distilled water, before placing into high-temperature storage.

High-temperature storage of the samples was carried out in air at temperatures of 200°C and 240°C. Most of the solder – substrate systems were stored at both temperatures for 48 and 96 or 120 hours. A few systems were also stored for 2, 24 26, 29 or 716 hours. After storage, the samples were potted and then polished to obtain the metallographic cross sections. Then scanning electron microscopy (SEM), together with an X-ray energy-dispersive (EDX) spectrometer, was employed to characterize the interfacial structures and IMCs formed between the substrates and the solders during the high-temperature storage. In addition, in order to observe the crystalline morphology of the IMCs, some samples were also etched with 18% nitric acid to selectively dissolve the remaining solders.
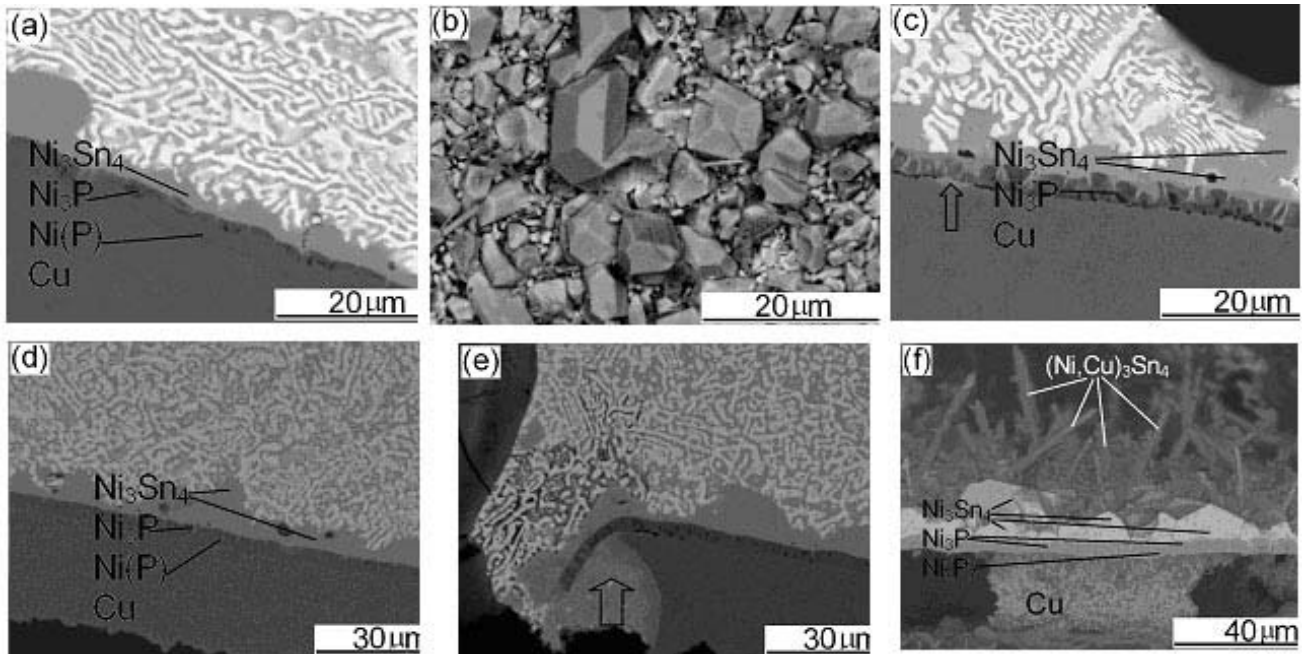

Figure 1 Typical SEM images of the BiSn42–Ni(P) system: (a) polished cross section, 200 °C, 24 h; (b) etched top surface, 200 °C, 24 h; (c) polished cross section, 200 °C, 48 h, the open arrow points at local failure; (d) polished cross section 240 °C, 48 h; (e) also polished cross section, 240 °C, 48 h ,the open arrow points at the failure at the base of the Cu/Ni/Au pads; (f) etched cross section, 240 °C, 48 h.

Results and Discussion

Ni(P) – solder

The results presented here start with the reactions of the basic eutectic Sn-Bi solder with the electroless Ni(P), which provides the benchmark for IMC growth in the rest of the paper. Figure 1 presents the SEM images showing typical features of the interfacial reaction and the IMC morphologies for this Ni(P) – solder system. No Au IMC was detected at the interfaces, and hence it is believed that the Au layer dissolved into the solder completely during the reflow process. Identified using EDX analysis, the interfacial reaction products are in agreement with what were reported for reactions of liquid Sn-Pb, Sn-Ag and also Sn-Bi solders with similar electroless Ni(P) substrates [6,9,10]. The IMC that forms is Ni_3Sn_4. A layer of crystalline Ni_3P, with numerous Kirkendall voids [9], was produced as the initially amorphous Ni(P) tends to crystallization, and Ni was depleted from this layer during IMC formation.

Compared with those for reaction times from 5 s to 5 h reported in Refs. [6,9,10], in the present study for longer reaction times, the interfaces between the IMC and the solder are relatively wavier. The IMC grains are larger and more heterogeneous, while their facets are more clearly developed (Figure 1b). Also the Kirkendall voids are significantly larger. It was especially found that at 200°C that the Ni layer begins to fail at around 48 hours, with Sn locally penetrating through the grain boundaries towards the underlying Cu metallization (Figure 1c). It was also observed that at the base of the Cu/Ni/Au pads, the Ni layer sometimes failed much earlier than elsewhere, allowing the solder to form IMCs with the underlying Cu, at a much faster rate than with Ni(P) (Figure 1e). In addition, a number of whiskers were found to protrude from the Ni_3Sn_4 IMC grains into the bulk of the SnBi solder (Figure 1f). According to the EDX results, these whiskers were identified as $(Ni,Cu)_3Sn_4$. Establishing a detailed mechanism for the formation of these whiskers is not the interest of this paper. Their formation is probably associated with the connective paths existing for the molten solder towards the underlying Cu metallization, grown up from the Kirkendall voids, and the chemical force [4] due to the reaction between Cu, Ni and Sn.

Figure 2 presents the thicknesses of the Ni(P), Ni_3P and Ni_3Sn_4 layers as functions of reaction time at both experimental temperatures. Here the plus and minus error bars, also in the following figures, stand for the measured maximum and minimum values, respectively. Obviously, these data are significantly scattered, which may be related to the fact that the experiments were carried out for long times. In order to determine the kinetics of the IMC growth more accurately, more experimental points than those in Figure 2 are necessary. Nonetheless, using the well established empirical power law for growth kinetics [9],

$$\delta = kt^{\alpha} \tag{1}$$

where δ is the average thickness, t is time, and k and α are constants, the average thickness of the Ni_3Sn_4 IMC approximately has a $t^{0.15}$ dependence on time at both temperatures, which is significantly lower than that as reported earlier for Sn-Pb and Sn-Ag solders in contact with

similar electroless Ni(P) substrates [9,10]. Thus, both the existing channel scallop model [11] and grain boundary model [9] that predict the dependence of the 1/3 order of time cannot be used to interpret the growth kinetics of Ni_3Sn_4 IMC formation over long reaction times.
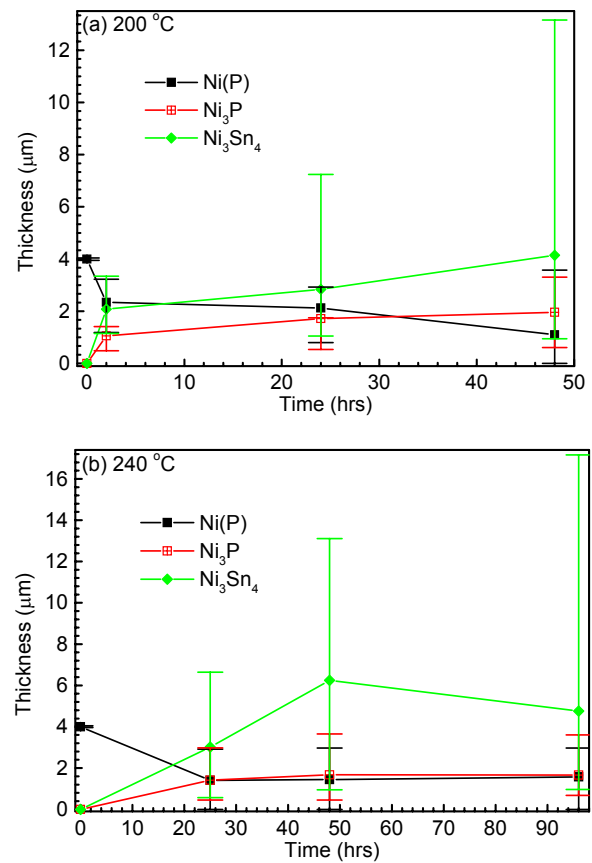

Figure 2 Thickness of Ni(P), Ni_3P and Ni_3Sn_4 for the BiSn42–Ni(P) system as a function of storage time.

This paper is mainly concerned with the effects of small quantities of one of the seven additional elements on the consumption rate of the Ni(P) substrate and the growth rate of the IMC. With addition of 2wt% Al into the eutectic Sn-Bi composition, the wettability of the solder to the contact metallization becomes very poor. The solder easily detached from the substrate during the reflow process. In the instances when the solder did adhere to the substrate, no real contact and IMC formation were observed between the solder and the substrate after the high-temperature storage. This may be due to the fact that Al is too active and the flux used is not matched to this type of alloyed solder. These experiments will be repeated using a more suitable flux. Both Au and Zn additives to the solder resulted in an increase in both the consumption rate of the substrate and growth rate of the IMC (Figure 3a and b), but have no appreciable effect on the interfacial microstructures. Cr, Si and Ag have been effective in reducing the consumption rate of the Ni(P) and the growth rate of the IMC, but their effects are all small (Figure 3c and d). Among these three elements, only Ag has been observed to produce minor additional IMC, Ag_3Sn, around the Ni_3Sn_4 IMC grain boundaries (Figure 4). The reduction in the IMC growth rate can be attributed to these tiny Ag_3Sn grains acting

443   2005 Electronic Components and Technology Conference

as local diffusion barriers. A higher level of Ag addition may thus be expected to further reduce the IMC growth rate. However, this is actually not practicable because a high content of Ag may increase the melting point of the alloyed solder to an extent that results in loss of the performance of liquid solder interconnects at the anticipated operating temperatures.

Significantly, Cu has been effective in modifying the IMC formed at the interface. The mechanism is similar to the reaction reported between molten Sn-3.5Ag solder saturated with Cu and electroless Ni(P) [12]. Cu in the molten

BiSn41.6Cu1 solder precipitated out as a layer of Cu-Ni-Sn IMC, instead of the Ni_3Sn_4 IMC formed with the molten BiSn42 solder, on the electroless Ni(P) substrate. The Cu-Ni-Sn IMC formed at both temperatures for storage times less than 120 h contains a higher percentage of Cu atoms than Ni atoms, and can hence be identified as $(Cu,Ni)_6Sn_5$ according to the EDX result. The structure of the IMCs was somewhat different from those at the Ni(P)/Au/SnAgCu interface, which mainly consisted of $(Cu,Ni)_6Sn_5$, but also contained some Ni_3Sn_4 [13]. The layer of $(Cu,Ni)_6Sn_5$ IMC seen in our work acts as a reaction barrier and significantly reduced the
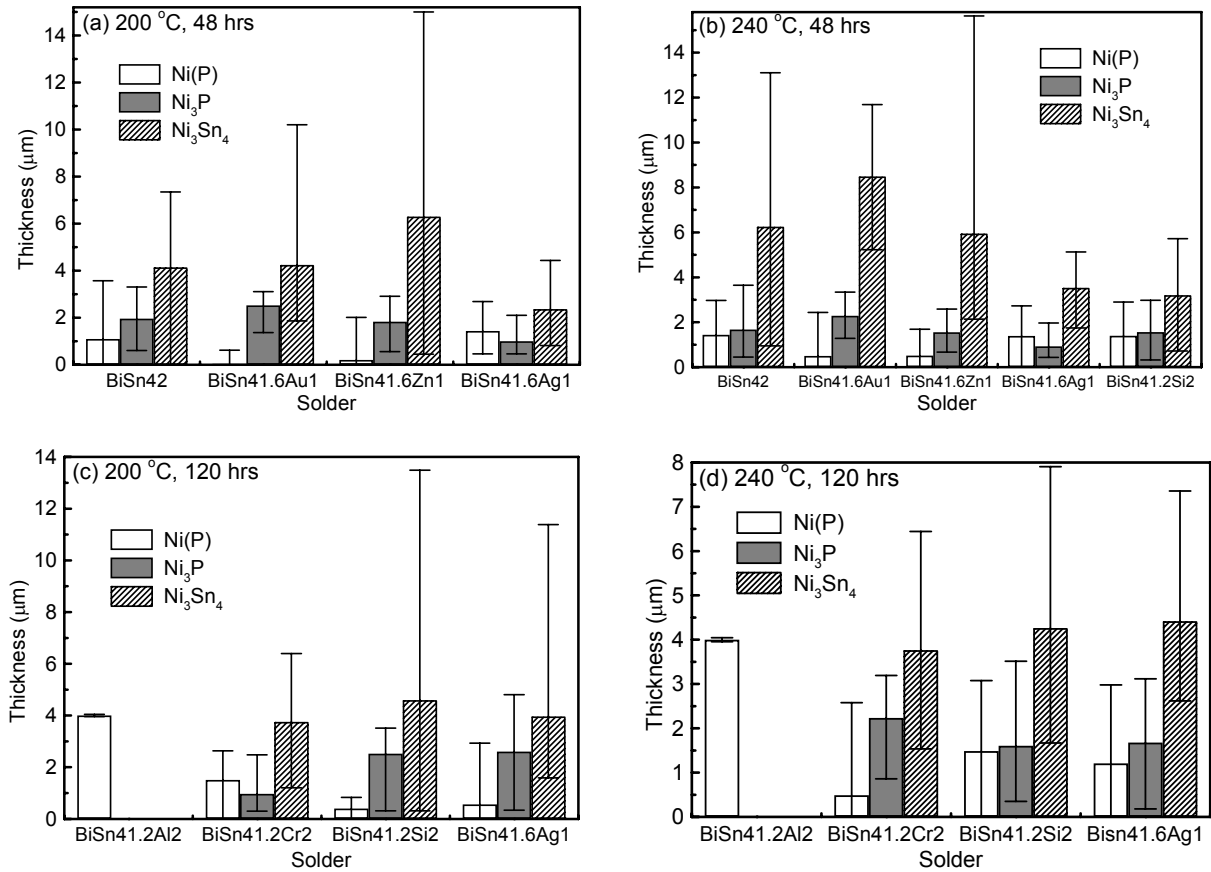

Figure 3 Comparison of thickness of Ni(P), Ni_3P and Ni_3Sn_4 for the Ni(P) substrate in contact with the different alloyed solders.
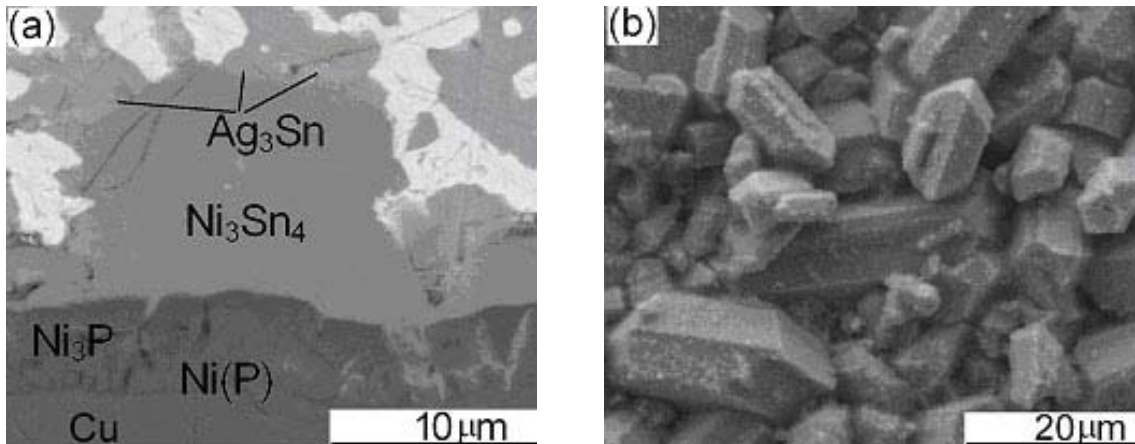

Figure 4 SEM images of the BiSn41.6Ag1–Ni(P) system: (a) polished cross section, 240 °C, 120 h; (b) etched top surface, 200 °C, 96 h.

444   2005 Electronic Components and Technology Conference

consumption rate of the Ni(P) substrate during the high-temperature storage (Figures 2 and 5). Only a few locations were converted to porous Ni_3P with limited size and thickness, and the majority of the Ni(P) metallization was intact following contact with the molten BiSn41.6Cu1 solder at 240 °C for 120 h (Figure 6a). The Cu-Ni-Sn IMC formed at 200 °C for 716 h may be identified as $(Cu,Ni)_6Sn_5$ or $Ni_{26}Cu_{29}Sn_{45}$ [13] (to be determined). In the case of a relatively long reaction time, the Ni(P) layer has been entirely converted to porous Ni_3P, through which Sn penetrates towards the underlying Cu metallization to form Cu_3Sn (Figure 6b). It should be noted that an amorphous substance always tends to transform towards the corresponding crystalline counterpart. Nonetheless, the results obtained here show the possibility of modification and limitation of IMC formation at the interface between molten solders and the substrate for extended periods, by adding a small quantity of an additional element.
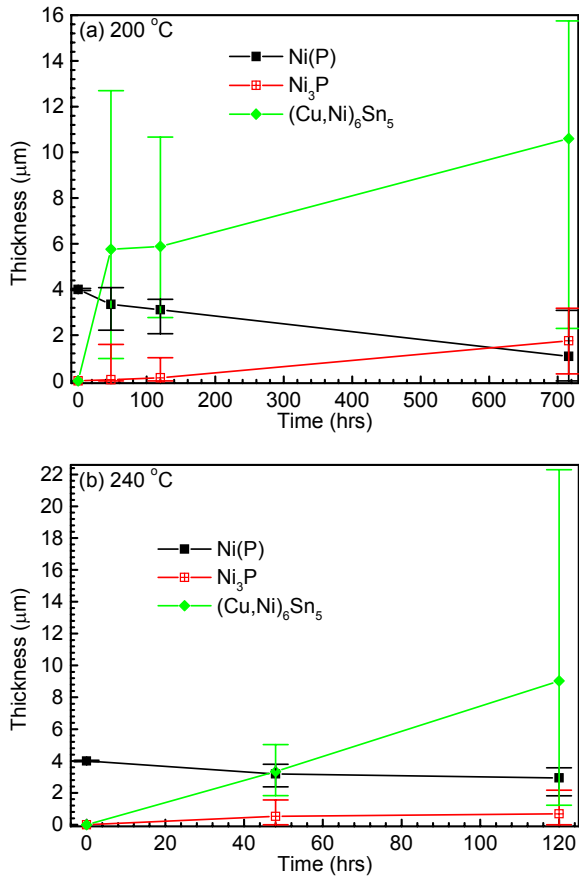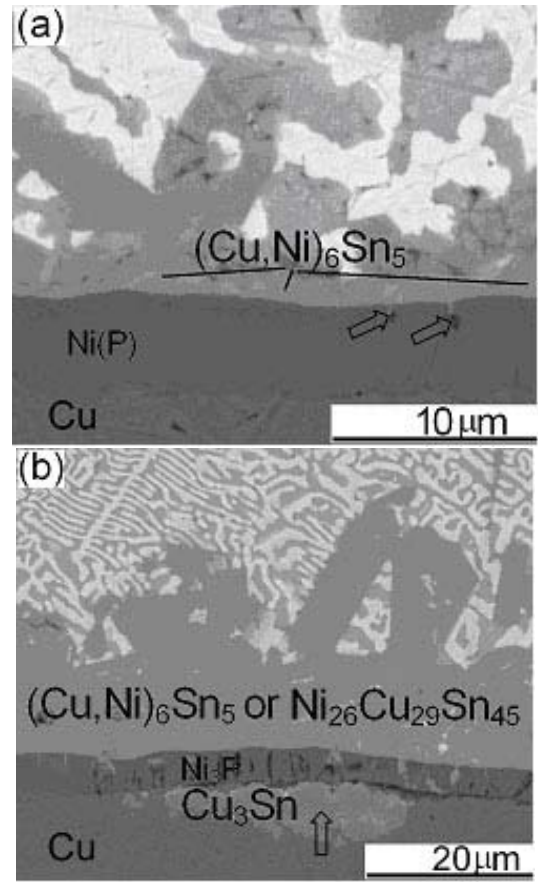

Figure 6 SEM images of the polished cross sections for the BiSn41.6Cu1–Ni(P) system: (a) 240 °C, 120 h, the open arrows point at locally formed Ni_3P; (b) 200 °C, 716 h, the open arrow points at the formed Cu_3Sn due to Sn penetration through the Ni_3P.

completely, only Cu_6Sn_5 was observed and migrated from the interface into the bulk of the molten solder (Figure 7b). The underlying Ti-W layer seems intact during continuous contact with the molten solders at both storage temperatures (Figure 7c). However, no evidence of an IMC containing Ti and/or W was observed. Also, the solder easily detached from the substrate during cross sectioning after storage at 240 °C for one month. In the polished cross section of a sample stored at 200 °C for one month, cracks were observed within the Ti-W layer (Figure 7d). Thus, further investigation is needed to determine the level of adhesion between the solder and the Ti-W substrates.

Among the investigated additional elements, Al resulted in poor wettability of the alloyed solder to the substrate, similar to the results with the electroless Ni(P) substrate. Cr and Si have no appreciable effect on the IMC growth at both storage temperatures. This may be due to the Cr and Si having extremely low solubility in the solder, and hence precipitating out. Addition of 1wt% Au into the eutectic Sn-Bi solder modified the IMC formation, which consisted of extremely large grains containing Au which spalled into the solder bulk (Figure 8a). Ag can slightly reduce the consumption rate of the Cu layer; however, it appears to have no effects on the interfacial IMCs (Figure 8b).

Figure 5 Thickness of Ni(P), Ni_3P and Ni_3Sn_4 for the BiSn41.6Cu1–Ni(P) system as a function of storage time.

Cu– and Ti-W – solder

As expected, the consumption rates of Cu in contact with the molten BiSn42 solder were high. Even at 200 °C, the as-sputtered Cu layer (~6μm) could survive for only 30 hours approximately. The interfacial IMCs are the same as those formed between the molten Sn-Ag, Sn-Pb, Sn-Ag-Cu solders and Cu substrate [7,8,14]. The IMC formed at the Cu side could be identified as Cu_3Sn, while that formed at the solder side as Cu_6Sn_5 (Figure 7a). Once the Cu layer was consumed

By contrast, Zn appears to be the most effective additive for modifying the IMC growth and the consumption rate of Cu in contact with the molten solder, as shown in Figure 9.
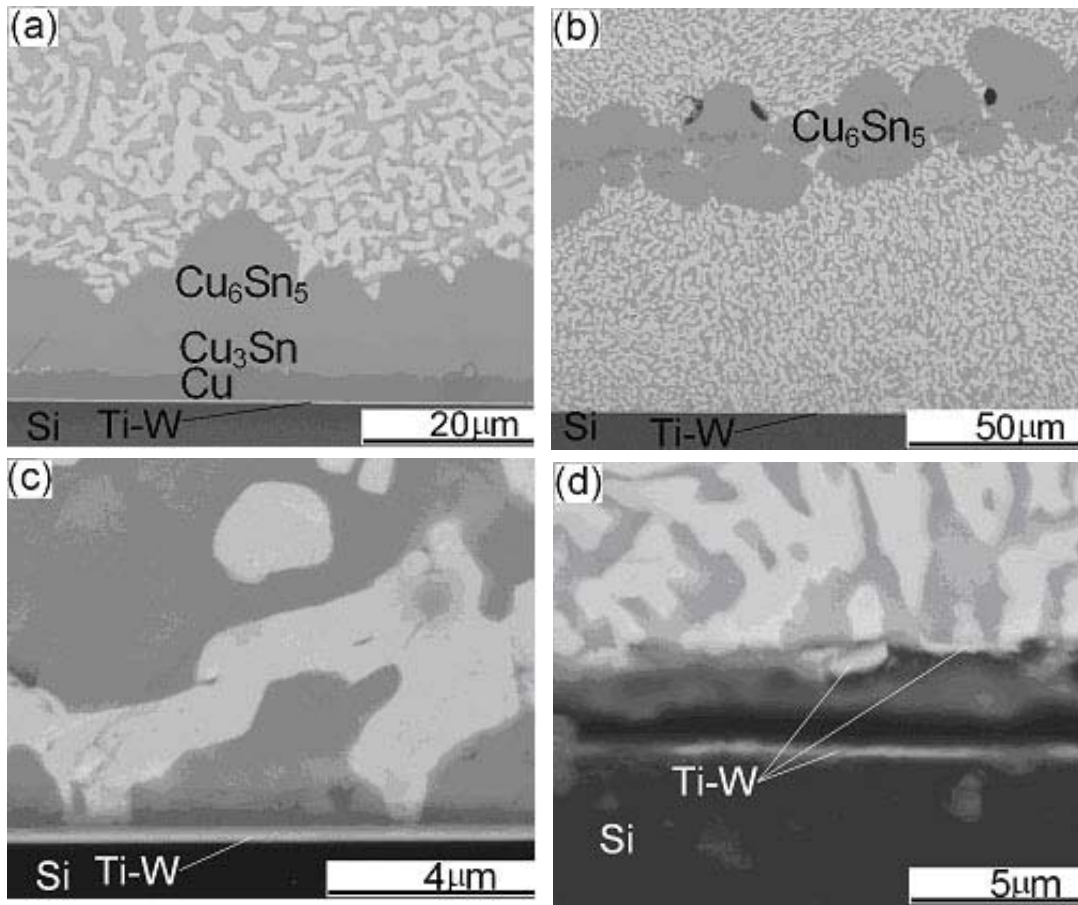

Figure 7 SEM images of the polished cross sections for the BiSn42–Cu/Ti-W system: (a) 200 °C, 29 h; (b) 240 °C, 26 h; (c) 240 °C, 96 h; (d) 200 °C, 716 h.
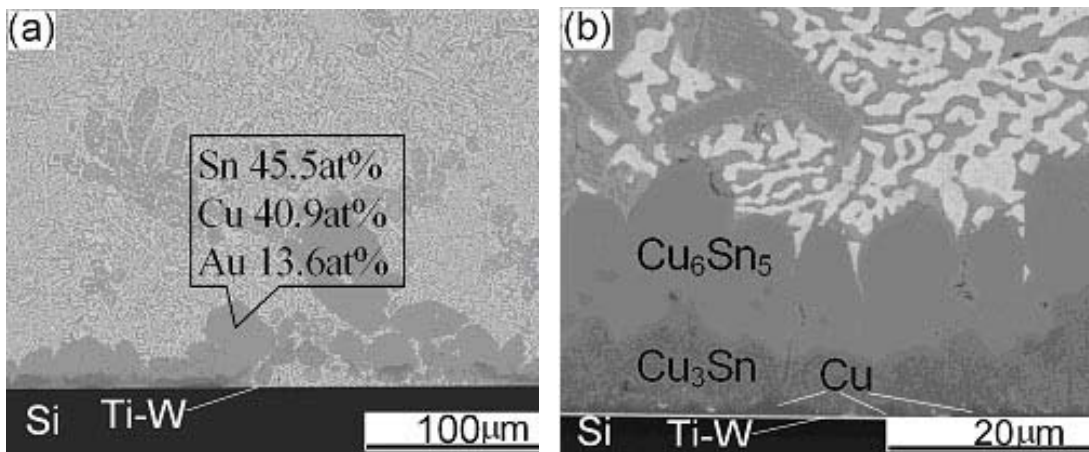

Figure 8 SEM images of the polished cross sections for (a) the BiSn41.6Au1–Cu/Ti-W system, 200 °C, 48 h; (b) the BiSn41.6Ag1–Cu/Ti-W system, 240 °C, 48 h. The callout in (a) presents the atomic ratio of the IMC quantified by EDX.

With the addition of 1wt% Zn into the Sn-Bi solder, a layer of γ-CuZn was produced between the solder and Cu substrate, instead of the Cu_3Sn and Cu_6Sn_5 (Figure 9a and b). A similar γ-CuZn IMC has been reported during reaction of Sn-Zn eutectic solder and Cu substrates [8,15]. This layer of γ-CuZn obviously retards the diffusion of both Cu and Sn, leading to a decreased consumption rate of the Cu in contact with the molten BiSn41.6Zn1 solder at 200 °C (Figure 9). However, the effect is limited and the γ-CuZn existing at 200 °C cannot survive at 240 °C for 48 h, as shown in Figure 9 c and d.
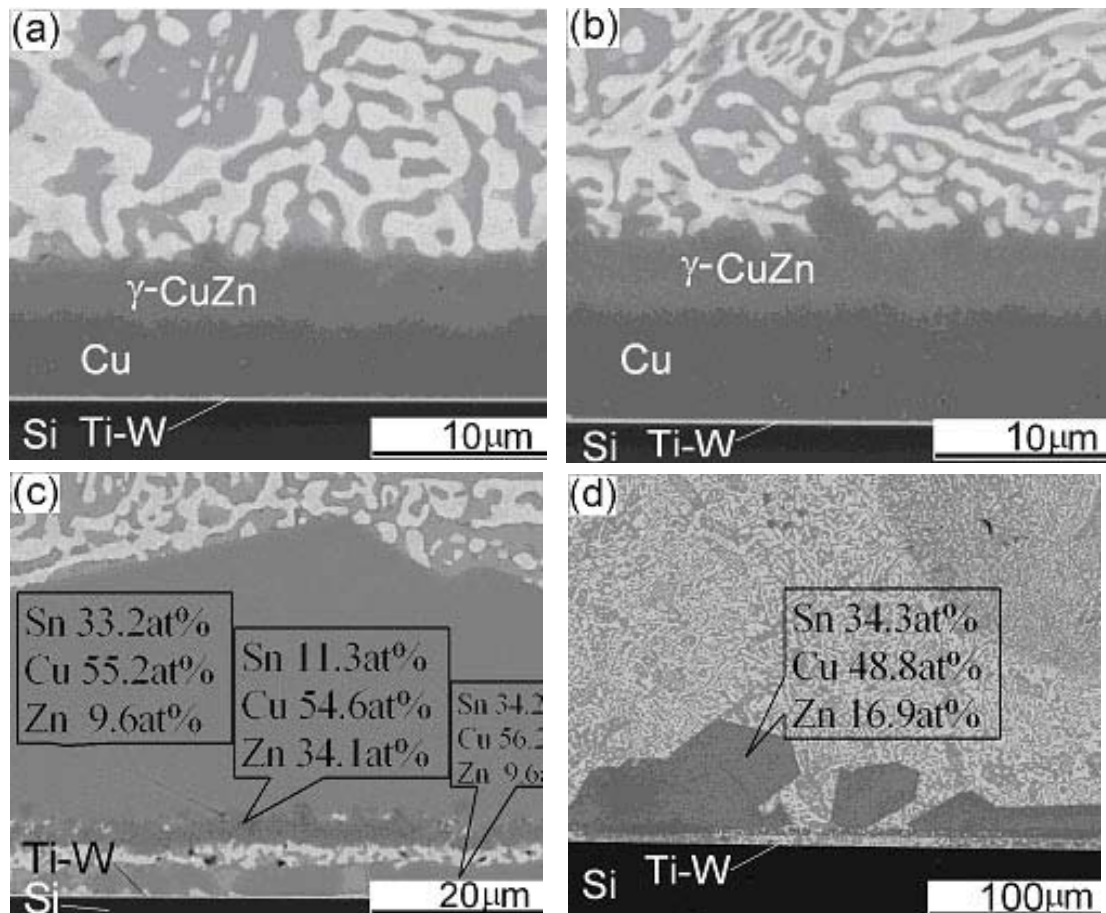
446   2005 Electronic Components and Technology Conference

Figure 9 SEM images of the polished cross sections for the BiSn41.6Zn1–Cu/Ti-W system: (a) 200 °C, 48 h; (b) 200 °C, 120 h; (c) 240 °C, 46 h; (d) 240 °C, 120 h. The callouts in (c) and (d) present the atomic ratios of the IMCs quantified by EDX.

Discussion

From the above results, it can be seen that significantly decreased IMC growth rates were only achieved for the BiSn41.6Cu1–Ni(P) and the BiSn41.6Zn1–Cu systems. The common factors between them include the following two aspects. The first is that the small quantity of an additional element effectively modified the IMC formed between the solder and the substrate. The other is that the additional element has excellent affinity with the corresponding substrate. This is contributed to Cu and Ni lying located just behind Zn and Cu respectively in the periodic table. The difference is that the IMC $(Cu,Ni)_6Sn_5$ formed at the BiSn41.6Cu1/Ni(P) system is more stable, and hence more effective in reducing IMC growth rate, than the IMC γ-CuZn formed at the BiSn41.6Zn1/Cu system. This is in good agreement with the fact that the melting point 1083 °C of Cu is higher than that of Zn (419 °C). In the case of the previously investigated Nb-In/Sn system [1], the extremely slow rate of IMC growth was attributed mainly to the high activation energy associated with the formation of the $NbSn_2$ IMC. This in turn is due to the refractory nature of Nb, with a melting point of 2467 °C. Therefore, high melting points and good affinity with the substrate metallizations are two practical criteria for identifying potential additional elements for further experimentation.

On the other hand, thermodynamic modeling by calculating metastable equilibria has been successful in prediction of primary IMC formation during interfacial reaction between Sn-based solders and various substrates [13,15,16]. Thermodynamic investigation was previously employed to implement sensitivity studies of different lead-free solder alloy systems [17]. It is also necessary to ensure that the alloyed solders with the inhibitor additives are in a liquid state at the anticipated operating temperatures. Therefore, the present experimental results, in combination with the thermodynamic investigation that is being undertaken using MTDATA software, will be very useful to rapidly screen possible elements as alloying additions to the various solder-substrate systems.

Conclusions

Both Ni_3Sn_4 and Ni_3P formed at the interface between the eutectic Sn-Bi solder and the electroless Ni(P) substrate. 1wt% Cu addition into the basic eutectic Sn-Bi solder modified the IMC growth from Ni_3Sn_4 to$(Cu,Ni)_6Sn_5$, resulting in significantly decreased growth rates for both Ni_3Sn_4 and Ni_3P formation at the interfaces at high temperatures.

The IMCs formed at the interface between the eutectic Sn-Bi solder and the Cu substrates included Cu_3Sn and Cu_6Sn_5. 1wt% Zn addition into the basic Sn-Bi solder led to the

447   2005 Electronic Components and Technology Conference

formation of the IMC γ-CuZn, instead of Cu_3Sn and Cu_6Sn_5. This layer of γ-CuZn was effective in reducing the consumption rate of the Cu in contact with the molten solder 200 °C, but was unstable at 240 °C.

The Ti-W layer appeared to be intact in contact with the molten solders at both experimental temperatures, but the mechanical adhesion between the solder (solid phase) and the substrate requires further investigation.

High melting points and good affinity with the substrates should be considered as criteria for identifying potential inhibitor additives for further experimentation.

References

1. Mannan, S. H., Clode, M. P., "Materials and Processes for Implementing High Temperature Liquid Interconnects," *IEEE Trans. on Adv. Packaging*, Vol. 27, No. 3 (2004), pp.508- 514.

2. M. Nowottnick, U. Pape, K. Wittke, W. Steel, "Solder Joints for High Temperature Electronics", *2003 SMTA International Conference Proceedings,* Chicago, IL, USA, September 21-25, 2003, pp. 693-699.

3. Miao, H. W., Duh, J. G., "Microstructure Evolution in Sn-Bi and Sn-Bi-Cu Solder Joints Under Thermal Aging," *Materials Chemistry and Physics*, Vol. 71 (2001), pp. 255-271.

4. Zeng, K., Tu, K. N., "Six Cases of Reliability Study of Pb-Free Solder Joints in Electronic Packaging Technology," *Materials Science and Engineering R*, Vol. 38 (2002), pp. 55-105.

5. He, M. et al, "Solid State Interfacial Reaction of Sn-37Pb and Sn-3.5Ag Solders with Ni-P Under Bump Metallization," *Acta Materialia*, Vol. 52 (2004), pp. 2047-2056.

6. Young, B. L., Duh, J. G., "Interfacial Reaction and Microstructural Evolution for Electroplated Ni and Electroless Ni in the Under Bump Metallurgy with 42Sn58Bi Solder During Annealing," *Journal of Electronic Materials,* Vol. 30, No. 7 (2001), pp. 878-884.

7. Prakash, K. H., Sritharan, T., "Interface Reaction Between Copper and Molten Tin-Lead Solders," *Acta Materialia*, Vol. 49 (2001), pp. 2481-2489.

8. Takaku, Y. et al, "Interfacial Reaction and Morphology Between Molten Sn Base Solder and Cu Substrate," *Materials transactions*, Vol. 45, No. 3 (2004), pp. 646-651.

9. He, M., et al, "Intermetallic Compound Formation Between Sn-3.5Ag Solder and Ni-based Metallization During Liquid State Reaction," Thin Solid Films, Vol. 462-463 (2004), pp. 376-383.

10. Jang, J. W. et al, "Solder Reaction-Assisted Crystallization of Electroless Ni-P Under Bump Metallization in Low Cost Flip Chip Technology," Journal of Applied Physics, Vol. 85, No. 12 (1999), pp. 8456-8463.

11. Kim, H. K., Tu, K. N., "Kinetic Analysis of the Soldering Reaction Between Eutectic SnPb Alloy and Cu Accompanied by Ripening," *Physical Review B*, Vol. 53 (1996), pp. 16027-16034.

12. Liu, C. Y., Wang, S. J., "Prevention of Spalling by the Self-Formed Reaction Barrier Layer on Controlled Collapse Chip Connections Under Bump Metallization," *Journal of Electronic Materials,* Vol. 32, No. 1 (2003), pp. L1-L3.

13. Laurila, T. et al, "Analyses of Interfacial Reactions at different Levels of Interconnection," *Materials Science in Semiconductor Processing*, Vol. 7 (2004), pp. 307-317.

14. Chuang, C. M., Lin, K. L., "Effect of Microelements Addition on the Interfacial Reaction Between Sn-Ag-Cu Solders and the Cu Substrate," *Journal of Electronic Materials,* Vol. 32, No. 12 (2003), pp. 1426-1431.

15. Lee, B. J. et al, " Prediction of Interface Reaction Products Between Cu and Various Solder Alloys by Thermodynamic Calculation," *Acta Materialia*, Vol. 45 (1997), pp. 1867-1874.

16. Lee, H. M., Choi, W. K., "Prediction of Primary Intermetallic Compound Formation During Interfacial Reaction Between Sn-based Solder and Ni Substrate," *Scripta Materialia*, Vol. 46 (2002), pp. 777-781.

17. Huang, Z. et al, "Inter-Dependence of Processing and Alloy Composition on the Reliability of Sn-Based Lead Free Solders in Fine Pitch FCOB Interconnection," *SEMI Technology Symposium: 28th International Electronics Manufacturing Technology*, San Jose, CA, USA, July 16-18, 2003.