Temperature dependency of the growth rate of (Cu,Ni)$_6$Sn$_5$ on Cu-xNi substrates

Xin Fu Tan$^{1,*}$, Nurul Razliana Abdul Razak$^1$, Muhammad Hafiz Husain$^1$, Stuart McDonald$^1$, and Kazuhiro Nogita$^1$

$^1$Nihon Superior Centre for the Manufacture of Electronic Materials (NS CMEM), School of Mechanical and Mining Engineering, The University of Queensland, Brisbane, Qld 4072, Australia

Abstract. Cu$_6$Sn$_5$ is the most common intermetallic compound (IMC) in lead-free solder joints, and is also a promising anode material for advanced lithium-ion batteries. It has been reported that the growth rates of (Cu,Ni)$_6$Sn$_5$ in Sn-based solder alloy/Cu-xNi substrate couples are greatly accelerated compared to the intermetallic layers that form on a pure Cu substrate. Due to the faster growth rates, solidification can progress through a transient-liquid-phase reaction in commercially relevant timeframes. The complete reaction of the liquid Sn in the couple will result in a joint that is stable at high temperatures. Furthermore, the presence of Ni in the intermetallic suppresses the formation of a Cu$_3$Sn layer and stabilises the (Cu,Ni)$_6$Sn$_5$ preventing a polymorphic transformation on cooling along with the associated induced strains. This study investigates the growth rates of (Cu,Ni)$_6$Sn$_5$ in Sn/Cu-xNi couples, where 0 $\leq$ x $\leq$ 14 wt%, and reports on the effect of temperature on the growth rates at temperatures above the melting point of Sn (231.9˚C) between 232˚C and 300˚C. The results show the highest growth rates occur in the Sn/Cu-6Ni couples, and there is an increase of the (Cu,Ni)$_6$Sn$_5$ growth rate with increasing temperature due to faster diffusion and reaction rates.

1 Introduction

Cu$_6$Sn$_5$ is a near ubiquitous intermetallic compound (IMC) in Sn-based lead-free solder joints made with copper substrates and plays an important role in the mechanical integrity of the joint [1]. Cu$_6$Sn$_5$ also has potential functional applications as an anode material in lithium-ion batteries due to its higher energy capacity relative to conventional carbon-based anodes [2, 3].

With the miniaturisation and the rapid increase in the density of electronic packaging, local service temperatures in the integrated circuits increase accordingly, creating a demand for high temperature bonding materials. Transient-liquid-phase (TLP) bonding is an attractive method for high temperatures applications as the fabrication can be carried out at relatively low temperatures, while the bonded joints can operate at much higher temperatures. Cu$_6$Sn$_5$ IMCs forms naturally at the interface of Cu substrates and Sn-based solder joints during typical reflow temperatures below 250˚C. The liquidus temperature of Cu$_6$Sn$_5$ is

* Corresponding author: xin.tan@uq.edu.au
408˚C, and it has better electromigration resistance [4] and a higher strength compared to bulk solder alloys and is therefore an ideal candidate material for the end product of a TLP bond.

However, the growth rate of Cu₆Sn₅ in a Cu/Sn-based solder alloy couple is often sluggish, and different methods have been therefore been explored to shorten the bonding time. These include enhancing the Cu/Sn interfacial reaction by applying an electric current [4], ultrasonic-assisted bonding [5] and the addition of Ni in the Cu substrates [6-8].

In this study, Cu-xNi substrates with varying concentrations of Ni, where x = 0, 2, 6, 10, and 14 wt%, were examined with respect to the growth rate of (Cu,Ni)₆Sn₅ that forms on this substrate during isothermal contact with liquid Sn. Furthermore, the effect of temperature on the growth rates was investigated at commercially relevant temperatures of 232˚C, 250˚C, 270˚C and 300˚C. It was hypothesised that the combined effect of optimising the temperature and Ni concentration in the substrate would greatly increase the rate of formation of (Cu,Ni)₆Sn₅.

2 Methods

Soldering flux was applied to the surface of Cu-xNi sheets, where x = 0, 2, 6, 10, and 14 wt%, to remove surface oxides. Sn (99.9%) sheets rolled to approximately 100 μm in thickness were placed on the Cu-xNi sheets. The Cu-xNi/Sn couples were sandwiched between two glass slides and clamped together with a metal clip. The samples were placed in an annealing furnace preheated to a temperature of either 250˚C, 270˚C or 300˚C for 3, 5, 7 and 10 minutes. For comparison, a set of control samples were held at 232˚C for 5 and 10 minutes. The Sn sheets liquefied and reacted with the Cu-xNi sheets to form (Cu,Ni)₆Sn₅ at the Cu-xNi/Sn interface. The samples were then removed from the furnace and cooled in air, and subsequently rinsed in ethanol.

To observe the cross-sections, the samples were cold mounted in epoxy resin. Standard metallography procedures were used to polish the surface of the samples for scanning electron microscopy (SEM) observations. SEM was conducted under backscatter electron (BSE) mode at an accelerating voltage of 15 kV.

3 Results and discussions

3.1 Growth rates at 232˚C

At a reaction time of 5 minutes at 232˚C, just above the melting point of Sn of 231.9˚C, very little bonding occurs between the Cu-xNi/Sn couples, and most of the couples detached as they were removed from the glass slides.

Fig. 1 shows the cross-section SEM images of the Cu-xNi/Sn couples placed at 232˚C for 10 minutes. Under BSE imaging mode, the top layers with the brightest shade of grey are the Sn sheets (highest Z-contrast), the bottom layers with the darkest shade are the Cu-xNi substrates, and a layer of (Cu,Ni)₆Sn₅ can be seen at the Cu-xNi/Sn interface. The thickness of the (Cu,Ni)₆Sn₅ layer varies dramatically with the Ni content in the substrate. In a pure Cu/Sn couple, approximately 4 μm of Cu₆Sn₅ with a scallop-like morphology is grown. As the concentration of Ni in the substrate is increased to 2 wt% Ni, the morphology of the (Cu,Ni)₆Sn₅ changes to a rod-like structure, although the growth rate remains relatively constant at around 4 μm in 10 minutes. As the amount of Ni in the substrate is increased to 6 wt%, the growth rate of (Cu,Ni)₆Sn₅ increases dramatically. Very little Sn remained in the Cu-6Ni/Sn couple and 48 μm of (Cu,Ni)₆Sn₅ was formed. However, further increasing the content of Ni results in a decrease of the growth kinetics and the same conditions see
(Cu,Ni)$_6$Sn$_5$ layers of about 28 μm and 10 μm form in the Cu-10Ni/Sn and the Cu-14Ni/Sn couple respectively.

The results show that the presence of 6-14 wt% Ni in the Cu substrate can significantly increase the growth rates of the interfacial (Cu,Ni)$_6$Sn$_5$ relative to Ni-free substrates, with a maximum growth rate observed in the Cu-6Ni/Sn couple. This result matches that found by Choquette [9], who reported a maximum growth rate at 5.5 wt% Ni in a Cu-xNi/Sn-0.7Cu-0.05Ni system, while they deviates slightly from the results of Vuorinen et. al., where the fastest rate was observed on Cu-10Ni substrates [7], both conducted at 240˚C. Furthermore, the minimal amount of bonding in the samples held for 5 minutes, including the Cu-6Ni/Sn couple, suggests that an incubation period between 5-10 minutes is required before the (Cu,Ni)$_6$Sn$_5$ formation reaction proceeds at this temperature.

Fig. 1. Cross-section SEM images of (Cu, Ni)$_6$Sns grown between Sn and Cu-xNi, where x = 0, 2, 6, 10 and 14, at 232˚C for 10 minutes. Images are shown at the same scale.

3.2 Growth rates at 250˚C, 270˚C and 300˚C

SEM images of cross-section of the couples showing the (Cu,Ni)$_6$Sn$_5$ grown at 250˚C, 270˚C and 300˚C are seen in Fig. 2. The average thicknesses of the (Cu,Ni)$_6$Sn$_5$ layers for the different samples and conditions are plotted in Fig. 3. In comparison to Fig. 1, the thickness of the interfacial (Cu,Ni)$_6$Sn$_5$ after 10 minutes of growth has increased with the increasing temperature. Increasing temperature has also reduced the incubation time for bonding, as shown by the formation of a layer of (Cu,Ni)$_6$Sn$_5$ in all the samples held at 250˚C, 270˚C and 300˚C.

Minimal bonding was observed in the Cu/Sn couple held for 3 minutes at 250˚C and part of the sample detached when the metal clip used to clamp the sample was removed, entrapping contaminants at the Cu/Sn interface as can be seen in Fig. 2 (a). At this initial bonding stage, instead of having a maximum growth rate in the 6 wt% Ni sample, the 3 minutes samples bonded at 250˚C show an increasing thickness of (Cu,Ni)$_6$Sn$_5$ with increasing amounts of Ni in the substrates, indicating that the addition of Ni in the substrates may reduce incubation time. At 5 minutes, the interface layer of (Cu,Ni)$_6$Sn$_5$ in the Cu-6Ni, Cu-10Ni and Cu-14Ni samples were significantly thicker than those in the Cu and Cu-2Ni samples. At 7 and 10 minutes, accelerated growth of (Cu,Ni)$_6$Sn$_5$ is also observed in the Cu-2Ni sample, while the Cu-6Ni sample again shows the maximum growth rate. In the Cu-6Ni and Cu-10Ni samples, (Cu,Ni)$_6$Sn$_5$ grains have grown to the top of the Sn layer within 7 minutes, and in the Cu-6Ni sample, the Sn was fully consumed within 10 minutes, forming a layer of (Cu,Ni)$_6$Sn$_5$ of about 34 μm.

For the samples reacted at 270˚C (Fig. 2 (b)) and 300˚C (Fig. 2 (c)), significantly shorter incubation times were observed with increasing temperature. Accelerated growth of (Cu,Ni)$_6$Sn$_5$ was observed in the Cu-6Ni sample within 3 minutes at 270˚C, while at 300˚C the Cu-10Ni and Cu-14Ni also showed accelerated growth. The Cu-6Ni sample formed a homogeneous layer of (Cu,Ni)$_6$Sn$_5$ of about 32 μm after 7 minutes at 300˚C. The grains had grown to the top of the Sn layer within 3 minutes, and Sn was fully consumed within 7 minutes.

As the thickness of the Sn layers in this study limits the growth of the (Cu,Ni)$_6$Sn$_5$ layers, it is difficult to quantify the growth rates. However, it is expected that the relationship
between the thickness of the (Cu,Ni)$_6$Sn$_5$ layer and the bonding temperature and time will follow an Arrhenius-type equation:

$$h = At^n \exp \left( \frac{-Q}{RT} \right)$$

(1)

where $h$ is the thickness at time, $t$; $A$ is a numerical constant derived empirically; $n$ is the time constant; $Q$ is the activation energy; $R$ is the universal gas constant; and $T$ is the temperature [10]. The equation can be rewritten in the form:

$$\ln h = \ln A + n \ln t - \frac{Q}{RT}$$

(2)

or

$$\ln h = \frac{-Q}{R} \left( \frac{1}{T} \right) + \ln A + n \ln t$$

(3)

which has the form of the linear equation $y = kx + c$. As a result, the equation predicts that $\ln h$ changes linearly with $-\left(1/T\right)$, while $h$ also changes parabolically with $tn$. It is often
Fig. 2. Cross-section SEM images of (Cu,Ni)₆Sn₅ grown between Sn and Cu-xNi, where x = 0, 2, 6, 10 and 14, at (a) 250°C, (b) 270°C, and (c) 300°C for 3, 5, 7 and 10 minutes. Images are shown at the same scale.

Fig. 3. The average thickness of (Cu,Ni)₆Sn₅ grown between Sn and Cu-xNi, where x = 0, 2, 6, 10 and 14, at different temperatures for (a) 3, (b) 5, (c) 7 and (d) 10 minutes. Samples where further (Cu,Ni)₆Sn₅ growth is limited due to the consumption of all available Sn in the solder by are marked “*”.

described that time constant of $n = 0.33$ is related to grain boundary diffusion controlled reactions, $n = 0.5$ is related to volume diffusion controlled reactions, while at $n = 1$ the reaction is not limited by diffusion [11]. It is expected that the constants $A$ and $n$ are different for the substrates with different amounts of Ni, and this will affect the growth rate of the (Cu,Ni)₆Sn₅ layer.

Another factor which may affect the incubation time and growth rate is the effect of temperature on the shifts in the equilibrium phase boundaries in the Sn-Cu-Ni ternary phase.
diagram as presented by Gourlay et al [12] (Fig. 4). As Cu and Ni dissolve in liquid Sn, the liquid composition of the remaining solder coupled with each Cu-xNi substrate follows the a line of constant Cu:Ni ratio as shown in Fig. 4. The plot suggests that for Cu and Cu-2Ni substrates, lower concentrations of Cu and Ni are required for the formation of (Cu,Ni)₆Sn₅ at 250°C compared to that at 268°C, which is likely to reduce incubation time and increase the growth rate at the lower temperature. This factor competes with the effect of temperature, and results in the abnormality observed in the Cu-2Ni samples, where a thicker layer of (Cu,Ni)₆Sn₅ is observed in the 250°C sample compared to those at 270°C and 300°C in Fig. 3 (d). At x = 6, the constant Cu:Ni ratio line crosses the liquid/liquid + (Cu,Ni)₆Sn₅ equilibrium phase boundaries for 250°C and 268°C at similar Cu and Ni compositions, while at x = 10 and 14, the plot predicts lower concentration of Cu and Ni are required to form (Cu,Ni)₆Sn₅ at the higher temperature, enhancing the growth rates of the IMCs.

Fig. 4. Very Sn-rich corner of Sn-Cu-Ni ternary phase diagram showing isothermal sections at 250°C and 268°C reconstructed from [12]. Dashed lines are constant Cu:Ni ratio lines for Cu-2Ni, Cu-6Ni, Cu-10Ni and Cu-14Ni.

3.3 Suppression of Cu₃Sn

Fig. 5 shows the Cu/Sn, Cu-2Ni/Sn and Cu-6Ni/Sn interfaces after 10 minutes at 300°C at higher magnifications. A thin layer of intermetallic compound (IMC) is observed between (Cu,Ni)₆Sn₅ and the substrates in the Cu/Sn and Cu-2Ni/Sn couples. The formation of a Cu₃Sn layer between Cu₆Sn₅ and Cu substrates is commonly reported for Cu/Sn-based solder alloys. As shown in Fig. 5, the formation of the (Cu,Ni)₃Sn layer is noticeably reduced with an increasing amount of Ni in the substrate, where the thickness of Cu₃Sn is lower in the Cu-2Ni/Sn couple compared to the Cu/Sn couple, and the (Cu,Ni)₃Sn layer is not visible in the Cu-6Ni/Sn couple and the couples with higher Ni content substrates. The effect of Ni in the suppression of Cu₃Sn formation is similar to what is reported in reactions between pure Cu substrates and Ni containing Sn-based solder alloys [13, 14], indicating that a similar effect is achieved regardless of the source of Ni.

Fig. 5. Cross-section SEM images of (Cu,Ni)₆Sn₅ and (Cu,Ni)₃Sn grown between Sn and Cu-xNi, where x = 0, 2, and 6 at 300°C for 10 minutes. Images are shown at the same scale.
4 Conclusions

This study shows the growth rate of (Cu,Ni)_6Sn_5 can be greatly accelerated by optimising the Ni content in the Cu-xNi substrate and increasing the bonding temperature. At temperatures above 250˚C, a homogeneous, Sn and Cu_3Sn-free layer of (Cu,Ni)_6Sn_5 can be obtained within 10 minutes. This enables TLP bonding and anode fabrication at commercially relevant times and temperatures. The results also show there are shorter incubation times for the initial formation of (Cu,Ni)_6Sn_5 with increasing Ni content in the substrates.

Quantitative analysis of the growth rates of (Cu,Ni)_6Sn_5 is not possible in this experiment as the thickness of the (Cu,Ni)_6Sn_5 layer in many samples were limited by the amount of Sn available. However this study does demonstrate the formation of a Sn-free (Cu,Ni)_6Sn_5 layer is possible if composition and processing variables are optimised. The relationship between these variables and growth rates will be quantified in future work.

This work was supported by the UQ-Nihon Superior cooperative research grant at the University of Queensland (UQ) [grant number 2016001895], Australia; an Australian Government Research Training Program (RTP) grant from the University of Queensland, Australia.

References

1. D.K. Mu, S.D. Mcdonald, J. Read, H. Huang, K. Nogita, Curr Opin Solid St M., 20(2), 55 (2016).
2. X.F. Tan, S.D. Mcdonald, Q. Gu, Y. Hu, L. Wang, S. Matsumura, T. Nishimura, K. Nogita, J. Power Sources, 415, 50 (2018).
3. K.D. Kepler, Electrochem. Solid-State Lett., 2(7), 307 (1999).
4. J. Feng, C. Hang, Y. Tian, B. Liu, C. Wang, Sci Rep, 8(1), 1775 (2018).
5. Z. Li, M. Li, Y. Xiao, C. Wang, Ultrason Sonochem, 21(3), 924 (2014).
6. S.M. Choquette, I.E. Anderson, Int J Powder Metall., 51(4), 9 (2015).
7. V. Vuorinen, H. Yu, T. Laurila, J.K. Kivilahti, J. Electron. Mater., 37(6), 792 (2008).
8. V.A. Baheti, S. Islam, P. Kumar, R. Ravi, R. Narayanan, D. Hongqun, V. Vuorinen, T. Laurila, A. Paul, Philos Mag., 96(1), 15 (2015).
9. S.M. Choquette, Materials Science And Engineering. 2018, Iowa State University.
10. P.T. Vianco, K.L. Erickson, P.L. Hopkins, J. Electron. Mater., 23(8), 721 (1994).
11. N. Zhao, Y. Zhong, M.L. Huang, H.T. Ma, W. Dong, Sci Rep, 5, 13491 (2015).
12. C.M. Gourlay, K. Nogita, J. Read, A.K. Dahle, J. Electron. Mater., 39(1), 56 (2009).
13. F. Gao, T. Takemoto, H. Nishikawa, Mat Sci Eng A, 420(1-2), 39 (2006).
14. S.U. Mehreen, K. Nogita, S. Mcdonald, H. Yasuda, D. Stjohn, J. Alloys Compd, 766, 1003 (2018).