Selective Interfacial Reaction between Ni and Eutectic BiSn Lead-Free Solder

W. H. Tao

Department of Chemical Engineering, Chinese Culture University, Taipei, Taiwan

C. Chen, C. E. Ho, W. T. Chen, and C. R. Kao*

Department of Chemical Engineering, National Central University, Chungli City, Taiwan

Received October 5, 2000

The chemical compatibility of the Ni surface with the eutectic BiSn lead-free solder was studied. According to the literature, the compound $NiBi_3$ is both soft and brittle and has a very high growth rate when Ni is reacted with Bi. Therefore, it is highly undesirable for $NiBi_3$ to form in a solder joint. The objective of this article is to study the reactions between Ni and 58Bi−42Sn in detail and to clarify whether the formation of $NiBi_3$ will be an issue. In this study, Ni was reacted with the eutectic BiSn solder at 180, 240, 300, 360, and 420 °C for times ranging from 0.5 to 48 h. At all temperatures only Ni_3Sn_4 was detected as the reaction product. None of the other Ni−Sn intermetallic compounds and none of the Ni−Bi intermetallic compounds were observed. The formation of only Ni_3Sn_4 is considered the best possible outcome from the standpoint of electronic packaging applications. At lower temperatures (180, 240, and 300 °C), Ni_3Sn_4 formed at the interface as a thin continuous layer, which was protective and resulted in the parabolic growth kinetics. However, reaction at a higher temperature (420 °C) produced at the interface a thick reaction zone, which was a two-phase mixture of Ni_3Sn_4 + solder. This morphology, which was nonprotective, led to the linear growth kinetics. The growth rates at temperatures below 300 °C were quite slow and were considered beneficial for packaging applications. The Ni_3Sn_4 formed near the interface had rounded edges. At locations away from the interface and inside the solder joint also existed a small amount of Ni_3Sn_4, but this Ni_3Sn_4 exhibited a faceted, needle-shaped morphology. It is believed that the Ni_3Sn_4 with rounded edges formed during reaction, while the needle-shaped Ni_3Sn_4 formed during the solidification of the solder.

Introduction

Currently, solders for microelectronic packaging applications are predominantly lead-bearing. In fact, Pb is a major constituent in almost all of the commercially important electronic solders, such as the 95Pb−5Sn (wt %) solder, frequently used for chip-to-package interconnections, and the 37Pb−63Sn solder, frequently used for package-to-board interconnections. Although Pb in electronic devices does not cause a direct hazard to human safety, it may pose an indirect threat when electronic devices become waste at the end of their life cycles. There is a concern that some of the Pb that ends up in landfills may migrate to the food chains accessed by both wildlife and humans. It is expected that the use of Pb-bearing solders will be restricted or banned soon. This concern has propelled extensive research for Pb-free replacements by both academe and industry in recent years.[1] The alloy 58Bi−42Sn is considered to be a very promising substitute for 37Pb−63Sn in the consumer electronics and telecommunications industry.[1] Many mechanical properties of this alloy have been reported to be comparable or better than those of the 37Pb−63Sn solder, but more studies are still needed to fully evaluate its other properties, especially its chemical properties. One such chemical property that needs more research is the reaction between the thin metallization layer(s) and the solder inside electronic packages.

Electrolytic and electroless Ni layer are very common metallizations for electronic packages, and the application of Ni as a metallization layer will increase as more advanced packaging technologies, such as the Ball-Grid-Array and Flip-Chip packaging, are used.[2−4] To prevent the oxidation of Ni, a thin (0.02−0.2 μm) layer of Au or Pd is deposited over the Ni layer. During soldering, this thin protective layer quickly reacts with the solder and disappears, exposing the Ni layer to the solder. The Ni layer will then start to react with the solder to form intermetallic compound(s) at the interface. The formation of intermetallic compound(s) is an indication of good wetting and bonding, but the presence of *thick* inter-

---

* To whom correspondence should be addressed. E-mail: kaocr@hotmail.com. Phone/Fax: +886-3-4227382.

(1) *Lead-Free Solder Project Final Report*; National Center for Manufacturing Sciences: Ann Arbor, MI, 1997.

(2) Romenesko, B. M. *Int. J. Microcircuits Electron. Packag.* **1996**, *19*, 64.

(3) Mei, Z.; Gallery, P.; Fisher, D.; Hua, F.; Glazer, *J. Adv. Electron. Packag.* **1997**, *2*, 1543.

(4) Bradley, E.; Banerji, K. *IEEE Trans. Compon. Packag. Manufact. Technol. B* **1996**, *19*, 320.

10.1021/cm000803l CCC: $20.00

metallic layer(s) has negative impacts on the strength of a solder joint.[5–7] Therefore, a detailed understanding on the interfacial reaction between Ni and the solder is important to obtain the optimal soldering conditions so that a low defect rate for the solder joints can be achieved.

Compared to the reaction between Ni and 37Pb–63Sn, where Pb is chemically inert with Ni, the reaction between Ni and 58Bi–42Sn has the potential to be more complicated because both Bi and Sn are reactive with Ni. According to the Ni–Pb phase diagram,[8] Pb forms a simple monotectic invariant with Ni and therefore is chemically inert to Ni. In other words, when Pb is in contact with Ni, the only interaction is the dissolution of Ni into Pb. Therefore, Pb does not actively participate in the chemical reaction between Ni and 37Pb–63Sn. The only reaction will be between Ni and Sn. (There are three intermetallic compounds between Ni and Sn, Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4.[8]) The situation for Bi, however, is quite different. According to the Ni–Bi phase diagram,[8] there are two intermetallic compounds in this system, NiBi and $NiBi_3$. Therefore, when 58Bi–42Sn reacts with Ni, the two Ni–Bi intermetallics and the three Ni–Sn intermetallics will compete with each other to form. In such type of reactions, not all the possible intermetallic compounds will form. Very often, only a few of the possible intermetallics become the reaction products. Experimental studies are needed to reveal what exactly will occur in such type of reactions.

According to the literature,[9–12] reaction between Ni and solid Bi produced a thick layer of $NiBi_3$ at the original Ni–Bi interface. The growth of $NiBi_3$ was extremely rapid for solid-state reactions, reaching 230 μm in 70 h at 250 °C.[9,10] The growth of $NiBi_3$ followed parabolic kinetics, suggesting diffusion-controlled kinetics.[9,10] The other stable compound NiBi was not detected. The possible rapid growth of $NiBi_3$ in a solder joint would be very troublesome. There is evidence showing that $NiBi_3$ has very inferior mechanical properties. This compound is both *soft* and brittle.[12] In view of the fact that $NiBi_3$ has a high growth rate and inferior mechanical properties, it is highly undesirable for $NiBi_3$ to form in a solder joint. The objective of this article is to study the reactions between Ni and 58Bi–42Sn in detail and to clarify whether the formation of $NiBi_3$ will be an issue.

Experimental Section

The 58Bi–42Sn solder used in this study was prepared from 99.999%-pure Bi and 99.99%-pure Sn. Each solder bath was formed by placing 6.50 g of solder into a 10-mm i.d. vial. Nickel disks, 6.35 mm in diameter, 0.50 mm in thickness, and 99.995% pure, were utilized to react with the solder. The mass of each disk was 0.142 g. Before the reaction, each Ni disk was metallurgically polished on both surfaces. One micrometer diamond abrasive was used as the last polishing step. The exact thickness of each disk was then recorded. These Ni disks were then cleaned with acetone, etched in a 50 vol % HCl–H_2O solution for 10 s, and fluxed with a mildly activated rosin flux (RMA#5, Indium Corporation of America). Each fluxed disk was then vertically inserted into a fresh molten solder bath held at a fixed temperature. Reaction temperatures included 180 ± 1, 240 ± 1, 300 ± 1, 360 ± 1, and 420 ± 1 °C. Reaction times ranged from 0.5 to 48 h. When each of the scheduled reaction times was reached, the solder bath together with the Ni disk were cooled to room temperature using an air-blower. The liquid solder solidified with little disturbance and cooled to touch in about 90 s. The samples were then removed from the vials, mounted in epoxy, sectioned by using a low-speed diamond saw, and metallographically polished in preparation for characterization.

The reaction zone for each sample was examined by using an optical microscope and a scanning electron microscope (SEM). The thickness of the reaction product for each sample was measured by using image analysis software. The thickness of the reaction product is defined as the total area occupied by that phase divided by the linear length of the interface. The composition of the reaction product was determined using a JEOL JXA-8800M electron microprobe, operated at 15 keV. During microprobe measurement, the measured X-ray peaks were Kα, Mα, and Lα for Ni, Bi, and Sn, respectively, and the standards used were pure Ni, Bi, and Sn for Ni, Bi, and Sn signals, respectively. In microprobe analysis, the concentrations of Ni, Bi, and Sn were measured independently, and the total weight percentage was within 100 ± 1% in each case. For every data point, at least four measurements were made and the average value was reported. It was estimated that the accuracy of the alloy compositions determined in this study was within 1 wt %.

Results

Reaction Product and Its Microstructures. Throughout this study, only the intermetallic compound Ni_3Sn_4 was detected as the reaction product at all temperatures. None of the other Ni–Sn compounds and none of the Ni–Bi compounds were observed. However, reaction at different temperatures produced Ni_3Sn_4 with distinctive microstructures. The first type of microstructure, which occurred in reaction at lower temperatures (180, 240, and 300 °C), had a thin continuous layer of Ni_3Sn_4 at the interface. The micrographs shown in Figure 1 are representative for this type of microstructure. The upper regions in these micrographs were the 58Bi–42Sn solder, which had the typical eutectic structure. The lower regions were the Ni disks. The reaction product Ni_3Sn_4 situated between the upper and lower regions. The second type of microstructure (Figure 2), which occurred in reaction at a higher temperature (420 °C), had a thick, nonplanar reaction zone, which was a Ni_3Sn_4 + solder two-phase mixture layer. In the reaction zone, the solder composition deviated from the original 58Bi–42Sn composition to more Bi-rich compositions, as revealed by the EPMA measurement. This is because the formation of Ni_3Sn_4 would consume Sn atoms. Between the first and second type of microstructures, there was a transition microstructure shown in Figure 3. This transition-type microstructure occurred at an intermediate temperature of 360 °C. In this transition-type microstructure, there were a continuous Ni_3Sn_4 layer at the interface and many isolated Ni_3Sn_4 particles near the interface inside the solder.

---

(5) Bradley, E.; Banerji, K. *ECTC Conf. Proc.* **1996**, 1028.

(6) Puttlitz, J. *IEEE Trans. Compon. Hybrids Manuf. Technol.* **1990**, *13*, 647.

(7) Hribar, V. F.; Bauer, J. L.; O'Donnell, T. P. *Third Int. SAMPE Electron. Conf. Proc.* **1989**, 1187.

(8) Baker, H. *ASM Handbook Volume 3: Alloy Phase Diagram*; ASM Intl.: Materials Park, OH, 1992.

(9) Duchenko, O. V.; Dybkov, V. I. *J. Mater. Sci. Lett.* **1995**, *14*, 1725.

(10) Dybkov, V. I.; Duchenko, O. V. *J. Alloys Compd.* **1996**, *234*, 295.

(11) Lee, M. S.; Liu, C. M.; Kao, C. R. *J. Electron. Mater.* **1999**, *28*, 57.

(12) Lee, M. S.; Chen, C.; Kao, C. R. *Chem. Mater.* **1999**, *11*, 292.

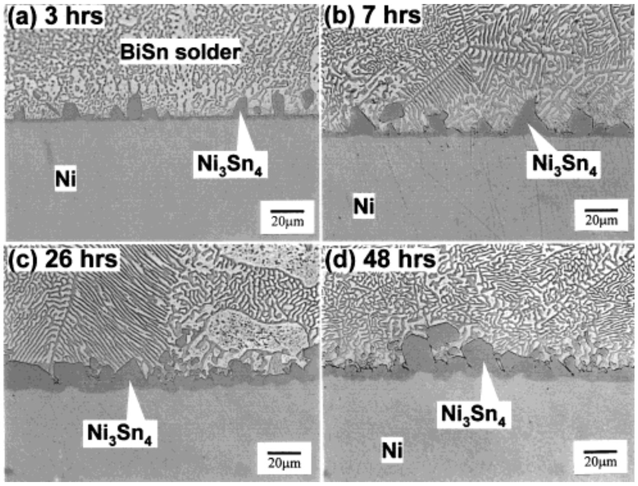

Figure 1. Micrographs for samples reacted at 240 °C for 3, 7, 26, and 48 h, respectively. The microstructure shown is representative for samples reacted at 180, 240, and 300 °C. In the solder, the bright phase is the Sn-rich phase and the dark phase is the Bi-rich phase.

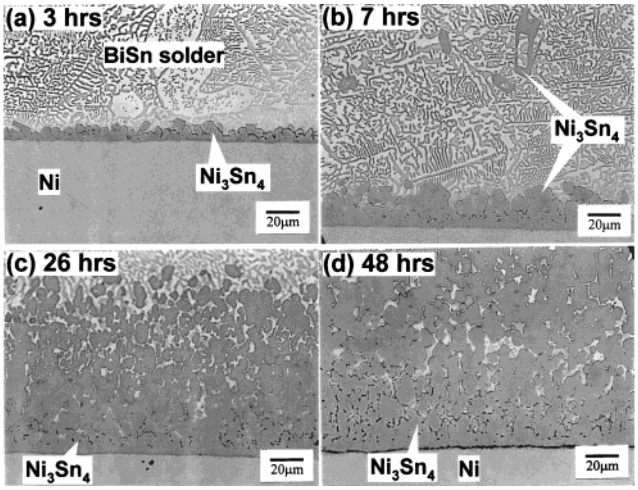

Figure 2. Micrographs for samples reacted at 420 °C for 3, 7, 26, and 48 h, respectively. The reaction zone exhibited a nonplanar structure and was a two-phase mixture of Ni_3Sn_4 + solder.

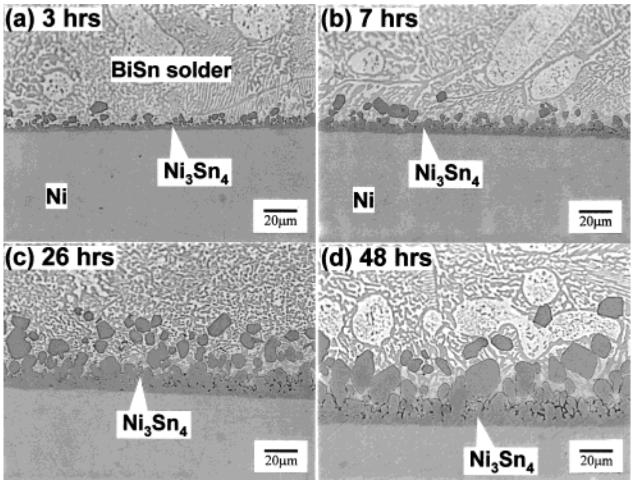

Figure 3. Micrographs for samples reacted at 360 °C for 3, 7, 26, and 48 h, respectively. This microstructure is a transition microstructure between the first type of microstructure shown in Figure 1 and the second type of microstructure shown in Figure 2.

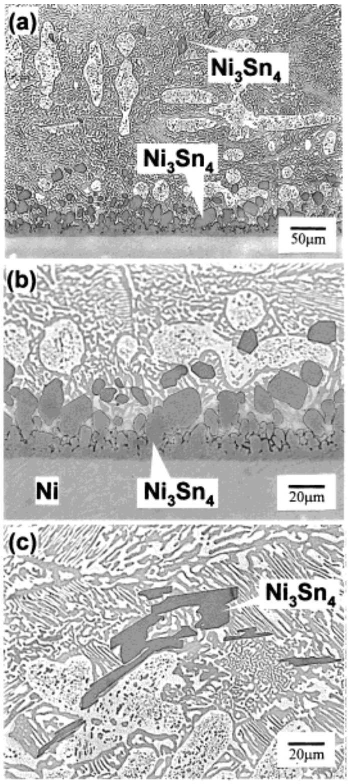

Figure 4. Micrographs for a sample reacted at 360 °C for 48 h. (a) This micrograph shows that Ni_3Sn_4 not only formed at locations near the interface but also formed in locations far away from the interface. (b) A zoom-in micrograph for Ni_3Sn_4 formed near the interface. (c) A zoom-in micrograph for Ni_3Sn_4 formed far away from the interface.

The reaction product Ni_3Sn_4 not only formed at locations near the interface as shown in Figures 1−3 but also formed in locations far away from the interface. This is illustrated in Figure 4 a. Those Ni_3Sn_4 particles near the interface had rounded edges, while those Ni_3Sn_4 particles far away from the interface had a faceted surface, as illustrated in Figure 4, b and c. To investigate the morphologies of Ni_3Sn_4 more closely, a 50 vol % HNO_3-H_2O solution was used to partially etch the solder away from a sample reacted at 420 °C for 48 h. The resulting microstructure of Ni_3Sn_4 particles away from the interface is shown in Figure 5, a and b. This etching solution preferentially attacked the Sn-rich phase, leaving more Bi-rich phase exposed. These two micrographs clearly revealed that those Ni_3Sn_4 far away from the interface had the morphology of hollow needles. Those Ni_3Sn_4 near the interface had a round, particle-like morphology, as shown in Figure 6, a−c, whose micrographs were also from a sample reacted at 420 °C for 48 h. In Figure 6 a, the solder had been completely etched away to reveal the top surface of the reaction zone. It is interesting to note that in Figure 6c the Ni_3Sn_4 grain size increased gradually from the Ni/Ni_3Sn_4 interface to the Ni_3Sn_4/solder interface.

The Ni_3Sn_4 surface shown in Figure 6a was then used to obtain the X-ray diffraction pattern for Ni_3Sn_4. The pattern was then compared with the data published in

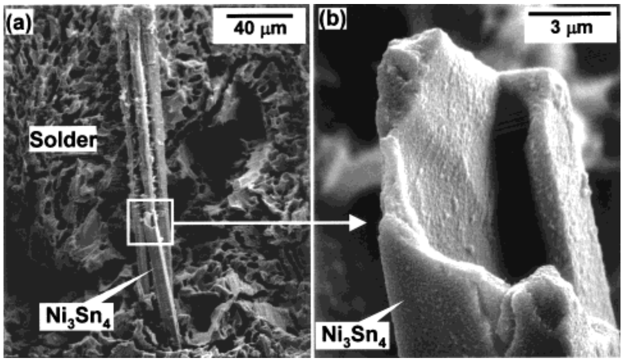

Figure 5. Two micrographs from a sample reacted at 420 °C for 48 h, revealing that Ni_3Sn_4 far away from the interface had the morphology of hollow needles.

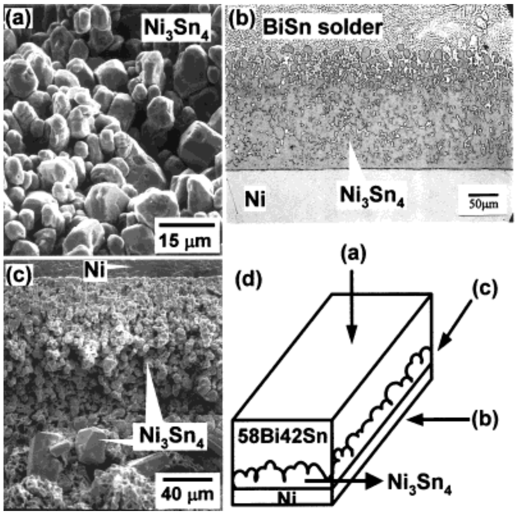

Figure 6. A top-view micrograph (a), a cross-section view micrograph (b), and a 45° view micrograph (c) of a sample reacted at 420 °C for 48 h.

the literature to confirm that it had the *mC*14 crystal structure as reported in the literature.

Growth Kinetics. The growth kinetics for Ni_3Sn_4 also showed distinctive behaviors at different temperatures. The main region of Figure 7 shows the thickness of Ni_3Sn_4 near the interface at different temperatures as a function of the square root of time. The thickness of Ni_3Sn_4 is defined as the total area occupied by Ni_3Sn_4 divided by the linear length of the interface. Included in the calculation for the area were the continuous Ni_3Sn_4 layer and those isolated Ni_3Sn_4 particles near the interface and had rounded edges. These Ni_3Sn_4 particles farther away from the interface and had a faceted surface were not included. The reason for the exclusion is because that the faceted Ni_3Sn_4 did not form during the reaction, but during the solidification of the solder (see Discussion section). It can be seen that the parabolic kinetics represents the data at 180, 240, and 300 °C very well and the data at 360 °C reasonably well. The parabolic kinetics, however, cannot describe the data for 420 °C at all. The 420 °C data were re-plotted as a function of time as the inset in the upper-left corner of Figure 7. From this inset, it can be seen that the reaction at 420 °C followed the linear kinetics nicely.

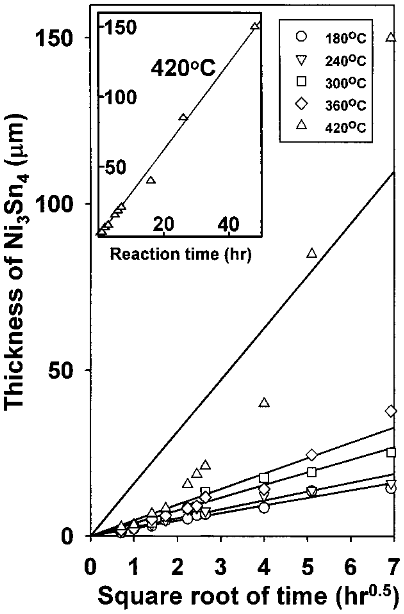

Figure 7. The thickness of Ni_3Sn_4 near the interface plotted as a function of the square root of time. The inset shows the 420 °C data re-plotted as a function of the time.

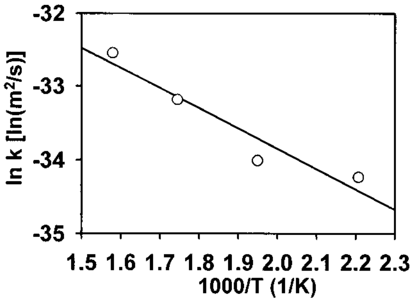

Figure 8. The growth constant *k* versus the inverse of the temperature for data between 180 and 360 °C. The activation energy was determined to be 23 kJ/mol.

The data for 180−360 °C was fitted to the following equation,

$$d = (kt)^{1/2} \tag{1}$$

where d is the thickness of Ni_3Sn_4 near the interface, t is the reaction time, and k is a constant with the dimension of diffusivity (m^2/s). The values of ln k were then plotted against the inverse temperature ($1/T$) in Figure 8 to obtain the activation energy for the growth of Ni_3Sn_4. From the slope in Figure 8, the activation energy for k was determined to be 23 kJ/mol.

Discussion

In this study only Ni_3Sn_4 was detected as the reaction product, and none of the other Ni−Sn and Ni−Bi intermetallic compounds were detected. Let us consider the case of missing Ni_3Sn and Ni_3Sn_2 first. According to the Ni−Sn binary phase diagram, Ni and Ni_3Sn_4 are not in thermodynamic equilibrium; therefore, there is a driving force for the formation of Ni_3Sn and Ni_3Sn_2 at the Ni/Ni_3Sn_4 interface in Figures 1−3. The reasons for one or more thermodynamically stable phases to be missing had been discussed elsewhere.[12,13] There are three possible reasons: (1) The missing phases were actually there, but were two thin to be resolved by the analysis techniques. (2) The missing phases had difficulty nucleating because they had smaller thermodynamic driving forces for nucleation. (3) The missing phases had substantially lower diffusion coefficients compared to its neighboring phases. For the present case, it cannot be concluded as to which reason is more important. Next, let us consider the case of missing NiBi and $NiBi_3$. The reason for Ni to preferentially react with Sn is probably the same with the common phenomenon of preferential oxidation of a binary alloy; that is, Ni has a higher affinity to Sn than to Bi. Under such circumstance, the laws of thermodynamics did not require NiBi or $NiBi_3$ to form. For electronic packaging applications, the fact that $NiBi_3$ is missing is very beneficial to the strength of a solder joint. As pointed out earlier, the growth rate of $NiBi_3$ is very rapid and $NiBi_3$ has very inferior mechanical properties, being both soft and brittle. If $NiBi_3$ had formed in the reaction between Ni and 58Bi−42Sn, the applications of 58Bi−42Sn would have been limited to Ni-free surface finishes.

In industrial soldering practice, the peak soldering temperature is generally 40−50 °C above the molten temperature of the solder, and the time period when the solder is molten is generally not longer than a few minutes. Considering the eutectic temperature of 138 °C for the 58Bi−42Sn solder, the peak soldering temperature for this solder should be around 180 °C and never exceed 200 °C. According to the results of this study, the thickness of Ni_3Sn_4 at the interface will be <0.5 μm, whose thickness is considered excellent for a solder joint. Therefore, this present study showed that 58Bi−42Sn is very compatible with Ni-bearing surface finishes from the viewpoint of intermetallic formation.

One interesting aspect of solid−liquid reactions is that the reaction products may have richer morphologies compared to their counterparts in solid−solid reactions. Shown in Figure 9 is the microstructure for the reaction of *solid* 58Bi−42Sn with Ni at 120 °C for 1000 h.[14] The Ni_3Sn_4 exhibited a simple layered morphology (planar interface). In the present study for reaction between liquid 58Bi−42Sn and a Ni, nonplanar interface developed. This was probably due to the additional physical processes, such as dissolution, convection, and surface tension effects of liquid that are not present or important in solid−solid reactions where only diffusion and reaction dominated.

In this study it was found that, at low temperatures (180, 240, and 300 °C), the growth of Ni_3Sn_4 followed parabolic kinetics, which suggested diffusion-controlled kinetics. At the high temperature (420 °C), the growth obeyed linear kinetics, suggesting reaction-controlled kinetics. At the intermediate temperature (360 °C), the growth is in transition from parabolic to linear kinetics. These observations are supported by the microstructures developed at different temperatures. At low temperatures, the Ni_3Sn_4 was more continuous, which was protective and had the function of a diffusion barrier. At high temperature, the reaction zone was a two-phase mixture of Ni_3Sn_4 + solder, which could not offer protection for Ni from the solder.

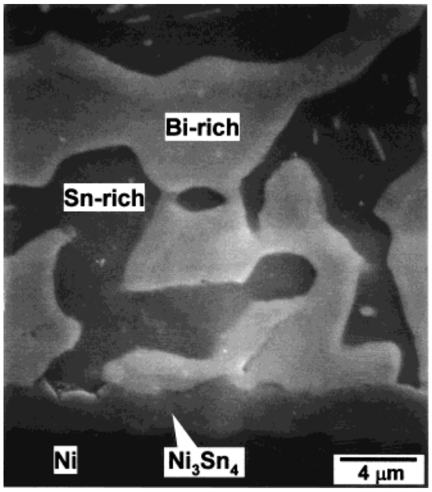

Figure 9. The microstructure for the reaction of solid 58Bi−42Sn with Ni at 120 °C for 1000 h.[14] The compound Ni_3Sn_4 had a simple layered morphology. This picture was taken with a SEM, so that the Bi-rich phase became bright and Sn-rich phase became dark.

The reason for those Ni_3Sn_4 particles near the interface to have a different morphology from those Ni_3Sn_4 particles far away from the interface (see Figure 4) was probably due to their different origins. Those Ni_3Sn_4 particles that had rounded edges formed during the reaction of Ni with 58Bi−42Sn and were in contact with liquid for a long period of time so that sharp edges had become rounded due to the Gibbs−Thomson effect. The hollow, needle-shaped Ni_3Sn_4 originated from those dissolved Ni atoms that reacted with Sn to form Ni_3Sn_4 during the solidification of the solder. This Ni_3Sn_4 was in contact with liquid for a short period of time so that it had a faceted surface.

The mechanism for the increasing Ni_3Sn_4 grain size from the Ni/Ni_3Sn_4 interface to the Ni_3Sn_4/solder interface shown in Figure 5c is an interesting phenomenon worthy of further study. The Ostwald ripening has been proposed as a very likely mechanism responsible for this phenomenon.[15]

The reaction between Ni and pure liquid Sn had been studied by Gur and Bamberger.[16] They found that the growth of Ni_3Sn_4 followed parabolic kinetics if Ni_3Sn_4 was continuous and protective. They estimated the activation energy for this parabolic growth to be 28 kJ/mol, which is close to our result of 23 kJ/mol for the temperature range of 180−360 °C. We suspect that the same mechanism governed these two reactions. This activation energy of 23 kJ/mol is substantially lower than that for the reaction between Ni and solid eutectic BiSn solder, which is 90 kJ/mol.[13] The Ni_3Sn_4 formed in solid−solid reaction was very planar (Figure 9) so that it was a better diffusion barrier. A more detailed study is needed to reveal the difference for the growth mechanism for the solid−liquid reaction and solid−solid reaction.

---

(13) Chen, C.; Ho, C. E.; Lin, A. H.; Luo, G. L.; Kao, C. R. *J. Electron. Mater.* **2000**, *29*, 1200.
(14) Chen, C. Master Thesis, National Central University, Taiwan, 1999.
(15) Kim, H. K.; Liou, H. K.; Tu, K. N. *J. Appl. Phys. Lett.* **1995**, *66*, 2337.
(16) Gur, D.; Bamberger, M. *Acta Mater.* **1998**, *46*, 4917.

Conclusions

The reaction between Ni and liquid eutectic BiSn solder produced only Ni_3Sn_4. All other Ni–Bi and Ni–Sn intermetallic compounds were not detected. The formation of only Ni_3Sn_4 indicated that eutectic BiSn lead-free solder is compatible with Ni-bearing surface finishes in electronic packages from the standpoint of intermetallic formation.

With increasing reaction temperature, the growth of Ni_3Sn_4 shifted from a parabolic kinetics with a slow growth rate (<300 °C) to a linear kinetics with a higher growth rate (>360 °C). Rapid growth of an intermetallic in a solder joint is undesirable because intermetallics are usually quite brittle, and a thick intermetallic at the interface will severely weaken a solder joint. Fortunately, in industrial soldering applications using this solder, the soldering temperature is below 200 °C so that the growth rate of Ni_3Sn_4 is very slow. Therefore, from the standpoint of intermetallic growth rate, eutectic BiSn solder is also compatible with a Ni-bearing surface finish.

Acknowledgment. The authors wish to thank the National Science Council of R.O.C. for the financial support of this study through Grant NSC89-2214-E-008-028. The authors also wish to thank the UNICAP Corp. and the Advanced Semiconductor Engineering, Inc. for their assistance in this study.

CM000803L