

Long-Term Aging Study on the Solid-State Reaction Between 58Bi42Sn Solder and Ni Substrate

C. CHEN,¹ C.E. HO,¹ A.H. LIN,¹ G.L. LUO,¹ and C.R. KAO^{1,2}

1.—National Central University, Department of Chemical Engineering, Chungli City, Taiwan.

2.—e-mail: kaocr@hotmail.com

The reaction between Ni and eutectic BiSn solder at 85°C, 100°C, 120°C, and 135°C was studied. Reaction times ranging from 25 h to 3600 h were used. Only Ni₃Sn₄ was detected as a result of the reaction. None of the other Ni-Sn intermetallic compounds and none of the Ni-Bi intermetallic compounds were observed. The growth of Ni₃Sn₄ followed diffusion-controlled kinetics and was very slow, with the layer thickness reaching only 16 μm after 3600 h of aging at 135°C. The eutectic BiSn microstructure coarsened very quickly. Substantial coarsening can be observed at 135°C for only 200 h of aging. In addition, fine Bi-rich particles within the Sn-rich phase of the solder were found. The amount of these fine Bi-rich particles increased with the aging temperature. It is believed that the formation of these fine Bi-rich particles is due to the fact that the Sn-rich phase can dissolve substantial amounts of Bi. It was also found that, as aging time increased, the region immediately adjacent to the Ni₃Sn₄ layer was preferentially occupied by the Bi-rich phase. This is because Sn in that region had reacted with Ni to form Ni₃Sn₄, leaving a nearly continuous Bi-rich phase above the Ni₃Sn₄. Since Bi-rich alloys tend to be brittle, a nearly continuous Bi-rich phase might weaken the strength of a solder joint. The Ni₃Sn₄ grain size increased gradually from the Ni/Ni₃Sn₄ interface to the Ni₃Sn₄/BiSn interface, which is probably an Ostwald ripening phenomenon.

Key words: 58Bi42Sn solder, Ni substrate, aging phenomenon

INTRODUCTION

The PbSn eutectic solder is widely used by the electronic industry for packaging applications. This solder has been used for years and meets the performance requirements very well, but lead in this solder has negative impacts on the environment. Because of this environmental concern, it is anticipated that lead-bearing solders will be phased out either voluntarily by industry or through legislation in a few years. Many lead-free solders have been proposed as possible replacements, and some of them have been used in industry for other reasons for quite some time. The eutectic BiSn solder (58 wt.% Bi-42 wt.% Sn, Bi42Sn) is an important candidate for replacing the PbSn eutectic solder in many applications.¹

In printed circuit boards (PCB) manufacturing, a solderable surface finish is coated over the Cu traces

to maintain solderability over a period of shelf time. Currently, lead-bearing PbSn surface finishes are the most widely used ones. There is also a pressure to eliminate the use of lead in surface finishes. Ni layers, both electrolytic and electroless, are used in several important lead-free finishes, such as the Au/Ni and Pd/Ni. These new surface finishes have the additional advantage of being very flat, making them ideal for fine lead-pitch and area-array surface mount components. The Au and Pd over-layers are used to protect the Ni layers from oxidizing. The Au and Pd layers are very thin (0.02–0.2 μm) and will disappear very quickly into the solder during the reflow operation, exposing the Ni layer to the solder. Therefore, in lead-free PCB soldering, the interactions between Ni and solder have to be considered. The objective of this paper is to study the reactions between Ni and the Bi42Sn solder in the solid state.

According to the Ni-Bi and Ni-Sn phase diagrams,² there are two intermetallic compounds in the Ni-Bi

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system (NiBi and NiBi₃), and three intermetallic compounds (Ni₃Sn, Ni₃Sn₂, and Ni₃Sn₄) in the Ni-Sn system, respectively. Therefore, the reactions between Bi42Sn with Ni can be potentially quite complicated. When Bi42Sn reacts with Ni, all the intermetallics of Ni-Bi and Ni-Sn will compete with each other to form. In such reactions, not all the possible intermetallic compounds in the binary phase diagrams will form. Very often, only a few of them become the reaction products. Experimental studies are needed to reveal what exactly will occur in such reactions. A literature search revealed that there was only one study on the reaction between Ni and liquid Bi42Sn,³ and there is not any study on the reaction between Ni and solid Bi42Sn. Kang et al.³ studied the reaction at 170°C for up to 20 minutes, and found that only Ni₃Sn₄ formed. It would be interesting to see if this is still the case for long-term aging in the solid-state.

In the literature, however, there are more studies on the binary reactions between Ni and Bi⁴⁻⁷ as well as between Ni and Sn.⁸⁻¹² The reaction between Ni and solid Bi produced a layer of thick NiBi₃ at the original Ni-Bi interface. The growth of NiBi₃ was very rapid for solid-state reactions, reaching 230 μm in 70 h at 250°C.^{4,5} The possible rapid growth of NiBi₃ in a solder joint would be very troublesome. This is because there is evidence showing that NiBi₃ has very inferior mechanical properties.^{6,7} This compound is both soft and brittle. In view of the fact that NiBi₃ has high growth rate and inferior mechanical properties, it is highly undesirable to form NiBi₃ in a solder joint. The reaction between Ni and Sn always produced Ni₃Sn₄. In some studies, Ni₃Sn and Ni₃Sn₂ were also detected.^{8-10,12} The mechanical properties of Ni₃Sn₄ are more typical for intermetallic compounds. Although this compound is still quite brittle, its properties are not as undesirable as NiBi₃.

EXPERIMENTAL PROCEDURE

The Bi42Sn solder used in this study was prepared from 99.999%-pure Bi and 99.99%-pure Sn. Each solder bath was formed by placing 35 g of solder into an 8 mm ID quartz tube with one end sealed. The Ni specimens were 99.99%-pure long slabs, each measuring 70 mm in length, 6.35 mm in width, and 0.5 mm in thickness. These Ni slabs were metallurgically polished on both surfaces. One μm diamond abrasive was used as the last polishing step. The exact thickness of each slab after polishing was then recorded. These Ni slabs were then cleaned with acetone, etched in a 50 vol.% HCl-H₂O solution for 10 sec, and fluxed with a mildly activated rosin flux (RMA#5, Indium Corporation of America). Each fluxed slab was then vertically inserted into a molten solder bath at 200°C, as shown schematically in Fig. 1. Care was taken to avoid any trapped voids in the solder. Immediately after the insertion, the whole setup was quenched very quickly into iced water to form a solid-state reaction couple.

Each reaction couple was then placed in an oven maintained at a constant reaction temperature. The

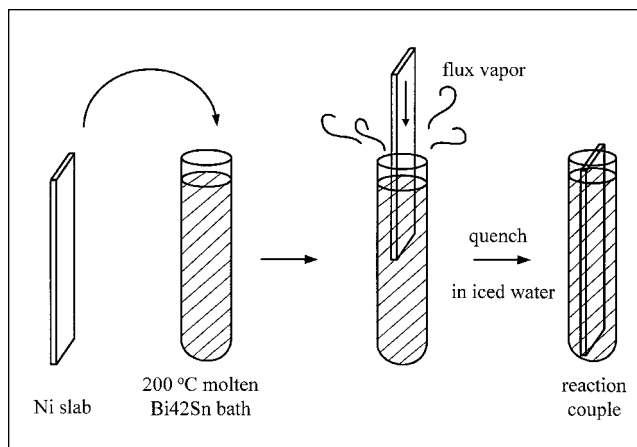


Fig. 1. A schematic drawing showing the preparation of the reaction couples. One reaction couple was used for each temperature. When each of the scheduled reaction times was reached, a 3 mm thick sample was sectioned from each of the reaction couples. The remaining pieces of the reaction couples were then returned to the ovens for further reaction.

temperature homogeneity and stability for each oven was better than $\pm 1^\circ\text{C}$. Four reaction temperatures, 85°C, 100°C, 120°C, and 135°C, were used in this study. When each of the scheduled reaction times was reached, the reaction couples were taken out of the ovens, and from each reaction couple a 3 mm thick sample was sectioned along the direction perpendicular to the longitudinal direction of the reaction couple. What remained of each reaction couple was then returned to its oven for further reaction. The reaction times used in this study included 0, 25, 50, 100, 150, 200, 300, 500, 1000, 1900, and 3600 hours. The zero reaction time refers to the condition right after the preparation of the reaction couple without aging.

The samples were then 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 zone and the thickness of the unreacted Ni for each sample were measured by using image analysis software. The thickness of a phase is defined as the total area occupied by that phase divided by the length. 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 $K\alpha$, $M\alpha$, and $L\alpha$ 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 $100 \pm 1\%$ 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.%. The crystal structure of the reaction product was determined by using a diffractometer using Cu $K\alpha_1$ radiation.

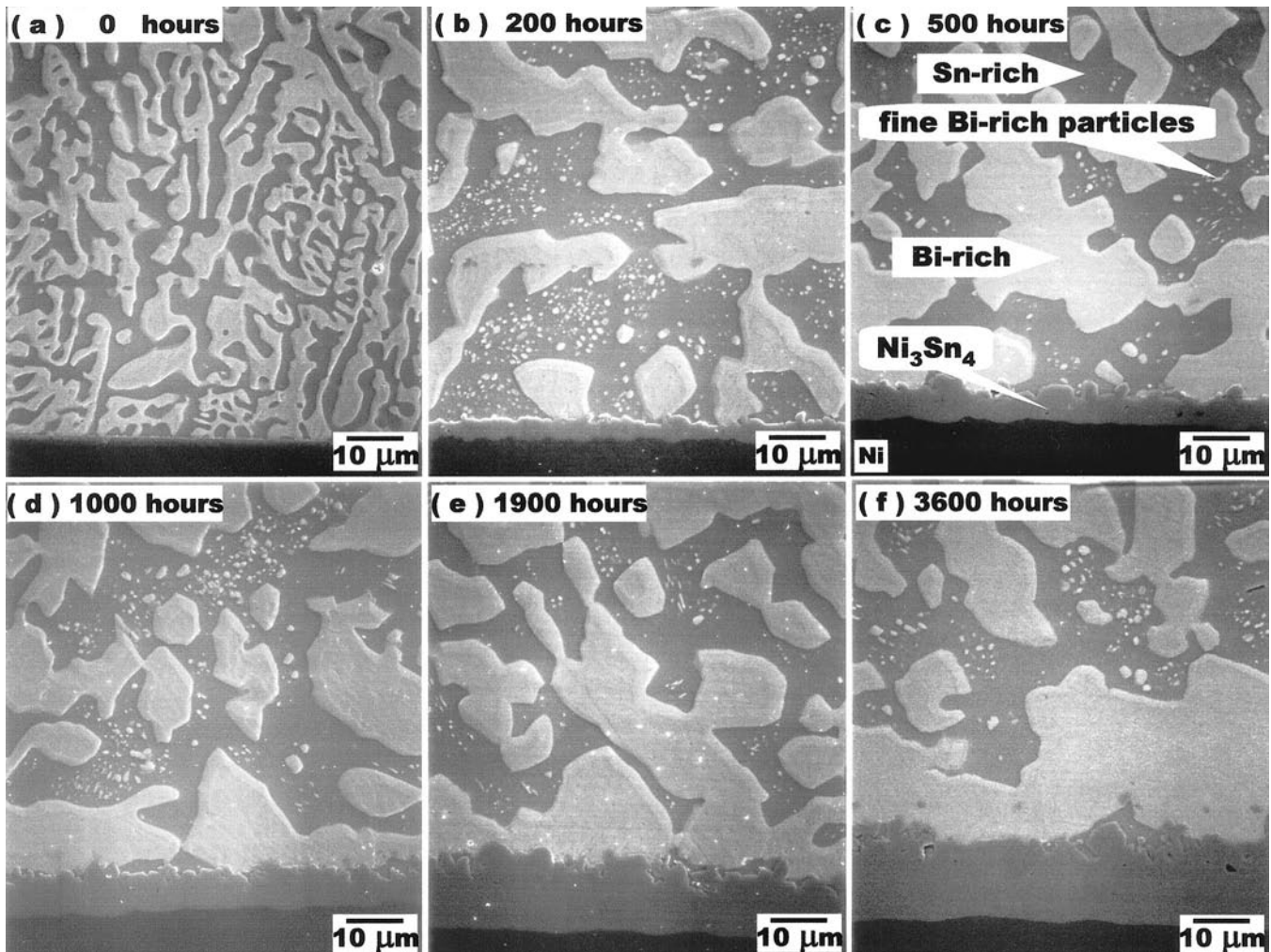


Fig. 2. Secondary electron micrographs for samples reacted at 135°C for 0, 200, 500, 1000, 1900, and 3600 h, respectively. (a) represents the sample conditions right after insertion into molten solder without any aging. These are cross-section micrographs with the section direction perpendicular to the faces of the Ni slabs. In all cases, only Ni_3Sn_4 was detected. Phases are labeled in c and d.

RESULTS

Figure 2 shows the secondary electron micrographs for reaction couples aged at 135°C for different aging times. Figure 2a represents the sample conditions right after insertion into molten solder and without any aging. In all the reaction couples, including those at other temperatures, only the intermetallic compound Ni_3Sn_4 was detected. The other Ni-Sn compounds and all the Ni-Bi compounds were not observed. The EPMA line-scan across the reaction zone of the reaction couple aged at 135°C for 3600 h is shown in Fig. 3. It can be seen from this line scan that Ni_3Sn_4 was essentially a line compound without any Bi dissolved. As shown in Fig. 2, Ni_3Sn_4 exhibited the layered structure, and its thickness increased rather slowly with aging time, reaching only 16 μm for 3600 h of aging at 135°C. This slow growth rate is considered favorable for packaging applications. The compound Ni_3Sn_4 was found only at the interface, and no Ni_3Sn_4 was detected within the solder. This is quite different from the reactions of metals with liquid solders, in which case intermetallic compounds can often be found within

the solder. It can also be seen that the BiSn eutectic structure coarsened substantially after 200 h of aging at 135°C. The microstructure evolution at other temperatures is not shown in this paper for the sake of brevity, but it is worthy of pointing out that the BiSn eutectic structure did not show an appreciable degree of coarsening after 3600 h of aging at 85°C. At 100°C and 120°C, substantial degrees of coarsening were observable at 500 h and 200 h, respectively. Moreover, as shown in Fig. 2, there are many fine Bi-rich particles in the Sn-rich phase after aging. These fine Bi-rich particles did not exist in the reaction couples right after preparation, as can be seen in Fig. 2a.

Figure 4 compares the microstructures of reaction couples after 3600 h of aging at 85°C, 100°C, 120°C, and 135°C. The grain sizes of the BiSn eutectic structure depended strongly on the aging temperatures. Moreover, there were fine Bi-rich particles in the Sn-rich phase at every temperature except for the one at 85°C. Although it is not apparent in Fig. 4 due to limited field of view of these micrographs, there was a general trend that the amount of these fine Bi-rich particles increased with the aging temperature.

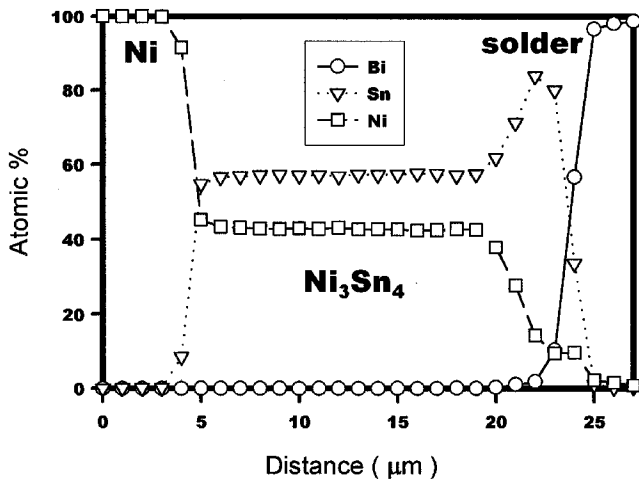


Fig. 3. The EPMA line-scan across the reaction zone of the reaction couple aged at 135°C for 3600 h. Only Ni₃Sn₄ was detected. According to this line scan, Ni₃Sn₄ was essentially a line compound without any Bi dissolved.

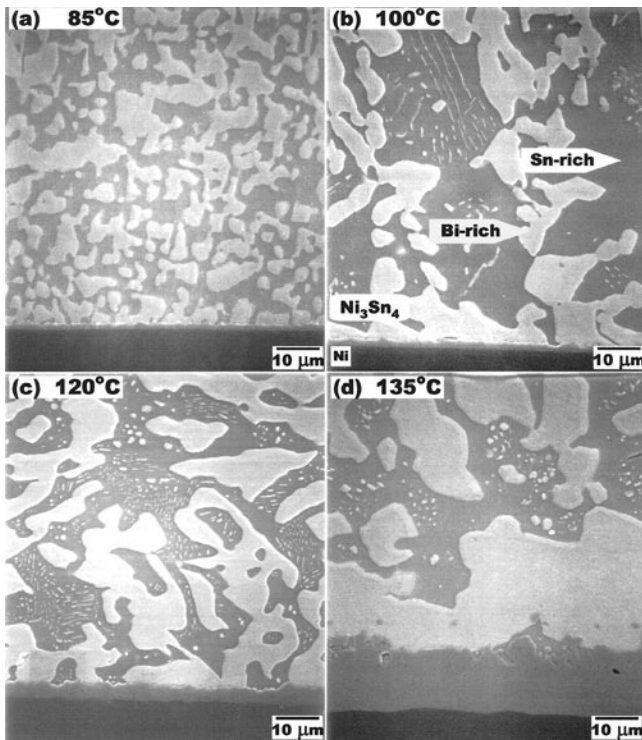


Fig. 4. A comparison of the microstructures for reaction couples after 3600 h of aging at 85°C, 100°C, 120°C, and 135°C. These are cross-section micrographs. Phases are labeled in Fig. 4b.

To investigate the microstructure of Ni₃Sn₄ more closely, a 50 vol.% HNO₃-H₂O solution was used to completely etch the solder away from a 3600 h-135°C reaction couple to reveal the Ni₃Sn₄ grains, as shown in Fig. 5a. Moreover, 45° view pictures are shown in Fig. 5b and c for a 3600 h-135°C reaction couple. In Fig. 5b and c, the solder was only partially etched away by using the 50 vol.% HNO₃-H₂O solution. This etching solution preferentially attacked the Sn-rich phase, leaving more Bi-rich phase exposed. It is interesting to note that the Ni₃Sn₄ grain sizes increased

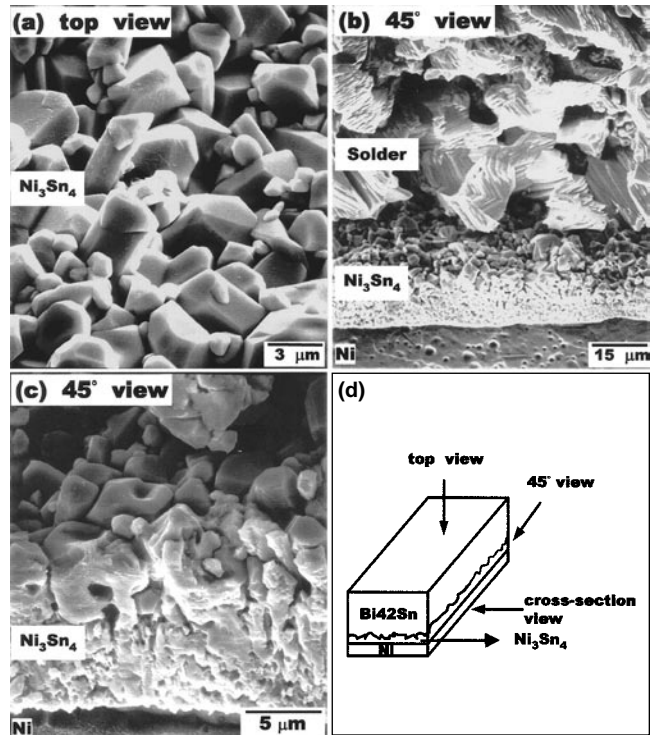


Fig. 5. A top-view and two 45° view micrographs for a reaction couple aged at 135°C for 3600 h. A 50 vol.% HNO₃-H₂O solution had been used to etch the solder. Phases are labeled in Fig. 5h.

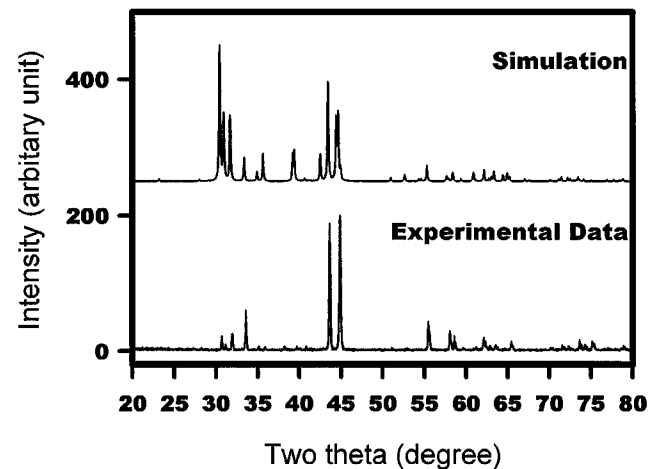


Fig. 6. X-ray diffraction pattern for the Ni₃Sn₄ surface shown in Fig. 5a. The Cu Kα₁ radiation was used. Also shown was a simulated powder diffraction pattern.

gradually from the Ni/Ni₃Sn₄ interface to the Ni₃Sn₄/BiSn interface.

The Ni₃Sn₄ surface shown in Fig. 5a was then used to obtain the x-ray diffraction pattern of Ni₃Sn₄, shown in Fig. 6. This pattern shows distinctive differences, in terms of both peak position and relative peak intensity, from the JCPDS pattern for Ni₃Sn₄ (JCPDS No. 4-0845). A commercial software package was then used to simulate the powder diffraction pattern for Ni₃Sn₄ using the structure data listed in the literature.¹³ The resulting simulated pattern is also shown in Fig. 6. These two patterns have the same peak

positions, although the relative peak intensities show some differences, which are probably because the grains in Fig. 5a have certain preferred orientation.

The growth kinetics for Ni_3Sn_4 is presented in Fig. 7. As can be seen parabolic kinetics describe the data reasonably well, suggesting the growth is diffusion-controlled. The growth of Ni_3Sn_4 is rather slow, especially at lower temperatures. This implies Ni will be a very good diffusion barrier for the BiSn solders. The growth constant k , with the dimension of the diffusion coefficient (m^2/s), can be determined by fitting the thickness d to the following equation:

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

where t is the aging time. The growth constant k was then plotted versus the inverse of the temperature in Fig. 8 in order to determine the activation energy Q for k . As shown in Fig. 8, a single straight line (the solid line) cannot represent all four data points well. Moreover, the resulting activation energy of 177 kJ/mol is considered too high for such system. Neglecting the 135°C data point (dash line) would give an activation energy of 90 kJ/mol, which is a more reasonable number.

DISCUSSION

In this study only Ni_3Sn_4 was observed, and none of the other Ni-Sn intermetallic phases and none of the Ni-Bi intermetallic phases were detected. Thermodynamically, Ni and Ni_3Sn_4 are not in equilibrium according to the Ni-Sn binary phase diagram; therefore, there is driving force for the formation of additional intermetallic phases at the Ni/ Ni_3Sn_4 interface. These missing phases were either too thin to be resolved by SEM, or they are simply not present. The first possibility can be ruled out by examining the interface carefully using instruments with higher resolution, such as a high-resolution transmission electron microscope. Let us discuss the second possibility in more detail. Two contributing reasons are widely accepted for the absence of a phase that should form but does not. The first reason is that the missing phase has difficulty nucleating, because it has a smaller thermodynamic driving force for nucleation. The second reason is that the missing phase has a substantially lower diffusion coefficient compared to other phases. In general, the phases with higher diffusion coefficients will grow faster. When the difference in diffusion coefficient is extreme, the phases with higher diffusion coefficients will even grow at the expense of those with lower diffusion coefficients. In other words, even if the missing phase(s) are present initially, they will shrink and eventually disappear. For the present case, it cannot be concluded which reason is more important. For packaging applications, the fact that NiBi_3 is missing is very beneficial for the strength of a solder joint. As pointed out earlier, the growth rate of NiBi_3 in a Ni-Bi diffusion couple is very rapid, reaching 230 μm in 70 h at 250°C. Furthermore, NiBi_3 has very inferior mechanical properties, being both soft and brittle. If NiBi_3 had formed in the reaction

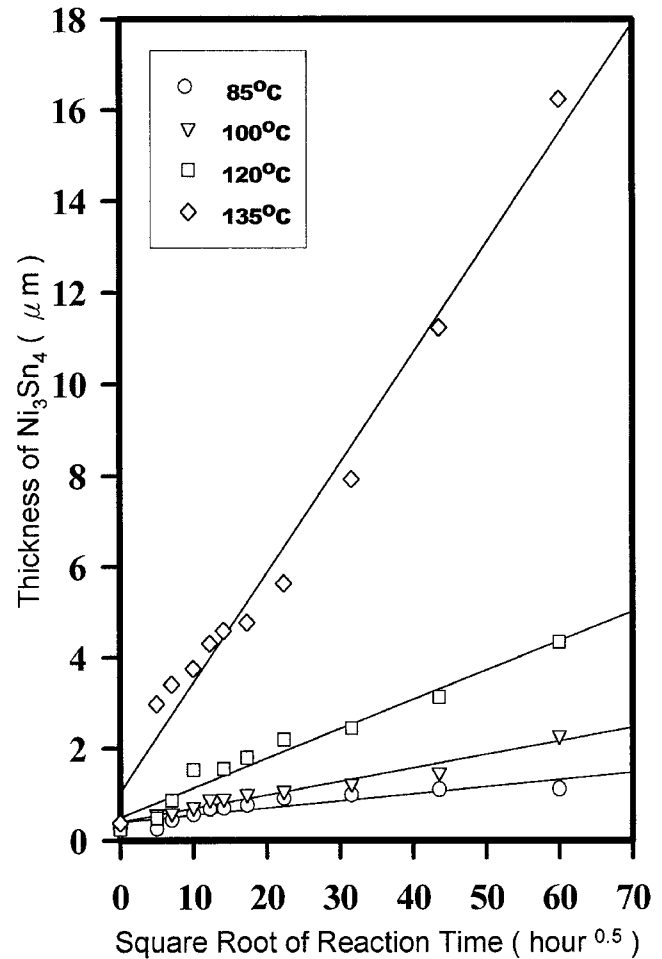


Fig. 7. A parabolic plot of the thickness of Ni_3Sn_4 at different times and temperatures.

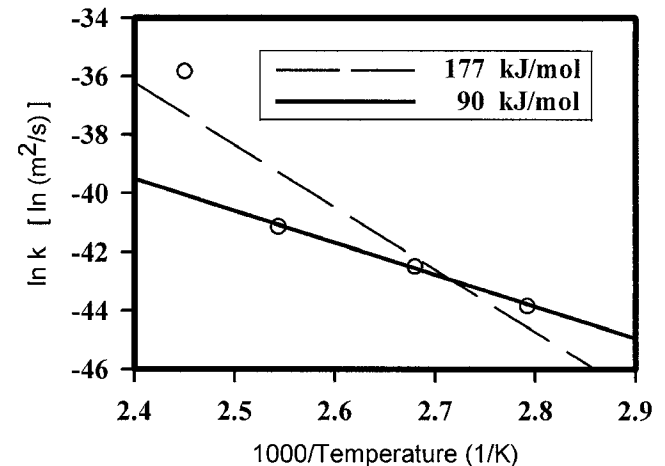


Fig. 8. The growth constant versus the inverse of the temperature. A single straight line can not represent the four data points very well.

between Ni and Bi42Sn, the applications of Bi42Sn would have been limited to Ni-free surface finishes. Nevertheless, the results of this study indicate that only Ni_3Sn_4 forms, and its growth rate is very slow. Therefore, Bi42Sn is quite compatible with Ni-bearing surface finishes from the standpoint of intermetallic formation.

One very interesting feature of the BiSn eutectic structure after aging is the existence of fine Bi-rich particles in the Sn-rich phase, as shown in Figs. 2 and 4. The amount of these fine Bi-rich particles increased with the aging temperature. We believe that the origin of the formation of these Bi-rich particles can be found in the BiSn binary phase diagram, which is shown in Fig. 9.² As shown in the BiSn phase diagram, the Sn-rich phase can dissolve substantial amount of Bi, while the Bi-rich phase shows almost no solubility for Sn. When a Bi42Sn alloy is aged at a temperature, the alloy will eventually reach thermodynamic equilibrium. In other words, the Sn-rich phase will dissolve the amount of Bi atoms according to the phase diagram, and this amount of Bi will increase with the aging temperature. After aging and the subsequent cooling to room temperature, these dissolved Bi atoms will precipitate out as the fine Bi-rich particle in the Sn-rich phase, and the amount of these particles increases with the amount of dissolved Bi atoms, which in turn increases with the aging temperature.

Another interesting microstructural feature in Figs. 2 and 4 is that, as aging time increased, the region immediately adjacent to the Ni_3Sn_4 became more and more preferentially occupied by the Bi-rich phase. This is of course because Sn in that region had reacted with Ni to form Ni_3Sn_4 , leaving a nearly continuous Bi-rich phase above the Ni_3Sn_4 . Since the Bi-rich alloys tend to be brittle, a nearly continuous Bi-rich phase above the Ni_3Sn_4 might weaken the strength of a solder joint.

The mechanism for the increase of Ni_3Sn_4 grain size shown in Fig. 5b and c is an interesting phenomenon worthy of further study. The Ostwald ripening has been proposed as a very likely mechanism responsible for this phenomenon.¹⁴

Another observation, which needs to be clarified, is the activation plot shown in Fig. 8. A single straight line fit of the data gives an activation energy of 177 kJ/mol, which is too high for such system. If the data point for 135°C is ignored, 90 kJ/mol is obtained for the other three temperatures, which is a more reasonable number. It is not clear at this point whether there is indeed a shift in activation energy around 135°C, or it is just an artifact. More experiments between 135°C and 120°C is needed to clarify this point.

Solid-state reaction between Cu and Bi42Sn had been studied by Vianco et al. from 55–120°C for up to 400 days.¹⁵ The compound Cu_6Sn_5 and a CuBiSn ternary compound formed as a result of the reactions, and the growth rate for Cu_6Sn_5 was several times faster than Ni_3Sn_4 . Moreover, repeating Cu_6Sn_5 /CuBiSn double-layers were found in some of the samples. It is believed that the formation of the double-layers was due to the faster growth rate of Cu_6Sn_5 . The rejected Bi atoms had no time to diffuse away from the interface so that a CuBiSn ternary compound formed. In the present study, the Ni_3Sn_4 growth rate was slower, and no such double-layer was observed. The activation energy for the growth of Cu_6Sn_5 is 55 kJ/mol, substantially lower than that for Ni_3Sn_4 .

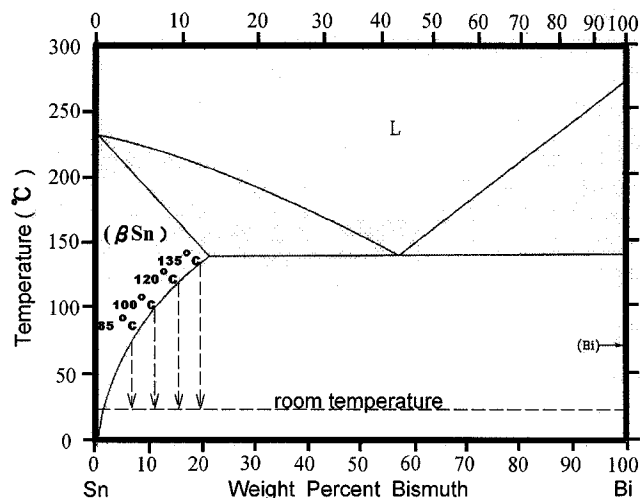


Fig. 9. Binary phase diagram of the BiSn system.² The origin of the fine-Bi-rich particles in the Sn-rich phase of the BiSn eutectic structure is from the high solubility of Bi in Sn.

SUMMARY

Intermetallic compound formation between solid Bi42Sn and Ni was studied. Temperature used ranged from 85°C to 135°C, and aging time ranged from 25 h to 3600 h. Composition analysis using EPMA revealed that only Ni_3Sn_4 formed, and none of the other Ni-Sn intermetallic compounds and none of the Ni-Bi intermetallic compounds were detected. The growth of Ni_3Sn_4 followed diffusion-controlled kinetics and was very slow, with the intermetallic layer thickness reaching only 16 μm at 135°C for 3600 h of aging. This suggests that Ni is compatible with the Bi42Sn from the standpoint of intermetallic formation. The eutectic BiSn microstructure coarsened very quickly. Substantial coarsening can be observed at 135°C after only 200 h of aging. This rapid coarsening might have a negative impact on the strength of a solder joint. In addition, fine Bi-rich particles in the Sn-rich phase of the solder were found. The amount of these fine Bi-rich particles increased with the aging temperature. It is proposed that the origin for the formation of these Bi-rich particles is precipitation from the Sn-rich phase during cooling after aging. This is due to the fact that the Sn-rich phase can dissolve a substantial amount of Bi during aging. It is also found that, as aging time increased, the region immediately about the Ni_3Sn_4 became preferentially occupied by the Bi-rich phase. This is because Sn in that region had reacted with Ni to form Ni_3Sn_4 , leaving a nearly continuous Bi-rich phase above the Ni_3Sn_4 . Since the Bi-rich alloys tend to be brittle, a nearly continuous Bi-rich phase above the Ni_3Sn_4 might weaken the solder joint.

ACKNOWLEDGEMENT

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