

Formation and Absence of Intermetallic Compounds during Solid-State Reactions in the Ni–Bi System

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The reactions between Ni and NiBi₃ at 330, 370, 410, and 450 °C were studied. The compound NiBi₃ was prepared by melting a mixture of 99.9994% Bi shots and 99.996%, –120 mesh Ni powder. It was found that the synthesized NiBi₃ is soft and brittle. This is contrary to the characteristics of common intermetallics, which are often hard and brittle. Such inferior mechanical properties make the formation of NiBi₃ in solder joints very undesirable. The reaction product was a layer of NiBi that grew parabolically, suggesting diffusion-controlled kinetics. The activation energy for the growth of NiBi is 84 kJ/mol. The fact that NiBi formed here, but not in the reaction between Ni and Bi as reported in the literature, suggests that the reason for absence of NiBi is not due to difficulty in nucleation. The more likely reason is that the interdiffusion coefficient of NiBi is much smaller than that of NiBi₃. The dominant diffusing species in NiBi was analyzed by a marker movement experiment. It was found that the Bi flux through NiBi is 3–9 times greater than Ni flux at 370 °C. An expression relating the marker position to the ratio of Bi flux to Ni flux was proposed.

Introduction

Recent advances in integrated circuit (IC) manufacturing technologies have produced larger chips, smaller feature sizes, increasing transistor count, and increasing input/output terminals. All these factors have put increased emphasis on microelectronic packaging. Currently, packaging expense can represent 40% of the overall cost in IC manufacturing, and this percentage is expected to increase in the future. There are many critical issues in microelectronic packaging that are materials chemistry in nature, and one of them is the reaction between the thin metallization layer(s) and soldering materials at the solder joints of an electronic package. The microelectronic industry demands an extremely low defect rate for the solder joints (<25 ppm). To achieve such a low defect rate, a detailed knowledge of the reactions between the metallization layer(s) and the soldering materials is important.

Nickel is one of the most common metallization materials in IC packages, and the use of Ni will increase as more advanced packaging technology, such as the ball–grid–array packaging, is used.^{1–3} Bismuth is an important ingredient in many microelectronic solders, especially those being lead-free. The use of Bi in microelectronic solders will also increase since environmental concerns tend to favor the use of lead-free solders. Therefore, the knowledge of how Ni reacts with Bi is important. The phase diagram is the most concise

presentation that summarizes the chemistry in a binary metallic system. According to the Ni–Bi phase diagram,⁴ there are two intermetallic compounds in the Ni–Bi system: NiBi, stable up to 654 °C, and NiBi₃, stable up to 469 °C. Duchenko and Dybkov^{5,6} have studied the solid-state reactions between Ni and Bi at 150–250 °C and found that a layer of NiBi₃ formed at the original Ni–Bi interface. According to their results, the growth of NiBi₃ was very rapid for solid-state reactions at such low temperatures. The thickness of NiBi₃ reached 230 μm in 70 h at 250 °C. They also found that the growth of NiBi₃ followed parabolic kinetics, suggesting that the growth was diffusion-controlled. The main diffusing species was Bi, as determined by the marker movement experiment. The other intermetallic compound, NiBi, which is also thermodynamically stable at 150–250 °C according to the Ni–Bi phase diagram, was not detected by using scanning electron microscopy (SEM) in their study. The reason for the absence of NiBi was not clear.

Intermetallic compounds are often hard and brittle, and the cracking of a solder joint usually occurs next to or within the intermetallic layer inside a solder joint. It has been shown that the strength of a solder joint decreases with increasing thickness of the intermetallic compounds in a solder joint.^{7,8} Therefore, the rapid growth of NiBi₃ in a solder joint would be very troublesome. Moreover, from our hardness measurement (this

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study), there is evidence showing that NiBi₃ has very inferior mechanical properties compared to other intermetallic compounds. 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 desirable to avoid the formation of NiBi₃ in solder joints. To achieve such a goal, a detailed understanding for the Ni–Bi system is needed. The objective of this paper is to study the reactions between Ni and Bi in more detail and the reason for the absence of NiBi was one of the main focuses of this study.

The absence of one or more thermodynamically stable phases in a binary diffusion couple is not rare, and the cause for the absence is a subject that has been discussed in the literature.^{9–13} An extensive reference list for this subject can be found in a paper by d'Heurle.¹³ Of course, it is always possible that the “missing phase” is actually there but is just too thin to be detected by the instruments used. Scanning electron microscopy is the most popular technique used to identify the number of the product phases, but SEM is not practical for identifying a phase with thickness smaller than 100 nm. Electron probe microanalysis (EPMA) is the method of choice for identifying the compositions of the product phases, but results are reliable only for a phase thicker than 1 μm. High-resolution transmission electron microscopy (HRTEM) is the only technique that can determine the existence or absence of a phase unambiguously. Careful studies using HRTEM have confirmed that in many cases the missing phase just did not form.¹³ There are two widely accepted views for why a phase does not form. The first view is that the missing phase has difficulty in nucleation, due to the smaller thermodynamic driving force for nucleation.¹³ The second view, which is purely kinetic in nature, is that the missing phase has a substantially lower interdiffusion coefficient compared to other phases.^{10,12} According to the second view, the phases with higher interdiffusion coefficients will grow faster than those with lower interdiffusion coefficients. When the difference in interdiffusion coefficient is extreme, i.e. several orders of magnitude, the phases with higher interdiffusion coefficients will even grow at the expense of those with lower interdiffusion coefficients. In other words, even if the missing phase is present initially, it will shrink and eventually disappear.

To determine the reason for NiBi to be missing, we reacted Ni with NiBi₃ at 330, 370, 410, and 450 °C and examined if NiBi would form. If a nucleation problem is the reason for the lack of NiBi in the reaction between Ni and Bi, then NiBi should also have the same problem in the reaction between Ni and NiBi₃ and will not form. This is because the local environment at the Ni/NiBi₃ interface is the same in both cases. More detailed rationale is presented in the Discussion section.

Experimental Section

In this study, NiBi₃ had to be synthesized first for use in the reaction between NiBi₃ and Ni. The compound NiBi₃ was

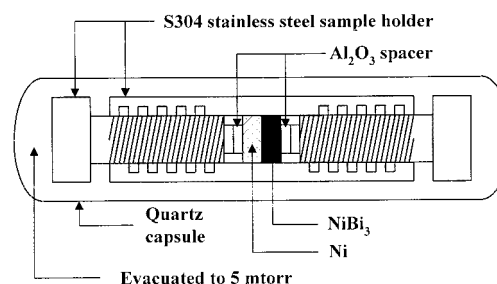


Figure 1. Schematic drawing of the sample holder used in the diffusion couple experiment. The screws of the sample holder were tightened to keep the two disks in contact. The whole sample holder was enclosed in an evacuated quartz capsule during reaction to prevent oxidation.

prepared by melting 99.9994% Bi shots and 99.996%, –120 mesh Ni powder in a 3-to-1 atomic ratio in a sealed, evacuated (5 mTorr) quartz tube of 6 mm inside diameter. The temperature used for melting was 800 °C. The sample was quenched and remelted several times to ensure homogeneity. After the last quench, the sample was homogenized at 450 °C for 7 days. (The intermetallic NiBi₃ decomposes peritectically into NiBi and liquid at 469 °C, according to the Ni–Bi phase diagram.⁴) After the homogenization, the sample rod became single-phased NiBi₃, as confirmed by metallography. EPMA, conducted at 15 keV, was used to verify the composition and homogeneity of NiBi₃. In EPMA, the standards used were pure Ni and pure Bi. In EPMA, the standards used were pure Ni and pure Bi. The weight percentages of Ni and Bi were measured independently, and the total percentage was within 100 ± 1 wt % in each case. It was estimated that the accuracy of the compositions determined in this study was within 1 wt %. A piece of NiBi₃ was grounded into powder for X-ray powder diffraction (XRD) analysis. The XRD analysis was used to verify that the synthesized NiBi₃ has the reported CaLiSi₂ type structure¹⁴ and is single-phased. The Vickers hardness for NiBi₃ was measured using a load of 100 g; 33 hardness measurements were made, and the average value was reported.

A 99.995%, 2 mm thick Ni disk (5 mm diameter) and a 5 mm thick NiBi₃ disk, sectioned from the synthesized NiBi₃ rod, were used in each diffusion couple study. The surface of each disk was polished using 1 μm diamond paste, ultrasonically cleaned in acetone, etched in a 50 vol % HCl–H₂O solution for 10 s, and cleaned in acetone again. Immediately after these steps, these two disks were then held in contact in a S304 stainless steel sample holder, shown schematically in Figure 1. Before the sample holder was loaded, it was sprayed with boron nitride powder to prevent the interaction between the sample holder and the disks. The sample holder with the disks was then placed in a 9 mm (i.d.) quartz tube, evacuated to a vacuum of 5 mTorr, sealed, and put into furnace to react. The reaction temperatures were 330, 370, 410, and 450 °C, and the reaction time ranged from 150 to 600 h. After the reaction, each diffusion couple was quenched in water, taken out of the sample holder, encapsulated in epoxy, and metallographically polished for analysis. The reaction zone of each sample was examined by an optical microscope. The thickness of the reaction product was measured at regular intervals on its optical micrograph. For each sample, about 30 data points were measured, and the average thickness was reported. An electron microprobe was used to measure the concentration profiles of the diffusion couples.

Results

Characterization of the Synthesized NiBi₃. The microstructure of the synthesized NiBi₃ after homogenization is single-phased with an average grain size

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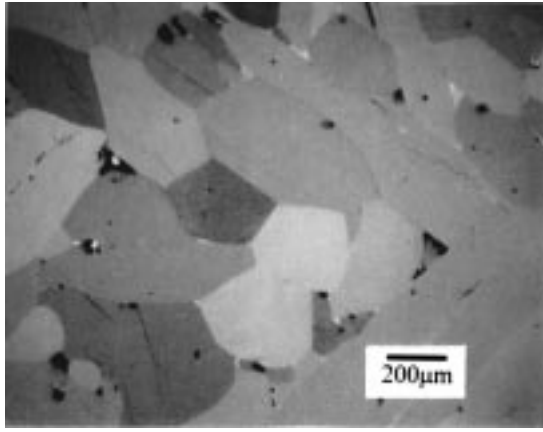


Figure 2. An optical micrograph (polarized) of NiBi₃. This picture shows that the synthesized NiBi₃ is single-phased with an average grain size of 200 μm.

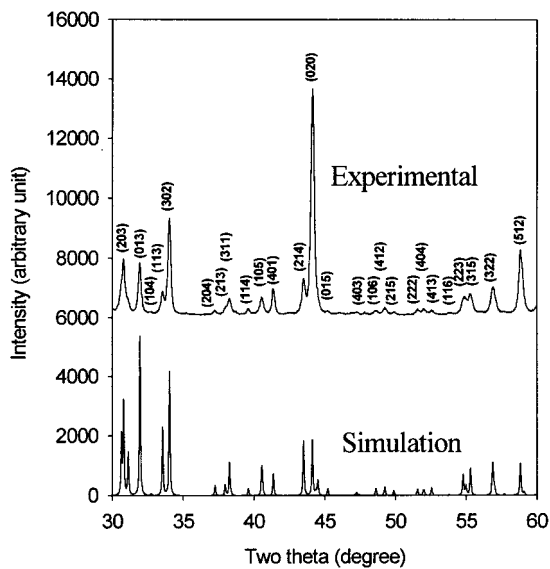


Figure 3. An X-ray powder diffraction pattern for NiBi₃. All the peaks are from NiBi₃ with the CaLiSi₂ type structure. The radiation used was Cu Kα₁. Also shown in Figure 3 is the calculated pattern using a commercial XRD simulation package. The crystal structure type and atom positions used in the calculation were taken from the literature,¹⁴ and the lattice parameters used were from this study.

of 200 μm. Figure 2 is a polarized optical micrograph of NiBi₃. The composition of this NiBi₃ was determined by EPMA to be 75 atom %, the same as the overall composition of the starting materials. EPMA also revealed that NiBi₃ was fully homogenized, since the compositions measured at different locations were the same. The XRD result, shown in Figure 3, confirmed that this NiBi₃ was single-phased. The crystal structure was determined to be the CaLiSi₂ type (*oP16*, *Pnma*), the same as that reported in the literature.¹⁴ Also shown in Figure 3 is the calculated pattern using a commercial XRD simulation package. As can be seen in Figure 3, the experimental and calculated patterns have the same peak positions, although there are differences in the relative intensities between peaks, especially the (020) peak. The reason for the differences is probably due to the preferred orientation generated during solidification. The lattice constants for NiBi₃ were determined to be $a = 0.888(7)$ nm, $b = 0.410(2)$ nm, and $c = 1.147(3)$ nm.

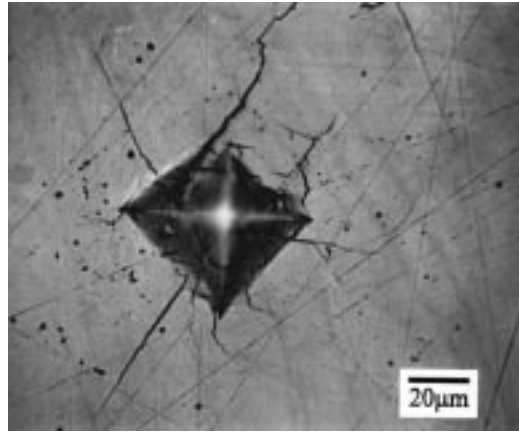


Figure 4. A picture showing one of the indentation marks made during the hardness measurement for NiBi₃. This phase is quite brittle, as demonstrated by the cracks along the edges of the indentation mark.

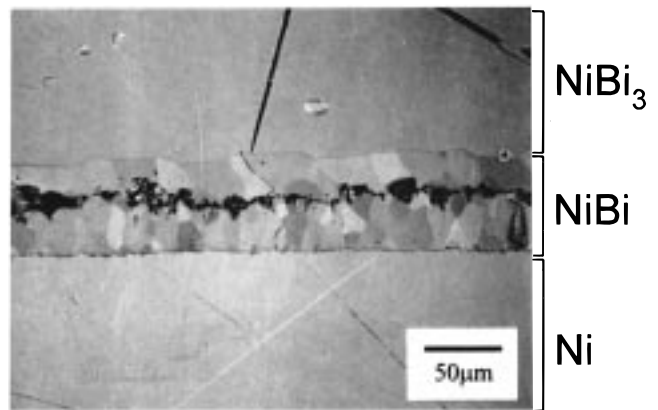


Figure 5. A cross sectional picture (polarized) showing the reaction product NiBi for the reaction between NiBi₃ and Ni at 370 °C for 600 h. From top to bottom, the three layers are NiBi₃, NiBi, and Ni, respectively. The crack within NiBi delineates the original interface between Ni and NiBi₃ before the reaction.

The intermetallic NiBi₃ is quite soft with a Vickers hardness of 25HV (100 g load). Figure 4 is a picture showing one of the indentation marks during the hardness measurement. Interestingly, this phase is also quite brittle, as demonstrated by the cracks along the edges of the indentation mark. As mentioned earlier, intermetallic compounds are often hard and brittle, but NiBi₃ shows the characteristics of being both soft and brittle. Consequently, NiBi₃ has very inferior mechanical properties and is very detrimental to the strength of a solder joint.

Reaction between Ni and NiBi₃ Figure 5 shows the product phase from the reaction of Ni and NiBi₃ at 370 °C for 600 h. Only one product phase was found and was identified by EPMA to be NiBi. Within NiBi, there is a crack running roughly parallel to the Ni/NiBi interface. This type of crack exists in all of the samples, and its width is very sensitive to the polishing steps. This crack presumably delineates the original interface between Ni and NiBi₃ before the reaction and therefore can serve as an internal marker. This assumption is supported by the observation that, in Figure 5, the sizes of every NiBi grain above the crack are consistently larger than those below the crack. This feature is quite general and was observed in diffusion couples with

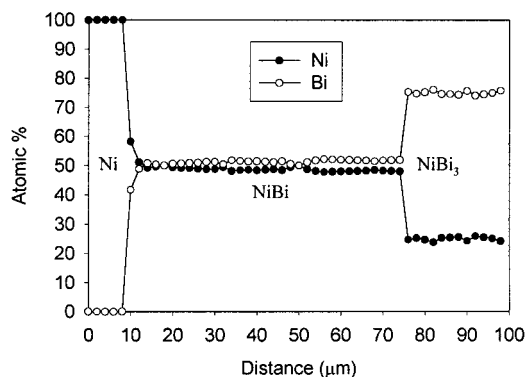


Figure 6. The EPMA line scan across the reaction zone for the diffusion couple reacted at 370 °C for 600 h.

different reaction temperatures and times. The reason for the formation of the crack is probably due to the volume decrease in the reaction $2\text{Ni} + \text{NiBi}_3 \rightarrow 3\text{NiBi}$. Nickel has a molar volume of $6.59 \text{ cm}^3/\text{mol}$. There are no literature values for the molar volumes of NiBi_3 and NiBi , but their molar volumes can be determined from their unit cells and lattice parameters,⁴ which were calculated to be 63 and $23 \text{ cm}^3/\text{mol}$, respectively. Using these values, the volume change for the reaction $2\text{Ni} + \text{NiBi}_3 \rightarrow 3\text{NiBi}$ is then -9.4% , which is quite appreciable. This decrease in volume induced an internal stress, which in turn caused the crack to occur at the weakest point, the original interface.

Figure 6 shows the EPMA line scan across the reaction zone for the diffusion couple reacted at 370 °C for 600 h. According to the Ni–Bi phase diagram,⁴ NiBi was estimated to have a range of homogeneity as wide as 4 atom % and to be Ni-rich (45–49 atom % Bi). Feschotte and Rosset later measured the range of homogeneity of NiBi to be very narrow and to be Bi-rich (51.0 ± 0.3 atom % Bi).¹⁵ From Figure 6, it can be seen that at 370 °C NiBi has a narrow range of homogeneity (within 1 atom %) and has a composition of 51 atom % Bi (Bi-rich). This finding is consistent with that of Feschotte and Rosset.¹⁵ The reason for NiBi to be Bi-rich is possibly due to the constitutional vacancies on the Ni sublattice. Bismuth interstitials are unlikely since Bi atoms are large in size.

The growth of NiBi as a function of time and temperature is shown in Figure 7. Regression analysis revealed that the growth of NiBi followed parabolic kinetics. This implies that the growth of NiBi is diffusion-controlled. The data in Figure 7 was fitted to the following equation:

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

where d is the thickness of NiBi , t is the reaction time, and k is a constant with the dimension of diffusivity (m^2/s). The values of $\ln k$ are plotted against the inverse temperature ($1/T$) in Figure 8 to obtain the activation energy for the growth of NiBi . From the slope in Figure 8, the activation energy for k was determined to be 84 kJ/mol. This value is larger than that for the growth of NiBi_3 , which was determined by Dybkov and Duchenko to be 67 kJ/mol.⁶ Extrapolation of the k value for NiBi

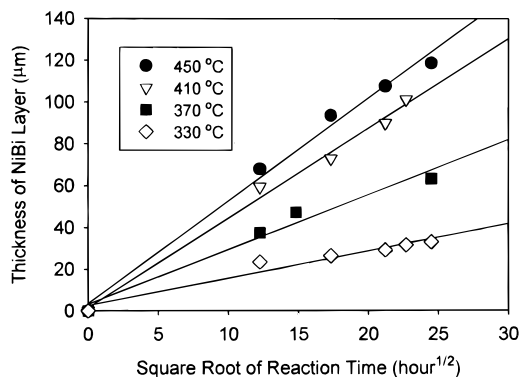


Figure 7. The thickness of NiBi as a function of time and temperature.

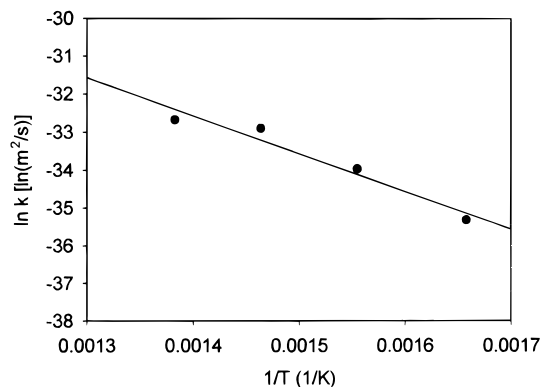


Figure 8. A plot of $\ln k$ versus the inverse temperature ($1/T$). From the slope of this plot, the activation energy for k was determined to be 84 kJ/mol.

using the activation energy to the temperature range used by Dybkov and Duchenko (150–250 °C)^{5,6} reveals that k for NiBi_3 is 10^3 – 10^4 times greater than that for NiBi .

Discussion

In the study of Duchenko and Dybkov, when Ni reacted with Bi, only NiBi_3 was detected, and the other stable phase NiBi was not.^{5,6} However, in this study, it was found that when Ni reacted with NiBi_3 , NiBi did form. The comparison for these two cases is illustrated in Figure 9. In cases a and b of Figure 9, they both have a Ni/ NiBi_3 interface, but one is on the right-hand side of the reaction (case a) and another is on the left-hand side (case b). Let us compare the Ni/ NiBi_3 interface in these two cases. The question is why in case a did NiBi not form (Duchenko and Dybkov) but in case b NiBi did (this study)? Clearly, the reason cannot be nucleation, since the local environment is the same at these two interfaces. In other words, if nucleation had been a problem in case a, it should also have been a problem in case b.

The reason for NiBi to be missing in case a is more likely to be purely kinetic. The interdiffusion coefficient in NiBi might be substantially lower than that in NiBi_3 . It has been shown by using numerical calculation that the phases with higher interdiffusion coefficients will grow faster than those with lower interdiffusion coefficients.¹² In extreme cases, the phases with higher interdiffusion coefficients will even grow at the expense of those with lower interdiffusion coefficients. This is

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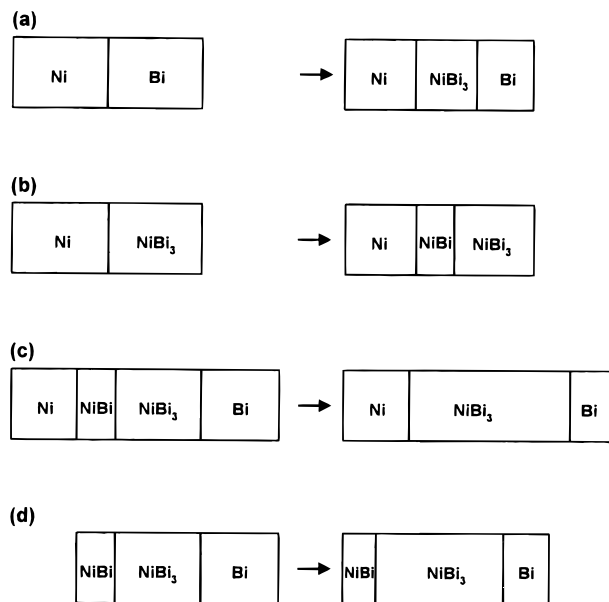


Figure 9. Schematic drawing showing the phase formation and disappearance in different diffusion couples. The local environment of the Ni/NiBi₃ interface in case a (on the right-hand side) is the same as that in case b (on the left-hand side). Case a was observed by Duchenko and Dybkov at 150–250 °C.^{5,6} Case b was observed in this study at 330–450 °C.

illustrated in Figure 9c. Here, an imaginary diffusion couple is formed by growing a Bi layer over the resulting diffusion couple formed in case b. If the Ni and Bi layers can be considered infinitely thick, the NiBi layer will shrink gradually with reaction time and eventually disappear completely. At the same time, NiBi₃ will grow. The final phase sequences of a and c are then the same. This phenomenon can be understood intuitively without resorting to numerical calculation, as outlined below. Since the interdiffusion coefficient of NiBi is orders of magnitude smaller than that of NiBi₃, NiBi can be considered a very effective diffusion barrier, blocking any atomic flux. Therefore, the diffusion couple on the left-hand side of Figure 9c does not “know” of the existence of the Ni layer to the left of NiBi. In other words, as long as NiBi still exists, this diffusion couple behaves like the one shown in Figure 9d. In this case, NiBi reacts with Bi to form NiBi₃, and therefore NiBi will shrink while NiBi₃ will grow. There is no published values for the interdiffusion coefficients of NiBi and NiBi₃, but the extrapolated k value for NiBi is 10³–10⁴ times smaller than k for NiBi₃ at 150–250 °C. The constant k has the same dimension as the interdiffusion coefficient and is considered a good indication of the values of interdiffusion coefficients.

In the present study, we did try to perform a diffusion couple study like the one illustrated in Figure 9c, but the Ni/NiBi/NiBi₃ diffusion couple from case b is very fragile and our experiment failed to produce useful results. Nevertheless, successful experiment similar to case c had been done by van Loo and Rieck.¹⁶ They reacted Ti with Al at 625 °C and found that only TiAl₃ formed, but at 625 °C Ti₃Al, TiAl, and TiAl₂ are also thermodynamically stable according to the Ti–Al binary phase diagram. Interestingly, when a Ti/TiAl₃ couple

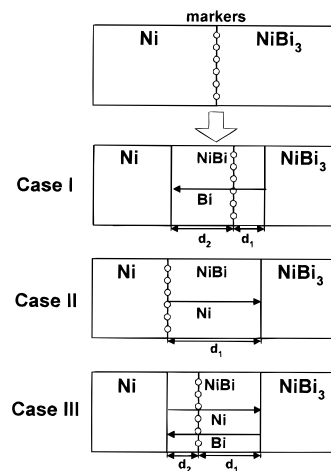


Figure 10. Schematic drawings showing the marker positions for three special cases. In case I, only Bi diffuses. In case II, only Ni diffuses. In case III, Ni flux to the right equals Bi flux to the left.

was reacted, Ti₃Al, TiAl, and TiAl₂ did form. However, when a layer of pure Al was joined on the outside of the remaining TiAl₃ layer of the above couple and then reacted, the three phases, Ti₃Al, TiAl, and TiAl₂, vanished completely in a few hours. The resulting configuration of the couple became Ti/TiAl₃/Al.

Next let us consider the dominant diffusing species in the reaction between Ni and NiBi₃. Since no actual diffusivity values are available in the literature, here we only consider the three special cases shown in Figure 10. Assuming the markers are placed at the original Ni/NiBi₃ interface before the reaction, let us consider where the markers will end up after the reaction. In case I, it is assumed that only Bi diffuses and the Ni intrinsic flux is zero. Here, the intrinsic flux denotes the atomic flux measured with respect to the lattice, not to a fixed outside reference point. Since Bi is the only diffusing species, the reaction at the NiBi/NiBi₃ interface is the decomposition of NiBi₃ into NiBi and Bi, i.e.



The 2 mol of Bi atoms released in eq 2 diffuse through the NiBi layer to the Ni/NiBi interface to react with 2 mol of Ni according to the following reaction:



Therefore, for the decomposition of every 1 mol of NiBi₃, 1 mol of NiBi forms at the NiBi/NiBi₃ interface (eq 2), and 2 mol of NiBi form at the Ni/NiBi interface (eq 3). The final marker position should then satisfy the following equation

$$d_2/d_1 = 2 \quad (\text{case I}) \quad (4)$$

where d_1 is the distance between the markers and the NiBi/NiBi₃ interface and d_2 is the distance between the Ni/NiBi interface and the markers (see Figure 10).

In case II, it is assumed that only Ni diffuses and the Bi intrinsic flux is zero. The reaction at the Ni/NiBi interface is the dissolution of Ni atoms into NiBi, i.e.



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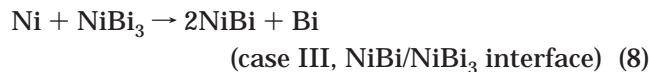
The dissolved Ni atoms diffuse through the NiBi layer to the NiBi/NiBi₃ interface to react with NiBi₃ according to the following reaction:



Therefore, NiBi only forms at the NiBi/NiBi₃ interface. The final marker position should then satisfy the following equation:

$$d_2/d_1 = 0 \quad (\text{case II}) \quad (7)$$

In case III, it is assumed that the Ni flux to the right through the NiBi layer equals the Bi flux to the left. This case corresponds to the combination of case I and II. The reaction at the NiBi/NiBi₃ interface is that, for every 1 mol of Ni diffusing through, 1 mol of NiBi₃ will be reacted to form 2 mol of NiBi and 1 mol of free Bi, which will then diffuse toward the Ni/NiBi interface. The reaction can be written as



The 1 mol of Bi released in eq 9 will react with Ni at the Ni/NiBi interface, i.e.



Note that in eqs 8 and 9, for every 1 mol of Ni diffusing to the right, 1 mol of Bi diffuse to the left. From eqs 8 and 9, one obtains

$$d_2/d_1 = 0.5 \quad (\text{case III}) \quad (10)$$

In summary, d_2/d_1 has the extreme values of 2 (case I, only Bi diffuses) and 0 (case II, only Ni diffuses). In reality, both Ni and Bi will diffuse, so $0 < d_2/d_1 < 2$. In the special case where the magnitude of the Ni flux equals that of the Bi flux (case III), $d_2/d_1 = 0.5$.

From Figure 5, taking the crack as an internal marker, one can find that $d_2/d_1 \approx 1-1.5$. Observation of other samples at 370 °C also revealed that the ratio d_2/d_1 is in this range. Such a d_2/d_1 ratio indicates that the reaction of Ni and NiBi₃ is between cases I and III.

In other words, at 370 °C both Ni and Bi diffuse, but the Bi flux is larger. More detailed analysis, which is omitted here for brevity, shows that when $d_2/d_1 = r$,

$$\frac{\text{magnitude of Bi flux}}{\text{magnitude of Ni flux}} = \frac{3r}{2-r} \quad (11)$$

From eq 11, we know that if $r = d_2/d_1 = 1-1.5$, then

$$3 < \frac{\text{magnitude of Bi flux}}{\text{magnitude of Ni flux}} < 9 \quad (\text{at } 370 \text{ }^\circ\text{C}) \quad (12)$$

In other words, the Bi flux is about 3–9 times greater than that of the Ni flux at 370 °C. The intrinsic diffusivities for Ni and Bi in NiBi may have different activation energies, and thus different temperature dependence. Therefore, at other temperatures, the values in eq 12 do not have to be the same.

Conclusions

The intermetallic compound NiBi₃ has very inferior mechanical properties. It is both soft and brittle. Formation of NiBi₃ in a solder joint will seriously deteriorate the strength of the joint and should be avoided. Unfortunately, in the reaction between Ni and Bi, NiBi₃ is the only phase formed. However, it is possible to avoid the formation of a certain intermetallic compound by adding an alloy element that has stronger affinity toward the substrate material.¹⁷ In other words, the approach is to find an element that will form a thermodynamically more favorable compound. Finding the proper alloy elements to serve such purpose is an important part of designing solders.

The reason for the other thermodynamically stable phase NiBi to be missing is more likely to be purely kinetic, not due to difficulty in nucleation. It is probably because the interdiffusion coefficient of NiBi is much smaller than that of NiBi₃. This observation also suggests a second possible approach to avoid the formation of NiBi₃, i.e. adding an alloy element that can form an intermetallic compound that has a diffusivity greater than that of NiBi₃.

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