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Interfacial Reaction between Sn-Bi Alloy and Ni Substrate

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Interfacial reactions between Sn-Bi alloys of different compositions and Ni substrates at 423 K for different durations were investigated. Only one interfacial phase, Ni_3Sn_4, was detected despite the existence of several other intermetallic compounds (IMCs) in Ni-Sn and Ni-Bi binary systems. This observation (only Ni_3Sn_4 was formed at the interface) was explained as a combination of the driving force for formation of the IMC and diffusion of Ni. The change of Ni_3Sn_4 layer thickness as a function of annealing time, which obeys a parabolic rule, was further confirmed. The thickness of Ni_3Sn_4 was also found to decrease with increasing Bi content in the Sn-Bi alloy.

Key words: Interfacial reaction, driving force, Sn-Bi alloy, Ni substrate

INTRODUCTION

Pb-Sn solder has been widely used in the electronics industry for packaging applications due to its low cost and excellent mechanical properties, wetting capability, and fatigue resistance. However, because Pb is harmful to both the environment and human health, intensive efforts have been conducted to search for a novel Pb-free solder as a replacement for Pb-Sn solder. So far, many different solder alloys have been proposed as potential Pb-free solder candidates; the most promising ones so far have been Sn-based alloys.[1–5] Among these alloys, Sn-Bi alloy, which has a low melting point, has been developed for step-by-step soldering processes and is suitable for soldering temperature-sensitive components and substrates. Moreover, when compared to the Sn-Pb solder, Sn-Bi solder offers a higher strength and superior creep resistance. Thus, Sn-Bi solder is an important candidate for Pb-free solder.

During the soldering process, solder alloys melt and then react with substrate to form IMCs at the joint interface. Fabrication of a reliable solder joint in a microelectronic package depends partly on the formation of IMCs at the interface, and IMCs play an important role in controlling the mechanical and electric properties.[6,7] It is necessary to understand the factors that govern the interfacial reaction between solder and substrate. In modern microelectronics packages, Ni coats are often plated as an under bump metallurgy (UBM) layer on the substrate prior to soldering.[8] Thus, the interfacial reaction between Ni and solder is becoming more and more interesting to materials scientists.

Several studies[9–14] have reported on the interfacial reaction between Sn-Bi eutectic alloy and Ni substrate. Kang et al.[9] studied the interfacial reaction between liquid Sn-Bi eutectic alloy and Ni substrate at 443 K for 20 min. Chen et al.[10] investigated the interfacial reaction between solid Sn-Bi eutectic alloy and Ni substrate at different temperatures for various reaction times. Recently, Young et al.[11] reported the interfacial reaction for electroplated Ni and electroless Ni with Sn-Bi eutectic alloy annealing at 418 and 453 K. In their work, [9–14] only Ni_3Sn_4 was found as a product of the interfacial reaction at each reaction temperature for various reaction times. This seems unreasonable, as two IMCs exist in the Ni-Bi binary system (NiBi and $NiBi_3$) and three (Ni_3Sn, Ni_3Sn_2, Ni_3Sn_4) in the Ni-Sn binary system according to the Ni-Bi and Ni-Sn binary phase diagram.[15] However, why only Ni_3Sn_4 was formed has not been reported. To better understand the kinetics of the interfacial reaction, diffusion couples of Sn-Bi alloys and Ni substrate were prepared and annealed at 423 K for specified times and the reaction products were studied.

EXPERIMENTAL PROCEDURES

Three Sn-Bi alloys (15 wt.%, 50 wt.%, and 70 wt.% Bi) used in this work were prepared from high-purity materials (Sn, 99.999%; Bi, 99.999%). Weighed amounts of Bi and Sn were encapsulated in a quartz tube filled with argon and the tubes were placed in the furnace at 873 K for 1 h. After melting, the tubes were shaken several times and removed

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from the furnace prior to ice-water quench. Ingots of the Sn-Bi alloys together with an acetone-cleaned pure Ni slab (99.99% Ni, 15 mm × 7 mm × 3 mm) were encapsulated in an argon-filled quartz tube. The tubes were then placed in a furnace at 573 K for 30 min. in order to melt the Sn-Bi alloy and immerse the Ni slab. Afterward, the tubes were quenched in ice-water to form reaction couples. Finally, the Sn-Bi/Ni couples were heated at 423 K for various durations, removed from the furnace, and quenched into ice-water.

The reaction couples were mounted by epoxy and polished mechanically. The interfacial reaction zone for each sample was examined using an optical microscope and scanning electron microscopy (SEM). The composition of the interfacial reaction layer was determined quantitatively by the electron probe microanalysis (EPMA) on a JEOL JXA-8800R (JEOL, Tokyo, Japan) microprobe under operating conditions of 20 kV, 20 nA current, and 40° take-off angle. Measurements of layer thickness were performed directly on the photomicrographs of the cross-sections of the interfacial reaction zone. Each measurement was an average value in the selected region. Because the thickness of the layer varied from place to place at the interface, each data reported was an average of five measurements at different regions in order to obtain a self-consistent result.

RESULTS AND DISCUSSION

The interfacial reaction zones of all samples, including the no-aging reaction couples at 423 K and those aged for different times at 423 K, were examined. Figure 1 illustrates the representative back-scattered electron (BSE) images of the Sn-Bi/Ni couples at 423 K for different times. Only one reaction layer was observed besides the parental materials. Composition profiles along a line perpendicular to the interface of the couples were measured by EPMA. One example of the composition profile for the Sn-15wt.%Bi/Ni couple is shown in Fig. 2. According to EPMA, the reaction layer appearing at the interface in Fig. 1 contains 55.8–58.4 at.% Sn, which corresponds to Ni_3Sn_4 without any Bi

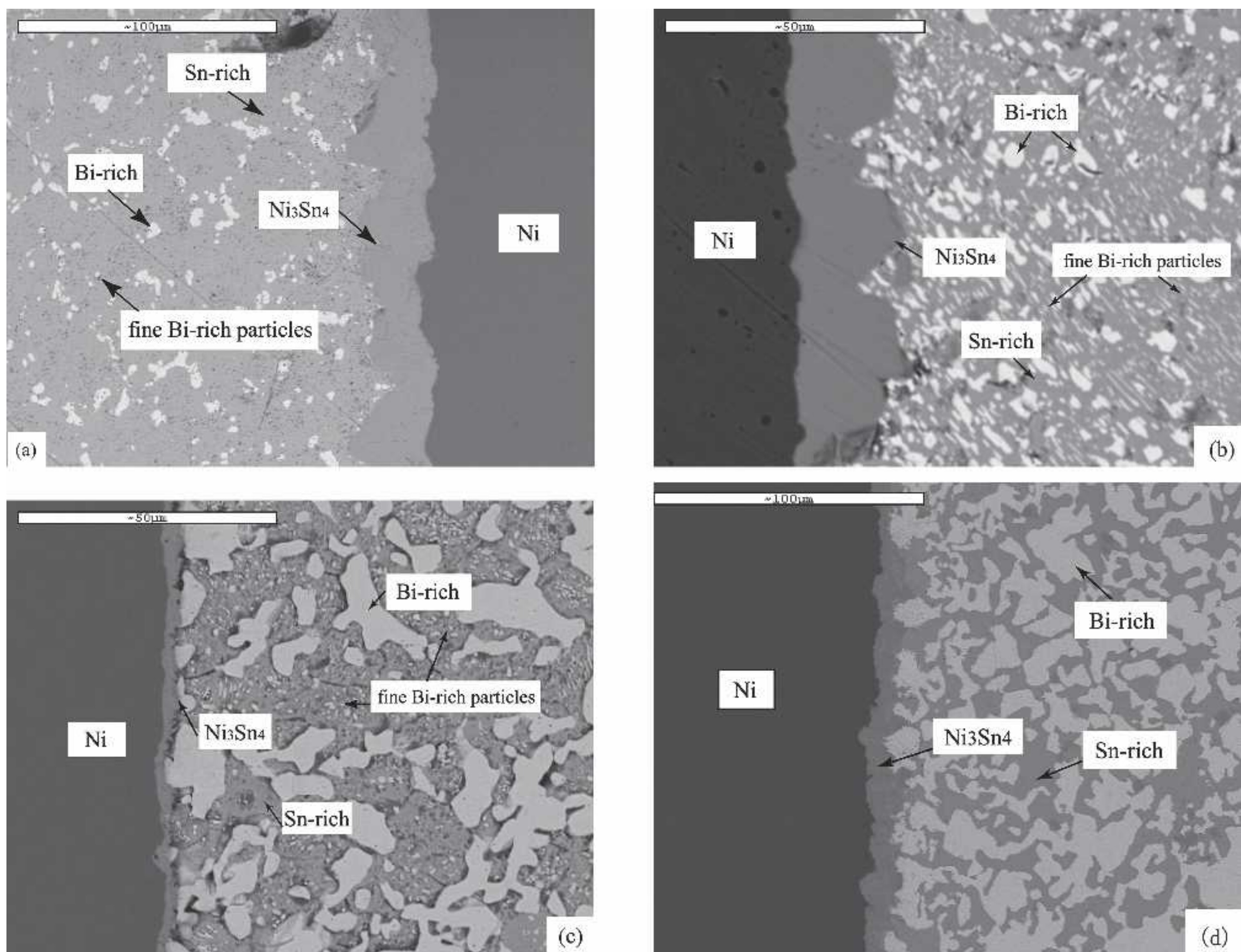

Fig. 1. Back-scattered electron images of interfacial reactions for the Sn-Bi/Ni couples at 423 K for different times: (a) Sn-15wt.% Bi/Ni for 200 h; (b) Sn-15wt.% Bi/Ni for 740 h; (c) Sn-50wt.% Bi/Ni for 200 h (sample was etched); (d) Sn-70wt.% Bi/Ni for 740 h.

dissolved. In addition to the Ni substrate, other phases in the Sn-Bi matrix alloys were also determined. The bright phase and the gray phase are Bi-rich (~98.6 at.% Bi) and Sn-rich (~97.2 at.% Sn) solid solutions, respectively.

Note that the Bi-enriched bright phase (Fig. 1) can appear as either fine particles or irregular bulk forms. Moreover, fine Bi particles exist in the Sn-15wt.%Bi/Ni and Sn-50wt.%Bi/Ni couples, while bulk Bi (in irregular forms) exists in the Sn-70wt.%Bi/Ni couple. This bright phase should be formed from the Sn-Bi matrix because only trace amounts of Ni are being detected (by EPMA) in the samples. To form the Ni_3Sn_4 phase, Sn must participate such that free Bi is left over in the Sn-Bi alloy during aging, and the concentration of the remaining free Bi must form a composition gradient against the interface and subsequently form fine particles in the matrix. The amount of these fine Bi particles increased with aging time (see Fig. 1a and b). However, in the Sn-70wt.%Bi/Ni couple, bulk Bi crystallizes from the Sn-Bi liquid on quenching as its composition falls within the co-existence phase field of liquid and Bi-based solid solution at 423 K. When this alloy was kept at 423 K, Bi appeared as irregular, bulky, primary crystals. Fine Bi particles and bulk Bi were also observed by Chen et al.[10] when they investigated the interfacial reaction between solid Sn-Bi eutectic alloy and Ni substrate.

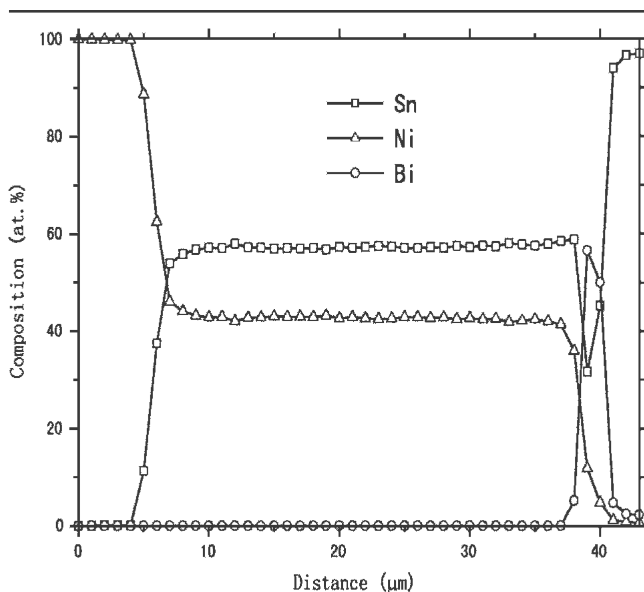

Fig. 2. Composition profiles across the reaction zone of the Sn-15wt.% Bi/Ni couple annealed at 423 K for 740 h.

The layer thickness of IMC formed in the couples can generally be expressed by the simple parabolic equation as follows:

$$d = d_0 + kt^n \quad (1)$$

where d_0 is the starting thickness of IMC, d is the average thickness at the time t, k is the growth rate constant, and n is the time exponent. This equation can be converted into a logarithmic expression as:

$$\ln(d - d_0) = n \ln t + \ln k \quad (2)$$

The time exponent (n) and the growth rate constant (k) are obtained from the slopes and intercepts of curves of $\ln(d - d_0)$ against ln t. Table I lists the time exponents and growth rate constants for different reaction couples at 423 K determined by the linear regression analysis using Eq. 2. As we can see in Table I, the time exponents (n) are approximated to 0.5, and most linear correlation coefficients (R^2) of these plots were greater than 0.98. Figure 3 illustrates changes of the average thickness of Ni_3Sn_4 versus square of time for all couples treated at 423 K. The average thickness of Ni_3Sn_4 at 423 K is likely increasing linearly with the square root of aging time. This indicates that the growth of Ni_3Sn_4 is controlled by a diffusion mechanism, in agreement with the literature.[9–14]

Moreover, the average thickness of Ni_3Sn_4 decreases with increasing Bi content (see Fig. 3). For example, after being heated at 423 K for 740 h, Ni_3Sn_4 is 9.83 μm thick for Sn-70wt.% Bi/Ni and 31.98 μm thick for Sn-15wt.%Bi/Ni reaction couples. The likely reason for thickness of Ni_3Sn_4 decreasing with increasing Bi content is that the supply of Sn necessary for the formation of Ni_3Sn_4 is inversely proportional to Bi content.

We also noted that the thickness of Ni_3Sn_4 in all couples is greater than zero, even when the reaction time is extrapolated to zero (Fig. 3). The reason behind this is that the Sn-Bi alloys melted at 573 K and reacted with Ni substrate for 30 min. during the preparation of the Sn-Bi/Ni couples, as already mentioned in Experimental Procedures. Consequently, an IMC layer has formed at the interface and grew before later heat treatment at 423 K.

Five stable intermediate phases, namely, Ni_3Sn, Ni_3Sn_2, Ni_3Sn_4, NiBi, and $NiBi_3$, exist at room temperature in Ni-Sn and Ni-Bi binary systems.[15] However, only the Ni_3Sn_4 phase is formed as the IMC at

Table I. Calculated Square of Growth Rate Constant (k^2), Linear Correlation Coefficient (R^2), and Time Exponent (n) in the Present Work

Alloy/substrate (intermetallic)	Temperature (K)	k^2 ($\times 10^{-17}$ m^2/sec)	R^2	n
Sn-15wt.%Bi/Ni (Ni_3Sn_4)	423	24.964	0.99	0.501
Sn-50wt.%Bi/Ni (Ni_3Sn_4)	423	4.624	0.99	0.492
Sn-70wt.%Bi/Ni (Ni_3Sn_4)	423	3.249	0.98	0.498

the interface between Sn-Bi alloys and Ni substrate according to the literature[9–14] and our present work. Two widely accepted explanations for this phenomenon have been proposed.[10,16–18] One indicated that the absent phases have substantially lower diffusion coefficients compared to the present phases. Due to the lack of the diffusion data of IMCs in Ni-Sn and Ni-Bi binary systems, this argument is not reasonable enough to explain this phenomenon. Another one showed that the absent phases have difficulty in nucleation with smaller driving forces available and larger activation energies for nucleation. However, this hypothesis cannot predict which phase would form first if two phases in a system have similar driving forces for formation. In a word, these theories emphasized only one factor and neglected others for the interfacial reaction.[10,16–18] They cannot explain the formation of IMCs at the interface.

In general, formation of a new phase at an interface is dependent not only on nucleation but also on growth rate. This work has attempted to combine the two models mentioned above and develop a new model to better explain the experimental phenomenon.

Phase transformation occurring in a closed system must satisfy one condition, i.e., the Gibbs free energy of the system shall decrease. Only if the driving force of the phase reaction is positive can the phase form accordingly. However, this is not necessary to ensure that the phase having the larger driving force will grow faster. The phase formed at the interface is related to the diffusion of the element involved. If one phase has a positive driving force and the diffusivities of relevant elements are high enough, the phase can form and grow faster. We shall use this method to study and predict the formation of Ni_3Sn_4 at the interface in Sn-Bi/Ni couples.

No ternary phase in the Sn-Bi-Ni system has yet been reported. Due to the lack of ternary thermodynamic parameters, the Sn-Bi-Ni system was extrapolated directly using the available thermodynamic parameters of the constituent binary systems[19–21] as represented in Fig. 4. According to the approach suggested by Lee et al.,[22] the driving forces for all possible IMCs in the Sn-Bi-Ni ternary system are calculated using Thermo-Calc software based on the CALPHAD method.[23,24] The calculated results are listed in Table II. It is clear that only Ni_3Sn_4 and Ni_3Sn_2 have positive driving forces while other phases, including the Ni-Bi binary IMCs, possess negative driving forces. Therefore, it can be concluded that either Ni_3Sn_4 or Ni_3Sn_2 could form at the interface in the Sn-Bi/Ni couples.

Which one will form first, Ni_3Sn_4 or Ni_3Sn_2? Let us analyze the diffusion of each element in different phases. Firstly, Ni diffuses much faster in liquid Sn-Bi alloy than do Sn and Bi in solid Ni. Therefore, the IMC formed at the interface must be formed at the side next to the Sn-Bi matrix. This indicates that transportation of Ni determines which phase

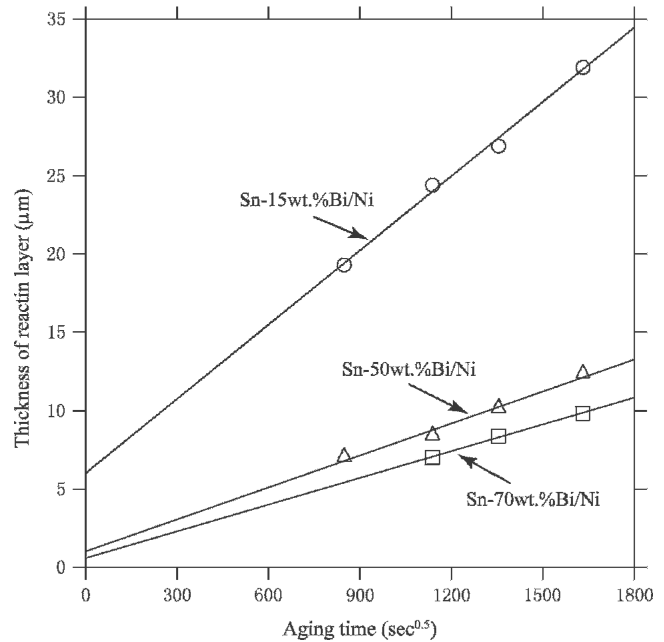

Fig. 3. Relationship between the thicknesses of reaction layer and aging time at 423 K.

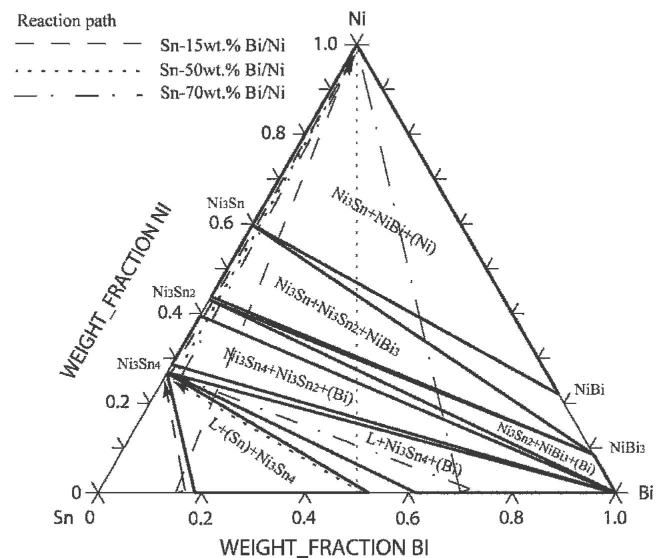

Fig. 4. Calculated isothermal section of the Sn-Bi-Ni ternary system at 423 K superimposed with the schematic reaction paths of the Sn-15wt.%Bi/Ni, Sn-50wt.%Bi/Ni, and Sn-70wt.%Bi/Ni reaction couples.

would form first. In Fig. 4, the straight lines that connect Ni (top corner) and the initial composition of Sn-Bi alloys intersect with various tie-lines and/or tie-triangles involving Ni_3Sn_4 and Ni_3Sn_2 in the Sn-Bi-enriched part. At the beginning of the interfacial reaction, composition of the Sn-Bi alloy could deviate from the initial value at the interface because Ni dissolving into Sn-Bi alloy and the diffusion of Sn and Bi into Ni is neglected. The layer adjacent to the Ni substrate becomes supersaturated with increasing time as a result of Ni dissolving continuously prior to formation of IMC in this part of the Sn-Bi alloys. The formation of Ni_3Sn_4 requires less Ni than formation of Ni_3Sn_2. This

Table II. Calculation of Driving Forces for Formation of IMCs for Various Diffusion Couples at 423 K Using Thermo-Calc Software[23]

Couple	Phase	Status*	Driving force (ΔG, J/mol)	Mole fraction
Sn-15wt.%Bi/Ni	FCC(Ni)	Entered	0	0.056
	BCT(Sn)	Entered	0	0.944
	Liquid	Entered	−150.33	0
Sn-50wt.%Bi/Ni	Rhombohedral (Bi)	Dormant	−1231.03	0
	Ni_3Sn_4	Dormant	6006.73	0
	Ni_3Sn_2	Dormant	3146.96	0
	Ni_3Sn	Dormant	−8431.58	0
	$NiBi_3$	Dormant	−6635.36	0
	NiBi	Dormant	−16892.00	0
	FCC(Ni)	Entered	0	0.0460
	BCT(Sn)	Entered	0	0.0004
	Liquid	Entered	0	0.9536
	Rhombohedral (Bi)	Dormant	−676.21	0
	Ni_3Sn_4	Dormant	6082.94	0
	Ni_3Sn_2	Dormant	3258.80	0
	Ni_3Sn	Dormant	−8253.98	0
	$NiBi_3$	Dormant	−6153.52	0
	NiBi	Dormant	−16485.10	0
Sn-70wt.%Bi/Ni	FCC(Ni)	Entered	0	0.058
	Rhombohedral (Bi)	Entered	0	0.215
	Liquid	Entered	0	0.727
	BCT(Sn)	Dormant	−331.69	0
	Ni_3Sn_4	Dormant	6634.26	0
	Ni_3Sn_2	Dormant	4083.13	0
	Ni_3Sn	Dormant	−6938.51	0
	$NiBi_3$	Dormant	−5163.93	0
	NiBi	Dormant	−15185.09	0

Note: "Entered" means that the phases are included in the calculation; "Dormant" means that the phases are not considered in the calculation, but their driving forces for precipitation are calculated.

implies that the growth of Ni_3Sn_4 can become easier. Moreover, the driving force of Ni_3Sn_4 is greater, which provides a larger nucleation rate. If the interfacial energy of the IMC/matrix is independent of the composition of the IMC, then Ni_3Sn_4 should have a larger nucleation rate leading to quicker formation of Ni_3Sn_4. Thus, the present work is consistent with previously reported experimental results.[9–14]

In addition, it is of value to note if other phases can form at the interface. According to Fig. 4, we know that other IMCs, such as $NiBi_3$, would form at the interface at 423 K if the amount of Sn in Sn-Bi alloy were extremely small. This is consistent with the experimental result that $NiBi_3$ was formed only in the Sn-98wt.%Bi/Ni couple at 573 K, while Ni_3Sn_4 formed in the Sn-Bi/Ni couples with Bi content varying from 92 to 97.5 wt.%, as reported by Lee et al.[16] Figure 4 also illustrates the schematic reaction paths of the Sn-15% Bi/Ni, Sn-50% Bi/Ni, and Sn-70wt.% Bi/Ni reaction couples.

CONCLUSIONS

Interfacial reactions between different Sn-Bi alloys and Ni substrate at 423 K have been studied experimentally. EPMA measurement revealed that only the Ni_3Sn_4 intermetallic compound was formed at the interface; this was explained as a combined effect of driving forces of phase formation and diffusion of Ni. Growth of Ni_3Sn_4 is predominated by a diffusion-controlled mechanism. The thickness of Ni_3Sn_4 increases with aging time, and the growth rate of the Ni_3Sn_4 layer decreases with Bi content. Only if the Sn content in the Sn-Bi alloy is extremely small is formation of other IMCs in the Ni-Bi binary system possible in the Sn-Bi/Ni couple.

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