Interfacial Reactions in In-Sn/Ni Couples and Phase Equilibria of the In-Sn-Ni System

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The In-Sn-Ni alloys of various compositions were prepared and annealed at 160°C and 240°C. No ternary compounds were found; however, most of the binary compounds had extensive ternary solubility. There was a continuous solid solution between the Ni_3Sn phase and Ni_3In phase. The Sn-In/Ni couples, made of Sn-In alloys with various compositions, were reacted at 160°C and 240°C and formed only one compound for all the Sn-In alloys/Ni couples reacted up to 8 h. At 240°C, $Ni_{28}In_{72}$ phase formed in the couples made with pure indium, In-10at.%Sn and In-11at.%Sn alloys, while Ni_3Sn_4 phase formed in the couples made of alloys with compositions varied from pure Sn to In-12at.%Sn. At 160°C, except in the In/Ni couple, Ni_3Sn_4 formed by interfacial reaction.

Key words: Interfacial reactions, phase equilibria, In-Sn, Ni, lead-free solder

INTRODUCTION

Due to the possible ban on Pb usage in electronic products, efforts have been conducted to develop Pb-free solders to replace conventional Pb-Sn alloys.[1–4] Although there is no fixed timetable, Europe already has a call for the phase out of lead by January 1, 2004.[4] The In-Sn alloys, which have low melting points and better fatigue properties, are one of the promising Pb-free solder candidates.[1–3,5–9] Nickel and nickel alloys are commonly used in electronic products. They are frequently plated on copper in printed circuit boards and are used for lead frames as well. Knowledge of interfacial reactions between In-Sn alloys and Ni substrates and the phase equilibria of the In-Sn-Ni ternary system provides basic understanding of the In-Sn alloys and is important for their usage as solders in electronic products.

When In-Sn alloys are in contact with Ni, concentration gradients form at the interface. If the temperature is sufficiently high, diffusion occurs as a result of the concentration gradient or, more precisely, the chemical potential gradient. New concentration profiles of the elements develop after certain annealing times, and new phases form as well if the thermodynamic and kinetic conditions are appropriate. These kinds of reactions occurring at interfaces have been studied by many investigators.[10–15] The new concentration profiles could be either smooth or discontinuous and are closely related to the phase equilibria of the respective system.

Many investigators have studied the phase equilibria of In-Sn,[16,17] In-Ni,[18] and Sn-Ni,[19] which are the constituent binary systems of the ternary In-Sn-Ni systems. Besides the terminal solid solutions, β-In_3Sn and γ-$InSn_4$ solid phases exist in the In-Sn system.[16,17] The most promising In-Sn solders are based on the eutectic composition, In-48.3at.%Sn. Phase equilibria of the In-Ni system is much more complicated. Besides the two terminal-solid phases, there are eight stable-solid phases: Ni_3In, Ni_2In, ζ-NiIn, $Ni_{13}In_9$, NiIn, δ-NiIn, Ni_2In_3, and $Ni_{28}In_{72}$.[18] Three stable intermetallic phases, Ni_3Sn, Ni_3Sn_2, and Ni_3Sn_4, form in the Ni-Sn system.[19] Only very limited phase-equilibrium data of the In-Sn-Ni system are available.[20,21] A partial isothermal section at 550°C[20] and one isothermal section at 700°C[21] are found in the literature. A Ni_6InSn_5 ternary compound was reported.[21] Phase relationships are complicated due to the existence of a ternary compound, large ternary solubility of various binary compounds, and continuous solid solutions that form in some regions.

Studies have been conducted to determine the interfacial reactions between Sn and Ni.[22–28] All these

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studies found the formation of Ni_3Sn_4 phase. The other two stable compounds, Ni_3Sn and Ni_3Sn_2, were observed only in some reaction couples.[27] Very few results are available for the experimental determination of interfacial reactions between pure In and Ni,[9,24] probably due to the soft nature of In that makes metallographical examination difficult. Tseng et al.[9] found the formation of $Ni_{10}In_{27}$ when the reaction temperature was lower than 300°C and found Ni_2In_3 instead when the temperature was higher. In a recent assessment of the In-Ni phase diagram by Singleton and Nash,[18] no $Ni_{10}In_{27}$ phase was observed, and it is likely that the $Ni_{28}In_{72}$ phase is the $Ni_{10}In_{27}$ phase. Marinkovic and Simic[24] reported the existence of both phases in the thin film couples annealed at room temperature. Lin and Chen[8,29] studied the reaction of eutectic In-Sn with electroless Ni deposits. They found the formation of Ni_2In_3 at 60°C and both the Ni_2In_3 and $Ni_{10}In_{27}$ ($Ni_{28}In_{72}$) phases at 80°C. Since only very limited phase equilibrium and interfacial reaction data are available in the literature, this study experimentally determines the phase equilibria of the In-Sn-Ni system with focus on the In-Sn side and investigates the interfacial reactions between In-Sn alloys and Ni substrate. These results are of importance in the development of In-Sn alloys in the usage of solders.

EXPERIMENTAL PROCEDURES

Indium shots of 99.9 wt.% purity, Sn shots of 99.95 wt.% purity, and 0.25-mm-thick Ni foils of 99.98 wt.% purity were used in this study. Proper amounts of metallic elements were weighed and sealed in a quartz tube. The quartz capsule was placed in a furnace at 400°C and 1100°C for the preparation of In-Sn and In-Sn-Ni alloys, respectively. At these temperatures, the metallic elements became molten and mixed together. After homogenization for 2 h, the capsule was removed from the furnace and quenched in ice water.

The In-Sn-Ni alloys were annealed at 160°C and 240°C for 4 weeks. After annealing, the alloys were quenched and removed from the quartz tube. The alloys were cut into two pieces. One piece was mounted, polished, and metallographically examined by optical microscopy. Electron probe microanalysis (EPMA) was used for compositional analysis. The other piece was prepared for powder x-ray diffraction (XRD) analysis. An x-ray diffractometer was used with a 45 kV accelerating voltage, 40 mA current, and a 4°/min scanning rate.

The In-Sn alloys were used for the preparation of reaction couples. Proper amounts of In-Sn alloys were cut and encapsulated in a quartz tube with a piece of Ni foil of size 10 mm × 6 mm × 0.25 mm. The sample capsule was placed in a furnace at 160°C and 240°C. The In-Sn alloys used in this study were molten at these temperatures. The molten metal surrounded the Ni foil, and interfacial reactions occurred. Reaction time varied from 30 min to 8 h. The couples were removed from the furnace and quenched in ice water after a predetermined length of time.

The quenched specimen was carefully mounted and polished so that the cross section of the interface was exactly exposed. The interface was metallographically examined. Due to the very soft nature of indium alloys, the specimen was polished with very light force and constantly washed with ice water. For microstructural analysis, light etching for 2–10 sec was conducted with a solution made of 2 mL HCl + 5 mL HNO_3 + 93 mL H_2O. Compositions of the reaction layers were analyzed by using either EPMA or a scanning electron microscope with an energy dispersive spectrometer (EDS).

RESULTS AND DISCUSSION

Thirty-nine In-Sn-Ni alloys were prepared and analyzed in this study. Their nominal compositions are shown in Figs. 1 and 10 and Table I. Alloys 1–19 were annealed at 240°C, and alloys 20–39 were annealed at 160°C. Figure 2 is the microstructure of alloy 1 (In-70at.%Sn-20at.%Ni) annealed at 240°C for 3 weeks. A large dark faceted phase and a matrix containing at least two different phases can be observed. The composition of the darker phase determined using EPMA is In-56.67at.%Sn-32.68at.%Ni. The Ni_3Sn_4, γ-$InSn_4$, and Sn phases can be found in the XRD results, as shown in Fig. 3. Based on the microstructure, EPMA, and XRD analysis, the large dark phase is Ni_3Sn_4, and the matrix is a mixture of γ phase and Sn phase. Considering the fact that binary In-Sn alloys are all molten at 240°C, and the matrix has a fine structure, it is presumed that the matrix was liquid prior to quenching. Similar microstructures were found for alloys 2, 3, and 4. As summarized in Table I, it is concluded that the liquid phase and Ni_3Sn_4 phases are in equilibrium at 240°C for alloys 1–4.

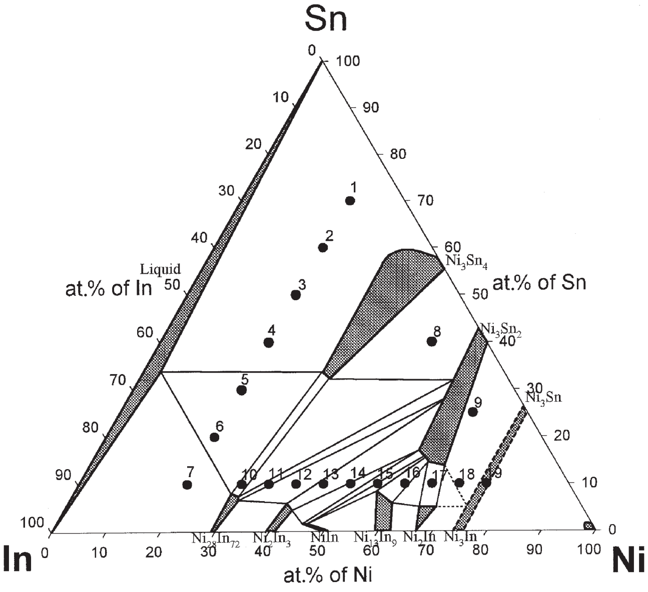


Fig. 1. The isothermal section of the In-Sn-Ni ternary system at 240°C superimposed with the nominal compositions of alloys examined in this study.

Table I. Nominal Compositions and Phase Identification of the Alloys Examined in This Study

ISN Number	Constitution (At.%) In	Sn	Ni	Phase Examination
1	10	70	20	Liquid, Ni_3Sn_4
2	20	60	20	Liquid, Ni_3Sn_4
3	30	50	20	Liquid, Ni_3Sn_4
4	40	40	20	Liquid, Ni_3Sn_4
5	50	30	20	Liquid, Ni_3Sn_4, $Ni_{28}In_{72}$
6	60	20	20	Liquid, Ni_3Sn_4, $Ni_{28}In_{72}$
7	70	10	20	Liquid, $Ni_{28}In_{72}$
8	10	40	50	Ni_3Sn_4, Ni_3Sn_2
9	10	25	65	Ni_3Sn_2, Ni_3Sn
10	60	10	30	Ni_3Sn_4, $Ni_{28}In_{72}$
11	55	10	35	Ni_3Sn_2, $Ni_{28}In_{72}$
12	50	10	40	Ni_3Sn_2, $Ni_{28}In_{72}$, Ni_2In_3
13	45	10	45	Ni_3Sn_2, Ni_2In_3
14	40	10	50	Ni_3Sn_2, Ni_2In_3, NiIn
15	35	10	55	Ni_3Sn_2, NiIn, $Ni_{13}In_9$
16	30	10	60	Ni_3Sn_2, $Ni_{13}In_9$
17	25	10	65	Ni_3Sn_2, Ni_2In
18	20	10	70	Ni_3Sn_2, $Ni_3(Sn,In)$
19	15	10	75	$Ni_3(Sn,In)$
20	10	10	80	$Ni_3(Sn,In)$, Ni
21	15	10	75	$Ni_3(Sn,In)$
22	20	10	70	Ni_3Sn_2, $Ni_3(Sn,In)$
23	25	10	65	Ni_3Sn_2, Ni_2In
24	30	10	60	Ni_3Sn_2, $Ni_{13}In_9$
25	35	10	55	Ni_3Sn_2, NiIn, $Ni_{13}In_9$
26	40	10	50	Ni_3Sn_2, Ni_2In_3, NiIn
27	45	10	45	Ni_3Sn_2, Ni_2In_{72}, Ni_2In_3
28	50	10	40	Ni_3Sn_2, $Ni_{28}In_{72}$, Ni_2In_3
29	55	10	35	Ni_3Sn_2, $Ni_{28}In_{72}$
30	60	10	30	Ni_3Sn_4, $Ni_{28}In_{72}$
31	10	40	50	Ni_3Sn_4, Ni_3Sn_2
32	10	25	65	Ni_3Sn_2, Ni,Sn
33	30	25	45	Ni_3Sn_4, Ni_3Sn_2, $Ni_{28}In_{72}$
34	30	20	10	Ni_3Sn_2, $Ni_{28}In_{72}$
35	2	88	10	Sn, Ni_3Sn_4
36	10	80	10	$InSn_4$, Ni_3Sn_4
37	15	75	10	$InSn_4$, Ni_3Sn_4
38	25	65	10	Liquid, $InSn_4$, Ni_3Sn_4
39	40	50	10	Liquid, Ni_3Sn_4

Figure 4 is the microstructure of alloy 6 (In-20at.%Sn-20at.%Ni) annealed at 240°C for 3 weeks. Three different kinds of phase regions can be observed, i.e., a dark phase, a gray phase, and a bright continuous phase. Based on the XRD and compositional analysis, four phases, In, β, Ni_3Sn_4, and $Ni_{28}In_{72}$, are found. Compositional analysis of the dark and gray phases using EPMA indicates that the dark phase is the Ni_3Sn_4 phase, while the gray phase is the $Ni_{28}In_{72}$ phase. Since four phases cannot exist at 240°C for a ternary alloy, the matrix-phase region was liquid prior to quenching. The indium phase precipitated from the liquid phase first during solidification, and then the β phase formed by a peritectic reaction. Similar results were found for alloy 5. The liquid phase, Ni_3Sn_4 phase, and $Ni_{28}In_{72}$ phase existed in alloys 5 and 6 annealed at 240°C, while the liquid phase transformed into In and β phases during quenching.

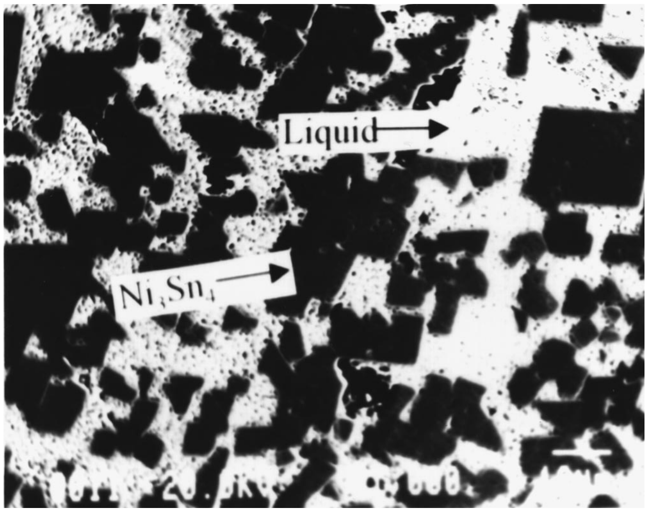


Fig. 2. The microstructure of alloy 1 (In-70at.%Sn-20at.%Ni) annealed at 240°C for 3 weeks.

The microstructure of alloy 10 (In-10at.%Sn-30at.%Ni) annealed at 240°C for 4 weeks is shown in Fig. 5. Two phases are observed. The darkest regions are voids. The composition of the brighter phase is In-7.89at.%Sn-30.32at.%Ni and that of the darker phase is In-35.37at.%Sn-33.62at.%Ni. The compositional determinations and XRD results indicate that the brighter phase is the $Ni_{28}In_{72}$ phase and the darker phase is the Ni_3Sn_4 phase. Figure 6 is the optical micrograph of alloy 11 (In-10at.%Sn-35at.%Ni). Compositions of the two phases are In-7.33at.%Sn-30.54at.%Ni and In-14.89at.%Sn-50.12at.%Ni. They are $Ni_{28}In_{72}$ and Ni_3Sn_2 phases, respectively. Based on the experimental results determined in this study and the phase equilibria information of the three constituent-binary systems,[17–19] the isothermal section of the In-Sn-Ni ternary system at 240°C proposed is shown in Fig. 1. Burkhardt and Schubert[20] studied the Ni-rich corner of the In-Sn-Ni system and suggested there should be a continuous solid solution between the Ni_3Sn phase and the Ni_3In phase at 550°C. A similar phase relationship, i.e., a continuous solid solution between Ni_3Sn and Ni_3In, is proposed. However, a continuous solid solution at high temperature does not guarantee the existence of one at lower temperature. Dash lines are, thus, used in the phase boundary in this region.

Figure 7 is the EPMA-BEI (back-scattered electron image) micrograph of alloy 35 (In-88 at.% Sn-10 at.% Ni) annealed at 160°C for 4 weeks. Two phases can be observed. Compositional analysis and XRD results indicate that the dark phase is the Ni_3Sn_4 phase and the bright phase is the Sn phase. A two-phase microstructure can be found for alloy 37 (In-75at.%Sn-10at.%Ni) as well. The XRD and compositional analysis indicate the dark phase is the Ni_3Sn_4 phase, while the continuous phase is the γ-$InSn_4$ phase. At 240°C, all the In-Sn alloys are molten; the most significant difference at 160°C is both solid and liquid can be found for the In-Sn alloys depending

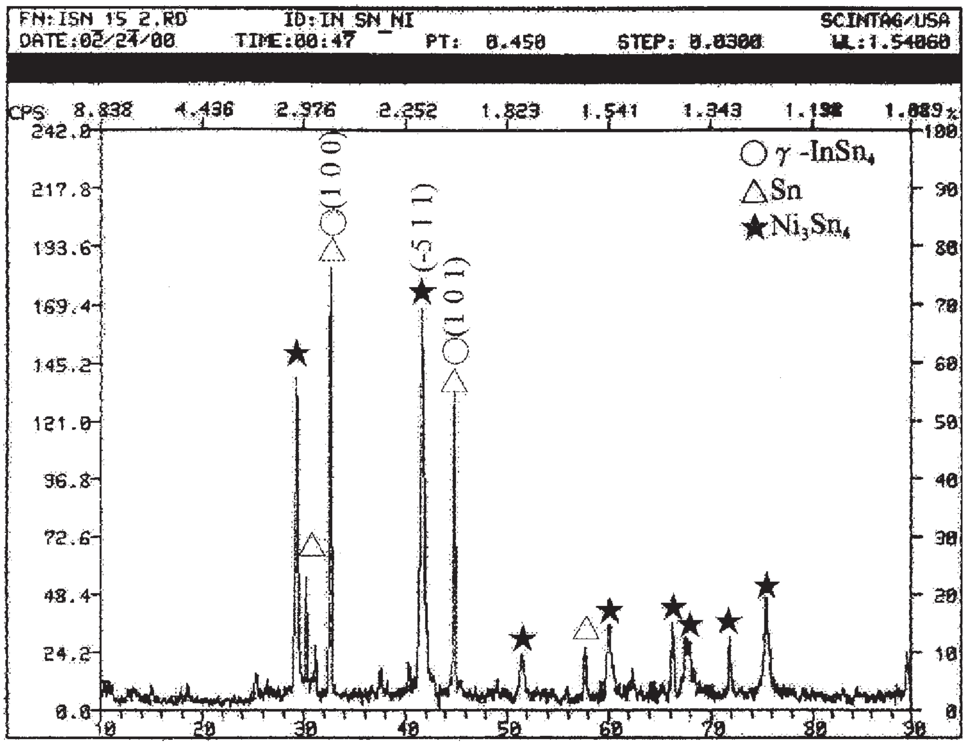


Fig. 3 The XRD pattern of alloy 1.

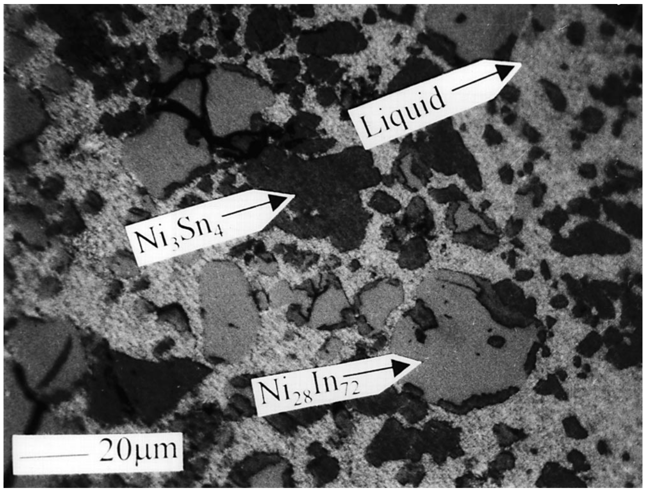


Fig. 4. The microstructure of alloy 6 (In-20at.%Sn-20at.%Ni) annealed at 240°C for 3 weeks.

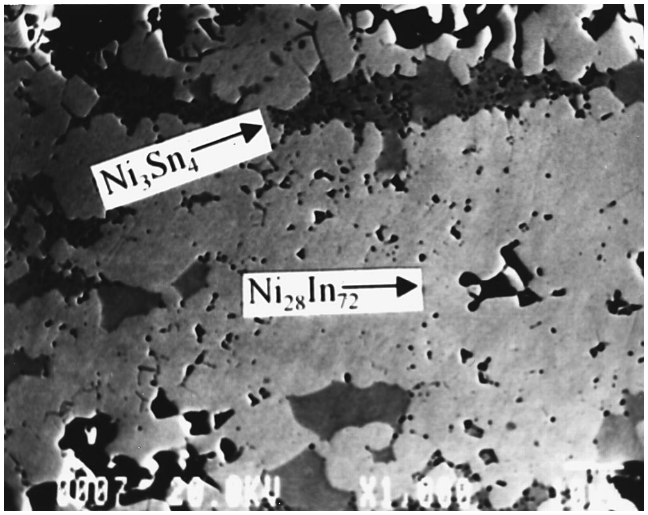


Fig. 5. The microstructure of alloy 10 (In-10at.%Sn-30at.%Ni) annealed at 240°C for 4 weeks.

upon their compositions. Only solid phases are stable for alloys 16 and 18 annealed at 160°C. Figure 8 is the micrograph of alloy 38 (In-65at.%Sn-10at.%Ni). A dark phase region, a bright phase region, and a fine-structure region can be observed. The XRD and compositional analysis indicate that the dark phase is the Ni_3Sn_4 phase, and the bright phase is the γ-$InSn_4$ phase. The two-phase mixture region was liquid and transformed into γ-$InSn_4$ phase and β-In_3Sn phase during quenching. Figure 9 is the micrograph of alloy 39 (In-50at.%Sn-10at.%Ni). The large phase is the primary Ni_3Sn_4 phase. The fine-structure region was the liquid-phase region at 160°C and transformed into γ-$InSn_4$ phase and β-In_3Sn phase during quenching. Figure 10 is the isothermal section at 160°C proposed from this study.

Bhargava and Schubert[21] determined the isothermal section of the In-Sn-Ni at 700°C, and they found there was another continuous solid solution between Ni_3Sn_2 phase and Ni_3In_2 phase in addition to the Ni_3Sn-Ni_3In solid solution, $Ni_3(Sn,In)$. A recent phase-diagram assessment of the Ni-In system[18] does not show the Ni_3In_2 phase at lower temperature. It is likely that the Ni_3In_2 phase is the ζ phase, which is only stable at a higher temperature. The structures of the Ni_3Sn_2[19] and $Ni_{13}In_9$[18] have not yet been determined; however, if there is a continuous

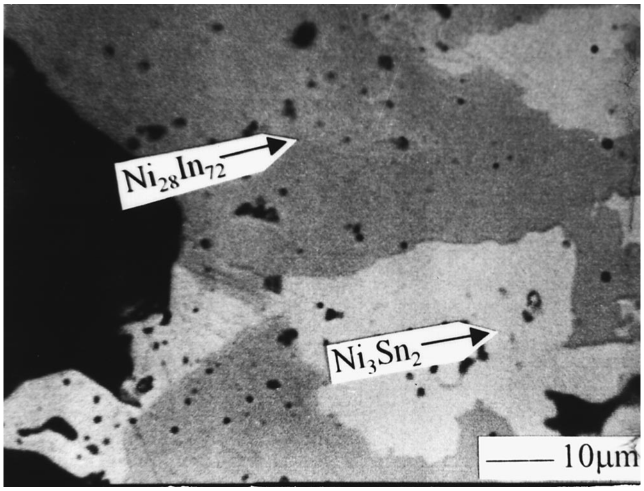


Fig. 6. The microstructure of alloy 11 (In-10at.%Sn-35at.%Ni) annealed at 240°C for 4 weeks.

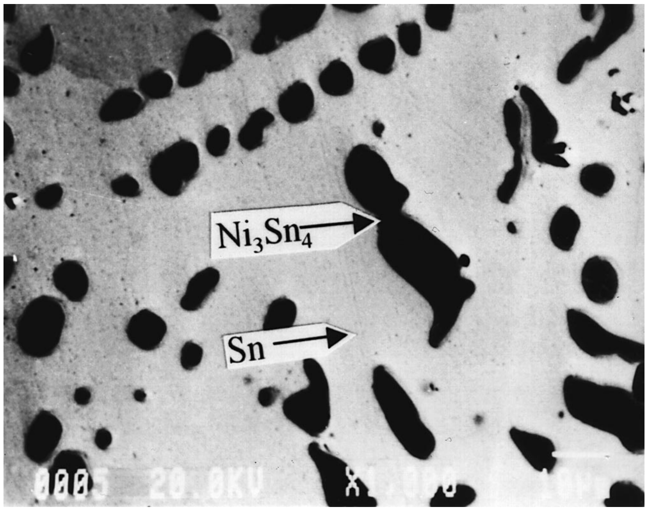


Fig. 7. The microstructure of alloy 35 (In-88at.%Sn-10at.%Ni) annealed at 160°C for 4 weeks.

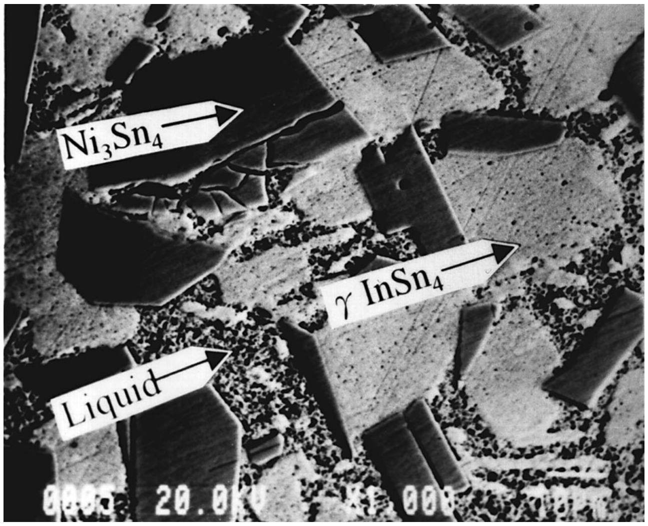


Fig. 8 The microstructure of alloy 38 (In-65at.%Sn-10at.%Ni) annealed at 160°C for 4 weeks.

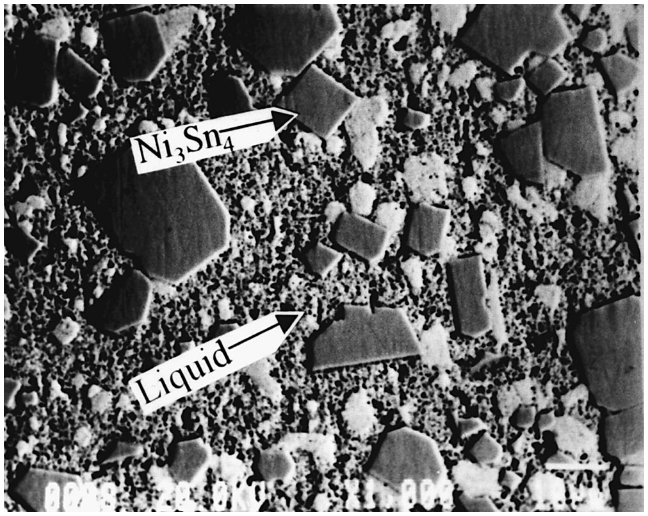


Fig. 9 The microstructure of alloy 39 (In-50at.%Sn-10at.%Ni) annealed at 160°C for 4 weeks.

solid solution between the two phases, their phase structures must be identical. Without further evidence showing that there is a phase in the Ni-In system with a Ni_3Sn_2 phase structure, it is not likely there is a continuous solid solution between Ni_3Sn_2 phase and $Ni_{13}In_9$ phase. Bhargava and Schubert also proposed the formation of a ternary compound, Ni_6InSn_5, at 700°C. In addition to the phase equilibria specimens mentioned above, several other specimens of compositions near Ni_6InSn_5 were prepared and examined; however, preliminary results indicate no evidence of the ternary compound either at 240°C or 160°C.

There are two other phases, In_3Sn and $InSn_4$, in the 700°C isothermal section proposed by Bhargava and Schubert.[21] This study did not find these two phases either. A recent phase-diagram assessment of the binary In-Sn system[16,17] indicates that all the In-Sn alloys are completely molten at temperatures higher than the melting point of Sn at 232°C, and there will be no stable solid compounds at 700°C. Bhargava and Schubert mentioned these two phases formed during solidification. However, if these two phases were not stable at 700°C, they should not appear in the isothermal section at 700°C. As shown in Fig. 1, the Ni_3Sn_4 phase has a very extensive solubility of the indium element. Although there is no ternary compound, most of the binary compounds in the In-Sn-Ni system have large solubility of ternary elements. This makes it difficult to experimentally determine the phase relationships in the In-Sn-Ni system. Moreover, indium and tin are very soft and have low melting points; on the contrary, nickel is hard and has a very high melting point. These make the preparation of specimens even more challenging. The isothermal section proposed in Fig. 1 is only a semiquantitative result. More experimental investigations are needed to examine the validity of the phase-equilibrium data and to further outline the exact boundary of the phase regions.

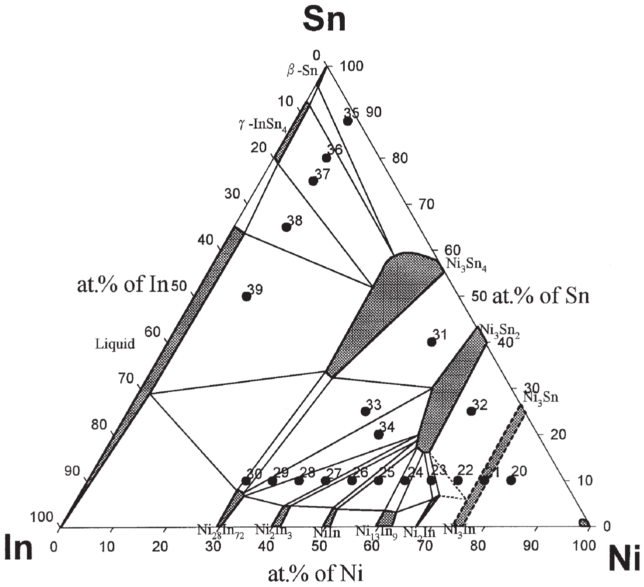


Fig. 10. The isothermal section of the In-Sn-Ni ternary system at 160°C superimposed with the nominal compositions of alloys examined in this study.

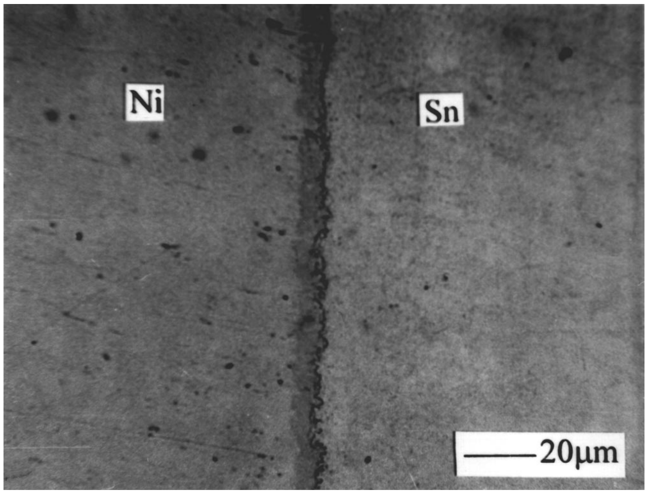


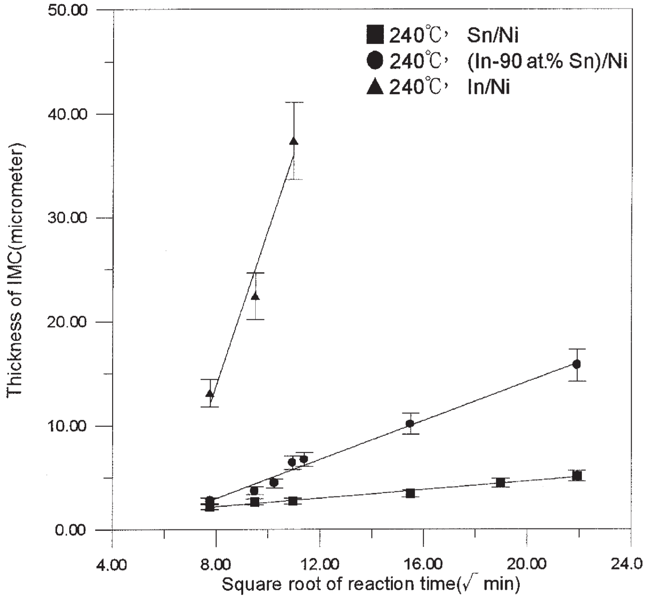
Fig. 11. An optical micrograph of the Sn/Ni couple reacted at 240°C for 8 h.

Table II. The Intermetallic Compounds Formed in the Couples Reacted at 240°C and 160°C

Temperature Couples	240°C	160°C
In/Ni	$Ni_{28}In_{72}$	$Ni_{28}In_{72}$
(In-10at.%Sn)/Ni	$Ni_{28}In_{72}$	Ni_3Sn_4
(In-11at.%Sn)/Ni	$Ni_{28}In_{72}$	—
(In-12at.%Sn)/Ni	Ni_3Sn_4	—
(In-20at.%Sn)/Ni	Ni_3Sn_4	Ni_3Sn_4
(In-30at.%Sn)/Ni	Ni_3Sn_4	Ni_3Sn_4
(In-40at.%Sn)/Ni	Ni_3Sn_4	Ni_3Sn_4
(In-48.3at.%Sn)/Ni	Ni_3Sn_4	Ni_3Sn_4
(In-60at.%Sn)/Ni	Ni_3Sn_4	Ni_3Sn_4
(In-70at.%Sn)/Ni	Ni_3Sn_4	Ni_3Sn_4
(In-80at.%Sn)/Ni	Ni_3Sn_4	Ni_3Sn_4
(In-90at.%Sn)/Ni	Ni_3Sn_4	Ni_3Sn_4
Sn/Ni	Ni_3Sn_4	Ni_3Sn_4

Figure 11 is an optical micrograph of the Sn/Ni couple reacted at 240°C for 8 h. One layer formed between Ni and Sn. The composition of the reaction layer, determined by probing on the center of the phase layer using EPMA, indicates that the phase layer is the Ni_3Sn_4. The phases formed in the couples are summarized and listed in Table II. This result is in agreement with most of the Sn/Ni reaction studies in the literature.[22–28] Although there are three intermetallic compounds between Sn and Ni,[19] only the Ni_3Sn_4 phase is formed by interfacial reaction. Not all the stable compounds can be found in the reaction couples. Two of the most important explanations for missing some stable phases are (1) the phases are not formed due to their high nucleation barrier and (2) those phases are too thin to be detected. Similar results were found in other Sn/Ni couples reacted at 240°C for various lengths of reaction time; only the Ni_3Sn_4 phase was formed, and its thickness increased with longer reaction time, as shown in Fig. 12.

Figure 13 is an optical micrograph of the In/Ni couple reacted at 240°C for 8 h. As shown in Fig. 13, only one reaction-phase layer formed. Embedding of alumina powders into indium can be found in Fig. 13 as well. Due to the extreme softness of indium, it is almost impossible to polish a pure indium specimen without the alumina embedding. The composition of the phase layer determined by using EPMA is In-28.6at.%Ni, which indicates the layer is the $Ni_{28}In_{72}$. This result is similar to that in the Sn/Ni system. Although there are six stable In-Ni compounds at 240°C, only one phase is formed by interfacial reaction. Tseng et al.[9] also studied the interfacial reactions between indium and nickel. They found that the $Ni_{10}In_{27}$ phase was formed at temper-



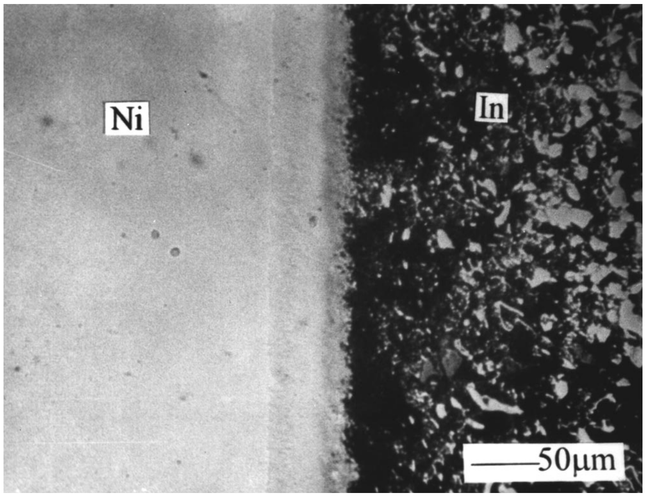


Fig. 13. An optical micrograph of the In/Ni couple reacted at 240°C for 8 h.

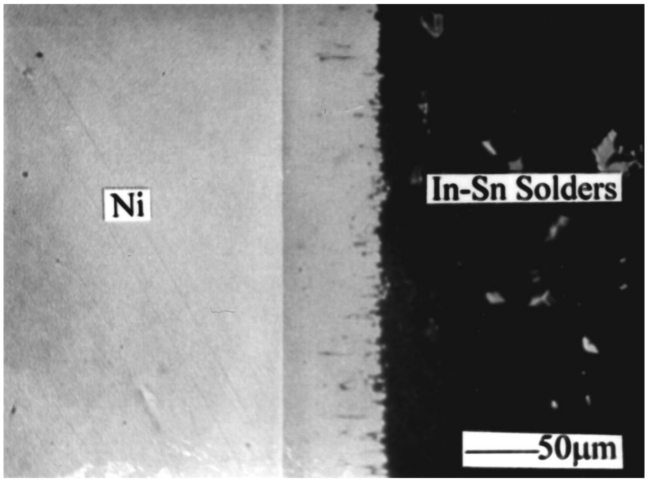


Fig. 15. An optical micrograph of the In-11at.%Sn/Ni couple reacted at 240°C for 12 h.

atures lower than 300°C. As mentioned previously, it is very likely that the $Ni_{10}In_{27}$ phase is the $Ni_{28}In_{72}$ phase. Thus, the results of the two studies are in agreement. Similar results were observed in all the other In/Ni couples reacted at 240°C for different lengths of time; only the $Ni_{28}In_{72}$ phase was formed, and its thickness increased with longer reaction time. As shown in Fig. 12, the growth rates of the $Ni_{28}In_{72}$ phase are faster than those of Ni_3Sn_4 phase.

Figure 14 is an optical micrograph of the In-90at.%Sn/Ni couple reacted at 240°C for 8 h. Only one compound is observed, and its composition determined by EPMA is In-55.62at.%Sn-38.38at.%Ni. Based on this compositional analysis result, this is the Ni_3Sn_4 phase. As shown in Fig. 1, the Ni_3Sn_4 phase has a large solubility of indium. The reaction path of the In-90at.%Sn/Ni couple is liquid/Ni_3Sn_4/Ni. Due to the formation of the Sn-rich Ni_3Sn_4 phase at the interface, the liquid phase at the liquid/Ni_3Sn_4 contact would be indium enriched. Figure 15 is an optical micrograph of the In-11at.%Sn/Ni couple reacted at 240°C for 12 h. The composition of the reacted-phase layer determined by EPMA was In-8.69at.%Sn-30.53at.%Ni and is the $Ni_{28}In_{72}$ phase. Its reaction path is liquid/$Ni_{28}In_{72}$/ Ni. Since the In-rich phase is formed at the liquid/solid interface, there is an Sn-rich (In-depleted) layer formed in the liquid phase adjacent to the $Ni_{28}In_{72}$ phase. Similar results were found in the In-10at.%Sn/Ni couples, and the $Ni_{28}In_{72}$ phase was formed in the couples.

Figure 16 is the micrograph of the In-12at.%Sn/Ni couple reacted at 240°C for 12 h. A Ni_3Sn_4 layer was formed. As summarized in Table II, similar results were found for all the In-Sn/Ni couples with Sn content higher than 12 at.% reacted at 240°C for various lengths of time; only the Ni_3Sn_4 phase was formed from interfacial reactions. There are no data available in the literature regarding the interfacial reaction between In-Sn alloys and pure Ni substrate. Lin and Chen[29] found that the $Ni_{10}In_{27}$ phase, i.e., the $Ni_{28}In_{72}$ phase, formed when molten In-49wt.%Sn (~In-48at.%Sn) alloy was in contact with an Ni-Cu-P deposit, and the $Ni_{10}In_{27}$ phase

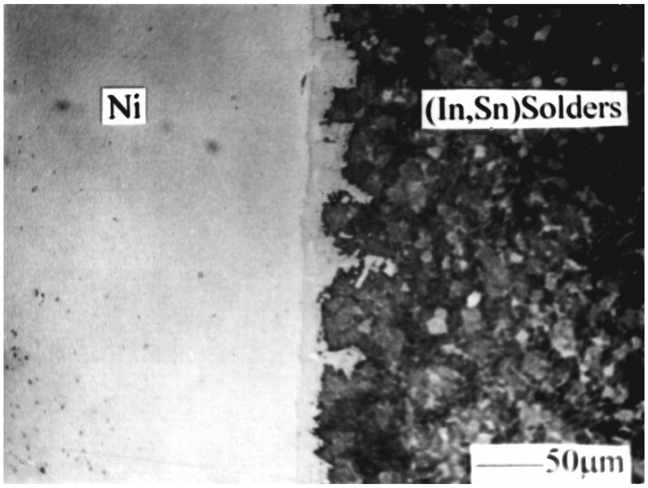


Fig. 14. An optical micrograph of the In-90at.%Sn/Ni couple reacted at 240°C for 8 h.

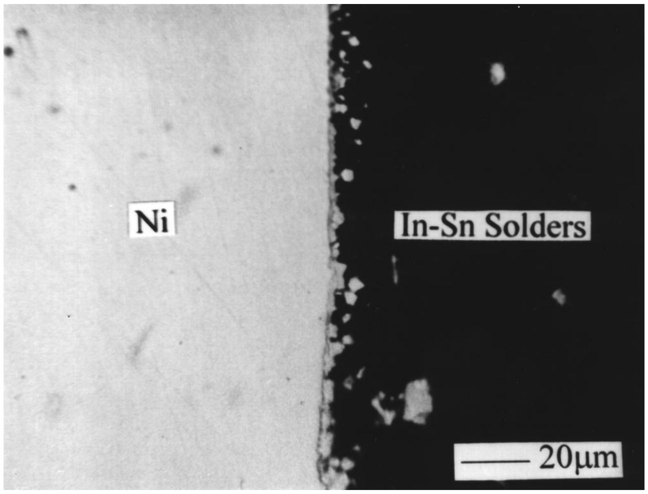


Fig. 16. An optical micrograph of the In-12at.%Sn/Ni couple reacted at 240°C for 12 h.

transformed into In_3Ni_2 phase after annealing at 80°C. Lin and Chen[29] proposed the formation of the $Ni_{10}In_{27}$ phase and In_3Ni_2 phase by EDS and XRD, but their results were not conclusive. For example, their EDS results indicated a higher content of tin than that of indium in the compound, and the matches of XRD peaks with $Ni_{10}In_{27}$ phase and In_3Ni_2 phase were not good either. It should also be pointed out that since both the $Ni_{10}In_{27}$ phase and Ni_3Sn_4 phase have a large solubility of a ternary element, which has different lattice constants, their XRD peaks would thus be shifted from those of binary compounds, without any solution of a ternary element. The disagreement between this study and that of Lin and Chen might have resulted from the different behavior of Ni-Cu-P and that of pure Ni or the different nucleation kinetics at 80°C and 240°C.

The growth rates of compounds in the In-Sn/Ni couples are shown in Fig. 12. The growth rate of the $Ni_{28}In_{72}$ phase is faster than that of the Ni_3Sn_4 phase. This is also shown in Figs. 15 and 16. Although the compositional difference of the two solder alloys in the In-11at.%Sn/Ni couple and the In-12at.%Sn/Ni couple is only 1%, the phases formed are different. The $Ni_{28}In_{72}$ phase is formed in the In-11at.%Sn/Ni couple and Ni_3Sn_4 phase is formed in the In-12at.%Sn/Ni couple. Besides the fact that the compositions of the reaction layers are different in the two reaction couples, the very significant difference of the layer thickness is another piece of strong evidence of the formation of different phases in the two kinds of couples. Another interesting phenomenon is that, although the concentration of Sn is lower in the In-90at.%Sn alloy than pure Sn, the growth rate of the Ni_3Sn_4 phase is faster in the In-90at.%Sn/Ni couple than that in the Sn/Ni couple. The melting point of pure Sn is 232°C, while that of In-90at.%Sn is about 215°C. The melting point of pure Sn is only 8° lower than the reaction temperature at 240°C; however, there is a 25° superheat for the In-90at.%Sn alloy at 240°C. It is very likely that the mobility of Sn in the molten In-90at.%Sn alloy with 25° superheat is higher than that in pure molten Sn with only 8° superheat. The high mobility is the explanation for the higher growth rate of the Ni_3Sn_4 phase in the In-90at.%Sn/Ni couple, although it has less Sn than that in the Sn/Ni couples.

Similar results are found for the In-Sn/Ni couples at 160°C. Only Ni_3Sn_4 phase was formed in the Sn/Ni and all the In-Sn/Ni couples examined in this study. Only $Ni_{28}In_{72}$ phase was formed in the In/Ni couple. As summarized in Table II, Ni_3Sn_4 phase formed in the In-10at.%Sn/Ni couples reacted at 160°C, while $Ni_{28}In_{72}$ phase formed in the same couples reacted at 240°C. As mentioned previously, the growth rates of $Ni_{28}In_{72}$ phase are much faster than those of Ni_3Sn_4 phase; however, the Ni_3Sn_4 phase is the dominant phase formed in the In-Sn/Ni couples. Similar results were found in other systems.[30] For example, the growth rate of $NiBi_3$ is faster than that of the Ni_3Sn_4 phase; however, the Ni_3Sn_4 phase is the more dominant phase in the Sn-Bi/Ni couples. It is likely that the nucleation of the $Ni_{28}In_{72}$ phase is more difficult than that of the Ni_3Sn_4 phase. At 160°C, the nucleation of the $Ni_{28}In_{72}$ phase is even unfavorable so that the Ni_3Sn_4 phase instead of the $Ni_{28}In_{72}$ phase is found in the In-10at.%Sn/Ni couples reacted at 160°C. As shown in Fig. 17, the reaction-layer thickness increases with longer reaction time and reaches a plateau after 225 h reaction of the In-90at.%Sn/Ni couple. Since the phases formed are the same before and after 225 h, the dramatic change of the growth rates indicates changes in the growth mechanism. The composition of the Ni_3Sn_4 phase formed in the couple, determined by using EPMA, is In-53at.%Sn-35at.%Ni. The Ni_3Sn_4 phase contains about 12at.%In, and it is higher than that in the bulk of the reaction couple, which is 10at.%In. It is likely that the formation of the In-containing Ni_3Sn_4 phase consumed all the nearby indium. When an In-depletion layer formed in the In-90at.%Sn/Ni couple, the interfacial reaction became similar to that in the Sn/Ni couple. Similar growth rates in the two couples, as shown in Fig. 17, provide support for this hypothesis.

CONCLUSIONS

Although metallographic studies of most of the Sn-In-Ni alloys have been difficult due to the very soft nature of indium, experimental examinations have been conducted on the phase equilibria of Sn-In-Ni system at 160°C and 240°C, and interfacial reaction in the Sn-In/Ni couples has been determined. There is no ternary compound found in the In-Sn-Ni system annealed at 160°C and 240°C. However, the phase relationships are complicated due to the fact that most of the binary compounds have extensive ternary solubility. There is a continuous solid solu-

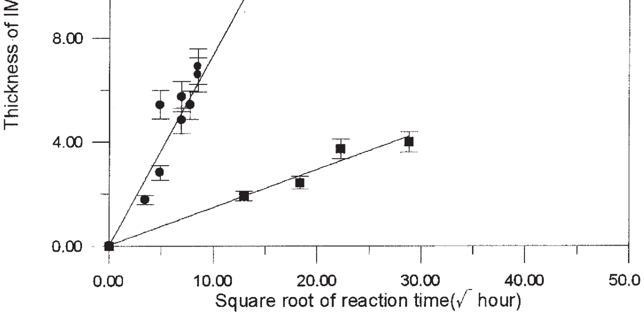


Fig. 17. The relationship between layer thickness and reaction time at 160°C.

tion between the Ni_3Sn phase and the Ni_3In phase. Although there are many intermetallic compounds in the Sn-In-Ni system, and the phase equilibrium relationships are complicated, there is only one compound formed, either $Ni_{28}In_{72}$ or Ni_3Sn_4 phase, in all the Sn-In alloys/Ni couples reacted at 160°C and 240°C up to 8 h. The growth rate of $Ni_{28}In_{72}$ phase was faster; however, the nucleation of Ni_3Sn_4 phase was kinetically favored. At 240°C, the $Ni_{28}In_{72}$ phase formed in the couples made with pure indium, In-10at.%Sn, and In-11at.%Sn alloys, while the Ni_3Sn_4 phase formed in the couples made of alloys with compositions varying from pure Sn to In-12at.%Sn. At 160°C, the $Ni_{28}In_{72}$ phase was only found in the couples made of pure indium.

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