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The Sn/Ni-7Wt.%V Interfacial Reactions

CHIH-CHI CHEN[1] and SINN-WEN CHEN[1,2]

1.—Department of Chemical Engineering, National Tsing Hua University, Hsin-Chu, Taiwan 300.
2.—swchen@che.nthu.edu.tw

Ni-7wt.%V(8at.%V) is an important under bump metallization material, and Sn is the primary element in most solders. This study examines the Sn/Ni-8at.%V interfacial reactions at 160°C, 200°C, 250°C, 300°C, 325°C, 350°C, and 400°C. Unlike the interfacial reactions in the Sn/Ni couples, a ternary T phase and the binary Ni_3Sn_4 phase are formed at 160°C. The vanadium solubility in the Ni_3Sn_4 phase is only 0.2 at.%, while the T phase contains 13.9at.%V. Similar results are found in the couples at 200°C, and the reaction paths are Sn/Ni_3Sn_4/T/Ni-V. The reaction paths are liquid/T/Ni_3Sn_4/Ni-V at 250°C and 300°C and are liquid/Ni_3Sn_4/Ni-V at 350°C and 400°C. Because the reaction products and the reaction rates in the Sn/Ni-8at.%V and Sn/Ni couples are different, reliabilities of the electronic products with the Ni-8at.%V barrier layer should not be assessed based only on the results of the Sn/Ni couples.

Key words: Interfacial reactions, Sn, Ni-7wt.%V, ternary phase

INTRODUCTION

Flip-chip technology is an emerging technology in the microelectronics industry. Most often Sn-based solders are used as bumping materials. To enhance the adhesion and prevent interfacial reactions between the solder bumps and the integrated circuit metal pads, under bump metallurgy (UBM) is required.[1] Nickel is usually used as the UBM barrier layer material because it has relatively lower reaction rates with solders.[2] However, Ni is a ferromagnetic material and its ferromagnetism hinders its sputtering deposition. The ferromagnetic interference can be overcome by adding the antiferromagnetic vanadium into the Ni target, and then the deposition rates can be enhanced. This process is known as the “Delco process,” and 7wt.%V addition is the most common industrial practice.[3] The Sn-based solders are in contact with the Ni-7wt.% (8at.%)V layer in the Delco process flip chip.

Although it has been recognized that the interfacial reactions between the solders and substrates are crucial for the products' reliabilities and there are very extensive investigations about the Sn/Ni interfacial reactions,[4–10] the vanadium addition effects upon the interfacial reactions are rarely examined.[11,12] Chun et al.[11] reported the formation of a Sn-Ni-V ternary compound at the peak reflow temperature of 260°C between the Pb-free solders and the Ti/Ni-V/Au UBM. Chen et al.[12] found that when the V addition in the Ni is above 5 wt.%, besides the Ni_3Sn_4 phase, an additional ternary phase is formed from the Sn/Ni-V interfacial reactions at 250°C. Since there are differences in the interfacial reactions in the Sn/Ni-8at.%V and Sn/Ni couples, the Sn/Ni-8at.%V interfacial reactions must be investigated in order to have accurate assessments of the joint properties with Ni-8at.%V barrier layer.

EXPERIMENTAL PROCEDURES

Reaction couples were prepared with the commercial Ni-7wt.%V (Ni-8at.%V) alloy (99.95wt.% purity) and pure Sn shots (99.999 wt.% purity). The reaction temperatures were at 160°C, 200°C, 250°C, 300°C, 325°C, 350°C, and 400°C. Since the melting points of pure Sn and Ni-8at.%V are 232°C and 1,455°C, respectively, two different kinds of Sn/Ni-8at.%V couples, solid/solid and liquid/solid, were prepared in this study. The Ni-8at.%V foil was cut into 1 mm × 10 mm × 20 mm pieces, polished, and cleaned prior to the preparation of couples.

For the preparation of the solid/solid couples, Sn shots were melted in a 40 mm × 10 mm × 20 mm graphite mold on a hot plate at 300°C. The Ni-V piece was inserted into the molten Sn at the center of the graphite mold, and then the graphite mold was quenched with cold water. The specimen bar was removed from the graphite mold and was cut into 40 mm × 1 mm × 1 mm Sn/Ni-V/Sn couples. The couples were encapsulated in quartz tubes and reacted at 160°C and 200°C for 120–168 h.

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For the preparation of the liquid/solid couples, the Ni–8at.%V piece and Sn shots were encapsulated together in a quartz tube. The sample capsules were then heated to 250°C, 300°C, 325°C, 350°C, and 400°C. At these temperatures, the solders were molten and encircled the Ni-V substrate to form the liquid/solid couples. The lengths of the reaction time were 1 h, 6 h, and 12 h. It warrants mentioning that the practical reaction temperature is around 250°C, and the soldering time is only for a couple of seconds. However, for better understanding of the Sn/Ni-V interfacial reactions, much elevated and larger temperature ranges and prolonged lengths of reaction time were used in this study.

After the predetermined lengths of reaction time, the couples were quenched into cold water. The reaction couples were cut, mounted, polished, and ground carefully to reveal the Sn/Ni-V interfaces. Optical microscopy and scanning electron microscopy with the second electron image (SEI) and backscattering electron image (BEI) were used for microstructural examinations. JEOL (Japan Electron Optics Ltd., Tokyo, Japan) JXA-8600SX electron probe microanalysis (EPMA) with wavelength dispersive spectroscopy was used for compositional analysis.

RESULTS AND DISCUSSION

Figure 1 is the BEI micrograph of the Sn/Ni-8at.%V couple reacted at 200°C for 120 h. Two reaction layers are formed. This result is different from that in the Sn/Ni couple in which only the Ni_3Sn_4 phase is formed.[10] The composition of the brighter phase, which is adjacent to the Ni-8at.%V substrate, is Sn-19.9at.%Ni-15.9at.%V, and that of the darker phase is Sn-42.9at.%Ni. Compared with previous Sn/Ni interfacial reaction results at 200°C[10] and the binary Sn-Ni phase diagram,[13] it is presumed that the darker phase adjacent to the Sn phase is the binary Ni_3Sn_4 phase with no detectable vanadium solubility.

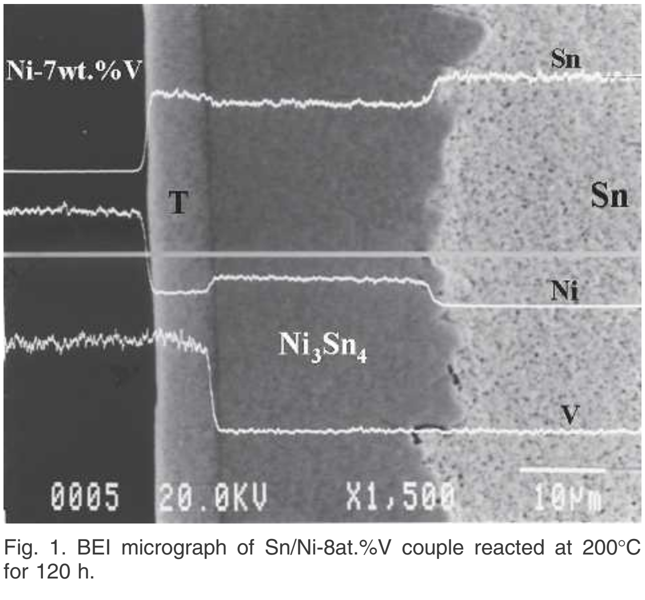

Fig. 1. BEI micrograph of Sn/Ni-8at.%V couple reacted at 200°C for 120 h.

Identification of the brighter phase is not as obvious. There are no corresponding binary phases in the Sn-Ni and Sn-V systems,[13,14] and there are no previous studies of the Sn-Ni-V intermetallic compounds either. Chun et al.[11] studied the interfacial reactions between Pb-free solders and Ti/Ni-V/Au UBM and they observed a Sn-Ni-V ternary compound between solders and Ni-V. Chen et al.[12] found the formation of a similar phase in the Sn/Ni-8at.%V couple reacted at 250°C, and the phase has been designated as the “T” phase. The brighter phase is presumed to be a ternary compound similar to the one mentioned in the 250°C study[12] and is thus also named “T” phase in this study.

Similar results are found in the Sn/Ni-8at.%V couples reacted at 160°C. The reaction paths are Sn/Ni_3Sn_4/T/Ni-V as well. The composition of the ternary phase is Sn-24.9at.%Ni-13.9at.%V. Slight compositional differences of the ternary phases formed at 160°C and 200°C are observed. Information of interfacial reactions between solders and the substrate layer is important for the assessment of the joint properties and selection of the optimal barrier layer thickness. Since the interfacial reaction results are different in the Sn/Ni and Sn/Ni-8at.%V couples, proper assessment for the flip-chip products with the Delco process should be evaluated based not on the interfacial reaction results of the Sn/Ni couples but on those of the Sn/Ni-8at.%V couples.

Because the amount of vanadium is negligible in the Ni_3Sn_4 phase, only diffusion fluxes of Ni and Sn need to be considered for the growth of the Ni_3Sn_4 phase. It is unlikely that the tin element is the fast diffusion species in the Ni_3Sn_4 phase. If it were the case in the Sn/Ni_3Sn_4/T/Ni-V couple, the growth front of the Ni_3Sn_4 phase should be at the T/Ni_3Sn_4 interface and then the Ni to V content ratios would be similar in both the T and Ni_3Sn_4 phases. However, the experimental results show differently. It is worth noting that in both of the reaction couples reacted at 160°C and 200°C, there are no noticeable Sn and V in the Ni-8at.%V substrate and in the Sn phase, respectively.

The T phase contains significant amounts of all three constituent elements. Vanadium is not the fastest diffusion species regarding the T phase formation. If vanadium element were the fastest in the Sn/Ni_3Sn_4/T/Ni-V couple, there should be a vanadium depletion zone between the T phase and Ni-V substrate, which has not been observed. If Sn is the fastest diffusion species in the T phase, then the growth front is at the Ni-8at.%V/T interface. Because there is no Sn in the Ni-V substrate, growth of the T phase would be just like dilution of the Ni-8at.%V substrate with the fastest arrived Sn element; then, the Ni to V content ratios should be the same in both the Ni-V and the T phases. The Ni/V content ratios in the Ni-V and T phases are different, indicating that Sn is not the fastest diffusion species in the T phase. It is likely that vanadium is relatively immobile; nickel diffuses out from the Ni-8at.%V and leaves vanadium behind. Some of the vacancies diffuse out as well, while some of the vacancies are occupied with the Sn atoms diffusing in from the Ni_3Sn_4 phase; thus, the T phase is more vanadium rich than the Ni-8at.%V substrate. The fact that the Sn atom is larger than the Ni atom could be another reason why there is less Sn inward flux than Ni outward flux in the T phase.

Figure 2 is the SEI micrograph of the Sn/Ni-8at.%V couple reacted at 250°C for 6 h. Only one reaction layer is found at the interface, and next to the layer is a two-phase region. The composition of the reaction layer determined by EPMA is Sn-11.6at.%Ni-16.1at.%V. The composition of the continuous phase in the two-phase mixture is nearly pure Sn, and that of the discontinuous phase is Sn-42.4at.%Ni-0.1at.%V. With a similar reasoning as mentioned above, it is presumed that the discontinuous phase is the Ni_3Sn_4 phase with negligible vanadium solubility, and the reaction layer is the ternary T phase. Since Sn is molten at 250°C, the continuous matrix in the two-phase region was the liquid phase prior to the sample's removal from the furnace. Figure 3 is the cross-sectional transmission electron microscopy (TEM) electron diffraction pattern of the T phase of the Sn/Ni-8at.%V couple reacted at 250°C for 1 h. The TEM specimen was prepared by using a focused ion beam with Ga as the ion source. The characterization was conducted by using JEOL 2000FXII TEM with a LaB_6 electron source and was operated at 120 kV. As shown in Fig. 3, the electron diffraction pattern of the T phase is a broad halo mixed with some random and weak spots. It is concluded that the T phase region is likely an amorphous phase mixed with some very fine crystalline domains or it is a reaction phase layer with ultra-fine grains.

Similar results are found in the 250°C Sn/Ni-8at.%V couples reacted for 1 h and 12 h. As shown in Fig. 4 in the SEI micrograph of the deep-etched 12-h reacted couples, the T phase is formed adjacent to the Ni-V substrate and the Ni_3Sn_4 phase is formed within the molten Sn matrix. There is only one continuous reaction phase formed at the interface. The darker part of the continuous reaction phase, as shown in Fig. 4, is the edge of the T phase. Higher amounts of Sn were removed by etching and the T phase was thus exposed; the darker part was originally adjacent to the solder matrix prior to deep etching. The compositions of the T phase are summarized in Table I and are Sn-15.6at.%Ni-15.4at.%V and Sn-12.7at.%Ni-16.2at.%V in the 1-h and 12-h reaction couples, respectively. The growth mechanism of T is presumed to be similar to those at 160°C and 200°C. Nickel atoms and some vacancies diffuse out of the Ni-V substrate, and then Sn atoms diffuse in to form the ternary T phase.

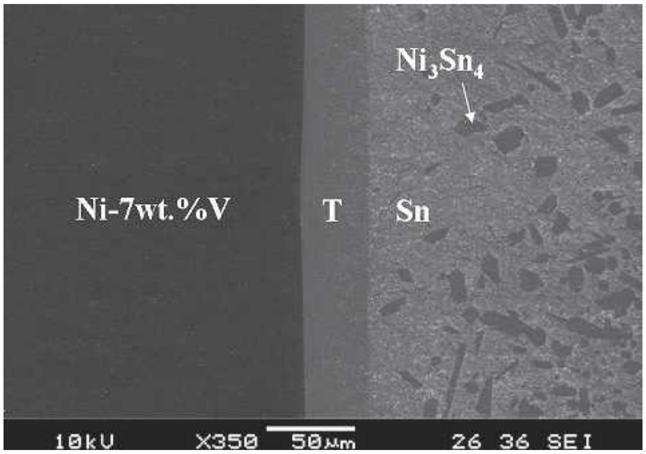

Fig. 2. SEI micrograph of Sn/Ni-8at.%V couple reacted at 250°C for 6 h.

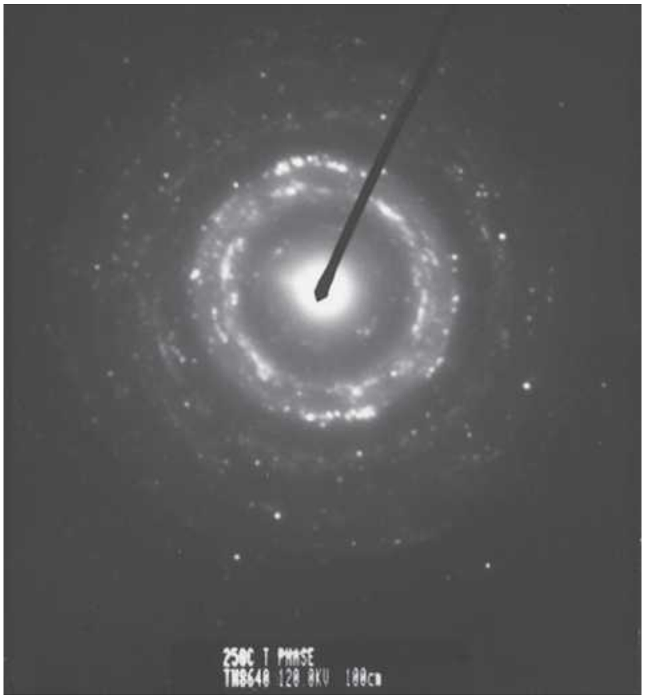

Fig. 3. Cross-sectional TEM electron diffraction pattern of the T phase of Sn/Ni-8at.%V couple reacted at 250°C for 1 h.

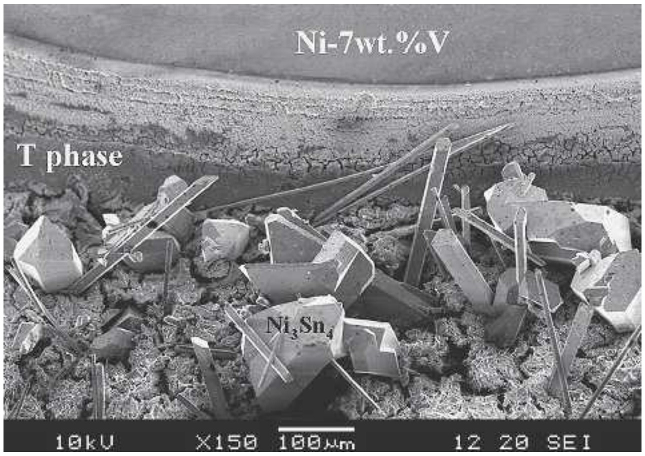

Fig. 4. SEI micrograph of the deep-etched Sn/Ni-8at.%V couple reacted at 250°C for 12 h.

Because there is negligible vanadium in the Ni_3Sn_4 phase, only diffusion of Ni and Sn needs to be considered for the formation of the Ni_3Sn_4 phase. The question that needs to be addressed is if the Ni_3Sn_4 phase

Table I. EPMA Compositional Analysis Results in This Study (At.%)

	Phases Formed in the Reaction Couples					
	Continuous Phases			Discontinuous Phases		
	1 h	6 h	12 h	1 h	6 h	12 h
400°C						
Sn	58.2	—	—	58.6	—	—
Ni	40.2	—	—	41.3	—	—
V	1.6	—	—	0.1	—	—
350°C						
Sn	59.3 57.2	57.8	57.6	57.9	57.7	57.8
Ni	36.2 39.8	38.4	39.7	40.9	42.2	41
V	4.5 3	3.8	2.7	1.2	0.1	1.2
325°C						
Sn	65	67.7(T) 59.8	68.4(T) 59.2	57.2	57.4	57.2
Ni	19.1	16.9(T) 36.2	16(T) 35.6	42.8	42.5	42.1
V	15.9	15.4(T) 4.0	15.6(T) 5.2	0	0.1	0.7
300°C						
Sn	65.1	72.4	73.5	57.6	58.1	57.7
Ni	19.3	11.9	10.3	42.3	41.4	42.3
V	15.6	15.7	16.2	0.1	0.5	0
250°C						
Sn	69	72.3	71.1	57.7	57.5	57.9
Ni	15.6	11.6	12.7	42.3	42.4	42.1
V	15.4	16.1	16.2	0	0.1	0
200°C	120 h					
Sn	—	—	64.2	—	—	57.1
Ni	—	—	19.9	—	—	42.9
V	—	—	15.9	—	—	0
160°C	168 h					
Sn	—	—	61.2	—	—	58.5
Ni	—	—	24.9	—	—	41.3
V	—	—	13.9	—	—	0.2

is formed by interfacial reaction or during solidification. The Ni solubility in the molten Sn in the binary Sn-Ni system[13] is very small even at 300°C, and according to the lever rule, only a very small amount of Ni_3Sn_4 phase could be formed during solidification. As shown in Figs. 2 and 4, significant amounts of Ni_3Sn_4 phase are formed. Therefore, the dispersive Ni_3Sn_4 phase is supposed to result from the interfacial reaction. The Ni_3Sn_4 phase is likely to grow on the T phase layer, detach, and then drift into the molten Sn. The reaction path is liquid/Ni_3Sn_4/T/Ni-V at 250°C. It can be noticed, as in Fig. 4, that the Ni_3Sn_4 phases are of two different morphologies. The round shaped one is likely formed by interfacial reactions, as mentioned above, while the faceted one is formed during solidification. However, further studies are needed to verify this presumption.

Figure 5 is the BEI micrograph of the Sn/Ni-8at.%V couple reacted at 300°C for 12 h. The composition of the continuous layer is Sn-10.3at.%Ni-16.2at.%V. The compositions of the T phase are summarized in Table I, and it can be noticed that the T phase has significant compositional homogeneity ranges. Since T phase is an amorphous phase formed by interfacial reactions, their compositions are likely to be influenced by the reaction kinetics, which differ with different reaction temperatures and lengths of reaction time. Similar to the couples reacted at 160°C, 200°C, and 250°C, there is no noticeable Sn in the Ni-8at.%V substrate and nearly negligible vanadium in the Sn phase. Figure 6 is the BEI micrograph of the Sn/Ni-8at.%V couple reacted at 325°C for 1 h. The result is similar to that in the couples reacted at 300°C. The dark and discrete phase is the Ni_3Sn_4 phase with no detectable vanadium. The composition of the continuous brighter layer is Sn-19.1at.% Ni-15.9at.%V and is the T phase.

When the reaction time in the 325°C-reacted couple is prolonged to 6 h, a new phase is formed, as shown in Fig. 7. The composition of the brighter

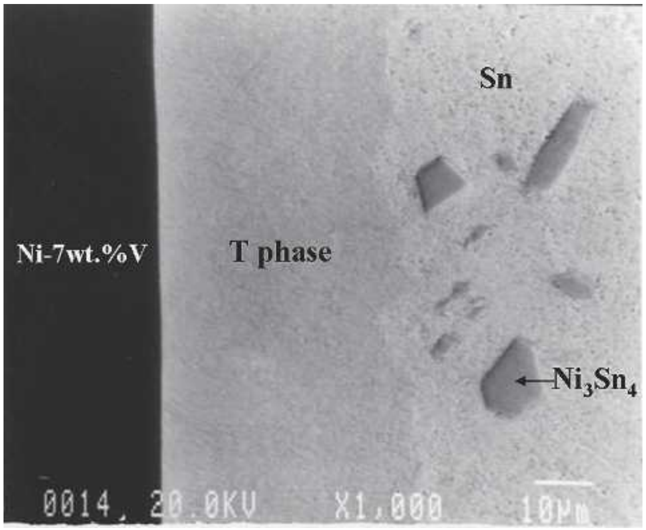

Fig. 5. BEI micrograph of Sn/Ni-8at.%V couple reacted at 300°C for 12 h.

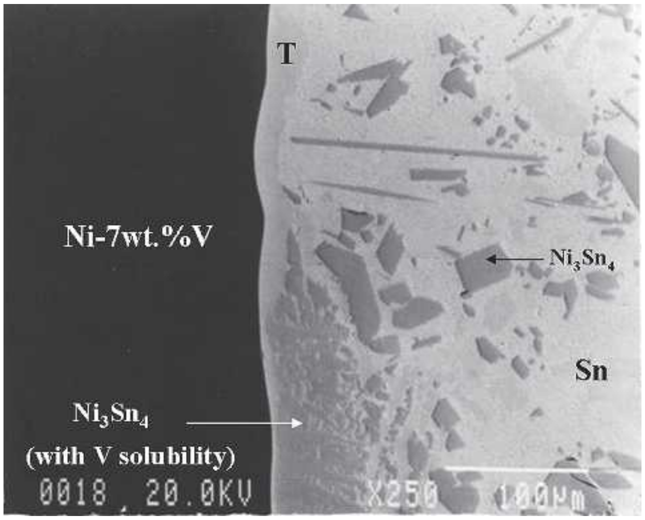

Fig. 7. BEI micrograph of Sn/Ni-8at.%V couple reacted at 325°C for 6 h.

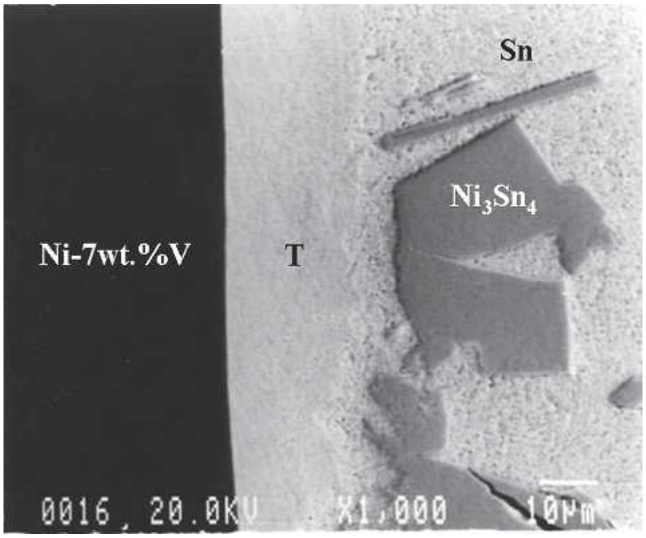

Fig. 6. BEI micrograph of Sn/Ni-8at.%V couple reacted at 325°C for 1 h.

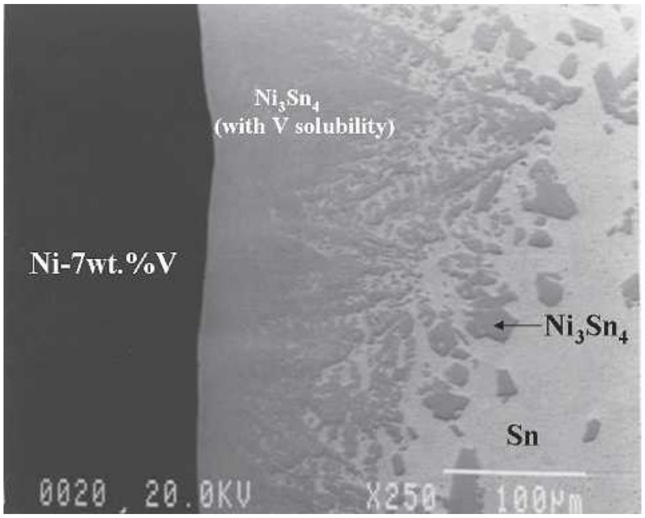

Fig. 8. BEI micrograph of Sn/Ni-8at.%V couple reacted at 325°C for 12 h.

phase adjacent to Ni-V substrate is Sn-16.9at.% Ni-15.4at.%V, and that of the darker layer attached to Ni-V substrate is Sn-36.2at.%Ni-4at.%V. The brighter phase is the T phase. Based on its composition, the darker phase is likely the Ni_3Sn_4 phase with 4 at.% vanadium solubility. Since no vanadium is noticeable in the Ni_3Sn_4 phase formed at lower temperatures, this phase is designated as the Ni_3Sn_4 phase with vanadium solubility. As shown in Fig. 7, unlike the Ni_3Sn_4 phase with no vanadium, which is mixed with the Sn phase, the Ni_3Sn_4 phase with vanadium is grown on the T phase. It is worth mentioning that the T phase layer becomes thinner and diminished with the Ni_3Sn_4 phase with vanadium growing on it.

Figure 8 is the BEI micrograph of the Sn/Ni-8at.%V couple reacted at 325°C for 12 h. A very thick reaction layer is formed. Its composition is Sn-35.6at.%Ni-5.2at.%V and is the Ni_3Sn_4 phase with vanadium solubility. The composition of the discrete dark particulates, which are far away from and not connected with the interface, is Sn-42.1at.%Ni-0.7at.%V. Careful examinations of the entire specimen reveal that about 80% of the interface is covered with the Ni_3Sn_4 phase with vanadium solubility and most of the T phase layer disappears, while the covered percentage is only about 10% in the 6-h reacted couple. Clearly, with longer reaction time, the T phase is consumed to form the Ni_3Sn_4 phase with vanadium solubility.

Figures 9–11 are the SEI micrographs of the Sn/Ni-8at.%V couples reacted at 350°C for 1 h, 6 h, and 12 h, respectively. For the 1-h reaction sample, as shown in Fig. 8, the composition of the thin layer adhered to the Ni-V substrate is Sn-36.2at.%Ni-4.5at.%V. The composition of the darker reaction layer next to the brighter layer is Sn-39.8at.%Ni-3at.%V, and that of the discrete phase closer to the Sn phase is Sn-40.9at.%Ni-1.2at.%V. All of the reaction products are the Ni_3Sn_4 phase with

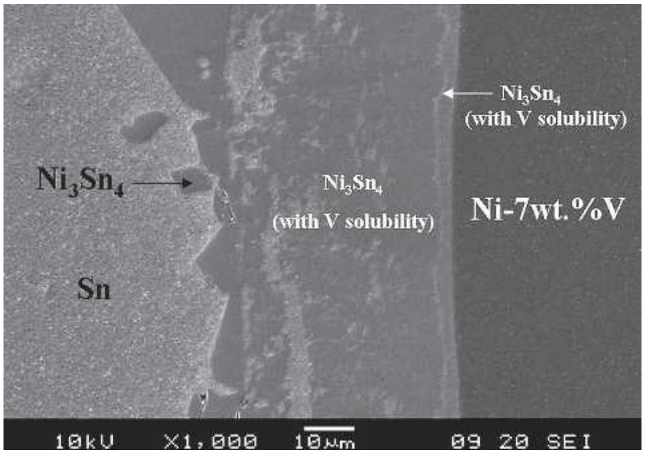

Fig. 9. SEI micrograph of Sn/Ni-8at.%V couple reacted at 350°C for 1 h.

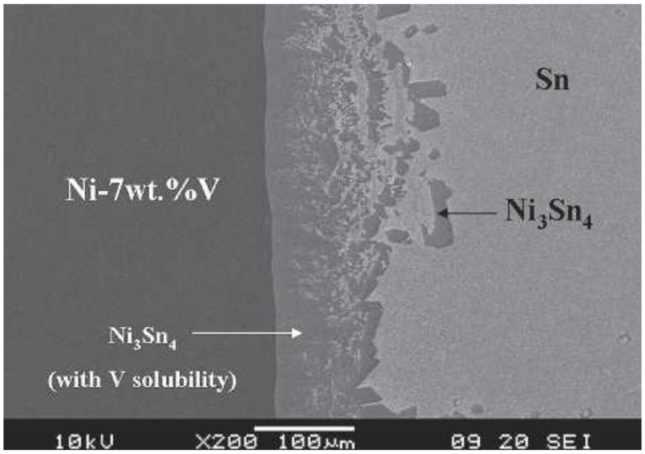

Fig. 10. SEI micrograph of Sn/Ni-8at.%V couple reacted at 350°C for 6 h.

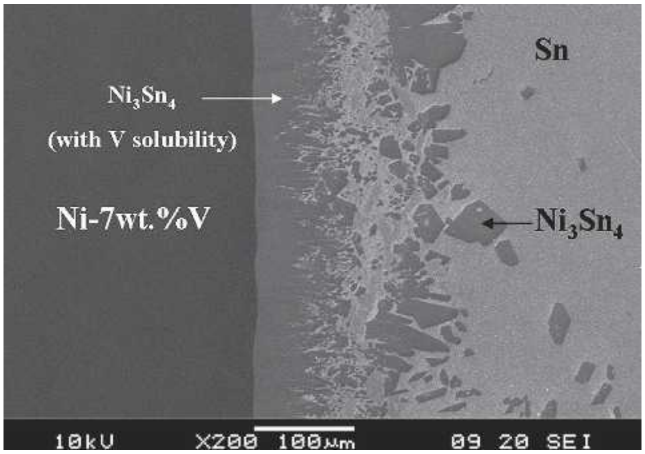

Fig. 11. SEI micrograph of Sn/Ni-8at.%V couple reacted at 350°C for 12 h.

different vanadium solubility. As can be seen from Figs. 8–10, the reaction layer grows with longer reaction time. The compositions of the continuous reaction layer are Sn-38.4at.%Ni-3.8at.%V and Sn-39.7at.%Ni-2.7at.%V for the 6-h and 12-h reaction couples, respectively. The reaction products are the Ni_3Sn_4 phase with vanadium solubility as well.

Figure 12 is the BEI micrograph of the Sn/Ni-8at.%V couple reacted at 400°C for 1 h. One reaction layer is formed on the Ni-V substrate, and its composition is Sn-40.2at.%Ni-1.6at.%V. The V content of the reaction layer varies slightly with vanadium content higher when it is closer to the Ni-V substrate. Similarly, the reaction products are the Ni_3Sn_4 phase with vanadium solubility, and the reaction paths are liquid/Ni_3Sn_4/Ni-V for the couples reacted at 350°C and 400°C. In comparison with the interfacial reactions in the Sn/Ni couples at 400°C,[7] the most significant difference is there is no formation of Ni_3Sn_2 and Ni_3Sn phases in the Sn/Ni-8at.%V couples. Besides that, the growth rates of the reaction layers are different. The growth rate of the reaction layer in the Sn/Ni-8at.%V couple is about 0.7 μm/min. at 400°C and is much higher than that in the Sn/Ni couple.

The reaction path of the Sn/Ni-8at.%V couple changes from Sn/Ni_3Sn_4/T/Ni-V at 160°C, to liquid/Ni_3Sn_4/T/Ni-V at 250°C, and then to liquid/Ni_3Sn_4/Ni-V at 400°C. The same tendency of the reaction path change is also observed in the couple reacted at 325°C from 1-h to 12-h reaction. Previous studies[15–18] have found that nucleation is more important in the initial stage of interfacial reactions, and thus, ternary compounds tend to nucleate and grow. In some cases, meta-stable compounds or even amorphous phases are formed from interfacial reactions as well.[17] However, with longer reaction time or reaction at higher temperatures, the mass transport factor becomes dominating, and the reaction path shifts toward the stable binary phases. The path changes in this study are in agreement with these previous observations. Since the amorphous T phase has never been examined, further studies are needed to characterize this T phase. Moreover,

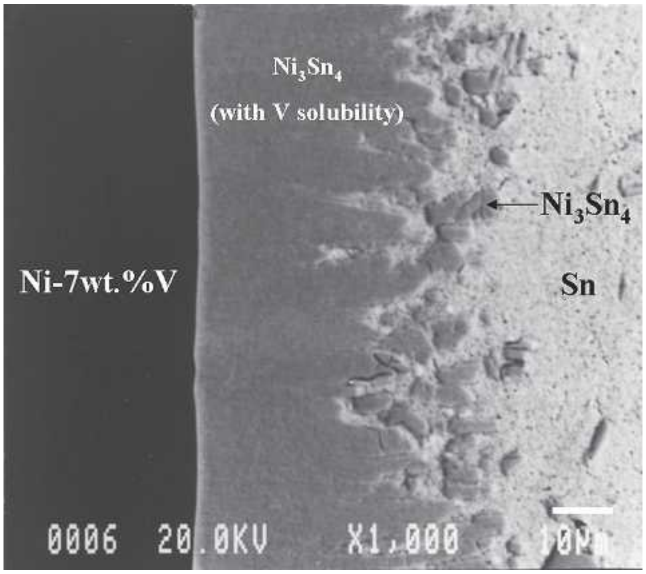

Fig. 12. BEI micrograph of Sn/Ni-8at.%V couple reacted at 400°C for 1 h.

phase equilibria of the ternary Sn-Ni-V system need to be determined, so that the compositional ranges of the Ni_3Sn_4 phase and the existence conditions of this amorphous T phase can be examined.

CONCLUSIONS

The interfacial reactions in the Sn/Ni-8at.%V couples are examined and are different from those in the Sn/Ni couples. Besides the Ni_3Sn_4 phase, a ternary T phase is formed in the Sn/Ni-8at.%V couple reacted at 160°C and 200°C. At 250°C, 300°C, and the beginning stage at 325°C, the reaction path is liquid/T/Ni_3Sn_4/Ni-8at.%V. At 350°C, 400°C, and the later stage at 325°C, the reaction path becomes liquid/Ni_3Sn_4/Ni-8at.%V. Because the interfacial reaction products are different at the Sn/Ni and Sn/Ni-8at.%V contacts, it is very important that reliability assessments of the flip-chip products with Ni-8at.%V barrier layer are evaluated based on the interfacial reaction results from the Sn/Ni-8at.%V couples. Further phase equilibria studies at various temperatures are needed to examine the thermodynamic stabilities of the T phase and the compositional ranges of the Ni_3Sn_4 phase.

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