Interfacial Reactions in the Sn-(Ag)/(Ni,V) Couples and Phase Equilibria of the Sn-Ni-V System at the Sn-Rich Corner

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

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

Ni-7wt.%V is commonly used as the barrier layer material in the under-bump metallurgy in the microelectronic industry. Although interfacial reactions between various solders with the nickel substrate have been investigated intensively, the effects of vanadium addition upon the solder/(Ni,V) interfacial reactions have not been studied. Sn/(Ni,V) and Sn-Ag/(Ni,V) interfacial reactions at 250°C were investigated in this study using the reaction couple technique. The vanadium contents of the (Ni,V) substrates examined in this study are 3 wt.%, 5 wt.%, 7 wt.%, and 12 wt.% and the reaction time is 12 h. The results indicate that when the vanadium contents in the (Ni,V) substrate are 5 wt.% and higher, the Sn/(Ni,V) and Sn-Ag/(Ni,V) interfacial reactions are different from those in the solder/Ni couples. Besides the Ni_3Sn_4 phase as commonly formed in the reaction with Ni substrate, a new ternary T phase has been found, and the reaction path is L/Ni_3Sn_4/T/(Ni,V). A 250°C Sn-Ni-V isothermal section is proposed based on the three constituent binary systems and limited experimental results obtained in this study. The reaction path is illustrated with the proposed Sn-Ni-V isothermal section. No stable ternary Sn-Ni-V phase is found from the phase equilibria study, and the new T phase is likely a metastable phase.

Key words: Under-bump metallization (UBM), interfacial reactions, Sn-Ni-V, Sn-Ag-Ni-V

INTRODUCTION

Flip chip technology is emerging in microelectronic packaging. Solders are replacing the gold wires used in the conventional wire bonding technology to connect the integrated circuits (ICs) chips and the substrates. To enhance the adhesion and to prevent severe interfacial reactions between the solder bumps and the IC metal pads, surface treatment known as under bump metallization (UBM) is required for the flip chip joining.[1] Metallic layers with various functions, such as adhesion layer and barrier layer, are formed between the solder bumps and the metal pads. Compared to most other metals, nickel has a relatively slower reaction rate with solders and thus is commonly chosen and used as the barrier layer material.

(Received February 6, 2005; accepted September 27, 2005)

In the industrial application, nickel is usually formed by a sputtering process. In order to overcome nickel ferromagnetism, 7wt.%V is usually added into the nickel to facilitate the nickel sputtering process.[2] Understanding the interfacial reactions between the solders and the barrier layers is crucial. Proper reliability assessment of the flip chip products and selection of the appropriate barrier layer thickness can only be determined with this understanding. Although interfacial reactions between various solders and the nickel substrate have been investigated intensively,[3–23] the effects of vanadium addition upon the solder/(Ni,V) interfacial reactions have not yet been studied.

The Pb-Sn alloys are the dominating solders in the modern electronics industry. However, due to health and environmental concerns, there are various continuous efforts to eliminate the use of Pb in electronic products. Recently, the European Union passed the resolution that no commercial electronic products should contain Pb after July 1, 2006.[24] Pb-free solders would become the dominating solders in the very near future, and Sn-Ag, Sn-Cu, and Sn-Ag-Cu alloys are among the most promising ones. The three alloys mentioned above and most of the other available Pb-free solders are all Sn-based alloys. The understanding of interfacial reactions between Sn and substrates is important for both the Pb-Sn and Pb-free solders.

The purpose of this study is to examine the effects of vanadium addition upon the interfacial reactions between solders and (Ni,V) substrates. For simplification and clarity purposes, instead of using the real flip-chip products, the interfacial reactions were investigated with the reaction couples prepared with solders and planar (Ni,V) substrates. As a first step, the solders used in this study are pure Sn and Sn-3.5wt.%Ag alloy. The selected vanadium contents are from 3 wt.% to 12 wt.%, and the industrial application, 7 wt.%, is within the compositional range of examination. Limited phase equilibria experiments were carried out as well, so that the Sn-Ni-V isothermal section at the Sn-rich corner can be constructed, and the reaction path can be illustrated.

EXPERIMENTAL PROCEDURES

Pure Sn shots of 99.999 wt.% purity and commercial Sn-3.5wt.%Ag ingots were used as solders. The V shots of 99.7 wt.% purity and Ni foil of 99.98 wt.% purity were used for the preparation of the (Ni,V) alloys. Proper amounts of V and Ni were weighed, alloyed together by arc melting, encapsulated in a quartz tube and homogenized at 1,000°C for 3 weeks. The Ni-V alloys were removed from the furnace and quenched in air. Besides the Ni-V alloys prepared in this study, the commercial Ni-7wt.%V alloy was also used as the substrate. Based on the binary Ni-V phase diagram,[25] the Ni-V alloys with 3 wt.%, 5 wt.%, 7 wt.%, and 12 wt.% contents at 250°C and 1,000°C are all in the single Ni solid solution phase region. Thus, the (Ni,V) substrates examined in this study are all in the single-phase region.

The homogenized (Ni,V) ingot was cut into 10 mm × 7 mm × 0.5 mm pieces. The (Ni,V) substrate was encapsulated in a quartz tube with Sn and Sn-Ag ingots. The sample capsule was placed in a furnace at 250°C. The reaction temperature was higher than the melting points of Sn and Sn-Ag alloys. The molten solder covers the Ni-V substrate, and a L/(Ni,V) reaction couple was prepared. After annealing for a predetermined duration, the sample was quenched into ice water. The samples were mounted carefully to reveal their exact vertical reaction interfaces and were metallographically examined. Electron probe microanalysis (EPMA) with wavelength dispersive spectroscopy was used for compositional analysis.

RESULTS AND DISCUSSION

Figure 1 is the secondary electron image (SEI) micrograph of the Sn/Ni-3 wt.%V couple reacted at 250°C for 12 h. Since Sn is molten at 250°C, the right-hand side region of Fig. 1 was a homogeneous liquid region in the beginning of the reaction at 250°C. Solid phases formed by either interfacial reactions with the (Ni,V) substrates or solidification from the molten matrix when the couple was removed from the furnace and quenched in the ice water. It is noticed that an interfacial layer is formed adjacent to the (Ni,V) substrate. The composition of this layer is quite uniform and is Sn-37.9at.%Ni-3.8at.%V determined by using EPMA. The interfacial reactions in the Sn/Ni systems have been examined quite extensively, and it has been found that the Ni_3Sn_4 phase is formed at the Sn/Ni interface when the temperature is at 250°C.[11,14] Based on the results of the layer's compositional analysis and the Sn/Ni interfacial reactions, it is presumed that the interfacial reactions in the Sn/Ni-3 wt.%V couples are similar to those in the Sn/Ni couples and the phase formed is the Ni_3Sn_4 phase with a 3.8 at.%V solubility.

Figure 2 is the SEI micrograph of the Sn/Ni-5wt.%V couple reacted at 250°C for 12 h. The microstructure is different from that as shown in Fig. 1. In addition to the formation of a layer adjacent to the (Ni,V) substrate, a region full of discontinuous phases is formed. The composition of the discontinuous phase determined by EPMA is Sn-41.4at.%Ni-0.2at.%V, and it is likely to be the Ni_3Sn_4 phase with almost no vanadium solubility. The EPMA determines the composition of the continuous layer to be Sn-26.4at.%Ni-10.4at.%V. Figure 3 is the line scan result through the continuous layer. The composition of this layer is quite uniform. The compositional and microstructural homogeneities clearly indicate that this continuous layer is a single-phase region. The composition of this continuous layer

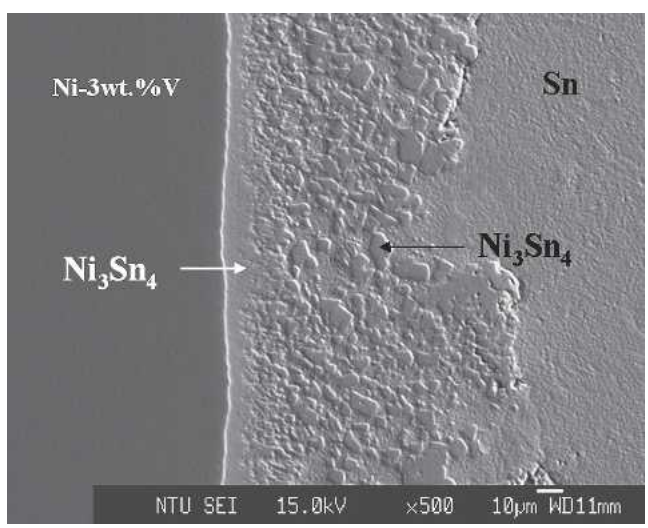

Fig. 1. SEI micrograph of the Sn/Ni-3wt.%V couple reacted at 250°C for 12 h.

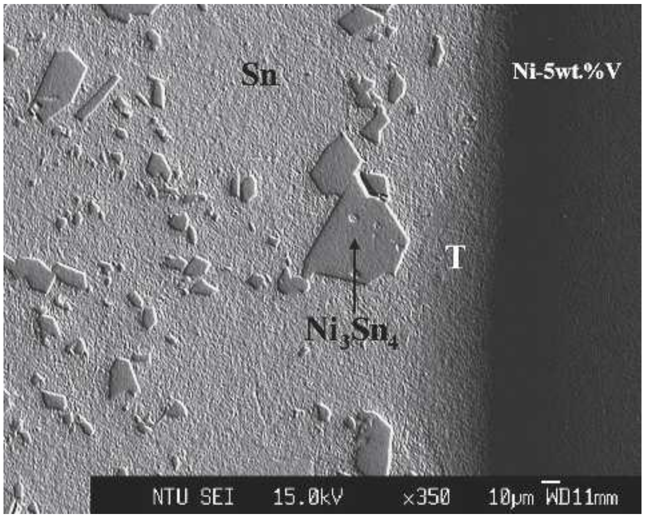

Fig. 2. SEI micrograph of the Sn/Ni-5wt.%V couple reacted at 250°C for 12 h.

phase is marked in the proposed Sn-Ni-V isothermal section, as shown in Fig. 4. Even though it cannot be determined for sure without the diffraction and structural analysis, based on the compositional results and the Sn-Ni-V isothermal section, it is likely that the phase of the continuous layer is not a binary compound with ternary solubility but a ternary T phase. Since there are no previous studies regarding the interfacial reactions of the Sn/(Ni,V) couples and the phase equilibria of the Sn-Ni-V ternary system, this ternary T phase is newly found in this study.

Besides the new T phase, the morphologies of the reaction layers are quite peculiar. As shown in Fig. 2, a large amount of Ni_3Sn_4 phase is mixed with the Sn phase. Since molten Sn at 250°C only has very limited solubility of Ni and V in the binary systems, it is very unlikely that the molten Sn can suddenly have large Ni and V solubility in the ternary solution. Without large solubility of Ni in the molten Sn phase, the large amount of Ni_3Sn_4 phase only can be formed by interfacial reactions at 250°C but not from precipitation during solidification. A possible formation mechanism of the Ni_3Sn_4 phase pieces is that they detached from the T phase layer after it formed by interfacial reactions because the Ni_3Sn_4

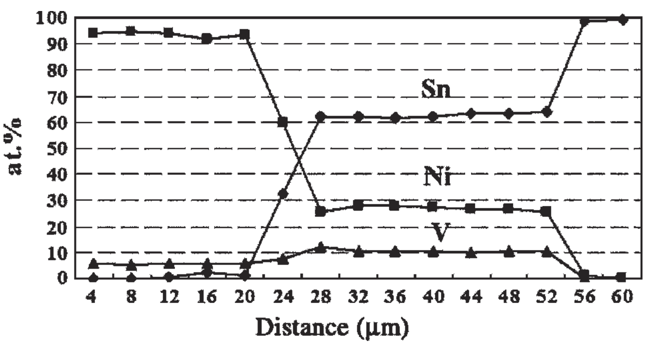

Fig. 3. Line scan result through the T phase in the Sn/Ni-5wt.%V couple.

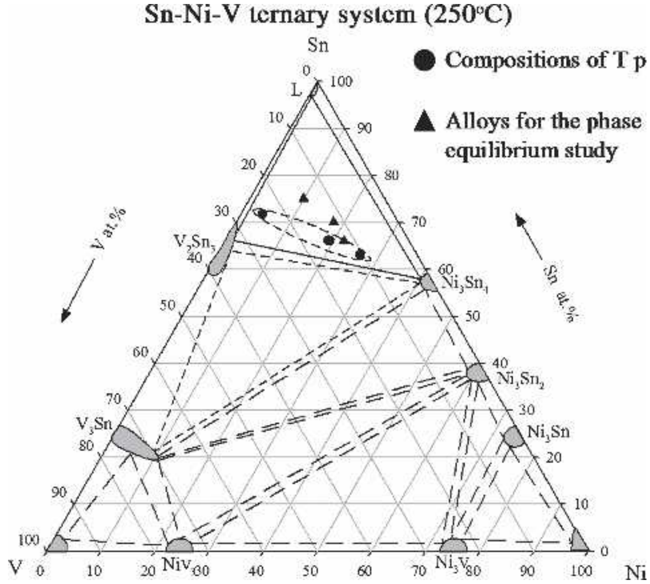

Fig. 4. Sn-Ni-V isothermal section at 250°C proposed in this study.

phase has a very poor wetting property with the T phase layer. As Ni and V are high melting point elements, their diffusivities are lower than that of Sn.[26–28] The Sn is assumed to be the dominate moving atom in the Sn/(Ni,V) couple, and the relative content of Ni to V in the interfacial region should be close to the original composition under this assumption. The composition of the ternary T phase is Sn-26.4at.%Ni-10.4at.%V, and its Ni to V content decreases in comparison with that in the original Ni-V alloy. The excess amount of the Ni reacted with Sn to form the Ni_3Sn_4 phase at 250°C. The reaction path in the Sn/Ni-5wt.%V is thus liquid/Ni_3Sn_4/T/Ni-5wt.%V substrate. Apparently, the result is different from that in the Sn/Ni system.[11,14] A proper assessment of the flip chip reliability with the Ni-V UBM should thus be examined with the Ni-V substrate, not only with the pure Ni substrate.

Since the T phase is a newly found phase, it is quite interesting to investigate its equilibrium phase relationship. Ternary Sn-Ni-V alloys were prepared from the pure elements, as mentioned previously. Proper amounts of constituent elements were weighed, arc melted together, encapsulated in a quartz tube, and homogenized at 1,000°C for 3 weeks. The alloys were then equilibrated at 250°C for 8 weeks. The nominal compositions of the three prepared alloys are Sn-18at.%Ni-12at.%V (01), Sn-10at.%Ni-15at.%V (02), and Sn-22at.%Ni-12at.%V(03). Figure 5 is the backscattered electron image (BEI) micrograph of alloy 01. Three different phase regions are observed. As summarized in Table I, the composition of the darkest phase is Sn-41.9at.%Ni-0.2at.%V, as determined by using EPMA. Based on this compositional analysis and the x-ray diffraction results, this phase is the Ni_3Sn_4 phase. The composition of the gray phase adjacent to Ni_3Sn_4 is Sn-2.1at.%Ni-30.9at.%V and is the V_2Sn_3 phase.[29]

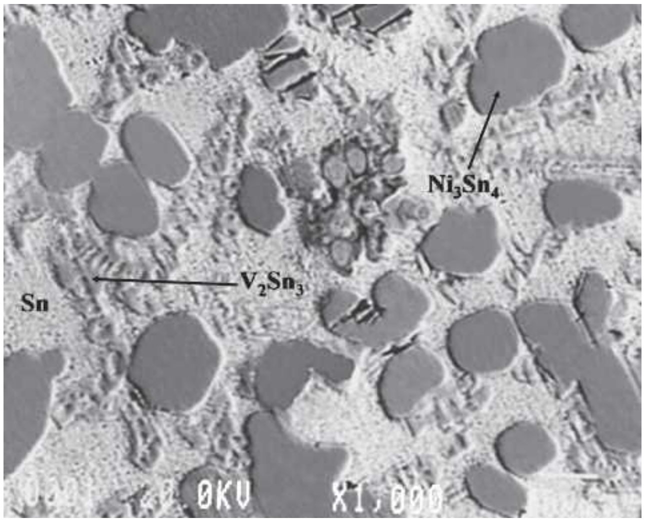

Fig. 5. BEI micrograph of alloy 01 (Sn-18at.%Ni-12at.%V) annealed for 8 weeks.

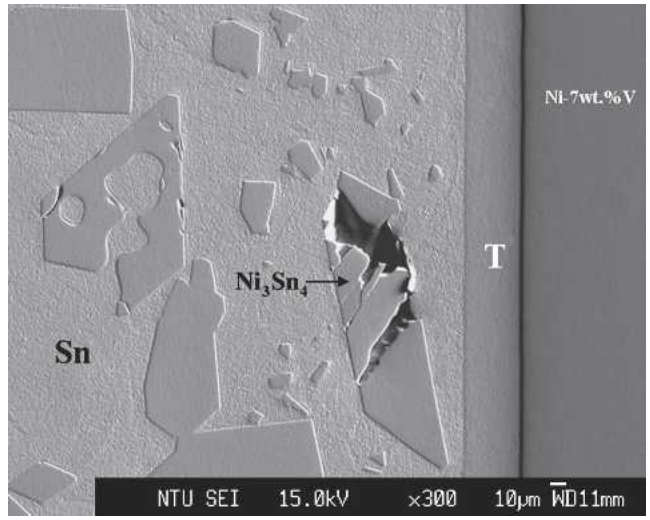

Fig. 6. SEI micrograph of the Sn/Ni-7wt.%V couple reacted at 250°C for 12 h.

The brightest continuous phase is Sn phase with Sn-0.2at.%Ni-0.1at.%V composition. The Sn phase is molten at 250°C and solidified when the specimen was removed from the furnace.

The equilibrium phase relationships determined for alloys 02 and 03 are similar to that of alloy 01. The results are summarized in Table I. Liquid phase, Ni_3Sn_4 phase, and the V_2Sn_3 phase are found in the three equilibrated alloys. At 250°C, the stable phases from the constituent binary systems are liquid (Sn), Ni_3Sn_4, Ni_3Sn_2, Ni_3Sn, Ni, Ni_8V, Ni_3V, Ni_2V, σ, NiV_3, V, V_3Sn, and V_2Sn_3.[25,29,30] Figure 4 is the Sn-Ni-V 250°C isothermal section proposed in this study based on the phase equilibria experiment samples and the information of the three binary constituent systems.[25,29,30] As shown in Fig. 4, the compositions of the three Sn-Ni-V alloys are prepared in the region so that if there is a thermodynamically stable T phase, the T phase would exist in the prepared alloys. However, the ternary T phase as observed in the Sn/Ni-5wt.%V couple has not been found from any of the phase equilibria studies. The ternary T phase could thus be a metastable phase formed in the reaction couple due to its formation kinetics. Further studies are needed to verify the phase relationship and the metastability of the T phase at the Sn-rich corner.

Figure 6 is the SEI micrograph of the Sn/Ni-7wt.%V couple reacted at 250°C for 12 h. The result is very similar to that shown in Fig. 2. A continuous interfacial layer and a region of dispersed solid phase pieces are found. The fractured phases are determined to be the Ni_3Sn_4 phase. The composition of the interfacial reaction layer determined by EPMA is Sn-19.2at.%Ni-14.6at.%V. Similar to the argument proposed in the discussion of the reaction with the Ni-5wt.%V substrate, the interfacial layer is a ternary phase, but not a binary compound with ternary solubility. Figure 7 is the SEI micrograph of the Sn/Ni-12wt.%V couple reacted at 250°C for 12 h. Similar results are found as in the couples with 5wt.%V and 7wt.%V substrates; a continuous ternary phase layer and Ni_3Sn_4 phase are formed from interfacial reactions. The composition of the continuous layer is Sn-4at.%Ni-24at.%V. It is also noticed that the Ni_3Sn_4 phases in Fig. 7 are with much larger pieces, but the explanation is still not clear.

The reaction path is thus liquid/Ni_3Sn_4/T/Ni-V substrate when the vanadium contents are 5wt.%V and higher. As summarized in Table II and shown

Table I. Results of Phase Equilibria Experiments at 250°C

Alloy	Nominal Compositions	Phases	Compositions (At.%) Sn	Ni	V
1	Sn-18at.%Ni-12at.%V	Liquid(Sn)	99.7	0.2	0.1
		V_2Sn_3	67.0	2.1	30.9
		Ni_3Sn_4	57.9	41.9	0.2
2	Sn-10at.%Ni-15at.%V	Liquid(Sn)	91.9	0.1	8.0
		V_2Sn_3	71.0	1.1	27.9
		Ni_3Sn_4	57.7	42	0.3
3	Sn-22at.%Ni-12at.%V	Liquid(Sn)	90.7	1.2	8.1
		V_2Sn_3	68.7	1.9	29.4
		Ni_3Sn_4	57.6	42.4	0

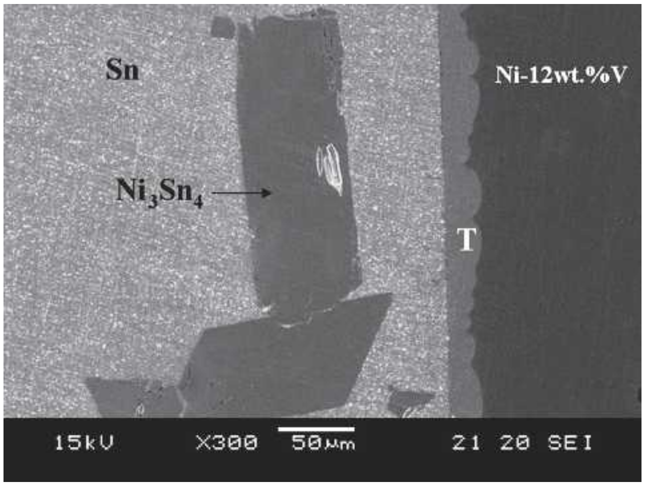

Fig. 7. SEI micrograph of the Sn/Ni-12wt.%V couple reacted at 250°C for 12 h.

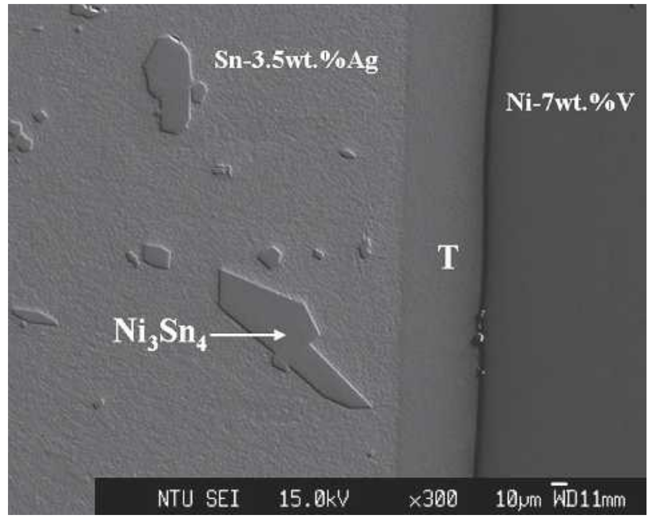

Fig. 8. SEI micrograph of the Sn-3.5wt.%Ag/Ni-7wt.%V couple reacted at 250°C for 12 h.

in Fig. 4, it can be observed that the vanadium contents in the ternary phase layers vary with the vanadium contents of the Ni-V substrates. It is very likely that the formation of the T phase is strongly controlled by the diffusion kinetics and the original mass balance at the interface, and thus, the composition of the ternary phase formed is strongly influenced by the original vanadium contents of the substrates. It also needs to be mentioned that the thickness of the T phase is thinner in the 12wt.%V couple, but no significant differences in the 5wt.%V and 7wt.%V couples. Future studies with different vanadium contents of the Ni-V substrates and with longer reaction times will be carried out to further investigate the characteristics of the T phase.

Figure 8 is the SEI micrograph of the Sn-3.5wt.%Ag/Ni-7wt.%V couple reacted at 250°C for 12 h. Similar to that found in the couple with pure solder, a continuous interfacial layer and pieces of Ni_3Sn_4 phase are formed. As summarized in Table II, the composition of the interfacial layer is Sn-19.9at.%Ni-15.3at.%V-0.3at.%Ag. With similar arguments, the continuous interfacial layer is a ternary phase layer. Figures 9 and 10 are SEI micrographs of the Sn-3.5wt.%Ag/(Ni,V) couples reacted at 250°C for 12 h, and the vanadium contents are 5 wt.% and 12 wt.%, respectively. Comparing the results of Sn-Ag/(Ni,V) as shown in Figs. 8–10 with those in the respective Sn/(Ni,V) couples, as shown in Figs. 6, 2, and 7, it can be found that their interfacial products are very similar. Both a ternary phase and the Ni_3Sn_4 phase are formed from interfacial reactions, and the Ag solubilities in both phases are very limited. Similar to the previous studies in the Sn-3.5wt.%Ag/Ni and Sn/Ni interfacial reactions,[11,14,23] Ag does not significantly participate in the interfacial reactions. Figure 11 is the SEI micrograph of the Sn-3.5wt.%Ag/Ni-3wt.%V reaction couple, similar to that in the Sn/Ni-3wt.%V couple; only the Ni_3Sn_4 phase is formed. The Sn-3.5wt.%Ag/(Ni,V) couple studies again indicate that the reaction paths are different from those with pure nickel substrate when the vanadium contents are 5 wt.% and higher. Since the vanadium content in the commercial UBM Ni-V layer is 7 wt.%, reliability assessment of the flip chip products must rely on the interfacial reaction results with the Ni-V substrates. Future studies to fully understand the interfacial reactions between solder and Ni-V substrates are thus very important.

Table II. Compositional Analysis of the Phases Formed in the Reaction Couples

		Phases Formed in the Reaction Couples							
		Ni_3Sn_4				Ternary Phase			
Solders	Substrates	Sn (at.%)	Ni (at.%)	V (at.%)	Ag (at.%)	Sn (at.%)	Ni (at.%)	V (at.%)	Ag (at.%)
Sn	Ni-3wt.%V	58.3	37.9	3.8	—	—	—	—	—
Sn-3.5wt.%Ag		60.0	36.0	4.0	0	—	—	—	—
Sn	Ni-5wt.%V	58.4	41.4	0.2	—	63.2	26.4	10.4	—
Sn-3.5wt.%Ag		57.4	42.5	0.1	0	63.9	25.1	10.7	0.3
Sn	Ni-7wt.%V	57.9	42.1	0	—	66.2	19.2	14.6	—
Sn-3.5wt.%Ag		57.8	42.1	0.1	0	64.5	19.9	15.3	0.3
Sn	Ni-12wt.%V	58.9	41.0	0.1	—	72.0	4.0	24.0	—
Sn-3.5wt.%Ag		57.7	42.2	0.1	0	72.0	4.5	23.3	0.2

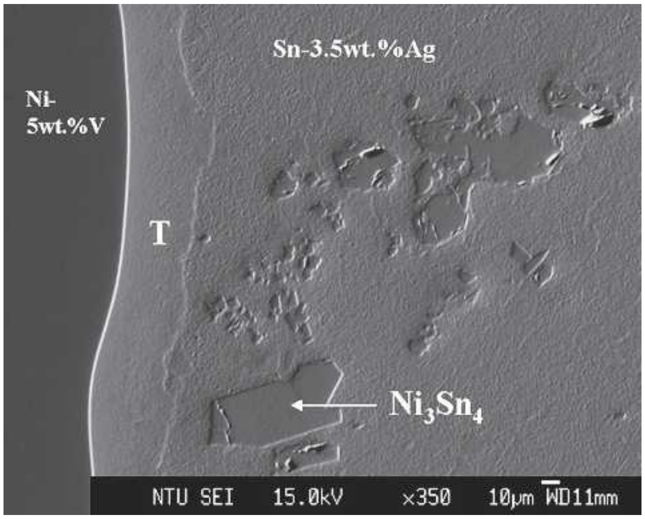

Fig. 9. SEI micrograph of the Sn-3.5wt.%Ag/Ni-5wt.%V couple reacted at 250°C for 12 h.

CONCLUSIONS

The interfacial reactions at 250°C in the Sn/(Ni,V) and Sn-3.5wt.%Ag/(Ni,V) systems are different from those in the solder/Ni system when the vanadium contents are 5 wt.% and higher. Besides the formation of the Ni_3Sn_4 phase, as commonly observed in the solder/Ni reaction couples, a new ternary phase is formed. The phase formation results in the Sn/(Ni,V) and Sn-3.5wt.%Ag/(Ni,V) couples being quite similar. When the vanadium contents of the substrate are 5 wt.% and higher, both the Ni_3Sn_4 phase and a ternary phase are formed. The ternary T phase has never been reported in the literature. Future studies are necessary to confirm its structure and the compositional regime. Since the reactions are different at the solder/Ni and at the solder/Ni-7wt.%V interfaces, the reliability of the commercial flip chip products with the Ni-7wt.%V barrier layer should be reassessed with proper interfacial reaction information.

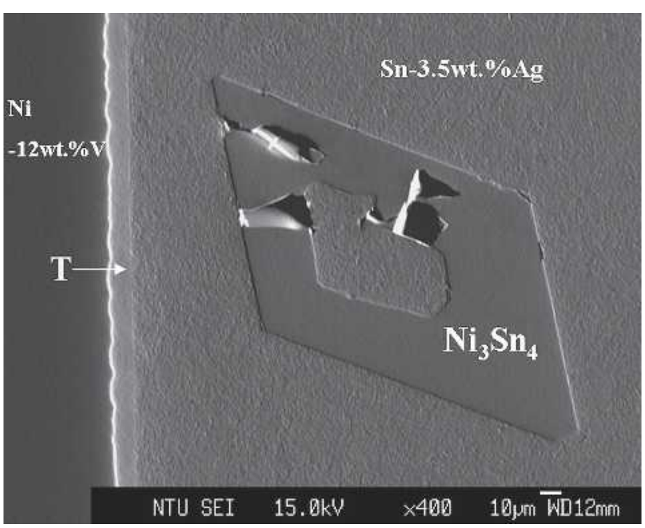

Fig. 10. SEI micrograph of the Sn-3.5 wt.%Ag/Ni-12wt.%V couple reacted at 250°C for 12 h.

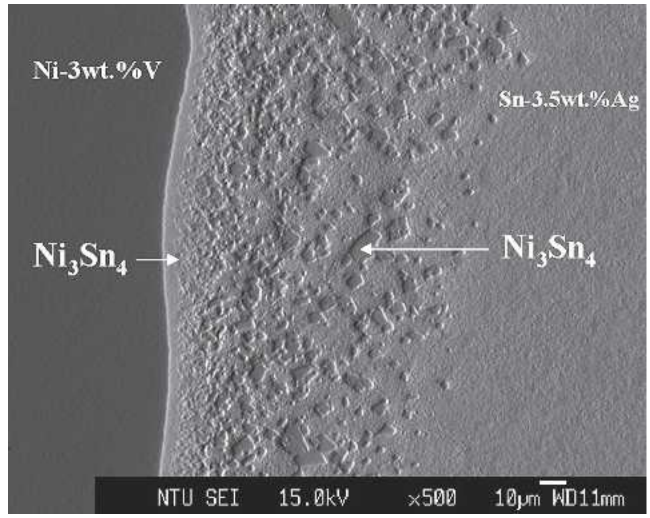

Fig. 11. SEI micrograph of the Sn-3.5wt.%Ag/Ni-3wt.%V couple reacted at 250°C for 12 h.

ACKNOWLEDGEMENT

The authors acknowledge the financial support of the National Science Council of Taiwan, Republic of China (Grant No. NSC93-2216-E007-043).

REFERENCES

1. D.R. Frear, J.W. Jang, J.K. Lin, and C. Zhang, *JOM* 53 (1), 28 (2001).
2. C.Y. Liu, K.N. Tu, T.T. Sheng, C.H. Tung, D.R. Frear, and P. Elenius, *J. Appl. Phys.* 87, 750 (2000).
3. S.K. Kang and V. Ramachandran, *Scripta Metall.* 14, 421 (1980).
4. Z. Marinkovic and V. Simic, *Thin Solid Films* 98, 95 (1982).
5. J.A. van Beek, S.A. Stolk, and J.J. Frans van Loo, *Z. Metallkd.* 73, 439 (1982).
6. W.J. Tomlinson and H.G. Rhodes, *J. Mater. Sci.* 22, 1769 (1987).
7. J. Haimovich, *Welding Res. Suppl.* March, 102s (1989).
8. C.Y. Lee and K.L. Lin, *Thin Solid Films* 249, 201 (1994).
9. S. Bader, W. Gust, and H. Hieber, *Acta Metall. Mater.* 43, 329 (1994).
10. S.K. Kang, R.S. Rai, and S. Purushothaman, *J. Electron. Mater.* 25, 1113 (1996).
11. S.-W. Chen, C.-M. Chen, and W.-C. Liu, *J. Electron. Mater.* 27, 1193 (1998).
12. D. Gur and M. Bamberger, *Acta Mater.* 46, 4917 (1998).
13. Y.D. Jeon and K.W. Paik, *Proc. Electron. Components. Technol. Conf.* (Piscataway, NJ:IEEE, 2001), pp. 1326–1332.
14. S.-W. Chen, S.-H. Wu, and S.-W. Lee, *J. Electron. Mater.* 32, 1188 (2003).
15. W.K. Choi and H.M. Lee, *J. Electron. Mater.* 28, 1251 (1999).
16. J.W. Jang, P.G. Kim, K.N. Tu, D.R. Frear, and P. Thompson, *J. Appl. Phys.* 85, 8456 (1999).
17. P.G. Kim, J.W. Jang, T.Y. Lee, and K.N. Tu, *J. Appl. Phys.* 86, 6746 (1999).
18. P.L. Liu and J.K. Shang, *J. Electron. Mater.* 29, 622 (2000).
19. T.M. Korhonen, P. Su, S.J. Hong, M.A. Korhonen, and C.Y. Li, *J. Electron. Mater.* 29, 1194 (2000).
20. J.W. Jang, D.R. Frear, T.Y. Lee, and K.N. Tu, *J. Appl. Phys.* 88, 6359 (2000).
21. J.Y. Park, C.W. Yang, J.S. Ha, C.U. Kim, E.J. Kwon, S.B. Jung, and C.S. Kang, *J. Electron. Mater.* 30, 1165 (2001).
22. C.E. Ho, R.Y. Tsai, Y.L. Lin, and C.R. Kao, *J. Electron. Mater.* 31, 584 (2002).
23. H.-F. Hsu and S.-W. Chen, *Acta Mater.* 52, 2541 (2004).
24. *Official Journal of the European Union,* L37/19–L37/23 (February 13, 2003).

25. J.F. Smith, O.N. Carlson, and P.G. Nash, *Phase Diagrams of Binary Nickel Alloys* (Materials Park, OH: ASM International, 1991), pp. 361–367.
26. ASM Handbook Committee, *Metals Handbook*, 10th ed. (Metals Park, OH, ASM, 1990), vol. 2, pp. 1166–1167.
27. E.A. Brandes, *Smithells Metals Reference Book*, 6th ed. (London: Butterworth & Co Ltd., 1983), pp. 13-1–13-14.
28. M.B. Bever, *Encyclopedia of Materials Science and Engineering* (Cambridge, United Kingdom: Oxford University Press, 1986), vol. 2, pp. 1175-86.
29. J.F. Smith, *Phase Diagrams of Binary Vanadium Alloys* (Metals Park, OH, ASM International, 1989), pp. 270–274.
30. P. Nash and A. Nash, *Bull. Alloy Phase Diagrams* 6, 350 (1985).