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ARTICLE

Phase Equilibria in the Ni-Al-Sn Ternary System at 800 and 1000 °C

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Abstract: The phase equilibria in the Ni-Al-Sn ternary system at 800 and 1000 °C was investigated by electron probe microanalysis and X-ray diffraction. The results show that: (1) No ternary compound is found at 800 and 1000 °C. (2) The Ni-Al side presents four binary compounds including NiAl, Ni_3Al, Al_3Ni and Al_3Ni_2 phases. The solubilities of Sn in the binary NiAl and Ni_3Al phases are 3.1 at% and 14.7 at% at 800 °C, and 3.0 at% and 8.0 at% at 1000 °C, respectively. As for the binary Al_3Ni and Al_3Ni_2 phases, the solubilities of Sn are almost negligible. (3) The Ni-Sn side displays three binary compounds including Ni_3Sn(r), Ni_3Sn(h) and Ni_3Sn_2(h). The Ni_3Sn(r) phase is stable at 800 °C dissolving 4.2 at% Al, but it is replaced by the Ni_3Sn(h) phase with a 5.5 at% Al solubility at 1000 °C. The solid solubility of Al in Ni_3Sn_2(h) is 8.4 at% and 12.1 at% at 800 and 1000 °C, respectively. (4) The Al-Sn side is occupied by an interconnected liquid region having only ~1 at% Ni solubility.

Key words: Ni-Al-Sn ternary system; phase equilibria; solubility; electron probe microanalysis

Nickel (Ni) is one of the most important substrates or coating materials in electronic devices because of its good oxidation resistance[1, 2]. Aluminum (Al) is generally used as an electronic packaging materials due to its low density and good electrical conductivity[3, 4]. During the soldering process, interfacial reactions will occur at soldering joint among Ni, Al and Sn elements[5]. Additionally, the addition of Ni and Al elements can improve the overall performance of lead-free solders[6-8]. In order to study the lead-free solder and the interfacial reactions on Ni substrate, it is important to determine the Ni-Al-Sn ternary equilibria experimentally.

Three binary subsystems of Ni-Al[9], Ni-Sn[10] and Al-Sn[11] constitute the Ni-Al-Sn ternary system, as shown in Fig.1. Nash et al[12,13] plotted the Al-rich Ni-Al binary phase diagram based on the experimental data available. Subsequently, Okamoto[9] made a complete revision, and Huang et al[14,15] conducted a thermodynamic evaluation for the Ni-Al binary system. The Ni-Sn binary system has been widely studied as an important lead-free soldering material system[16], and assessed by Ghosh[17], Liu[18] and Zemanova[19] et al. The Al-Sn is a simple eutectic system with the eutectic point close to the tin side. The mutual solubility in the solid metals is quite low, and no intermetallic compounds were found in the Al-Sn binary system[20].

Although there have been a large number of investigations about the above subsystems, the experimental information of the Ni-Al-Sn ternary system is still scarce. Up to now, there are only the phase diagrams of the Ni-Al-Sn ternary system at room temperature[21], as shown in Fig.2. Despite the fact that soldering temperature is usually lower than 450 °C[22], it is necessary to obtain the phase equilibrium information at high temperature, and it will provide a theoretical basis for the thermodynamic calculation of the Ni-Al-Sn ternary system.

1 Experiment Procedures

In this work, high purity metals were used: nickel (99.9 wt%),

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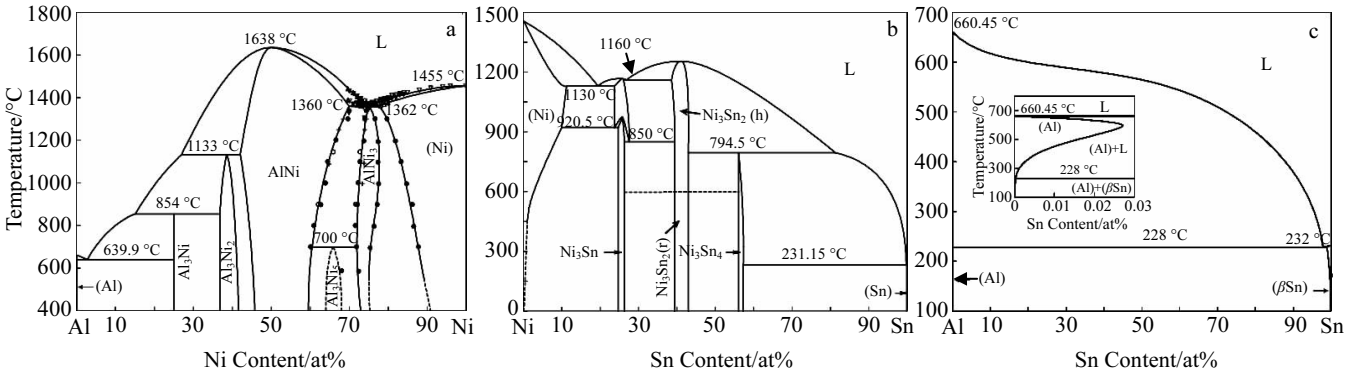

Fig.1 Binary phase diagrams that constitute the Ni-Al-Sn ternary system: (a) Al-Ni[9] binary system, (b) Ni-Sn[10] binary system, and (c) Al-Sn[11] binary system

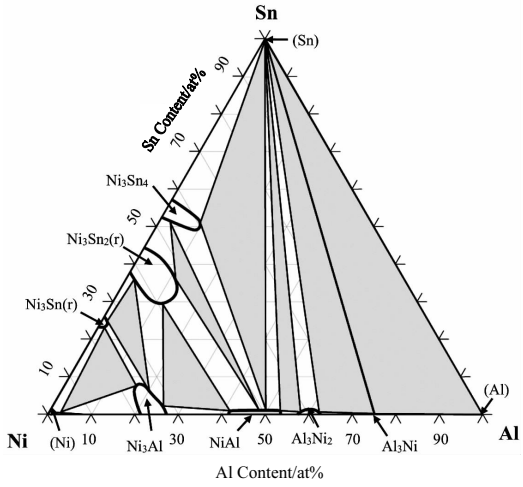

Fig.2 Isothermal section of Ni-Al-Sn ternary system at room temperature[21]

aluminum (99.8 wt%), and tin (99.9 wt%). Each Ni-Al-Sn ternary alloy weighed around 20 g was prepared by arc smelting in an argon atmosphere. Afterwards, the ternary Ni-Al-Sn alloys were cut into small pieces and were sealed in quartz tubes with argon for further annealing treatment. The specimens in the quartz capsules were annealed at 800 and 1000 ºC for various durations. After the end of heat treatment, the specimens were quenched into ice water.

After standard metallographic preparation, microstructure observations and chemical analyses of the equilibrium phases were carried out on electron-probe-microanalyzer (EPMA, JXA-8100, JEOL, Japan). High purity metals were used as standard metallographic and the measurements were carried out at a voltage of 20 kV and a current of 20 nA. In addition, the composition of liquid phase was determined by EDS-Mapping analysis in this work, and the final phase composition comes from the statistical averaging of five liquid region. The crystal structure analysis was conducted using X-ray diffraction (XRD) on a Philips Panalytical X-pert diffractometer (Cu Kα radiation at 40 kV and 30 mA). The data were collected in the range of 2θ from 20° to 110° at a step size of 0.01°. Corresponding XRD evaluations were carried out using the Jade software, version 6.5.

2 Results and Discussion

2.1 Phase equilibrium at 800 and 1000 °C

In the present study, 15 samples with different composition were prepared in order to determine the phase equilibria at 800 and 1000 °C in the Ni-Al-Sn ternary system. Alloys with different composition were marked with different numbers for reading convenience. The related equilibrium composition of the Ni-Al-Sn ternary system at 800 and 1000 ºC is summarized in Table 1. Back-scattered electron (BSE) images and X-ray diffraction (XRD) patterns for most of the Ni-Al-Sn ternary specimens are shown in Fig.3 and Fig.4, respectively. All the mentioned chemical compositions in this work were given in the form of an atomic fraction (at%). All observed phases were identified via two methods: the equilibrium composition measured by EPMA, and the crystal structure analysis by XRD. Most of the identification of equilibrium phases could be confirmed by taking advantage of the available composition ranges and crystal structure information of the intermetallic compounds in the binary and ternary systems[14,19,21].

A BSE image of the alloy 2# ($Ni_{30}Al_{40}Sn_{30}$) annealed at 800 °C is presented in Fig.3a, showing three-phase co-existence of (NiAl + Al_3Ni_2 + L). The corresponding XRD pattern, shown in Fig.4a, shows the characteristic diffraction peak of βSn originated from the liquid solidification process during quenching. In the alloy 5# ($Ni_{30}Al_{65}Sn_5$) annealed at 800 ºC for 3 d, a three-phase equilibrium of (Al_3Ni (black) + Al_3Ni_2 (gray) +L (rest)) is found, as shown in Fig.3b. The XRD analysis (Fig.4b) further matches up with them. The annealed alloy 8# ($Ni_{50}Al_{15}Sn_{35}$) is composed of three-phase microstructure of

Table 1 Equilibrium composition of the Ni-Al-Sn ternary system at 800 and 1000 ºC

Temperature /°C	Sample No.	Alloy composition/ at%	Annealing time/d	Phase equilibria	Composition/at%					
					Phase 1		Phase 2		Phase 3	
				Phase 1/Phase 2/Phase 3	Al	Sn	Al	Sn	Al	Sn
800	1#	$Ni_{18}Al_{77}Sn_5$	3	Al_3Ni/L	75.5	0.0	80.0	18.6	-	-
	2#	$Ni_{30}Al_{40}Sn_{30}$	3	NiAl/Al_3Ni_2/L	57.7	0.4	55.2	0.2	2.5	96.1
	3#	$Ni_{30}Al_{50}Sn_{20}$	3	Al_3Ni_2/L	62.3	0.1	8.2	90.4	-	-
	4#	$Ni_{30}Al_{60}Sn_{10}$	3	Al_3Ni_2/L	61.8	0.1	46.0	53.0	-	-
	5#	$Ni_{30}Al_{65}Sn_5$	3	Al_3Ni_2/Al_3Ni/L	62.0	0.1	75.6	0.0	56.0	42.0
	6#	$Ni_{38}Al_{52}Sn_{10}$	3	Al_3Ni_2/L	57.6	0.4	3.0	95.8	-	-
	7#	$Ni_{42}Al_{48}Sn_{10}$	3	NiAl/L	54.3	0.4	1.7	93.8	-	-
	8#	$Ni_{50}Al_{15}Sn_{35}$	3	NiAl/Ni_3Sn_2(h)/L	49.0	1.1	2.2	43.5	1.3	87.0
	9#	$Ni_{55}Al_{30}Sn_{15}$	20	NiAl/Ni_3Sn_2(h)	45.1	1.3	3.0	38.2	-	-
	10#	$Ni_{65}Al_{25}Sn_{10}$	20	NiAl/Ni_3Al/Ni_3Sn_2(h)	36.4	3.1	27.0	2.4	8.4	29.7
	11#	$Ni_{67}Al_{23}Sn_{10}$	20	NiAl/Ni_3Al/Ni_3Sn_2(h)	36.3	3.0	26.5	2.1	8.2	29.3
	12#	$Ni_{68}Al_{18}Sn_{14}$	20	Ni_3Al/Ni_3Sn_2(h)	25.7	2.5	6.8	30.1	-	-
	13#	$Ni_{70}Al_6Sn_{24}$	20	Ni_3Al/Ni_3Sn(r)/Ni_3Sn_2(h)	11.9	14.7	4.2	21.4	1.9	36.7
	14#	$Ni_{80}Al_8Sn_{12}$	20	(Ni)/Ni_3Al/Ni_3Sn(r)	10.5	3.9	12.2	11.3	3.9	21.3
	15#	$Ni_{80}Al_{12}Sn_8$	27	(Ni)/Ni_3Al/Ni_3Sn(r)	10.6	3.7	12.5	11.2	4.0	21.4
1000	4#	$Ni_{30}Al_{60}Sn_{10}$	3	Al_3Ni_2/L	58.8	0.3	62.0	37.0	-	-
	5#	$Ni_{30}Al_{65}Sn_5$	3	Al_3Ni_2/L	61.2	0.0	77.7	20.2	-	-
	6#	$Ni_{38}Al_{52}Sn_{10}$	3	Al_3Ni_2/NiAl/L	58.5	0.1	53.3	0.1	3.1	96.6
	7#	$Ni_{42}Al_{48}Sn_{10}$	3	NiAl/L	53.3	0.7	1.8	96.2	-	-
	8#	$Ni_{50}Al_{15}Sn_{35}$	3	NiAl/Ni_3Sn_2(h)/L	48.3	0.7	4.7	38.4	0.5	72.9
	9#	$Ni_{55}Al_{30}Sn_{15}$	20	NiAl/Ni_3Sn_2(h)	46.6	0.9	5.4	35.6	-	-
	10#	$Ni_{65}Al_{25}Sn_{10}$	20	NiAl/Ni_3Sn_2(h)	32.7	2.8	12.1	24.3	-	-
	11#	$Ni_{67}Al_{23}Sn_{10}$	20	NiAl/Ni_3Al/Ni_3Sn_2(h)	32.3	3.0	24.9	2.0	12.1	24.3
	12#	$Ni_{68}Al_{18}Sn_{14}$	20	Ni_3Al/Ni_3Sn_2(h)	20.6	2.3	10.8	25.6	-	-
	13#	$Ni_{70}Al_6Sn_{24}$	20	Ni_3Al/Ni_3Sn(h) / Ni_3Sn_2(h)	16.5	8.0	5.5	20.6	4.2	32.2
	14#	$Ni_{80}Al_8Sn_{12}$	20	(Ni)/Ni_3Sn(h)	10.7	4.4	4.5	20.6	-	-
	15#	$Ni_{80}Al_{12}Sn_8$	20	(Ni)/Ni_3Al/Ni_3Sn(h)	11.7	4.5	14.7	7.9	4.6	20.2

(NiAl + Ni_3Sn_2(h) + L) at 800 °C, as shown in Fig.3c, and the Fig.4c reveals the corresponding XRD pattern.

Fig.3d shows a typical two-phase microstructure from the annealed alloy 9# ($Ni_{55}Al_{30}Sn_{15}$). The corresponding XRD pattern is presented in Fig.4d, which shows all the diffraction peaks of the NiAl and Ni_3Sn_2(h) phase. The EPMA analysis indicates that the black phase is NiAl, and the grey one is Ni_3Sn_2(h). The BSE image and corresponding XRD pattern of 15# ($Ni_{80}Al_{12}Sn_8$) alloy is shown in Fig.3e and Fig.4e, respectively. According to the determined phase composition and crystal structure, 15# ($Ni_{80}Al_{12}Sn_8$) alloy shows the co-existence of the three-phases of (Ni) (black) + Ni_3Al (dark grey) + Ni_3Sn(r) (light grey). The BSE image of 5# ($Ni_{30}Al_{65}Sn_5$) alloy is shown in Fig.3f, in which the two-phase microstructure of (Al_3Ni_2 + L) is established using EPMA and XRD (Fig.4f) analysis. As the liquid phase of 5# alloy precipitates Al and *β*Sn during solidification, corresponding peaks of Al and *β*Sn appear in Fig.4f. The BSE images presented in Fig.3g and Fig.3h show that the annealed alloy 11# ($Ni_{67}Al_{23}Sn_{10}$) and 13# ($Ni_{70}Al_6Sn_{24}$) are three-phase co- existence microstructure at 1000 °C. Fig.5 is the element mapping of 11# ($Ni_{67}Al_{23}Sn_{10}$) alloy analyzed by EPMA. Combined with the XRD pattern shown in Fig.4g, a three-phase microstructure of NiAl + Ni_3Al + Ni_3Sn_2(h) could be identified. Also, it could be concluded that 13# alloy consists of Ni_3Sn(h), Ni_3Al, and Ni_3Sn_2(h) based on EPMA and XRD results.

2.2 Isothermal section at 800 and 1000 °C

Based on the above experimental data, the 800 and 1000 ºC isothermal section diagram was established. Fig.6a shows the 800 isothermal setion. In total, six three-phase regions and one liquid region are experimentally confirmed at 800 ºC and are marked with different symbols. The solubility of Al in the Ni_3Sn(r) and Ni_3Sn_2(h) phase was measured to be about 4.2 at% and 8.4 at%, respectively. The solubility of Sn in the Ni_3Al and NiAl phase is about 14.7 at% and 3.1 at%, respectively. In addition, the solid solubility of Sn in Al_3Ni_2 and Al_3Ni is almost negligible. Fig.6b shows the isothermal section of Ni-Al-Sn ternary system at 1000 ºC. Five three-phase equilibria, Ni+Ni_3Al+Ni_3Sn(h), Ni_3Al+Ni_3Sn(h)+ Ni_3Sn_2(h), Ni_3Al+Ni_3Sn_2(h)+NiAl, NiAl+Ni_3Sn_2(h)+Liquid

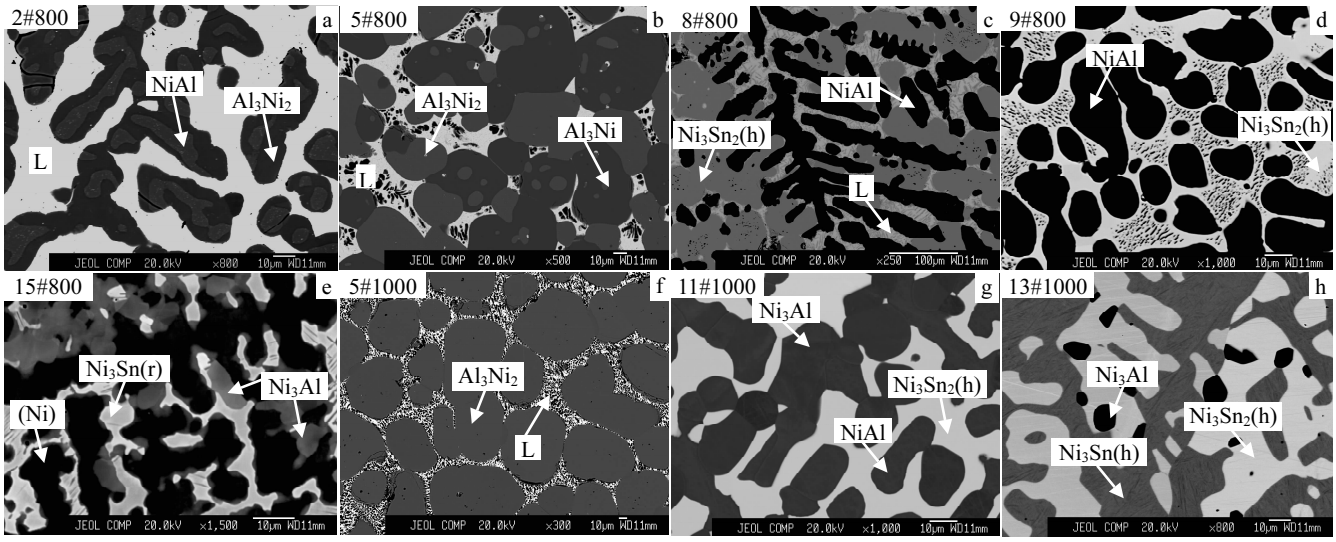

Fig.3 Microstructures of ternary Ni-Al-Sn system obtained from different samples: (a) 2#, (b) 5#, (c) 8#, (d) 9# and (e) 15# alloys annealed at 800 °C; (f) 5#, (g) 11# and (h) 13# alloys annealed at 1000 °C

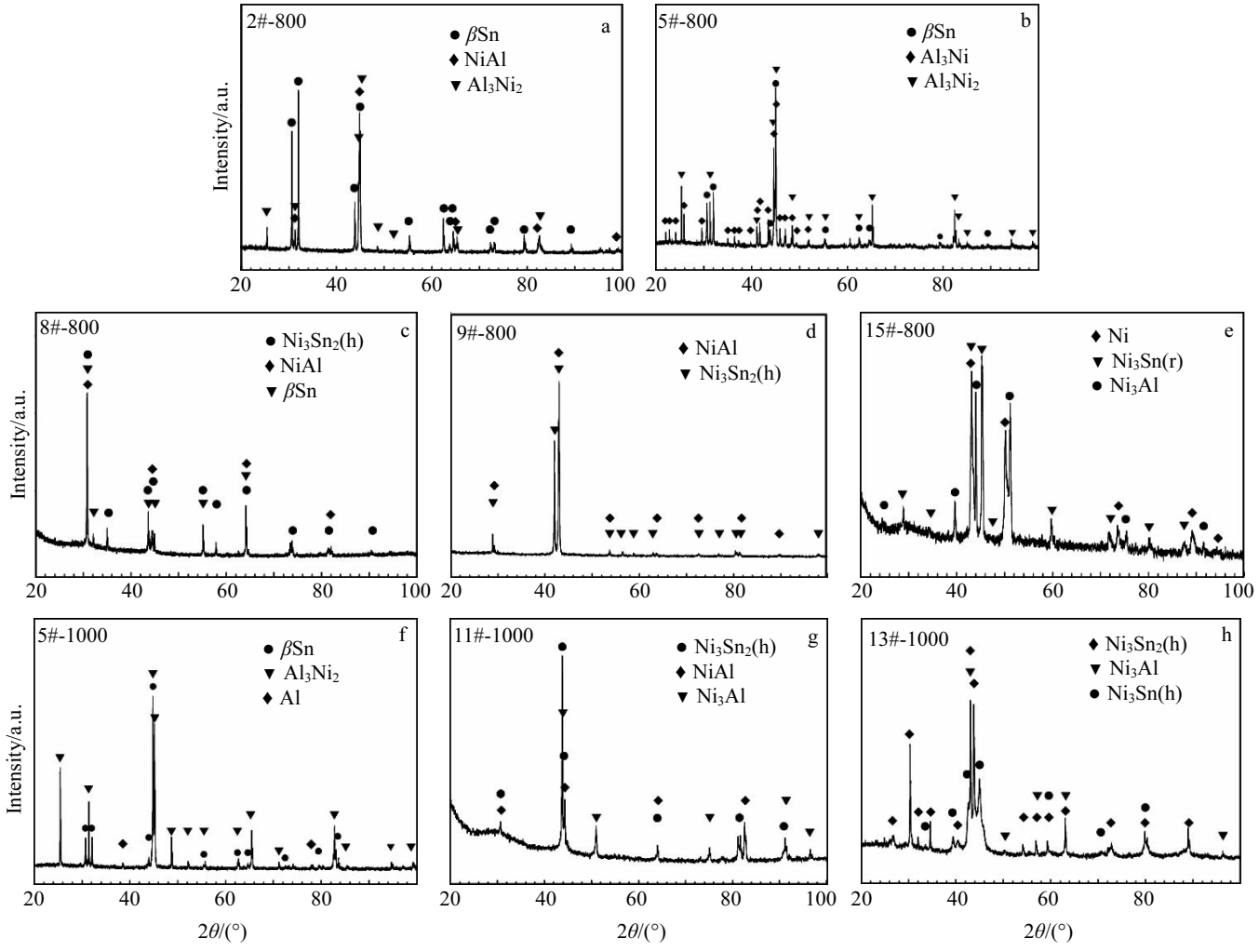

Fig.4 XRD patterns of Ni-Al-Sn ternary alloy obtained from different samples: (a) 2#, (b) 5#, (c) 8#, (d) 9#, and (e) 15# alloys annealed at 800 °C; (f) 5#, (g) 11#, and (h) 13# alloys annealed at 1000 °C

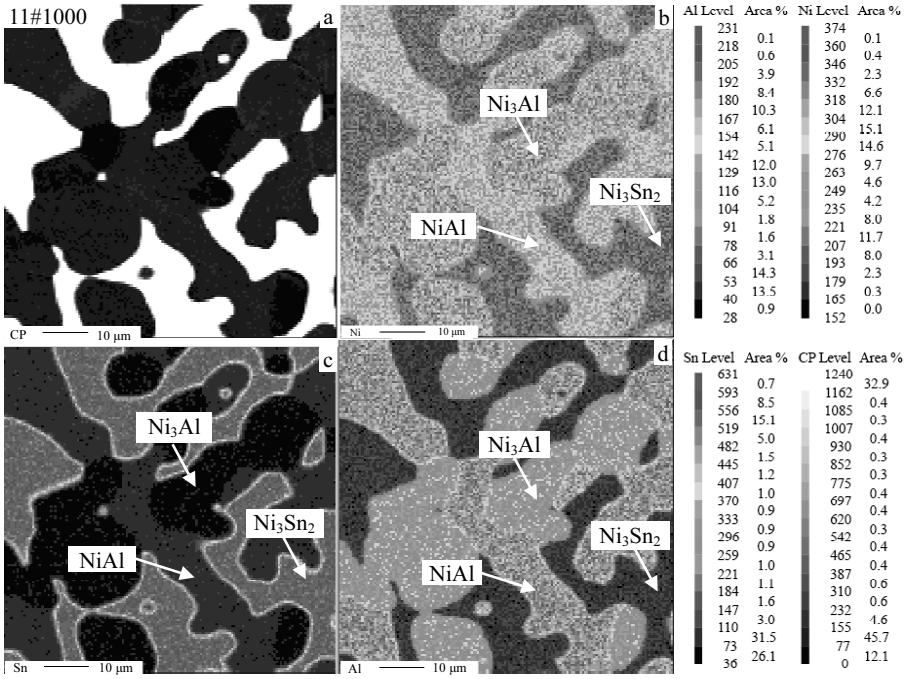

Fig.5 BSE image (a) and element mapping (b~d) of 11# alloy annealed at 1000 °C for 20 d: (b) Ni, (c) Sn, and (d) Al

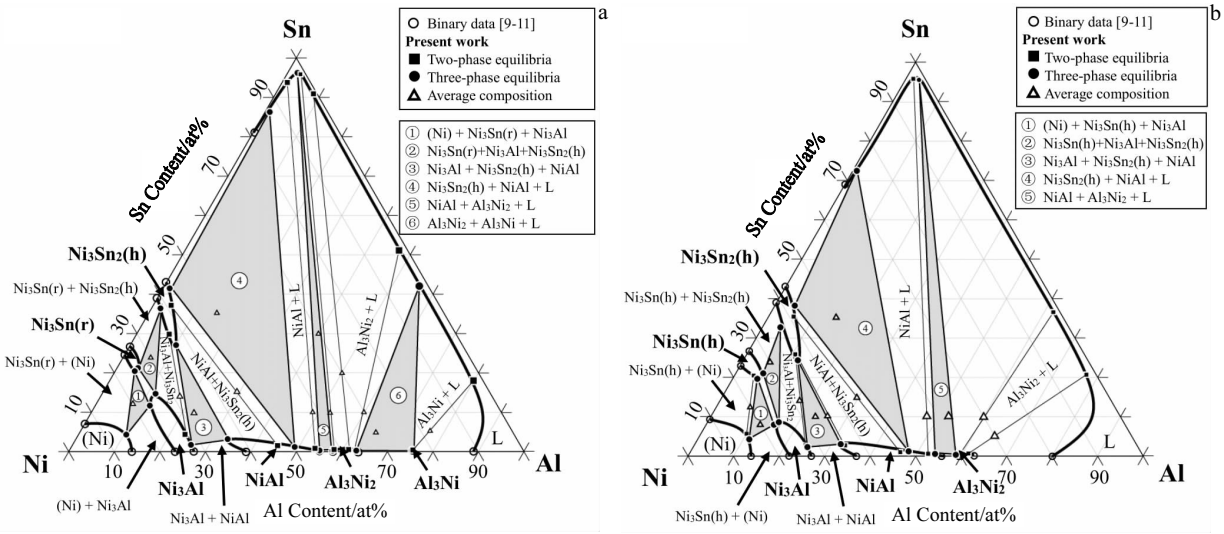

Fig.6 Experimentally determined isothermal section diagram of Ni-Al-Sn ternary system at 800 °C (a) and 1000°C (b)

and NiAl+Al_3Ni_2+Liquid are confirmed at 1000 ºC. Compared the 1000 ºC isothermal section with that at 800 ºC, it is noteworthy that the solubility of Sn in Ni_3Al has significantly reduced from 14.7 at% to 8.0 at%. Besides, according to the Ni-Sn binary phase diagram, the crystal structure of the Ni_3Sn phase changed from Ni_3Sn(r) to Ni_3Sn(h) at 1000 °C. The solubility of Al in the Ni_3Sn(h) and Ni_3Sn_2(h) phase was measured to be about 5.5 at% and 12.1 at% at 1000 ºC, respectively. The solubility of Sn in the Ni_3Al and NiAl phase is about 8.0 at% and 3.0 at% at 1000 ºC, respectively.

The phase diagram of the Ni-Al-Sn ternary system at room temperature was determined by Zheng[21], as shown in Fig.2. Comparing the present work with that of Zheng[21], there is a great difference due to the appearance of liquid region and the disappearance of Ni_3Sn_4 phase caused by higher temperature. In the present work, the liquid region could dissolve ~1 at% Ni at the middle of Al-Sn side. Additionally, there is a great change in the homogeneity range of each compound, especially in NiAl, Ni_3Al and Ni_3Sn. Another difference is that Ni_3Sn_2(h) phase, instead of Ni_3Sn_2(r), is stable at both 800 and

1000 ºC. Moreover, the present work will provide a theoretical basis for the thermodynamic evaluation of the Ni-Al-Sn ternary system. In that way, it will present a useful guide for the design of lead-free solder and the interfacial reaction at welding joint.

3 Conclusions

1) The isothermal sections of the Ni-Al-Sn ternary system at 800 and 1000 °C can be experimentally determined. Total 6 and 5 three-phase regions exist at 800 and 1000 °C, respectively. No any ternary compound is found.

2) 4 Al-Ni binary compounds (Al_3Ni_2, Al_3Ni, NiAl and Ni_3Al) show absolutely different solubilities for the elemental Sn. On the one hand, almost no solubility is detected in both the Al_3Ni_2 and Al_3Ni phases from 800 °C to 1000 °C. On the other hand, the maximum solubility of Sn in Ni_3Al and NiAl phases at 800 °C is 14.7 at% and 3.1 at%, and the value changes into 8.0 at% and 3.0 at% at 1000 °C, respectively.

3) The Ni_3Sn(r) phase is stable at 800 °C dissolving 4.2 at% Al but it is replaced by the Ni_3Sn(h) phase with a 5.5 at% Al solubility at 1000 °C. The solid solubility of Al in Ni_3Sn_2(h) is 8.4 at% and 12.1 at% at 800 and 1000 °C, respectively.

4) The Al-Sn side presents an interconnected liquid region at both 800 and 1000 ºC although its solubility for Ni is extremely low to ~1 at%.

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Ni-Al-Sn 三元系在 800 和 1000 ℃时的相平衡

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摘　要：采用电子探针显微分析和 X 射线衍射分析等方法研究了 Ni-Al-Sn 三元系在 800 和 1000 ℃时的相平衡。结果表明：(1) Ni-Al-Sn 三元系在 800 和 1000 ℃时均未发现三元化合物；(2) Ni-Al 侧存在 NiAl、Ni_3Al、Al_3Ni 和 Al_3Ni_2 4 个化合物，800 ℃时，Sn 在 NiAl 和 Ni_3Al 中的固溶度分别为 3.1 at%和 14.7 at%，在 1000 ℃时分别为 3.0 at%和 8.0 at%。而 Sn 在 Al_3Ni 和 Al_3Ni_2 中几乎没有固溶度；(3) Ni-Sn 侧有 Ni_3Sn(r)、Ni_3Sn(h)和 Ni_3Sn_2(h)3 个化合物。800 ℃时，Al 在 Ni_3Sn(r)相的固溶度为 4.2 at%，1000 ℃时，Ni_3Sn(r)相转变为 Ni_3Sn(h)相，拥有 5.5 at% Al 的固溶度。另外，800 ℃时，Al 在 Ni_3Sn_2(h)相中的固溶度为 8.4 at%，1000 ℃时为 12.1 at%；(4) Ni-Al-Sn 三元系 Al-Sn 侧为相互贯通的液相区域，Ni 在 Al-Sn 侧的溶解度约为 1 at%。

关键词：Ni-Al-Sn 三元系；相平衡；固溶度；电子探针显微分析

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