

Experimental Investigation of the Phase Equilibria in the Ni-Co-Sn Ternary System

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Abstract: Phase equilibria of the Ni-Co-Sn ternary system at 700 °C and 1000 °C were experimentally determined by using electron probe microanalyzer and X-ray diffraction. No ternary compound was found at 700 °C and 1000 °C. There was an extensive region of mutual solubility existing between $\beta\text{Co}_3\text{Sn}_2$ phase and $\text{Ni}_3\text{Sn}_2(h)$ phase. Three Ni-Sn binary compounds [$\text{Ni}_3\text{Sn}(l)$, $\text{Ni}_3\text{Sn}(h)$ and Ni_3Sn_4] showed absolutely different solubilities for the element Co. The maximum solubility of Co in $\text{Ni}_3\text{Sn}(l)$ and Ni_3Sn_4 phases at 700 °C were 6.9 at% and 25.6 at%, respectively, and the solubility of $\text{Ni}_3\text{Sn}(h)$ phases changed into 15.5 at% at 1000 °C. The Ni-Co side presented an interconnected (αCo , Ni) phase region at both 700 and 1000 °C and its homogeneity range for Sn was from 1 at% to 10.5 at%. The solubility of Ni in the linear compound CoSn phase was about 15.9 at%.

Key words: Ni-Co-Sn ternary system; phase diagram; linear compound

Lead-free soldering plays an important role in the electronic packaging industry^[1-4]. During the soldering process, interfacial reactions will occur at the soldering joint among Ni, Co and Sn elements^[5]. Additionally, the additions of Ni and Co elements can improve the overall performance of lead-free solders^[6-8]. According to the results of Huang, Chen et al.^[9,10], the addition of a small amount of Co can significantly reduce the overcooling effect and effectively refine the microstructure of the solder. In order to study the lead-free solder and the interfacial reactions on Ni and Co substrate, it is important to determine the Ni-Co-Sn ternary equilibria experimentally.

The corresponding sub-binary systems of Ni-Co-Sn ternary system, have been well studied. The Co-Ni phase diagram is a very simple system without any intermetallic compounds which has been reported by S. U. Jen and R. Kainuma. An infinite mutual solubility of Co and Ni has been found^[11,12]. Co-Sn phase diagram has been reported by M. Jiang which demonstrated four stable compounds CoSn_2 , CoSn , $\alpha\text{Co}_3\text{Sn}_2$, $\beta\text{Co}_3\text{Sn}_2$ ^[13]. The Ni-Sn binary system has been widely studied as an important lead-free soldering material system^[14], and assessed by Ghosh^[15], Liu^[16] and Dong^[17] et al. Ni-Sn phase

diagram has been reported by A. Zemanova^[18] which demonstrated five stable compounds $\text{Ni}_3\text{Sn}(l)$, $\text{Ni}_3\text{Sn}(h)$, $\text{Ni}_3\text{Sn}_2(l)$, $\text{Ni}_3\text{Sn}_2(h)$, Ni_3Sn_4 . The 250 °C isothermal section of the Ni-Co-Sn ternary system is proposed by Y. H. Chao^[3]. In their research, it is worthy to pay attention to the fact that both intermetallic compounds: the $\beta\text{Co}_3\text{Sn}_2$ phase (in the Co-Sn system), and the $\text{Ni}_3\text{Sn}_2(h)$ phase (in the Ni-Sn system), have the same orthorhombic structure. There is an extensive region of mutual solubility existing between the two binary isomorphous phases, $\beta\text{Co}_3\text{Sn}_2$ and $\text{Ni}_3\text{Sn}_2(h)$.

The three binary phase diagrams of Co-Ni, Co-Sn and Ni-Sn constituting the Ni-Co-Sn ternary system are shown in Fig.1 and the information of stable solid phases and their crystal structures in three binary systems are summarized in Table 1.

Although there are a large number of investigations about the above subsystems, the experimental equilibria of the Ni-Co-Sn ternary system is still scarce. Up to now, there is only one phase diagram of the Ni-Co-Sn ternary system at 250 °C^[3]. Despite the fact that soldering temperature is usually lower than 450 °C, it is necessary to obtain the phase equilibria

Received date: June 25, 2019

Foundation item: National Natural Science Foundation of China (51771158); Joint Fund to Promote Cross-Strait Scientific and Technological (U1605243)

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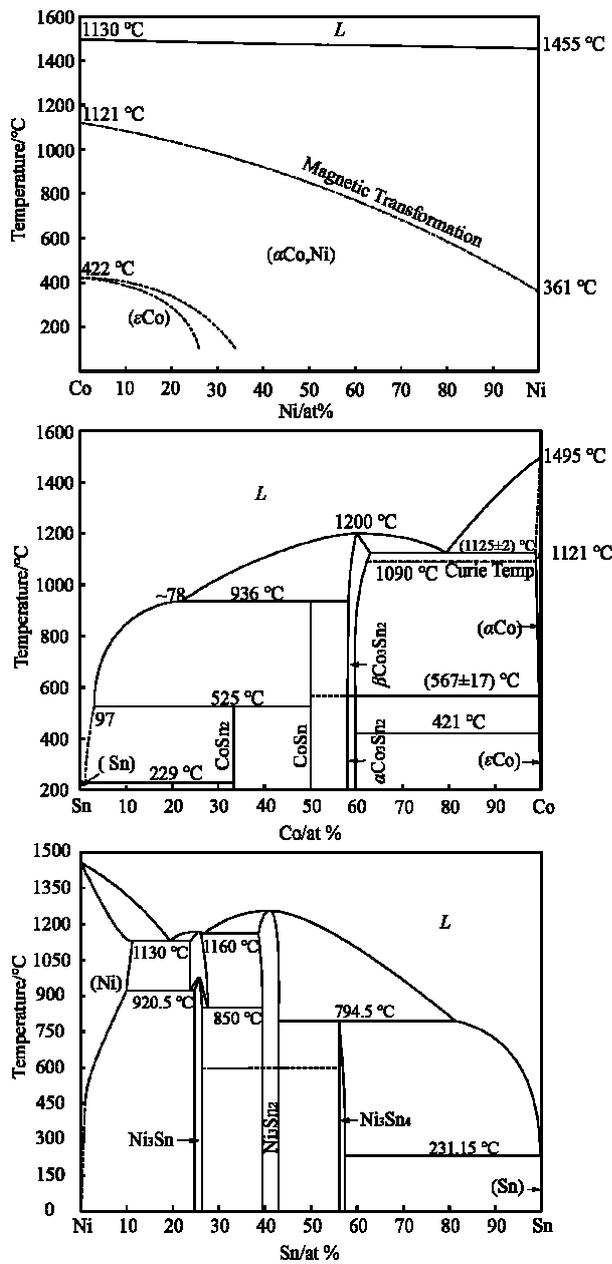


Fig.1 Binary phase diagrams constituting the Ni-Co-Sn ternary system^[11,13,18]

rium information at high temperature, and it will provide a theoretical basis for the thermodynamic calculation of the Ni-Co-Sn ternary system.

1 Experiment

Pure metals Nickel (99.9 wt%), Cobalt (99.9 wt%) and Tin (99.9 wt%) were used as raw materials and the bulk buttons were prepared by arc melting under high purity argon atmosphere. The mass of each sample was about 15 g. In order to achieve their homogeneity, the ingots were remelted at least 4 times and the mass losses were less than 0.5 wt%.

Table 1 Stable solid phases in the three binary systems^[11, 13, 18]

Phase	Pearson symbol	Prototype	Space group	Strukturbericht
(αCo,Ni)	<i>cF4</i>	Cu	<i>Fm-3m</i>	A1
(εCo)	<i>hP2</i>	Mg	<i>P6₃/mmc</i>	A3
(αCo)	<i>cF4</i>	Cu	<i>Fm-3m</i>	A1
(εCo)	<i>hP2</i>	Mg	<i>P6₃/mmc</i>	A3
(βSn)	<i>tI4</i>	βSn	<i>P4₁/amd</i>	A5
(αSn)	<i>cF8</i>	C(diamond)	<i>Fd-3m</i>	...
βCo ₃ Sn ₂	<i>hP6</i>	Ni ₂ In	<i>P6₃/mmc</i>	B8 ₁
αCo ₃ Sn ₂	<i>oP20</i>	Ni ₃ Sn ₂	<i>Pnma</i>	B8 ₁
CoSn	<i>hP6</i>	CoSn	<i>P6/mmm</i>	B35
CoSn ₂	<i>tI12</i>	CuAl ₂	<i>I4/mcm</i>	C16
βCoSn ₃	<i>tI64</i>	βCoSn ₃	<i>I4₁/acd</i>	A2
αCoSn ₃	<i>oC32</i>	PdSn ₃	<i>Cmca</i>	...
Co ₃ Sn	<i>cI2</i>	W	<i>Im-3m</i>	A2
(Ni)	<i>cF4</i>	Cu	<i>Fm-3m</i>	A1
(βSn)	<i>tI4</i>	βSn	<i>P4₁/amd</i>	A5
(αSn)	<i>cF8</i>	C(diamond)	<i>Fd-3m</i>	...
Ni ₃ Sn(h)	<i>cF16</i>	BiF ₃ ^b	<i>Fm-3m</i>	D0 ₃
Ni ₃ Sn(l)	<i>hP8</i>	Mg ₃ Cd	<i>P6₃/mmc</i>	D0 ₁₉
Ni ₃ Sn ₂ (h)	<i>hP6</i>	InNi ₂	<i>P6₃/mmc</i>	B8 ₁
Ni ₃ Sn ₂ (l)	<i>oP20</i>	Ni ₃ Sn ₂	<i>Pnma</i>	B8 ₁
Ni ₃ Sn ₄	<i>mC14</i>	CoGe	<i>C2/m</i>	...

The ternary Ni-Co-Sn alloys were cut into small pieces and then put into quartz capsules and filled with argon gas. In addition, the samples containing liquid phase were wrapped in pure Nickel slice to prevent the contact reaction with quartz. Specimens were annealed at 700 °C for 720 h and 1000 °C for 168 h. And the samples which are containing liquid phase were annealed 700 °C for 5 h and 1000 °C for 2 h. Specimens were quenched into ice water after heat treatment.

After standard metallographic preparation, the backscatter electron (BSE) images and equilibrium composition of the equilibrium phases were obtained on electron-probe-micro-analyzer (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 1.0×10^{-8} A. The crystal structure analysis was conducted using X-ray diffraction (XRD) on a Philips Panalytical X-pert diffractometer (Cu K α radiation at 40 kV and 40 mA). The data were collected in the range of 2θ from 20° to 90° at a step size of 0.0167°.

2 Results and Discussion

2.1 An extensive region of mutual solubility

According to Y. H. Chao's study^[3], it is worthy to pay attention to the fact that both intermetallic compounds: the βCo₃Sn₂ phase (in the Co-Sn system), and the Ni₃Sn₂(h) phase (in the Ni-Sn system), not only have the same orthorhombic structure, but also have very similar values in terms of lattice parameters.

Therefore, it is reasonable to speculate that there is an extensive region of mutual solubility between $\beta\text{Co}_3\text{Sn}_2$ and $\text{Ni}_3\text{Sn}_2(h)$. For the validation of the existence of a continuous solid solution between $\beta\text{Co}_3\text{Sn}_2$ and $\text{Ni}_3\text{Sn}_2(h)$ phases in the isothermal section of the Ni-Co-Sn ternary system at 700 °C, three different alloys ($\text{Ni}_{16}\text{Co}_{42}\text{Sn}_{42}$, $\text{Ni}_{29}\text{Co}_{32}\text{Sn}_{39}$, $\text{Ni}_{44}\text{Co}_{18}\text{Sn}_{38}$) in this single-phase region were prepared. Their BSE micrographs show the appearance of a single phase and their compositions determined using EPMA. Their XRD results are shown in Fig.2, where the characteristic peaks of the $\beta\text{Co}_3\text{Sn}_2$ and $\text{Ni}_3\text{Sn}_2(h)$ phases are only confirmed and well marked by star symbols. Based on the analyses of EPMA and XRD, an extensive region of mutual solubility existing between $\beta\text{Co}_3\text{Sn}_2$ and $\text{Ni}_3\text{Sn}_2(h)$ was confirmed and labeled as $(\text{Ni, Co})_3\text{Sn}_2$.

2.2 Phase equilibria at 700 °C

Typical BSE images of the Ni-Co-Sn equilibrated alloys quenched from 700 °C are shown in Fig.3a~3f while their phase equilibrium compositions are listed in Table 2. All the mentioned chemical compositions in this work is given in the form of an atomic ratio (at%). Phase identification was based on the equilibrium composition as measured by EPMA and XRD results. 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^[11,13,18].

The $\text{Ni}_{11}\text{Co}_{70}\text{Sn}_{19}$ alloy annealed at 700 °C for 720 h has formed a eutectic organization of $(\text{Ni, Co})_3\text{Sn}_2$ and $(\alpha\text{Co, Sn})$

phases, as illustrated in Fig.3a. This sample composition crosses the eutectic reaction line during the cooling process; therefore, a eutectic reaction occurred and a strip phase ($\alpha\text{Co, Sn}$) was formed. The corresponding XRD pattern, as presented in Fig.4a, shows all the diffraction peaks of the $(\alpha\text{Co, Sn})$ and $(\text{Ni, Co})_3\text{Sn}_2$ phases. Fig.3b shows the two-phase microstructure (Ni_3Sn_4 +Liquid phase) of the $\text{Ni}_{20}\text{Co}_{20}\text{Sn}_{60}$ alloy annealed at 700 °C for 5 h. The BSE image of $\text{Ni}_{62}\text{Co}_{11}\text{Sn}_{27}$ alloy

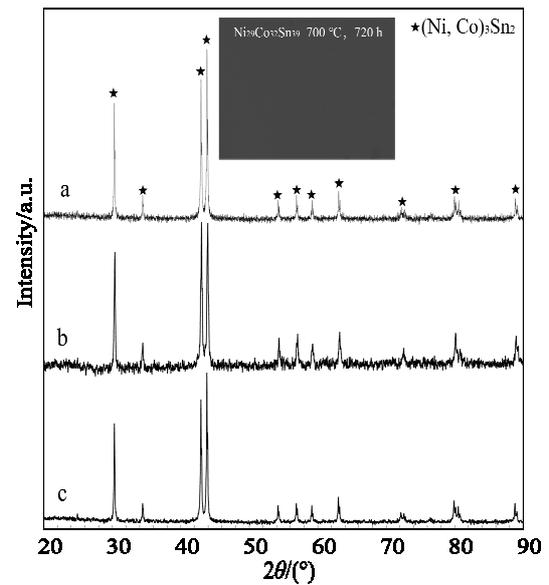


Fig.2 XRD patterns of partial Ni-Co-Sn ternary alloys annealed at 700 °C for 720 h obtained from $\text{Ni}_{16}\text{Co}_{42}\text{Sn}_{42}$ (a), $\text{Ni}_{29}\text{Co}_{32}\text{Sn}_{39}$ (b), and $\text{Ni}_{44}\text{Co}_{18}\text{Sn}_{38}$ (c)

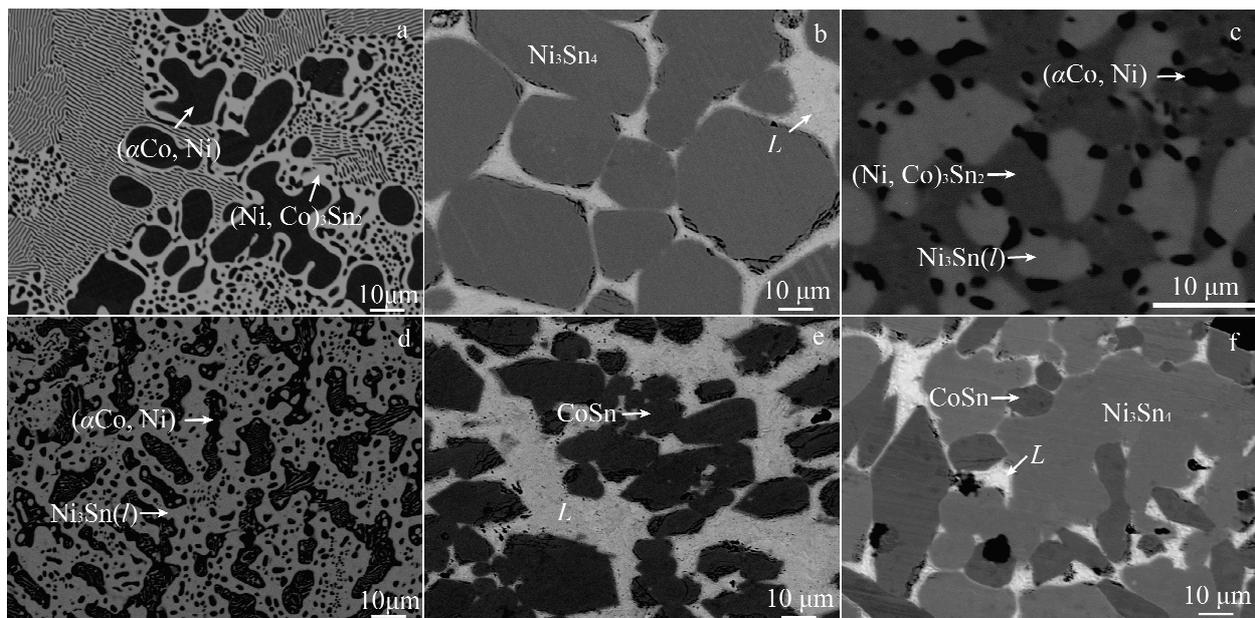


Fig.3 Typical ternary BSE images obtained from Ni-Co-Sn ternary alloys: (a) $\text{Ni}_{11}\text{Co}_{70}\text{Sn}_{19}$ alloy annealed at 700 °C for 720 h, (b) $\text{Ni}_{20}\text{Co}_{20}\text{Sn}_{60}$ alloy annealed at 700 °C for 5 h, (c) $\text{Ni}_{62}\text{Co}_{11}\text{Sn}_{27}$ alloy annealed at 700 °C for 720 h, (d) $\text{Ni}_{75}\text{Co}_{11}\text{Sn}_{14}$ alloy annealed at 700 °C for 720 h, (e) $\text{Ni}_{10}\text{Co}_{30}\text{Sn}_{60}$ alloy annealed at 700 °C for 5 h, and (f) $\text{Ni}_{20}\text{Co}_{27}\text{Sn}_{53}$ alloy annealed at 700 °C for 5 h

Table 2 Equilibrium composition of the Ni-Co-Sn ternary system at 700 °C determined in the present work

Alloy/ at%	Annealed time/h	Phase equilibrium		Composition/at%					
		Phase 1/Phase 2/Phase 3	Phase 1		Phase 2		Phase 3		
			Ni	Co	Ni	Co	Ni	Co	
Ni ₁₁ Co ₇₀ Sn ₁₉	720	(α Co, Ni)/(Ni, Co) ₃ Sn ₂	4.75	92.63	19.95	40.03	
Ni ₁₀ Co ₅₆ Sn ₃₄	720	(α Co, Ni)/(Ni, Co) ₃ Sn ₂	1.44	96.25	12.02	47.33	
Ni ₁₆ Co ₄₂ Sn ₄₂	720	(Ni, Co) ₃ Sn ₂	16.01	42.24	
Ni ₂₉ Co ₃₂ Sn ₃₉	720	(Ni, Co) ₃ Sn ₂	29.35	30.68	
Ni ₄₄ Co ₁₈ Sn ₃₈	720	(Ni, Co) ₃ Sn ₂	46.37	14.62	
Ni ₆₅ Co ₁₂ Sn ₂₃	720	(α Co, Ni)/Ni ₃ Sn(<i>l</i>)	29.88	68.85	68.39	6.61	
Ni ₁₀ Co ₃₀ Sn ₆₀	5	<i>L</i> /CoSn	0.24	1.16	11.77	39.05	
Ni ₂₀ Co ₂₀ Sn ₆₀	5	<i>L</i> /Ni ₃ Sn ₄	1.17	0.88	24.16	21.35	
Ni ₃₀ Co ₁₀ Sn ₆₀	5	<i>L</i> /Ni ₃ Sn ₄	1.4	0.76	27.16	18.82	
Ni ₆₂ Co ₁₁ Sn ₂₇	720	(α Co, Ni)/(Ni, Co) ₃ Sn ₂ /Ni ₃ Sn(<i>l</i>)	33.89	65.15	59.68	2.7	68.45	6.39	
Ni ₅₀ Co ₂₃ Sn ₂₇	720	(α Co, Ni)/(Ni, Co) ₃ Sn ₂	32.29	66.55	58.19	3.84	
Ni ₃₀ Co ₄₃ Sn ₂₇	720	(α Co, Ni)/(Ni, Co) ₃ Sn ₂	7.78	91.16	40.9	20.03	
Ni ₇₅ Co ₁₁ Sn ₁₄	720	(α Co, Ni)/Ni ₃ Sn(<i>l</i>)	73.84	25.37	71.46	3.81	
Ni ₂₀ Co ₃₂ Sn ₄₈	720	(Ni, Co) ₃ Sn ₂ /CoSn	22.19	35.83	14.06	36.57	
Ni ₂₇ Co ₂₅ Sn ₄₈	720	(Ni, Co) ₃ Sn ₂ /Ni ₃ Sn ₄	29.19	28.19	27.15	20.63	
Ni ₂₄ Co ₃₁ Sn ₄₅	720	(Ni, Co) ₃ Sn ₂ /Ni ₃ Sn ₄	25.09	33.42	25.29	23.27	
Ni ₂₀ Co ₂₇ Sn ₅₃	5	<i>L</i> /CoSn/Ni ₃ Sn ₄	0.97	1.07	15.80	34.58	22.81	23.90	

annealed at 700 °C for 720 h is shown in Fig.3c. According to the determined phase composition Ni₆₂Co₁₁Sn₂₇ alloy showed a three-phases co-existence of [(α Co, Sn) + (Ni, Co)₃Sn₂ + Ni₃Sn(*l*)]. The corresponding XRD pattern, as shown in Fig. 4b, all the diffraction peaks of the (α Co, Sn), (Ni, Co)₃Sn₂ and Ni₃Sn(*l*) phases was presented. A two-phase microstructure of [(α Co, Sn)+Ni₃Sn(*l*)] was found in the Ni₇₅Co₁₁Sn₁₄ alloy annealed at 700 °C for 720 h, as indicated in Fig. 3d, where the (α Co, Sn) phase with the flat plate shape distributes in the matrix of the Ni₃Sn(*l*) phase. The corresponding XRD pattern, as presented in Fig.4c, showed all the diffraction peaks of the (α Co, Sn) and Ni₃Sn(*l*) phases. The Ni₁₀Co₃₀Sn₆₀ alloy annealed at 700 °C for 5 h has formed a two-phase microstructure of CoSn phase and liquid phase, as illustrated in Fig.3e. Fig.3f shows a three-phase microstructure (CoSn+Ni₃Sn₄+ Liquid phase) of the Ni₂₀Co₂₇Sn₅₃ alloy annealed at 700 °C for 5 h.

Based on the above experimental data, the corresponding phase compositions of the annealed alloys is summarized in Table 2, while the 700 °C isothermal section of Ni-Co-Sn ternary system is constructed and shown in Fig.5. In total, two three-phase regions of [(α Co, Sn) + (Ni, Co)₃Sn₂ + Ni₃Sn(*l*)] and [Ni₃Sn₄ + CoSn + *L*], and one liquid region were experimentally confirmed at 700 °C and they were marked with different symbols. An undetermined three-phase regions of [Ni₃Sn₄ + CoSn + (Ni, Co)₃Sn₂] was labeled in dashed lines. As can be seen in Fig.5, the solubility of Sn in the (Ni,

Co)₃Sn₂ phase was about 39 at% to 42 at%. The solubility of Co in the Ni₃Sn(*l*) and Ni₃Sn₄ phase was measured to be about 6.9 at% and 25.6 at%, respectively. The solubility of Ni in the linear compound CoSn phase was about 15.9 at%. The Ni-Co side presents an interconnected (α Co, Sn) phase region.

2.3 Phase equilibria at 1000 °C

Fig.6 presents some typical BSE images of the Ni-Co-Sn alloys annealed at 1000 °C for 168 h or 2 h. As shown in Fig. 6a, two different phases were found in the Ni₆₅Co₁₂Sn₂₃ alloy annealed at 1000 °C for 168 h.

Combined with the composition analysis, the light gray phase was identified as Ni₃Sn(*h*), and the black phase was (α Co, Sn) phase. The corresponding XRD pattern, as presented in Fig.7a, shows all the diffraction peaks of the (α Co, Sn) and Ni₃Sn(*h*) phases. Fig.6b shows a BSE image of the Ni₆₂Co₁₁Sn₂₇ alloy annealed at 1000 °C for 168 h, where the two-phase equilibrium [Ni₃Sn(*h*) + (Ni, Co)₃Sn₂] was identified. The corresponding XRD pattern is shown in Fig.7b, the characteristic diffraction peaks of the (Ni, Co)₃Sn₂ and Ni₃Sn(*h*) phases are only confirmed. In the Ni₅₉Co₁₃Sn₂₈ alloy annealed at 1000 °C for 168 h, a three-phase equilibrium [(α Co, Sn)(black) + Ni₃Sn(*h*)(gray) + (Ni, Co)₃Sn₂(white)] was found as shown in Fig.6c. The corresponding XRD pattern, as presented in Fig.7c, shows all the diffraction peaks of the (α Co, Sn), Ni₃Sn(*h*) and (Ni, Co)₃Sn₂ phases. Moreover, as it can be seen in Fig.6d, there is a two-phase equilibrium [(Ni,

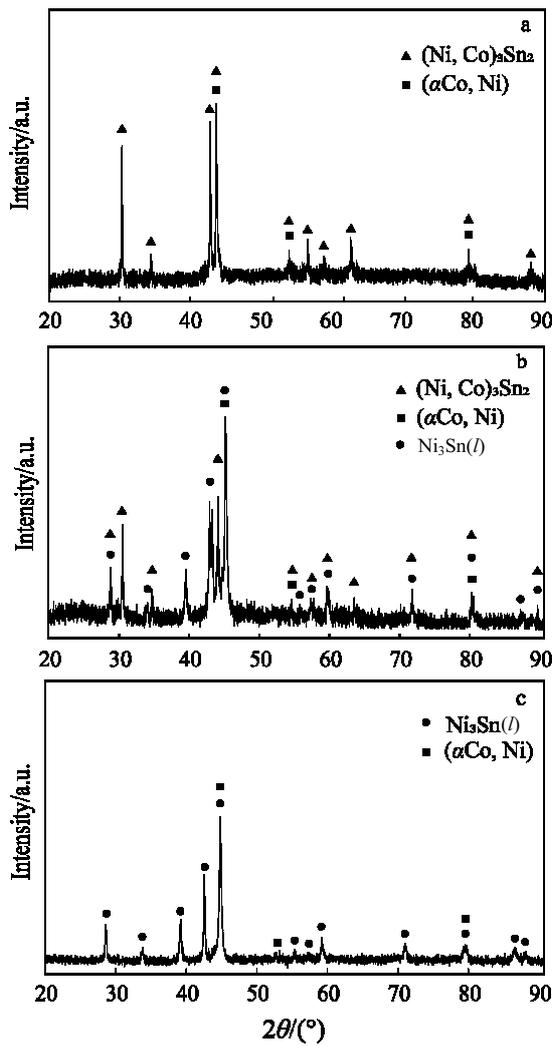


Fig.4 XRD patterns of partial Ni-Co-Sn ternary alloy obtained from Ni₁₁Co₇₀Sn₁₉ (a), Ni₂₄Co₁₁Sn₂₇ (b), Ni₇₅Co₁₁Sn₁₄ alloys (c) annealed at 700 °C

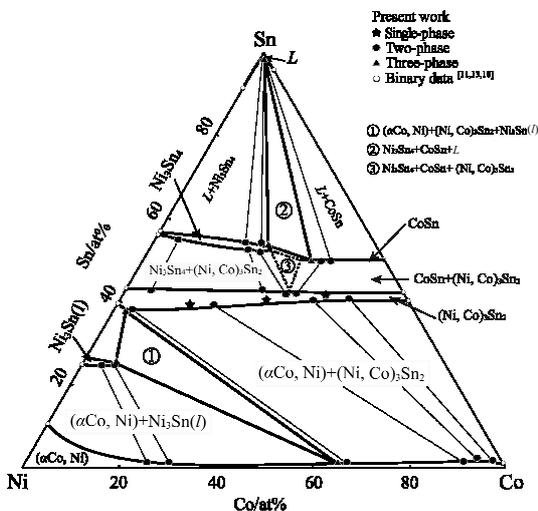


Fig.5 Experimentally determined isothermal section of the Ni-Co-Sn system at 700 °C

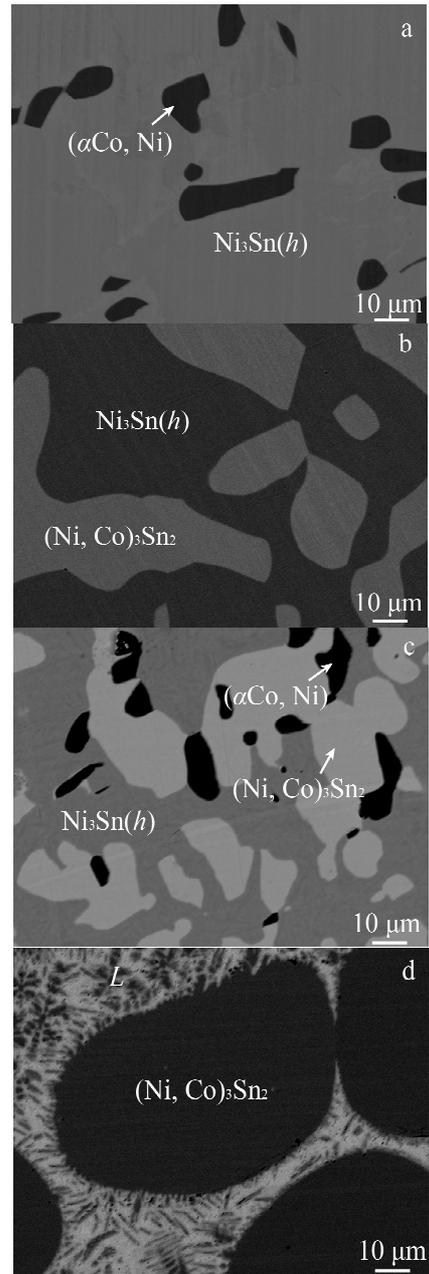


Fig.6 Typical ternary BSE images obtained from Ni-Co-Sn ternary alloys: (a) Ni₆₅Co₁₂Sn₂₃ alloy annealed at 1000 °C for 168 h, (b) Ni₆₂Co₁₁Sn₂₇ alloy annealed at 1000 °C for 168 h, (c) Ni₅₉Co₁₃Sn₂₈ alloy annealed at 1000 °C for 168 h, and (d) Ni₁₀Co₃₀Sn₆₀ alloy annealed at 1000 °C for 2 h

Co)₃Sn₂ + L] occurring in the Ni₁₀Co₃₀Sn₆₀ alloy annealed at 1000 °C for 2 h.

The corresponding phase composition of the annealed alloys is summarized in Table 3, and the 1000 °C isothermal section was established as presented in Fig.8. Only one three-phase regions of [(αCo, Sn) + Ni₃Sn(h) + (Ni,Co)₃Sn₂] was found.

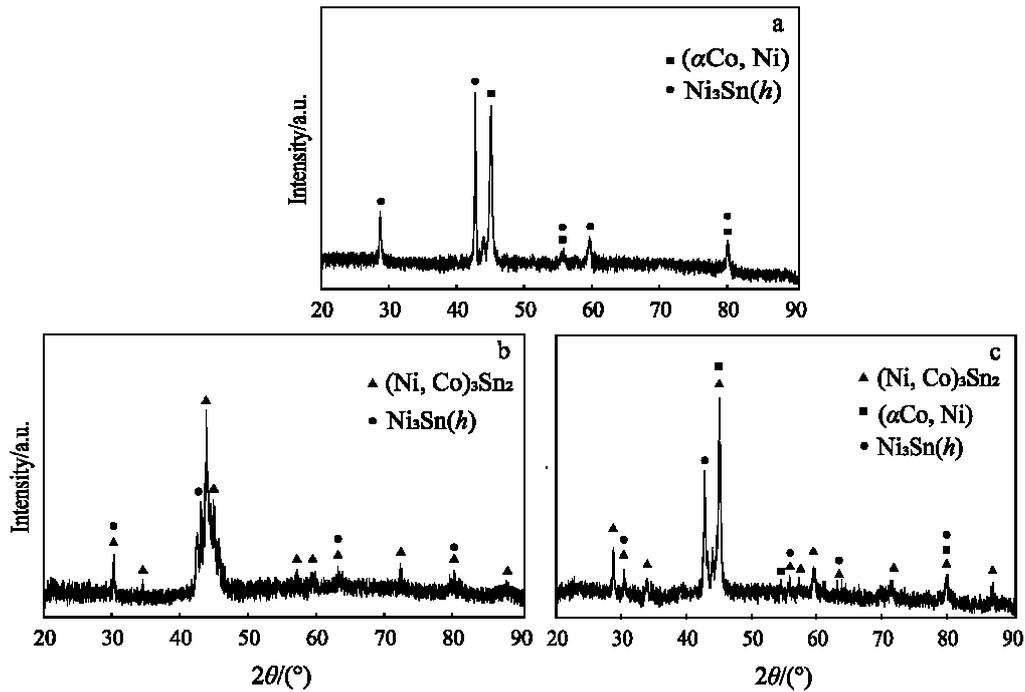


Fig.7 XRD patterns of partial Ni-Co-Sn ternary alloy obtained from $\text{Ni}_{65}\text{Co}_{12}\text{Sn}_{23}$ (a), $\text{Ni}_{62}\text{Co}_{11}\text{Sn}_{27}$ (b), and $\text{Ni}_{59}\text{Co}_{13}\text{Sn}_{28}$ alloys (c) annealed at 1000 °C

Table 3 Equilibrium composition of the Ni-Co-Sn ternary system at 700 °C determined in the present work

Alloy/ at %	Annealing time/h	Phase equilibrium		Composition/at%					
		Phase 1/Phase 2/Phase 3		Phase 1		Phase 2		Phase 3	
		Ni	Co	Ni	Co	Ni	Co		
$\text{Ni}_{11}\text{Co}_{70}\text{Sn}_{19}$	168	$(\alpha\text{Co, Ni})/(\text{Ni, Co})_3\text{Sn}_2$		4.6	93.64	18.15	42.97
$\text{Ni}_{10}\text{Co}_{56}\text{Sn}_{34}$	168	$(\alpha\text{Co, Ni})/(\text{Ni, Co})_3\text{Sn}_2$		2.65	95.45	11.24	49.9
$\text{Ni}_{16}\text{Co}_{42}\text{Sn}_{42}$	168	$(\text{Ni, Co})_3\text{Sn}_2$		30.95	30.1
$\text{Ni}_{29}\text{Co}_{32}\text{Sn}_{39}$	168	$(\text{Ni, Co})_3\text{Sn}_2$		16.32	42.58
$\text{Ni}_{44}\text{Co}_{18}\text{Sn}_{38}$	168	$(\text{Ni, Co})_3\text{Sn}_2$		45.81	15.97
$\text{Ni}_{65}\text{Co}_{12}\text{Sn}_{23}$	168	$(\alpha\text{Co, Ni})/\text{Ni}_3\text{Sn}(h)$		63.79	30.63	68.2	7.8
$\text{Ni}_{10}\text{Co}_{30}\text{Sn}_{60}$	2	$L/(\text{Ni, Co})_3\text{Sn}_2$		12.36	7.77	22.79	35.12
$\text{Ni}_{20}\text{Co}_{20}\text{Sn}_{60}$	2	$L/(\text{Ni, Co})_3\text{Sn}_2$		13.88	6.81	26.15	31.82
$\text{Ni}_{62}\text{Co}_{11}\text{Sn}_{27}$	168	$\text{Ni}_3\text{Sn}(h)/(\text{Ni, Co})_3\text{Sn}_2$		62.47	12.13	57.47	5.82
$\text{Ni}_{63}\text{Co}_{13}\text{Sn}_{24}$	168	$(\alpha\text{Co, Ni})/\text{Ni}_3\text{Sn}(h)$		51.2	45.03	63.44	11.6
$\text{Ni}_{50}\text{Co}_{23}\text{Sn}_{27}$	168	$(\alpha\text{Co, Ni})/(\text{Ni, Co})_3\text{Sn}_2$		38.91	56.28	53.42	8.89
$\text{Ni}_{30}\text{Co}_{43}\text{Sn}_{27}$	168	$(\alpha\text{Co, Ni})/(\text{Ni, Co})_3\text{Sn}_2$		13.71	83.25	36.99	24.06
$\text{Ni}_{75}\text{Co}_{11}\text{Sn}_{14}$	168	$(\alpha\text{Co, Ni})/\text{Ni}_3\text{Sn}(h)$		76.68	15.66	68.26	7.48
$\text{Ni}_{59}\text{Co}_{13}\text{Sn}_{28}$	168	$(\alpha\text{Co, Ni})/(\text{Ni, Co})_3\text{Sn}_2/\text{Ni}_3\text{Sn}(h)$		46.14	50.30	56.72	6.73	60.10	13.64
$\text{Ni}_{61}\text{Co}_{15}\text{Sn}_{24}$	168	$(\alpha\text{Co, Ni})/\text{Ni}_3\text{Sn}(h)$		48.77	47.53	61.90	13.36
$\text{Ni}_{50}\text{Co}_5\text{Sn}_{45}$	2	$L/(\text{Ni, Co})_3\text{Sn}_2$		23.26	1.66	51.21	4.98
$\text{Ni}_{40}\text{Co}_{15}\text{Sn}_{45}$	2	$L/(\text{Ni, Co})_3\text{Sn}_2$		18.33	3.85	41.24	15.06

With the temperature increasing from 700 to 1000 °C, there are several differences as summarized in the following: (1) Ni_3Sn_4 phase and CoSn phase disappeared at 1000 °C. (2) According to the Ni-Sn binary phase diagram, the crystal structure of the Ni_3Sn

phase changed from $\text{Ni}_3\text{Sn}(l)$ to $\text{Ni}_3\text{Sn}(h)$ at 1000 °C. The solubility of Co in the $\text{Ni}_3\text{Sn}(l)$ phase was measured to be about 6.9 at% at 700 °C and in the $\text{Ni}_3\text{Sn}(h)$ was measured to be about 15.5 at%. (3) The liquid phase on the Sn-rich side has increased.

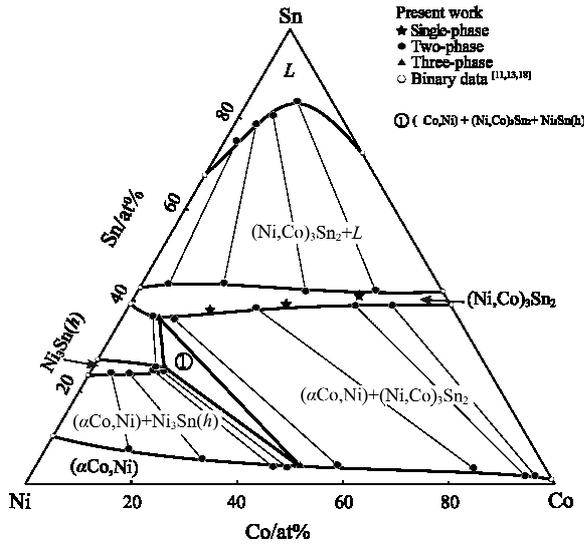


Fig.8 Experimentally determined isothermal section of the Ni-Co-Sn system at 1000 °C

3 Conclusions

1) The isothermal sections of the Ni-Co-Sn ternary system at 700 and 1000 °C have been experimentally investigated. No any ternary compound is found.

2) There is an extensive region of mutual solubility existing between $\beta\text{Co}_3\text{Sn}_2$ phase and $\text{Ni}_3\text{Sn}_2(h)$ phase, which is labeled as $(\text{Ni}, \text{Co})_3\text{Sn}_2$. The $(\text{Ni}, \text{Co})_3\text{Sn}_2$ phase is a stable phase with dissolving about 39 at% to 42 at% Sn.

3) Three Ni-Sn binary compounds [$\text{Ni}_3\text{Sn}(l)$, $\text{Ni}_3\text{Sn}(h)$ and Ni_3Sn_4] show absolutely different solubilities of Co. The $\text{Ni}_3\text{Sn}(l)$ phase is stable at 700 °C dissolving 6.9 at% Co but it is replaced by the $\text{Ni}_3\text{Sn}(h)$ phase at 1000°C, and the solubility of Co changed to 15.5 at%. The maximum solubility of Co in Ni_3Sn_4 phase at 700 °C is 25.6 at%, and the Ni_3Sn_4 phase disappears at 1000 °C.

4) The Ni-Co side presents an interconnected $(\alpha\text{Co}, \text{Ni})$ phase region at both 700 and 1000 °C and its solubility for Sn

is from 1 at% to 10.5 at%. The solubility of Ni in the linear compound CoSn phase is about 15.9 at%.

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Ni-Co-Sn 三元系相平衡的实验研究

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摘要: 采用电子探针显微分析和X-ray衍射分析方法研究了Ni-Co-Sn三元体系在700和1000 °C时的相平衡。在这两个温度截面中均未发现三元化合物。 $\beta\text{Co}_3\text{Sn}_2$ 相和 $\text{Ni}_3\text{Sn}_2(h)$ 相形成了一个贯穿连续固溶体相。Ni-Sn侧包含 $\text{Ni}_3\text{Sn}(l)$ 、 $\text{Ni}_3\text{Sn}(h)$ 和 Ni_3Sn_4 3个化合物相, 它们中Sn的固溶度是有很大的区别的。700 °C时, Co在 $\text{Ni}_3\text{Sn}(l)$ 和 Ni_3Sn_4 中的最大固溶度分别约为6.9 at%和25.6 at%, 在1000 °C时, Co在 $\text{Ni}_3\text{Sn}(h)$ 中的最大固溶度约为15.5 at%。在700和1000 °C下, Ni-Co侧的 $(\alpha\text{Co}, \text{Ni})$ 相为一个贯穿连续固溶体相, 并且Sn在 $(\alpha\text{Co}, \text{Ni})$ 相中的固溶度为1 at%~10.5 at%。Ni在线性化合物 CoSn 相中的溶解度约为15.9 at%。

关键词: Ni-Co-Sn三元系; 相平衡; 线性化合物

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