Article ID: 1003-6326(2004)05-0870-05

Determination of isothermal sections of Ni-Cr-Nb ternary system①

WANG Ri-chu(王日初), FENG Yan(冯 艳), JIN Zhan-peng(金展鹏), HUANG Bai-yun(黄伯云)
(School of Materials Science and Engineering, Central South University, Changsha 410083, China)

Abstract: The isothermal sections of Ni-Cr-Nb ternary system at 1 323 K and 1 423 K were determined by means of diffusion triple and energy spectrum analysis (ESA). By analyzing the diffusion layers in the diffusion couples, the compounds forming in this system were identified. There are three similar compounds found at these two temperatures: Ni_3Nb, NiNb and $NbCr_2$-R, and four similar three-phase regions are found: (Ni) + (Cr) + Ni_3Nb, Ni_3Nb+ $NbCr_2$-R+ NiNb, $NbCr_2$-R+ (Cr) + Ni_3Nb, $NbCr_2$-R+ NiNb+ (Nb). The results show that no phase transformation happens between these tow temperatures. But the solid solubilities of the binary compounds at 1 423 K become bigger than those at 1 323 K, especially the solid solubility of $NbCr_2$-R. No ternary compound is observed.

Key words: Ni-Cr-Nb ternary system; diffusion triple; isothermal section
CLC number: TG 113.14 **Document code:** A

1 INTRODUCTION

Because of the good thermal stability, the nickel-based alloys have found wide applications in high temperature fields[1]. They have the widest application and are the most mature material, by which modern aero-engine, combustion turbine and rocket engine are produced. The addition of chromium into the nickel-based alloy can strengthen the properties of creep resistance and corrosion resistance of super alloys. The addition of Re, Mo, W, Ta and Nb can enhance the stability of alloys and increase the high-temperature strength[2-5]. The addition of Nb can further improve the property of high temperature corrosion resistance of Ni-based super alloy, at the same time Nb can strengthen grain boundary and precipitated phase[6].

The Ni-Cr binary system has important commercial value, but the phase relations always exist argument. Nash[7] made a detailed thermodynamics evaluation on the Ni-Cr binary system, there was a simple eutectic reaction at high temperature and a formation reaction of peritectoid Ni_2Cr at low temperature. There are liquid phase, solid solution (fcc and bcc) and Ni_2Cr at low temperature found in the system. The polymorphism of Cr and the formation of σ phase initiate various complex forms of this phase diagram, but the existence of σ phase as a stable phase hasn't been certified.

Okamoto[8], Bolcavage et al[9], Zeng et al[10], Nash et al[11] made thermodynamics evaluation on the Ni-Nb binary system. There were one peritectic reaction and two eutectic reactions, and in this system there existed liquid phase, solid solution (Ni and Nb) and three intermediate compounds: Ni_8Nb, Ni_3Nb and NiNb. The formation of Ni_8Nb needs research, but it can be commonly thought that peritectoid reaction form Ni_8Nb.

Venkatraman et al[12], Joaquim et al[13] made detailed thermodynamics evaluation on the Nb-Cr binary system. They discovered that there were two eutectic reactions and there existed liquid phase, solid solution (Nb and Cr) and an intermediate compound $NbCr_2$ which formed eutectic structure with solid solution. When the temperature went down, there was a transformation of C14 → C15. The structure of $NbCr_2$ is cubic $MgCu_2$-type (C15), which turns into hexagonal $MgZn_2$-type (C14) at high temperature. The transformation temperature isn't stable.

The experimental data of the Ni-Cr-Nb ternary system are very limited. In this paper, the authors aim to determine the isothermal sections of Ni-Cr-Nb ternary system at 1 323 K and 1 423 K by means of diffusion triple[14, 15] and energy spectrum analysis, which are important either to study the phase relationship and phase diagram of Ni-Cr-Nb ternary system or to optimize and select processing of Ni-based alloys.

2 EXPERIMENTAL

The raw materials for preparing the Ni-Cr-Nb diffusion triple are 99.9% (mass fraction) purity niobium, nickel and chromium ingots. The dimensions of niobium, nickel are 10 mm × 8 mm × 6 mm, and the dimension of chromium is 20 mm × 8 mm × 6 mm. The melting point of chromium is lower than that of niobium and a little higher than that of nickel, but chromium is too crisp to thermocompress together

① **Received date:** 2004-02-10; **Accepted date:** 2004-06-29
Correspondence: WANG Ri-chu, Professor, PhD; Tel: +86-10-13755199741; E-mail: fenyanfenyan_0@etang.com

at high temperature. So binary Ni-Nb diffusion triples were first made by heat pressing in GLEEBLE1500-type thermo-compressor filled with high-purity argon at 1 001 K, 370 MPa for 10 min. The samples were annealed in a quartz ampoule filled with high-purity argon at (1 323 ±5) K for 96 h, then quenched in cool water.

The binary Ni-Nb couples and Cr pieces were planished, polished and tightened by wolfram filament as shown in Fig. 1. Then the Ni-Cr-Nb diffusion triples were annealed in a quartz ampoule filled with high-purity argon at (1 323 ±5) K for 690 h and (1 423 ±5) K for 170 h. The triples were quenched to prevent cracking and polished parallel to the diffusion direction.

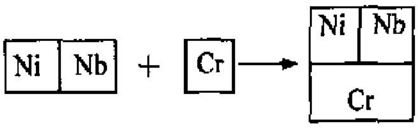

Fig. 1 Schematic diagram of construction of Ni-Cr-Nb diffusion triple

3 RESULTS AND DISCUSSION

3.1 Isothermal section of Ni-Cr-Nb ternary system at 1 323 K

Fig. 2 shows the back-scattered electron images of Ni-Cr-Nb diffusion triple after annealing at 1 323 K for 690 h. Fig. 2(b) is on the top of Fig. 2 (a) and Fig. 2(c) is on the right of Fig. 2(a). It can be seen that there are three diffusion layers, of which two are Ni-Nb compounds and one is Nb-Cr compound. Although there is a field whose color is different from the other one between NiNb and Nb, it can be see in Table 1 that this field has the same component as Nb, Ni and Cr form complete solid solution. No ternary compounds are formed in the Ni-Cr-Nb diffusion triple at 1 323 K. The characteristics of phase distribution and the phase relations are schematically shown in Fig. 3.

The chemical compositions of diffusion equilibrium phases were determined by means of energy spectrum analysis. Parts of the typical data are listed in Table 1. By combining Table 1 with Fig. 2, the Ni-Nb compounds are Ni_3Nb and NiNb, and the Nb-Cr compound is $NbCr_2$-R. The largest solubility of Cr in Ni-Nb compounds is 3.51% (mole fraction). From Nb-Cr binary phase diagram, it can be seen that $NbCr_2$ has a structure transforma-

Table 1 Lines and tie triangles determined by ESA for Ni-Cr-Nb diffusion triple(mole fraction, %)

Tie line and tie triangle	Ni	Cr	Nb	Ni	Cr	Nb
(Ni)/Ni_3Nb	73.70	22.59	3.71	76.10	3.51	20.39
Ni_3Nb/NiNb	77.58	0.67	21.75	37.50	1.55	60.95
	77.12	0.97	21.91	36.74	1.43	61.83
NiNb/(Nb)	18.61	0.63	80.76	0.92	0.00	99.08
(Ni)/(Cr)	56.21	41.85	1.93	6.83	92.99	0.18
(Nb)/$NbCr_2$-R	0.00	0.19	99.81	0.00	66.67	33.33
$NbCr_2$-R/(Cr)	0.00	66.67	33.33	0.01	99.81	0.18
Ni_3Nb/(Cr)	76.28	2.45	21.27	6.83	92.99	0.18
Ni_3Nb/$NbCr_2$-R	77.12	0.97	21.91	0.00	66.67	33.33
NiNb/$NbCr_2$-R	36.74	1.43	61.83	0.00	66.67	33.33
(Ni)/(Cr)/$NbCr_2$-R	56.22	41.85	1.93	6.83	92.99	0.18
	6.83	92.99	0.18	0.00	66.67	33.33
	0.00	66.67	33.33	56.22	41.85	1.93
Ni_3Nb/$NbCr_2$-R/NiNb	77.12	0.97	21.91	0.00	66.67	33.33
	0.00	66.67	33.33	36.74	1.43	61.83
	36.74	1.43	61.83	77.12	0.97	21.91
(Nb)/$NbCr_2$-R/NiNb	0.00	0.34	99.66	0.00	66.67	33.33
	0.00	66.67	33.33	36.74	1.43	61.83
	36.74	1.43	61.83	0.00	0.34	99.66
Ni_3Nb/$NbCr_2$-R/(Cr)	77.12	0.97	21.91	0.00	66.67	33.33
	0.00	66.67	33.33	0.01	99.81	0.18
	0.01	99.81	0.18	77.12	0.97	21.91

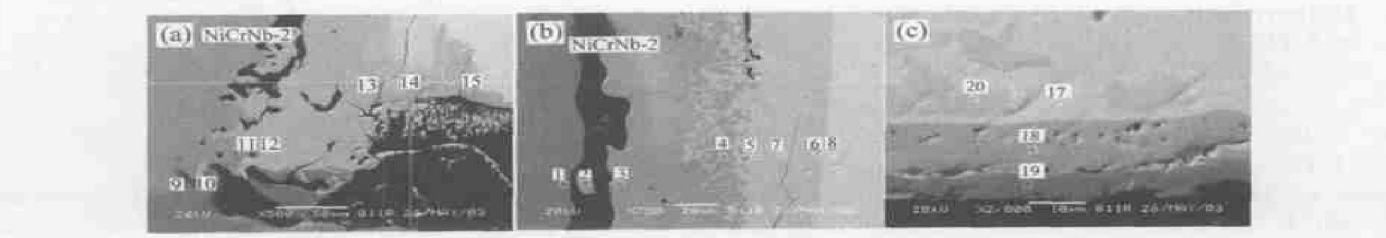

Fig. 2 Back-scattered electron images of Ni-Cr-Nb diffusion triple after annealing at 1 323 K for 690 h

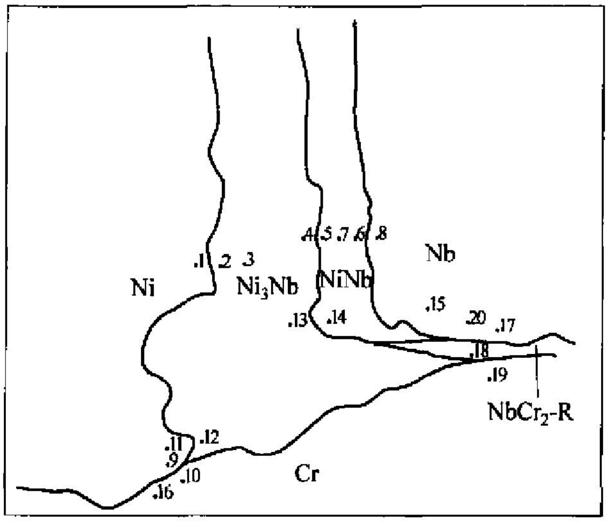

Fig. 3 Schematic diagram of phase distribution

tion at 2 101 K and $NbCr_2H$ only exists at above this temperature. Although only $NbCr_2$ can be determined by the energy spectrum analysis, it can be inferred to be $NbCr_2$-R at this temperature. By comparing Fig. 2 with Fig. 3, it can be seen that the layer $NbCr_2$-R is so thin that the component at the edge of the three phases ($NbCr_2$-R, NiNb, Nb) can not be determined by ESA. So the solubility of Ni at this point exists question. The largest solubility of Cr in Ni is 41.85% (mole fraction). The largest solubility of Ni in Cr is 6.83% (mole fraction). The largest solubility of Ni in Nb is 0.92% (mole fraction). The largest solubility of Nb in Ni is 3.71% (mole fraction). The largest solubility of Cr in Nb is 0.34% (mole fraction). The largest solubility of Nb in Cr is 0.18% (mole fraction).

By analyzing Fig. 3 and Table 1, the following three-phase equilibria in the Ni-Cr-Nb system at 1 323 K can be determined: 1—(Ni) + (Cr) + Ni_3Nb; 2—Ni_3Nb + $NbCr_2$-R + NiNb; 3—$NbCr_2$-R + (Cr) + Ni_3Nb; 4—$NbCr_2$-R + NiNb + (Nb)

Referring to Table 1, the tie lines and tie triangles of equilibrium phases in the concentration triangle can be obtained. Thus the isothermal section of the Ni-Cr-Nb ternary system of 1 323 K is established, as shown in Fig. 4.

3.2 Isothermal section of Ni-Cr-Nb ternary system at 1 423 K

Fig. 5 shows the back-scattered electron image of Ni-Cr-Nb diffusion triple after annealed at 1 423 K for 170 h. It can be seen that there are three diffusion layers, of which two are Ni-Nb compounds and one is Nb-Cr compound. Ni and Cr form complete solid solution. No ternary compounds are formed in the Ni-Cr-Nb diffusion triple. The characteristics of phase distribution and the phase relations are schematically shown in Fig. 6.

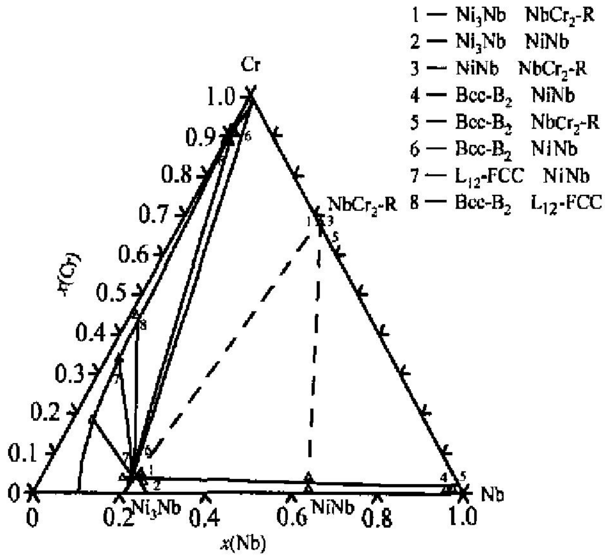

Fig. 4 Isothermal section of Ni-Cr-Nb ternary system at 1 323 K

Fig. 5 Back-scattered electron image of Ni-Cr-Nb diffusion triple after annealing at 1 423 K for 170 h

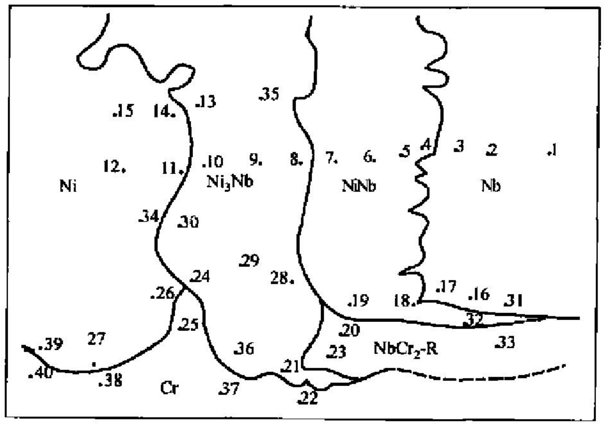

Fig. 6 Schematic diagram of phase distribution

The chemical compositions of diffusion equilibrium phases were determined by means the energy spectrum analysis. Parts of the typical data are listed in Table 2. By combining Table 2 with Fig. 5, the Ni-Nb compounds are Ni_3Nb and

Table 2 Lines and tie triangles determined by ESA for Ni-Cr-Nb diffusion triple(mole fraction, %)

Tie line and tie triangle	Ni	Cr	Nb	Ni	Cr	Nb
(Ni) / Ni_3Nb	68.07	28.28	3.65	75.11	3.45	21.44
	76.92	18.40	4.68	76.09	3.11	20.80
	73.52	22.30	4.18	75.84	0.50	23.66
	57.63	39.67	2.70	77.53	3.68	18.79
	55.66	40.95	3.39	72.86	4.88	22.26
	63.49	33.75	2.76	74.64	3.74	21.62
Ni_3Nb / NiNb	75.86	0.48	23.66	35.75	0.80	63.45
	75.84	0.50	23.66	36.13	0.49	63.38
	74.56	1.86	23.58	34.05	4.15	61.80
NiNb/ (Nb)	32.55	10.55	56.90	2.31	0.55	97.14
	35.85	0.79	63.36	0.57	0.01	99.42
	35.60	0.93	63.47	3.66	0.57	95.77
	34.05	4.15	61.80	2.31	0.55	97.14
$NbCr_2$- R / NiNb	46.04	25.62	28.34	34.05	4.15	61.80
	27.79	38.20	34.01	32.55	10.55	56.90
(Nb) / $NbCr_2$- R	0.00	0.38	99.62	27.79	38.20	34.01
(Cr) / Ni_3Nb	8.79	91.20	0.01	72.86	4.88	22.26
	4.31	95.47	0.22	73.32	3.48	23.20
	10.92	88.95	0.13	77.53	3.68	18.79
(Ni) / (Cr)	57.63	39.67	2.70	10.92	88.95	0.13
	55.66	40.95	3.39	8.79	91.20	0.01
	53.97	44.44	1.59	11.23	88.77	0.00
(Cr) / $NbCr_2$- R	4.31	95.47	0.22	43.54	29.46	27.00
$NbCr_2$- R/ Ni_3Nb	43.54	29.46	27.00	73.32	3.48	23.20
	46.04	25.62	28.34	74.56	1.86	23.58
(Nb) / $NbCr_2$- R/ NiNb	27.79	38.20	34.01	0.00	0.38	99.62
	0.00	0.38	99.62	32.55	10.55	56.90
	32.55	10.55	56.90	27.79	38.20	34.01
NiNb/ Ni_3Nb/ $NbCr_2$- R	46.04	25.62	28.34	34.05	4.15	61.80
	34.05	4.15	61.80	74.56	1.86	23.58
	74.56	1.86	23.58	46.04	25.62	28.34
$NbCr_2$- R/ Ni_3Nb/ (Cr)	43.54	29.46	27.00	73.32	3.48	23.20
	73.32	3.48	23.20	4.31	95.47	0.22
	4.31	95.47	0.22	43.54	29.46	27.00
(Ni) / (Cr) / Ni_3Nb	55.66	40.95	3.39	72.86	4.88	22.26
	72.86	4.88	22.26	8.79	91.20	0.01
	8.79	91.20	0.01	55.66	40.95	3.39

NiNb. The solubility of Cr at point 15 is 16. 30% (mole fraction, the same below) , but only 0. 33% at point 16. It can be inferred that the diffusion velocity of Cr in Ni is bigger than that in Nb. The largest solubility of Ni in Cr is 44. 44% and 3. 66% in Nb. The largest solubility of Cr in Ni is 12. 50% and 0. 57% in Nb. The largest solubility of Nb in Cr is 0. 22% and in Ni 4. 68%. The solubility of Ni in Ni_3Nb ranges from 72. 86% to 73. 55% and the solubility of Nb in Ni_3Nb ranges from 18. 79% to 23. 66%. It's the same as Ni-Nb binary system. The component range of Ni in NiNb is 32. 55% - 36. 31% and the component range of Nb is 48. 25% - 63. 47%. Cr substitutes Ni partly because of the diffusion of Cr into Ni and the mole proportion is about 1∶ 1. The largest solubility of Ni in $NbCr_2$-R is 46. 04%. It can be seen from Fig. 5 that the layer $NbCr_2$-R is very thin. Considering the component of point 33 isn't accurate, part lines in the isothermal section in Fig. 7 are imaginary lines.

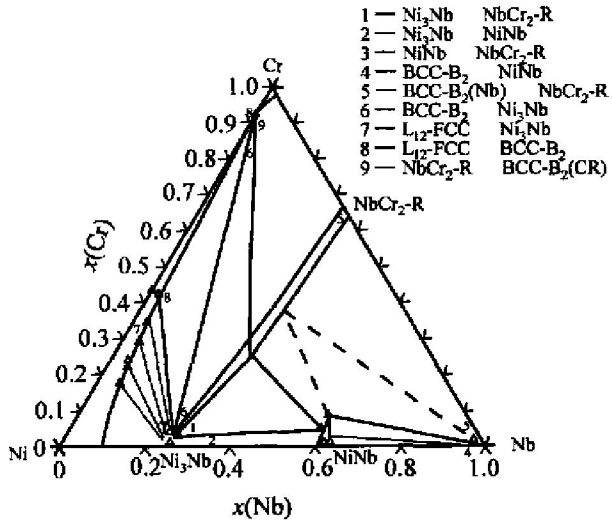

Fig. 7 Isothermal section of Ni-Cr-Nb ternary system at 1 423 K

By analyzing Fig. 6 and Table 2, the following three-phase equilibria in the Ni-Cr-Nb system at 1423K can be determined: 1—(Ni) + (Cr) + Ni_3Nb; 2 — Ni_3Nb+ $NbCr_2$-R+ NiNb; 3 —$NbCr_2$-R+ (Cr) + Ni_3Nb; 4 —$NbCr_2$-R+ NiNb+ (Nb) .

Referring to Table 2, the tie lines and tie triangles of equilibrium phases in the concentration triangle can be obtained. Thus the isothermal section of the Ni-Cr-Nb ternary system of 1 423 K is established, as shown in Fig. 7.

Comparing Fig. 4 with Fig. 7, it can be seen that the phase diagram doesn't change except the solubility, especially the solubility of Ni in $NbCr_2$-R.

4 CONCLUSIONS

The isothermal sections of Ni-Cr-Nb ternary system at 1 323 K and 1 423 K were determined by means of diffusion triple and energy spectrum analysis

(ESA). It can be found that no ternary compounds are formed in the Ni-Cr-Nb ternary system at 1 323 K and 1 423 K. There is no phase transformation in the Ni-Cr-Nb ternary system when cooling from 1 423 K to 1 323 K except the solubility turning bigger. At 1 423 K the diffusion velocity of Cr in Nb is smaller than that in Ni and the solubilities among the three elements is larger than that at 1 323 K. At 1 423 K the largest solubility of Ni in Cr is 11.23% and 3.66% in Nb. The largest solubility of Cr in Ni is 44.44% and 0.57% in Nb. The largest solubility of Nb in Ni is 4.68% and 0.22% in Cr. At 1 323 K the largest solubility of Ni in Cr is 6.83% and 0.92% in Nb. The largest solubility of Cr in Ni is 41.85% and 0.34% in Nb. The largest solubility of Nb in Ni is 3.71% and 0.18% in Cr.

REFERENCES

[1] Furrer D, Fecht H. Ni-based super-alloys for turbine discs[J]. JOM, 1999, 2: 31-34.

[2] Zhao J C, Jzckson M R. A diffusion multiple approach for the a celerated design of structural materials[J]. MRS Bulletin, 2002, 4: 324-329.

[3] CUI Yu-wen, LU Xiao-gang, JIN Zhan-peng. Experimental study and thermodynamic assessment of the Ni-Mo-Ta system[J]. Metall Mater Trans, 1999, 30A(11): 2735-2744.

[4] ZENG Ke-jun, JIN Zhan-peng, HUANG Pei-yun. The effect of Nb on the hot corrosion behavior of Ni-based superalloy[J]. Z Metallkde, 1989, 80(2): 129-134.

[5] Liu B X, Bai H Y, Zhang Z J, et al. Thermally induced transition from metastable Ni-Nb hexagonal phase to amorphous and its thermodynamic interpretation[J]. Journal of Alloys and Compounds, 1993, 196: 37-40.

[6] Subramanian P R, Mendiratta M G, Dimiduk D M. The development of Nb-Based advanced intermetallic alloys for structural applications[J]. JOM, 1996: 33-38.

[7] Nash P. The Cr-Ni(chromium-nickel) system[J]. Bulletin of Alloy Phase Diagrams, 1986, 7(5): 466-476.

[8] Okamoto H. Nb-Ni(niobium-nickel)[J]. Journal of Phase Equilibria, 1992, 13(4): 44-45.

[9] Bolcavage A, Kattner U R. A reassessment of the calculated Ni-Nb phase diagram[J]. Journal of Phase Equilibria, 1996, 17(2): 92-100.

[10] ZENG Ke-jun, JIN Zhan-peng. Thermodynamic modelling of intermetallic compounds in the Ni-Nb system[J]. Scripta Mettallurgica et Materialia, 1992, 26: 417-422.

[11] Nash P, Nash A. The Nb-Ni(niobium-nickel) system[J]. Bulletin of Alloy Phase Diagrams, 1986, 17(2): 124-130.

[12] Venkatraman M, Neumann J P. The Cr-Nb (chromium-niobium) system[J]. Bulletin of Alloy Phase Diagrams. 1986, 7(5): 462-465.

[13] Joaquim G, Costa N, Suzana G, Fries, Hans L L. Thermodynamic optimization of the Nb-Cr system[J]. CALPHAD, 1993, 3: 219-228.

[14] LIANG Jing-kui. Phase and Phase Structure[M]. Beijing: Science and Technology Publishing Company, 1993. 150-154. (in Chinese)

[15] JING Zhan-peng. Ternary triple and its application in phase study [J]. Journal of Central-South Institute of Mining and Metallurgy, 1984(1): 27-34. (in Chinese)

(Edited by LONG Huai-zhong)