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Transformations and phase relations in Nb-Ti-Si ternary system at 1 373~ 1 473 K①

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[Abstract] The isothermal sections of the Nb-Ti-Si ternary system at 1 473 K and 1 373 K were determined by means of diffusion triple technique and electron microprobe analysis. By analyzing the diffusion layers in the diffusion couples, the titanium silicides and niobium silicides forming in this system were identified. The results show that no ternary compounds formed in the Nb-Ti-Si ternary system at the test temperatures. The phase transformations occurring on cooling from 1 473 K to 1 373 K were discussed.

[Key words] Nb-Ti-Si ternary system; diffusion triple technique; isothermal sections; phase transformations; phase relations

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1 INTRODUCTION

Because of their high strength, good plasticity and corrosion resistance, especially low density and excellent fracture toughness, the titanium and its alloys have found wide applications in many fields[1].

In the Nb-Si binary system, an in-situ composite can form with Nb_5Si_3 phase as reinforcement and (Nb) phase as matrix. Even at a temperature high up to 2 757 K, the Nb_5Si_3 still has enough strength (hardness) to act as reinforcement[2]. The addition of titanium into the Nb-Si system can further improve the properties of the matrix as well as the Nb-Si compounds, which is due to the fact that continuous solid solution can form between niobium and titanium in a certain range of temperature and sometimes niobium and titanium can replace each other to form silicides.

Schlesinger et al[3] made a detailed evaluation on the Nb-Si binary system, and found there are three compounds namely Nb_3Si, Nb_5Si_3 and $NbSi_2$ in this system. Many other researchers[4,5] have also done a lot of work on this system, respectively.

The Nb-Ti binary system is relatively simple. Murray[6] made an evaluation on it, and he believed that above 1 155 K, a continuous solid solution forms between niobium and titanium.

Murray[7], Vahlas[8], Seifert et al[9] made thermodynamic evaluation or optimized calculation on the Ti-Si binary system, and found there are five compounds namely Ti_3Si, Ti_5Si_3, Ti_5Si_4, $TiSi$ and $TiSi_2$ in this system.

The experimented data of the Nb-Ti-Si ternary system are very limited. Bewlay et al[10] determined the liquid face and the Nb-Ti-Si isothermal section of the Nb-Ti-Si ternary system through studying 29 alloys by means of directional solidification. ZHANG et al[11] made a thermodynamic evaluation on the liquid face of the Nb-Ti-Si ternary system. In this paper, the authors aim to determine isothermal sections of the Nb-Ti-Si ternary system at 1 473 K and 1 373 K by means of diffusion triple technology and electron microprobe analysis.

2 EXPERIMENTAL

The raw materials for preparing the Nb-Ti-Si diffusion triple are 99.9% purity niobium and titanium ingots and 99.99% purity silicon ingot. The dimensions of niobium, titanium and silicon ingots are 5 mm × 5 mm × 10 mm, 5 mm × 5 mm × 10 mm and 5 mm × 10 mm × 10 mm, respectively. The schematic diagram of construction of the Nb-Ti-Si ternary system is shown in Fig. 1. After long time annealing at 1 473 K and 1 373 K, the transformations and phase relations were determined by analyzing the diffusion layers using electron microprobe analysis technique.

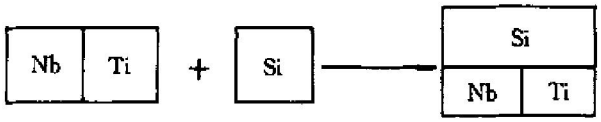

Fig. 1 Schematic diagram of construction of Nb-Ti-Si diffusion triple

3 RESULTS AND DISCUSSION

3.1 Isothermal section of Nb-Ti-Si ternary system at 1 473 K

Fig. 2(a) shows the back-scattered electron image of the Nb-Ti-Si diffusion triple after annealing for 360 h at 1 473 K. It can be found in Fig. 2(a) that there are seven diffusion layers, of which four are Ti-

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Si compounds, two are Nb-Si compounds and one is a compound forming between (NbTi) and Si. The characteristics of phase distribution and the phase relations are schematically shown in Fig. 2(b).

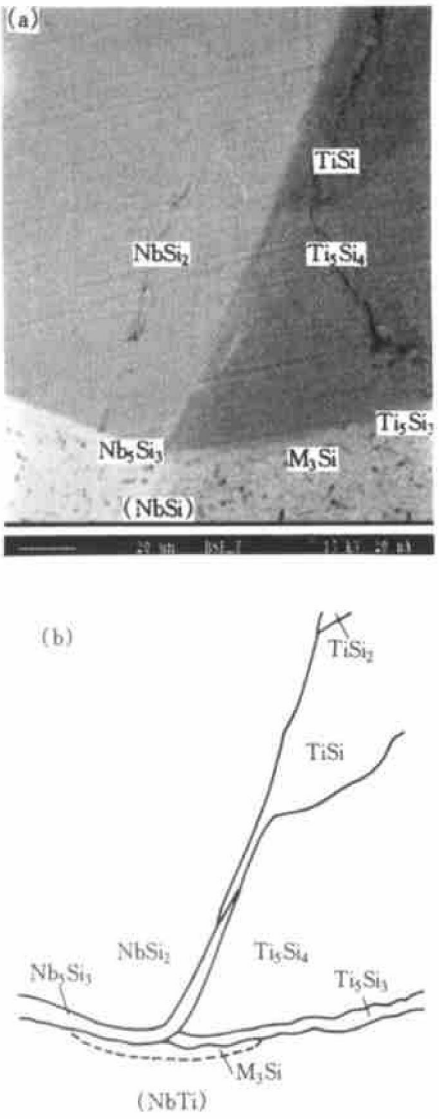

Fig. 2 Back-scattered electron image (a) and schematic diagram of phase distribution (b) of Nb-Ti-Si diffusion triple after annealing for 360 h at 1 473 K

The chemical compositions of the equilibrium phases were determined by the electron microprobe analysis. Part of the typical data are listed in Table 1. The diffusion layers in the diffusion triple can be demarcated based on the experimental data. In the Ti-Si side, the diffusion layers are $TiSi_2$, TiSi, Ti_5Si_4 and Ti_5Si_3 successively from silicon to titanium. In the Nb-Si side, the diffusion layers are $NbSi_2$ and Nb_5Si_3 successively from silicon to niobium.

In Nb-Si side, there are mainly two layers of compounds namely Nb_5Si_3 and $NbSi_2$. The largest solubility of titanium in Nb_5Si_3 is 3.0% (mole fraction). While that in $NbSi_2$ is only 1.2% (mole fraction).

Table 1 Tie lines and tie triangles of Nb-Ti-Si diffusion triple at 1 473 K (mole fraction)

Tie lines	Nb	Si	Ti	Nb	Si	Ti
Ni_5Si_3 / $NbSi_2$	0.634	0.366	0	0.348	0.652	0
	0.620	0.371	0.009	0.346	0.654	0
	0.616	0.360	0.024	0.343	0.651	0.006
Nb_5Si_3 / Nb(Ti)	0.639	0.331	0.030	0.945	0.055	0
	0.658	0.342	0	0.990	0.010	0
	0.640	0.342	0.018	0.987	0.013	0
TiSi / $TiSi_2$	0.133	0.512	0.355	0.110	0.651	0.239
	0.096	0.514	0.390	0.043	0.650	0.307
	0.056	0.495	0.449	0.027	0.654	0.319
$TiSi_2$ / $NbSi_2$	0.052	0.657	0.291	0.338	0.650	0.012
	0.052	0.651	0.297	0.330	0.661	0.009
	0.110	0.651	0.239	0.318	0.665	0.027
Ti_5Si_3 / Ti_5Si_4	0.200	0.360	0.540	0.171	0.421	0.408
	0.166	0.364	0.470	0.135	0.423	0.442
	0.105	0.354	0.541	0.073	0.427	0.500
Tie triangles	**Nb**	**Si**	**Ti**	**Nb**	**Si**	**Ti**
TiSi/ $NbSi_2$ / $TiSi_2$	0.133	0.512	0.355	0.318	0.665	0.027
	0.110	0.651	0.239	0.133	0.512	0.355
	0.318	0.665	0.027	0.110	0.651	0.239
Ti_5Si_4 / TiSi	0.171	0.421	0.408	0.133	0.512	0.355
	0.135	0.423	0.442	0.098	0.504	0.398
	0.073	0.427	0.500	0.055	0.495	0.450
Ti(Nb) / Ti_5Si_3	0.078	0.028	0.875	0.031	0.357	0.612
	0.098	0.019	0.883	0.033	0.357	0.610
	0.001	0.045	0.954	0.001	0.347	0.652
TiSi/ $NbSi_2$ / Nb_5Si_3	0.133	0.512	0.355	0.318	0.665	0.027
	0.617	0.360	0.023	0.133	0.512	0.355
	0.318	0.665	0.027	0.617	0.360	0.023
M_3Si/ Nb_5Si_3 / Ti_5Si_3	0.0273	0.246	0.481	0.617	0.360	0.023
	0.617	0.360	0.023	0.200	0.360	0.540
	0.200	0.360	0.540	0.273	0.246	0.481
TiSi/ Ti_5Si_4 / Nb_5Si_3	0.133	0.512	0.355	0.171	0.421	0.408
	0.171	0.421	0.408	0.617	0.360	0.023
	0.617	0.360	0.023	0.133	0.512	0.355
(NbTi) / M_3Si / Nb_5Si_3	0.898	0.043	0.059	0.273	0.246	0.481
	0.273	0.246	0.481	0.617	0.360	0.023
	0.617	0.360	0.023	0.898	0.043	0.059
Ti_5Si_4/ Nb_5Si_3 / Ti_5Si_3	0.171	0.421	0.408	0.617	0.360	0.023
	0.617	0.360	0.023	0.200	0.360	0.540
	0.200	0.360	0.540	0.171	0.421	0.408
(TiNb) / M_3Si / Ti_5Si_3	0.098	0.019	0.883	0.191	0.253	0.556
	0.191	0.253	0.556	0.041	0.357	0.602
	0.041	0.357	0.602	0.098	0.019	0.883

By analyzing Fig. 2 and Table 1, the following three-phase equilibria in the Nb-Ti-Si ternary system at 1 473 K can be determined:

1) $NbSi_2$ + $TiSi_2$ + TiSi;
2) $NbSi_2$ + TiSi + Nb_5Si_3;
3) Nb_5Si_3 + TiSi + Ti_5Si_4;
4) Nb_5Si_3 + Ti_5Si_4 + Ti_5Si_3;
5) Nb_5Si_3 + Ti_5Si_3 + M_3Si;
6) Nb_5Si_3 + (NbTi) + M_3Si;
7) Ti_5Si_3 + (NbTi) + M_3Si.

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 Nb-Ti-Si ternary system of 1 473 K is established, as shown in Fig. 3.

3.2 Isothermal section of Nb-Ti-Si ternary system at 1 373 K

Fig. 4(a) shows the back-scattered electron image of Nb-Ti-Si diffusion triple after annealing for 480 h at 1 373 K. It can be seen that there form seven diffusion layers, of which five are Ti-Si compounds, and two are Nb-Si compounds. The characteristics of phase distribution and phase relations are shown in Fig. 4(b).

The chemical compositions of different equilibrium phases were determined by means of the electron microprobe analysis. Part of the typical data are listed in Table 2. By combining Table 2 with Fig. 4, the Ti-Si compounds can be determined to be $TiSi_2$, TiSi, Ti_5Si_4, Ti_5Si_3 and Ti_3Si, among which $TiSi_2$, TiSi and Ti_5Si_4 diffusion layers are obvious and relatively thick, but Ti_5Si_3 diffusion layer is relatively thin. By local magnification, it can be found that there also exists a very thin diffusion layer, see Fig. 5. Through the electron microprobe analysis, this thin layer is identified to be Ti_3Si. The Nb-Si compounds are divided into two layers, namely Nb_5Si_3 and $NbSi_2$.

The compositions of silicon in Ti-Si compounds are in a narrow range, which agrees with those reported in references. But the solubility of niobium in

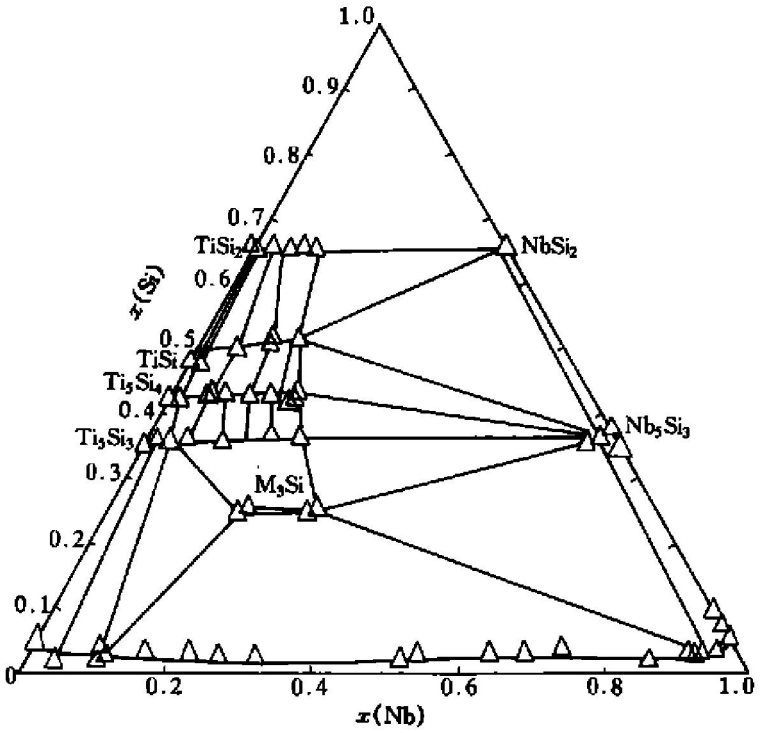

Fig. 3 Isothermal section of Nb-Ti-Si ternary system at 1 473 K

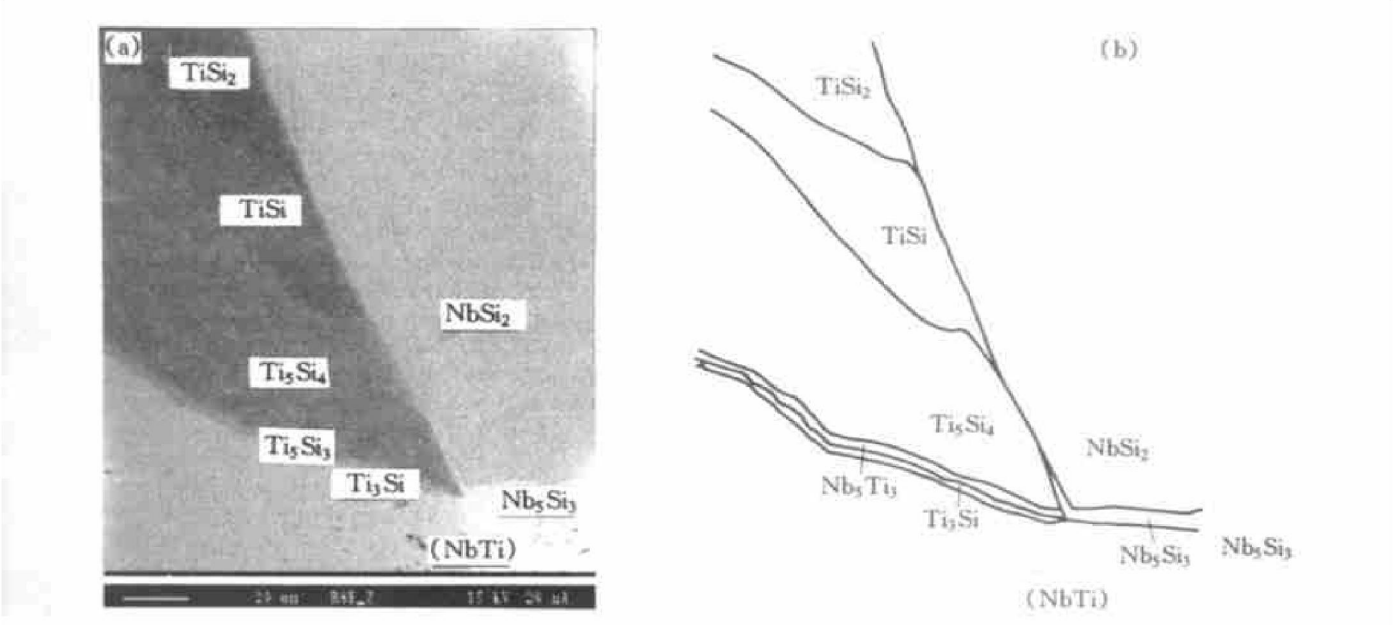

Fig. 4 Back-scattered electron image (a) and schematic diagram of phase distribution (b) of Nb-Ti-Si diffusion triple after annealing for 480 h at 1 373 K

Table 2 Tie lines and tie triangle of Nb-Ti-Si ternary triple at 1 373 K (mole fraction)

Tie lines	Nb	Si	Ti	Nb	Si	Ti
Nb_5Si_3 / $NbSi_2$	0.604	0.360	0.036	0.351	0.648	0.001
	0.620	0.358	0.022	0.362	0.638	0
	0.635	0.363	0.001	0.347	0.652	0.001
Nb_5Si_3 / Nb(Ti)	0.604	0.360	0.036	0.964	0.021	0.015
	0.630	0.358	0.012	0.996	0.002	0.002
	0.632	0.367	0.001	0.998	0	0.002
TiSi / $TiSi_2$	0.117	0.481	0.402	0.105	0.656	0.239
	0.108	0.490	0.402	0.081	0.646	0.273
	0.085	0.480	0.435	0.062	0.655	0.283
$TiSi_2$ / $NbSi_2$	0.105	0.656	0.239	0.311	0.661	0.028
	0.081	0.646	0.273	0.308	0.668	0.024
	0.062	0.655	0.283	0.315	0.665	0.020
Ti_5Si_3 / Ti_5Si_4	0.155	0.364	0.481	0.132	0.431	0.437
	0.103	0.361	0.536	0.107	0.430	0.463
	0.073	0.366	0.561	0.063	0.423	0.514
Tie triangles	**Nb**	**Si**	**Ti**	**Nb**	**Si**	**Ti**
Ti_5Si_4 / TiSi	0.132	0.431	0.437	0.117	0.481	0.402
	0.097	0.440	0.463	0.108	0.490	0.402
	0.063	0.423	0.514	0.085	0.480	0.435
TiSi/ $NbSi_2$ / $TiSi_2$	0.117	0.481	0.402	0.311	0.661	0.028
	0.311	0.661	0.028	0.105	0.656	0.239
	0.105	0.656	0.239	0.117	0.481	0.402
Ti(Nb) / Ti_3Si	0.980	0.004	0.016	0.145	0.258	0.597
	0.322	0.008	0.670	0.129	0.253	0.618
	0.127	0.011	0.862	0.068	0.255	0.677
TiSi/ $NbSi_2$ / Ti_5Si_4	0.117	0.481	0.402	0.311	0.661	0.028
	0.311	0.661	0.028	0.132	0.431	0.437
	0.132	0.431	0.437	0.117	0.481	0.402
Ti_3Si/ Nb_5Si_3 / Ti_5Si_3	0.145	0.258	0.597	0.604	0.360	0.036
	0.604	0.360	0.036	0.155	0.364	0.481
	0.155	0.364	0.481	0.145	0.258	0.597
Ti_5Si_4/ $NbSi_2$ / Nb_5Si_3	0.132	0.431	0.437	0.311	0.661	0.028
	0.311	0.661	0.028	0.604	0.360	0.036
	0.604	0.360	0.036	0.132	0.431	0.437
(TiNb) / Ti_3Si / Nb_5Si_3	0.980	0.004	0.016	0.145	0.258	0.597
	0.145	0.258	0.597	0.604	0.360	0.036
	0.604	0.360	0.036	0.980	0.004	0.016
Ti_5Si_4/ Nb_5Si_3 / Ti_5Si_3	0.132	0.431	0.437	0.604	0.360	0.036
	0.604	0.360	0.036	0.155	0.364	0.481
	0.155	0.364	0.481	0.132	0.431	0.437

Ti-Si compounds at 1 373 K is layer; it is 10.5% in $TiSi_2$, 11.7% in TiSi, 13.2% in Ti_5Si_4, 15.5% in Ti_5Si_3 and 14.5% in Ti_3Si (mole fraction), respectively.

The solubility of titanium in Nb-Si compounds is relatively small. The largest value in $NbSi_2$ is 2.77% (mole fraction) and that in Nb_5Si_3 is 3.6% (mole fraction). The solubility of silicon in (NbTi) is very small.

There can form continuous solid solution between niobium and titanium at 1 373 K, but the Nb/Ti interface can be clearly seen in the diffusion couple.

It can be known from Fig. 4 and Table 2 that there exist the following three-phase equilibria in the Nb-Ti-Si ternary system at 1 373 K:

1) $NbSi_2$ + $TiSi_2$ + TiSi;
2) $NbSi_2$ + $TiSi_2$ + Ti_5Si_4;
3) $NbSi_2$ + Ti_5Si_4 + Nb_5Si_3;
4) Nb_5Si_3 + Ti_5Si_4 + Ti_5Si_3;
5) Nb_5Si_3 + Ti_5Si_3 + Ti_3Si;
6) Nb_5Si_3 + Ti_3Si + (NbTi).

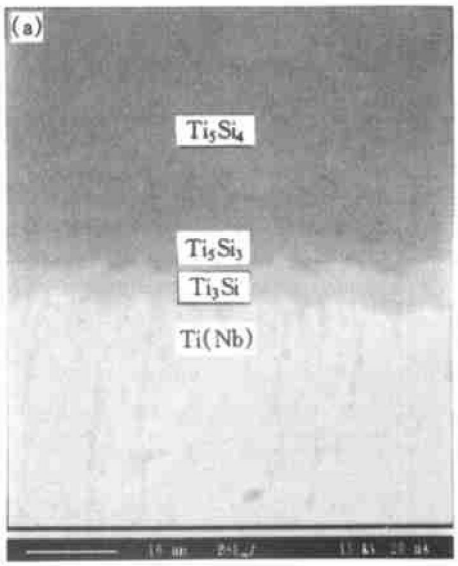

Fig. 5 Local magnification of Ti_3Si thin layer

Referring to Fig. 4 and Table 2, the tie lines and tie triangles of the equilibrium phases in the concentration triangle can be obtained, thus the isothermal section of the Nb-Ti-Si ternary system at 1 373 K is established, as shown in Fig. 6.

3.3 Phase transformations and phase relations from 1 473 K to 1 373 K in Nb-Ti-Si ternary system

The three-phase equilibria of the Nb-Ti-Si ternary system at 1 373 K and 1 473 K are summarized in Table 3. It is clear from Table 3 and the isothermal sections in Fig. 3 and Fig. 5 that there are two main changes from 1 473 K to 1 373 K. 1) There occurs a peritectoid-eutectoid reaction: Nb_5Si_3 + TiSi $\longrightarrow$ Ti_5Si_4 + $NbSi_2$; 2) With decreasing temperature, the Ti_5Si_3 + M_3Si + (NbTi) phase field moves to the Ti-Si side and disappears at some temperature between 1 473 K and 1 373 K, and correspondingly M_3Si compound changes to Ti_3Si compound.

Table 3 Three-phase equilibria in Nb-Ti-Si ternary system at 1 473 K and 1 373 K

T / K	Equilibria	
1 473	1) $TiSi_2$ + $NbSi_2$ + TiSi	5) Nb_5Si_3 + Ti_5Si_3 + M_3Si
	2) $NbSi_2$ + TiSi + Nb_5Si_3	6) Ti_5Si_3 + M_3Si + (NbTi)
	3) Nb_5Si_3 + TiSi + Ti_5Si_4	7) Nb_5Si_3 + M_3Si + (NbTi)
	4) Nb_5Si_3 + Ti_5Si_4 + Ti_5Si_3	
1 373	1) $TiSi_2$ + $NbSi_2$ + TiSi	4) Nb_5Si_3 + Ti_5Si_4 + Ti_5Si_3
	2) $NbSi_2$ + TiSi + Ti_5Si_4	5) Nb_5Si_3 + Ti_5Si_3 + Ti_3Si
	3) Nb_5Si_3 + Ti_5Si_4 + $NbSi_2$	6) Nb_5Si_3 + Ti_3Si + (NbTi)

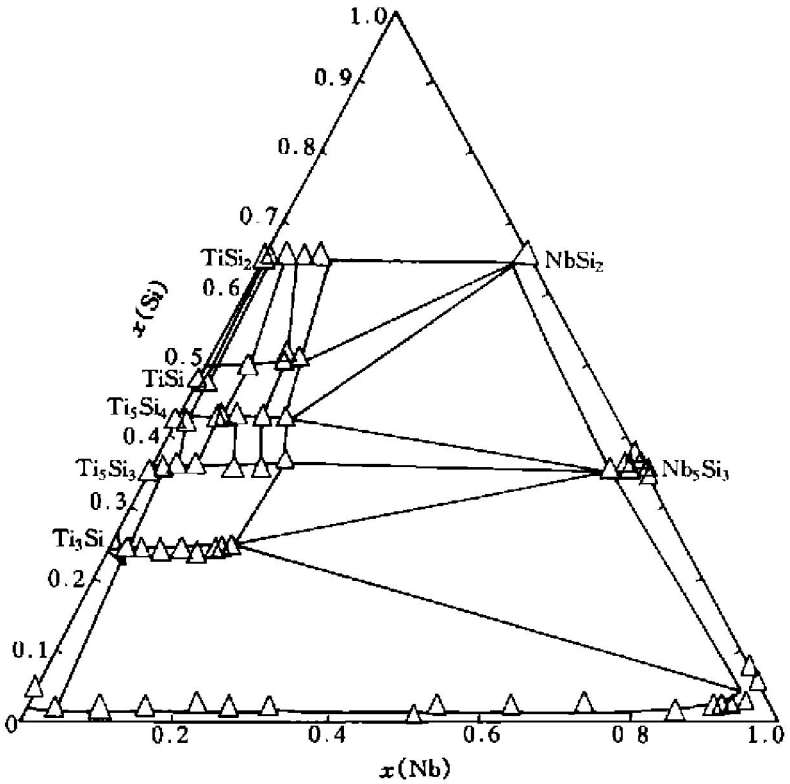

Fig. 6 Isothermal section of Nb-Ti-Si ternary system at 1 373 K

4 CONCLUSIONS

1) No ternary compounds form in the Nb-Ti-Si ternary system at 1 473 K and 1 373 K.

2) There occurs a peritectoid-eutectoid reaction: $Nb_5Si_3 + TiSi \longrightarrow Ti_5Si_4 + NbSi_2$ in the Nb-Ti-Si ternary system on cooling from 1 473 K and 1 373 K.

3) With decreasing temperature, the Ti_5Si_3 + M_3Si+ (NbTi) phase field moves to the Ti-Si side and disappears at some temperature between 1 473 K and 1 373 K, and correspondingly M_3Si compound changes to Ti_3Si compound.

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