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Experimental investigation and thermodynamic assessment of phase equilibria in the Nb–Si–Zr ternary system

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ABSTRACT

In this study, the phase equilibria of Nb–Si–Zr at 1373 K, 1473 K and 1573 K were experimentally determined by means of back-scattered electron (BSE), electron probe microanalysis (EPMA) and X-ray diffraction (XRD). The results show that there were five three-phase regions and sixteen two-phase regions in the studied isothermal sections, and no any ternary compounds were found. The solubility of Si in the Nb–Zr side is very small. Large solubilities of Nb in αZr_5Si_4, Zr_3Si_2 and Zr_2Si phases were observed, otherwise the solubilities of Nb in $ZrSi_2$, $\alpha ZrSi$ and Zr_3Si phases are relatively small. Based on the present experimental results, the thermodynamic assessment of Nb–Si–Zr system was carried out using the CALPHAD (Calculation of Phase Diagrams) method. The current calculated phase diagrams are in reasonable agreement with the present experimental data.

1. Introduction

With the development of aircraft engines and gas turbines, the airfoil temperature at the hottest location is approaching 1423 K, which is close to the limit for the Ni-based alloys. The present Ni-based superalloys were difficult to meet the demand of development of aircraft and gas turbines, in order to promote the progress in turbine engines, more advanced high temperature structural materials are in dire need. The intermetallic compounds of Nb–Si based refractory alloys have been investigated extensively for potential candidates in these fields [1–3]. According to numbers of previous researches results, the Nb–Si binary composites exhibit high melting point, low density and excellent mechanical properties [4–6]. However, practical applications of Nb–Si based alloys were hindered for the poor oxidation resistance at high temperature [7] and low fracture toughness at room temperature [8–10]. In order to overcome these drawbacks and improve the property balance of Nb–Si based refractory alloys, many significant efforts have been made by alloying, such as adding Ti, Hf, Cr, Al, Zr, Ta, V, W, Mo [11–17]. The alloying effects of Zr in Nb–Si based alloys have been investigated widely, and results indicated that alloying with proper content of Zr can enhance the kinetics of the eutectoid decomposition of high-temperature Nb_3Si phase into Nb and Nb_5Si_3 phases in the binary Nb–Si system [18]. Furthermore, addition of Zr can bring some visible microstructural change and improvement of mechanical properties of the alloys [16,19–21]. Thus, the high-performance Nb–Si based alloys may play a more and more important role in the development of advanced aircraft engines. In order to well understand the effects of Zr on the microstructure and properties of Nb–Si based alloys, the knowledge of phase equilibrium in the Nb–Si–Zr system is a prerequisite. Moreover, establishing a comprehensive thermodynamic database of Nb–Si based alloys also requires detailed information of phase equilibrium in Nb–Si–Zr system. Recently, more and more attentions were paid to the phase equilibrium involved Nb–Si based alloys [22–24], however, the phase equilibrium about Nb–Si–Zr system were rare. To the best of our knowledge, only the mutual solubility of disilicides of $ZrSi_2$–$NbSi_2$ was studied [25], and the isothermal section of Nb–Si–Zr system at 1173 K was reported [26]. It is not beneficial to materials design in Nb–Si based alloys for aircraft engines. Thus the purpose of this work is to determine the phase equilibrium of Nb–Si–Zr ternary system at 1373 K, 1473 K and 1573 K experimentally by using BSE, EPMA and XRD methods. And then, based on the present experimental results, a thermodynamic calculation of the Nb–Si–Zr system is carried out by using the CALPHAD method. For the Nb–Si–Zr system, the experimental temperature at 1373 K, 1473 K and 1573 K are relatively low temperature. Because many intermediate phases stable at higher temperature, such as $\beta ZrSi$, βZr_5Si_4, βNb_5Si_3, and Zr_5Si_3

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phases, were not involved in the present experimental work. And in thermodynamic calculation these phases are not considered due to the lacking of experimental data at high temperature. Despite this blemish mentioned above, all of these results of this work can make a contribution to the materials design of Nb–Si based refractory alloys.

In the Nb–Si–Zr ternary system, the three sub-binary systems Nb–Si [27–29], Si–Zr [30] and Nb–Zr [31] have been investigated several times. The Nb–Si binary phase diagram was edited by Schlesinger [27], in which four intermediate phases are predicted: Nb_3Si, αNb_5Si_3, βNb_5Si_3 and $NbSi_2$. In the Si–Zr binary phase diagram, edited by Okamoto [30], there are nine intermediate phases: $ZrSi_2$, $\alpha ZrSi$, $\beta ZrSi$, αZr_5Si_4, βZr_5Si_4, Zr_3Si_2, Zr_5Si_3, Zr_2Si and Zr_3Si. The Nb–Zr binary system [31] is a simple system without any intermediate phase. At higher temperatures, there is a liquidus/solidus minimum of 2013 K at 78.3 at.% Zr. At 893 K, the bcc solid solution between Nb and β(Zr) undergoes a monotectoid reaction $\beta_1 \rightarrow \beta_2 + \beta(Zr)$, where the β(Zr) is the terminal solid solution (β(Nb, Zr)). At 1261 K, the critical point of the monotectoid reaction occurs at 39.4 at.% Zr. The phase diagrams of the Nb–Si, Nb–Zr and Si–Zr binary systems are shown in Fig. 1, and the information of all stable solid phases in the three binary systems is listed in Table 1 [27,30,31].

Table 1
The stable solid phases in three binary systems.

System	Phase	Pearson's symbol	Prototype	Strukturbericht designation	Reference
Nb–Si	(Nb)	*cI*2	W	A2	[27]
	Nb_3Si	*tP*32	PTi_3	–	[27]
	βNb_5Si_3	*tI*32	Si_3W_5	$D8_m$	[27]
	αNb_5Si_3	*tI*32	Cr_5B_3	$D8_l$	[27]
	$NbSi_2$	*hP*9	$CrSi_2$	C40	[27]
	(Si)	*cF*8	C(diamond)	A4	[27]
Nb–Zr	(Nb)	*cI*2	W	A2	[31]
	βZr	*cI*2	W	A2	[31]
	αZr	*hP*2	Mg	A3	[31]
Si–Zr	(Si)	*cF*8	C(diamond)	A4	[30]
	$ZrSi_2$	*oC*26	Si_2Zr	C49	[30]
	βZrSi	*oC*8	CrB	B_f	[30]
	αZrSi	*Op*8	FeB	B26	[30]
	βZr_5Si_4	–	–	–	[30]
	αZr_5Si_4	*tP*36	–	–	[30]
	Zr_3Si_2	*tP*10	Si_2U_3	$D5_a$	[30]
	Zr_5Si_3	*hP*16	Mn_5Si_3	$D8_8$	[30]
	Zr_2Si	*tI*26	Al_2Cu	C16	[30]
	Zr_3Si	*tP*32	PTi_3	–	[30]
	βZr	*cI*2	W	A2	[30]
	αZr	*hP*2	Mg	A3	[30]

2. Experimental procedures

Bulk alloy buttons were prepared by arc melting in a water-cooled copper crucible with a non-consumable tungsten electrode under a high purity argon atmosphere from pure materials niobium (99.8 wt.%), silicon (99.9 wt.%) and zirconium (99.9 wt.%). In order to achieve homogeneity, all of the ingots (around 20 g) were melted five times and the weight loss during melting were generally less than 0.50%. Then the ingots were cut into small pieces for heat treatments and further observations. These small specimens were sealed into quartz capsules evacuated and backfilled with argon gas and annealed at 1373 K, 1473 K and 1573 K respectively. Depending on the annealing temperature and composition of the specimen, the time of heat treatment varied from 15 days to 45 days. Afterward, the specimens were quenched into ice water.

After annealing and standard metallographic preparation, the microstructural observations were carried out by BSE. The equilibrium compositions of the equilibrated alloys were examined by EPMA (JXA-8100R, JEOL, Japan). Five analyses were carried out for each phase and standard deviation of the measured concentration were ±0.5 at.%. Pure elements were used as standards and the measurements were carried out at 20.0 kV. The XRD was used to identify the crystal structure. The XRD of the sample was carried out on a Phillips Panalytical X-pert diffractometer using Cu Kα radiation at 40.0 kV and 30 mA. The data were collected in the range of 2θ from 20° to 90° at a step of 0.0167°.

3. Thermodynamic models

In the present work, the thermodynamic parameters of the Nb–Si, Si–Zr, and Nb–Zr binary sub-systems are taken from Geng et al. [32], Chen et al. [33], and Armando [34].

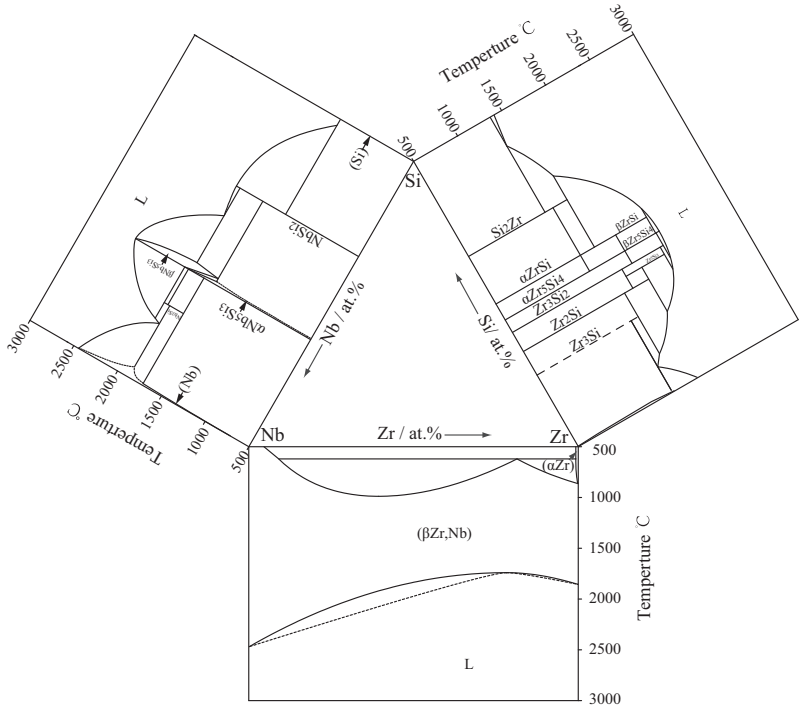

Fig. 1. Binary phase diagrams constituting the Nb–Si–Zr ternary system [27,30,31].