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Experimental investigation of phase equilibria in the Zr–Nb–Cr system at 1573 K and 1373 K

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ABSTRACT

Phase equilibria in the Zr–Nb–Cr system at 1573 K and 1373 K were characterized by X-ray diffraction (XRD) and electron probe microanalysis (EPMA) coupled with wavelength-dispersive spectroscopy (WDS). Three single-phase regions and two two-phase regions were identified in the isothermal sections of 1573 K and 1373 K. The single-phase regions are BCC (Cr), C15 and BCC (Zr, Nb), and the two-phase regions are BCC (Cr) + C15 and BCC (Zr, Nb) + C15. With the temperature decreasing from 1573 K to 1373 K, the BCC (Zr, Nb) phase region narrows slightly, while the C15 phase region shrinks noticeably in the Nb-rich direction. The problems concerning sample equilibration and weight loss in the experiments were discussed, and the C15 single-phase region was explored based on the site occupancy modelled by the compound energy formalism (CEF) coupled with first-principles calculations.

1. Introduction

Zirconium alloys are widely used as cladding materials in harsh conditions, such as high temperature and pressure, hydro-sour erosion and intensive neutron radiation etc., for their excellent mechanic properties, irradiation stability and corrosion resistance [1,2]. Since Nb and Cr have pronounced effects on thermal and physical properties of zirconium alloys [3,4], the examination on the phase diagram of the Zr–Nb–Cr system is essential for providing efficient support when developing high performance alloys and searching for optimized processes in production.

Up to now, the binary phase diagrams Zr–Nb [5], Zr–Cr [6] and Nb–Cr [7] have been evaluated, yet the precise information of the phase equilibrium in the Zr–Nb–Cr ternary system is still limited and incomplete. Savel'yeva and Grum-Grzhimaylo [8] studied the partial isothermal sections at 1473 K and 1273 K in 1969 by using optical microscope (OM) examination supplemented by X-ray diffraction (XRD) analysis. However, the composition analysis was considered as qualitative and the exact phase relation was not conclusively determined. Kim and Takasugi [9] explored the isothermal sections of the Zr–Nb–Cr and Zr–Hf–Cr systems at 1573 K, and put emphasis on the Laves phase research. In their work, the alloys were furnace-cooled to room temperature at a rate of about 13 K/min, a process that cannot keep the equilibrium state at 1573 K. The related problem is how the composition range of the C15 Laves phase varies with temperature. With this consideration, accurate solubility of the constituent phases should be examined at different temperatures by appropriate characterization techniques and on quenched samples.

In this study, the isothermal sections of the Zr–Nb–Cr system at 1573 K and 1373 K were investigated by electron probe micro-analysis (EPMA) coupled with wavelength-dispersive spectroscopy (WDS) and XRD. The problems concerning sample equilibration and weight loss in the experiments were discussed, and the site occupancy of the C15 phase was examined by thermodynamic modelling assisted by first principles calculations.

2. Experimental procedure

To facilitate the following discussions, all samples are organized as A- and B-series and divided into 4 groups as listed in Table 1, together with the annealing conditions.

Button ingots with nominal compositions given in Tables 2 and 3 were prepared by a non-consumable tungsten electrode arc melting with a water-sealed copper hearth in purified argon atmosphere. Zr (99.95 wt.%) of nuclear purity from State Nuclear Baoti Zirconium Industry Company, Nb (99.95 wt.%), and Cr (99.99 wt.%) were used as raw materials. To reduce possible

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Table 1
Summary of sample groups and annealing conditions.

Group ID	Sample ID[a]	Annealing and time
T1	A1, A2, A3	1573 K, 100 h
	B1, B2, B3	1373 K, 340 h
T2	A4, A5, A6, A7	1573 K, 100 h
	B4, B5, B6, B7	1373 K, 340 h
T3	A8, A9, A10, A11	1573 K, 200 h
	B8, B9, B10	1373 K, 480 h
Binary	A12, A13, A14, A15	1573 K, 100 h

[a] The compositions of the A- and B-series samples are listed in Tables 2 and 3

contamination of oxygen, titanium ingot as getter was melted before the zirconium alloys. The 10 g ingots were flipped after each melting and re-melted six times to ensure chemical homogeneity. The final ingots were weighted, and the melting loss was found to be less than 0.5 wt.%.

The samples were heat-treated in a pit type furnace. To prevent contamination and oxidation, the specimens were wrapped with niobium foils, and then encapsulated in quartz tubes filled with argon of about 200 Pa after pumping vacuum to 10^{-3} Pa. Special thick quartz tubes were used in the experiment at 1573 K to avoid rupture when they soften at high temperatures for longtime annealing. Quartz tubes with samples were finally broken and quenched in ice water.

Microstructures of the prepared alloys were characterized by OM firstly, and then by EPMA in the back scattering (BS) condition. EPMA/WDS was performed on alloys to examine compositions of the constituent phases, and the values finally obtained were an average of more than five data points. Characterization of phases in selected samples was conducted by XRD with CuKα radiation and graphite monochromator. Tube voltage, current, and scan rate were selected as 40 kV, 250 mA, and 4°/min in 2θ, respectively.

3. Results and discussion

3.1. Isothermal section at 1573 K

Table 2 presents the experimental results of the alloys quenched from 1573 K by using EPMA/WDS and XRD techniques. Fig. 1 is the phase relation of the Zr–Nb–Cr system at 1573 K based on the present experimental results, from which C15 Laves phase, the BCC (Cr) solid solution and the BCC (Zr, Nb) are found. The C15 phase region exists in a broad composition range of Cr, from 52 to 68 at%. The BCC (Zr, Nb) is a continuous solid solution between β-Zr and β-Nb, *i.e.*, Zr atoms and Nb atoms substitute each other completely. In addition, there are two wide two-phase regions, C15 + BCC (Cr) and C15 + BCC (Zr, Nb), which are divided by the C15 phase field.

In the slow furnace-cooling condition in Kim and Takasugi's work [9], the measured phase relation corresponded to the equilibrium below 1573 K, where the solubility range for the single-phase region should be smaller by comparing with the results measured on the quenched samples in the present work. This is clearly demonstrated in Fig. 1 by the single-phase regions of C15 and BCC (Zr, Nb) close to the Cr–Zr binary. In fact, the measured solubility ranges for C15 and BCC (Zr, Nb) in Kim and Takasugi's work are comparable to those shown in Fig. 4, especially for data close to the Cr–Zr binary.

Back scattering (BS) microstructures and XRD patterns for some samples representing the different groups at 1573 K are shown in Fig. 2. The phases were identified by the XRD patterns and the standard PDF cards for C15–Cr_2Zr, C15–Cr_2Nb and pure Nb, Zr and Cr. As shown in Fig. 2a, in sample A3 (T1 group), the two-phase equilibrium between BCC (Cr) and C15 is observed. The black phase is BCC (Cr), and the gray phase is C15. Comparing the diffraction patterns with the PDF card for BCC Cr (PDF#06-0694), the peak positions fit well with the experiments. However, all peak

Table 2
Summary of experimental results for the Zr–Nb–Cr alloys at 1573 K by using XRD and EPMA/WDS.

No.	Nominal composition (at.%)			Phase identification	Composition (at.%)			Lattice Parameters (nm)
	Zr	Nb	Cr		Zr	Nb	Cr	a
A1	4	16	80	C15	4.78	28.21	67.01	0.6996 (4)
				BCC (Cr)	0.07	1.07	98.86	0.2883 (9)
A2	10	10	80	C15	14.13	19.79	66.08	0.7105 (0)
				BCC (Cr)	0.05	0.8	99.15	0.2892 (9)
A3	16	4	80	C15	25.56	6.69	67.75	0.7202 (7)
				BCC (Cr)	0.84	0.45	98.71	0.2891 (3)
A4	47.5	2.5	50	C15	33.92	2.76	63.32	0.6997 (1)
				BCC (Zr,Nb)	92.90	2.77	4.33	0.3545 (3)
A5	43.7	6.3	50	C15	32.27	7.52	60.21	0.7009 (4)
				BCC (Zr,Nb)	98.38	0.75	0.87	0.3547 (2)
A6	37.5	12.5	50	C15	30.55	12.85	56.60	0.7200 (2)
				BCC (Zr,Nb)	82.06	13.53	4.41	0.3545 (3)
A7	31.3	18.7	50	C15	28.02	19.94	52.04	0.7025 (0)
				BCC (Zr,Nb)	67.49	28.91	3.60	0.3541 (4)
A8	30	30	40	C15	23.86	22.92	53.22	0.7205 (0)
				BCC (Zr,Nb)	42.12	51.28	6.60	0.3313 (3)
A9	20	40	40	C15	21.45	23.74	54.81	0.7194 (8)
				BCC (Zr,Nb)	17.54	75.56	6.90	0.3306 (3)
A10	12.5	37.5	50	C15	13.27	26.34	60.39	0.7000 (9)
				BCC (Zr,Nb)	7.82	84.15	8.03	0.3306 (6)
A11	6.3	43.7	50	C15	6.76	30.70	62.54	0.6965 (5)
				BCC (Zr,Nb)	3.83	85.02	11.15	0.3545 (3)
A12	20	–	80	C15–Cr_2Zr	30.09	–	69.91	0.7225 (1)
				BCC (Cr)	1.29	–	98.71	0.2889 (8)
A13	60	–	40	C15–Cr_2Zr	34.54	–	65.46	0.7221 (4)
				β-Zr	99.4	–	0.6	0.3259 (1)
A14	–	20	80	C15–Cr_2Nb	–	33.37	66.63	N/A
				BCC (Cr)	–	4.80	95.20	N/A
A15	–	40	60	C15–Cr_2Nb	–	35.81	64.19	0.7018 (7)
				β-Nb	–	88.47	11.53	0.3306 (6)