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1 100 ℃ isothermal section of Nb-W-Zr-C quaternary system①

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Abstract: An isothermal section of the Nb-W-Zr-C system at 1 100 ℃ was established by means of multiphase diffusion couples along with electron microprobe analysis and X-ray diffraction analysis. The isothermal section consists of two single-phase regions, α(Nb, W, Zr) and (W, Nb)$_2$Zr and one double-phase region, α(Nb, W, Zr) + (W, Nb)$_2$Zr. It is concluded that (W, Nb)$_2$Zr is an interstitial intermediate phase with the face-centered cubic (Cu_2Mg) lattices. The maximum solid solubility of carbon in (W, Nb)$_2$Zr phase is determined as about 4.18% C(mole fraction). The composition ranges of tungsten in the (W, Nb)$_2$Zr phase are 55.41% to 65.98% and the maximum solid solubility of niobium in (W, Nb)$_2$Zr is determined as 7.78%.

Key words: Nb-W-Zr-C quaternary system; diffusion couple; isothermal section

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1 INTRODUCTION

Much interest has been focused on niobium-based superalloy, which can be used for refractory structural materials in the advanced space power system due to its good high-temperature properties and good creep-rupture properties. The carbon, tungsten and zirconium are important alloy additives to the niobium-based superalloy and through solid solution hardening, precipitation hardening and deformation heat treatment, the niobium-based superalloy can obtain excellent high-temperature strength and plasticity.[1,2]

There are very few reports on the Nb-W-Zr-C quaternary system. In 1973, Cavitskii et al[3] investigated the phase relations of the Nb-10W-Zr-C system in the rich niobium range at 1 800 ℃ using a large number of equilibrium alloys. Apart from the α(Nb) solid solution single-phase, there coexist three 2-phase fields and two 3-phase regions at 1800 ℃ as follows: α+ Nb_2C, α+ (Zr, Nb, W)C, α+ W_2Zr, α+ Nb_2C+ (Zr, Nb, W)C, α+ W_2Zr+ (Zr, Nb, W)C. There only exist α and α+ W_2Zr fields in the system when the carbon content is less than 0.2% (mole fraction). In 1985, Zakhagow et al[4] reported the phase relations of the (Nb+ 4.42W+ 0.9Zr)-C pseudobinary phase diagram and there exist α + (Zr, Nb, W)$_2$C 2-phase fields in the system at 1 100 ℃. The (Zr, Nb, W)$_2$C phase is a secondary solid solution based on Nb_2C.

In this study, diffusion couples along with electron probe microanalysis (EPMA)[5-11], scanning electron microscope and X-ray diffraction (XRD) analysis were used to establish an isothermal section of Nb-W-Zr-C system at 1 100 ℃.

2 EXPERIMENTAL

The specimens used in the present work were prepared from elemental materials as follows: iodide zirconium (99.9%), tungsten 99.6%, and Nb-0.1% C (mole fraction) alloy. These components were assembled into a diffusion couple after being ground and polished. The samples were sealed into quartz capsules under vacuum (1.33×10^{-2} Pa) and annealed at 1 100 ℃ for 255 h in a GK-2B type diffusion furnace to produce local equilibrium interfaces[12]. The temperature was controlled with a thyristor regulator and was found to be within ±1 ℃ as measured with a calibrated Ni-Cr/Ni-Al thermocouple. After the heat treatments these samples were water quenched by breaking the capsules, and then prepared by mechanical polishing using a cloth with chromium oxide parallel to the diffusion direction.

The microstructural investigations were done in a scanning electron microscope(JSM-5600LV). XRD analysis was done on a XD-98 diffractometer in unfiltered copper radiation (a = 1.54056 Ù, 30° ≤2θ ≤88°, step scan mode with a step size of 0.03°). The diffraction graphs were calculated using software of Peking University XRD analysis system. The composition of each phase in the annealed samples was determined by electron probe microanalysis (EPMA) (CAMEBAX-CAMECA-SX51) using accelerating voltage of 15 kV and take off angle 40°.

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3 RESULTS AND DISCUSSION

Fig. 1 shows the back-scattered electron image of the Nb-W-Zr-C diffusion triple annealed at 1 100 ℃ for 255 h. A layer of intermetallic compound with a thickness of approximately 20 μm was found between the zirconium and tungsten component. The layer was identified by EPMA as being $(W, Nb)_2Zr$ phase. Table 1 lists some of the experimental tie-lines

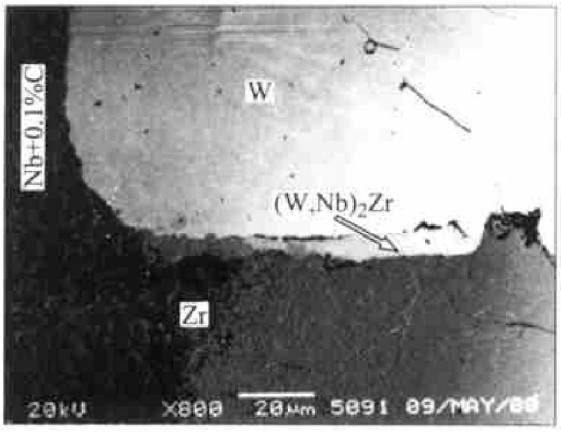

Fig. 1 SEM back-scattered image of Nb-W-Zr-C diffusion triple annealed at 1 100 ℃ for 255 h

Table 1 Microprobe measurements of phase equilibria in Nb-W-Zr-C diffusion triple annealed at 1 100 ℃ for 255 h(mole fraction, %)

$(W, Nb)_2Zr$				α(Nb, W, Zr)			
Nb	W	Zr	C	Nb	W	Zr	C
0	65.98	32.51	1.51	0	99.65	0.24	0.11
1.76	63.18	33.25	1.81	0.37	98.48	1.07	0.08
2.24	62.95	32.47	2.34	4.90	93.86	1.13	0.11
3.31	61.90	32.70	2.09	6.68	91.86	1.37	0.09
4.07	61.42	32.46	2.05	9.24	89.12	1.57	0.07
5.06	60.34	31.04	3.56	41.77	56.08	2.07	0.08
5.60	61.58	30.26	2.66	55.49	41.54	2.85	0.12
6.03	60.42	30.79	3.76	70.36	26.03	3.50	0.11
6.12	58.95	31.09	3.84	85.66	6.12	8.10	0.12
6.70	58.71	32.19	2.40	82.69	3.84	13.36	0.11
7.78	55.41	33.02	3.79	82.03	2.91	14.94	0.12
7.45	55.56	32.81	4.18	78.16	2.39	19.37	0.08
7.02	56.09	33.20	3.69	60.91	2.11	36.81	0.10
6.51	57.25	33.11	3.09	53.78	1.98	44.16	0.08
6.08	57.49	33.36	3.07	45.26	2.35	52.28	0.11
5.33	58.65	33.24	2.78	36.30	2.14	61.46	0.10
4.48	58.89	33.66	2.97	28.06	1.07	70.76	0.09
3.54	59.73	33.57	3.16	21.48	1.09	77.34	0.09
2.79	60.87	34.11	2.23	12.30	0.99	86.62	0.09
1.92	63.04	34.01	1.03	9.62	0.88	89.38	0.12
1.86	63.22	32.96	1.96	4.98	1.25	93.68	0.09
0.16	65.29	33.10	1.45	0.27	1.01	98.62	0.10

in the diffusion triple annealed at 1 100 ℃ for 255 h. These data were made on a CAMEBAX-CAMECA-SX51 set with accelerating voltage of 15 kV and take off angle of 40°. The zirconium, niobium, tungsten and carbon standards were taken from parts of the corresponding components far away from the diffusion region. The microprobe measurements of each tie line were taken at a pair of points close to each interface.

From the results of EPMA (Table 1) it is established that the composition range of tungsten in the $(W, Nb)_2Zr$ phase is from 55.41% to 65.98% (mole fraction) and the niobium content in the $(W, Nb)_2Zr$ phase ranges is about from 0 to 7.78%. The maximum solid solubilities of carbon in $(W, Nb)_2Zr$ is about 4.18%.

The annealed diffusion triple was examined by XRD analysis. The XRD spectra were shown in Fig. 2. From the XRD profile, the intermetallic compound $(W, Nb)_2Zr$ has the face-centered cubic lattice (Cu_2Mg). Comparing the XRD pattern of $(W, Nb)_2Zr$ phase with the PDF card of W_2Zr (JCPDS-ICDD (c) 1996 No. 2-1117), it can be seen that the 2θ angles of the former appreciably shift to the left side and the lattice spacing d is greater than that of the latter W_2Zr phase. It is concluded that the $(W, Nb)_2Zr$ phase is an interstitial solid solution phase based on the intermetallics W_2Zr and the carbon atoms hold the tetrahedral interstice of the W_2Zr phase.

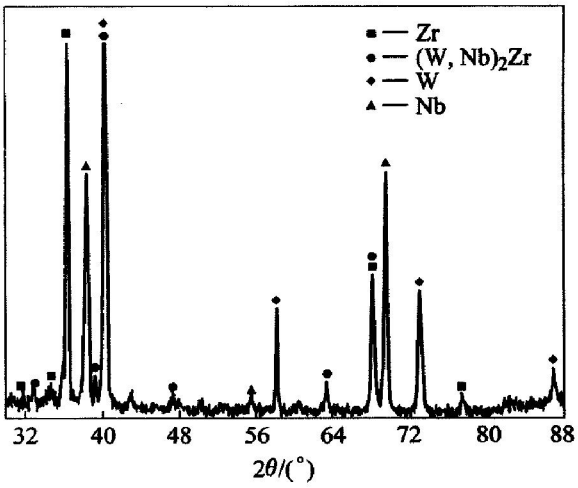

Fig. 2 XRD pattern of Nb-W-Zr-C diffusion triple annealed at 1 100 ℃ for 255 h

An isothermal section of the Nb-W-Zr-C system at 1 100 ℃ derived from the present investigations carried out by XRD, SEM and EPMA and corresponding binary phase diagrams[13-15] is shown in Fig. 3. There coexist two phases, α (Nb, W, Zr) and $(W, Nb)_2Zr$ in the system at 1 100 ℃. The α (Nb, W, Zr) solid solution is in equilibrium with the $(W, Nb)_2Zr$ phase and the

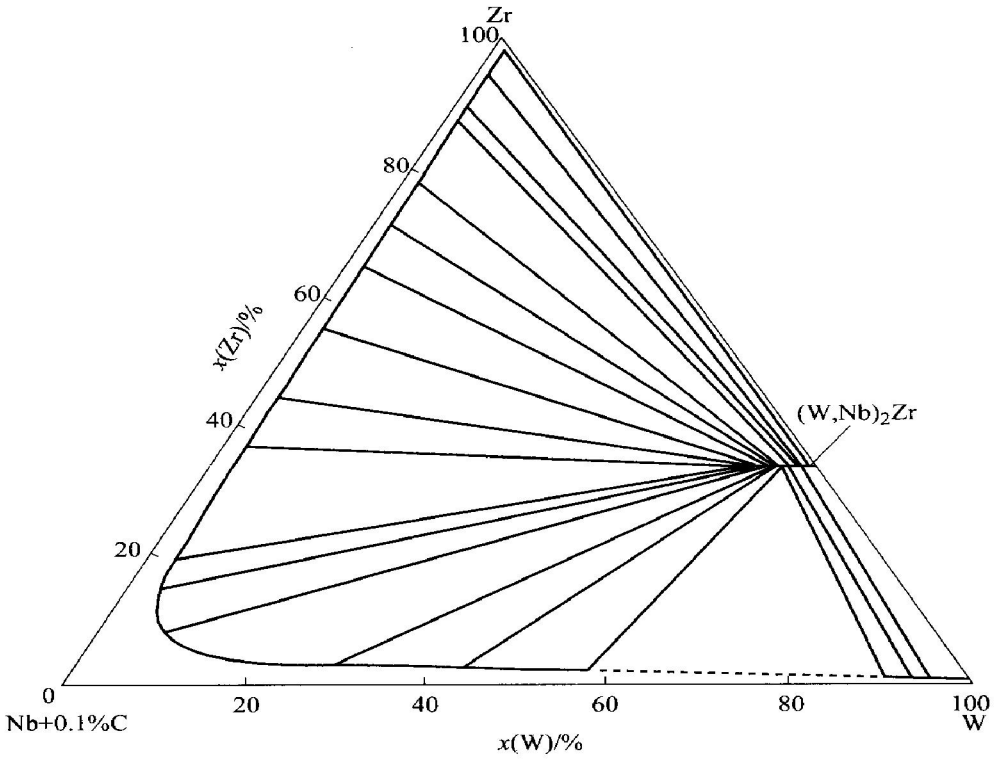

Fig. 3 Isothermal section of Nb-W-Zr-C system at 1 100 ℃

isothermal section consists of two single-phase fields, α(Nb, W, Zr) and (W, Nb)$_2$Zr, and one double-phase field, α(Nb, W, Zr) + (W, Nb)$_2$Zr.

4 CONCLUSIONS

1) The isothermal section of the Nb-W-Zr-C system at 1 100 ℃ was constructed. The isothermal section consists of two single-phase regions, α(Nb, W, Zr) and (W, Nb)$_2$Zr, and one double-phase region, α(Nb, W, Zr) + (W, Nb)$_2$Zr.

2) The maximum solubility of carbon in the (W, Nb)$_2$Zr phase was determined as about 4.18% (mole fraction) at 1 100 ℃, whilst the composition range of tungsten and niobium in (W, Nb)$_2$Zr phase are 55.41% to 65.98% and 0 to 7.78%, respectively.

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