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Determination of isothermal section of Fe-Ti-Zr ternary system at 1 173 K

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Abstract: Phase relations in the Fe-Ti-Zr ternary system at 1 173 K were investigated by means of diffusion-triple approach together with electron probe microanalysis(EPMA) technique. A series of tie lines and tie-triangles were determined and the isothermal section at 1 173 K was established, which consists of four three-phase fields: β(Ti, Zr)+$FeZr_2$+FeTi, $FeZr_2$+FeTi+Fe_2Zr, FeTi+Fe_2Zr+Fe_2Ti and Fe_2Zr+Fe_2Ti+Fe. The results show that the largest solubility of Ti in Fe_2Zr is about 11.3%(mole fraction) and the solid solubility of Ti in $FeZr_2$ is about 26.9%, the solid solubility of Zr in Fe_2Ti is about 8.1% and the solid solubility of Zr in FeTi is 7.2%. The binary compound $FeZr_2$ is nearly a linear compound. No ternary compound is found.

Key words: Fe-Ti-Zr; diffusion triple; isothermal section; phase diagram

1 Introduction

It is well known that the AB_2 Laves phase alloys show considerable promise as hydrogen storage materials because of their large hydrogen absorption capacity and rapid reaction rate with hydrogen[1]. The hydrogen absorption characteristics of AB_2 compounds such as ZrV_2, $ZrCr_2$ and $ZrFe_2$ were first studied by SHALTIEL et al[2]. They were found to absorb large quantities of hydrogen, but hydrides formed were too stable to be of practical significance. Therefore many studies performed so far have paid attention to increasing the vapour pressure of Zr-based Laves phase alloys without markedly reducing the absorption capacity by partial substitution of the A or B element by other elements, and the substitution usually involves transition elements, i.e. Ti, Cr, C, Ni and Cu[1].

The binary systems of the Fe-Ti and Ti-Zr have been well studied. There are two intermediate phases in the Fe-Ti system, namely $TiFe_2$ and TiFe. JONSSON[3] thermodynamically evaluated the Fe-Ti system. The Ti-Zr binary system consists of two solid solutions, α- and β-phase, and liquid with a congruent minimum at 50% Zr[4]. For the phase diagram of the Fe-Zr system, however, there still remain uncertainties and controversies even about the intermetallic phases actually present in this system. Very little work has been done about the phase equilibria in the Fe-Ti-Zr ternary system. In order to further understand the phase relations in this system, the knowledge about the phase diagram of the Fe-Ti-Zr system is indispensable. In the present work, phase equilibria in the Fe-Ti-Zr system at 1 173 K were investigated by means of diffusion-triple approach. Details about this approach are referred to Jin[5].

2 Experimental

The Fe-Ti-Zr diffusion triple specimens were prepared from blocks of pure metals: Fe (99.9%), Zr (99.9%), Ti (99.5%) (mass fraction). Firstly, to make a Ti-Zr diffusion couple, the Ti and Zr blocks were diffusionally welded under 3 MPa in argon flow at 1 073 K for 10 min, then cooled to ambient temperature. Subsequently, the Fe-Ti-Zr diffusion triple was assembled from the obtained Ti-Zr couple and pure Fe block by diffusion welding under 4.5 MPa at 1 073 K in argon flow for 10 min. Finally, the triple was encapsulated in evacuated quartz tube backfilled with pure argon and annealed at (1 173±2) K for 1 440 h. After the heat treatment, the diffusion triple was taken out from the furnace and quenched in water by breaking the quartz tube. The fabricating diffusion triple is shown in Fig.1.

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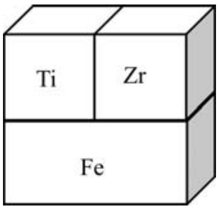

Fig.1 Schematic diagram of fabricating Fe-Ti-Zr diffusion triple

The obtained diffusion triple was ground, polished and then examined by means of electron probe microanalysis(EPMA) (JX−8800R, Japan, electron Optics Ltd, Tokyo) under the operation condition of 20 kV, 2×10^{-8}A and take-off angle of 40˚.

3 Results and discussion

The back-scattered electron image of the Fe-Ti-Zr triple annealed at 1 173 K is shown in Fig.2. The chemical compositions of the equilibrium phases at the tie lines and tie triangles are listed in Table 1. It is clear from Fig.2 and Fig.3 that there are three diffusion layers of Fe_2Ti, FeTi and $FeZr_2$ in the Fe-Ti side, two diffusion layers of Fe_2Zr and $FeZr_2$ in the Fe-Zr side. Ti and Zr are completely soluble at 1 173 K, thus no diffusion layers are formed. No ternary compound was found.

Based on the experimental data in Table 1, a series phase equilibrium tie lines and tie triangles can be drawn. Referring to Fig.2 and Fig.3, the isothermal section of the Fe-Ti-Zr system at 1 173 K is established by connecting the boundary lines of different equilibrium phase fields, as shown in Fig.4. There are four three-phase fields in this plot, namely β(Ti,Zr)+$FeZr_2$+FeTi, $FeZr_2$+FeTi+Fe_2Zr, FeTi+Fe_2Zr+Fe_2Ti and Fe_2Zr+Fe_2Ti+Fe.

It can also be seen from Fig.4 and Table 1 that the solubility of Ti in Fe_2Zr is about 11.3% and that of Ti in $FeZr_2$ is about 26.9%; and the solid solubility of Zr in Fe_2Ti is about 8.1% and that of Zr in FeTi is 7.2%. The intermetallic phase Fe_2Ti has a solubility range from 65.7% to 72.1% Fe and the phase FeTi has a solubility range from 48.7% to 50.2% Fe. Meanwhile the intermetallic phase Fe_2Zr has a solubility range from 66.1% to 71.3% Fe. The binary compound $FeZr_2$ is nearly a linear compound. Additionally, the phase $FeZr_2$ is very thick and long in the intersections of Ti/Zr and Ti/Fe shown in areas *C* and *D* in Fig.2(a). It is believed that the diffusion drive force in the intersection is very large.

With regard to literature data, our current work showed some results worth further discussion. Accord-

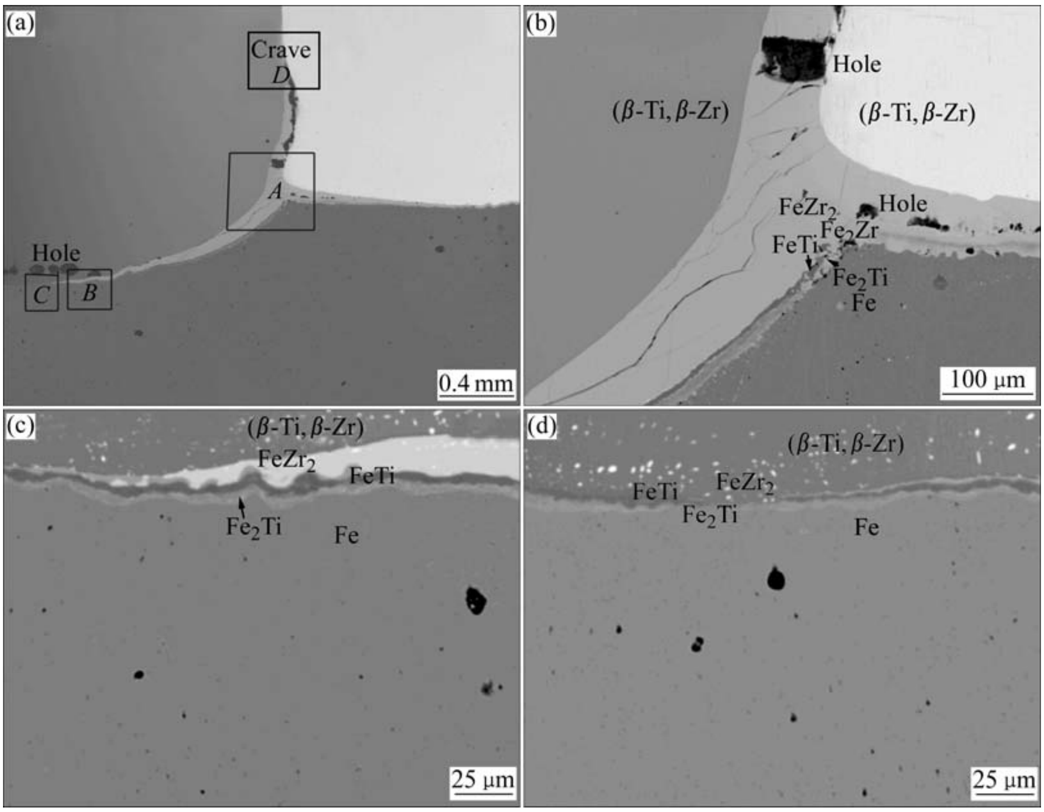

Fig.2 Back-scattered electron images of Fe-Ti-Zr ternary system at 1 173 K by EPMA: (a) Panoramic view; (b), (c) and (d) High-magnification images of areas *A*, *B* and *C* in Fig.2(a)

Table 1 Extrapolated compositions of phases in equilibrium at 1 173 K (mole fraction, %)

Ti	Zr	Fe	Ti	Zr	Fe
(Fe_2Ti)			(α-Fe)		
25.82	1.10	73.08	4.38	0.000	95.62
26.83	0.81	72.36	3.86	0.000	96.14
27.43	1.09	71.48	4.22	0.000	95.78
27.12	0.98	71.90	4.35	0.000	95.65
25.00	3.12	71.88	4.27	0.000	95.73
(Fe_2Zr)			(α-Fe)		
4.78	23.92	71.30	0.20	4.33	95.47
3.52	25.37	71.11	0.41	4.65	94.94
(FeTi)			($FeTi_2$)		
50.52	0.22	49.26	33.22	1.11	65.67
49.69	0.41	49.90	30.93	2.14	66.93
48.73	1.29	49.98	28.78	4.15	67.07
48.41	1.41	50.18	26.61	6.27	67.12
($FeZr_2$)			(Fe_2Zr)		
1.04	66.12	32.84	0.89	32.78	66.33
2.17	65.00	32.83	1.83	32.00	66.17
7.56	59.47	32.97	2.74	30.74	66.52
9.02	58.33	32.65	5.66	28.05	66.29
($FeZr_2$)			β(Ti, Zr)		
3.21	64.67	32.12	0.45	95.67	3.88
4.19	63.72	32.09	2.13	93.73	4.14
5.53	62.22	32.25	4.30	91.85	3.85
16.32	51.56	32.12	25.71	70.56	3.73
18.41	49.71	31.88	34.55	59.93	5.52
23.01	45.10	31.89	46.27	47.66	6.07
(FeTi)			β(Ti, Zr)		
50.17	1.07	48.76	80.87	0.77	18.36
49.48	1.72	48.80	79.95	2.94	17.11
47.03	4.30	48.67	68.00	19.73	12.27
(FeTi)			(Fe_2Zr)		
42.23	7.58	50.19	7.66	25.89	66.45
43.15	7.21	49.64	7.78	26.15	66.07
(FeTi)			($FeZr_2$)		
44.04	7.21	48.75	21.62	45.52	32.86
44.56	6.90	48.54	25.70	41.23	33.07
(Fe_2Ti)			(Fe_2Zr)		
21.94	8.11	69.95	11.35	20.07	68.58

ing to the present study, the Laves phase $Fe_{23}Zr_6$ and $FeZr_3$ have not been found. Contradictory results were also published concerning the existence of the phase $Fe_{23}Zr_6$ (or Fe_3Zr as denoted in earlier work). It was first described by SVECHNIKOV et al[6]. Although this phase was later also found in several investigations [7−12], it was generally observed only in comparably small amounts and in combination with the phases (α-Fe) and Fe_2Zr. In the experimental studies of AUBERTIN et al[13] and ALEKSEEVA et al[14] on the Fe-Zr phase

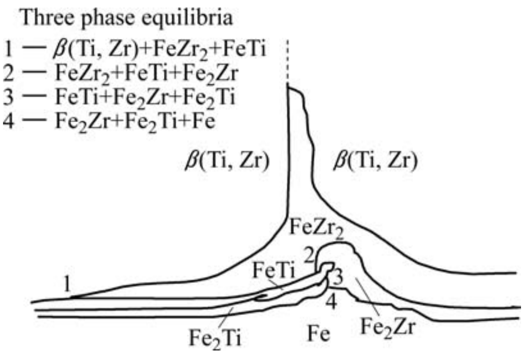

Fig.3 Schematic diagram of diffusion triple of Fe-Ti-Zr system at 1 173 K

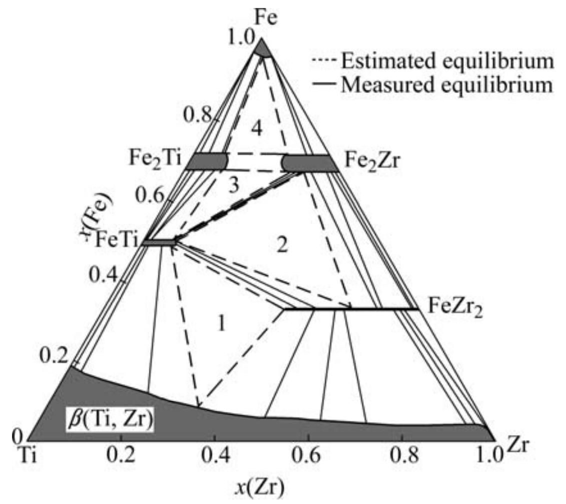

Fig.4 Isothermal section of Fe-Ti-Zr ternary system at 1 173 K

diagram, no $Fe_{23}Zr_6$ was found. A completely different explanation for the occurrence of the $Fe_{23}Zr_6$ phase was given by LIU et al[15] that the Laves phase is only a metastable phase. Recently, the Fe-Zr phase diagram has been redetermined by STEIN et al[16] over the entire composition range, and thought that the previously reported cubic phase $Fe_{23}Zr_6$ is not an equilibrium phase but oxygen-stable and the another intermetallic phase $FeZr_3$ occurs below 851 ℃. In our present work, all these compounds are in good agreement with the Fe-Ti [3] and Fe-Zr[16] binary phase diagrams.

4 Conclusions

1) The isothermal section of the Fe-Ti-Zr ternary system at 1 173 K is determined by means of diffusion trip approach and EMPA technique. A tentative isothermal section at 1 173 K is present, which consists of 4 three-phase fields, β(Ti, Zr)+$FeZr_2$+FeTi, $FeZr_2$+FeTi+Fe_2Zr, FeTi+ Fe_2Zr +Fe_2Ti and Fe_2Zr +Fe_2Ti +Fe.

2) The binary compound $FeZr_2$ is nearly linear compounds. No ternary compound is found.

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