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Experimental investigation of phase equilibria in the Ti-Fe-Zr system

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ABSTRACT

The phase relations of the Ti-Fe-Zr system at 873 and 1173 K were experimentally investigated by using the equilibrated alloys. Four ternary phases were determined stable at 1173 K. Two of them were line compounds with fixed Fe/(Ti, Zr) ratio, while the other two showed ellipse-shaped homogeneity. There were eight three-phase equilibria and a continuous single phase field of β(Ti, Zr) in the isothermal section at 1173 K. The solubility of Zr in Fe_2(Ti, Zr) and Ti in (Fe, Ti)$_2$Zr was measured to be 25.5 at% and 6.1 at%, respectively. The remaining binary intermetallic phases hardly dissolved the third component. The phase relationships in the isothermal section at 873 K were similar to those at 1173 K over the composition range of 0–50 at% Fe. In this isothermal section, five three-phase equilibria were observed and they were all related with the newly found ternary phases. The phase relations measured in this work are of significant difference from the existing ones obtained with the diffusion couple.

1. Introduction

Owing to the combination of favorable properties such as high specific strength, good biocompatibility, relatively low elastic modulus and high corrosion resistance, titanium alloys have attracted significant attention for their biomedical application as orthopedic implants [1,2]. Among them, as a typical biomedical titanium alloy, the Ti-6Al-4V alloy with (α + β)-type microstructure has been commercially utilized for a long period. However, the high Young's modulus of this alloy (~110 GPa), the toxicity of vanadium to the human body and the neurological disease potentially induced by aluminum [1] are disadvantageous from the biological point of view. In comparison with other phase structures in Ti, the β-phase has the relatively low elastic modulus [3–6]. Hence, biocompatible β-phase stabilizing alloying elements (e.g. Nb, Ta, Fe and Mo) are preferable in the development of bio-titanium alloys. The addition of Zr into β-type Ti alloys has been reported to improve alloy mechanical properties and corrosion resistance, and also to inhibit the martensitic transformation in alloy, regardless of the slight effect of Zr on the β-transus [7–9]. As a low cost β-phase stabilizer, Fe is quite attractive to develop alloys of both high strength and low Young's modulus [10]. As the phase diagram is an important basis for the materials design and application [11–13], the exploration of phase equilibria in the Ti-Fe-Zr system is of importance in developing high performance-to-cost ratio bio-titanium alloys.

Phase diagrams of the three constitutive binary subsystems, i.e. Fe-Ti, Fe-Zr and Ti-Zr, in the Ti-Fe-Zr ternary system are presented in Fig. 1. Crystallographic data of all solid phases in these binary subsystems [14–19] are given in Table 1.

For the Fe-Ti system, lots of studies have been carried out [20–30]. Murry [25] conducted a critical review on the phase diagram, Jonsson [27] presented an overview on the available thermodynamic data. Up to now, the thermodynamic assessment has been implemented by different groups [25–30]. The phase diagram of the Fe-Ti system has been given in Fig. 1(a) according to the latest thermodynamic description in Ref. [30]. Two stable intermetallic phases (i.e. FeTi and Fe_2Ti) are present in phase diagram and both exhibit visible homogeneity ranges. The homogeneity range of FeTi is nearly symmetric with respect to the stoichiometric composition, while that of Fe_2Ti leans significantly towards the Fe-rich side.

For the Fe-Zr system, the intermetallic phases are listed in Table 1. Although the phase diagram has been investigated experimentally by many researchers [31–34], it still remains controversial that whether the $Fe_{23}Zr_6$ or Fe_2Zr with a hexagonal structure (denoted as hex.-Fe_2Zr in short) phase is stable in the Fe-rich side. A series of thermodynamic assessments of this system have been conducted with the $Fe_{23}Zr_6$ [33,35,36] or hex-Fe_2Zr phase [37,38] alternatively serving as a stable phase. Due to the fact that the $Fe_{23}Zr_6$ phase was found in most experimental studies (e.g. the recent investigations of the Cu-Fe-Zr [39] and Fe-Nb-Zr [40] systems), the Fe-Zr phase diagram assessed lately by Lu et al. [36] is accepted in present work. As shown in Fig. 1(b), among the four intermetallic phases, only the Fe_2Zr phase has a noticeable homogeneity range. For the other three phases, $FeZr_2$ appears only

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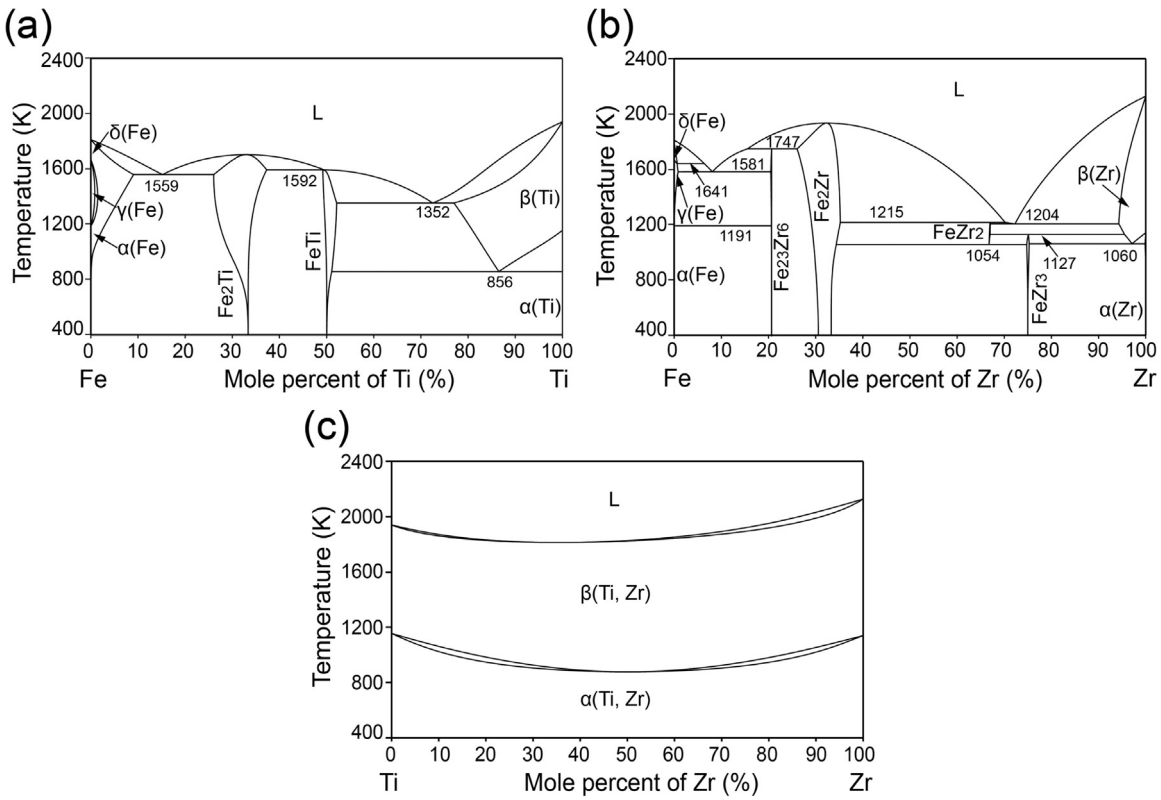

Fig. 1. Phase diagrams of constitutive binary systems in the Ti-Fe-Zr system, calculated based on the data given in: (a) Fe-Ti [30]; (b) Fe-Zr [36]; (c) Ti-Zr [45].

Table 1
Crystallographic data of all phases involved in the Ti-Fe-Zr system.

System	Phase	Strukturbericht designation	Pearson symbol	Space group	Prototype	Lattice parameter(s) (nm)	Ref.
Fe	α(Fe)	A2	*cI*2	$Im\bar{3}m$	W	$a = b = c = 0.2887$	[14,15]
	γ(Fe)	A1	*cF*4	$Fm\bar{3}m$	Cu	$a = b = c = 0.3660$	[14,15]
	δ(Fe)	A2	*cI*2	$Im\bar{3}m$	W	$a = b = c = 0.2932$	[14,15]
Ti	α(Ti)	A3	*hP*2	$P6_3/mmc$	Mg	$a = b = 0.2950,\ c = 0.4681$	[14,15]
	β(Ti)	A2	*cI*2	$Im\bar{3}m$	W	$a = b = c = 0.3311$	[14,15]
Zr	α(Zr)	A3	*hP*2	$P6_3/mmc$	Mg	$a = b = 0.3252,\ c = 0.5180$	[15,16]
	β(Zr)	A2	*cI*2	$Im\bar{3}m$	W	$a = b = c = 0.3540$	[15,16]
Fe-Ti	Fe_2Ti	C14	*hP*12	$P6_3/mmc$	Zn_2Mg	$a = b = 0.4785,\ c = 0.7799$	[14,15]
	FeTi	B2	*cP*2	$Pm\bar{3}m$	CsCl	$a = b = c = 0.2979$	[14,15]
	Ti_2Fe*	–	*cF*96	$Fd\bar{3}m$	Ti_2Ni	$a = b = c = 1.1328$	[17]
Fe-Zr	$Fe_{23}Zr_6$	$D8_2$	*cF*116	$Fm\bar{3}m$	$Mn_{23}Th_6$	$a = b = c = 1.1690$	[15,18]
	Fe_2Zr*	C36	*hP*24	$P6_3/mmc$	Ni_2Mg	$a = b = 0.4954,\ c = 1.6304$	[19]
	Fe_2Zr	C15	*cF*24	$Fd\bar{3}m$	Cu_2Mg	$a = b = c = 0.7070$	[15,16]
	$FeZr_2$	C16	*tI*12	*I*4/*mcm*	Al_2Cu	$a = b = 0.6385,\ c = 0.5596$	[15,16]
	$FeZr_3$	$E1_{12}$	o*S*16	*Cmcm*	Re_3B	$a = 0.3324,\ b = 1.0990,\ c = 0.8810$	[15,16]
Ti-Zr	–	–	–	–	–	–	

The phase marked with '* ' symbol denotes metastable phase.

within the temperature range of 1215–1054 K, and $FeZr_3$ is formed through a peritectoid reaction.

For the Ti-Zr system, several thermodynamic descriptions [41–46] have been performed based on the experimental data reported in studies [47–55]. The first thermodynamic assessment was performed by Murry [41]. In comparison with other existing assessments, the one recently conducted by Cui et al. [45] is believed more reliable due to the consideration of the enthalpy of mixing of liquid alloys reported by Thiedemann et al. [54]. In Fig. 1(c), the full isomorphous phase diagram does not exhibit any intermetallic phases or invariant reactions, in comparison with those of the Fe-Ti (Fig. 1(a)) and Fe-Zr (Fig. 1(b)) systems.

For the Ti-Fe-Zr ternary system, many studies have been conducted on the phase relations [56–64]. By means of diffusion couples, two groups constructed the isothermal sections at 1173 [56] and 1073 K [57] after annealing for 1440 and 5760 h, respectively. In these two isothermal sections, all binary intermetallic phases exhibited noticeable solubility of the third component. Phase relations in Refs. [56,57] were determined solely relying on the compositional measurement while without crystal structure analysis. This may lead to some uncertainty in measuring the limited solubility of the third component for the intermetallic phases, especially for the Fe_2Ti and Fe_2Zr (i.e. $Fe_2(Ti, Zr)$ and $(Fe, Ti)_2Zr$ in this study) phases which have the same stoichiometric ratio and may be misidentified without the structure analysis [56,57]. Ardisson et al. [58] annealed specimens at 1223 K for 60 h to determine the solubility in $FeZr_2$ and at 1073 K for 48 h for the solubility in $FeZr_3$. Nevertheless, Ti was found insoluble in above two phases. This result was in contradiction with that in studies [56,57], in which notable

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