Experimental Investigation of Phase Equilibria in the Fe-Si-Zr Ternary System

C.P. Wang, Y. Hu, S.Y. Yang, Y. Lu, Q.W. Jiang, and X.J. Liu

(Submitted January 15, 2013; in revised form April 8, 2013; published online May 8, 2013)

The phase equilibria of the Fe-Si-Zr ternary system at 1273 and 1373 K have been experimentally investigated using scanning electron microscopy, electron probe microanalyzer and x-ray diffraction. In the present study, the established isothermal sections are characterized by a series of binary phases, ternary compounds and solid solutions. FeZr_2 and SiZr_2 do not form a continuous solid solution at 1273 and 1373 K. A new phase denoted here as τ_9 ($29\text{Fe}_{42}\text{Si}_{29}\text{Zr}$) was found at both temperatures. The measured composition of the τ_8 phase agrees with the formula $\text{Fe}_4\text{Si}_2\text{Zr}$ found in the previous structural investigations. The newly determined phase equilibria of the Fe-Si-Zr system will provide important information for the development of silicon steels.

Keywords electron microprobe, microstructure, phase diagrams, ternary alloy systems

1. Introduction

As a significant material utilized in electrical devices, such as transformers, the silicon steels play an important role on the technical features, operating costs and comprehensive performance of these devices.^[1–4] The magnetic flux (B_{10}) and core loss value ($W_{17/50}$) are basic parameters indicating the quality of the silicon steels, and both of them are sensitive to the composition of silicon steels.^[5] Additionally, it has been reported that Zr addition (0.05–0.3 wt.%) into silicon steels can form a stable compound ZrN , which will lead to the grain refinement, a decrease of iron loss and an obvious increase in the recrystallization temperature of the alloys.^[6] It can thus be seen that Zr element in the Fe-Si alloys has a great impact on the performance of silicon steels. Therefore, the Fe-Si-Zr ternary system is an important subsystem for the silicon steels.

The three binary systems Fe-Si, Zr-Fe and Si-Zr, constituting the Fe-Si-Zr ternary system, are shown in Fig. 1. The Fe-Si binary phase diagram reviewed by Kubaschewski^[7] shows the presence of seven intermediate phases: ξ_α (FeSi_2), ξ_β (FeSi_2), ϵ (FeSi), η (Fe_5Si_3), α_1 (Fe_3Si), α_2 (Fe_2Si), and β (Fe_2Si). The Zr-Fe binary phase diagram was determined by Stein et al.^[8] Four intermediate phases exist: α (Fe_2Zr), β (Fe_2Zr), FeZr_3 and FeZr_2 . The Si-Zr binary phase diagram provided by Okamoto^[9] depicts the following intermediate phases: SiZr_3 , SiZr_2 , Si_3Zr_5 , Si_2Zr_3 , α (Si_4Zr_5), β (Si_4Zr_5), α (SiZr),

β (SiZr), and Si_2Zr . The stable solid phases and their crystal structures in the three binary systems are listed in Table 1.

Regarding the experimental data of phase equilibria in the Fe-Si-Zr system, only one partial isothermal section at 1073 K studied by Lisenko et al.^[10] is available, as shown in Fig. 1. The data and ternary compounds in this system were reviewed by Raghavan^[11] and Du et al.^[12] Furthermore, the existence of ternary compounds is reported: τ_1 (FeSiZr),^[10,13] τ_2 (Fe_3SiZr_2),^[10,14] τ_3 ($\text{Fe}_4\text{Si}_4\text{Zr}_7$),^[10,13,15] τ_4 ($\text{Fe}_2\text{Si}_2\text{Zr}$),^[10,16] τ_5 ($\text{Fe}_{16}\text{Si}_7\text{Zr}_6$),^[10,17] τ_6 ($\text{Fe}_5\text{Si}_{12}\text{Zr}_3$),^[18] τ_7 ($\text{Fe}_2\text{Si}_3\text{Zr}_3$),^[19] τ_8 ($\text{Fe}_4\text{Si}_2\text{Zr}$),^[20,21] (Fe,Zr) $_5\text{Si}_3$,^[10,18] (Fe,Si) $_2\text{Zr}$,^[10,18,22] see Table 1. The structures of the τ_4 ($\text{Fe}_2\text{Si}_2\text{Zr}$), τ_5 ($\text{Fe}_{16}\text{Si}_7\text{Zr}_6$), τ_6 ($\text{Fe}_5\text{Si}_{12}\text{Zr}_3$), τ_7 ($\text{Fe}_2\text{Si}_3\text{Zr}_3$), τ_8 ($\text{Fe}_4\text{Si}_2\text{Zr}$), (Fe,Zr) $_5\text{Si}_3$ and (Fe,Si) $_2\text{Zr}$ have not been assigned PDF numbers (calculated powder diffraction data), except τ_1 (FeSiZr), τ_2 (Fe_3SiZr_2) and τ_3 ($\text{Fe}_4\text{Si}_4\text{Zr}_7$). Regarding the isothermal section of the Fe-Si-Zr system at 1073 K, the addition of about 10–20 at.% Zr stabilizes a ternary phase of the Fe_5Si_3 structure at 37.5 at.% Si.^[10] Here, it should be noted that limited experimental data will restrict the compositional design of silicon steels. Only one partial isothermal section at 1073 K is not enough to do research for compositional design of silicon steels, while considering that the heat treatment temperature of silicon steels belongs to high-temperature range. Therefore, it is necessary to comprehensively determine the phase equilibria of the Fe-Si-Zr ternary system, especially at high temperature. The present research has thus been done to tackle this issue. In this study, the phase equilibria of the Fe-Si-Zr ternary system at 1273 and 1373 K were experimentally investigated by using scanning electron microscopy (back-scattered electron, BSE), electron probe microanalyzer (EPMA) and x-ray diffraction (XRD).

2. Experimental Procedure

Iron (99.8 wt.%), zirconium (99.8 wt.%) and silicon (99.9 wt.%) were used as starting materials. Bulk alloy

C.P. Wang, Y. Hu, S.Y. Yang, Y. Lu, and X.J. Liu, Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, People's Republic of China; Q.W. Jiang, Anshan Iron and Steel Group Corporation, Anshan 114021, People's Republic of China. Contact e-mail: lxj@xmu.edu.cn.

Table 1 The stable solid phases in the three binary systems

System	Phase	Pearson's symbol	Prototype	Space Group	Strukturbericht	Lattice parameters, pm	References
Fe-Si	ξ_α (FeSi ₂)	<i>tP3</i>	FeSi ₂	<i>P4/mmm</i>	...	<i>a</i> = 286.65	[7]
	ε (FeSi)	<i>cP8</i>	FeSi	<i>P2₁3</i>	<i>B20</i>	<i>a</i> = 246.8, <i>c</i> = 396.0	[7]
	η (Fe ₅ Si ₃)	<i>hP16</i>	Mn ₅ Si ₃	<i>P6₃/mcm</i>	<i>D8₈</i>	<i>a</i> = 675.9, <i>c</i> = 472.0	[7]
	β (Fe ₂ Si)	<i>hP6</i>	Fe ₂ Si	<i>P3m1</i>	...	<i>a</i> = 405.2, <i>c</i> = 508.55	[7]
	α_1 (Fe ₃ Si)	<i>cF16</i>	BiF ₃	<i>Fm3m</i>	<i>D0₃</i>	<i>a</i> = 565	[7]
	α_2 (Fe-Si)	<i>cP2</i>	CsCl	<i>Pm3m</i>	<i>B2</i>	<i>a</i> = 281	[7]
	α Fe	<i>cI2</i>	W	<i>Im3m</i>	<i>A2</i>	<i>a</i> = 286.65	[7]
	ξ_β (FeSi ₂)	<i>oC48</i>	FeSi ₂	<i>Cmca</i>	...	<i>a</i> = 986.3, <i>b</i> = 779.1, <i>c</i> = 783.3	[7]
	γ Fe	<i>cF4</i>	Cu	<i>Fm3m</i>	<i>A1</i>	<i>a</i> = 366.60	[7]
	α (ZrFe ₂)	<i>cF24</i>	MgCu ₂	<i>Fd3m</i>	<i>C15</i>	<i>a</i> = 0.702	[8]
Zr-Fe	β (ZrFe ₂)	<i>hP24</i>	MgNi ₂	<i>P6₃/mmc</i>	<i>C36</i>	<i>a</i> = 0.495, <i>c</i> = 1.614	[8]
	Zr ₂ Fe	<i>tI12</i>	CuAl ₂	<i>I4/mcm</i>	<i>C16</i>	<i>a</i> = 0.638, <i>c</i> = 0.560	[8]
	Zr ₃ Fe	<i>oC16</i>	Re ₃ B	<i>Cmcm</i>	<i>E1_a</i>	<i>a</i> = 0.332, <i>b</i> = 1.100, <i>c</i> = 0.882	[8]
	SiZr ₃	<i>tP32</i>	Ti ₃ P	<i>P4₂/n</i>	...	<i>a</i> = 1101, <i>c</i> = 545	[9]
Si-Zr	SiZr ₂	<i>tI12</i>	CuAl ₂	<i>I4/mcm</i>	<i>C16</i>	<i>a</i> = 660.9, <i>c</i> = 529.8	[9]
	Si ₂ Zr ₃	<i>tP10</i>	Si ₂ U ₃	<i>P4/mbm</i>	<i>D5_a</i>	<i>a</i> = 708.2, <i>c</i> = 371.5	[9]
	α (Si ₄ Zr ₅)	<i>tP36</i>	Si ₄ Zr ₅	<i>P4₁2₁2</i>		<i>a</i> = 712.25, <i>c</i> = 1300.0	[9]
	α (SiZr)	<i>oP8</i>	FeB	<i>Pnma</i>	<i>B27</i>	<i>a</i> = 699.5, <i>b</i> = 378.6, <i>c</i> = 529.6	[9]
	Si ₂ Zr	<i>oC12</i>	Si ₂ Zr	<i>Cmcm</i>	<i>C49</i>	<i>a</i> = 372.1, <i>b</i> = 1468, <i>c</i> = 368.3	[9]
	β (SiZr)	<i>oC8</i>	CrB	<i>Cmcm</i>	...		[9]
	β (Si ₄ Zr ₅)	...	...	...	...		[9]
	Si ₃ Zr ₅	<i>hP16</i>	Mn ₅ Si ₃	<i>P6₃/mcm</i>	<i>D8₈</i>	<i>a</i> = 788.6, <i>c</i> = 555.8	[9]
	Si	<i>cF8</i>	C	<i>Fd3m</i>	<i>A4</i>	<i>a</i> = 543.06	[9]
	α Zr	<i>hP2</i>	Mg	<i>P6₃/mmc</i>	<i>A3</i>	<i>a</i> = 323.2, <i>c</i> = 514.7	[9]
Fe-Si-Zr	β Zr	<i>cI2</i>	W	<i>Im3m</i>	<i>A2</i>	<i>a</i> = 356.8	[9]
	τ_1 (FeSiZr)	<i>oP12</i>	TiNiSi	<i>Pnma</i>	<i>C23</i>	<i>a</i> = 640.5, <i>b</i> = 393.5, <i>c</i> = 719.9	[10,13]
	τ_2 (Fe ₃ SiZr ₂)	<i>hP12</i>	MgZn ₂	<i>P6₃/mmc</i>	...	<i>a</i> = 498.5, <i>c</i> = 809.6	[10,14]
	τ_3 (Fe ₄ Si ₇ Zr ₄)	<i>tI60</i>	Zr ₄ Co ₄ Ge ₇	<i>I4/mmm</i>	...	<i>a</i> = 1305.6, <i>c</i> = 509.0	[10,13,15]
	τ_4 (Fe ₂ Si ₂ Zr)	<i>tP10</i>	Al ₂ Ga ₂ Ge	<i>I4/mmm</i>	<i>DI₃</i>	<i>a</i> = 375.0, <i>c</i> = 966.0	[10,16]
	τ_5 (Fe ₁₆ Si ₇ Zr ₆)	<i>cF116</i>	Mg ₆ Cu ₁₆ Si ₇	<i>Fm3m</i>	...	<i>a</i> = 1168.0	[10,17]
	τ_6 (Fe ₅ Si ₁₂ Zr ₃)	...	...	...	...	<i>a</i> = 1430.0, <i>b</i> = 1904.0, <i>c</i> = 515.0	[18]
	τ_7 (Fe ₂ Si ₃ Zr ₃)	<i>oP32</i>	...	<i>Pnma</i>	...	<i>a</i> = 389.8, <i>b</i> = 974.3, <i>c</i> = 1304.2	[19]
	τ_8 (Fe ₄ Si ₂ Zr)	<i>tP14</i>	Fe ₄ Si ₂ Zr	<i>P4₂/mmm</i>	...	<i>a</i> = 375.0, <i>c</i> = 966.0	[20,21]
	(Fe,Zr) ₅ Si ₃	<i>hP16</i>	Mn ₅ Si ₃	<i>P6₃/mcm</i>	<i>D8₈</i>	<i>a</i> = 674.0-677.0, <i>c</i> = 472.0-474.0	[10,18]
	(Fe,Si) ₂ Zr	<i>hP12</i>	MgZn ₂	<i>P6₃/mmc</i>	<i>C14</i>	<i>a</i> = 498.9, <i>c</i> = 811.0	[10,18,22]

identification was based on the equilibrium composition measured by EPMA (Tables 2, 3) and XRD results (Fig. 5). Comparing with isothermal section at 1073 K shown in Fig. 1, the ternary phases (τ_1 , τ_2 , τ_3 , τ_4 , τ_5), the phase (Zr,Fe)₅Si₃ and the large solubility of Fe in the Si₂Zr also appear at 1273 K and 1373 K. However, in this study, FeZr₂ and SiZr₂ do not form a continuous solid solution at 1273 and 1373 K. The phase τ_8 (57Fe₂₉Si₁₄Zr) appears at 1273 K and 1373 K, which agrees with the formula Fe₄Si₂Zr found in the structural investigations of Yarmolyuk et al.^[20,21] and listed in the review of Raghavan.^[11] In addition, a new phase τ_9 was observed in the present work, which indicates the existence of a new phase.

Figure 2(a) shows the three-phase microstructure (ε (FeSi) + ξ_α (FeSi₂) + τ_3 (Fe₄Si₇Zr₄)) of the Fe₃₅Si₅₅Zr₁₀ (at.%) alloy annealed at 1273 K for 1440 h. A three-phase equilibrium ((Zr,Fe)₅Si₃ + τ_8 (Fe₄Si₂Zr) + τ_9) was identified in the Fe₅₀Si₃₅Zr₁₅ (at.%) alloy annealed at 1273 K for 1440 h, and indicated in Fig. 2(b). The homogeneity of

phase τ_9 ranges from 40.7 to 43.2 at.% Si, from 27.8 to 30.3 at.% Zr, and from 27.2 to 28.8 at.% Fe. Considering the composition of τ_7 (Fe₂Si₃Zr₃) given by Raghavan^[11] and the standard deviation of the measured concentration, τ_9 may not be τ_7 (Fe₂Si₃Zr₃),^[19] which appears in the isothermal section at 1273 K.^[11] Figure 2(c) presents the three-phase microstructure ((Zr,Fe)₅Si₃ + α Fe + τ_8 (Fe₄Si₂Zr)) of the Fe₆₀Si₃₀Zr₁₀ (at.%) alloy equilibrated at 1273 K for 1440 h. In the Fe₄₂Si₃₉Zr₁₉ (at.%) alloy annealed at 1273 K for 1440 h, a three-phase equilibrium ((Zr,Fe)₅Si₃ + τ_9 + τ_4 (Fe₂Si₂Zr)) was found, and shown in Fig. 2(d). Two three-phase equilibria of the (τ_4 (Fe₂Si₂Zr) + τ_9 + ε (FeSi)) and (τ_5 + τ_8 (Fe₄Si₂Zr) + τ_1 (FeSiZr)) were observed in the Fe₄₁Si₄₄Zr₁₅ (at.%) and Fe_{51.5}Si_{27.5}Zr₂₁ (at.%) alloys both quenched from 1273 K for 1440 h, and indicated in Fig. 2(e) and (f), respectively. Figure 3(a) shows the three-phase microstructure (α (Fe₂Zr) + γ Fe + τ_5 (Fe₁₆Si₇Zr₆)) of the Fe₆₈Si₁₂Zr₂₀ (at.%) alloy annealed at 1273 K for 1440 h, where the gray,

Fig. 2 BSE images of typical ternary alloys annealed at 1273 K for 1440 h: (a) the $\text{Fe}_{35}\text{Si}_{55}\text{Zr}_{10}$ (at.%); the $\text{Fe}_{50}\text{Si}_{35}\text{Zr}_{15}$ (at.%); (c) the $\text{Fe}_{60}\text{Si}_{30}\text{Zr}_{10}$ (at.%); (d) the $\text{Fe}_{42}\text{Si}_{39}\text{Zr}_{19}$ (at.%); (e) the $\text{Fe}_{41}\text{Si}_{44}\text{Zr}_{15}$ (at.%); and (f) the $\text{Fe}_{51.5}\text{Si}_{27.5}\text{Zr}_{21}$ (at.%)

Table 2 Equilibrium compositions of the Fe-Si-Zr system determined at 1273 K

Alloy, at.%	Phase equilibrium	Composition, at.%					
		Phase 1		Phase 2		Phase 3	
		Si	Zr	Si	Zr	Si	Zr
Fe ₂₀ Si ₇₀ Zr ₁₀	(Si) + Si ₂ Zr + ξ_α (FeSi ₂)	99.5	0.1	63.0	29.5	66.7	7.5
Fe ₃₅ Si ₅₅ Zr ₁₀	ε (FeSi) + ξ_α (FeSi ₂) + τ_3	51.5	0.1	66.6	7.1	51.8	23.4
Fe ₂₀ Si ₆₀ Zr ₂₀	ξ_α (FeSi ₂) + Si ₂ Zr + τ_3	66.5	6.9	63.9	27.9	53.0	22.8
Fe ₅ Si ₅₅ Zr ₄₀	Si ₂ Zr + α (SiZr) + τ_3	62.6	30.3	50.6	48.8	50.3	25.7
Fe _{27.5} Si ₄₉ Zr _{23.5}	ε (FeSi) + τ_3 + τ_9	50.4	0.3	50.5	24.3	43.2	28.3
Fe ₁₇ Si ₄₈ Zr ₃₅	τ_3 + α (SiZr) + τ_9	49.0	25.6	50.1	49.7	42.9	28.7
Fe ₄₁ Si ₄₄ Zr ₁₅	ε (FeSi) + τ_4 + τ_9	49.8	0.1	40.5	19.5	42.8	27.8
Fe ₇ Si ₄₆ Zr ₄₇	α (SiZr) + α (Si ₄ Zr ₅) + τ_9	50.1	49.1	45.5	54.2	42.5	30.3
Fe ₅₀ Si ₄₀ Zr ₁₀	ε (FeSi) + (Zr,Fe) ₅ Si ₃ + τ_4	49.9	0.0	36.0	10.4	41.3	17.5
Fe ₄₂ Si ₃₉ Zr ₁₉	τ_4 + (Zr,Fe) ₅ Si ₃ + τ_9	40.7	19.2	36.2	11.4	41.9	29.3
Fe ₅₀ Si ₃₅ Zr ₁₅	τ_9 + (Zr,Fe) ₅ Si ₃ + τ_8	40.6	29.3	35.1	11.5	29.3	13.9
Fe ₄₀ Si ₃₅ Zr ₂₅	τ_1 + τ_9 + τ_8	35.0	30.5	41.3	27.9	29.4	13.1
Fe ₆₀ Si ₃₀ Zr ₁₀	α Fe + (Zr,Fe) ₅ Si ₃ + τ_8	27.2	0.1	36.4	11.3	29.8	13.8
Fe _{51.5} Si _{27.5} Zr ₂₁	τ_1 + τ_5 + τ_8	33.9	32.2	24.4	20.0	28.8	14.2
Fe ₆₈ Si ₁₉ Zr ₁₃	α Fe + τ_5 + τ_8	11.8	0.6	24.0	19.9	28.5	14.0
Fe _{62.5} Si _{16.5} Zr ₂₁	τ_1 + τ_2 + Si ₂ Zr ₃	34.1	32.2	17.7	35.1	39.0	60.6
Fe ₆₈ Si ₁₂ Zr ₂₀	γ Fe + α (Fe ₂ Zr) + τ_5	2.8	0.3	14.0	18.3	12.4	23.2
Fe ₂₀ Si ₂₀ Zr ₆₀	Liquid + SiZr ₂ + α (Fe ₂ Zr)	0.5	67.0	31.4	66.1	3.0	34.1
Fe ₃ Si ₄₂ Zr ₅₅	τ_1 + α (Si ₄ Zr ₅) + Si ₂ Zr ₃	34.5	32.5	45.5	54.1	38.9	60.6
Fe ₂₇ Si ₃₈ Zr ₃₅	τ_9 + α (Si ₄ Zr ₅) + τ_1	40.7	30.5	45.7	54.0	34.8	33.8
Fe _{29.5} Si ₂₃ Zr _{47.5}	α (Fe ₂ Zr) + SiZr ₂ + Si ₂ Zr ₃	8.7	32.9	33.6	64.4	38.8	60.8
Fe ₁₀ Si ₁₀ Zr ₈₀	β Zr + SiZr ₂ + liquid	0	95.9	30.6	65.8	0.2	72.6
Fe _{62.5} Si _{16.5} Zr ₂₁	τ_5 + α (Fe ₂ Zr)	17.5	20.5	13.2	25.2	...	...
Fe ₃₃ Si ₄₂ Zr ₂₅	τ_4 + τ_9	40.7	18.2	42.4	27.9	...	...
Fe ₃₉ Si ₄₈ Zr ₁₃	ε (FeSi) + τ_9	50.2	0.1	43.1	27.8	...	...
Fe ₄₅ Si ₂₅ Zr ₃₀	α (Fe ₂ Zr) + τ_1	15.5	27.1	34.2	30.9	...	...
Fe _{81.5} Si _{2.5} Zr ₁₇	γ Fe + α (Fe ₂ Zr)	0.5	0.6	5.0	26.7	...	...
Fe ₆₂ Si ₂₀ Zr ₁₈	α Fe + τ_5	22.8	20.0	8.3	1.5	...	...
Fe ₇₀ Si ₁₇ Zr ₁₃	α Fe + τ_5	9.8	3.1	22.5	20.1	...	...
Fe _{43.5} Si ₂₅ Zr _{31.5}	τ_1 + τ_2	32.7	33.2	17.4	30.8	...	...
Fe _{61.5} Si _{11.5} Zr ₂₇	α (Fe ₂ Zr)	10.6	29.1	...	...	...	...

Seven analyses were carried out for each phase and the standard deviation of the measured concentration is ± 0.5 at.%

the dark gray and the black represent τ_5 (Fe₁₆Si₇Zr₆) phase, α (Fe₂Zr) phase and γ Fe phase, respectively. A two-phase equilibrium (τ_4 (Fe₂Si₂Zr) + τ_9) was identified in the Fe₃₅Si₄₀Zr₂₅ (at.%) alloy at 1273 K for 1440 h, and indicated in Fig. 3(b), where the τ_9 phase with the strip shape distributes in the τ_4 matrix. Figure 3(c) presents the two-phase microstructure (τ_5 (Fe₁₆Si₇Zr₆) + α Fe) of the Fe₇₁Si₁₅Zr₁₄ (at.%) alloy equilibrated at 1273 K for 1440 h.

In the Fe₂₀Si₇₀Zr₁₀ (at.%) alloy annealed at 1373 K for 720 h, the three-phase microstructure (ξ_α (FeSi₂) + Si + Si₂Zr) was observed, as shown in Fig. 3(d). Figure 3(e) shows the three-phase microstructure ((Zr,Fe)₅Si₃ + ε (FeSi) + τ_4 (Fe₂Si₂Zr)) of the Fe₅₀Si₄₀Zr₁₀ (at.%) alloy annealed at 1373 K for 720 h. In the Fe₃Si₄₂Zr₅₅ (at.%) alloy quenched from 1373 K for 720 h, the three-phase microstructure (Si₂Zr₃ + τ_1 (FeSiZr) + α (Si₄Zr₅)) was observed (Fig. 3f) and substantiated by the XRD result, as shown in Fig. 5(a), where the characteristic peaks of the

Si₂Zr₃, τ_1 (FeSiZr) and α (Si₄Zr₅) phases were found and well marked by different symbols. In the Fe₅Si₅₅Zr₄₀ (at.%) alloy annealed at 1373 K for 720 h, the three-phase microstructure (τ_3 (Fe₄Si₇Zr₄) + Si₂Zr + α (SiZr)) was observed (Fig. 4a) and substantiated by XRD result, as shown in Fig. 5(b), where the characteristics peaks of τ_3 (Fe₄Si₇Zr₄), Si₂Zr and α (SiZr) are confirmed and well marked by different symbols. In the Fe_{33.5}Si_{43.5}Zr₂₃ (at.%) alloy annealed at 1373 K for 720 h, the three-phase equilibrium of (τ_4 (Fe₂Si₂Zr) + τ_9 + ε (FeSi)) was found, as presented in Fig. 4(b). In addition, the three-phase equilibrium of ((Zr,Fe)₅Si₃ + β (Fe₂Si) + ε (FeSi)) was identified in the Fe₅₇Si₄₀Zr₃ (at.%) alloy annealed at 1373 K for 720 h, and its equilibrium microstructure is presented in the Fig. 4(c). As illustrated in Fig. 4(d), the three-phase equilibrium microstructures (τ_3 (Fe₄Si₇Zr₄) + Si₂Zr + ξ_α (FeSi₂)) was detected in the Fe₂₀Si₆₀Zr₂₀ (at.%) alloys quenched from 1373 K for 720 h. As shown in Fig. 4(e), a

Table 3 Equilibrium compositions of the Fe-Si-Zr system determined at 1373 K

Alloy, at. %	Phase equilibrium	Composition, at. %					
		Phase 1		Phase 2		Phase 3	
		Si	Zr	Si	Zr	Si	Zr
Fe ₂₀ Si ₇₀ Zr ₁₀	(Si) + ξ_α (FeSi ₂) + Si ₂ Zr	99.5	0.1	66.8	7.2	63.5	29.5
Fe ₃₅ Si ₅₅ Zr ₁₀	ξ_α (FeSi ₂) + ε (FeSi) + τ_3	66.3	7.7	51.2	0.2	51.5	23.4
Fe ₂₀ Si ₆₀ Zr ₂₀	ξ_α (FeSi ₂) + Si ₂ Zr + τ_3	65.6	7.4	63.1	29.3	51.4	23.6
Fe ₅ Si ₅₅ Zr ₄₀	Si ₂ Zr + α (SiZr) + τ_3	63.8	29.7	50.5	49.2	52.1	24.3
Fe _{27.5} Si ₄₉ Zr _{23.5}	ε (FeSi) + τ_3 + τ_9	50.5	0.2	50.9	24.1	43.5	27.8
Fe _{33.5} Si _{43.5} Zr ₂₃	ε (FeSi) + τ_4 + τ_9	49.9	0.6	40.3	19.5	43.4	27.7
Fe ₅₀ Si ₄₀ Zr ₁₀	ε (FeSi) + (Zr,Fe) ₅ Si ₃ + τ_4	50.5	0	36.4	11.3	41.0	18.8
Fe ₅₇ Si ₄₀ Zr ₃	ε (FeSi) + (Zr,Fe) ₅ Si ₃ + β (Fe ₂ Si)	49.7	0	36.3	10.6	34.6	0
Fe ₄₃ Si ₃₈ Zr ₁₉	τ_4 + (ZrFe) ₅ Si ₃ + τ_9	40.9	19.2	36.5	11.2	42.3	28.8
Fe ₆₀ Si ₃₀ Zr ₁₀	α Fe + (Zr,Fe) ₅ Si ₃ + τ_8	27.0	0.1	36.2	11.3	29.9	13.8
Fe ₄₀ Si ₃₅ Zr ₂₅	τ_1 + τ_9 + τ_8	35.5	31.2	40.9	28.7	29.6	13.8
Fe ₇ Si ₄₆ Zr ₄₇	α (SiZr) + α (Si ₄ Zr ₅) + τ_9	50.2	49.4	44.9	55.1	43.3	29.7
Fe ₆₈ Si ₁₉ Zr ₁₃	α Fe + τ_5 + τ_8	14.6	0	24.7	19.6	29.3	13.7
Fe _{51.5} Si _{27.5} Zr ₂₁	τ_1 + τ_5 + τ_8	34.1	33.0	25.1	20.2	28.7	14.4
Fe ₉ Si ₃₆ Zr ₅₅	τ_1 + Si ₂ Zr ₃ + τ_2	33.4	33.7	39.6	60.3	13.9	34.5
Fe ₆₈ Si ₁₂ Zr ₂₀	γ Fe + α (Fe ₂ Zr) + τ_5	2.9	0.2	12.5	24.7	13.7	20.3
Fe ₂₀ Si ₂₀ Zr ₆₀	Liquid + SiZr ₂ + α (Fe ₂ Zr)	0.7	62.8	29.1	63.6	2.9	31.0
Fe ₂ Si ₂₀ Zr ₇₈	β Zr + SiZr ₂ + SiZr ₃	0.1	97.3	29.8	63.8	24.8	74.1
Fe ₅₀ Si ₃₅ Zr ₁₅	τ_9 + (Zr,Fe) ₅ Si ₃ + τ_8	39.7	28.9	36.4	11.5	30.5	13.8
Fe ₁₉ Si ₄₇ Zr ₃₄	τ_3 + α (SiZr) + τ_9	49.0	25.2	50.9	47.9	42.5	29.9
Fe ₃ Si ₄₂ Zr ₅₅	τ_1 + α (Si ₄ Zr ₅) + Si ₂ Zr ₃	33.9	34.2	44.4	55.4	39.6	60.3
Fe ₂₇ Si ₃₈ Zr ₃₅	τ_9 + α (Si ₄ Zr ₅) + τ_1	41.5	30.1	44.8	55.0	34.1	32.9
Fe _{29.5} Si ₂₃ Zr _{47.5}	α (Fe ₂ Zr) + SiZr ₂ + Si ₂ Zr ₃	8.5	32.7	33.7	64.0	38.8	60.3
Fe ₄₉ Si ₂₅ Zr ₂₆	τ_1 + τ_5 + α (Fe ₂ Zr)	33.0	32.4	20.8	20.3	16.2	26.2
Fe ₁₀ Si ₁₀ Zr ₈₀	β Zr + SiZr ₂ + liquid	0	96.5	29.2	65.1	0.5	74.6
Fe ₅₃ Si ₃₆ Zr ₁₁	FeSi + (Zr,Fe) ₅ Si ₃ + β (Fe ₂ Si)	49.4	0	35.6	11.5	33.1	0
Fe ₃₄ Si ₄₆ Zr ₂₀	ε (FeSi) + τ_9	50.9	0.2	43.5	27.5	...	...
Fe ₆₂ Si ₂₀ Zr ₁₈	α Fe + τ_5	9.1	1.3	22.5	20.1	...	...
Fe ₄₅ Si ₂₅ Zr ₃₀	α (Fe ₂ Zr) + τ_1	15.9	28.2	33.0	32.6	...	...
Fe _{62.5} Si _{16.5} Zr ₂₁	τ_5 + α (Fe ₂ Zr)	18.5	20.3	14.3	24.1	...	...
Fe _{81.5} Si _{2.5} Zr ₁₇	γ Fe + α (Fe ₂ Zr)	0.4	0.6	4.1	26.6	...	...
Fe ₄₃ Si ₂₅ Zr ₃₂	τ_1 + τ_2	32.4	33.3	14.5	30.6	...	...
Fe ₆₇ Si ₁₈ Zr ₁₅	α Fe + τ_5	9.9	0.6	23.0	19.8	...	...
Fe ₇₁ Si ₁₅ Zr ₁₄	α Fe + τ_5	11.7	0.1	23.5	20.0	...	...
Fe _{60.5} Si _{11.5} Zr ₂₈	α (Fe ₂ Zr)	10.2	28.4	...	...	...	...

Seven analyses were carried out for each phase and the standard deviation of the measured concentration is ± 0.5 at. %

two-phase equilibrium (ε (FeSi) + τ_9) was indentified in the Fe₃₄Si₄₆Zr₂₀ (at. %) alloy at 1373 K for 720 h, where the τ_9 phase irregularly distributes in the ε (FeSi) matrix, and the XRD result is indicated in Fig. 5(c). In the Fe₁₉Si₄₇Zr₃₄ (at. %) alloy quenched from 1373 K for 720 h, the three-phase microstructure (α (SiZr) + τ_9 + τ_3 (Fe₄Si₇Zr₄)) was observed (Fig. 4f) and the XRD result was presented in Fig. 5(d). Therefore, the phase regions around the phase τ_9 were measured by EPMA and known phases were identified by the component position. At this moment, it might infer the existence of a new phase. The effect of slightly differing compositions can be ignored, because the ternary-phase regions around the phase τ_9 were large enough and the

standard deviation of the measured concentration is ± 0.5 at. %. Through composition contrast, the new phase τ_9 is not same as τ_7 (Fe₂Si₃Zr₃) given by Raghavan.^[11] Furthermore, In Fig. 5(c), the ε (FeSi) phase is figured out by a circle symbol, and the rest peaks probably indicate the new phase τ_9 . If the characteristic peaks of α (SiZr) and τ_3 (Fe₄Si₇Zr₄) were removed in Fig. 5(d), the rest peaks of them are exactly identical with the rests in Fig. 5(c). Thus, according to the EPMA and XRD results, the existence of phase τ_9 at the temperature of 1373 K was confirmed in the Fe-Si-Zr ternary system. The crystal parameters of phase τ_9 are under determination and will be revealed in our further report.

Fig. 3 BSE images of typical ternary alloys at 1273 K and 1373 K: (a) the $\text{Fe}_{68}\text{Si}_{12}\text{Zr}_{20}$ (at.%) alloy annealed at 1273 K for 1440 h; (b) the $\text{Fe}_{35}\text{Si}_{40}\text{Zr}_{25}$ (at.%) alloy annealed at 1273 K for 1440 h; (c) the $\text{Fe}_{71}\text{Si}_{15}\text{Zr}_{14}$ (at.%) alloy annealed at 1273 K for 1440 h; (d) the $\text{Fe}_{20}\text{Si}_{70}\text{Zr}_{10}$ (at.%) alloy annealed at 1373 K for 720 h; (e) the $\text{Fe}_{50}\text{Si}_{40}\text{Zr}_{10}$ (at.%) alloy annealed at 1373 K for 720 h; and (f) the $\text{Fe}_3\text{Si}_{42}\text{Zr}_{55}$ (at.%) alloy annealed at 1373 K for 720 h

Fig. 4 BSE images of typical ternary alloys annealed at 1373 K for 720 h: (a) the $\text{Fe}_5\text{Si}_{55}\text{Zr}_{40}$ (at.%); (b) the $\text{Fe}_{33.5}\text{Si}_{43.5}\text{Zr}_{23}$ (at.%); (c) the $\text{Fe}_{57}\text{Si}_{40}\text{Zr}_3$ (at.%); (d) the $\text{Fe}_{20}\text{Si}_{60}\text{Zr}_{20}$ (at.%); (e) the $\text{Fe}_{34}\text{Si}_{46}\text{Zr}_{20}$ (at.%); and (f) the $\text{Fe}_{19}\text{Si}_{47}\text{Zr}_{34}$ (at.%)

Fig. 5 XRD patterns obtained from alloys annealed at 1373 K for 720 h: (a) the $\text{Fe}_3\text{Si}_{46}\text{Zr}_{20}$ (at.%) alloy; (b) the $\text{Fe}_5\text{Si}_{55}\text{Zr}_{40}$ (at.%) alloy; (c) the $\text{Fe}_{34}\text{Si}_{46}\text{Zr}_{20}$ (at.%) alloy; and (d) the $\text{Fe}_{19}\text{Si}_{47}\text{Zr}_{34}$ (at.%) alloy. Vertical red marks with numbers indicate the position of possible Bragg reflections of the α (Si_4Zr_5), Si_2Zr_3 , τ_1 , α (SiZr), Si_2Zr , ϵ (FeSi), and τ_3 phase

Fig. 6 Experimentally determined isothermal sections of the Fe-Si-Zr system at: (a) 1273 K and (b) 1373 K

3.2 Isothermal Section

All the equilibrium compositions of the Fe-Si-Zr ternary system at 1273 and 1373 K determined by EPMA were listed in Tables 2 and 3, respectively. Based on the experimental data mentioned above, two isothermal sections at 1273 and 1373 K were constructed in Fig. 6(a) and (b), respectively.

In the isothermal section at 1273 K shown in Fig. 6(a), several ternary phases were experimentally determined and a new phase τ_9 was observed for the first time in this work. The solubility of Zr in the ξ_α (FeSi_2) phase is found to be 7.5 at.%, the solubility of Fe in the Si_2Zr is measured to be 8 at.% and the solubility of Fe in the SiZr_2 phases is shown to be 4 at.%. Furthermore, the solubility of Si in the Fe_2Zr phase is found to be about 16 at.%. Compared with isothermal section at 1073 K shown in Fig. 1, the single-phase regions of the ternary phases (τ_1 , τ_3 , τ_4 , τ_8) identified in the isothermal section at 1273 K, change to be one-phase regions. On the other hand, the τ_5 phase changes to be a linear compound, and the Zr content in the τ_5 phase is 20 at.%. In addition, the ternary phase named τ_9 indicated in Fig. 2(b), (d) and (e), separates the ternary region (ε (FeSi) + τ_3 + τ_4) into two new ternary regions: (ε (FeSi) + τ_3 + τ_9) and (ε (FeSi) + τ_4 + τ_9). Compared with isothermal section given by Raghavan,^[11] the phase ($\text{Fe,Si})_2\text{Zr}$, τ_6 ($\text{Fe}_5\text{Si}_{12}\text{Zr}_3$) and τ_7 ($\text{Fe}_2\text{Si}_3\text{Zr}_3$) disappear, as well as a continuous series of solid solution formed by FeZr_2 and SiZr_2 . Also, the solubility of Si in the Fe_2Zr phase and the solubility of Zr in the ξ_α (FeSi_2) phase increase. For the phase τ_9 , although the standard deviation of the measured concentration is taken into consideration, the composition position of τ_9 is still far away from known ternary phase (τ_1 (FeSiZr), τ_3 ($\text{Fe}_4\text{Si}_4\text{Zr}_7$), τ_7 ($\text{Fe}_2\text{Si}_3\text{Zr}_3$)). Moreover, through XRD patterns, the unknown peaks cannot be calibrated by other peaks of Fe-Si-Zr metal compounds. Therefore, it is indicated that the phase τ_9 exists.

The phase relationships in the isothermal section at 1373 K (Fig. 6b) are similar to that at 1273 K. Compared with the isothermal section at 1273 K, the apparent difference happens in the binary Fe-Zr side, where Si content varies from 28 to 50 at.%. The η (Fe_5Si_3) phase disappears and the β (Fe_2Si) appears, which leads to appearance of a ternary region ($(\text{Zr,Fe})_5\text{Si}_3$ + ε (FeSi) + β (Fe_2Si)). It can be seen from the Fe-Si binary phase diagram that, the Fe_5Si_3 only exists in the temperature range between 1098 K and 1333 K. According to the previous and current study, Zr can stabilize a ternary phase of the Fe_5Si_3 structure^[10] and make presence of Fe_5Si_3 to be extended within larger temperature range. The solubility of Fe in the SiZr_2 phases increases, being up to 8 at.% at 1373 K. Additionally, the liquid region in the Zr-rich corner becomes larger.

4. Conclusions

The phase equilibria of the Fe-Si-Zr alloy system at 1273 and 1373 K were experimentally determined in the whole compositional range, which consists of a series of ternary

phase equilibria, two phase equilibria and solid solutions. The newly determined phase equilibria will provide additional support for the thermodynamic assessment of this Fe-Si-Zr system and compositional design of new silicon steels. The important conclusions drawn from the present study are as follows:

- (1) The previously-reported phases τ_1 , τ_2 , τ_3 , τ_4 , τ_5 , τ_8 and $(\text{Zr,Fe})_5\text{Si}_3$ were found both at 1273 K and 1373 K. The phases τ_6 and τ_7 were not found at either temperature. Also, FeZr_2 and SiZr_2 do not form a continuous solid solution at 1273 and 1373 K. A new phase denoted here as τ_9 was found at both temperatures.
- (2) The measured homogeneity range of the newly found phase τ_9 ($29\text{Fe}42\text{Si}29\text{Zr}$) is sufficiently narrow to conclude that it is distinctly different from the ternary phase τ_7 denoted as τ_6 by Raghavan^[11] with the nominal composition $\text{Fe}_2\text{Si}_3\text{Zr}_3$ ($25\text{Fe}37.5\text{Si}37.5\text{Zr}$). Available structural evidence supports this conclusion.
- (3) The measured composition of the τ_8 phase ($57\text{Fe}29\text{Si}14\text{Zr}$) agrees with the formula $\text{Fe}_4\text{Si}_2\text{Zr}$ found in the structural investigations of Yarmolyuk et al.^[20,21] and listed in the review of Raghavan.^[11]

Acknowledgments

Authors wish to acknowledge the National Natural Science Foundation of China (Grant No. 51031003, Grant No. 51171159), the Ministry of Education, PR CHINA (Grant No. 20120121130004), National Key Basic Research Program of China (973 Program, 2012CB825700) and Aviation Industry Corporation of China for funding this research.

References

1. C.M.B. Bacaltchuk, G.A. Castello-Branco, M. Ebrahimi, H. Garmestani, and A.D. Rollett, Effect of Magnetic Field Applied During Secondary Annealing on Texture and Grain Size of Silicon Steel, *Scr. Mater.*, 2003, **48**, p 1343-1347
2. N. Takahashi and J. Harase, Recent Development of Technology of Grain Oriented Silicon Steel, *Mater. Sci. Forum.*, 1996, **204-206**, p 143-154
3. C.W. Chen, *Magnetism and Metallurgy of Soft Magnetic Materials*, Dove Publications, New York, 1986, p 377
4. F.G. Caballero, M.K. Miller, S.S. Babu, and C. Garcia-Mateo, Atom Scale Observations of Bainite Transformation in a high Carbon high Silicon Steel, *Acta Mater.*, 2007, **55**, p 381-390
5. K. Matsumura and B. Fukuda, Recent Developments of Non-oriented Electrical Steel Sheets, *IEEE Trans. Magn.*, 1984, **20**, p 1533-1538
6. Z.Z. He, Cold Rolled Non Grain Oriented Steel, *Electrical Steel*, Z.Z. He, Ed., Metallurgical-Industry Publishing, Beijing, 1997, p 416-417, in Chinese
7. O. Kubaschewski, *Iron-Binary Phase Diagrams*, Springer, New York, 1982, p 1-4
8. F. Stein, G. Sauthoff, and M. Palm, Experimental Determination of Intermetallic Phases, Phase Equilibria, and Invariant

- Reaction Temperatures in the Fe-Zr System, *J. Phase Equilib.*, 2002, **23**, p 480-494
9. H. Okamoto, The Si-Zr (Silicon-Zirconium) System, *Bull. Alloy Phase Diagr.*, 1990, **11**, p 513-519
 10. L.A. Lisenko, Z. Ban, and E.I. Gladisevskii, Investigation of the System Zr-Fe-Si, *Croat. Chem. Acta.*, 1971, **43**, p 113-118
 11. V. Raghavan, The Fe-Si-Zr (Iron-Silicon-Zirconium) System, *Phase Diagrams of Ternary Iron Alloys*, Part 6B, Indian Institute of Metals, Calcutta, 1992, p 1189-1194
 12. Y. Du, W. Xiong, W. Zhang, H. Chen, and W. Sun, Iron-Silicon-Zirconium, *Landolt-Bornstein New Series IV*, Vol 11D5, 2009, p 605-620
 13. W. Jeitschko, A.G. Jordan, and P.A. Beck, V and E Phases in Ternary Systems with Transition Metals and Silicon or Germanium, *Trans. Met. Soc. AIME*, 1969, **245**, p 335-339
 14. R.C. Mittal, S.K. Si, and K.P. Gupta, Si-Stabilised C14 Laves Phases in the Transition Metal Systems, *J. Less-Common Met.*, 1978, **60**, p 75-82
 15. Ch.B.H. Evers and W. Jeitschko, Crystal Structure of Tetra-zirconium Tetrairon Heptasilicide, $Zr_4Fe_4Si_7$, *Z. Kristallogr.*, 1996, **211**, p 119
 16. Yu.V. Voroshilov, V.Ya. Markiv, and E.I. Gladyshevskii, The Zirconium-Nickel-Silicon System, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, 1967, **3**(8), p 1140-1148, in Russian
 17. P. Chaudouet, B. Lambert, R. Madar, and R. Fruchart, Existence of a G-type Phase in the Fe-Zr-Si System, *Ann. Chi. Fr.*, 1984, **9**(2), p 119-121
 18. L.A. Lysenko, Z. Ban, Ya.P. Yarmolyuk, and E.I. Gladisevskii, Reaction of Zr with Fe-Group Transition Metals and Si, *Struktura Faz. Faz. Prevrashcheniya i Diagrammy Sostoyaniya Metal. Sistem.*, O.S. Ivanov, Ed., Nauka, Moscow, 1974, p 21-25, in Russian
 19. Y.P. Yarmolyuk, Y.N. Grin, and E.I. Gladyshevskii, Crystal Structure of $Hf_3Ni_2Si_3$, *Sov. Phys. Crystallogr.*, 1977, **22**, p 416-419, in Russian
 20. Y.P. Yarmolyuk, L.A. Lysenko, and E.I. Gladyshevskii, The $ZrFe_4Si_2$ Crystal Structure: A New Structure Type in the Ternary Silicides of Transition Metals, *Dopov. Akad. Nauk Ukrain. RSA(A)*, 1975, p 279-282, in Ukrainian
 21. Y.P. Yarmolyuk, L.A. Lysenko, and E.I. Gladyshevskii, Crystal Structure of New Ternary Compounds in the Zr-Fe-Si System, *Tezisy Dokl.-Vses. Konf. Kristallokhim. Intermetall. Soedin.*, 2nd ed., R.M. Rykhal, Ed., L'Vov Gos. Univ., USSR, 1974, p 21-22
 22. O.Z. Blazina and R. Trojko, On Friauf-Laves Phases in the $Zr_{1-x}Al_xT_2$, $Zr_{1-x}Si_xT_2$, and $Zr_{1-x}Ti_xT_2$ ($T = Mn, Fe, Co$) Systems, *J. Less-Common Met.*, 1987, **133**, p 277-286