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Experimental investigation of phase equilibria in the Co–Si–Zr ternary system

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ABSTRACT

The phase equilibria in the Co–Si–Zr ternary system were investigated by means of back-scattered electron (BSE), electron probe microanalysis (EPMA) and X-ray diffraction (XRD). Two isothermal sections of the Co–Si–Zr ternary system at 1273 and 1373 K were experimentally established, and the compositions of the two ternary compounds ($Zr_5Co_8Si_9$ and $Zr_4Co_4Si_7$) were confirmed. The isothermal sections of the system at 1273 and 1373 K respectively consist of 29 and 30 three-phase regions, and also six ternary compounds was found in both two isothermal sections. The solubility of Zr in the intermediate and solution phases (i.e. αCo_2Si, $\alpha CoSi$, $CoSi_2$, αCo and εCo) at the Co–Si side is extremely small, whereas the situation of Si in the Co-rich corner (especially for $Co_{23}Zr_6$ and Co_2Zr phases) is reverse.

1. Introduction

Amorphous Co–Si thin films have received much interest over the years due to their application as contacts and interconnects in very large scale integrated (VLSI) technology [1–3]. Since doping Zr into amorphous Co–Si films can significantly improve the higher thermal stability of the films [4], the Co–Si–Zr base alloys can be highly promising as candidate for the amorphous alloys [5,6]. For the advanced development of high-performance Co–Si–Zr base alloys, the accurate information on the phase equilibria of Co–Si–Zr ternary system is especially required. However, to the best of our knowledge, only the isothermal section of Co–Si–Zr system at 1073 K was investigated by Lysenko et al. [7]. It is indicated from Ref. [7] that there are seven ternary compounds in the isothermal section (i.e. $ZrCo_5Si_3$, $ZrCo_2Si_2$, Zr_2CoSi_2, $ZrCo_2Si$, $Zr_7Si_9Zr_4$, ZrCoSi and Zr_9CoSi_{10}). More recently, Villars et al. [8] re-edited this isothermal section of Co–Si–Zr ternary system and suggested that there exist two ternary compounds ($Zr_4Co_4Si_7$ and $Zr_5Co_8Si_9$), which are inconsistent with the $ZrCoSi_2$ and $Zr_7Co_9Si_4$ reported in Ref. [7]. In addition, the phase equilibrium information of the Co–Si–Zr ternary system at Zr–Si side is still uncertainty. Based on above reason, it is important and highly necessary to investigate the phase equilibria in the Co–Si–Zr ternary system comprehensively.

In the Co–Si–Zr ternary system, the three sub-binary systems Co–Si [9], Co–Zr [10–12] and Si–Zr [13] had been experimentally investigated. The Co–Si binary phase diagram was edited by Ishida et al. [9], in which five intermediate phases were predicted: Co_3Si, αCo_2Si, βCo_2Si, CoSi and $CoSi_2$. In the Co–Zr binary system, five intermediate phases (i.e. $\gamma Co_{11}Zr_2$, $\delta Co_{23}Zr_6$, εCo_2Zr, $\zeta CoZr$ and $\eta CoZr_2$) were reported by Pechin et al. [10]. Later, Bataleva et al. [11] confirmed the existence of the Co_3Zr phase, and predicted that the εCo_2Zr and Co_3Zr phases have a range of homogeneity. The main information of the Co–Zr phase diagram was obtained by Pechin et al. [10] and our previous work [12]. The Si–Zr binary phase diagram provided by Okamoto [13] depicts the following intermediate phases: Si_2Zr, $\alpha ZrSi$, αZr_5Si_4, Zr_3Si_2, Zr_2Si and Zr_3Si. The phase diagram in the Co–Si, Co–Zr and Si–Zr binary systems are shown in Fig. 1 [9,10,13]. The information of all stable solid phases in the three binary systems mentioned above is summarized in Table 1 [9,12,14].

Recently, our group has been focused on establishing a thermodynamic database of the phase diagrams in the Co-based alloys [14–24]. In order to obtain the detailed information of the phase equilibria for the thermodynamic assessment, the purpose of the present work was to determine the isothermal sections of Co–Si–Zr ternary system at 1273 and 1373 K experimentally by using the back-scattered electron, electron probe microanalysis and X-ray diffraction. The obtained results will meet the need for the thermodynamic description of the Co–Si–Zr ternary system and provide a better understanding of microstructures of promising alloys for practical applications.

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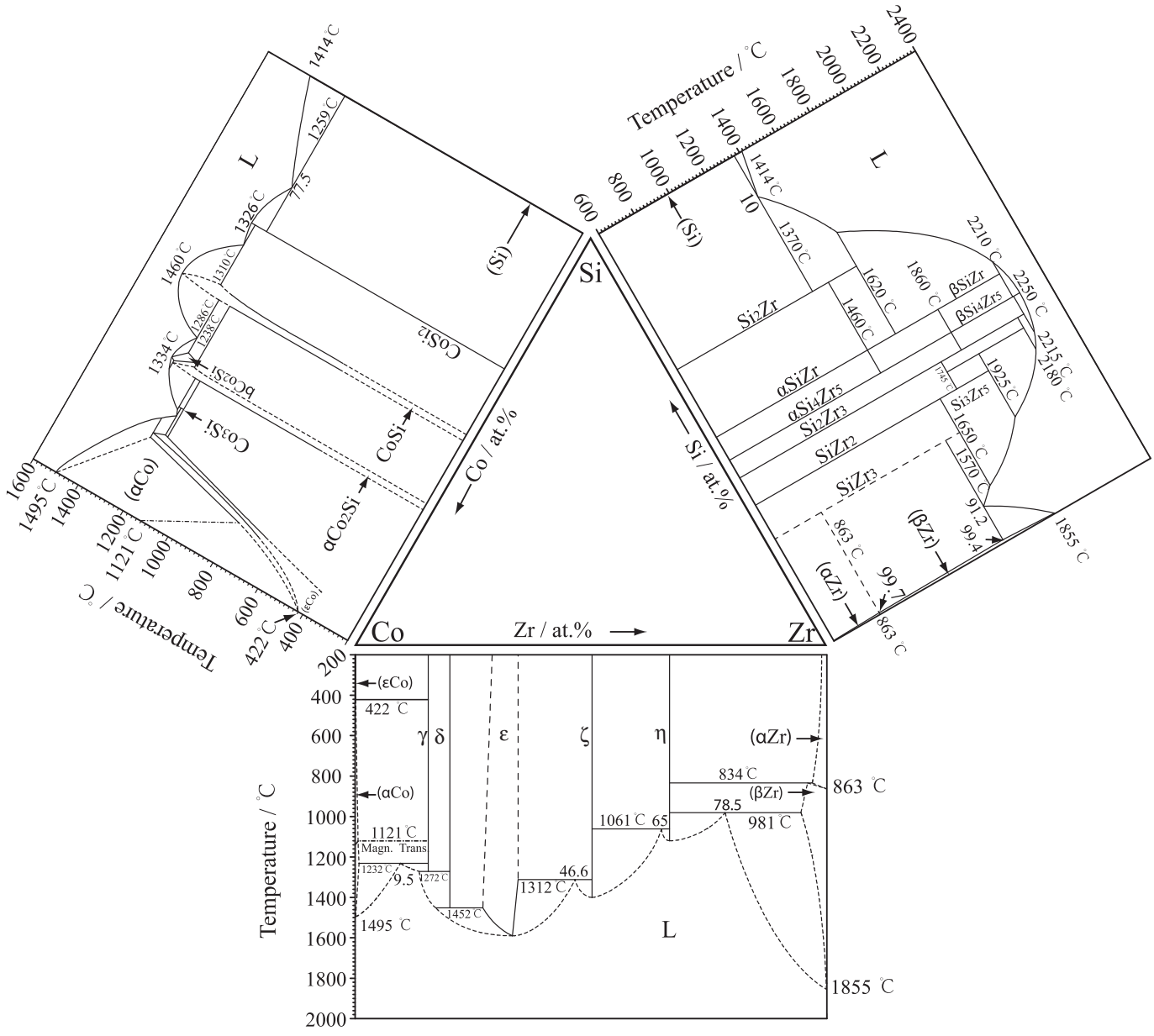

Fig. 1. Binary phase diagrams constituting the Co–Si–Zr ternary system [9,10,13].

Table 1
The stable solid phases in three binary systems.

System	Phase	Pearson's symbol	Prototype	Strukturbericht designation	Refs.
Co–Si	αCo	*cF*4	Cu	*A*1	[14]
	εCo	*hP*2	Mg	*A*3	[14]
	Co_3Si	*hp*8	Mg_3Cd	–	[14]
	αCo_2Si	*oP*12	Co_2Si	*C*23	[14]
	βCo_2Si	–	–	–	[14]
	CoSi	*cP*8	FeSi	*B*20	[14]
	$CoSi_2$	*cF*12	CaF_2	*C*1	[14]
	(Si)	*cF*8	C (diamond)	*A*4	[14]
Co–Zr	αCo	*cF*4	Cu	*A*1	[12]
	εCo	*hP*2	Mg	*A*3	[12]
	$\gamma Co_{11}Zr_2$	–	–	–	[12]
	$\delta Co_{23}Zr_6$	*cF*116	$Mn_{23}Th_6$	$D8_a$	[12]
	εCo_2Zr	*cF*24	Cu_2Mg	*C*15	[12]
	ζCoZr	*cP*2	CsCl	*B*2	[12]
	$\eta CoZr_2$	*tI*12	Al_2Cu	*C*16	[12]

Table 1 (*continued*)

System	Phase	Pearson's symbol	Prototype	Strukturbericht designation	Refs.
	βZr	*cI*2	W	*A*2	[12]
	αZr	*hP*2	Mg	*A*3	[12]
Si–Zr	(Si)	*cF*8	C (diamond)	*A*4	[13]
	Si_2Zr	*oC*12	Si_2Zr	*C*49	[13]
	βSiZr	*oC*8	CrB	B_f	[13]
	αSiZr	*Op*8	FeB	*B*27	[13]
	βSi_4Zr_5	–	–	–	[13]
	αSi_4Zr_5	*tP*36	–	–	[13]
	Si_2Zr_3	*tP*10	Si_2U_3	$D5_a$	[13]
	Si_3Zr_5	*hP*16	Mn_5Si_3	$D8_8$	[13]
	$SiZr_2$	*tI*12	Al_2Cu	*C*16	[13]
	$SiZr_3$	*tP*32	Ti_3P	–	[13]
	βZr	*cI*2	W	*A*2	[13]
	αZr	*hP*2	Mg	*A*3	[13]