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# Experimental study of the phase relations in the Co-Si-Zn ternary system at 723 and 873 K

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#### ABSTRACT

The 723 and 873 K isothermal sections of the Co–Si–Zn system have been determined using equilibrated alloys with the aid of a diffusion couple approach. The specimens were investigated by means of scanning electron microscopy equipped with energy dispersive X-ray spectroscopy, electron probe microanalysis and X-ray diffraction. There are nine three-phase regions exist in the isothermal section at 723 K and eight three-phase regions at 873 K. The CoSi phase can coexist with all compounds in Co–Zn binary system except  $\beta_1$  phase. The solubility of Si in Co–Zn binary compounds is limited. The maximum solubility of Zn in CoSi<sub>2</sub>, CoSi and Co<sub>2</sub>Si is 2.0, 6.2, and 5.4 at.%, respectively.

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#### 1. Introduction

Hot-dip galvanizing is one of the most important processes used to protect steel and iron substrates exposed to corrosion environments [1]. This technique has been in practice for almost a century. However, it is still a technical challenge in galvanizing Si-containing steels [2]. In general galvanizing, silicon in steels will give rise to thick, dull grey coatings that adhere poorly to the steel substrate, and deteriorate the coating quality, which is referred to as silicon reactivity or Sandelin effect in the galvanizing industry [3]. Many researches have been done to resolve this problem. One method is to raise the galvanizing temperature to avoid the formation of the  $\zeta$ -FeZn<sub>13</sub> phase [4], but it will reduce the life expectancy of the galvanizing equipment. Another common used method is to add some alloy elements into the zinc bath such as Ni [5] and Al to restrain the growth of  $\zeta$ -FeZn<sub>13</sub> phase [6]. Li et al. [7] have investigated the effect of Co in zinc bath on the microstructures and growth dynamics of the hot-dip galvanizing coating. The results showed that the addition of Co into zinc bath can control the silicon reactivity. When Co element is added to Zinc bath, the reaction region between the steel substrate and the Zn-Co bath essentially becomes a Zn-Fe-Co-Si quaternary system. Therefore, the information of the phase equilibrium of the Zn-Fe-Co-Si quaternary system at the galvanizing temperature is important to understand

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the effect of Co in zinc bath on the Si reactivity during hot-dip galvanizing Si-containing steels. The Zn-Fe-Co-Si quaternary system reference to four ternary system, i.e. Zn-Fe-Co, Zn-Co-Si, Zn-Fe-Si and Fe-Co-Si system. Until now, there has been no information about phase equilibria of the Co-Si-Zn ternary system in the literature. The present work is constitutes part of the authors' endeavor to determine the Zn-rich corner of the Zn-Fe-Co-Si quaternary system. Besides, Co-based alloy can be used for the submerged pot hardware in galvanizing operation [8]. The information of the phase relationship of the Co-Si-Zn ternary system is useful to understand the effect of Si on the reaction of Co-based alloy with molten zinc. In the present work, the 723 and 873 K isothermal sections of the Co-Si-Zn ternary system have been determined experimentally using combined techniques of the scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), electron probe microanalysis (EPMA), and X-ray diffraction (XRD).

#### 2. Literature data

The experimental phase diagram data of Co–Si system available in the literatures were reviewed by Ishida et al. [9]. This binary system was first calculated by Kaufman [10], and then Ishida et al. [9] performed a thermodynamic assessment of the experimental phase diagram and thermodynamic information. Most recently, it has been re-assessed by Zhang et al. [11] via experiments and modeling. There are five intermetallic compounds in the Co–Si system, viz.  $\text{Co}_3\text{Si}$ ,  $\alpha$ -Co $_2\text{Si}$ ,  $\beta$ -Co $_2\text{Si}$ , CoSi and  $\text{CoSi}_2$ . However, The Co $_3\text{Si}$  and  $\beta$ Co $_2\text{Si}$  do not exist at 723 and 873 K. Many of the experimental data of the Co–Zn phase diagram have been summarized by Hansen and Anderko [12] and Massalski [13]. Recently, Vassilev and Jiang [14] carried out a thermodynamic optimization of the Co–Zn binary system. There are six intermetallic compounds in this system, viz.  $\beta_1$  (CoZn),  $\beta$  (CoZn),  $\gamma$  (Co $_2\text{Sn}_2$ 1),  $\gamma_1$  (CoZn $_2$ 1),  $\gamma_2$ 

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**Table 1**Crystallographic data of the binary compounds in the Co–Si–Zn ternary system at 723 and 873 K.

Compound	Crystal class	Space group	Cell parameters (Å)			References
			a	b	С	
β <sub>1</sub> -CoZn	Cubic		6.345			[16]
β <sub>1</sub> -CoZn	Cubic	P4 <sub>1</sub> 32	6.319			[17]
β <sub>1</sub> -CoZn	Cubic	P213	6.336			[19]
$\gamma$ -Co <sub>5</sub> Zn <sub>21</sub>	Cubic	P215	8.9525			[18]
$\gamma$ -Co <sub>5</sub> Zn <sub>21</sub>	Cubic		8.9257			[16]
$\gamma$ -Co <sub>5</sub> Zn <sub>21</sub>	Cubic	I4 <sub>1</sub> 32	8.9412			[19]
$\gamma_1$ -CoZn <sub>7.8</sub>	Monoclinic	F2/m	9.030	4.338, $\beta$ = 89.90	12.511	[20]
$\gamma_2$ -CoZn <sub>13</sub>	Monoclinic	C2/m	13.306	7.535, $\beta$ = 126.8	4.992	[21]
Co <sub>2</sub> Si	Orthorhombic	Pnma	4.918	3.738	7.109	[22]
CoSi	Cubic	P213	4.446			[23]
CoSi <sub>2</sub>	Cubic	Fm-3m	5.364			[24]

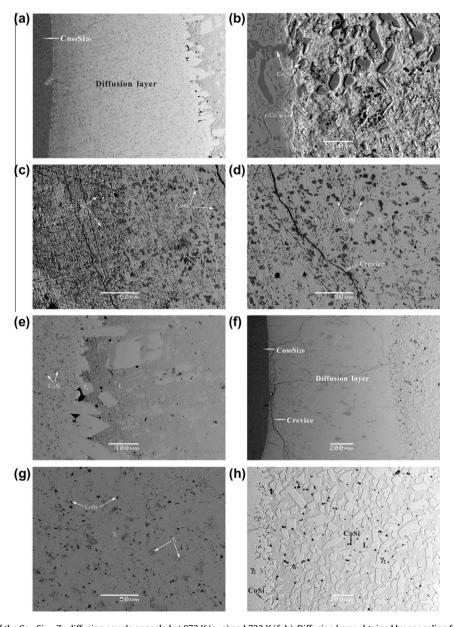


Fig. 1. The microstructures of the  $Co_{80}Si_{20}$ –Zn diffusion couple annealed at 873 K (a–e) and 723 K (f–h). Diffusion layer obtained by annealing for 48 h at 873 k is shows in (a); (ε–Co + αCo<sub>2</sub>Si + β<sub>1</sub>) and (αCo<sub>2</sub>Si + β<sub>1</sub> + γ) two three-phase conjunction interface can be seen in (b); (αCo<sub>2</sub>Si + γ + CoSi) three-phase coexist interface can be seen in (c); (d) shows (CoSi + γ + γ<sub>1</sub>) three-phase coexist interface; (e) shows (CoSi + L + γ<sub>1</sub>) three-phase coexist interface; Diffusion layer obtained by annealing for 96 h at 723 K is shows in (f), (CoSi + γ<sub>1</sub> + γ<sub>2</sub>) and (L + CoSi + γ<sub>2</sub>) two three-phase conjunction interface can be seen in (g and h), respectively.

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