Phase Relationships in the Zn-Rich Corner of the Zn-Fe-Zr System

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(Submitted November 14, 2010; in revised form March 23, 2011)

The phase relationships in the Zn-rich corner of the Zn-Fe-Zr system at 450, 600 and 800 °C were investigated by means of x-ray powder diffraction (XRD) and scanning electron microscopy coupled with energy/wave dispersive spectroscopy (SEM-EDS/WDS). Two ternary compounds were found in the system. One of them was designated as $\text{ZrFe}_2\text{Zn}_{20}$ according to its narrow composition range. It is a $\text{CeCr}_2\text{Al}_{20}$ -type compound with lattice parameter $a = 1.3941$ nm. $\text{ZrFe}_2\text{Zn}_{20}$ is stable below 878.6 °C and can co-exist with all binary compounds in the Zn rich corner of the system. The other one was designated as $\text{Zr}_2\text{Fe}_3\text{Zn}_5$. SEM-WDS analysis indicated that Fe was hardly detected in ZrZn_{22} , $\text{Zr}_5\text{Zn}_{39}$ and ZrZn_3 . And no Zr was dissolved in all Fe-Zn intermetallic compounds.

Keywords intermetallic compound, phase diagram, thermodynamic equilibrium, Zn-Fe-Zr

1. Introduction

Hot-dip galvanizing is a popular and mature process that offers steel components effective corrosion protection. However, galvanizing Si-containing steels remains a technical challenge as it produces dull and excessively thick coatings with poor adhesion. This phenomenon is referred to as the Sandlin effect or Si reactivity by the galvanizers.^[1–3] A practical solution to this problem is galvanizing the steels in alloyed baths. At present, Zn-Ni alloys are commonly used in the galvanizing industry.^[4] However, they afford control of Si reactivity only when the Si content in the steel is below 0.2 wt.%. Mackowiak and Short^[5] demonstrated that Zr in the Zn bath effectively suppressed the excessive growth of Fe-Zn compounds by forming a ternary compound at the growth front of the ζ (FeZn_{13}) layer in the coating.

The investigation of addition of Zr to Zn bath is very limited. Sebisty^[6,7] reported that additions of 0.1 and 0.3 wt.%Zr decreased the coating thickness. He suggested that the limiting growth of the ζ phase is probably due to the formation of the intermetallic particles rich in Fe and Zr which involves the dissolution of the ζ phase. Zhang^[6] believed that both Zr and Mn can inhibit the layer growth of

active steels with high Si content. Thus, Mn and Zr might be an alternative addition to Ni for controlling the excessive reaction of the active steels in general galvanizing.

When Zr is added to the Zn bath, the bath essentially becomes a Zn-Fe-Zr ternary system. Gross et al.^[8] reported a ternary compound $\text{ZrFe}_2\text{Zn}_{20}$ with the $\text{CeCr}_2\text{Al}_{20}$ -type structure in the ternary system. However, no information about the phase diagram was reported. To understand the effect of Zr on Si reactivity control, determination of the phase relationship in the Zn-Fe-Zr ternary system at the galvanizing temperature is essential. In the present work, the phase equilibria in the Zn-rich corner of the Zn-Fe-Zr system at 450 and 600 °C were determined experimentally using combined techniques of x-ray diffraction (XRD), optical microscopy and scanning electron microscopy coupled with energy/wave dispersive x-ray spectroscopy (SEM-EDS/WDS).

Due to its importance to the galvanizing industry, the Fe-Zn binary system has been investigated repeatedly.^[9–11] The most recent thermodynamic assessment of the system was carried out by Xiong et al.^[12] There are four intermetallic compounds, the ζ (FeZn_{13}), the δ (FeZn_{10}), the Γ_1 ($\text{Fe}_5\text{Zn}_{21}$) and the Γ ($\text{Fe}_3\text{Zn}_{10}$) phases, in the system.

The Zn-Zr phase diagram has been thermodynamically assessed by Arroyave and Liu^[13] based on previous investigation results.^[14,15] Six stoichiometric compounds exist in the system: ZrZn_{22} , $\text{Zr}_5\text{Zn}_{39}$, ZrZn_3 , ZrZn_2 , ZrZn , and Zr_2Zn . It needs to be mentioned that the compounds of Zn_{14}Zr and Zn_6Zr reported by Chiotti and Kilp^[16] were found to be Zn_{22}Zr and $\text{Zn}_{39}\text{Zr}_5$ instead, respectively, in a recent study. The crystal data of all the binary and ternary compounds relevant to the equilibria in the Zn-rich corner are listed in Table 1.

2. Experimental Methods

Series of alloys were prepared to determine the equilibrium phases in the Zn-Fe-Zr system. The purity of raw

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Table 1 Crystallographic parameters for the binary and ternary compounds in Zn-rich corner of the Zn-Fe-Zr system

Compound	Prototype	Pearson symbol	Space group	Composition range (at.%)	Ref.
ZrZn ₂₂	Mg ₅ Cr ₂ Al ₁₈	cF184	Fd $\bar{3}$ m (227)	4.3%Zr	[17,18]
Zr ₅ Zn ₃₉	Ce ₅ Mg ₄₁	mS88	C2/m(12)	11.4%Zr	[18]
ZrZn ₃	TiZn ₃	cP4	Pm $\bar{3}$ m(221)	25%Zr	[15]
ζ (FeZn ₁₃)	CoZn ₁₃	mS28	C2/m (12)	5.9-7.1%Fe	[19,20]
δ (FeZn ₁₀)	FeZn ₁₀	hP555	P6 ₃ mc (186)	8.1-13.2%Fe	[20,21]
Γ_1 (Fe ₅ Zn ₂₁)	Fe ₅ Zn ₂₁	cF408	F43m (216)	18.9-24%Fe	[20]
Γ (Fe ₃ Zn ₁₀)	Fe ₃ Zn ₁₀	cI52	I43m (217)	18-31%Fe	[20,21]
ZrFe ₂ Zn ₂₀	CeCr ₂ Al ₂₀	cF184	Fd $\bar{3}$ m (227)		[8]

materials, i.e., Fe and Zr powders and Zn chips, was 99.99 wt.%. The mixture of the raw materials, with the weight of each constituent precisely measured, was put into a tantalum inner corundum crucible, and then sealed in an evacuated quartz tube. Each sample was heated to 1100 °C and kept for 24 h, then quenched in water. During the course of the work, in order to minimize Zn loss and obtain a relatively compact sample, a bottom-quenching technique^[22] was used. The quenched samples were then resealed and annealed at 450, 600 and 800 °C for 40, 30 and 20 days, respectively, to ensure the establishment of an equilibrium state. The treatment was completed with rapid water quenching to preserve the equilibrium state at high temperature.

Sections of the specimens were prepared in the conventional way for metallographic examinations. A nital etching solution was used for revealing their microstructural details and a conventional optical microscope was used for the preliminary examination of all specimens. Detailed metallographic examinations and compositional analyses of various phases in the samples were performed using a JSM-6510 scanning electron microscope (SEM) equipped with an OXFORD INCA energy dispersive x-ray spectroscope (EDS). More precise determinations of the phase composition and the solubility were conducted using the wave dispersive x-ray spectroscopy (WDS). The compositions reported in this study were the averages of at least five measurements. In addition, some critical alloys were carefully studied by analyzing XRD patterns generated using a BEVKER-AXS/D8 advanced x-ray diffractometer with Cu K α -radiation and a step increase of 0.01° in the 2 θ angle.

To determine the transition point of the new compound, NETZSCH DSC 404 F3 high temperature calorimeter was used. In order to prevent oxidation and the evaporation of Zn during the heating, the specimens were sealed in evacuated quartz tubes. Vassilev^[23] used this method in study of Ni-Sn-Bi system. The DTA calibration was performed by measuring the heat of melting of pure elements (Bi, Zn, Al, Ag and Au) using the same working conditions. The base line was determined by performing measurements on two empty quartz tubes. And the temperature uncertainty was about ± 0.6 °C. The measurement was repeated three times.

Table 2 Alloys and phase compositions at 450 °C (at.%)

Alloys	Designed composition	Phase	Zn	Fe	Zr
A1	Zn93Fe5Zr2	ZrFe ₂ Zn ₂₀	87.1	8.4	4.5
		η -Zn	100.0	...	...
		ζ	92.7	7.3	...
A2	Zn90Fe8Zr2	ZrFe ₂ Zn ₂₀	86.9	8.8	4.3
		ζ	92.6	7.4	...
		δ	91.1	8.9	...
A3	Zn84Fe14Zr2	ZrFe ₂ Zn ₂₀	85.5	9.8	4.7
		δ	84.8	15.2	...
		Γ_1	81.1	18.9	...
A4	Zn75Fe24Zr1	ZrFe ₂ Zn ₂₀	85.2	9.9	4.9
		Γ_1	77.5	22.5	...
		Γ	71.2	28.8	...
A5	Zn67Fe32Zr1	ZrFe ₂ Zn ₂₀	85.1	9.8	5.1
		Γ	68.5	31.5	...
		α -Fe	4.8	95.2	...
A6	Zn94Fe3Zr3	ZrFe ₂ Zn ₂₀	87	8.2	4.8
		η -Zn	99.8	...	0.2
		ZrZn ₂₂	95.7	...	4.3
A7	Zn84Fe3Zr7	ZrFe ₂ Zn ₂₀	86.5	8.5	5.0
		ZrZn ₂₂	95.7	...	4.3
		Zr ₅ Zn ₃₉	88.1	...	11.9
A8	Zn73Fe3Zr13	ZrFe ₂ Zn ₂₀	86.3	8.6	5.1
		Zr ₅ Zn ₃₉	88.3	...	11.7
		ZrZn ₃	74.8	...	25.2
9	Zn80Fe15Zr10	ZrFe ₂ Zn ₂₀	85.7	9.2	5.1
		ZrZn ₃	74.2	...	25.8
		Zr ₂ Fe ₃ Zn ₅	49.2	29.6	21.2
A10	Zn80Fe30Zr6	ZrFe ₂ Zn ₂₀	85.2	9.8	5.0
		α -Fe	95.5	...	4.5
		Fe ₂₃ Zr ₆	12.3	66.2	21.5
A11	Zn87Fe9Zr5	ZrFe ₂ Zn ₂₀	86.3	9.0	4.7

3. Results and Discussion

3.1 Phase Equilibrium in Zn-Rich Corner at 450 °C

All phases and their chemical compositions detected in the three phase regions in the Zn-Fe-Zr alloys, after being annealed at 450 °C for 40 days, are summarized in Table 2. The ternary compound which had a narrow composition range of 4.3-5.1 at.%Zr, 8.4-9.9 at.%Fe and 85.1-87.1 at.%Zn was firmly identified. It can be approximately represented by stoichiometric formula of ZrFe₂Zn₂₀, which is the same as that reported by Gross et al.^[8] The ternary compound is similar to those existing in the Zn-Fe-Ti,^[24] Zn-Fe-Ni^[25] and Zn-Fe-Nb^[26] systems.

As shown in Table 2, ZrFe₂Zn₂₀ was in equilibria with all Zn-Fe binary compounds at 450 °C. Three phases were clearly distinguished in alloys A1-A5. ZrFe₂Zn₂₀ was more resistant to etching by nital and can be clearly distinguished from all Zn-Fe binary compounds. Figure 1 and 2 show the microstructures of alloys A2 and A5, which are located in the three-phase region of $\delta + \zeta + \text{ZrFe}_2\text{Zn}_{20}$ and $\alpha\text{-Fe} + \Gamma + \text{ZrFe}_2\text{Zn}_{20}$, respectively. SEM-WDS analysis indicated that no Zr was dissolved in any of the Zn-Fe

Fig. 1 BSE image of alloy A2 (Zn90Fe8Zr2). It consists of δ , ζ and $\text{ZrFe}_2\text{Zn}_{20}$

Fig. 2 BSE image of alloy A5 (Zn67Fe32Zr1). α -Fe, Γ and $\text{ZrFe}_2\text{Zn}_{20}$ coexist

Fig. 3 BSE image of alloy A7 (Zn84Fe3Zr7) consists of $\text{ZrFe}_2\text{Zn}_{20}$, ZrZn_{22} , and $\text{Zr}_5\text{Zn}_{39}$

Fig. 4 X-ray pattern of alloy A1 (Zn93Fe5Zr2)

Fig. 5 X-ray pattern of alloy A4 (Zn75Fe24Zr1)

binary compounds. As can be seen from the microstructure of alloy A7 in Fig. 3, $\text{ZrFe}_2\text{Zn}_{20}$ coexists with ZrZn_{22} and $\text{Zr}_5\text{Zn}_{39}$. $\text{ZrFe}_2\text{Zn}_{20}$ was more difficult to be etched than ZrZn_{22} , but less than $\text{Zr}_5\text{Zn}_{39}$ and ZrZn_3 . Fe was hardly detected in ZrZn_{22} , $\text{Zr}_5\text{Zn}_{39}$ and ZrZn_3 by SEM-WDS analysis.

To further identify the $\text{ZrFe}_2\text{Zn}_{20}$ phase and confirm the relative phase equilibrium states determined by SEM-WDS, the XRD patterns of some selective alloys were generated, as shown in Fig. 4-9. It needs to be noted that the patterns of single ζ , δ , Γ_1 and Γ were gathered from Cook and Grant^[20] and that of α -Fe, η -Zn, ZrZn_{22} and $\text{Zr}_5\text{Zn}_{39}$ were calculated from available crystal structure data from Samson^[17] and

Fig. 6 X-ray pattern of alloy A7 (Zn₈₄Fe₃Zr₇)

Fig. 7 X-ray pattern of alloy A8 (Zn₇₃Fe₃Zr₁₃)

from Chen and Jeitsehko^[18]. However, the XRD pattern of ZrZn_3 in Fig. 7 and 8(b) was generated from the Zn-25 at.%Zr alloy which was prepared by annealing the cold-pressed mixture of the Zn and Zr powders in evacuated tube at 700 °C for 30 days. Arroyave et al.^[15] first-principle calculated the enthalpies of formation for ZrZn_3 with the AB_3 -type structures. They believed that the cubic L1_2 structure is likely to be the ground state for the ZrZn_3 composition. However, it had no experiment supporting.

Fig. 8 (a) BSE image and (b) XRD pattern of alloy A9. It consists of three phases: ZrZn_3 , $\text{ZrFe}_2\text{Zn}_{20}$ and $\text{Zr}_2\text{Fe}_3\text{Zn}_5$. The peaks, denoted by dots, may belong to the $\text{Zr}_2\text{Fe}_3\text{Zn}_5$

The XRD pattern of $\text{ZrFe}_2\text{Zn}_{20}$ contained in all figures was generated from alloy A11. The alloy was prepared by the way described in Section 2 and was confirmed to be a single phase by SEM-EDS. As can be seen from Fig. 4-9, the characteristic peaks of $\text{ZrFe}_2\text{Zn}_{20}$ are clearly distinguished from all binary compounds in all alloys.

The TREOR program^[27] was used to index and calculate the pattern automatically and finally all peaks were indexed in the cubic system, resulting in the figure of merit, $M(40) = 26$, $F(40) = 30$. The lattice parameter of the crystal was 1.3941 nm, which agreed well with that reported by Gross et al.^[8] As discussed by Gross et al., both the $\text{ZrFe}_2\text{Zn}_{20}$ and ZrZn_{22} had the $\text{CeCr}_2\text{Al}_{20}$ -type structure. Therefore, the profiles of the XRD patterns of them were similar, as shown in Fig. 6. They had a difference of 0.45° (2θ) in all peaks with ZrZn_{22} having the larger lattice parameter of 1.4101 nm.^[17] The BSE image and XRD pattern of the alloys A7, shown in Fig. 3 and 6, respectively, indicated that $\text{ZrFe}_2\text{Zn}_{20}$ containing 9 at.% of Fe is a different phase from ZrZn_{22} .

Fig. 9 (a) BSE image and (b) XRD pattern of alloy A10. $\text{Fe}_{23}\text{Zr}_6$, $\text{ZrFe}_2\text{Zn}_{20}$ and $\alpha\text{-Fe}$ co-exist

Another ternary compound was found in alloy A9, as shown in Fig. 8(a). It coexisted with ZrZn_3 and $\text{ZrFe}_2\text{Zn}_{20}$ with a little color difference from ZrZn_3 . SEM-WDS analysis indicated that it contained 20 at.%Zr, 30 at.%Fe and 50 at.%Zn. Therefore, it was designated as $\text{Zr}_2\text{Fe}_3\text{Zn}_5$. An XRD pattern of alloy A9 in Fig. 8(b) clearly shows that there are some peaks, denoted by dots, not belong to the patterns of $\text{ZrFe}_2\text{Zn}_{20}$ or ZrZn_3 . They can not be indexed as attributable to any of binary compound in the system.

It is important to note that 12.3 at.%Zn was detected in the $\text{Fe}_{23}\text{Zr}_6$ phase in alloy A10. Three phases were clearly distinguished in the BSE image of alloy A10 in Fig. 9(a). And $\text{Fe}_{23}\text{Zr}_6$ was successfully index in the XRD pattern (Fig. 9b) but with 2θ difference of about 0.244° . It may be a ternary compound which has a crystal structure similar to $\text{Fe}_{23}\text{Zr}_6$ and needs further examination. At present, it was considered as $\text{Fe}_{23}\text{Zr}_6$.

Fig. 10 The Zn-rich corner of the Zn-Fe-Zr phase diagram at 450°C

Fig. 11 SEM image of alloy B1 ($\text{Zn}_{91}\text{Fe}_7\text{Zr}_2$)

Based on the experimental results obtained in this study and the information of relevant binary systems in the literatures, the 450°C isothermal section of the Zn-rich corner of the Zn-Fe-Zr system was constructed, as shown in Fig. 10. The ternary compound $\text{ZrFe}_2\text{Zn}_{20}$, which has a narrow composition range, is in equilibrium with all phases in the Zn-rich corner and is designated as T_1 .

3.2 Phase Equilibrium in Zn-Rich Corner at 600°C and 800°C

In the present work, phase equilibrium in the Zn-rich corner of the Zn-Fe-Zr system at 600°C was also investigated. Some typical SEM images and XRD patterns are clearly shown in Fig. 11-13. For concise, the BSE images and XRD patterns of the alloys which lie in the same ternary phase field with that at 450°C , i.e.,

Fig. 12 (a) BSE image and (b) XRD pattern of alloy B2 ($\text{Zn}_{83}\text{Fe}_{15}\text{Zr}_2$). δ , Γ and $\text{ZrFe}_2\text{Zn}_{20}$ were equilibrated in the alloy

$\text{ZrFe}_2\text{Zn}_{20} + \text{Zr}_5\text{Zn}_{39} + \text{ZrZn}_3$ and $\alpha\text{-Fe} + \text{ZrFe}_2\text{Zn}_{20} + \Gamma$, were not shown again.

The $\text{ZrFe}_2\text{Zn}_{20}$ phase stably existed at 600 °C and coexisted with all the compounds in the Zn-rich corner. ZrZn_{22} , ζ and Γ_1 were not found at this temperature which agrees well with the binary boundaries. The equilibria of $\delta + \text{Liq.} + \text{ZrFe}_2\text{Zn}_{20}$ in alloy B1 is shown in Fig. 11. It should be pointed out that the $\eta\text{-Zn}$ marked in the figure was the liquid phase at the annealing temperature. The BSE image and XRD pattern of alloy B2, which show the coexistence of $\delta + \Gamma + \text{ZrFe}_2\text{Zn}_{20}$, was shown in Fig. 12(a) and (b), respectively. The pattern of alloy A11 was used to index the $\text{ZrFe}_2\text{Zn}_{20}$ phase at 600 °C. SEM-WDS results in Table 3 suggested that Zr can not dissolve in δ and Γ at 600 °C. Besides, the XRD pattern of alloy B4 is shown in Fig. 13. Liquid, $\text{Zr}_5\text{Zn}_{39}$ and $\text{ZrFe}_2\text{Zn}_{20}$ were coexisting in the alloy. No Fe was detected in $\text{Zr}_5\text{Zn}_{39}$ and ZrZn_3 by

Fig. 13 XRD pattern of alloy B4 ($\text{Zn}_{92}\text{Fe}_3\text{Zr}_5$)

Table 3 Alloys and phase compositions at 600 °C (at.%)

Alloys	Designed composition	Phase	Zn	Fe	Zr
B1	$\text{Zn}_{91}\text{Fe}_7\text{Zr}_2$	$\text{ZrFe}_2\text{Zn}_{20}$	86.9	8.5	4.6
		δ	89.9	10.1	...
		$\eta\text{-Zn}$	97.9	2.1	...
B2	$\text{Zn}_{83}\text{Fe}_{15}\text{Zr}_2$	$\text{ZrFe}_2\text{Zn}_{20}$	85.4	9.6	5
		δ	85.3	14.7	...
		Γ	78.5	21.5	...
B3	$\text{Zn}_{67}\text{Fe}_{32}\text{Zr}_1$	$\text{ZrFe}_2\text{Zn}_{20}$	85	10.1	4.9
		Γ	67.8	32.2	...
		$\alpha\text{-Fe}$	17.4	82.3	0.3
B4	$\text{Zn}_{92}\text{Fe}_3\text{Zr}_5$	$\text{ZrFe}_2\text{Zn}_{20}$	87.2	8.3	4.5
		Liq.	97.8	...	2.2
		$\text{Zr}_5\text{Zn}_{39}$	87.7	...	12.3
B5	$\text{Zn}_{84}\text{Fe}_3\text{Zr}_{13}$	$\text{ZrFe}_2\text{Zn}_{20}$	86.1	8.7	5.2
		$\text{Zr}_5\text{Zn}_{39}$	87.4	...	12.6
		ZrZn_3	74.4	...	25.6
B6	$\text{Zn}_{75}\text{Fe}_{10}\text{Zr}_{15}$	$\text{ZrFe}_2\text{Zn}_{20}$	84.49	9.41	6.1
		ZrZn_3	69.95	28.45	1.6
		$\text{Zr}_2\text{Fe}_3\text{Zn}_5$	18.31	51.69	30.0

SEM-WDS analysis. The Zn-rich corner of the Zn-Fe-Zr system at 600 °C was outlined in Fig. 14.

As shown above, the $\text{ZrFe}_2\text{Zn}_{20}$ phase stably exists at 600 °C. The alloy A11, which was annealed at 450 °C for 40 days and confirmed to be a single phase, was used to determine the transition point of the $\text{ZrFe}_2\text{Zn}_{20}$ phase. The alloy was enclosed in an evacuated quartz tube in DTA examination to prevent oxidation and the evaporation of Zn. The DTA curve in Fig. 15 indicates that the transformation point of the $\text{ZrFe}_2\text{Zn}_{20}$ phase is 878.6 °C. At the same time,

Fig. 14 The Zn-rich corner of the Zn-Fe-Zr phase diagram at 600 °C

Fig. 16 The Zn-rich corner of the Zn-Fe-Zr phase diagram at 800 °C

Fig. 15 DTA curve of alloy A11, the single $\text{ZrFe}_2\text{Zn}_{20}$ phase, with heating rate of 5 °C/min

the equilibria of $\text{Liq.} + \alpha\text{-Fe} + \text{ZrFe}_2\text{Zn}_{20}$ and $\text{Liq.} + \text{ZrFe}_2\text{Zn}_{20} + \text{ZrZn}_3$ at 800 °C were observed in the present work. The Zn-rich corner of the Zn-Fe-Zr system at 800 °C was outlined in Fig. 16.

4. Conclusions

Based on SEM-EDS and WDS analyses and x-ray diffraction studies, the phase relationship in the Zn-rich corner of Zn-Fe-Zr ternary system at 450, 600 and 800 °C

was outlined in the present work. The solubility of Zr in four Fe-Zn compounds is too limited to be detected. And Fe can not be dissolved into the ZrZn_{22} , $\text{Zr}_5\text{Zn}_{39}$ and ZrZn_3 .

Two ternary compounds, designated as $\text{ZrFe}_2\text{Zn}_{20}$ and $\text{Zr}_2\text{Fe}_3\text{Zn}_5$ according their narrow chemical composition, were found in the system. DTA test indicated that $\text{ZrFe}_2\text{Zn}_{20}$ can stably exist below 878.6 °C. The XRD pattern of the single $\text{ZrFe}_2\text{Zn}_{20}$ phase was successfully indexed. It is a $\text{CeCr}_2\text{Al}_{20}$ -type compound with lattice parameter $a = 1.3941$ nm. $\text{ZrFe}_2\text{Zn}_{20}$ can be in equilibrium with all phases in the Zn-rich corner of the system. Moreover, $\text{Zr}_2\text{Fe}_3\text{Zn}_5$ was found coexisting with $\text{ZrFe}_2\text{Zn}_{20}$ and ZrZn_3 .

Acknowledgments

The authors gratefully acknowledge the financial support from Qinlan project, and National Natural Science Foundation of China (Nos. 50971110 and 50971111). Discussions with Dr. Nai-Yong Tang at Teck Metals are much appreciated.

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