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The phase equilibria in the Pr–Si–Zr ternary system at 773 K

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ABSTRACT

The phase relationships in the Pr–Si–Zr ternary system at 773 K have been investigated mainly by means of X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and differential thermal analysis (DTA). 9 binary compounds, i.e. Pr_5Si_3, Pr_5Si_4, PrSi, $PrSi_2$, $ZrSi_2$, ZrSi, Zr_5Si_4, Zr_3Si_2 and Zr_2Si were confirmed. The isothermal section of the Pr–Si–Zr ternary system at 773 K consists of 12 single-phase regions, 21 two-phase regions and 10 three-phase regions. None of the intermediate compound phases in this system exhibits a remarkable solid solution range at 773 K.

1. Introduction

Due to the favorable neutronic properties like low neutron absorption, good elevated-temperature mechanical properties and outstanding corrosion resistance in pressurized heavy water reactor condition, Zr-based alloys are used as important structural materials for reactor core components [1–3]. For the future nuclear reactors like gas fast reactors, the cores may work at high temperatures range from 500 °C to 1000 °C. Moreover, current trends towards extended burn-up of the nuclear fuel in pressurized water reactors have accentuated the demand for Zr-based alloys with higher uniform corrosion resistance under irradiation and high temperature mechanical properties [4]. The Zr_xSi_y was believed to be the potential structural materials for nuclear reactors [5]. Processing and characterization of Zr_3Si_2 have been studied. It is confirmed that the thermal properties (from room temperature to 1273 K) of Zr_3Si_2 satisfy the requirements related to gas fast reactors. On the other hand, as rare earth (RE) elements can greatly increase the properties (such as tensile strength, ductility and anti-creep properties) of alloys, they are widely used in industry [6–8].

Therefore, it is of academic interest to investigate the RE–Si–Zr alloy systems. However, up to now, very few information can be found on the RE–Si–Zr alloy systems. For the light RE–Si–Zr systems, the interaction of Pr with the Si and Zr elements was experimentally studied here for the first time.

It is reported that there are five binary compounds, i.e. Pr_5Si_3, Pr_5Si_4, PrSi, Pr_3Si_4 and $PrSi_2$, exist in the Pr–Si binary system at 773 K [9]. Five compounds, i.e. $ZrSi_2$, ZrSi, Zr_5Si_4, Zr_3Si_2 and Zr_2Si were observed in the Zr–Si system [10]. The Pr–Zr binary system [11] has been investigated in our previous work which shows that there is no binary compound at 773 K. The crystal structure data for the intermetallic compounds in the Pr–Si, Si–Zr and Pr–Zr binary systems at 773 K are given in Table 1.

2. Experimental details

2.1. Materials processing

All the 51 alloys buttons were prepared by arc melting on a water-cooled copper cast with a non-consumable tungsten electrode under pure argon atmosphere. Titanium was used as an O_2 getter during the melting process. Each sample was prepared with a total weight of 2 g by weighting appropriate of the pure components (Pr: 99.9 wt.%, Si: 99.99 wt.%, Zr: 99.95 wt.%). Each arc-cast button was melted three times and turned around after melting for better homogeneity. The homogenization temperature was determined by differential thermal analysis (DTA). For most alloys, the weight loss is less than 1% after melting.

All the melted alloy buttons were sealed in evacuated quartz tubes for homogenization heat treatment. The homogenize temperature at 1173 K for 360 h and cooled down to 773 K at a low cooling rate of 0.15 K/min during the heat treatment process, the high homogenize temperature and low cooling rate were chosen to ensure complete solid state transition of the as annealed samples. Finally, all these annealed buttons were quenched in liquid nitrogen.

2.2. Phase identifications

Considering that the Pr-rich alloys oxidize quickly in the air, the equilibrated samples were carefully treated in alcohol in every

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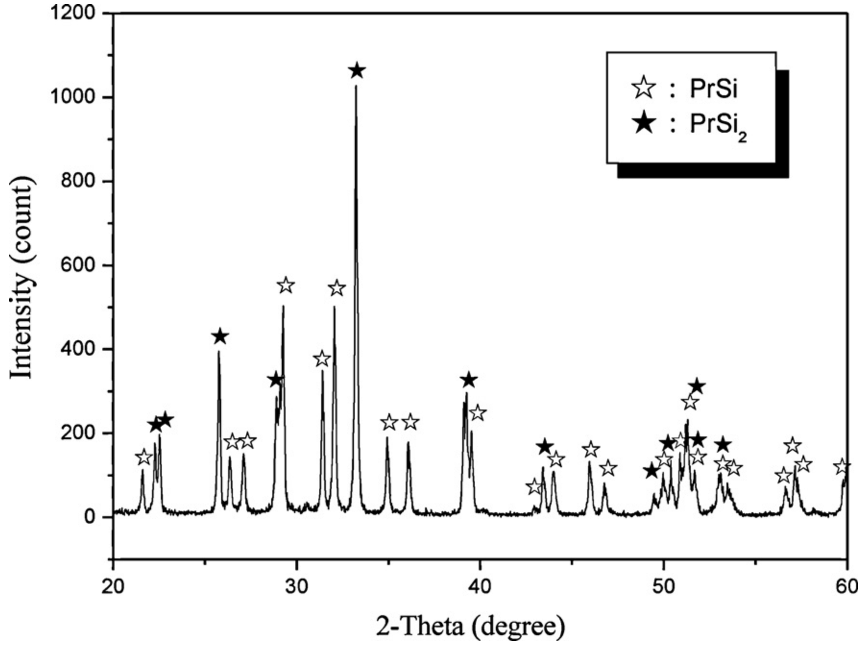

Fig. 1. XRD pattern of the equilibrated sample prepared with atomic proportion of Pr 42.9% and Si 57.1% (Pr_3Si_4) showing the existence of $PrSi_2$ and PrSi at 773 K.

Table 1
The crystal structure data of intermetallic compounds in the Pr–Si–Zr system at 773 K.

Compound	Space group	Lattice parameters (nm)			Reference
		a	*b*	*c*	
Pr_5Si_3	*I4/mcm*	0.7814(5)	–	1.374(2)	[12]
Pr_5Si_4	$P4_12_12$	0.790	–	1.491	[12]
PrSi	*Pnma*	0.8240	0.3941	0.5920	[12]
$PrSi_2$	$I4_1/amd$	0.4205(5)	–	1.373(2)	[12]
$ZrSi_2$	*Cmcm*	0.3721	1.468	0.3683	[12]
ZrSi	*Pnma*	0.6995(3)	0.3786(2)	0.5296(3)	[12]
Zr_5Si_4	$P4_12_12$	0.7123(1)	–	1.3002(1)	[12]
Zr_3Si_2	*P4/mbm*	0.7082	–	0.3714	[12]
Zr_5Si_3	$P6_3/mcm$	0.7903	–	0.5581	[12]
Zr_2Si	*I4/mcm*	0.6609(3)	–	0.5298(3)	[12]

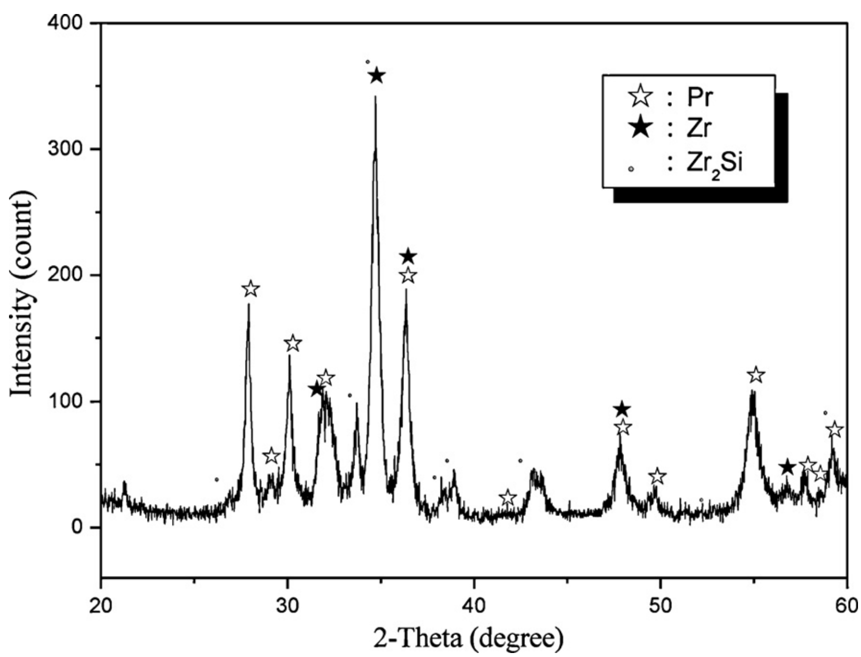

Fig. 2. XRD pattern of the equilibrated sample with atomic proportion of Pr 30%, Si 15% and Zr 55%, showing the phase equilibrium of Zr, Pr and Zr_2Si at 773 K.

Table 2
Details of the three-phase regions in the Pr–Si–Zr system at 773 K.

Phase regions	Alloy composition (at.%)			Phase composition
	Pr	Si	Zr	
1	15	75	10	$PrSi_2 + Si + ZrSi_2$
2	5	58	37	$PrSi_2 + ZrSi_2 + ZrSi$
3	35	55	10	$PrSi_2 + ZrSi + PrSi$
4	25	50	25	$ZrSi + PrSi + Zr_5Si_4$
5	40	48	12	$PrSi + Zr_5Si_4 + Pr_5Si_4$
6	39.8	42.4	17.8	$Zr_5Si_4 + Pr_5Si_4 + Pr_5Si_3$
7	14.7	40.8	44.5	$Zr_5Si_4 + Pr_5Si_3 + Zr_3Si_2$
8	30.1	36.7	33.2	$Pr_5Si_3 + Zr_3Si_2 + \alpha$-Pr
9	12.3	32.2	55	$Zr_3Si_2 + Pr + Zr_2Si$
10	30	15	55	$Zr + Pr + Zr_2Si$

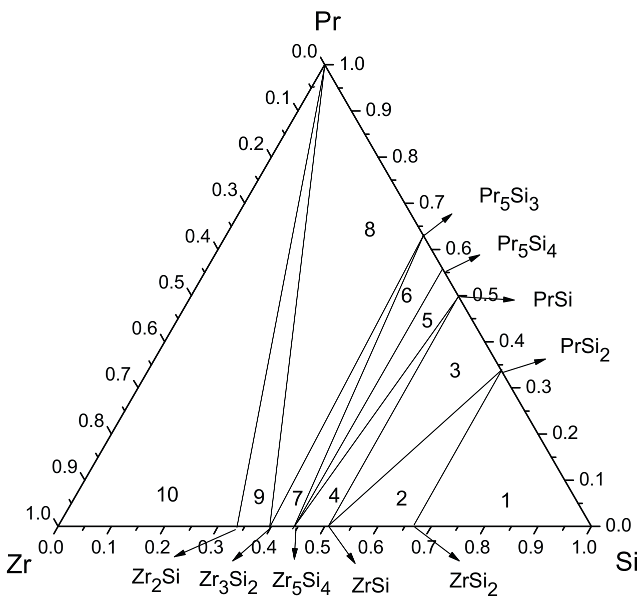

Fig. 3. The 773 K isothermal section of the Pr–Si–Zr ternary system.

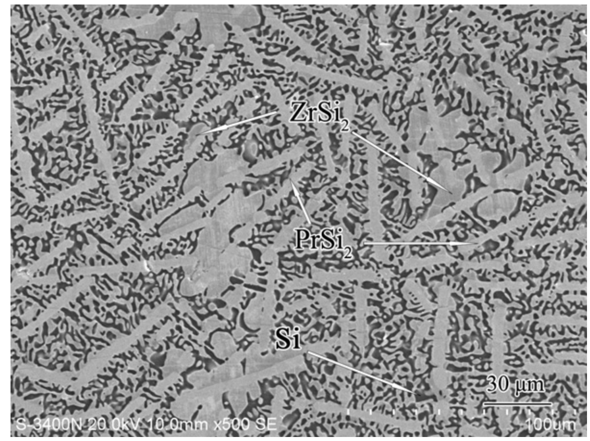

Fig. 5. SEM micrograph of the equilibrated Pr15Si75Zr10 sample at 773 K.

steps of the experiment. Possible oxidized surfaces of the samples were removed before grounding into powder, and then analyzed on a Rigaku D/Max-2500 V diffractometer with Cu Kα radiation and graphite monochromator. The scan ranges of the samples were from 20° to 60° (2θ) with a speed of 10°/min. The software Jade 5.0 and Powder Diffraction File (PDF release 2003) were used for phase identification [13]. Using the microstructural analysis to identify the phase compositions, the metallographic samples were cut from the samples and prepared using conventional grinding and mechanical polishing techniques. The polished samples were etched in an etchant with composition of HNO_3:HCl:water = 1:3:6 (ratio by volume). The images were obtained in the Hitachi S-3400 scanning electron microscope (SEM) equipped with energy dispersive X-ray analysis (EDX).

3. Results and discussion

3.1. Binary system

From Ref. [9], it is reported that in the Pr–Si system there exist five binary compounds, i.e. Pr_5Si_3, Pr_5Si_4, PrSi, Pr_3Si_4 and $PrSi_2$ at

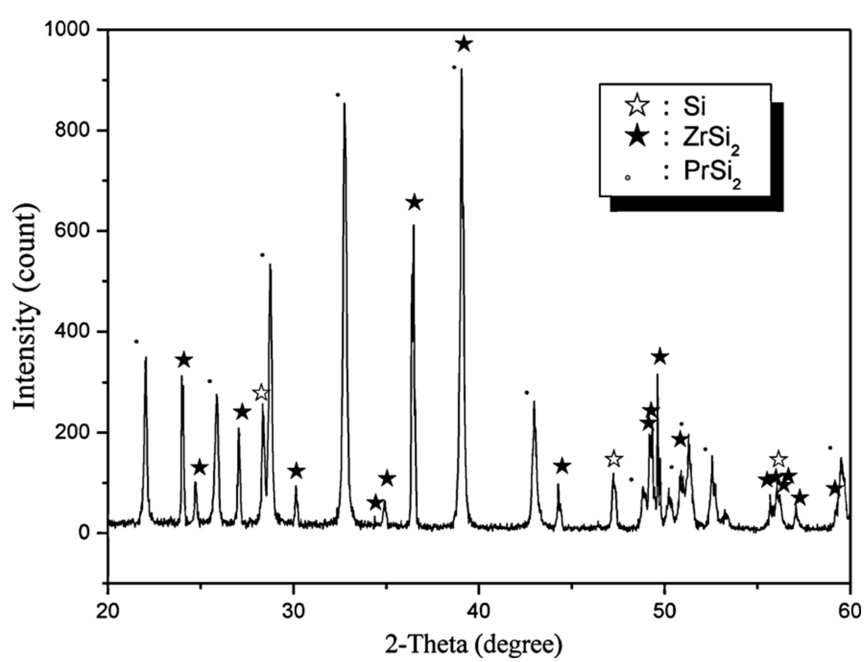

Fig. 4. The XRD pattern of the Pr15Si75Zr10 sample showing the equilibrium of $PrSi_2$, Si and $ZrSi_2$ at 773 K.

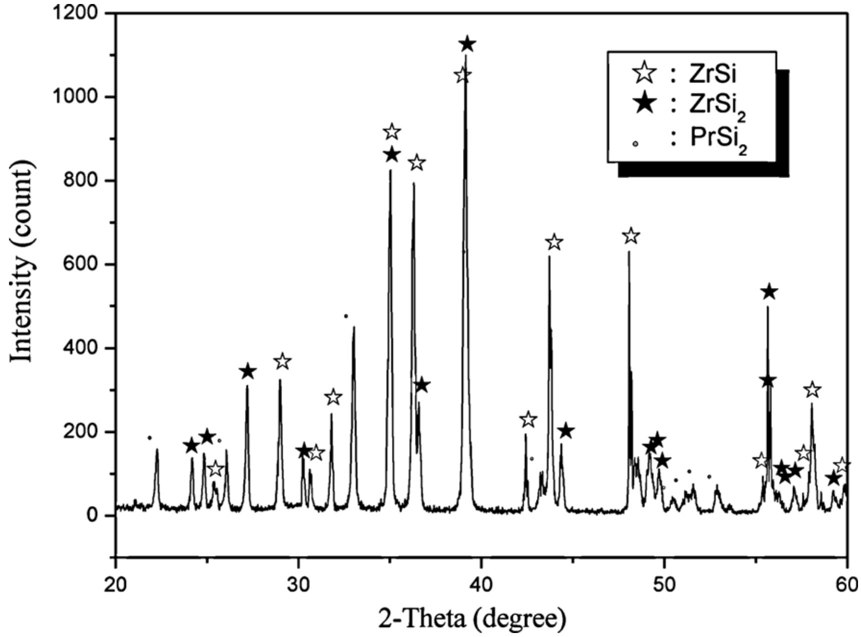

Fig. 6. XRD pattern of the equilibrated sample Pr5Si58Zr37 showing the equilibrium of $PrSi_2$, $ZrSi_2$ and ZrSi at 773 K.

773 K. In the present work, the Pr_3Si_4 was not found at 773 K. As shown in Fig. 1, the XRD pattern of the alloy Pr30Si40 shows two phases, i.e. $PrSi_2$ and PrSi. By all of the analysis results, this work confirms that four binary compounds, i.e. Pr_5Si_3, Pr_5Si_4, PrSi, and $PrSi_2$ exist in the Pr–Si system at 773 K.

Five compounds, i.e. $ZrSi_2$, ZrSi, Zr_5Si_4, Zr_3Si_2 and Zr_2Si, have been confirmed here for the Zr–Si system. The compound Zr_5Si_3 was not found in the present work at 773 K. Ref. [10] reported that Zr_5Si_3 exists in the temperature ranges from 2018 K to 2353 K and decomposes below 2018 K by the eutectoid reaction $Zr_5Si_3 \rightarrow Zr_3Si_2 + Zr_2Si$. Moreover, Zr_3Si was not found in this work. From the XRD pattern in Fig. 2, the equilibrated sample with atomic proportion of Pr 30%, Si 15% and Zr 55% consists three phases, i.e. Zr, Pr and Zr_2Si, which confirms that the binary compound Zr_3Si does not exist at 773 K.

3.2. Solid solubility

The phase-disappearing method and comparison of the shift of the XRD diffraction patterns of the samples near to the compositions of the binary phases have been employed to determine the solid solubility ranges of all of the single phases [14]. The results indicate that all the intermediate compound phases in this system do not have a remarkable solid solution at 773 K.

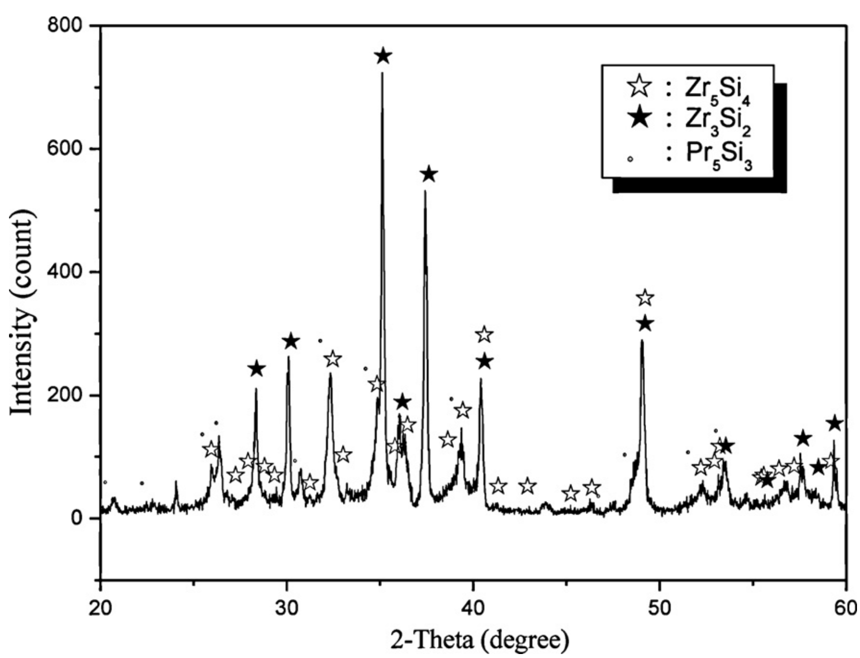

Fig. 7. The XRD pattern of the equilibrated sample Pr14.7Si44.8Zr40.5 showing the equilibrium of Zr_5Si_4, Pr_5Si_3 and Zr_3Si_2 at 773 K.

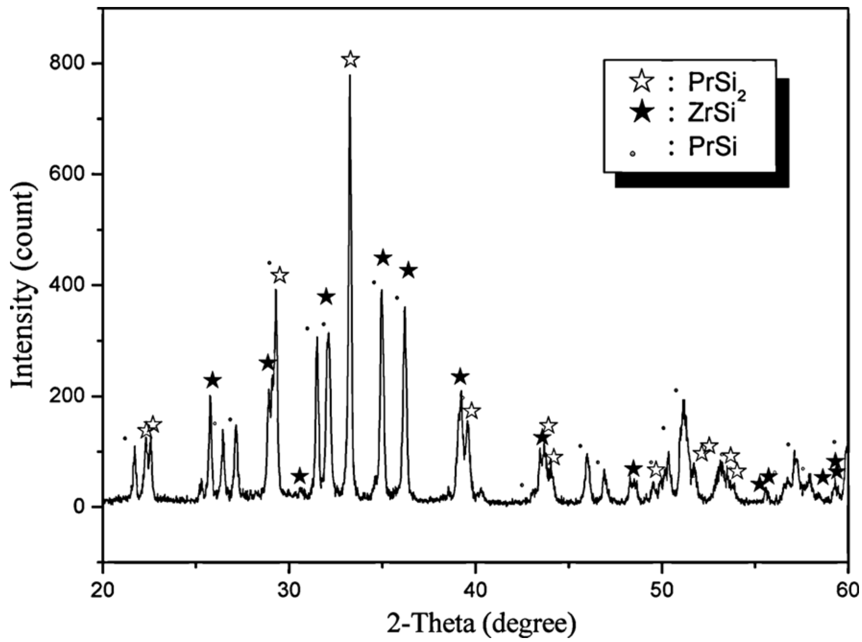

Fig. 8. The XRD pattern of the equilibrated sample Pr35Si55Zr10 showing the equilibrium of $PrSi_2$, ZrSi and PrSi at 773 K.

3.3. Isothermal section

Based on the results of phase analysis of XRD diffraction patterns of all the samples, the 773 K isothermal section of the Pr–Si–Zr ternary system was determined, as shown in Fig. 3. The isothermal section consists of 12 single-phase regions, 21 two-phase regions and 10 three-phase regions. The details of the three-phase regions and compositions of the typical alloys of the Pr–Si–Zr system at 773 K are shown in Table 2.

The X-ray diffraction patterns for some representative samples located in the three-phase regions are shown in Figs. 4–6. Fig. 4 illustrates that the sample Pr15Si75Zr10 located in the $PrSi_2 + Si + ZrSi_2$ three-phase region, and the SEM photograph in Fig. 5 also clearly indicates the existence of the above phases (identified by EDX). Fig. 6 indicates that the sample Pr5Si58Zr37 located in the $PrSi_2 + ZrSi_2 + ZrSi$ three-phase region. Fig. 7 shows that the equilibrated sample of Pr14.7Si40.8Zr44.5 consists of three phases namely Zr_5Si_4, Pr_5Si_3 and Zr_3Si_2. Figs. 8–10 illustrate the equilibrated samples Pr35Si55Zr10, Pr40Si42.2Zr17.8 and Pr25Si50Zr25 located in the $PrSi_2 + ZrSi + PrSi$, $Zr_5Si_4 + Pr_5Si_4 + Pr_5Si_3$ and $PrSi + Zr_5Si_4 + Pr_5Si_4$ three-phase regions, respectively.

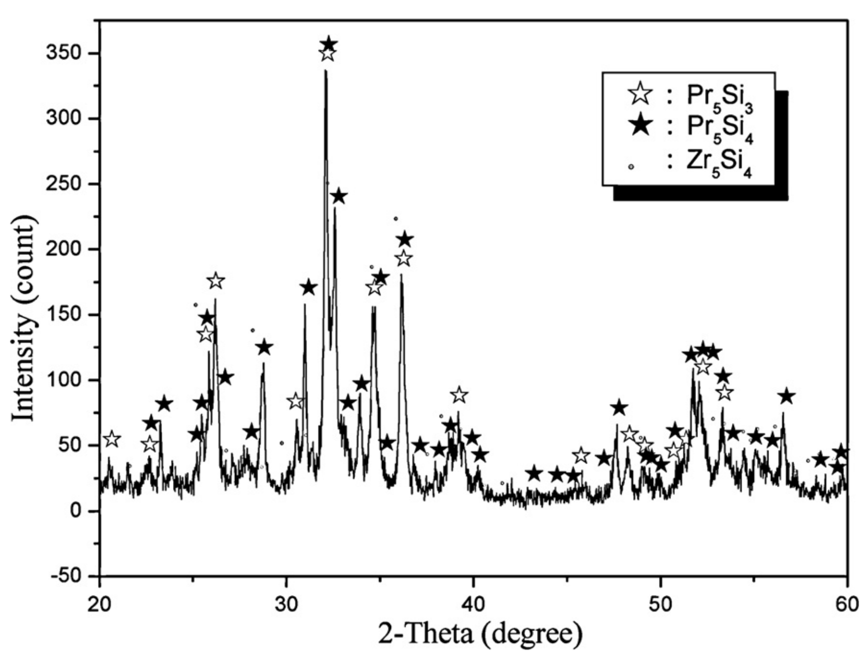

Fig. 9. The XRD pattern of the equilibrated sample Pr40Si42.2Zr17.8 showing the equilibrium of Zr_5Si_4, Pr_5Si_4 and Pr_5Si_3 at 773 K.

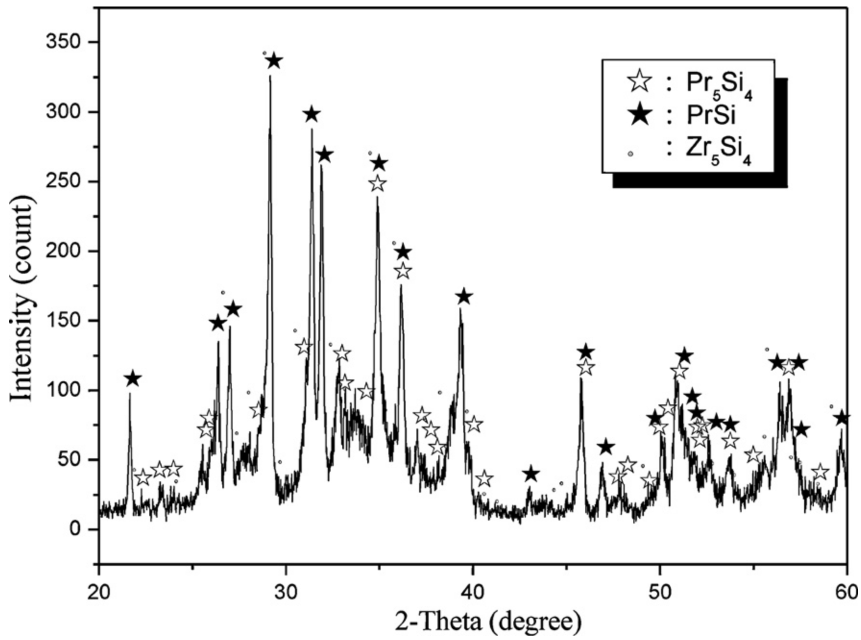

Fig. 10. The XRD pattern of the equilibrated sample Pr25Si50Zr25 showing the equilibrium of PrSi, Zr_5Si_4 and Pr_5Si_4 at 773 K.

4. Conclusions

In this work, the phase relationships of the Pr–Si–Zr ternary system at 773 K have been determined using equilibrated alloy method. 9 binary compounds, i.e. Pr_5Si_3, Pr_5Si_4, PrSi, $PrSi_2$, $ZrSi_2$, ZrSi, Zr_5Si_4, Zr_3Si_2 and Zr_2Si were confirmed. The Pr–Si–Zr ternary system isothermal section at 773 K consists of 12 single-phase regions, 21 two-phase regions and 10 three-phase regions. All the intermediate compound phases in this system do not show remarkable solid solution at 773 K. No intermediate compound phase in the Pr–Zr binary system and no ternary compound in the Pr–Si–Zr ternary system have been found at 773 K.

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