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Phase equilibria of the Al–Pr–Zr ternary system at 773 K

Jia She [a], Yongzhong Zhan [a,*], Chunliu Li [a], Yong Du [b], Honghui Xu [b], Yuehui He [b]

[a] Laboratory of Nonferrous Metal Materials and New Processing Technology, Ministry of Education, Guangxi University, Nanning, Guangxi 530004, PR China
[b] State Key Laboratory of Powder Metallurgy, Central South University, Changsha, Hunan 410083, PR China

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ABSTRACT

The phase equilibria of the Al–Pr–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). The 14 binary compounds, i.e. $AlZr_3$, $AlZr_2$, Al_2Zr_3, Al_3Zr_4, AlZr, Al_3Zr_2, Al_2Zr, Al_3Zr, α-$Al_{11}Pr_3$, Al_3Pr, Al_2Pr, β-AlPr, $AlPr_2$ and β-$AlPr_3$ were confirmed. No binary compound was found in the Pr–Zr binary system. The result shows that the isothermal section of the Al–Pr–Zr ternary system at 773 K consists of 17 single-phase regions, 31 two-phase regions and 15 three-phase regions. All the intermediate compounds phases in this system have not a remarkable solid solution at 773 K. No ternary compound is found in this work.

1. Introduction

Al–based and Zr–based bulk metallic glasses (BMGs) have absorbed more and more attentions for their potential applications [1,2]. These bulk metallic glasses have such promising properties as high yield strength, hardness, and elastic strain limit, along with relatively high fracture toughness, fatigue resistance and corrosion resistance. Furthermore, the Al-based bulk metallic glasses showed very high tensile strength. Some Al-based amorphous alloys have high tensile strength, as much as 1000 MPa, which is about two times higher than that of conventional aluminum alloys [1]. On the other hand, the Zr-base bulk metallic glasses have been used to produce sport instruments and have promising application as structural materials. Many bulk metallic glasses have been found in the Al–Zr–TM (TM = transition metals) multi-component systems [3]. It is reported that rare earth elements (RE), i.e. Pr and Ce added in the Al–Zr–TM bulk metallic glasses can greatly increase the properties of alloys such as tensile strength, ductility and anti-creep properties [4]. Phase diagrams are regarded as the "maps" for materials scientists to design new materials. Using equilibrated alloys to determine phase diagram is a traditional, important and widely used method. The obtained phase equilibria are important experimental data for the optimization of thermodynamic parameters, which in turn can be utilized for calculation of phase diagrams (CALPHAD). Therefore, there is an interest in the phase diagrams of relevant alloy systems, namely Al–Zr–RE ternary system.

The structure of aluminum rich Al–Zr alloys was studied by Fink and Willey [5,6], who found only two phases, i.e. Al_3Zr and an Al–Zr solid solution. A full phase diagram of the Al–Zr system has been compiled by McPherson and Hansen [7]. The phase equilibria in the Al–Zr system have been studied [8–10]. There are eight intermetallic phases namely $AlZr_3$, $AlZr_2$, Al_2Zr_3, Al_3Zr_4, AlZr, Al_3Zr_2, Al_2Zr and Al_3Zr reported at 773 K. The Al–Pr binary system is mainly described in Refs. [11–14]. This system is characterized by six intermediate phases, i.e. α-$Al_{11}Pr_3$, Al_3Pr, Al_2Pr, AlPr, $AlPr_2$ and β-$AlPr_3$ at 773 K. The Pr–Zr binary system has not been reported yet. The reported crystal structure data for the intermetallic compounds in the Al–Zr, Al–Pr and Pr–Zr binary systems at 773 K are given in Table 1. Up to now, however, the phase relationship of the Al–Pr–Zr ternary system has not been reported yet. This paper was undertaken to investigate the phase relationships of the Al–Pr–Zr ternary system as well as the intermediate compound in the Pr–Zr binary system mainly be means of experimental methods.

2. Experimental

2.1. Materials processing

All the 59 alloy buttons were produced 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 1.5 g by weighing appropriate of the commercially available pure components (Al 99.9 wt.%, Zr 99.95 wt.%, Pr 99.95 wt.%). Each arc-cast button had been melted three times and turned around after melting for better homogeneity. The homogenization temperature was determined by differential thermal analysis (DTA) as well as the reported binary phase diagrams. For most alloys, the weight loss was less than 1% after melting.

All the melted alloy buttons were sealed in evacuated quartz tubes for homogenization heat treatment. The alloys at the Al rich corner were homogenized at 900 K for 960 h and the rest alloys were homogenized at 1173 K for 360 h, and then cooled

* Corresponding author. Tel.: +86 771 3272311; fax: +86 771 3233530.
E-mail address: zyzmatres@yahoo.com.cn (Y. Zhan).

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

Compound	Space group	Lattice parameters (nm)			Reference
		a	*b*	*c*	
$AlZr_3$	$Pm\bar{3}m$	0.43917(1)	–	–	[15]
$AlZr_2$	$P6_3/mmc$	0.4894	–	0.5928	[15]
Al_2Zr_3	$P4_2/mnm$	0.7630(1)	–	0.69981(2)	[15]
Al_3Zr_4	$P\bar{6}$	0.5433(2)	–	0.5390(2)	[15]
AlZr	*Cmcm*	0.3353	1.0866	0.4266	[15]
Al_3Zr_2	*Fdd*2	0.9601(0	1.3906(20	0.5574(2)	[15]
Al_2Zr	$P6_3/mmc$	0.43601(2)	–	0.87482(5)	[15]
Al_3Zr	*I*4/*mmm*	0.4005	–	1.7285	[15]
α-$Al_{11}Pr_3$	*Immm*	0.4446	1.2949	1.0005	[15]
Al_3Pr	$P6_3/mmc$	0.65111	–	0.4605	[15]
Al_2Pr	$Fd\bar{3}m$	0.7967	–	–	[15]
β-AlPr	*Cmcm*	0.922	0.764	0.570	[15]
$AlPr_2$	*Pnma*	0.6729	0.5248	0.9759	[15]
β-$AlPr_3$	$Pm\bar{3}m$	0.4962(6)	–	–	[16]

down to 773 K at a rate of 9 K/h and maintained for more than 240 h. Finally, all these annealed buttons were quenched in liquid nitrogen.

2.2. Phase identifications

The equilibrated samples were ground 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 [17]. Samples for scanning electron microscopy (HITACHI S-3400N) with energy dispersive spectrometer (EDS) were cut from the samples. Then the samples were prepared using conventional techniques of grinding and mechanical polishing. The samples were etched in the liquor with composition of 1 ml HF, 3 ml HNO_3 and 100 ml water.

3. Results and discussions

3.1. Phase analysis and solid solubility

3.1.1. Al–Zr system

In the previous work [18], all eight binary compounds, i.e. $AlZr_3$, $AlZr_2$, Al_2Zr_3, Al_3Zr_4, AlZr, Al_3Zr_2, Al_2Zr and Al_3Zr have been confirmed at 773 K in the Al–Zr system and well agree with the work in Ref. [8]. In this work, the XRD pattern of the alloy with the atomic proportion Al 30%, Pr 20% and Zr 50% (shown in Fig. 1) shows that there is no Al_3Zr_5 phase. Therefore, this result again approve that the Al_3Zr_5 is a high temperature phase, which agrees with the result of Okamoto [10]. The binary compound Al_4Zr_5 also has a high temperature transformation at about 1273 K and from Fig. 2 the result shows that Al_4Zr_5 did not exist at 773 K, which is in accordance with the result of Rigaud et al. [9] and Okamoto [10]. The existences of these two binary compounds at 773 K have also been studied on the analysis of the equilibrated samples with the stoichiometric compositions.

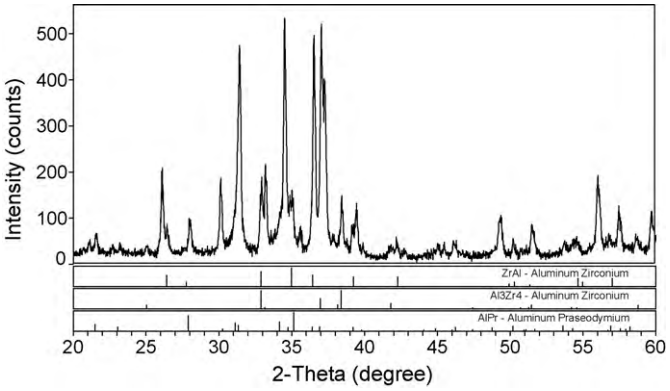

Fig. 2. The XRD pattern of the equilibrated sample prepared with the atomic proportion of Al 47.8%, Pr 17.2% and Zr 35%.

3.1.2. Al–Pr system

In the Al–Pr system, all the six compounds, i.e. α-$Al_{11}Pr_3$, Al_3Pr, Al_2Pr, β-AlPr, $AlPr_2$ and β-$AlPr_3$ at 773 K were confirmed here, which agrees well with Ref. [12]. In Ref. [12], the phase β-$Al_{11}Pr_3$ exists at temperatures higher than 1238 K. From Fig. 3, it is clear that the XRD patterns of the equilibrated alloy with composition of Al 76 at.%, Pr 14 at.% and Zr 10 at.% consists of three phases, i.e. α-$Al_{11}Pr3$, Al_3Pr and Al_3Zr. Thus it is confirmed that the β-$Al_{11}Pr_3$ phase does not exist at 773 K. SEM micrograph of this sample clearly

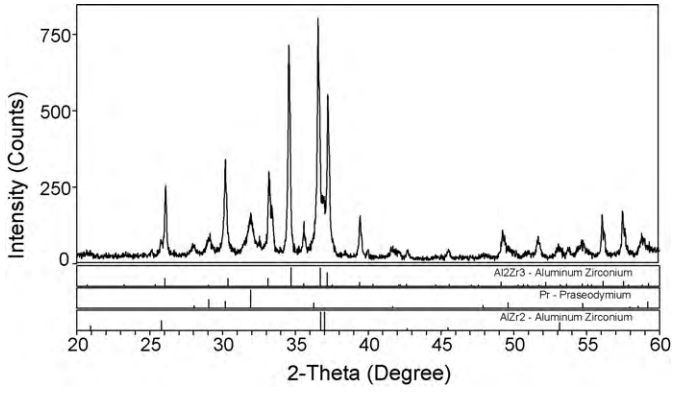

Fig. 1. The XRD pattern of the equilibrated sample prepared with the atomic proportion of Al 30%, Pr 20% and Zr 50%.

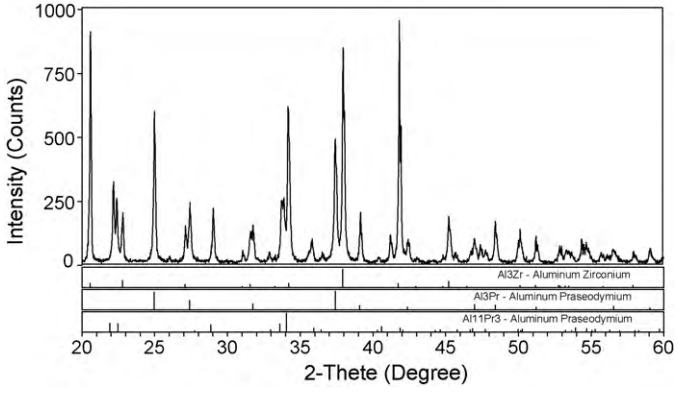

Fig. 3. The XRD pattern of the equilibrated sample prepared with the atomic proportion of Al 76%, Pr 14% and Zr 10%.

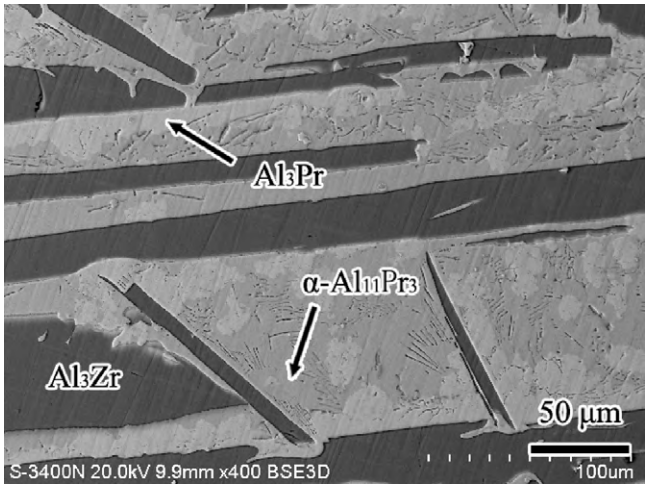

Fig. 4. The SEM micrograph of the equilibrated alloy with the atomic proportion of Al 76%, Pr 14% and Zr 10%.

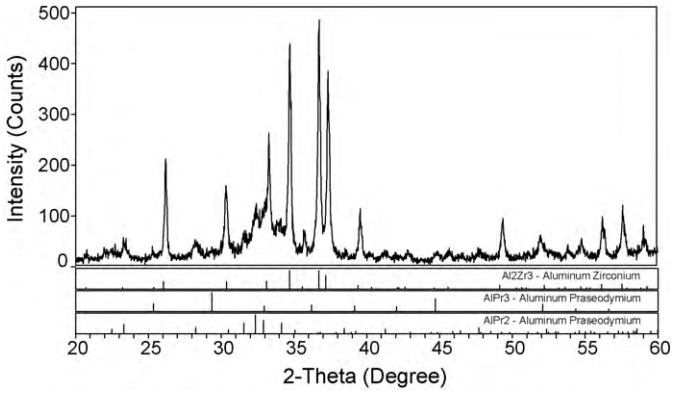

Fig. 5. The XRD pattern of the equilibrated alloy prepared with the atomic proportion of Al 37%, Pr 20% and Zr 43%.

indicates the existence of three phases (Fig. 4). EDX result indicates that the pale phase is Al_3Pr, the gray one is α-$Al_{11}Pr_3$ and the dark phase is Al_3Zr. From Fig. 5, the XRD pattern of the equilibrated alloy (Al 37%, Pr 20% and Zr 43%) consists of the patterns of three phases, i.e. β-$AlPr_3$, $AlPr_2$ and Al_2Zr_3. Thus it is confirmed that the phase α-$AlPr_3$ does not exist at 773 K.

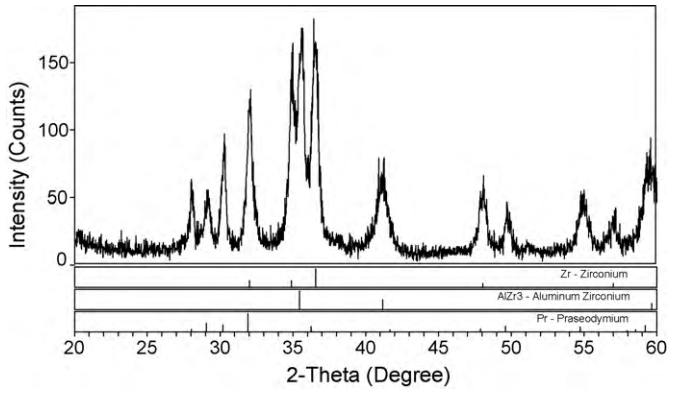

Fig. 6. The XRD pattern of the equilibrated sample prepared with the atomic proportion of Al 10%, Pr 30% and Zr 60%.

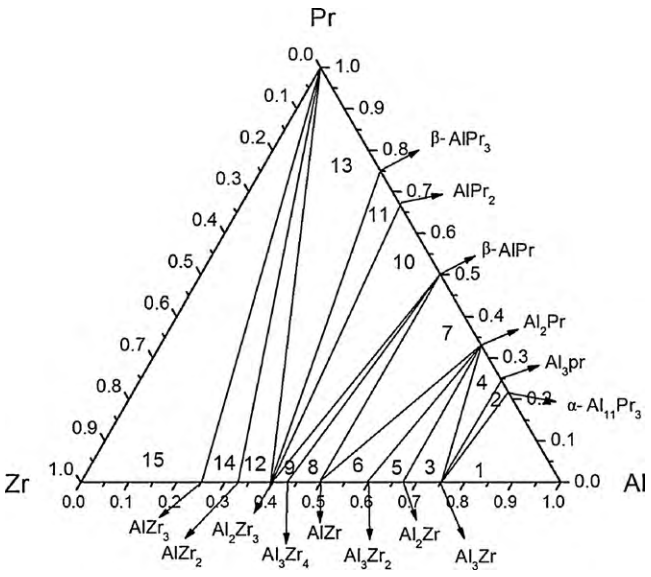

Fig. 7. The 773 K isothermal section of the Al–Pr–Zr ternary system.

3.1.3. Pr–Zr system

As the Pr–Zr binary system has not been reported, the present work was carried out to verify the existence of any intermediate compounds in this system. All the experimental results have shown that no binary compound exists in the Pr–Zr system. As an example, the XRD pattern of the equilibrated alloy with the atomic proportion of Al 10%, Pr 30% and Zr 60% (shown in Fig. 6) indicates that it locates in the α-Pr + $AlZr_3$ + α-Zr three-phase region, which clearly shows that there is no binary compound exists in the Pr–Zr binary system.

3.1.4. Solid solubility

The phase-disappearing method and comparing the shift of the XRD 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 [19]. The results indicate that none of the intermediate compounds in this system has a remarkable solid solution at 773 K.

3.2. Isothermal section

Based on the result of phase analysis of XRD patterns of all the samples, the 773 K isothermal section of the Al–Pr–Zr ternary sys-

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

Phase regions	Alloy composition (at.%)			Identified phases
	Al	Pr	Zr	
1	80	10	10	Al + α-$Al_{11}Pr_3$ + Al_3Zr
2	76	14	10	α-$Al_{11}Pr_3$ + Al_3Pr + Al_3Zr
3	69	14	17	Al_2Pr + Al_3Zr + Al_2Zr
4	72	20	8	Al_3Pr + Al_2Pr + Al_3Zr
5	65	10	25	Al_2Pr + Al_3Zr_2 + Al_2Zr
6	55	5	40	Al_2Pr + AlZr + Al_3Zr_2
7	60	30	10	Al_2Pr + β-AlPr + AlZr
8	47.8	17.2	35	β-AlPr + Al_3Zr_4 + AlZr
9	45	20	35	β-AlPr + Al_3Zr_4 + Al_2Zr_3
10	42	23	35	β-AlPr + $AlPr_2$ + Al_2Zr_3
11	37	20	43	β-$AlPr_3$ + $AlPr_2$ + Al_2Zr_3
12	25	30	45	α-Pr + $AlZr_2$ + Al_2Zr_3
13	33	20	47	α-Pr + β-$AlPr_3$ + Al_2Zr_3
14	25	15	60	α-Pr + $AlZr_3$ + $AlZr_2$
15	10	30	60	α-Pr + $AlZr_3$ + α-Zr

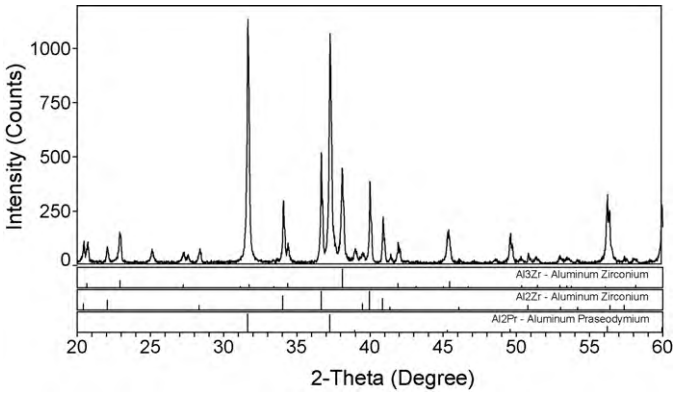

Fig. 8. The XRD pattern of the equilibrated sample prepared with the atomic proportion of Al 69%, Pr 14% and Zr 17%.

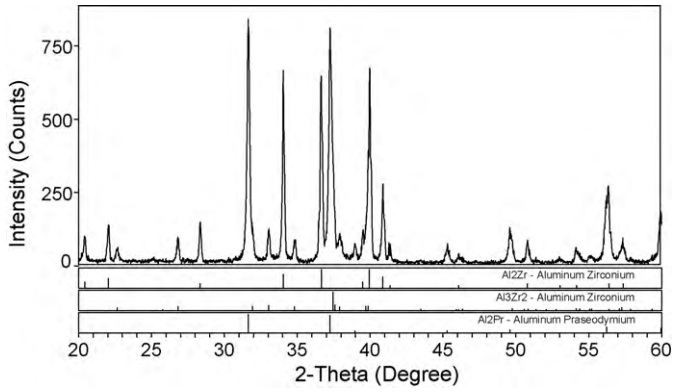

Fig. 9. The XRD pattern of the equilibrated sample prepared with the atomic proportion of Al 65%, Pr 10% and Zr 25%.

tem has been determined, as shown in Fig. 7. The isothermal section consists of 17 single-phase regions, 31 two-phase regions and 15 three-phase regions. The details of the three-phase regions and compositions of the typical alloys of the Al–Pr–Zr system at 773 K are shown in Table 2.

The XRD patterns of some representative samples located in some three-phase regions are shown in Figs. 8–11. Fig. 8 illustrates the XRD pattern of the sample Al69Pr14Zr17 located in the $Al_3Pr + Al_2Pr + Al_3Zr$ three-phase region. Fig. 9 illustrates

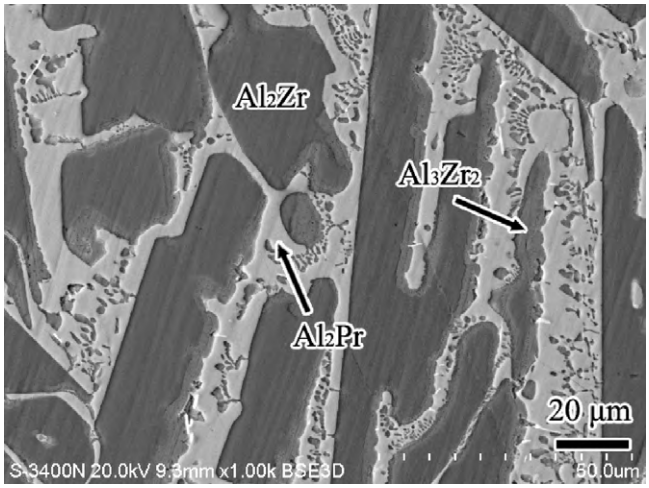

Fig. 10. SEM micrograph of the equilibrated alloy with the atomic proportion of Al 65%, Pr 10% and Zr 25%.

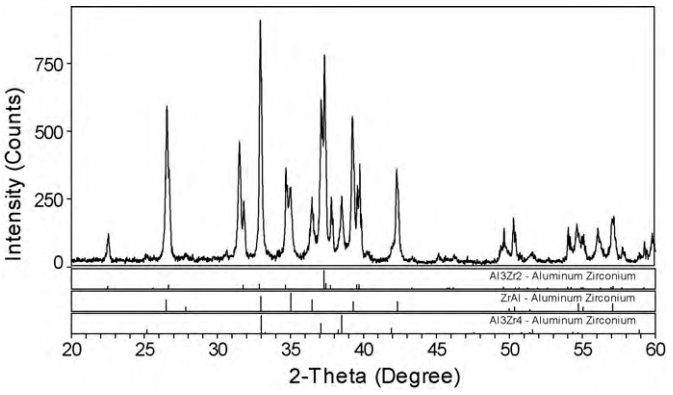

Fig. 11. The XRD pattern of the equilibrated sample prepared with the atomic proportion of Al 55%, Pr 5% and Zr 40%.

the XRD pattern of the sample Al65Pr10Zr25 located in the $Al_2Pr + Al_3Zr_2 + Al_2Zr$ three-phase region (Fig. 10). SEM micrograph clearly indicates the existence of three phases which have been indicated by EDX to be Al_2Pr, Al_3Zr_2 and Al_2Zr, respectively. Fig. 11 illustrates the XRD pattern of the sample Al55Pr5Zr40 located in the $Al_2Pr + AlZr + Al_3Zr_2$ three-phase region.

4. Conclusions

In this work, the 14 binary compounds, i.e. $AlZr_3$, $AlZr_2$, Al_2Zr_3, Al_3Zr_4, AlZr, Al_3Zr_2, Al_2Zr, Al_3Zr, α-$Al_{11}Pr_3$, Al_3Pr, Al_2Pr, β-AlPr, $AlPr_2$ and β-$AlPr_3$ are confirmed. No binary compound is found in the Pr–Zr binary system at 773 K. The isothermal section of the Al–Pr–Zr ternary system at 773 K consists of 17 single-phase regions, 31 two-phase regions and 15 three-phase regions. None of the intermediate compounds phases in this system has a remarkable solid solution at 773 K. No ternary compound is found in the present work.

Acknowledgements

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References

[1] B.A. Sun, M.X. Pan, D.Q. Zhao, W.H. Wang, X.K. Xi, M.T. Sandor, Y. Wu, Scripta Mater. 59 (2008) 1159–1162.
[2] S.H. Xie, X.R. Zeng, H.X. Qian, J. Alloys Compd. 480 (2009) L37–L40.
[3] Q. Wang, C. Dong, J.B. Qiang, Y.M. Wang, Mater. Sci. Eng. A 449–451 (2007) 18–23.
[4] C.Z. Zhang, X.F. Bian, J. Guo, S.H. Wang, K.K. Song, C.D. Wang, B. Zhang, J. Alloys Compd. 436 (2007) 95–98.
[5] W.L. Fink, L.A. Willey, Trans. Am. Inst. Min. Metall. Eng. 133 (1939) 69–79.
[6] W.L. Fink, L.A. Willey, Metals Handbook, American Society for Metals, Metals Park, OH, 1948, p1168.
[7] D.J. McPherson, M. Hansen, Trans. Am. Soc. Met. 46 (1954) 354–374.
[8] M. Poetzschke, K. Schubert, Z. Metallkd. 53 (1962) 548–561.
[9] V. Rigaud, B. Sundman, D. Daloz, G. Lesoult, CALPHAD 33 (2009) 442–449.
[10] H. Okamoto, J. Phase Equilib. 23 (2002) 455–456.
[11] K.H.J. Buschow, J.H.N. Van Vucht, Z. Metallkd. 57 (1966) 162.
[12] A.H. Gomes de Mesquita, K.H.J. Buschow, Acta Crystallogr. 22 (1967) 497.
[13] M.E. Drits, E.S. Kadaner, N.D. Shoa, Izv. Akad, Nauk SSSR Met. 1 (1969) 219.
[14] K.H.J. Buschow, J.H.N. Van, Vucht, Philips Res. Rep. 22 (1967) 233.
[15] P. Villars, Pearson's Handbook of Crystallographic Data, ASM International, Materials Park, OH, 1997.
[16] K.H.J. Buschow, J.H.N. Van Vuch Philips, Res. Rep. 22 (1967) 233–245.
[17] Materials Data JADE Release 5.0, XRD Pattern Processing, Materials Data Inc., Livermore, CA, 2003.
[18] Z. Hu, Y. Zhan, J. She, Y. Du, H. Xu, J. Alloys Compd. 491 (2010) 200–202.
[19] Y. Zhan, Y. Du, Y. Zhuang, in: J.-C. Zhao (Ed.), Methods for Phase Diagram Determination, 1st ed., Elsevier Science Press, Amsterdam, The Netherlands, 2007, pp. 108–150.