Journal of Alloys and Compounds 507 (2010) 62–66

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Phase equilibria in the ternary Al–Zr–La system

Dan Peng[a], Yongzhong Zhan[a,*], Jia She[a], Mingjun Pang[a], Yong Du[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

ARTICLE INFO

Article history:
Received 5 July 2010
Accepted 10 July 2010
Available online 23 July 2010

Keywords:
Metals and alloys
Phase diagrams
X-ray diffraction
Scanning electron microscope

ABSTRACT

The phase relationships in the Al–Zr–La ternary system at 773 K have been investigated for the first time mainly by means of X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy dispersive analysis (EDX). The existence of the Al_4La_5 and $AlLa_2$ binary compounds has been confirmed in this ternary system. The isothermal section consists of 18 single-phase regions, 33 two-phase regions and 16 three-phase regions. No ternary compound was observed in this work.

1. Introduction

Aluminum alloys are widely used in aerospace and automobile industries due to their low density, good mechanical properties, high corrosion and wear resistance, and lower thermal coefficient of expansion [1–3]. Zirconium based alloys are used extensively in the nuclear industry. They have distinct advantages of low neutron absorption cross-section coupled with required mechanical properties and good corrosion resistance, which makes them indispensable as structural materials in thermal reactors. Formation of Al_3Zr precipitates in aluminum alloys has been used for a long time, especially in alloys for aerospace applications (such as AA7000 series) [4]. The stronger covalence Al–Zr bond in Al_3Zr is not easily to be broken down by dislocation cutting and thus can hinder dislocation moving. In other words, the strong Al–Zr covalent bond network can greatly strengthen the matrix of Al alloys [5].

Al–R (rare-earth) alloys have been investigated for a long time due to their interesting physical properties and possibility of commercial application. As the solubility of R in aluminum is very low, the mixture of Al with Al_3R ($Al_{11}R_3$) is always important for the design of new materials [6]. These intermetallic compounds show rather outstanding electrical and magnetic properties. For example, Al_3Ce and Al_2Ce are considered to be model systems in the investigations of “heavy fermions”. Kondo effect and peculiarities in phase transitions of the second order were found for these and similar Al–R compounds at low temperatures [7–9]. It is a common place for many works that rare-earth elements exist in the R^{3+} or R^{2+} states in Al-based alloys [10]. It means that the magnetic moment per R-atom in the alloys is the same as that for pure R and 4f-electrons which are not involved into chemical bonds formation. However, this idea has to be checked experimentally, especially for high temperatures.

In order to discover further application characteristics of the aluminum and zirconium alloys, it is necessary to investigate the phase relationships in the Al–Zr–RE ternary systems. However, up to now very few information can be found on the ternary system of the Al–Zr–La. This work was undertaken to experimentally investigate on the phase diagram of this ternary system and shed light on the phase equilibrium information.

In Refs. [11–13], the binary phase diagrams of Al–Zr, Al–La and Zr–La systems have been reported. Eight binary compounds, i.e. Al_3Zr, Al_2Zr, Al_3Zr_2, AlZr, Al_3Zr_4, Al_2Zr_3, $AlZr_2$ and $AlZr_3$ are shown in the Al–Zr binary phase diagram at 773 K. For the Al–La binary system, five intermediate phases namely $AlLa_3$, AlLa, $AlLa_2$, Al_3La and $Al_{11}La_3$ have been reported in the previous binary phase diagram at 773 K. In addition the existence of Al_4La_5 [14], a new compound $AlLa_2$ has been reported in the previous literature [15]. There is no binary compound reported in the Zr–La system. Structural data for the intermetallic compounds in the three binary systems are given in Table 1.

2. Experimental procedure

Each sample was prepared with a total weight of 1.5 g by weighing appropriate of the pure components (Al 99.9 wt.%, Zr 99.99 wt.% and La 99.99 wt.%). Sixty-one alloy buttons were made in an electric arc furnace under an argon atmosphere and a water-cooled copper crucible. Titanium was used as an oxygen getter during the melting process. The alloys were re-melted four times in order to achieve complete fusion and homogeneous composition. For most alloys, the weight loss is less than 1% after melting.

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

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2010.07.133

Table 1
Crystallographic data of the binary phases in the ternary Al–Zr–La system.

Compound	Conditions (°C)	Space group	Lattice parameters (nm)			Reference
			a	*b*	*c*	
Al_3Zr	<980	I4/*mmm*	0.4005	–	1.7285	[16]
			0.400967		1.729368	This work
Al_2Zr	<1250	P6$_3$/*mmc*	0.52824 (5)	–	0.87482 (5)	[16]
			0.528334		0.874973	This work
Al_3Zr_2	<1480	*Fdd*2	0.9601 (2)	1.3906 (2)	0.5574 (2)	[16]
			0.95831	1.386968	0.556662	This work
AlZr	<1275	*Cmcm*	0.3353	1.0866	0.4266	[16]
			0.33516	1.08361	0.426421	This work
Al_3Zr_4	<1030	$P\bar{6}$	0.5433 (2)	–	−0.5390 (2)	[16]
			0.542897		0.534973	This work
Al_2Zr_3	<1275	P4$_2$/*mnm*	0.7630 (1)	–	0.6998 (1)	[16]
			0.763362		0.703534	This work
$AlZr_2$	<1595	P6$_3$/*mmc*	0.4894	–	0.5928	[16]
			0.485921		0.593844	This work
$AlZr_3$	<1490	$Pm\bar{3}m$	0.43917 (1)	–	–	[16]
			0.438000			This work
$Al_{11}La_3$	<915	*Immm*	0.4431	1.3142	1.0132	[17]
			0.443219	1.31573	1.013753	This work
Al_3La	<1170	*P*6$_3$/*mmc*	0.6667	–	0.4616	[18]
			0.666098		0.462609	This work
Al_2La	<1405	$Fd\bar{3}m$	0.81489	–	–	[19]
			0.814267			This work
AlLa	<873	*Cmem*	0.9531 (6)	0.7734 (6)	0.5809 (5)	[20]
Al_4La_5	–	$P\bar{6}2m$	0.9163	–	1.1231	[14]
$AlLa_2$	–	Tetragonal	1.70942 (1)	–	0.53790 (3)	[15]
$AlLa_3$	520–400	$Pm\bar{3}m$	0.5093	–	–	[21]
			0.510014			This work

The melted alloys were sealed in an evacuated quartz tube containing titanium chips as an oxygen getter. The tube was placed in a resistance furnace for homogenization treatment and then annealed at different temperatures in order to attain good homogenization. The heat treatment temperature of the alloys was determined by differential thermal analysis (DTA) results of some typical ternary alloys or based on previous works of the three binary phase diagrams. The alloys at the Al-rich corner or those contained $AlLa_3$ phase were homogenized at 873 K for 960 h, and the rest alloys were homogenized at 1173 K for 360 h. Then all of them were cooled down to 773 K at a rate of 9 K/h and maintained for more than 240 h. Finally, all these annealed alloys were quenched in liquid nitrogen.

Finally, the equilibrated samples in the Al–Zr–La system were determined from X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive analysis (EDX). Samples for XRD analyses were firstly powdered and then analyzed on a Rigaku D/Max-2500 V diffractometer with CuKα radiation and graphite monochromator operated at 40 kV, 200 mA. The Materials Data Inc. software Jade 5.0 and Powder Diffraction File (PDF release 2004) were used for phase identification. Some typical alloys were analyzed by optical microscopy (OM) and SEM.

3. Results and discussion

3.1. Phase analysis and solid solubility

In this work, the binary systems Al–Zr, Al–La and Zr–La at 773 K have been studied to identify the binary compounds before the analysis of the ternary system.

Eight binary compounds, i.e. Al_3Zr, Al_2Zr, Al_3Zr_2, AlZr, Al_3Zr_4, Al_2Zr_3, $AlZr_2$ and $AlZr_3$, have been confirmed in the Al–Zr binary system at 773 K, which agrees well with the other works [11,22].

In the present work, seven binary compounds, i.e. $AlLa_3$, $AlLa_2$, Al_4La_5, $AlLa_3$, AlLa, $AlLa_2$, Al_3La and $Al_{11}La_3$, have been confirmed at 773 K in the Al–La system which agrees well with the previous works [12,14,15]. To our knowledge, two binary compounds (i.e. $AlLa_2$ and Al_4La_5) and their crystal structural data have been reported [14,15]. The XRD pattern of the equilibrated sample which contains 33.5 at.% Al and 66.5 at.% La clearly indicates the existence of the $AlLa_2$ phase. It is noted that there are some minor unknown peaks (which has been labeled in the figure) exist, as illustrated in Fig. 1. This unknown crystal structure needs additional study. The existence of the Al_4La_5 compound was also confirmed in this work. As an example, the XRD pattern of the equilibrated alloy with atomic proportion of 43 at.% Al, 23 at.% Zr and 34 at.% La shows the existence of the Al_4La_5 phase, as shown in Fig. 2. This result is in accordance with that reported in Refs. [14,15].

In the Zr–La system, it is confirmed here that no binary compounds exists. This result is in good agreement with that reported in Ref. [13]. Moreover, in the present work, no ternary compounds have been found in the Al–Zr–La ternary system at 773 K.

Fig. 3 illustrates the XRD patterns of the equilibrated Al86Zr10La4 alloy and Al85Zr5La10 alloy. The results indicate the existence of three phases, i.e. $Al_{11}La_3$, Al_3Zr and Al. It is clear from Fig. 4 that the equilibrated alloys Al72Zr16La12 and Al70Zr5La25 consist of three phases, i.e. Al_2La, Al_3Zr and Al_3La. From Fig. 5, it can be observed that, at 773 K, there are three phases in the alloys of Al55Zr40La5 and Al62Zr20La18, i.e. Al_3Zr_2, AlZr and Al_2La. Another two equilibrated alloys of Al54Zr22La24 and Al57Zr15La28 consist of the patterns of three phases, i.e. AlZr, AlLa and Al_2La, as shown in Fig. 6.

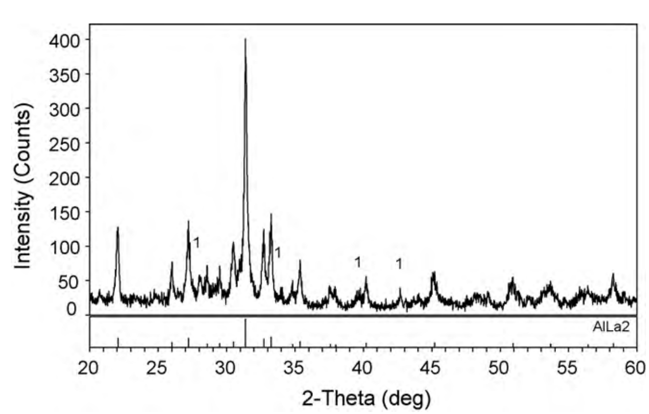

Fig. 1. The XRD patterns of the equilibrated sample with atomic proportion of 33.5 at.% Al and 66.5 at.% La showing the existence of $AlLa_2$ single phase.

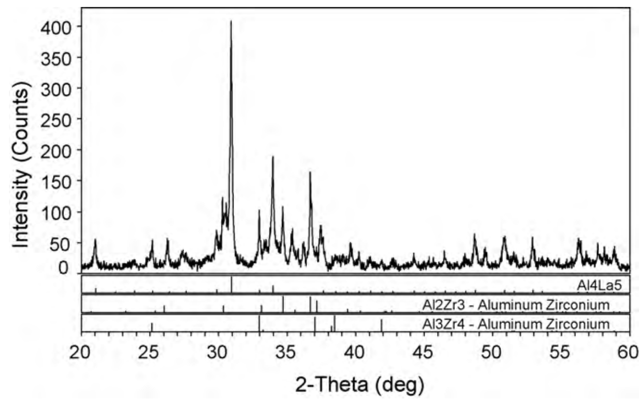

Fig. 2. The XRD pattern of the equilibrated sample prepared with atomic proportion of 43 at.% Al, 23 at.% Zr and 34 at.% La.

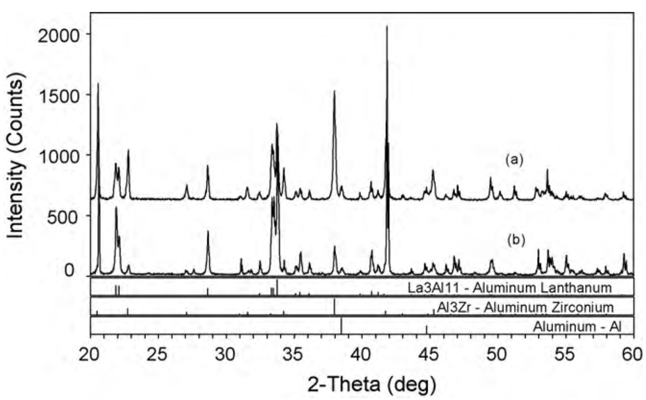

Fig. 3. The XRD patterns of two equilibrated Al–Zr–La ternary samples with compositions of (a) 86 at.% Al, 10 at.% Zr and 4 at.% La, and (b) 85 at.% Al, 5 at.% Zr and10 at.% La.

It is clear from Fig. 7 that the equilibrated alloy with composition of 68 at.% Al, 22 at.% Zr and 10 at.% La consists of three phases, i.e. Al_3Zr, Al_2Zr and Al_2La. SEM result also clearly shows the existence of these three phases (Fig. 8). EDX result indicates that the pale phase is Al_2La, the gray one is Al_2Zr, and the rest is Al_2Zr (which is surrounded by the Al_3Zr phase).

The solid solubility ranges of all of the single phases were determined using the phase-disappearing method and by comparing the shift of the XRD patterns of the samples near to the compositions of the binary phases have been employed to determine [23]. The results showed that the diffraction patterns did not shift and the diffraction patterns of the second phase could easily be detected when the composition of the alloys deviated from its single-phases region by 1.0 at.%. Therefore, none of these phases in this system revealed a remarkable homogeneity range at 773 K.

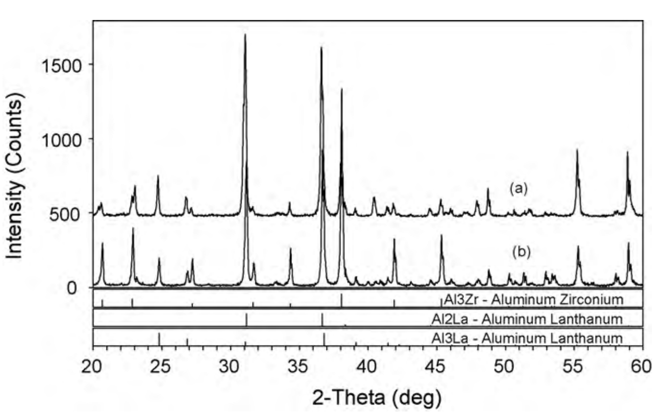

Fig. 4. The XRD patterns of two equilibrated Al–Zr–La ternary samples with compositions of (a) 72 at.% Al, 10 at.% Zr and 18 at.% La, and (b) 70 at.% Al, 5 at.% Zr and 25 at.% La.

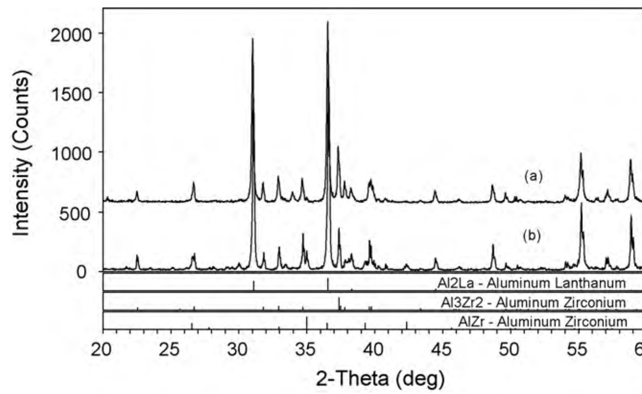

Fig. 5. The XRD patterns of two equilibrated Al–Zr–La ternary samples with compositions of (a) 55 at.% Al, 40 at.% Zr and 5 at.% La, and (b) 62 at.% Al, 20 at.% Zr and 18 at.% La.

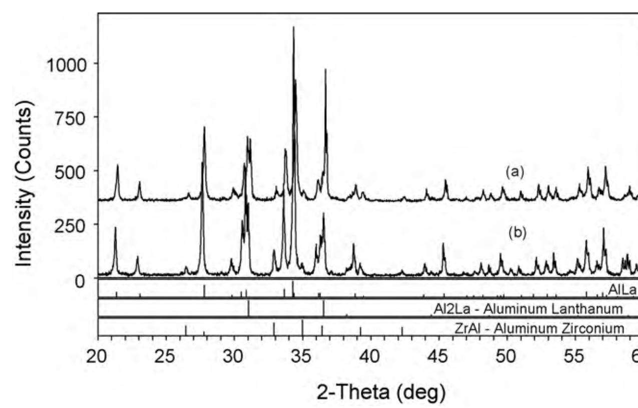

Fig. 6. The XRD patterns of two equilibrated Al–Zr–La ternary samples with compositions of (a) 54 at.% Al, 22 at.% Zr and 24 at.% La, and (b) 57 at.% Al, 15 at.% Zr and 28 at.% La.

3.2. Isothermal section

The isothermal section of the ternary Al–Zr–La system at 773 K was determined by XRD, SEM and optical microscopy. Fig. 9 indicates a part of the investigated compositions within the Al–Zr–La system in this work. The isothermal sec-

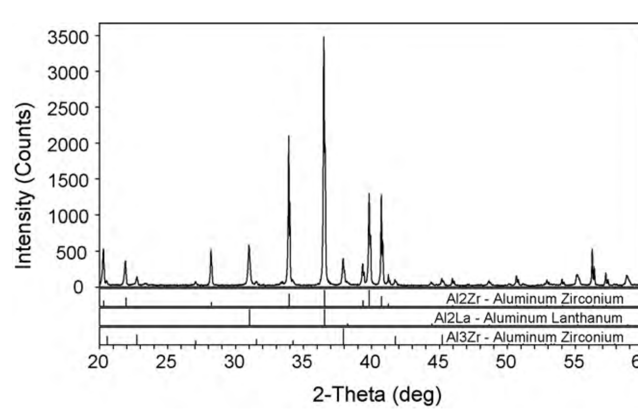

Fig. 7. The XRD pattern of the equilibrated sample prepared with atomic proportion of 68 at.% Al, 22 at.% Zr and 10 at.% La.

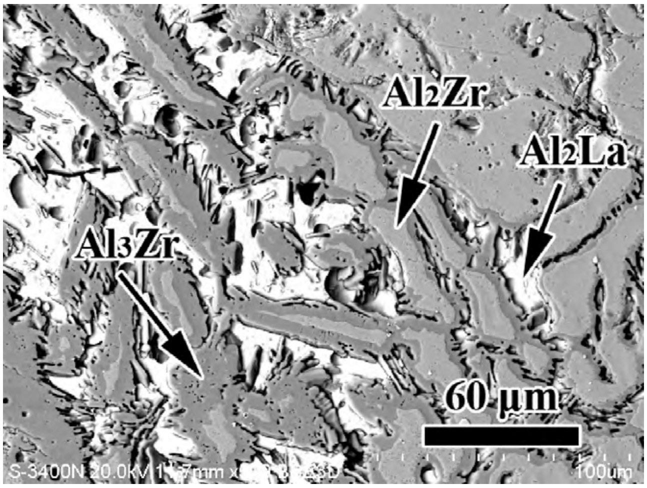

Fig. 8. The SEM micrograph of the equilibrated alloy containing 68 at.% Al, 22 at.% Zr and 10 at.% La.

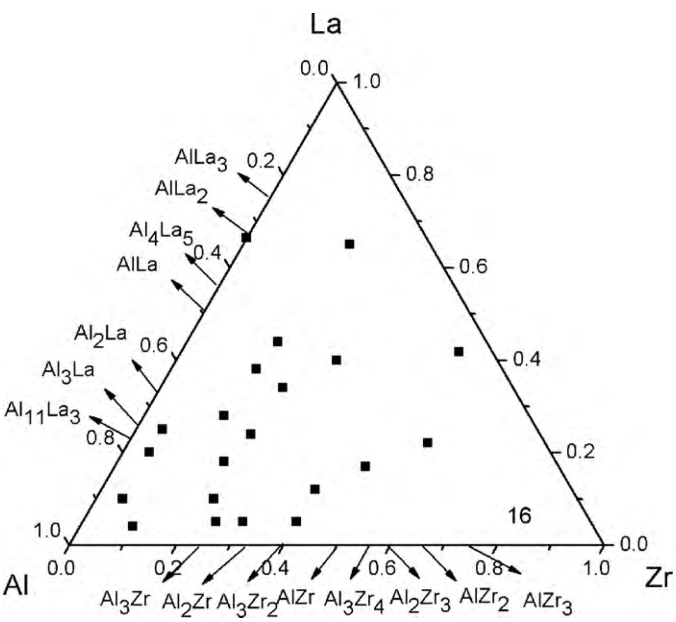

Fig. 9. The compositions of the typical ternary Al–Zr–La samples annealed at 773 K.

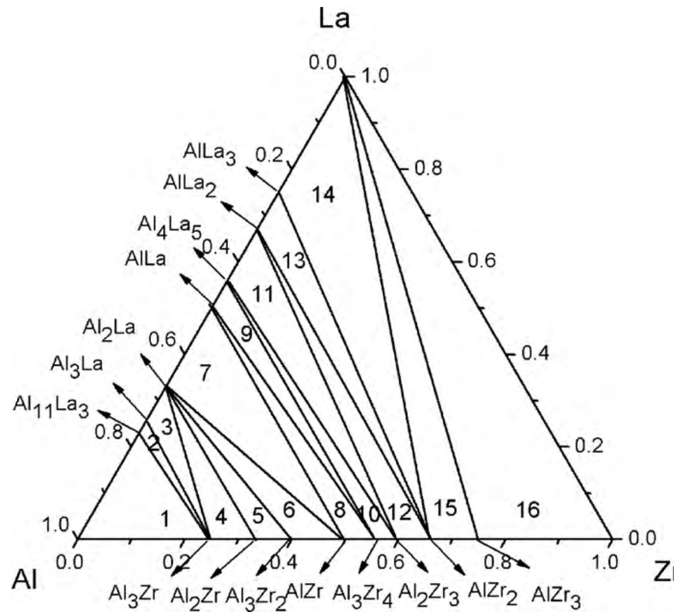

Fig. 10. The 773 K isothermal section of the Al–Zr–La ternary system.

tion, shown in Fig. 10, consists of 18 single-phase regions, 33 binary-phase regions and 16 ternary-phase regions. The following three-phase equilibria namely $Al + Al_{11}La_3 + Al_3Zr$, $Al_3La + Al_{11}La_3 + Al_3Zr$, $Al_3La + Al_2La + Al_3Zr$, $Al_2La + Al_2Zr + Al_3Zr$, $Al_2La + Al_2Zr + Al_3Zr_2$, $Al_2La + Al_3Zr_2 + AlZr$, $AlLa + Al_2La + AlZr$, $AlLa + AlZr + Al_3Zr_4$, $AlLa + Al_4La_5 + Al_3Zr_4$, $Al_4La_5 + Al_2Zr_3 + Al_3Zr_4$, $Al_4La_5 + AlLa_2 + Al_2Zr_3$, $AlLa_2 + AlZr_2 + Al_2Zr_3$, $AlZr_2 + AlLa_3 + AlLa_2$, $AlZr_2 + AlLa_3 + La$, $AlZr_3 + AlZr_2 + La$ and $AlZr_3 + La + Zr$, have been determined at 773 K. Details of the three-phase regions and compositions of the typical alloys are given in Table 2. No ternary compounds were found in this system.

Table 2
Details of the three-phase regions and compositions of the typical alloys in the Al–Zr–La system at 773 K.

Phase region	Typical alloy composition (at.%)			Phase composition
	Al	Zr	La	
1	86	10	4	$Al + Al_{11}La_3 + Al_3Zr$
2	75	5	20	$Al_3La + Al_{11}La_3 + Al_3Zr$
3	70	5	25	$Al_3La + Al_2La + Al_3Zr$
4	70	25	5	$Al_2La + Al_2Zr + Al_3Zr$
5	65	30	5	$Al_2La + Al_2Zr + Al_3Zr_2$
6	62	20	18	$Al_2La + Al_3Zr_2 + AlZr$
7	54	22	24	$AlLa + Al_2La + AlZr$
8	48	40	12	$AlLa + AlZr + Al_3Zr_4$
9	46	16	38	$AlLa + Al_4La_5 + Al_3Zr_4$
10	43	23	34	$Al_4La_5 + Al_2Zr_3 + Al_3Zr_4$
11	39	17	44	$Al_4La_5 + AlLa_2 + Al_2Zr_3$
12	36	47	17	$AlLa_2 + AlZr_2 + Al_2Zr_3$
13	30	30	40	$AlZr_2 + AlLa_3 + AlLa_2$
14	15	20	65	$AlZr_2 + AlLa_3 + La$
15	22	56	22	$AlZr_3 + AlZr_2 + La$
16	12	55	33	$AlZr_3 + La + Zr$

4. Conclusions

In this work, 15 binary compounds, i.e. Al_3Zr, Al_2Zr, Al_3Zr_2, $AlZr$, Al_3Zr_4, Al_2Zr_3, $AlZr_2$, $AlZr_3$, $AlLa_3$, $AlLa$, $AlLa_2$, Al_3La, $Al_{11}La_3$, Al_4La_5 and $AlLa_2$, were confirmed. The phase equilibria of the ternary Al–Zr–La system at 773 K have been determined. The existence of the two binary compounds Al_4La_5 and $AlLa_2$ was confirmed in the isothermal section. No ternary compound is found in the ternary system. The isothermal section consists of 18 single-phase regions, 33 two-phase regions and 16 three-phase regions. Remarkable homogeneity range for all phases was not observed.

Acknowledgement

This work is supported by the National Natural Science Foundation of China (Grant No. 50831007).

References

[1] D.L. McDanels, Metall. Trans. A 16 (1985) 1105–1115.
[2] B. Ralph, H.Y. Yuen, W.B. Lee, J. Mater. Process. Technol. 63 (1997) 339–353.
[3] M.K. Surappa, P.K. Rohatgi, J. Mater. Sci. 16 (1981) 983–993.
[4] A. Deschamps, L. Lae, P. Guyot, J. Acta Mater. 55 (2007) 2775–2783.
[5] Y.J. Gao, Q.F. Mo, J. Mater. Sci. 499 (2009) 299–303.
[6] N.P. Lyakishev (Ed.), Phase Diagrams for Binary Metallic Systems, vol. 1, Moscow, Mashinostroenie, 1996, pp. 991 (in Russian).
[7] L. Degiorgi, Rev. Mod. Phys. 71 (3) (1999) 690.
[8] D.E. MacLaughlin, M.S. Rose, B.-L. Young, J. Phys. B: Condens. Mater. 326 (2003) 387–389.
[9] R.E. Majewski, A.S. Edelstein, A.E. Dwight, J. Appl. Phys. 50 (B3) (1979) 2336.
[10] K.N.R. Taylor, Adv. Phys. 20 (1971) 551.

[11] H. Okamoto, J. Phase Equilibria 23 (2002) 455–456.
[12] T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kacprzak (Eds.), Alloy Phase Diagrams 2 (1990) 1718–1719.
[13] H. Okamoto, J. Phase Equilibria 3 (1992) 162.
[14] N.M. Belyavina, V.Ya. Markiv, V.V. Zavodyanny, J. Alloy Compd. 367 (2004) 132–136.
[15] Y. Chen, Q. Feng, L. Zeng, J. Alloy Compd. 492 (2010) 208–212.
[16] P. Villars, Pearson's Handbook of Crystallographic Data, ASM International, Materials Park, OH, 1997, pp. 488–489.
[17] A.H. Gomes de Mesquita, K.H.J. Buschow, Acta Cryst. 22 (1967) 497–501.
[18] E.E. Havinga, J. Less-Common Met. 41 (1975) 241–254.
[19] B. Appa Rao, P. Kistaiak, N. Rajasekhar Reddy, K. Satyanarayana, J. Mater. Sci. Lett. 1 (1982) 432–434.
[20] K.H.J. Buschow, Philips Res. Rep. 20 (1965) 337–348.
[21] A. Iandelli, Natl. Phys. Lab. 1 (9) (1959), 3F-2–3F-11.
[22] Z. Hu, Y. Zhan, J. She, J Alloy Compd. 491 (2010) 200–202.
[23] Y. Zhan, Y. Du, Y. Zhuang, Determination of phase diagrams using equilibrated alloys, in: J.-C. Zhao (Ed.), Methods for Phase Diagram Determination, first ed., Elsevier Science Press, Amsterdam, The Netherlands, 2007, pp. 108–150.