

Contents lists available at ScienceDirect

Journal of Alloys and Compounds



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

# Determination of the phase equilibria in the Al-Er-V ternary system at 773 K

# Zhulin Yang<sup>a</sup>, Yongzhong Zhan<sup>a,\*</sup>, Honglou Mo<sup>a</sup>, Yong Du<sup>b</sup>, Honghui Xu<sup>b</sup>

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

### ARTICLE INFO

Article history: Received 26 March 2010 Received in revised form 23 April 2010 Accepted 2 May 2010 Available online 7 May 2010

*Keywords:* Metals and alloys Phase diagrams X-ray diffraction

#### 1. Introduction

Aluminum alloys have been used extensively in many fields like motor industry, aircraft industry, electronic industry and buildings, etc., due to the characteristics such as light weight, corrosion resistance, reasonably good strength and ductility, easy fabrication and favorable economics [1]. Rare earth (RE) is an important kind of alloying additive for metallic materials. It is well known that the addition of small amount of rare earth element can improve the microstructures and properties of the alloys [2,3]. In order to discover further application characteristics and regularities concerning phase formation in the Al–Er–V ternary system, it is necessary to investigate the phase relationships in the system.

In Refs. [4–6], five different phases have been found to exist in the binary Al–V system:  $Al_{10}V$  (cF184, *Fd*-3*m*,  $Al_{10}V$ -type),  $Al_{45}V_7$ (mC104, C2/*m*,  $Al_{45}V_7$ -type),  $Al_{23}V_4$  (hP54, *P*6<sub>3</sub>/*mmc*,  $Al_{23}V_4$ -type),  $Al_3V$  (t18, *I4/mmm*, Al<sub>3</sub>Ti-type) and  $Al_8V_5$  (cI52, *I*-43*m*, Cu<sub>5</sub>Zn<sub>8</sub>type). However, it is reported that there are two other compounds, i.e. AlV<sub>3</sub> and  $Al_{50}V_{50}$  exist [7]. Richter et al. [8,9] reinvestigated the Al–V phase diagram using differential thermal analysis, Xray diffraction, and electron probe microanalysis and confirmed the existence of the two compounds. The Al–Er binary phase diagram [10] shows five intermediate phases namely  $Al_3$ Er,  $Al_2$ Er, AlEr,  $Al_2$ Er<sub>3</sub> and AlEr<sub>2</sub>. The existence of five binary compounds was confirmed in the Al–Er system at 873 K by Pukas et al. [11]. There is no binary compound reported in the Er–V system at 773 K, however there is an extended miscibility gap in the liquid in this system

# ABSTRACT

The phase equilibria of the Al–Er–V ternary system at 773 K has been investigated over the whole concentration range mainly by powder X-ray diffraction (XRD), scanning electron microscope (SEM) and optical microscopy (OM). This isothermal section consists of 14 single-phase regions, 26 two-phase regions, and 13 three-phase regions. There are 10 binary compounds, i.e. Al<sub>3</sub>Er, Al<sub>2</sub>Er, AlEr, Al<sub>2</sub>Er<sub>3</sub>, AlEr<sub>2</sub>, Al<sub>10</sub>V, Al<sub>45</sub>V<sub>7</sub>, Al<sub>23</sub>V<sub>4</sub>, Al<sub>3</sub>V and Al<sub>8</sub>V<sub>5</sub> confirmed in the Al–Er–V system. The ternary compound Al<sub>43</sub>Er<sub>6</sub>V<sub>4</sub> is confirmed and its lattice parameter is calculated and refined. The solid solubility of V in Al<sub>2</sub>Er<sub>3</sub>, AlEr and Al<sub>2</sub>Er are determined to be about 1–2 at.%, and the solubility of Al in V is 39 at.% at 773 K.

© 2010 Elsevier B.V. All rights reserved.

[12]. The previous work has shown that one ternary compound  $Al_{43}Er_6V_4$  exist in the Al-Er-V system [13,14]. The reported crystal structure data of the intermediate compounds are given in Table 1.

Up to now, no report on the isothermal section of the ternary Al–Er–V system has been found. The purpose of the present work was to investigate experimentally the Al–Er–V phase diagram, mainly by constructing an isothermal section at 773 K, so as to provide essential information for the design and fabrication of new-type aluminum and vanadium alloys.

#### 2. Experimental details

In this work, the purities of Al, Er and V were 99.99 wt.%, 99.99 wt.% and 99.9 wt.%, respectively. 58 alloy buttons have been produced. Each sample was prepared to have a total weight of 1.5 g by weighing appropriate amounts of the pure components. All the alloy buttons were prepared in an electric arc furnace under an argon atmosphere, using a water-cooled cooper crucible. Titanium was used as an oxygen getter during the melting process. Each asarc-cast button was melted three times and turned around after melting for better homogeneity. For most alloys, the weight loss is less than 1% after melting.

The melted alloys were sealed in an evacuated quartz tube. 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 Al-rich alloys containing more than 40 at.% Al were homogenized at 873 K for 720 h. The other alloy samples were homogenized at 1173 K for 480 h. Subsequently, the

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

<sup>0925-8388/\$ -</sup> see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2010.05.006

# Table 1 Crystal structure data of intermediate compounds in the Al-Er-V system at 773 K.

Compound	Space group	Lattice parameters (nm)			Reference
		а	b	С	
Al <sub>3</sub> Er	Pm <u>3</u> m	0.4215	-	-	[15]
Al <sub>2</sub> Er	Fd <del>3</del> m	0.7775	-	-	[15]
AlEr	Pbcm	0.5801	1.1272	0.5570	[15]
AlEr <sub>2</sub>	Pnma	0.6516	0.5015	0.9279	[15]
$Al_2Er_3$	$P4_2/mnm$	0.81323	-	0.75039	[15]
Al <sub>10</sub> V	Fd3m	1.4492	-	-	[7]
$Al_{45}V_7$	C2/m	2.5604	0.76213	1.1081	[7]
Al <sub>23</sub> V <sub>4</sub>	P6₃/mmc	0.76928	-	1.7040	[7]
Al <sub>3</sub> V	I4/mmm	0.3772	-	0.8305	[7]
Al <sub>8</sub> V <sub>5</sub>	I <del>4</del> 3m	0.9234	-	-	[7]
AlV <sub>3</sub>	Pm3n	0.47982	-	-	[7]
AlV	P42212	1.08451	-	0.43755	[9]
$Al_{43}Er_6V_4$	$P6_3/mcm$	1.0935	1.0935	1.7627	[16]

furnace was cooled down to 773 K and kept at this temperature for 240 h. Then, the samples were removed and quenched in liquid nitrogen.

All the equilibrated samples were powdered and then analyzed on a Rigaku D/Max-2500V diffractometer with Cu K<sub> $\alpha$ </sub> radiation and graphite monochromator operated at 40 kV, 200 mA. The Materials Data Inc. software Jade 5.0 and Powder Diffraction File (PDF release 2003) were used for phase identification. Optical microscopy (OM) and scanning electron microscopy (SEM) were used for microstructural analysis. By all these means, the phase relationships of the Al–Er–V ternary system at 773 K were determined.

#### 3. Results and discussion

#### 3.1. Binary system

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

The present work has indicated that no binary compound exist in the Er–V system, which agrees well with the results of Ref. [12].

In the Al–Er system, the phase diagram [10] shows five intermediate phases, i.e. Al<sub>3</sub>Er, Al<sub>2</sub>Er, AlEr, Al<sub>2</sub>Er<sub>3</sub> and AlEr<sub>2</sub>. The PDF files of the compounds Al<sub>3</sub>Er, Al<sub>2</sub>Er, AlEr and Al<sub>2</sub>Er<sub>3</sub> are available on JCPDS PDF cards (2003). The calculated XRD patterns of the compound AlEr<sub>2</sub>, of which the PDF files is not available and crystallographic data is known, is obtained by using the PowderCell for Windows program. Based on the analysis of the details of the XRD pattern (shown in Fig. 1) of #41 sample (77.2 at.% Al, 18.6 at.% Er and 4.2 at.% V), the binary compounds Al<sub>3</sub>Er and Al<sub>2</sub>Er can be con-



Fig. 1. The XRD pattern of #41 sample (77.2 at.% Al, 18.6 at.% Er and 4.2 at.% V) indicating the phase equilibrium of Al<sub>3</sub>Er, Al<sub>2</sub>Er and Al<sub>43</sub>Er<sub>6</sub>V<sub>4</sub>.



**Fig. 2.** The XRD pattern of #46 sample (25.5 at.% Al, 44.5 at.% Er and 30 at.% V) indicating the phase equilibrium of Al<sub>2</sub>E<sub>3</sub>, AlEr<sub>2</sub> and V.

firmed, and the three-phase region  $Al_3Er + Al_2Er + Al_{43}Er_6V_4$  can be determined. The intermediate compounds  $Al_2Er_3$  and  $AlEr_2$  were confirmed based on the XRD pattern (shown in Fig. 2) of #46 sample (25.5 at.% Al, 44.5 at.% Er and 30 at.% V). Consequently, it is demonstrated that five binary compounds  $Al_3Er$ ,  $Al_2Er$ , AlEr,  $Al_2Er_3$  and  $AlEr_2$  exist in the Al–Er system at 773 K.

In the Al–V system, the previous binary diagram [4] shows five intermediate phases, they are  $Al_{10}V$ ,  $Al_{45}V_7$ ,  $Al_{23}V_4$ ,  $Al_3V$  and  $Al_8V_5$ . Two other binary compounds, i.e.  $AlV_3$  and  $Al_{50}V_{50}$  have been reported in Ref. [7]. It also was reported that the new compound AlV was discovered in the course of a re-investigation of the system at 500 °C [8]. In this work, the two compounds  $AlV_3$  and  $Al_{50}V_{50}$  (AlV) were not found, which agrees well with Refs. [4–6]. From Fig. 3, it is clear that the XRD pattern of #32 sample (45 at.% Al, 10 at.% Er and 45 at.% V) consists of the patterns of three phases, i.e. V,  $Al_8V_5$  and  $Al_2Er$ . This result indicates the existence of the binary compound  $Al_8V_5$  in the Al–V system, as well as the phase equilibrium of the three phases, i.e. V,  $Al_8V_5$  and  $Al_2Er$  at 773 K.

#### 3.2. Ternary phase

In this work, the XRD pattern of #29 sample (85 at.% Al, 8 at.% Er and 7 at.% V) clearly indicates the existence of the  $Al_{43}Er_6V_4$  phase, as illustrated in Fig. 4. In addition, from the XRD pattern of #27 sample (74 at.% Al, 10 at.% Er and 16 at.% V) in Fig. 5a, the existence of the ternary compound  $Al_{43}Er_6V_4$  is indicated. The microstructure of #27 sample examined by both SEM and OM clearly exhibited the existence of three phases, i.e.  $Al_{43}Er_6V_4$ ,  $Al_3V$  and  $Al_2Er$ . EDX result indicated that the black phase was  $Al_3V$ , the gray one was  $Al_{43}Er_6V_4$  while the white phase was  $Al_2Er$ , as is



Fig. 3. The XRD pattern of #32 sample (45 at.% Al, 10 at.% Er and 45 at.% V) indicating the phase equilibrium of V,  $Al_8V_5$  and  $Al_2Er$ .



Fig. 4. The XRD pattern of #29 sample (85 at.% Al, 8 at.% Er and 7 at.% V) indicating the phase equilibrium of  $Al_{43}Er_6V_4$ ,  $Al_{10}V$  and Al.

shown in Fig. 5b. Moreover, the SEM micrograph (shown in Fig. 6) of #13 sample (85 at.% Al, 10 at.% Er and 5 at.% V) also indicated the existence of the ternary compound  $Al_{43}Er_6V_4$ , as well as the equilibrium of the three phases, i.e.  $Al_{43}Er_6V_4$ ,  $Al_3Er$  and Al at 773 K. Combined with the above results, the existence of the ternary compound  $Al_{43}Er_6V_4$  reported in Refs. [13,14] can be confirmed in this work.

The crystal structure of the  $Al_{43}Er_6V_4$  was investigated using X-ray power diffraction. The X-ray power diffraction pattern of the single phase (Fig. 7) was indexed using Jade 5.0. The results indicate that the single phase has a hexagonal structure with space group  $P6_3/mcm$  (no. 193) and parameters of a = 1.08967 nm, c = 1.76236 nm, and Vol = 1.81224 nm<sup>3</sup>. The composition of the sample, the intensities of the reflections and the obtained lat-



Fig. 5. The XRD pattern (a) and the SEM micrograph (b) of #27 sample (74 at.% Al, 10 at.% Er and 16 at.% V) indicating the phase equilibrium of  $Al_{43}Er_6V_4$ ,  $Al_3V$  and  $Al_2Er$ .



Fig. 6. The SEM micrograph of #13 sample (85 at.% Al, 10 at.% Er and 5 at.% V) indicating the phase equilibrium of Al +  $Al_3Er + Al_{43}Er_6V_4$ .

tice parameters proved that this compound is isostructural with  $Ho_6Mo_4Al_{43}$ . The results are shown in Table 2.

# 3.3. Solid solubility

The solid solubility ranges of all single phases in the isothermal section were determined by XRD using phase-disappearing method and comparing the shift of the XRD pattern of the samples near the compositions of the binary phases [17]. The solid solubility of V in Al<sub>2</sub>Er<sub>3</sub>, AlEr and Al<sub>2</sub>Er are determined to be about 1–2 at.%, as shown in Fig. 8. The solubility of Al in V is 39 at.% at 773 K. For the other binary compounds and the ternary compound Al<sub>43</sub>Er<sub>6</sub>V<sub>4</sub>, the results showed that the diffraction patterns did not show shift and the diffraction patterns of the second phase could easily be detected when the composition of the alloys deviated from its single-phase region by 1.0 at.%. Therefore, it is concluded that there is no detected solid solubility in these compounds at 773 K.



**Fig. 7.** XRD pattern of the single-phase  $Al_{43}Er_6V_4$ .

### Table 2

Crystal structure data of the ternary compound  $Al_{43}Er_6V_4$ .

Compound	$Al_{43}Er_6V_4$
Structure type	$Ho_6Mo_4Al_{43}$
Cell parameters	$p_{0_3}/mcm$ (110, 193) a=b=1.08967  nm
cen parameters	c = 1.76236  nm,
	$\alpha = \beta = 90^\circ$ , $\gamma = 120^\circ$
Volume of unit cells (nm <sup>3</sup> )	1.81224
Calculated density (g/cm <sup>3</sup> )	4.3387
Formula units per cell	Z=2



Fig. 8. The isothermal section of the Al-Er-V ternary system at 773 K.

Table 3

Details of the three-phase regions and compositions of the typical alloys of the Al-Er-V at 773 K

Phase region	Alloy co	ompositior	n (at.%)	Phase composition
	Al	Er	V	
1	73.6	25	1.4	$Al_3Er + Al_2Er + Al_{43}Er_6V_4$
2	85	12.5	2.5	$Al + Al_3Er + Al_{43}Er_6V_4$
3	90	4	6	$Al + Al_{10}V + Al_{43}Er_6V_4$
4	87	3	10	$Al_{10}V + Al_{45}V_7 + Al_{43}Er_6V_4$
5	85	2	13	$Al_{45}V_7 + Al_{23}V_4 + Al_{43}Er_6V_4$
6	80	5	15	$Al_{23}V_4 + Al_3V + Al_{43}Er_6V_4$
7	75	15	10	$Al_2Er + Al_3V + Al_{43}Er_6V_4$
8	70	5	25	$Al_2Er + Al_3V + Al_8V_5$
9	50	10	40	$Al_2Er + Al_8V_5 + V$
10	40	30	30	$Al_2Er + AlEr + V$
11	30	40	30	$AIEr + Al_2Er_3 + V$
12	25	45	30	$Al_2Er_3 + AlEr_2 + V$
13	15	55	30	$AIEr_2 + Er + V$

#### 3.4. Isothermal section

The isothermal section of the Al-Er-V ternary system at 773 K has been determined on the basis of XRD, SEM and OM, as is shown

in Fig. 8. This isothermal section consists of 14 single-phase regions, 26 two-phase regions and 13 three-phase regions. Constitutions of the three-phase regions and compositions of the typical alloys are listed in Table 3.

# 4. Conclusions

The phase relationships of the Al-Er-V ternary system at 773 K have been determined using equilibrated alloys for the first time. The 773 K isothermal section consists of 14 single-phase regions, 26 two-phase regions and 13 three-phase regions. The existences of 10 binary compounds namely Al<sub>3</sub>Er, Al<sub>2</sub>Er, AlEr, Al<sub>2</sub>Er<sub>3</sub>, AlEr<sub>2</sub>, Al<sub>10</sub>V, Al<sub>45</sub>V<sub>7</sub>, Al<sub>23</sub>V<sub>4</sub>, Al<sub>3</sub>V and Al<sub>8</sub>V<sub>5</sub> were confirmed at 773 K. The ternary compound Al<sub>43</sub>Er<sub>6</sub>V<sub>4</sub> which is isostructural with Ho<sub>6</sub>Mo<sub>4</sub>Al<sub>43</sub> was confirmed in this ternary system at 773 K. The solid solubility of V in Al<sub>2</sub>Er<sub>3</sub>, AlEr and Al<sub>2</sub>Er are determined to be about 1–2 at.%, and the solubility of Al in V is 39 at.% at 773 K.

#### Acknowledgement

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

#### References

- Z. Hu, Y. Zhan, J. She, Y. Du, H. Xu, J. Alloys Compd. 491 (2009) 200-202.
- C.M.L. Wu, D.Q. Yu, C.M.T. Law, L. Wang, Mater. Sci. Eng. R 44 (2004) 1-44. [2]
- [3] Y. Zhan, J. Ma, G. Zhang, Z. Hu, C. Li, J. Alloys Compd. 475 (2009) 281-285.
- J.L. Murray, Bull. Alloy Phase Diagrams 10 (4) (1989) 351-357. [4]
- [5] W. Gong, Y. Du, B. Huang, R. Schmid-Fetzer, C. Zhang, H. Xu, Thermodynamic reassessment of the Al-V system, Z. Metallkd. 95 (2004) 978-986.
- [6] B. Huber, H.S. Effenberger, K.W. Richter, Intermetallics 18 (2010) 606-615. [7] P. Villars, Pearson's Handbook of Crystallographic Data, ASM International,
- Materials Park, OH, 1997, pp. 484-485. [8] K.W. Richter, H. Ipser, Z. Metallkd. 91 (2000) 383-388.
- [9] B. Huber, K.W. Richter, J. Alloys Compd. 493 (2010) L33-L35.
- [10] K.A. Gschneidner Jr., F.W. Calderwood, Bull. Alloy Phase Diagrams 9 (6) (1988).
- [11] S. Pukas, W. Lasocha, R. Gladyshevskii, CALPHAD 33 (2009) 23-26.
- [12] J.F. Smith, K.J. Lee, Phase Diagrams of Binary Vanadium Alloys. (1989). [13] M.W. Wolff, S. Niemann, T. Ebel, W. Jeitschko, J. Magn. Magn. Mater. 223 (2001)
- 1-15. [14] S. Niemann, W. Jeitschko, J. Solid State Chem. 116 (1995) 131-135.
- [15] P. Villars, Pearson's Handbook of Crystallographic Data, ASM International, Materials Park, OH, 1997, pp. 364-365.
- [16] Materials Data JADE Release 5.0, XRD Pattern Processing, Materials DaTa Inc, Livermore, CA, 2002.
- [17] Y. Zhan, Y. Du, Y. Zhuang, Determination of phase diagrams using equilibrated alloys, in: J.-C. Zhao (Ed.), Methods for Phase Diagram Determination, 1st ed., Elsevier Science Press, Amsterdam, The Netherlands, 2007, pp. 108-150.