

# Isothermal Section of the Al-Mn-Dy System at 500 °C

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Phase relationships in the Al-Mn-Dy ternary system at 500 °C have been investigated by X-ray diffraction, scanning electron microscopy with energy dispersive spectroscopy, and electron probe microanalysis. From the experimental results it was concluded that the isothermal section consists of 16 single-phase regions, 26 two-phase regions and 12 three-phase regions. Two extensive solid solutions,  $(\text{Al}_x\text{Mn}_{1-x})_{12}\text{Dy}$  and  $(\text{Al}_{1-x}\text{Mn}_x)_2\text{Dy}$ , were observed. The solid solution  $(\text{Al}_x\text{Mn}_{1-x})_{12}\text{Dy}$  forms by Al replacing Mn in  $\text{Mn}_{12}\text{Dy}$ , while the continuous solid solution  $(\text{Al}_{1-x}\text{Mn}_x)_2\text{Dy}$  forms by Mn and Al mutually substituting in  $\text{Al}_2\text{Dy}$  and  $\text{Mn}_2\text{Dy}$ , respectively. The maximum solid solubility of Al in  $\text{Mn}_{12}\text{Dy}$  is 79.3 at. %.

**Keywords** Al-Mn-Dy alloy, phase diagram, x-ray diffraction

## 1. Introduction

Phase diagrams and thermodynamics provide basic knowledge for alloy design. For example, thermodynamic descriptions of multi-component Al-based alloys have been applied to alloy development.<sup>[1]</sup> Rare earth (RE) elements and transition metals play important roles in the improvement of the microstructure as well as the mechanical properties of Al-based alloys. Scandium was reported to greatly improve the properties of Al alloys due to the formation of coherent  $\text{Al}_3\text{Sc}$ .<sup>[2,3]</sup> The presence of  $\text{Al}_3\text{Dy}$  was observed to significantly reduce the microelectronic resistivity of the Al-Dy alloy thin films.<sup>[4]</sup>

A major alloying element in 3000 series commercial Al alloys is Mn. Work on the interaction of RE metals with transition metals and aluminum has been reported.<sup>[5-11]</sup> However, little work on phase equilibria of RE metals, manganese and aluminum was found in the open literature. In order to clarify the interaction of Mn and RE metals in commercial aluminum alloys, it is necessary to investigate phase equilibria in the Al-Mn-RE ternary system. Specifically, this work aims to investigate the phase equilibria in the Al-Mn-Dy system.

Five intermetallic compounds have been reported in the Al-Dy system<sup>[12]</sup> at 500 °C, i.e.  $\text{Al}_3\text{Dy}$  (rhombohedral  $\text{Al}_3\text{Ho}$  type),  $\text{Al}_2\text{Dy}$  (cubic  $\text{Cu}_2\text{Mg}$  type),  $\text{AlDy}$  (orthorhombic  $\text{AlEr}$  type),  $\text{Al}_2\text{Dy}_3$  (tetragonal  $\text{Al}_2\text{Zr}_3$  type) and  $\text{AlDy}_2$  (orthorhombic  $\text{Co}_2\text{Si}$  type); three intermediate phases have been reported in the Mn-Dy system,<sup>[13]</sup> i.e.,  $\text{Mn}_2\text{Dy}$  (cubic  $\text{Cu}_2\text{Mg}$  type),  $\text{Mn}_{23}\text{Dy}_6$  (cubic  $\text{Mn}_{23}\text{Th}$  type) and  $\text{Mn}_{12}\text{Dy}$  (tetragonal  $\text{Mn}_{12}\text{Th}$  type); and six intermetallic compounds have been reported in the Al-Mn system, i.e.  $\text{Al}_{12}\text{Mn}$  (cubic  $\text{Al}_{12}\text{W}$  type),  $\text{Al}_6\text{Mn}$  (orthorhombic  $\text{Al}_6\text{Mn}$  type),  $\lambda\text{-Al}_4\text{Mn}$ ,

$\mu\text{-Al}_4\text{Mn}$ ,  $\text{Al}_{11}\text{Mn}_4$  (triclinic  $\text{Al}_{11}\text{Mn}_4$  type), and  $\text{Al}_8\text{Mn}_5$  (rhombohedral  $\text{Al}_8\text{Cr}_5$  type).<sup>[14,15]</sup> The  $\lambda\text{-Al}_4\text{Mn}$  and  $\mu\text{-Al}_4\text{Mn}$  phases are compositionally and structurally different. For example,  $\lambda\text{-Al}_4\text{Mn}$  is in the Al-rich side with space group  $\text{P}6_3/\text{mmc}$ , while  $\mu\text{-Al}_4\text{Mn}$  is in the Al-poor side with space group  $\text{Pnnn}$ . With temperature decreasing,  $\text{Al}_{11}\text{Mn}_4$  transforms from the high temperature structure (Space group  $\text{Pnma}$ ) to the low temperature form (space group  $\text{P}\bar{1}$ ) at 916 °C. Table 1 lists crystallographic data of compounds stable at 500 °C in Al-Mn-Dy and one can see that there are no ternary compounds in this system.

## 2. Experimental Procedure

The starting materials were high purity Al (99.95%), Mn (99.8%) and Dy (99.95%) (in mass%) and the total weight of each sample was 1.5 g. Specimens were melted in an arc furnace under an environment of pure Ar (99.99%). To compensate for the loss of Mn, an additional 20 wt.% Mn was added to each alloy. To guarantee homogeneity, the alloy buttons were melted at least three times. The final measured compositions were observed to slightly deviate from the nominal or synthesis composition of alloy, which shows that the loss of Mn in the alloy is compensated by the above mentioned method. After melting, the buttons were sealed in vacuum quartz tubes and then annealed at 500 °C for 30 days. The tubes were quenched into water after annealing, and then broken to recover the samples. The quenched alloys were cut into two pieces, one for x-ray examination and the other for microscopic analysis. The x-ray diffraction radiation was  $\text{Cu}_{K\alpha}$ .

Samples for x-ray diffraction were directly ground into powder, while samples for microstructure analysis were prepared by grinding and polishing. The microstructure of unetched samples was observed on the Zeiss EVO-18 scanning electronic microscope (SEM) equipped with energy dispersive spectroscopy (EDS). Some samples were analyzed using the JEOL JXA-8230 electron probe micro-analyzer (EPMA), as well. Reported compositions are the average of three measurements.

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**Table 1 Crystallographic data of the compounds in Al-Mn-Dy system**

Phases	Space group	Pearson symbol	Prototype	Lattice parameter (nm)			References
				a	b	c	
Al	Fm-3m	cF4	Cu	0.4049			16
Mn	P4 <sub>1</sub> 32	Cp20	βMn	0.629			17
	I-43m	cI58	αMn	0.8894			18
Dy	P6 <sub>3</sub> /mmc	Hp2	Mg	0.3458		0.5466	19
Al <sub>3</sub> Dy	R-3m	hR20	Al <sub>3</sub> Ho	0.608		3.594	20,21
	P6 <sub>3</sub> /mmc	hP16	Ni <sub>3</sub> Ti	0.6091		0.9533	22
Al <sub>2</sub> Dy	Fd-3m	cF24	Cu <sub>2</sub> Mg	0.7843			23
AlDy	Pbcm	oP16	AlDy	0.5822	1.1369	0.5604	24
	Pm-3m	cP2	CiCs	0.3682			25
Al <sub>2</sub> Dy <sub>3</sub>	P4 <sub>2</sub> nm	tP20	Al <sub>2</sub> Gd <sub>3</sub>	0.8170		0.7523	26
	P4 <sub>2</sub> mnm	tP20	Al <sub>2</sub> Zr <sub>3</sub>	0.8218		0.755	27
AlDy <sub>2</sub>	Pnma	oP12	Co <sub>2</sub> Si	0.6543	0.5075	0.9397	28
Mn <sub>12</sub> Dy	I4/mmm	tI26	Mn <sub>12</sub> Th	0.8579		0.4763	29
Mn <sub>23</sub> Dy <sub>6</sub>	Fm-3m	CfI16	Mn <sub>23</sub> Th <sub>6</sub>	1.2358			30
Mn <sub>2</sub> Dy	Fd-3m	cF24	Cu <sub>2</sub> Mg	0.7564			31
Al <sub>12</sub> Mn	Im-3m	cI26	Al <sub>12</sub> W	0.747			32
Al <sub>6</sub> Mn	Cmcm	oC28	Al <sub>6</sub> Mn	0.7551	0.6497	0.8870	33
	Cmcm	oC28	Al <sub>6</sub> Mn	0.7555	0.6499	0.8872	34
Al <sub>4</sub> Mn(μ)	Pnnn	oP60		0.7217	0.7674	0.875	35
Al <sub>4</sub> Mn(λ)	P6 <sub>3</sub> /mmc	hP574	Al <sub>4</sub> Mn	1.998(1)		2.4673	36
Al <sub>11</sub> Mn <sub>4</sub>	P-1	aP15	Al <sub>11</sub> Mn <sub>4</sub>	0.5095	0.8879	0.5051	37
Al <sub>8</sub> Mn <sub>5</sub>	R3m	hR52	Al <sub>8</sub> Cr <sub>5</sub>	1.2645		1.5855	38
AlMnDy	Fd-3m	cF-24	Cu <sub>2</sub> Mg	0.778			31
Al <sub>7</sub> Mn <sub>5</sub> Dy	I4/mmm	tI26	Mn <sub>12</sub> Th	0.8812		0.5096	39
Al <sub>6</sub> Mn <sub>6</sub> Dy	I4/mmm	tI26	Mn <sub>12</sub> Th	0.8823		0.5061	39
Al <sub>8</sub> Mn <sub>4</sub> Dy	I4/mmm	tI26	Mn <sub>12</sub> Th	0.885		0.511	39

Al<sub>7</sub>Mn<sub>5</sub>Dy, Al<sub>6</sub>Mn<sub>6</sub>Dy and Al<sub>8</sub>Mn<sub>4</sub>Dy are the solid solution phases in the form of (Al<sub>x</sub>Mn<sub>1-x</sub>)<sub>12</sub>Dy. AlMnDy is solid solution phase in the form of (Al<sub>1-x</sub>Mn<sub>x</sub>)<sub>2</sub>Dy

### 3. Results and Discussions

Table 2 lists the experimental results obtained from XRD and SEM/EDS analysis of 22 alloy buttons, as well as EPMA measurements on selected alloys.

A phase with nearly constant Dy (about 6-10 at.%) and various Mn/Al ratios was observed in alloys 7-22, as shown in Table 2. Some peaks of the x-ray pattern in these alloys are a match to Mn<sub>12</sub>Dy, with slightly different lattice parameters. It was concluded that a solid solution, corresponding to (Al<sub>x</sub>Mn<sub>1-x</sub>)<sub>12</sub>Dy, formed by Al substituting for Mn in Mn<sub>12</sub>Dy in this system. The maximum solid solubility of Al in Mn<sub>12</sub>Dy is 79.3 at.%, which is the average of alloys 20 and 21.

Note that both Al<sub>2</sub>Dy and Mn<sub>2</sub>Dy have the same cubic Cu<sub>2</sub>Mg-type crystal structure. Similarly, phases with constant Dy content (about 30-33 at.%) and different Al/Mn ratio were observed in alloys 1-9,15-16 and 22, as listed in Table 2. The x-ray diffraction patterns of these phases were indexed by Al<sub>2</sub>Dy or Mn<sub>2</sub>Dy with slightly different lattice parameters. Thus it was concluded that, Al<sub>2</sub>Dy and Mn<sub>2</sub>Dy form a continuous solid solution, (Al<sub>1-x</sub>Mn<sub>x</sub>)<sub>2</sub>Dy, in all these alloys.

Figure 1 is the backscattered electron (BSE) image and x-ray diffraction pattern of alloy 14. The light gray phase is (Al<sub>x</sub>Mn<sub>1-x</sub>)<sub>12</sub>Dy, and the gray phase is Al<sub>8</sub>Mn<sub>5</sub>, while the dark needle phase is Al<sub>11</sub>Mn<sub>4</sub>. These three phases were identified by x-ray diffraction. Identification of phases in alloy 14 showed that there is a tie-triangle of [(Al<sub>x</sub>Mn<sub>1-x</sub>)<sub>12</sub>Dy + Al<sub>8</sub>Mn<sub>5</sub> + Al<sub>11</sub>Mn<sub>4</sub>] in this system.

The phases (Al<sub>x</sub>Mn<sub>1-x</sub>)<sub>12</sub>Dy, Al<sub>11</sub>Mn<sub>4</sub>, and Al<sub>4</sub>Mn were observed to co-exist in alloy 17, as shown in Fig. 2. The EDS analysis showed that the white gray phase is (Al<sub>x</sub>Mn<sub>1-x</sub>)<sub>12</sub>Dy, and the gray phase is Al<sub>11</sub>Mn<sub>4</sub>, while the dark gray phase is Al<sub>4</sub>Mn. The dark gray phase was identified as Al<sub>4</sub>Mn from its lower Al content.

The co-existence of (Al<sub>x</sub>Mn<sub>1-x</sub>)<sub>12</sub>Dy, Al<sub>6</sub>Mn, and (Al) was found in alloy 19, as shown in Fig. 3. Compositions of the identified phases are listed in Table 2. X-ray diffraction and EPMA confirmed the results of SEM/EDS analysis.

Direct evidences to support the tie-triangles of [(Al) + Al<sub>3</sub>Dy + (Al<sub>x</sub>Mn<sub>1-x</sub>)<sub>12</sub>Dy], [Al<sub>3</sub>Dy + (Al<sub>1-x</sub>Mn<sub>x</sub>)<sub>2</sub>Dy + (Al<sub>x</sub>Mn<sub>1-x</sub>)<sub>12</sub>Dy], and [Mn<sub>23</sub>Dy<sub>6</sub> + (Al<sub>1-x</sub>Mn<sub>x</sub>)<sub>2</sub>Dy + (Al<sub>x</sub>Mn<sub>1-x</sub>)<sub>12</sub>Dy] are shown in Fig. 4, 5 and 6.

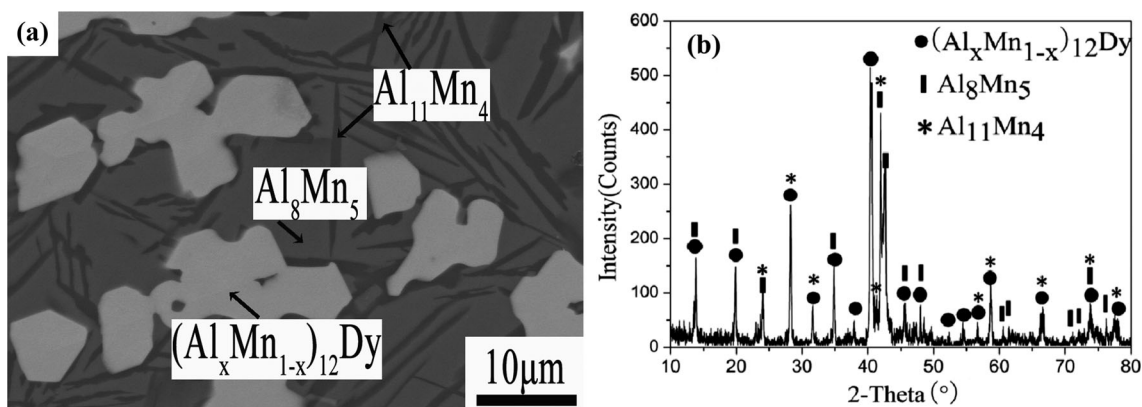
According to the Al-Dy phase diagram,<sup>[12]</sup> Al<sub>2</sub>Dy<sub>3</sub> is formed by the peritectic reaction

**Table 2 Phase identification by using XRD, SEM/EDS and EPMA for the selected Al-Mn-Dy alloys**

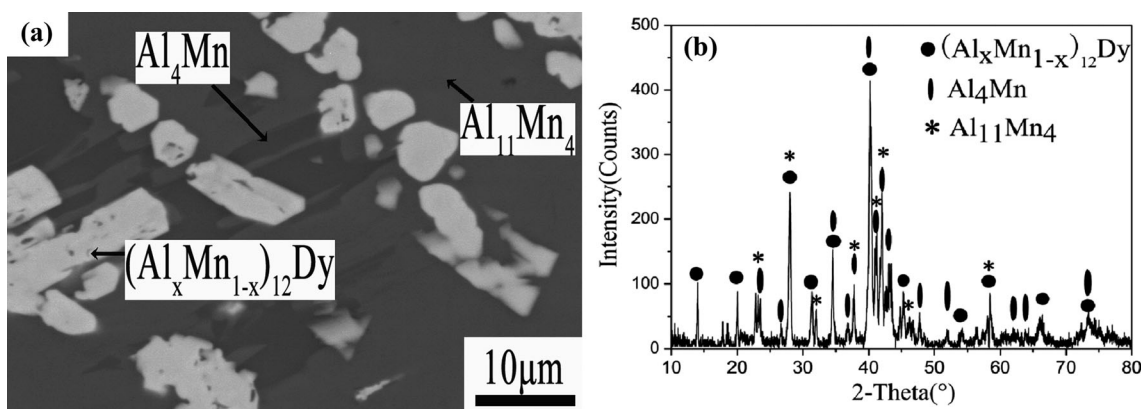
No.	Compositions (at.%)						Phase identified	Measured Compositions EDS (at.%)			Measured Compositions EPMA (at.%)		
	Nominal			Measured				Al	Mn	Dy	Al	Mn	Dy
	Al	Mn	Dy	Al	Mn	Dy							
1	50	10	40	52.42	8.8	38.8	(Al <sub>1-x</sub> Mn <sub>x</sub> ) <sub>2</sub> Dy	56.9	10.9	32.2	56.9	12.0	31.1
							AlDy	51.4	1.0	47.6	40.8	7.4	51.8
							AlDy <sub>2</sub>	34.6	0.9	64.5	32.4	1.9	65.7
2	40	15	45	41.8	16.3	41.9	(Al <sub>1-x</sub> Mn <sub>x</sub> ) <sub>2</sub> Dy	47.6	20.3	32.1	45.4	22.6	32.0
							AlDy <sub>2</sub>	36.7	0.6	62.8	34.3	1.0	64.7
							(Dy)	13.9	2.0	84.0			
3	35	12.5	52.5	36.98	13.0	50.0	(Al <sub>1-x</sub> Mn <sub>x</sub> ) <sub>2</sub> Dy	44.1	23.5	32.5			
							AlDy <sub>2</sub>	34.9	1.2	63.8			
							(Dy)	13.9	2.0	84.0			
4	27.5	17.5	55	31.33	16.5	52.2	(Al <sub>1-x</sub> Mn <sub>x</sub> ) <sub>2</sub> Dy	33.4	33.1	33.5			
							AlDy <sub>2</sub>	34.4	1.8	63.8			
							(Dy)	5.1	2.1	92.8			
5	10	25	65	13.6	25.8	60.6	(Al <sub>1-x</sub> Mn <sub>x</sub> ) <sub>2</sub> Dy	18.2	49.4	32.4			
							AlDy <sub>2</sub>	30.1	3.3	66.5			
							(Dy)	4.9	1.5	93.6			
6	15	40	45	18.55	36.8	44.7	(Al <sub>1-x</sub> Mn <sub>x</sub> ) <sub>2</sub> Dy	21.3	46.3	32.4	18.7	47.4	33.9
							AlDy <sub>2</sub>	26.4	5.7	67.9	28.4	2.7	68.9
							(Dy)	3.2	2.8	94.0	0.1	0.1	99.8
7	17.5	60	22.5	23.63	47.6	28.8	(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	11.3	80.6	8.0	11.0	82.3	6.7
							(Al <sub>1-x</sub> Mn <sub>x</sub> ) <sub>2</sub> Dy	29.9	39.0	31.1	29.3	38.4	32.3
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	33.1	58.3	8.6			
8	32.5	47.5	20	33.17	44.5	22.4	(Al <sub>1-x</sub> Mn <sub>x</sub> ) <sub>2</sub> Dy	46.5	22.5	31.0			
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	22.7	47.4	29.9	21.6	46.7	31.7
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	11.4	80.6	8.1	20.7	72.7	6.6
9	20	67.5	12.5	13.65	69.1	17.3	Mn <sub>23</sub> Dy <sub>6</sub>	10.7	70.9	18.4	8.4	70.0	21.6
							(βMn)	12.7	87.3	0.0	11.7	87.2	1.1
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	15.7	77.6	6.7	23.5	68.8	7.7
10	15	80	5	14.81	82.0	3.2	(βMn)	32.0	68.0	0.0	33.0	65.3	1.7
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	40.4	53.5	6.1	36.3	55.1	8.6
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	51.0	41.7	7.3	52.4	38.8	8.8
11	37.5	60	2.5	34.66	64.1	1.3	(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	40.4	53.5	6.1	36.3	55.1	8.6
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	51.0	41.7	7.3	52.4	38.8	8.8
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	56.6	36.6	6.8	52.9	39.3	7.8
12	47.5	42.5	10	48.82	42.2	9.0	(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	63.8	30.0	6.2	62.1	28.7	9.2
							Al <sub>8</sub> Mn <sub>5</sub>	62.9	37.1	0.0	61.5	36.2	2.3
							Al <sub>11</sub> Mn <sub>4</sub>	72.8	27.2	0.0	72.5	24.4	3.1
13	55	35	10	55.79	35.4	8.8	(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	58.6	10.9	30.5	58.0	12.9	29.1
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	48.9	41.0	10.1	47.6	43.8	8.6
							(Al <sub>1-x</sub> Mn <sub>x</sub> ) <sub>2</sub> Dy	63.1	3.9	33.0	63.5	3.5	33.0
14	65	32.5	2.5	68.94	29.4	1.7	(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	64.9	28.4	6.8	62.7	27.8	9.5
							Al <sub>3</sub> Dy	72.1	4.8	23.1	68.5	4.5	27.0
							Al <sub>4</sub> Mn	81.8	18.2	0	81.0	18.7	0.3
15	50	27.5	22.5	53.71	25.4	20.9	(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	71.1	22.5	6.5	66.3	24.8	8.9
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	75.7	24.1	0.2	73.2	24.9	1.9
							Al <sub>11</sub> Mn <sub>4</sub>	75.7	24.1	0.2	73.2	24.9	1.9
16	62.5	17.5	20	65.06	16.6	18.4	Al <sub>3</sub> Dy	76.1	0.9	23.0	73.4	1.7	24.9
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	74.5	19.4	6.1	69.3	21.8	8.9
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	75.0	18.6	6.4	71.6	19.9	8.5
17	82.5	12.5	5	88.09	8.8	3.2	(Al)	99.7	0.3	0.05	99.5	0.3	0.2
							Al <sub>6</sub> Mn	85.9	14.1	0.0	84.7	13.7	1.6
							Al <sub>3</sub> Dy	77.2	0.6	22.2	75.5	0.5	24.0
18	85	7.5	7.5	89.45	5.6	5.0	(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	76.3	17.0	6.7	74.1	17.2	8.7
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	76.3	17.0	6.7	74.1	17.2	8.7
							(Al <sub>x</sub> Mn <sub>1-x</sub> ) <sub>12</sub> Dy	76.3	17.0	6.7	74.1	17.2	8.7

**Table 2 continued**

No.	Compositions (at.%)						Phase identified	Measured Compositions EDS (at.%)			Measured Compositions EPMA (at.%)		
	Nominal			Measured				Al	Mn	Dy	Al	Mn	Dy
	Al	Mn	Dy	Al	Mn	Dy							
21	92.5	2.5	5	96.04	1.3	2.7	(Al)	99.6	0.3	0.1	99.6	0.1	0.3
							$(Al_xMn_{1-x})_{12}Dy$	82.3	8.6	9.1	81.4	10.7	7.9
							$Al_3Dy$	77.4	0.2	22.4	78.4	0.4	21.2
22	60	10	30	64.85	8.4	26.7	(Al)	99.5	0.2	0.3	99.7	0.2	0.1
							$(Al_{1-x}Mn_x)_2Dy$	65.4	4.1	30.6	65.5	3.9	30.6
							$(Al_xMn_{1-x})_{12}Dy$	59.3	33.0	7.7	61.0	31.2	7.8



**Fig. 1** (a) BSE image of the microstructure and (b) XRD results of alloy 14 annealed at 500 °C for 30 days

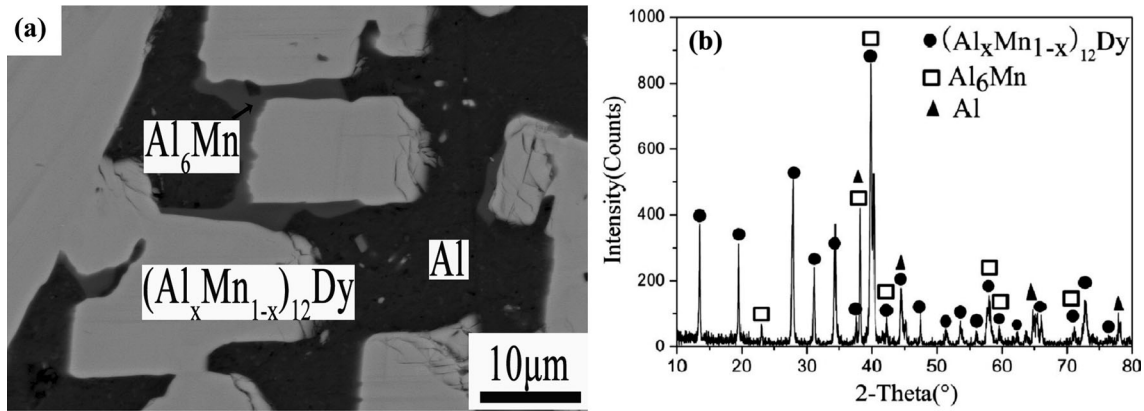


**Fig. 2** (a) BSE image of the microstructure and (b) XRD results of alloy 17 annealed at 500 °C for 30 days

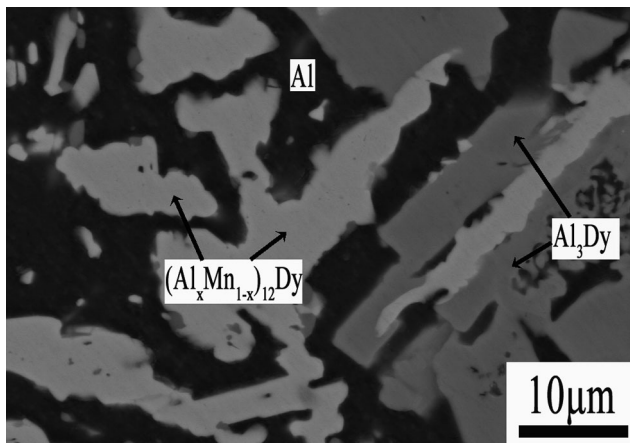
$AlDy + Liquid \rightarrow Al_2Dy_3$ , but  $Al_2Dy_3$  was not observed in the current work. It is most likely that the phase does not form during rapid cooling following melting. Although  $AlDy$  and  $AlDy_2$  will not co-exist when the alloy is in equilibrium, the co-existence of  $AlDy$ ,  $AlDy_2$  and  $(Al_{1-x}Mn_x)_2Dy$  is observed in alloy 1, as shown in Table 2. That means that alloy 1 is off-equilibrium.

Phases with ~64 at.% Dy in alloys 1-6 were proven by XRD to be  $AlDy_2$  rather than  $Al_2Dy_3$ . The crystal structure

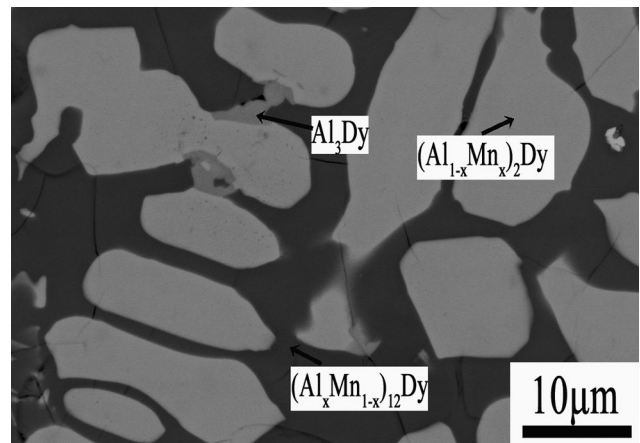
of  $Al_2Dy_3$  was determined before in Ref 26 and 27. The  $Al_2Gd_3$  type compounds  $Al_2Ho_3$  and  $Al_2Er_3$  form in the Al-Ho and Al-Er systems,<sup>[26,40]</sup> respectively. These are examples of the similarity between heavy RE metal compounds. Also,  $Al_2Dy_3$  was observed in the determination of the Al-Mo-Dy ternary phase diagram at 600 °C.<sup>[5]</sup> Finally,  $Al_2Dy_3$  appears stable below 600 °C according to the Al-Dy phase diagram in Ref 12. Thus, it is concluded that  $Al_2Dy_3$  is stable at 500 °C.



**Fig. 3** (a) BSE image of the microstructure and (b) XRD results of alloy 19 annealed at 500 °C for 30 days



**Fig. 4** BSE image of the microstructure of alloy 21, the dark phase is Al, the phase grey with point dispersed is  $\text{Al}_3\text{Dy}$ , the light gray phase is  $(\text{Al}_x\text{Mn}_{1-x})_{12}\text{Dy}$



**Fig. 5** BSE image of the microstructure of alloy 16, the gray phase is  $\text{Al}_3\text{Dy}$ , the light gray phase is  $(\text{Al}_{1-x}\text{Mn}_x)_2\text{Dy}$ , and the dark gray matrix phase is  $(\text{Al}_x\text{Mn}_{1-x})_{12}\text{Dy}$

The similar compound,  $\text{Al}_2\text{Ho}_3$ , forms by the peritectic reaction  $\text{AlHo} + \text{liquid} \rightarrow \text{Al}_2\text{Ho}_3$  at 994 °C.<sup>[41]</sup> Also,  $\text{Al}_2\text{Ho}_3$  was confirmed to exist at 500 °C in the Al-V-Ho system.<sup>[42]</sup> The Al-V-Ho alloys were heated at 900 °C for 20 days to guarantee homogeneity before the 500 °C final heat treatment. The temperature of 900 °C was high enough for diffusion to enable the formation of  $\text{Al}_2\text{Ho}_3$ . In this work, alloys were kept at 500 °C and had no high temperature anneal. Apparently 500 °C is too low for sufficient diffusion to occur. Therefore it is assumed that  $\text{Al}_2\text{Dy}_3$  is a stable phase at 500 °C and should be included in Fig. 7, although it was absent in the current work.

In the Al-Dy system,<sup>[12]</sup> the solubility of Al in (Dy) is negligible. A large amount of Al was detected in (Dy) in alloys 3, which shows that this alloy is off-equilibrium. Contents of Al in (Dy) in alloys 4-6 are smaller than that in alloy 3, which suggests that these alloys are closer to equilibrium.

Based on data available in Table 2, the phase diagram of the Al-Mn-Dy system was drawn, as shown in Fig. 7. It should be noted that the tie-triangles with solid lines are

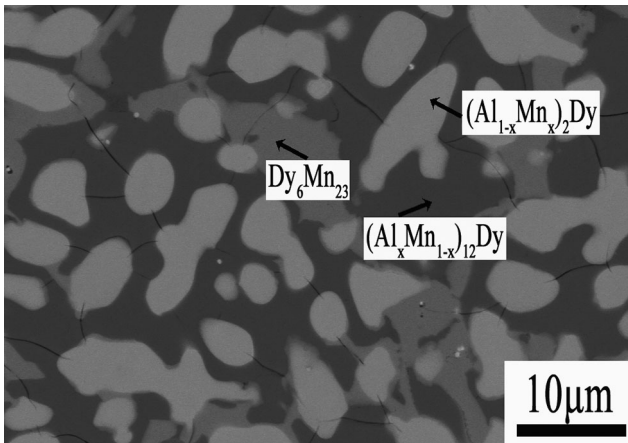
directly supported by the equilibrated alloys, and those with dash lines were deduced from the surrounding phase relationships.

The maximum solubility of Mn in  $\text{Al}_3\text{Dy}$  is 4.8 at.%, which was observed in alloy 16. Thus, the composition at the  $\text{Al}_3\text{Dy}$  corner of the tie-triangle [ $\text{Al}_3\text{Dy} + (\text{Al}_{1-x}\text{Mn}_x)_2\text{Dy} + (\text{Al}_x\text{Mn}_{1-x})_{12}\text{Dy}$ ] is 72.1 at.% Al, 4.8 at.% Mn and 23.1 at.% Dy.

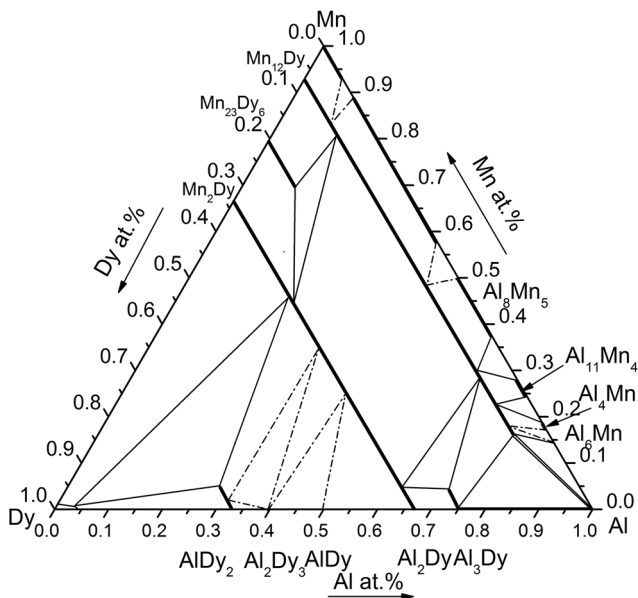
The maximum solubility of Mn in  $\text{AlDy}_2$  is 5.7 at.%, which was observed in alloy 6. Thus the composition of the  $\text{AlDy}_2$  corner in the tie-triangle [ $\text{AlDy}_2 + (\text{Al}_{1-x}\text{Mn}_x)_2\text{Dy} + (\text{Dy})$ ] is 26.4 at.% Al, 5.7 at.% Mn and 67.9 at.% Dy.

The maximum solubility of Al in  $\text{Mn}_{23}\text{Dy}_6$  is 10.7 at.%, which was observed in alloy 9. Thus the composition of the  $\text{Mn}_{23}\text{Dy}_6$  corner of the tie-triangle [ $\text{Mn}_{23}\text{Dy}_6 + (\text{Al}_{1-x}\text{Mn}_x)_2\text{Dy} + (\text{Al}_x\text{Mn}_{1-x})_{12}\text{Dy}$ ] is 10.7 at.% Al, 70.9 at.% Mn and 18.4 at.% Dy.

For the Al-rich alloy, the annealing temperature of 500 °C seems high enough for sufficient Al diffusion to



**Fig. 6** BSE image of the microstructure of alloy 9, the gray phase is  $Mn_{23}Dy_6$ , the light gray phase is  $(Al_{1-x}Mn_x)_2Dy$ , and the matrix phase is  $(Al_xMn_{1-x})_{12}Dy$



**Fig. 7** The phase diagram of the Al-Mn-Dy system at 500 °C

achieve equilibrium, since the Al melting point is only 660 °C. The phase boundary in alloy 19 (Fig. 3) is very clear suggesting equilibrium. Results from alloy 19 are consistent with the previous experimental investigation of the Al-Mn phase diagram,<sup>[14, 15, 43, 44]</sup> which show that only  $Al_6Mn$  exists in the Al-rich corner at 500 °C, and disagrees with the thermodynamic description of the Al-Mn system.<sup>[45-47]</sup>

In addition, Gordillo et al.<sup>[6]</sup> studied the effect of heat treatment on an Al-5Mn-2Ce (at.%) alloy by using x-ray diffraction and electron microscopy. The master alloy was prepared by powder processing and extruding. The extrudate contained a mixture of fcc Al,  $Al_{20}Mn_2Ce$ ,  $Al_6Mn$  and a small amount of  $Al_{12}Mn$  and  $Al_{11}Ce_3$ . After heat treatment at 450 °C for 48 h, the  $Al_{20}Mn_2Ce$  and  $Al_6Mn$  phases

decomposed completely and the volume fraction of  $Al_{12}Mn$  increased to 72-73 vol.%. Heat treatment at 500 °C for 48 h resulted in the decrease of  $Al_{12}Mn$  volume fraction to 9 vol.%, while amounts of each phase in the Al-5Mn-2Ce alloy becomes 60 vol.% fcc Al, 22 vol.%  $Al_3(Mn,Ce)$ , 8 vol.%  $Al_6Mn$  and 1 vol.%  $Al_{11}Ce_3$ . After prolonged annealing for 30 days in our work, the  $Al_{12}Mn$  phase was not observed. These results suggest that  $Al_{12}Mn$  is metastable at 500 °C, and that the temperature of the peritectoid reaction  $Al + Al_6Mn \rightarrow Al_{12}Mn$  is below 500 °C. That is lower than the reaction temperature of 507 °C predicted in the assessment work of Jansson.<sup>[45]</sup> Thus,  $Al_{12}Mn$  is not included in the Al-rich corner in Fig. 7. In addition, it is hard to distinguished  $\lambda$ - $Al_4Mn$  from  $\mu$ - $Al_4Mn$ . Therefore these two phases are treated as single  $Al_4Mn$  in this work.

#### 4. Summary

1. The ternary phase equilibria relationships in the Al-Mn-Dy system at 500 °C have been established by XRD, SEM/EDS combining with EPMA techniques and deduced from the surrounding phase relationships. There are 12 tie-triangles in this system, of which five were measured and seven were deduced.
2. Two extensive solid solutions were found in this system. One was a continuous solid solution between  $Al_2Dy$  and  $Mn_2Dy$  to form  $(Al_{1-x}Mn_x)_2Dy$ . In the other solid solution, Al substitutes for Mn in  $Mn_{12}Dy$  to form  $(Al_xMn_{1-x})_{12}Dy$ . The maximum solubility of Al in  $Mn_{12}Dy$  is 79.3 at.%.
3.  $Al_2Dy_3$  was not observed in the current work, which is assumed to be caused by difficulty forming  $Al_2Dy_3$  both by the peritectic reaction  $AlDy + Liquid \rightarrow Al_2Dy_3$  on cooling and by heat treatment at 500 °C.

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