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Journal of Alloys and Compounds 218 (1995) 127–130

Journal of ALLOYS AND COMPOUNDS

Subsolidus phase relations of the La–Fe–Al ternary system

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Received 24 June 1994; in final form 19 August 1994

Abstract

The subsolidus phase relations of the La–Fe–Al ternary system have been investigated by X-ray powder diffraction. In this ternary system, there exist six kinds of ternary compounds and their solid solutions, i.e. A (La/Fe/Al (at.%) = 10/12/78), B (36/44/20), $LaFe_4Al_8$, $LaFe_{13-x}Al_x$ ($2.34 \leqslant x \leqslant 7.28$), $La_2Fe_7Al_{10}$ and $LaAl_{2-x}Fe_x$ ($0 \leqslant x \leqslant 0.4$). A and B are two kinds of new ternary compounds with unknown crystal structures. For the $LaFe_{13-x}Al_x$ solid solution with cubic $NaZn_{13}$-type structure, the solid solubility has been determined by a parametric method. The ternary system can be divided into 17 three-phase and four two-phase regions. The subsolidus phase relations of the La–Fe–Al ternary system are presented.

Keywords: Phase relations; X-ray powder diffraction; Rare earths

1. Introduction

$LaCo_{13}$ has the highest 3d metal content among the known rare earth intermetallic compounds. Its excellent magnetic properties have attracted the interest of many researchers [1–5]. Since it has the cubic $NaZn_{13}$-type structure, it is unlikely to have appreciable magnetocrystalline anisotropy. Thus it should be important to search for 1:13 phase intermetallic compounds with lower symmetry. Several researchers made efforts to improve the magnetocrystalline anisotropy of $LaCo_{13}$-based intermetallic compounds by elemental substitution [4] and nitrogenation [5], but did not degrade their crystal symmetry. Palstra et al. [6] reported their results for $LaFe_{13-x}Al_x$ ($1.04 \leqslant x \leqslant 7.02$) with the cubic $NaZn_{13}$-type structure. With the increase of Al content, three kinds of magnetic transitions (anti-ferromagnetic, ferromagnetic and mictomagnetic) had been observed. From the point of view of crystal structure, a disorder–order structural transition might exist in the $La(T,M)_{13}$ (T represents transition metal elements and M non-transition metal elements) systems. Our previous work on $La(Fe,Al)_{13}$, $La(Fe,Si)_{13}$ and $La(Co,Si)_{13}$ [7–10] confirmed the disorder–order structural transition in these systems, and we obtained lower crystal symmetry (orthorhombic or tetragonal symmetry). To our knowledge, no results have been reported on the phase relations of the La–Fe–Al ternary system. To clarify the solid solubility of $LaFe_{13-x}Al_x$ and the structural transition, we have systematically investigated the subsolidus relation of the La–Fe–Al ternary system.

2. Experimental procedures

2.1. Sample preparation

The La–Fe–Al samples were prepared by repeated arc melting in an atmosphere of ultrapure argon gas. The purities of the starting materials Fe and Al are higher than 99.9%, and 99.5% for La. The melted samples were wrapped in Ta foil and annealed in evacuated quartz tubes for several weeks at 773–1173 K. The weight loss of each sample is less than 0.5 wt.%.

2.2. X-ray diffraction

A Guinier–de Wolff X-ray monochromatic focusing transmission camera with Fe Kα radiation ($\lambda = 1.9373$ Å) was used to examine the samples before and after annealing. By comparing the X-ray diffraction (XRD) patterns to those of the reported compounds, we can determine the phase composition in the samples. The XRD patterns used to determine their crystal structure parameters were collected by a Rigaku automatic X-

SSDI 0925-8388(94)01382-9

ray diffractometer with Cu Kα radiation and a graphite monochrometer ($\lambda = 1.5405$ Å). High purity Si was added to the samples as an internal standard to correct the 2θ positions of the diffraction in the case of precision measurements. The lattice parameters were then calculated using a standard least-squares reduction method.

3. Experimental results and discussion

3.1. Binary systems

For the binary La–Fe system, our results show that no La–Fe binary compounds exist, which accords with the reported results [11]. We had calculated the heat of formation of the La–Fe–Al ternary system by using the Miedema semiexperimental method [12], indicating that the heat of formation between La and Fe is positive; thus there is no stable La–Fe binary compound.

In the binary La–Al system, five kinds of binary La–Al compounds were reported, i.e. La_3Al [13], $LaAl_2$ [14], $LaAl_3$ [15], $LaAl_4$ [15] and La_3Al_{11} [16]. Under our present experimental conditions, we obtained only four kinds of binary La–Al compounds, but not $LaAl_4$. According to the phase diagram of the binary La–Al system, $LaAl_4$ can exist in two phases. One is the high temperature phase, with the tetragonal ($D1_3$) structure isotypic with $BaAl_4$ [14]. Gomes de Mesquita and Buschow [16] reported it might actually be La_3Al_{11}. However, Zalutskii and Kripykevich [17] reported an orthorhombic structure. The other is the low temperature phase, with an orthorhombic structure, different from the orthorhombic structure of La_3Al_{11} reported by Gomes de Mesquita and Buschow [16]. The transition temperature from the high temperature to the low temperature phase is 1180 K. Our samples were annealed at 773 K. If $LaAl_4$ does exist, then its low temperature phase should be obtained. However, under our synthesis conditions, there is no evidence of the existence of $LaAl_4$. We think that the structure of $LaAl_4$ might be actually the same as that of La_3Al_{11}, since their compositions are very close. Thus it is difficult to obtain separately $LaAl_4$ and La_3Al_{11}.

For the binary Fe–Al system, we only obtained two kinds of binary Fe–Al compounds, i.e. FeAl and $FeAl_2$. In fact, the binary Fe–Al system diagram is very complex, and these binary compounds are strongly related to the synthesis conditions.

3.2. Ternary compounds

In the ternary system, we obtained six kinds of ternary compounds and solid solutions, i.e. A (La/Fe/Al (at.%) = 10/12/78), B (36/44/20), $LaFe_4Al_8$, $LaFe_{13-x}Al_x$ ($2.34 \leqslant x \leqslant 7.28$), $La_2Fe_7Al_{10}$ and $LaAl_{2-x}Fe_x$ ($0 \leqslant x \leqslant 0.4$). A and B are two kinds of new ternary compounds with unknown crystal structures. The structural parameters of the ternary compounds are listed in Table 1.

Table 1
Structural parameters of La–Fe–Al ternary compounds

Compound	Lattice parameters	Space group
A	Unknown	Unknown
B	Unknown	Unknown
$LaFe_4Al_8$	$a = 8.900$ Å, $c = 5.075$ Å	*I4/mmm*
$LaFe_{13-x}Al_x$ ($2.34 \leqslant x \leqslant 7.28$)	$a = 11.983$–11.668 Å, $Z = 8$	*Fm3c*
$La_2Fe_7Al_{10}$	$a = 8.962$ Å, $c = 12.98$ Å, $Z = 3$	*R3m*
$LaAl_{2-x}Fe_x$ ($0 \leqslant x \leqslant 0.4$)	$a = 8.147$–8.111 Å, $Z = 8$	*Fd3m*

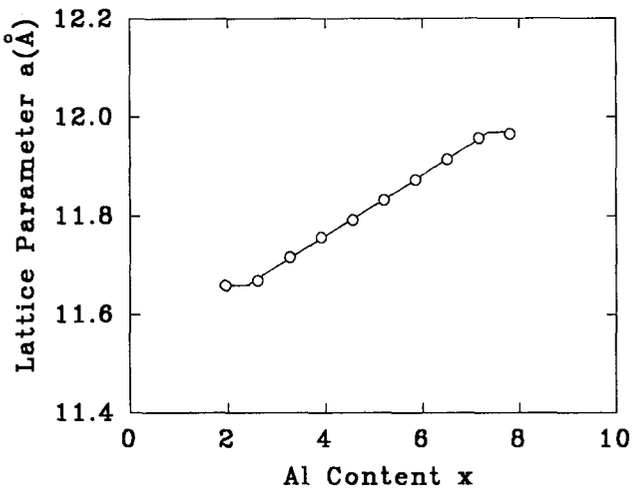

Fig. 1. The variation of the lattice parameter a vs. the Al content x for $LaFe_{13-x}Al_x$.

For the $LaFe_{13-x}Al_x$ solid solution with cubic $NaZn_{13}$-type structure, the solid solubility has been determined by a parametric method. In Fig. 1, we show the dependence of the lattice parameter a on the Al content x. According to the variation between the lattice parameter a and the Al content x, we can determine the solid solubility of $LaFe_{13-x}Al_x$ solid solution, which is $2.34 \leqslant x \leqslant 7.28$. Comparing our results with of those Palstra et al. [6], where the lower limit of the solid solution is 1.04, we found a lower limit of 2.34, which is much higher. The higher limit was determined as $x = 7.28$, which is almost the same as the results of Palstra et al. [6]. As to the structure of the $LaFe_{13-x}Al_x$ solid solution, Helmholt et al. [18] reported neutron diffraction results which showed that the 8b crystal position is fully occupied by Fe atoms and the 96i crystal position is occupied statistically by Fe and Al atoms. We also used the Lazy program (a computer program to calculate XRD intensity) to calculate the XRD intensity of $LaFe_{13-x}Al_x$ solid solution. The calculated intensities agree with the observed intensities very well, which also supports the suggested way of atomic occupancy. In Table 2 we list indices and the

Table 2
List of indices and the calculated and observed spacings and diffraction intensities for $LaFe_{10.4}Al_{2.6}$

Number	*hkl*	d_{obs} (Å)	d_{cal} (Å)	I_{obs}	I_{cal}
1	220	4.116	4.1255	25	23
2	222	3.355	3.3685	21	19
3	400	2.901	2.9172	20	12
4	420	2.5981	2.6092	62	64
5	422	2.3735	2.3819	100	100
6	531	1.9697	1.9724	98	98
7	442(600)	1.9444	1.9448	18	13
8	620	1.8442	1.8450	32	32
9	444	1.6838	1.6842	14	17
10	640	1.6171	1.6182	19	17
11	642	1.5594	1.5593	26	25
12	800	1.4589	1.4586	14	9
13	644(820)	1.4151	1.4150	18	16
14	660(822)	1.3754	1.3752	7	5
15	753(911	1.2821	1.2808	12	8
16	931	1.2235	1.2232	9	8

[a] = 11.668(2) Å; space group, *Fm3c*; $Z = 8$.

Table 3
Atomic parameters for $LaFe_{10.4}Al_{2.6}$

Atom	Position	*x*	*y*	*z*	*N*
La	8a	0.25	0.25	0.25	8
Fe	8b	0.0	0.0	0.0	8
Fe	96i	0.0	0.1750	1.1135	74
Al	96i	0.0	0.1750	0.1135	22

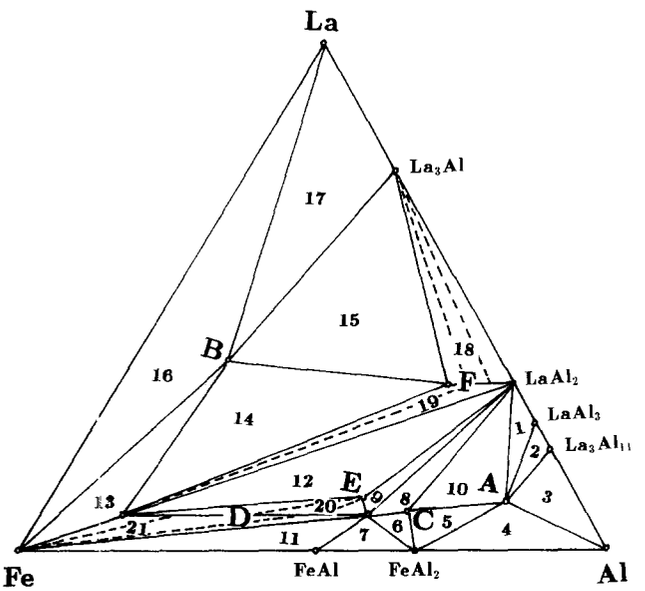

Fig. 2. The subsolidus phase relations of the La–Fe–Al ternary system: A, B, C, $LaFe_4Al_8$; D, $LaFe_{13-x}Al_x$; E, $La_2Fe_7Al_{10}$; F, $LaAl_{2-x}Fe_x$.

calculated and observed spacings and intensities for $LaFe_{10.4}Al_{2.6}$. The atomic parameters for $LaFe_{10.4}Al_{2.6}$ are listed in Table 3.

Table 4
Phase regions and phase compositions in the La–Fe–Al ternary system

Phase region	Phase compositions
1	$LaAl_2 + LaAl_3 + A$
2	$LaAl_3 + La_3Al_{11} + A$
3	$La_3Al_{11} + Al + A$
4	$FeAl_2 + Al + A$
5	$LaFe_4Al_8 + FeAl_2 + A$
6	$LaFe_4Al_8 + FeAl_2 + LaFe_{13-x}Al_x$
7	$LaFe_{13-x}Al_x + FeAl_2 + FeAl$
8	$LaFe_{13-x}Al_x + LaFe_4Al_8 + LaAl_2$
9	$LaFe_{13-x}Al_x + La_2Fe_7Al_{10} + LaAl_2$
10	$LaFe_4Al_8 + LaAl_2 + A$
11	$LaFe_{13-x}Al_x + FeAl + Fe$
12	$LaFe_{13-x}Al_x + La_2Fe_7Al_{10} + LaAl_2$
13	$LaFe_{13-x}Al_x + B + Fe$
14	$LaFe_{13-x}Al_x + LaAl_{2-x}Fe_x + B$
15	$La_3Al + LaAl_{2-x}Fe_x + B$
16	$La + Fe + B$
17	$La + La_3Al + B$
18	$La_3Al + LaAl_{2-x}Fe_x$
19	$LaFe_{13-x}Al_x + LaAl_{2-x}Fe_x$
20	$La_2Fe_7Al_{10} + LaFe_{13-x}Al_x$
21	$LaFe_{13-x}Al_x + Fe$

For $LaAl_2$, Zarechnyuk et al. [19] stated that there exists no solubility of Fe in $LaAl_2$. However, according to our experimental results, there exists a small solubility of Fe in $LaAl_2$. The solubility is $0 \leqslant x \leqslant 0.4$ (for $LaAl_{2-x}Fe_x$).

The compound $LaFe_4Al_8$ crystallizes in a tetragonal structure isotypic with $ThMn_{12}$, space group *I4/mmm*, which is consistent with the results obtained by Buschow et al. [20]. $La_2Fe_7Al_{10}$ was also obtained, which agrees with the diffraction data and structural parameters given by the JCPDS 34-261 card.

3.3. Ternary system

According to results of a phase analysis, the ternary La–Fe–Al system can be divided into 17 three-phase regions and four two-phase regions. Fig. 2 shows the subsolidus phase relations of the La–Fe–Al ternary system. In Table 4, we list all phase regions and phase compositions of each phase region in the La–Fe–Al ternary system.

4. Conclusion

The subsolidus phase relations of the La–Fe–Al ternary system have been determined, and six kinds of ternary compounds and their solid solutions, i.e. A (La/Fe/Al (at.%) = 10/12/78), B (36/44/20), $LaFe_4Al_8$, $LaFe_{13-x}Al_x$ ($2.34 \leqslant x \leqslant 7.28$), $La_2Fe_7Al_{10}$ and $LaAl_{2-x}Fe_x$ ($0 \leqslant x \leqslant 0.4$) were obtained. A and B are two kinds of new ternary compounds with unknown crystal

structures. The ternary system can be divided into 17 three-phase and four two-phase regions.

Acknowledgement

This work was supported by the National Natural Science Foundation of China.

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