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Y–Fe–Al ternary system: partial isothermal section at 1070 K Powder X-ray diffraction and Mössbauer spectroscopy study

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Abstract

Phase equilibria were established in the Y–Fe–Al ternary system within the concentration region 50–100 at.% Al for an isothermal section at 1070 K by means of scanning electron microscopy and powder X-ray diffraction. Two ternary aluminides were observed, YFe_xAl_{12-x} ($4 \leq x \leq 5.6$) with the $ThMn_{12}$-type structure, $a=8.6467(9)$–$8.7604(7)$ Å, $c=5.0374(6)$–$5.0504(5)$ Å and YFe_2Al_{10}, $YbFe_2Al_{10}$-type structure, $a=8.9649(6)$ Å, $b=10.1568(6)$ Å, $c=9.0113(6)$ Å. The only binary which forms a prolonged solid solution range is YAl_2. The unit cell edge of the YFe_xAl_{2-x} compounds, $MgCu_2$-type structure, decreases with Fe content from 7.834(9) Å for $x=0$ down to 7.689(4) Å for $x=0.5$. ^{57}Fe Mössbauer spectroscopy data of YFe_2Al_{10} show an unusually large isomer shift for Fe in Al-containing intermetallics and confirm that no magnetic ordering occurs down to 5 K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Intermetallics; X-Ray diffraction; Phase diagrams; Nuclear resonances

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1. Introduction

YFe_xAl_{12-x} ($4 \leq x \leq 6$) alloys with $ThMn_{12}$-type structure have attracted much interest as they are isostructural with the intermetallic systems containing an *f* element and Fe, potential candidates for permanent magnets with the lowest *f*-element content. However controversial results on these compounds have been published in the literature and it was recently shown that at least for the composition $4 \leq x \leq 4.2$ those results might be explained by insufficient chemical and structural characterization of the samples used in the study of the magnetic properties [1].

Phase equilibria in the Y–Fe–Al ternary system, at 770 K and within the concentration range 0–33.3 at.% Y, had already been investigated [2]. The existence of three ternary compounds were reported: Y(Fe, Al)$_{12}$ with $ThMn_{12}$-type structure, YFe_2Al_{10} crystallizing with an unknown structure and $YFe_{1+x}Al_{1-x}$ belonging to the $MgZn_2$-type. Later, and based on the powder X-ray diffraction (XRD) of the Nd(Fe, Al)$_{12}$ and Dy(Fe, Al)$_{12}$ systems, the same authors claimed that no formation of individual ternary RFe_2Al_{10} compounds was observed [3]. Recently, however, the LnT_2Al_{10} (Ln=Y, La–Nd, Sm, Gd–Lu and T=Fe, Ru, Os) compounds were prepared and found to crystallize with the $YbFe_2Al_{10}$-type structure [4].

An investigation of the phase formation and characterization of the Y–Fe–Al ternary alloys within the concentration range 50–100 at.% Al, was initiated [1,5]. Particular attention was devoted to the YFe_xAl_{12-x} ($1 \leq x \leq 7$) alloys and to the isothermal section at 1070 K, since in the preparation of samples for physical measurements most of the heat treatments are performed at this temperature. Phase analyses of samples ‘as cast’ as well as annealed at 870 and 1070 K were performed. The crystal structure refinement from powder XRD data and the ^{57}Fe Mössbauer spectra of YFe_2Al_{10} are reported for the first time.

2. Experimental

Thirty ternary samples with ≥50% at. Al and covering

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Table 1
Estimated parameters from the Rietveld refinement of the $ThMn_{12}$-type phases in the YFe_xAl_{12-x} samples with nominal composition $4.4 \leq x \leq 6$[a]

Sample	x	4.4	5	6
Unit cell parameters (Å)	a	8.7268(4)	8.6784(6)	8.6467(9)
	c	5.0459(4)	5.0418(4)	5.0374(6)
Unit cell volume (Å^3)		384.29(4)	379.72(5)	377.01(7)
Site occupation factors				
(2*a*) (0,0,0)	Y	1.0	1.0	1.0
(8*f*) (0.25,0.25,0.25)	Fe	4.0	4.0	4.0
(8*j*) (x_1,0.5,0)	Al	3.5(1)	2.9(1)	2.4(1)
	Fe	0.5(1)	1.1(1)	1.6(1)
(8*i*) (x_2,0,0)	Al	4.0(1)	4.0(1)	3.7(1)
Position parameters	x_1	0.2796(5)	0.2778(5)	0.2762(5)
	x_2	0.3455(6)	0.3428(6)	0.3419(8)
Equivalent isotropic temperature factors [6]	B_{eq} 2*a*	1.0(9)	1.1(9)	1.9(9)
	B_{eq} 8*f*	1.2(9)	1.1(9)	1.8(9)
	B_{eq} 8*j*	1.3(9)	1.5(9)	2.6(9)
	B_{eq} 8*i*	1.2(9)	1.0(9)	1.4(9)
Agreement factors	R_{Bragg}	7.56	3.84	4.67
	R_F	8.49	4.22	4.83
Estimated composition		$YFe_{4.5(1)}Al_{7.5(1)}$	$YFe_{5.1(1)}Al_{6.9(1)}$	$YFe_{5.6(1)}Al_{6.1(1)}$

[a] Refinement performed in the $I4/mmm$ space group and in the 2θ range 20.00–100.00° (CuKα radiation); 72 measured reflections, 29 refined parameters. In the bottom line composition estimated from the site occupation factors.

all the identified phase fields [2] were arc melted and annealed under vacuum at 870 and 1070 K for 30 days. The details on sample preparation are presented in Ref. [1]. Diffracted X-ray intensities were collected on a Philips automated diffractometer system PW1710. The experimental details and Rietveld refinement details are described in Ref. [1] and Tables 1 and 2. Powdered samples were pressed together with lucite powder into perspex holders, in order to obtain homogeneous and isotropic ^{57}Fe Mössbauer absorbers containing ~5 mg/cm^2 of natural iron. Details on the spectra data collection and analysis may be found in Ref. [1].

Table 2
Estimated atomic positions (x,y,z), site occupation factors (s.o.f.) and B_{eq} equivalent isotropic temperature factors [6] from the Rietveld analysis of the powder XRD data of the YFe_2Al_{10} sample [$YbFe_2Al_{10}$-type structure, *Cmcm* space group, $a=8.9649(6)$ Å, $b=10.1568(6)$ Å, $c=9.0113(6)$ Å, V=820.52(6) Å^3, Z=4, 2θ range 20–100° (CuKα radiation), 242 measured reflections, 41 refined parameters ($R_{Bragg}=0.0880$, $R_F=0.0589$)]

Atom	Site	x	y	z	s.o.f.	B_{eq}
Y	4*c*	0	0.1271(4)	0.25	1.0	2.9(9)
Fe	8*d*	0.25	0.25	0	1.0	2.4(9)
Al1	8*g*	0.2299(9)	0.361(1)	0.25	1.0	2.4(9)
Al2	8*g*	0.3496(9)	0.128(1)	0.25	1.0	3.4(9)
Al3	8*f*	0	0.1569(9)	0.5995(9)	1.0	2.3(9)
Al4	8*f*	0	0.379(1)	0.0508(9)	1.0	3.1(9)
Al5	8*e*	0.2242(8)	0	0	1.0	2.2(9)

3. Results and discussion

3.1. Phase equilibria diagram of the Y–Fe–Al system

The phase field distribution is consistent with the phase equilibria at 770 K suggested in Ref. [2]. The solubilities of the third element in the binary compounds were found to be insignificantly small except in the case of YAl_2 that forms a prolonged solid solution range with the $MgCu_2$-type structure. At 1070 K the unit-cell edge of the YFe_xAl_{2-x} decreased with Fe content from $a=7.834(9)$ Å for $x=0$ down to $a=7.689(4)$ Å for $x=0.5$, in agreement with previous results [7].

As far as the YFe_xAl_{12-x} ($1 \leq x \leq 7$) alloys are concerned, powder XRD and scanning electron microscopy (SEM) analyses have shown that all the ‘as cast’ samples within the above mentioned concentration range were multiphase. Small single crystals of the compound with the $ThMn_{12}$-type structure could only be found in the $3 \leq x \leq 4.5$ samples [5]. After annealing at 870 K only $YFe_{4.2}Al_{7.8}$ was obtained as a single phase. It was necessary to anneal at 1070 K to obtain YFe_xAl_{12-x} single phases within the composition range $4 \leq x \leq 4.2$ [1].

For $x>4.2$ the presence of the strongest diffraction peaks of Fe–Al binary alloys could still be detected by powder XRD after annealing at 1070 K. Results of the Rietveld refinements of the main $ThMn_{12}$-type phases for the samples $x=4.4$, 5 and 6 are presented in Table 1 and for $x=5$ and 6 in Fig. 1. On both patterns, at $2\theta \approx 44°$, the

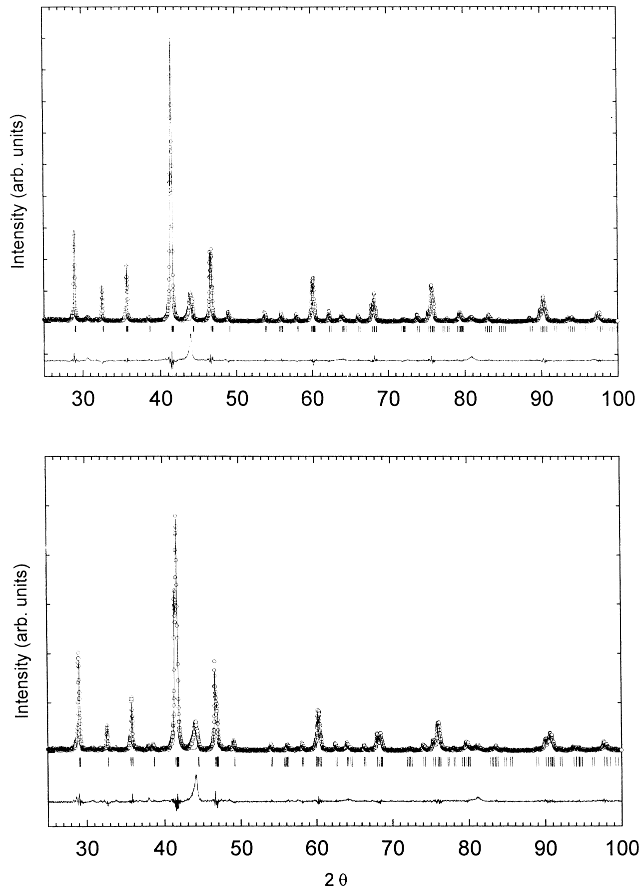

Fig. 1. X-Ray patterns for the YFe_5Al_7 (a) and YFe_6Al_6 (b) samples. For each sample the powder diffraction profile calculated by the Rietveld refinement is plotted on the observed data. The short vertical lines below each pattern represent the positions of all possible Bragg reflections and the lower curves show the difference between the observed and the calculated intensities in the same scale as the intensity data.

strongest diffraction peaks of the Al-rich FeAl binary alloys [1] are clearly visible, overlapping the (330) reflections of the $ThMn_{12}$ phases. Those peaks may be easily mistaken by the $ThMn_{12}$ (330) reflections if the Rietveld refinement is not performed. Small quantities of those impurity Fe–Al alloys may be thus overlooked. Considering the estimated site occupation factors, the composition of the $ThMn_{12}$ phase with the largest Fe concentration is $YFe_{5.6}Al_{6.1}$ (Table 1). A linear relationship is obtained between the unit-cell parameters, a and c, and the estimated Fe content of the $ThMn_{12}$-type phases (Fig. 2). Previously, although only for three samples, a similar dependence was reported [8]. However, the a and c values were plotted against the total Fe content of the samples, although the refinement of neutron powder diffraction data indicated that the actual Fe content of the $ThMn_{12}$-type phases were significantly lower for $x \geq 5$. The linear decrease of a and c with the increase of the actual Fe content of the $ThMn_{12}$-type phases (Fig. 2) is consistent with a gradual replacement of the Al atoms by the smaller

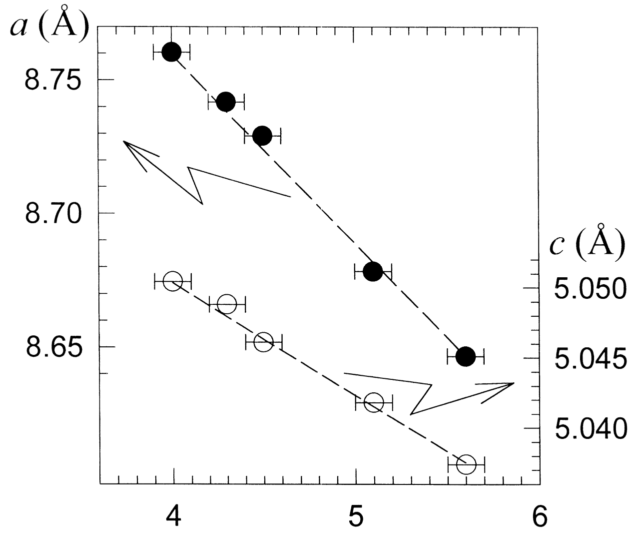

Fig. 2. Unit-cell parameters of the YFe_xAl_{12-x} ($4 \leq x \leq 5.6$) compounds vs. their Fe content estimated from the Rietveld refinement. Data for $4 \leq x \leq 4.3$ were taken from Ref. [1]. Horizontal error bars represent the errors estimated by the Rietveld refinement for the Fe contents. Estimated errors for the unit-cell parameters are much smaller than the width of the circles (cf. Table 1).

Fe atoms on only one crystallographic site, 8*j*, in agreement with the estimated site occupation factors.

3.2. Rietveld refinement and ^{57}Fe Mössbauer spectra of the YFe_2Al_{10} compound

At 1070 K the powder X ray diffractogram of the $x=2$ sample suggest the formation of a structure related to the $ThMn_{12}$ one. At the approximate 2θ angles where the strongest diffraction peaks of this phase were expected sets of two or three very close peaks were observed. The powder XRD data could be refined assuming the $YbFe_2Al_{10}$-type structure [4], *Cmcm* space group (No. 63). Details of the crystallographic data are given in Table 2. Calculated interatomic distances for Y and Fe are summarized in Table 3. Besides the peaks indexed to the new YFe_2Al_{10} phase only weak extra peaks assigned to YAl_3 were observed from the powder XRD data of the sample annealed at 1070 K (Fig. 3).

Although only one peak is observed in the Mössbauer

Table 3
Interatomic distances (d) and average numbers of nearest neighbors (NNs) of Y and Fe in YFe_2Al_{10}

	NN	Atom	d (Å)		NN	Atom	d (Å)
Y(4*c*)	2	Al(8*f*)	3.124	Fe(8*f*)	2	Al(8g)	2.524
	2	Al(8*g*)	3.134		2	Al(8*f*)	2.550
	2	Al(8*g*)	3.143		2	Al(8*f*)	2.592
	2	Al(8*f*)	3.164		2	Al(8*f*)	2.636
	2	Al(8*g*)	3.187		2	Al(8*g*)	2.724
	4	Al(8*f*)	3.283		2	Y(4*c*)	3.414
	4	Fe(8*d*)	3.414				

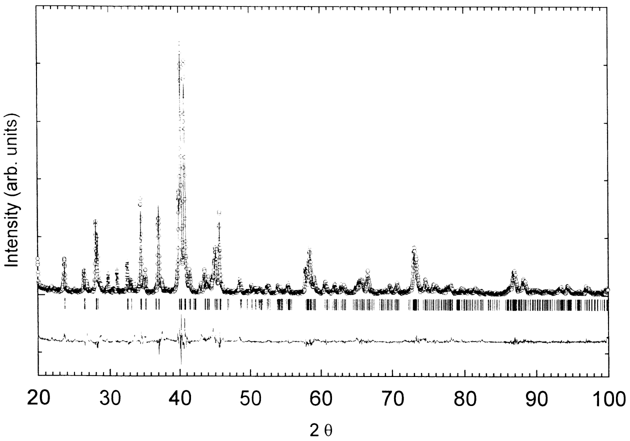

Fig. 3. X-Ray pattern for the YFe_2Al_{10} compound. See Fig. 1 caption.

spectra taken at room temperature and 5 K (Fig. 4), it is too narrow at the base to be reproduced by the shape of a single Lorentzian line. Fitting the spectra with an unresolved quadrupole doublet gives therefore a significantly better fit. The estimated hyperfine parameters are: the isomer shift relative to metallic Fe at room temperature $\delta=0.31$ mm/s at 298 K and 0.43 mm/s at 5 K; the quadrupole splitting $\Delta=0.13$ mm/s, constant with temperature. The quadrupole interaction should in fact be nonzero since the point symmetry on the Fe site is lower than cubic. The Fe atoms are surrounded by 10 Al atoms at similar distances 2.62±0.1 Å (Table 3) with the spatial arrangement shown in Fig. 5. Beyond this shell of Al atoms, the next-nearest atoms are Y at a distance 30% higher: 3.414 Å. The increase in the δ values as the temperature decreases is due to the second-order Döppler shift. In Fe–Al alloys, as well as on Fe–Al intermetallics positive δ relative to α-Fe, increasing with the number of Al nearest neighbors, are always observed. According to calculations based on the Miedema cellular atomic model for the Mössbauer δ [9], the room-temperature δ of an Fe atom in a strain-free Al structure is expected to be ≈0.26 mm/s, in agreement with the observed δ values for Al_6Fe (0.22 mm/s) and $Al_{13}Fe_4$ (0.20 mm/s) where Fe atoms are completely surrounded by nine to 11 Al atoms. In YFe_2Al_{10}, where they are surrounded by 10 Al atoms, the observed $\delta=0.31$ mm/s is even larger than the theoretical 0.26 mm/s value. The unusual values of δ and Δ of YFe_2Al_{10}, as well as the very good fit of the spectrum, confirm the absence of Fe-containing impurity phases as deduced from the X-ray diffractogram of this sample.

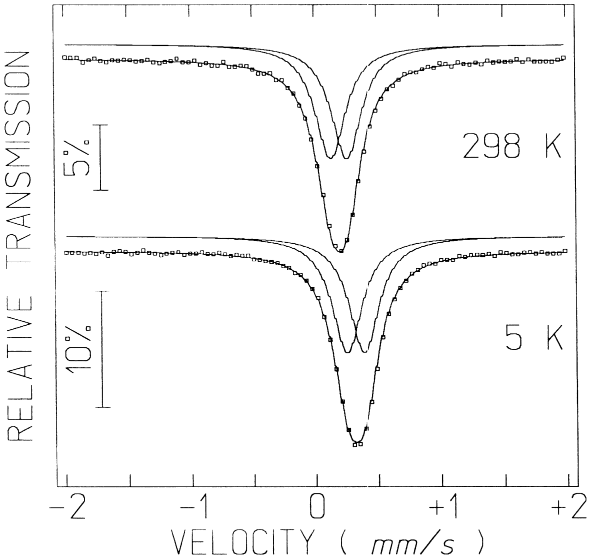

Fig. 4. Mössbauer spectra of YFe_2Al_{10} taken at 298 and 5 K. The lines over the experimental points are the calculated quadrupole doublets. Both peaks of the quadrupole doublet at each temperature are shown slightly shifted for clarity.

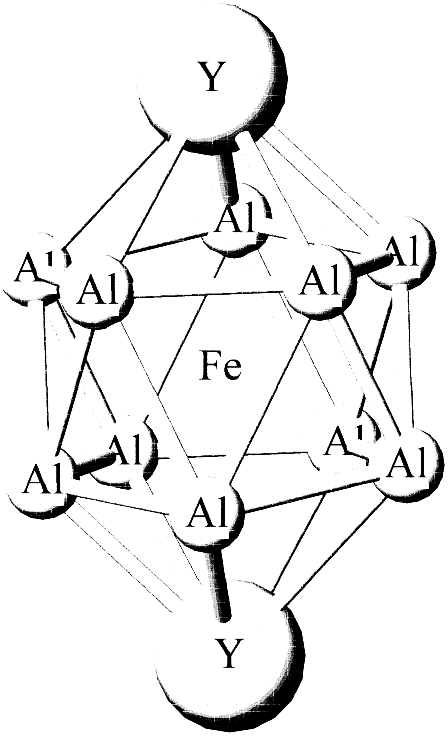

Fig. 5. Environment of an Fe atom in YFe_2Al_{10}. Nearest-neighbors up to 3.41 Å are shown.

4. Conclusion

Within the concentration range 50–100 at.% Al of the ternary Y–Fe–Al system at 1070 K two ternary compounds have been characterized using SEM and X-ray powder diffraction, YFe_xAl_{12-x} ($4\leq x\leq5.6$) ($ThMn_{12}$-type structure) and YFe_2Al_{10} ($YbFe_2Al_{10}$-type structure). At 1070 K only the YFe_xAl_{12-x} in the range $4\leq x\leq4.2$ could be obtained as single phases. Further experiments at higher annealing temperatures are in progress. For compositions richer in Al, Mössbauer spectra of YFe_2Al_{10} showed an unusually large isomer shift, 0.31 mm/s, for Fe atoms in Al containing intermetallics [9]. Larger δ values ($\approx$0.4 mm/s) were only reported for solid solution of Fe atoms in Al. These data also confirm previous magnetization results [4] showing that no magnetic ordering is detected down to 5 K, which is not surprising considering the low concentration of Fe atoms and that both Y and Al are nonmagnetic.

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