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NEW PHASES MELT QUENCHED UNDER HIGH PRESSURE IN R–Fe SYSTEMS (R ≡ Pr, Sm, Dy, Tb, Ho, Er, Tm, Yb, Lu)

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Summary

New phases were detected in alloys of the R–Fe series which were obtained by quenching from the melt at a constant pressure of 7.7 GPa. These compounds have the following imperfect disordered Laves phase structures: $MgZn_2$ type (C14) for R≡Tb, Ho, Er, Tm, Yb, Lu, and $MgCu_2$ type (C15) for R≡Pr, Sm, Dy. The connection between the structures of the new phases and the structure of metallic RFe_2 glasses is discussed.

1. Introduction

Rapid quenching of the melt is extensively used to obtain alloys in metastable states: supersaturated solid solutions, new phases and metallic glasses. These effects are observed when the cooling rate is more than 10^5 K s^{-1}. However, Bridgman's data for the increase in the viscosity of liquid mercury under pressure [1] suggest that the same effects can be obtained under high pressure at a lower cooling rate.

In this work we investigated the new phases in the R–Fe (R≡Pr, Sm, Tb, Dy, Ho, Er, Tm, Yb, Lu) systems obtained by quenching from the melt at a cooling rate of 10^2 - 10^3 K s^{-1} and a constant pressure of 7.7 GPa. Only four intermediate phases are known in these systems [2, 3]; RFe_2 ($MgCu_2$-type structure), RFe_3 (PNi_3-type structure), R_6Fe_{23} (Th_6Mn_{23}-type structure) and R_2Fe_{17} (Th_2Ni_{17}-type structure).

2. Experimental procedure

The experiments were carried out in a chamber constructed by Khvostantsev *et al.* [4]. The samples were prepared from a mixture of powdered rare earth metals (purity, 99.5%) and iron (purity, 99.99%). The powdered metals were mixed well and then compressed in an Al_2O_3 pipe ampoule. The sample was directly heated electrically to above the melting temperature of the mixture and was then quenched to room tem-

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perature at a cooling rate of 10^2 - 10^3 K s^{-1} and a constant pressure of 7.7 GPa. The melting temperature was controlled using a voltage–current plot.

The runs for the Yb–Fe system were carried out with initial ytterbium compositions of 80, 50, 33 and 20 at.%. The other R–Fe systems were investigated for only one composition (80 at.% R–Fe). The alloy composition was determined by X-ray microanalysis. It was found that the compositions of the alloys obtained after the high pressure–high temperature treatment differed from the initial composition of the powdered mixtures (see Table 1). This effect is explained by selective oxidation of the rare earth metals. The densities of the Yb–Fe compounds were determined using a pycnometric method. The phases were detected on X-ray powder photographs obtained using Cu Kα radiation and a camera of diameter 114 mm. Analysis of the reflection intensities was undertaken only for the ytterbium phase.

3. Results

New phases with compositions $YbFe_2$, $YbFe_4$ and approximately RFe were obtained using the high pressure–high temperature treatment. The unit cell dimensions and interatomic distances for these alloys are given in Tables 1 and 2.

TABLE 1

The unit cell dimensions and interatomic distances for the Yb–Fe compounds

Compound	AB	AB_2	AB_2	AB_4
Structure	C14	C14	C15	C15
a (Å)	5.272(2)	5.131(3)	7.239(5)[a] 7.231(5)	7.211(5)
c (Å)	8.487(5)	8.34(2)		
c/a	1.610	1.624		
$\bar{a}$ (Å)	7.42	7.25	7.24 7.23	7.21
d_{A-A} (Å)	3.21	3.14	3.14 3.13	3.12
d_{A-B} (Å)	3.08	3.01	3.00 3.00	2.99
d_{B-B} (Å)	2.62	2.56	2.56 2.56	2.55
Initial composition (at.%)	80 - 20	50 - 50	33 - 67	20 - 80
Observed composition (at.%)	48 - 52	31 - 69	30 - 70	19 - 81
Observed density (g cm^{-3})	7.90	—	9.90	8.61

[a] From ref. 2.

TABLE 2

The unit cell dimensions and the interatomic distances for the R–Fe compounds

R	*Structure*	*a* (Å)	*c* (Å)	*c/a*	$\bar{a}$ (Å)	d_{A-A} (Å)	d_{A-B} (Å)	d_{B-B} (Å)
Pr	C15	7.71			7.71	3.34	3.20	2.73
Nd	X[a]							
Sm	C15	7.71			7.71	3.34	3.20	2.73
Gd	X[a]							
Tb	C14	5.27	8.64	1.639	7.46	3.23	3.09	2.64
Dy	C15	7.59			7.59	3.29	3.15	2.68
Ho	C14	5.30	8.54	1.611	7.46	3.23	3.09	2.64
Er	C14	5.33	8.57	1.608	7.50	3.25	3.11	2.65
Tm	C14	5.29	8.54	1.614	7.45	3.23	3.09	2.63
Lu	C14	5.27	8.51	1.615	7.42	3.21	3.08	2.62

[a] X, unknown structure.

The YbFe alloy has a hexagonal unit cell with $a = 5.272(1)$ Å and $c = 8.487(2)$ Å; the observed density ρ is 7.9(1) g cm^{-3}. From this it follows that the number A of atoms in the unit cell is equal to 8.5. The Laves phase C14 was chosen as the model structure; this structure has space group $P6_3/mmc$ with the ytterbium and iron atoms occupying the 4f, 2a and 6h sites. Preliminary values of the atomic coordinates ($x = 0.83$, $z = 0.06$) were determined using the Paterson one-dimensional functions and were found to be close to the corresponding values of the Laves phase. X-ray data for the new phase $Yb_{0.48}Fe_{0.52}$ are listed in Table 3. Various types of atomic occupation structures were considered (Table 4). The atomic

TABLE 3

X-ray data for the new phase $Yb_{0.48}Fe_{0.52}$ (C14 structure) with $a = 5.272(1)$ Å, $c = 8.487(2)$ Å, $x = 0.834$, $z = 0.065$ and $R = 0.21$

N	*hkl*	I/I_0	d_{obs} (Å)	d_{calc} (Å)	F_{obs}	$\lvert F_{calc}\rvert$
1	100	20.4	4.564	4.569	0.46	0.32
2	002	16.8	4.240	4.241	0.73	0.62
3	101	18.7	4.022	4.023	0.31	0.29
4	102	16.0	3.110	3.108	0.32	0.26
5	110	77.6	2.637	2.637	1.07	1.17
6	103	89.9	2.404	2.404	0.85	0.98
7	200	16.2	2.281	2.283	0.51	0.53
8	112	100	2.239	2.239	0.92	1.02
9	201	61.0	2.204	2.205	0.73	0.67
10	004	8.9	2.122	2.121	0.69	0.46
11	202	0.0	—	2.010	0.00	0.01
12	104	8.4	1.925	1.923	0.29	0.26
13	203	44.9	1.776	1.777	0.68	0.51

(continued)

TABLE 3 *(continued)*

N	*hkl*	I/I_0	d_{obs} (Å)	d_{calc} (Å)	F_{obs}	$\lvert F_{calc}\rvert$
14	210	9.9	1.726	1.726	0.33	0.28
15	105	50.6	1.591	1.591	0.88	0.87
16	212	50.0	1.597	1.598	0.41	0.52
17	114	0.0	—	1.652	0.00	0.01
18	204	7.5	1.553	1.554	0.30	0.03
19	300	47.5	1.522	1.522	1.05	0.97
20	301	0.0	—	1.499	0.00	0.01
21	213	99.5	1.473	1.473	0.77	0.83
22	302	62.8	1.432	1.433	0.87	0.86
23	006	18.4	1.415	1.414	1.16	0.84
24	205	59.7	1.362	1.362	0.86	0.92
25	106	19.9	1.352	1.351	0.50	0.43
26	303	0.0	—	1.340	0.00	0.00
27	214	4.1	1.339	1.338	0.22	0.21
28	220	42.9	1.318	1.318	1.05	1.28
29	310	0.0	—	1.266	0.00	0.25
30	222	15.3	1.259	1.259	0.44	0.44
31	311	8.0	1.252	1.252	0.23	0.21
32	116	8.0	1.246	1.246	0.32	0.43
33	304	0.0	—	1.236	0.00	0.01
34	312	0.0	—	1.213	0.00	0.20
35	215	39.8	1.211	1.210	0.51	0.56
36	206	8.0	1.202	1.202	0.32	0.58
37	107	8.0	1.172	1.171	0.32	0.27
38	313	34.5	1.156	1.156	0.47	0.74
39	305	0.0	—	1.133	0.00	0.00

TABLE 4

The various types of the atomic occupation in the space group $P6_3/mmc$ for $Yb_{0.42}$-$Fe_{0.58}$

N	*4f positions*		*2a positions*		*6h positions*		*R*
	Yb	*Fe*	*Yb*	*Fe(1)*	*Yb*	*Fe(2)*	*(x = 0.834, z = 0.065)*
1	4	0	0	2	0	6	0.26
2	4	0	2	0	0	6	0.37
3	4	0	0	2	2	4	0.43
4	4	0	1	1	1	5	0.38
5	4	0	0.5	0	0	4.5	0.23
6	4	0	0	2	0.5	2.5	0.21
7	1.5	1.5	0.75	0.75	2.5	2.5	0.49
8	0	4	2	0	2.5	0.5	0.61
9	0	4	0	0.5	4.5	0	0.59

site filling for the minimum value of R ($R = 0.21$) was as follows: 4 Yb (f), 2 Fe (a), 0.5 Yb (h), 2.5 Fe (h). A distribution with ordered holes was also considered, but it gave rather high values of R. The close relation with the Laves phases is common for all R–Fe alloys. The heavy rare earth metals (terbium, holmium, erbium, thulium, ytterbium and lutetium) form compounds with the $MgZn_2$-type structure, and the light rare earths (praseodymium and samarium) and dysprosium form compounds with the $MgCu_2$-type structure.

The $YbFe_2$ alloy with the $MgZn_2$-type structure obtained by quenching from the melt is the first representative of the set of cubic RFe_2 compounds [3].

4. Conclusions

The lanthanide contraction in the series of rare earth–3d transition metal alloys usually increases with increasing concentration of rare earth metals. In addition the structure type changes with the variation of concentration. Figure 1 shows that there is no increase in the lanthanide contraction for the R–Fe series.

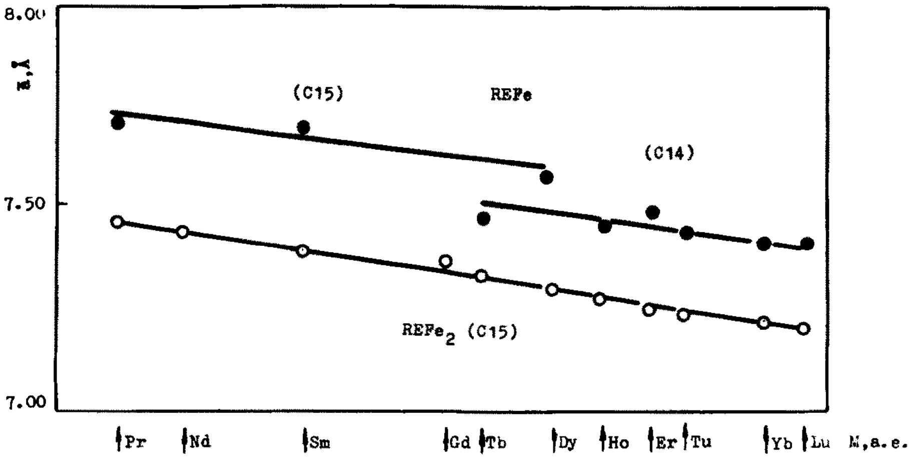

Fig. 1. Plots of the conventional cubic lattice parameters $\bar{a} = (8V_m)^{1/3}$, where V_m is the molecular volume, of RFe (●) and RFe_2 (○) *vs.* the atomic mass of the rare earth metals.

The coordination number (CN) of the rare earth atom in the Laves phase is equal to 16 (4R + 12Fe), and the neigbouring atoms form a Friauf polyhedron; for the iron atom CN = 12 and its neighbours form an icosahedral polyhedron. In the Yb–Fe alloy the CN of the ytterbium atom is decreased owing to the presence of holes, but the number of ytterbium atoms in the coordination sphere is increased as a result of disordering in the structure. A similar phenomenon is observed in the metallic glasses of the R–Fe system. For example, in amorphous $GdFe_2$ [5, 6] the number of Gd–Gd

TABLE 5

The nearest neighbours, coordination numbers and interatomic distances *d* in the Laves phases (AB_2 and AB compositions) and the amorphous alloys

Atom	*$YbFe_2$ ($MgZn_2$ type)*			*$Yb_{0.48}Fe_{0.52}$ ($MgZn_2$ type)*			*Amorphous $GdFe_2$* [5, 6]		
	Nearest neighbour	*d* (Å)	*CN*	*Nearest neighbour*	*d* (Å)	*CN*	*Nearest neighbour*	*d* (Å)	*CN*
A (f)	4 Yb	3.13	16	(1 + 3) Yb	3.14, 3.24	11.5	6(1) Gd	3.47	12.7
	3 Fe(1)	2.96		(0.25 + 0.5) Yb	3.09, 3.07		6.7(0.6) Fe	3.04	
	(3 + 6) Fe(2)	2.96, 3.00		3 Fe(1)	3.09				
				(1.25 + 2.5) Fe(2)	3.09, 3.07				
B(1) (a)	6 Yb	3.00	12	(6. + 0.5) Yb	3.09, 2.61	9			
	6 Fe(2)	2.56		2.5 Fe(2)	2.61		3.3(0.3) Gd	3.04	9.6
B(2) (h)	(2 + 4) Yb	2.96, 3.00	12	(2 + 4) Yb	3.09, 3.07	10	6.3(0.5) Fe	2.54	
				(0.17 + 0.17) Yb	2.64, 2.63				
	(2 + 2) Fe(2)	2.57, 2.56		(0.83 + 0.83) Fe(2)	2.64, 2.63				
	2 Fe(1)	2.56		2 Fe(1)	2.61				

neighbours is increased to six and the number of Gd–Fe neighbours is decreased to six. Therefore the coordination spheres of the R–Fe alloys can be considered as possible models of short-range order in the amorphous RFe_2 alloys (Table 5).

In the $YbFe_4$ alloy the iron atoms are distributed randomly in the ytterbium sublattice so that the Laves phase (C15) structure is maintained. Indeed the existence of alloys with the Laves phase structures over a wide range of concentrations agrees with calculations by Hafner [7] of the stability of Laves phases. However, we do not accept the role of the oxygen or aluminium admixtures in the stabilization of disordered compounds.

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