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The Fe-Gd Phase Diagram

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Abstract. The results of an experimental investigation of the iron-rich portion of the Fe-Gd system have confirmed previous studies showing that four incongruently melting intermetallic compounds exist, namely, $Fe_{17}Gd_2$, $Fe_{23}Gd_6$, Fe_3Gd and Fe_2Gd. The investigation also provided information about the crystal structures and ranges of stoichiometry of these intermetallic compounds.

Keywords: Fe-Gd phase diagram, Fe-Gd alloys, intermetallic compounds

Introduction

Transition metal-rare earth (TM-RE) alloy systems, both binary and higher orders, are of considerable interest in relation to the development of materials with attractive magnetic properties, such as large magnetostriction and high energy products. A characteristic feature of these TM-RE systems is the occurrence of a series of intermetallic compounds. The work reported here was part of a wider programme of research on certain binary and ternary transition metal-rare earth alloy systems (rare earths (RE) = Gd, Tb; transition metals (TM) = Fe, Co). The results on binary Fe-Gd alloys are specially reported here, which aim at resolving certain differences in previously reported studies.

Early work by Novy *et al*. (1961) reported seven intermetallic compounds with the Fe : Gd ratios of 17 : 2, 5 : 1, 4 : 1, 7 : 2, 3 : 1, 2 : 1, and 3 : 2. Another study (Savitskii *et al*., 1961) showed the presence of only four compounds, namely, 17 : 2, 23 : 6, 3 : 1, and 2 : 1. Other papers have been published on various aspects of this system including constitutional data, which have been the subject of several recent assessments (Zhang and Han, 1998; Okamoto, 1996; Savitskii *et al*., 1970). A reassessment has been also presented very recently (Zinkevich *et al*., 2000). This report incorporates a comprehensive list of references and also presents a thermodynamically calculated version of the phase diagram, which confirms the general features of the system and the four compounds reported by Savitskii *et al*. (1961).

The experimental results reported here are in general agreement with the assessment of Zinkevich *et al*. (2000). The stoichiometery ranges of the intermetallic compounds are also reported.

Materials and Methods

Alloys of nominal compositions, as listed in Table 1, were prepared as 5-10 g buttons by arc melting 99.99% purity iron and gadolinium under titanium gettered argon. Melting was carried out several times to ensure homogeneity. Samples of each alloy were subjected to homogenization heat treatment at 1050 °C for 2 weeks, followed by quenching in iced brine. Samples were sealed in evacuated silica tubes with partial pressure of argon prior to heat treatment.

Metallographic examination of both the as-solidified and homogenized samples, was carried out by optical and scanning electron microscopy. The composition of the phases appearing in various alloy samples was determined by energy dispersive X-ray (EDX) analysis with ZAF corrections. The compositions reported in Table 2 are the average of 5 measurements, the scatter was < ~0.5% and the error was ~±1% of the values reported. The X-ray diffractometry was carried out on powdered alloy samples employing Cu-Ká radiation so as to determine crystal structure and lattice parameter(s) of the compounds by applying the Nelson-Riley function.

Table 1. Nominal compositions of the Fe-Gd alloys investigated

Alloy designation	Composition (atomic, %)	
	Fe	Gd
GF-5	95.0	5.0
GF-11	88.5	11.5
GF-13	86.5	13.5
GF-16	83.4	16.6
GF-22	78.0	22.0
GF-25	74.5	25.5
GF-33	66.5	33.5

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Phase transformation temperatures were determined by differential thermal analysis (DTA) using homogenized samples, weighing 50 mg. An alumina crucible was used with platinum as the reference material and titanium gettered argon as the inert atmosphere. Data were recorded for heating cycle (with rates of 10 °C/min) and the extrapolated onset temperatures were measured to represent the phase transformation temperatures. The peritectoid temperatures were estimated to have an accuracy of ~±2 °C, while for other parts of the solidus the range was ~±5 °C.

A diffusion couple was prepared by clamping a 4 mm thick sample of gadolinium between two strips of iron (Rawlings and Neway, 1968). The couple was wrapped in tantalum foil and encapsulated in an evacuated silica tube with partial pressure of argon. The couple was annealed for 720 h at 1050 °C and subsequently quenched in iced brine. This was followed by EDX analysis of the phases appearing in the section of the couple.

Results and Discussion

Phase diagram. On the basis of the evidence, as discussed below and taking account of the results of all the experimental techniques used, the binary phase diagram is shown in Fig. 1. The phase diagram incorporates four intermetallic compounds corresponding, respectively, to Fe : Gd atomic ratios of 17 : 2, 23 : 6, 3 : 1, and 2 : 1. The basic features of the diagram agree closely with those reported in the recent assessment by Zinkevich *et al*. (2000). Some details of the experimental results, on which the diagram was based, are presented and discussed below.

Alloy phases and microstructure. The EDX data for the four intermetallic compounds found in the homogenized and as-solidified alloys are shown in Table 2. Some aspects of the compositional and microstructural features of the individual alloys investigated, in relation to the phase diagram (Fig. 1), are of interest to note. Previously reported versions of the phase diagram have shown the intermetallic as “line compounds” with no range of compositions. However, the EDX data reported here (Table 2) indicate the possible existence of small ranges of stoichiometry (see dashed lines in Fig. 1) for the 17 : 2 and 2 : 1 compounds (up to ~0.5 atomic %) and for 3 : 1 compound (up to ~1 atomic %) but the evidence for the 23 : 6 compound is lacking. Also, there was a general trend for the Fe-Gd atomic ratios (Table 2) to extend slightly in excess (i.e., Gd-rich) of the ideal stoichiometries. However, this feature was not seen in every case, particularly for the non-equilibrium structures of the as-solidified alloys. The existence of deviation from ideal stoichiometry has been discussed earlier (Atiq *et al*., 1997) in the context of the results of X-ray and density measurements of Fe-Gd and Fe, Co-Gd alloys and has been interpreted in terms of vacant lattice sites on the trace metal (TM) lattice.

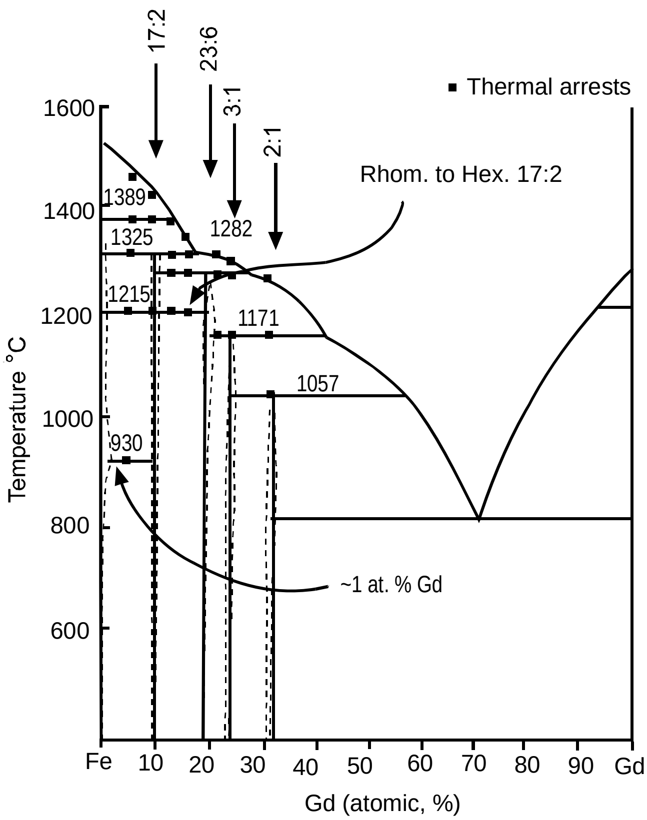

Fig. 1. The Fe-Gd phase diagram (intermetallic compounds have been shown as the ratios of Fe : Gd); Rhom. to Hex. = rhombohedral to hexagonal type.

Investigation of alloys GF-13 and GF-16 confirmed the absence of the compound Fe_5Gd, reported by Novy *et al.* (1961) and supported the results of Savitskii (1970), which have been incorporated in a later assessment (Novy *et al*., 1971). However, bearing in mind the report that in some rare earth systems a compound Co_5 RE exists, but only at temperatures above 1150 °C, alloy GF-16 was heated at 1250 °C for four days and quenched to retain any high temperature phase that might be present. The microstructure showed no difference, apart from coarsening, from the alloy homogenized at 1050 °C, indicating the absence of a different phase existing at high temperatures.

The homogenized GF-22 alloy provided information on the equilibria between 23 : 6 and 3 : 1 compounds, while the homogenized alloys GF-25 and GF-33 were very close to the single phase 3 : 1 and 2 : 1 structures, respectively. Some features of the as-solidified structures are of interest to note for the alloys

GF-22 (Fig. 2a), GF-25 (Fig. 3a) and GF-33 (Fig. 4a), in which the absence of equilibrium is shown by the presence of three phases associated with the incomplete progress of the relevant peritectic reactions. In these three alloys, the as-solidified material contained some 17 : 2 compounds. The homogenization treatment did not remove the 17 : 2 compound in alloy GF-22 (Fig. 2b). However, in alloy GF-25 and GF-33 the 17 : 2 compound was removed by homogenization (Fig. 3a, Fig. 4b). Concerning alloy GF-25 (Fig. 3a), reference to Fig. 1, suggests that some $Fe_{23}Gd_6$ should form as the primary phase during solidification, but instead some $Fe_{17}Gd_2$ was found in the as-solidified state. Similarly, in alloy GF-33 (Fig. 4a), where the primary phase should be the 23 : 6 compound, the 17 : 2 compound was present, instead, in the as-solidified state. Thus, it appears that nucleation of $Fe_{23}Gd_6$ during the solidification was relatively difficult. A similar observation on the nucleation of $Fe_{23}Tb_6$ has been reported in Fe-Tb alloys by Dariel *et al.* (1976).

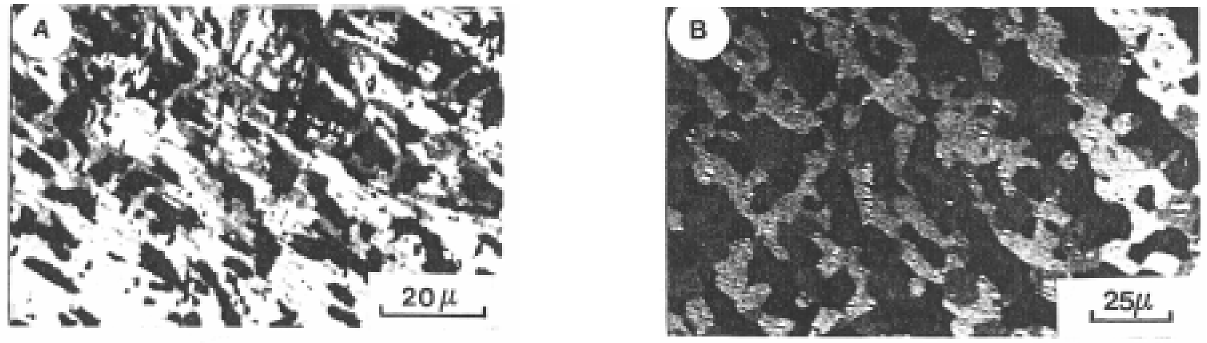

Fig. 2. Microstructures of alloy GF-22 (Sem/Bei): **(a)** as-solidified, showing $Fe_{17}Gd_2$ (dark) formed as primary phase, $Fe_{23}Gd_6$ (grey) and Fe_3Gd (bright); **(b)** homogenized, showing $Fe_{17}Gd_2$ (dark) formed as primary phase, $Fe_{23}Gd_6$ (grey) and Fe_3Gd (bright).

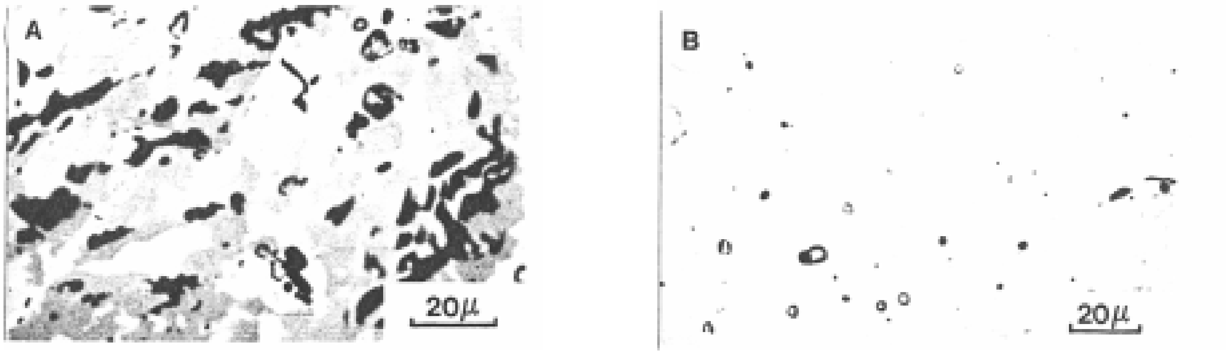

Fig. 3. Microstructures of alloy GF-25 (Sem/Bei): **(a)** as-solidified, showing $Fe_{17}Gd_2$ (dark) formed as primary phase, Fe_3Gd (grey) and Fe_2Gd (bright); **(b)** homogenized, showing a single phase microstructure comprising of Fe_3Gd (bright).

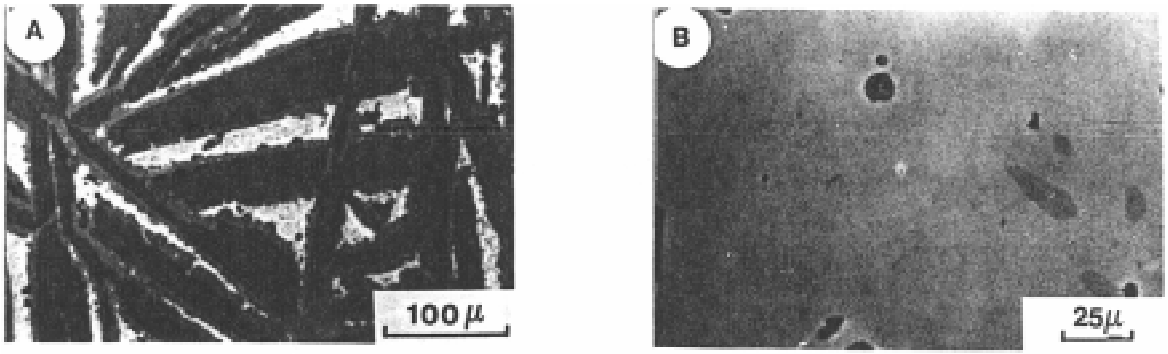

Fig. 4. Microstructures of alloy GF-33 (Sem/Bei): **(a)** as-solidified, showing $Fe_{17}Gd_2$ (dark) formed as primary phase, Fe_3Gd (grey) and Fe_2Gd (bright); **(b)** homogenized, showing a nearly single phase microstructure, Fe_2Gd matrix with some Fe_3Gd (dark).

Table 2. Microanalysis of the compounds present in the as-cast and homogenized binary Fe-Gd alloys

Alloy designation	Compound	Fe %	Gd %	Fe : Gd
GF-5*	$Fe_{17}Gd_2$	89.7	10.3	17:1.95
	Iron S.S.	99.7	0.3	
GF-5**	$Fe_{17}Gd_2$	89.5	10.5	17:1.99
	Iron S.S.	99.1	0.9	
GF-11*	$Fe_{17}Gd_2$	89.2	10.8	17:2.05
	$Fe_{23}Gd_6$	79.5	20.5	23:5.93
GF-11**	$Fe_{17}Gd_2$	89.3	10.7	17:2.03
GF-13*	$Fe_{17}Gd_2$	89.5	10.5	17:1.99
	$Fe_{23}Gd_6$	79.5	20.5	23:5.93
GF-13**	$Fe_{17}Gd_2$	89.1	10.9	17:2.07
	$Fe_{23}Gd_6$	79.3	20.7	23:6.0
GF-16*	$Fe_{17}Gd_2$	89.5	10.5	17:1.99
	$Fe_{17}Gd_2$	79.6	20.4	23:5.89
GF-16**	$Fe_{17}Gd_2$	89.2	10.8	17:2.05
	$Fe_{23}Gd_6$	79.3	20.7	23:6.0
GF-22*	$Fe_{17}Gd_2$	89.4	10.4	17:1.97
	$Fe_{23}Gd_6$	79.7	20.3	23:5.85
	Fe_3Gd	75.1	24.9	3:0.99
GF-22**	$Fe_{17}Gd_2$	89.4	10.6	17:2.01
	$Fe_{23}Gd_6$	79.2	20.8	23:6.04
	Fe_3Gd	74.7	25.3	3:1.01
GF-25*	$Fe_{17}Gd_2$	88.4	11.6	17:2.23
	Fe_3Gd	73.5	26.5	3:1.08
	Fe_2Gd	65.6	34.4	2:1.05
GF-25**	Fe_3Gd	73.9	26.1	3:1.06
GF-33*	$Fe_{17}Gd_2$	89.2	10.8	17:2.05
	Fe_3Gd	74.2	25.8	3:1.04
	Fe_2Gd	66.3	33.7	2:1.01
GF-33**	Fe_3Gd	74.6	25.4	3:1.02
	Fe_2Gd	66.1	33.9	2:1.03

*as-cast; **homogenized

Crystal structure. X-ray diffraction data identified intermetallic compounds with Fe-Gd ratios of 17 : 2, 23 : 6, 3 : 1 and 2 : 1 (Table 3) and the lattice parameters were consistent with those previously reported (Zinkevich *et al.*, 2000).

Phase transformation temperatures. The onset temperatures of thermal arrests during DTA heating, with corresponding temperatures as assessed by Zinkevich *et al.* (2000), are shown in Table 4. The temperatures of the incongruent melting points of the compounds are in reasonable agreement with those reported by Savitskii *et al.* (1961) and Zinkevich *et al.* (2000), except for Fe_2Gd, which showed a significant difference. In the thermodynamically calculated diagram by Zinkevich *et al.* (2000), there was a good agreement with the experimental data for the peritectic reaction temperature. However, the experimentally determined data (from the current work; Novy *et al.*, 1961; Savitskii, 1970) for the onset of primary solidification in alloys with Gd between ~5 and 20%, showed considerable scatter and were significantly higher than the liquidus values shown in the thermodynamically calculated diagram. The solid state transformation at ~1215 °C in the alloys containing $Fe_{17}Gd_2$ corresponds to the allotropic transformation from the

Table 3. Lattice parameters for various Fe-Gd intermetallic compounds

Compounds	Structure	Lattice parameters	
		“a” (Å)	“c” (Å)
$Fe_{17}Gd_2$	Rhombohedral	8.501	12.492
$Fe_{23}Gd_6$	Cubic	12.141	-
Fe_3Gd	Rhombohedral	5.167	24.692
Fe_2Gd	Cubic	7.3895	-

Table 4. Thermal arrests (°C) on heating corresponding to phase transformations in Fe-Gd system

Alloy	Phase transformations							
	Peritectoid ã-iron + $Fe_{17}Gd_2$ to á-iron	Fe_3Gd*	Fe_2Gd*	$Fe_{23}Gd_6$*	$Fe_{17}Gd_2$*	$Fe_{17}Gd_2$ rhom. to hex.	.ä- iron to L+ã¯ iron	Melting
GF-5	930	-	-	-	1325	1215	1389	1465
GF-11	931	-	-	-	1324	1216	1389	1429
GF-13	-	-	-	1283	1325	1215	-	1418
GF-16	-	-	-	1283	1324	1214	-	1387
GF-22	-	-	1171	1282	-	-	-	1331
GF-25	-	-	1173	1281	-	-	-	1311
GF-33	-	1057	1171	-	-	-	-	1289
Reported data**	932 ± 5	1080 ± 10	1160 ± 10	1280 ± 10	1335 ± 10	1215 ± 2	1380 ± 10	

*Incongruent melting temperatures of compounds; **Zinkevich *et al.*, 2000; rhom. to hex. = rhombohedral to hexagonal type low temperature allotrope (rhombohedral, $Zn_{17}Th_2$ type) to the high temperature form (hexagonal, $Ni_{17}Th_2$), as previously repor-ted (Atiq *et al.*, 1990a; 1990b).

Conclusion

The results reported here showing the equilibria involving four intermetallic compounds, namely, $Fe_{17}Gd_2$, $Fe_{23}Gd_6$, Fe_3Gd, and Fe_2Gd are in agreement with the recent assessment of the Fe-Gd system (Zinkevich *et al.*, 2000). The data reported here indicate the possibility of small composition ranges of stoichiometry and of a trend for the ratios to be slightly rich in gadolinium as compared with the ideal values. The temperatures of the peritectic and solid state transformations generally agree reasonably with the data as assessed by Zinkevich *et al*. (2000), but often the experimental melting temperatures were higher. The crystal structure and lattice parameters of the compounds were consistent with previous works.

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