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Structural and magnetic properties of the novel compound $Dy_3(Fe,Ti)_{29}$

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Abstract

Microstructural characterisation, by means of energy dispersive X-ray microanalysis and X-ray diffraction of a $Dy_3Fe_{27.5}Ti_{1.4}$ alloy annealed at 960°C for 7 days, has revealed the existence of a novel compound having the recently reported monoclinic $Nd_3(Fe,Ti)_{29}$-type structure. Thermogravimetric analysis (TGA) gives a magnetic ordering temperature of 438 K. Refinement of powder X-ray diffraction data by using the $P2_1/c$ ($a = 10.5759$ Å, $b = 8.4962$ Å, $c = 9.6704$ Å and $\beta = 97.0472°$) and $A2/m$ ($a = 10.5759$ Å, $b = 8.4958$ Å, $c = 9.6697$ Å and $\beta = 97.0416°$) space groups yields reliability R factors of 10.4% and 9.8% respectively. ^{57}Fe Mössbauer spectroscopy measurements at room temperature yield an average ^{57}Fe magnetic hyperfine field of 19.9(2) T, which corresponds to an average Fe magnetic moment of 1.3 μ_B.

Keywords: Fe-rich intermetallics; Ternary rare earth compounds; Structure determination, Magnetic properties; Mössbauer spectroscopy

1. Introduction

In a world wide search to identify a new rare-earth intermetallic compound to replace $Nd_2Fe_{14}B$, research has been focused on Fe-rich rare-earth intermetallic compounds interstitially modified with nitrogen or carbon. $Nd_2Fe_{14}B$ is a well established and widely used magnetic material, although it is limited in application owing to its relatively low Curie temperature. Compounds such as $Sm_2Fe_{17}N_{3-\delta}$ and $NdFe_{11}TiN_{1-\delta}$ have been reported to be possible alternatives to $Nd_2Fe_{14}B$ as both compounds exhibit uniaxial anisotropy and Curie temperatures above 700 K.

In 1992, Collocott et al. [1] reported the identification of a novel ternary phase $Nd_2(Fe,Ti)_{19}$ ('2:19') which existed at a composition between those of the well-known $Nd_2(Fe,Ti)_{17}$ and $Nd(Fe,Ti)_{12}$ phases. Originally the structure of the '2:19' was assigned a $2 \times a$ and $4 \times c$ superlattice of hexagonal $TbCu_7$. The structure of this phase was solved independently by Li et al. [2] from powder X-ray diffraction (XRD) and by Hu and Yelon [3] utilising neutron diffraction. Both refinements showed the compound had a monoclinic structure (space group $P2_1/c$, No. 14) and that the 'ideal' composition was $Nd_3(Fe,Ti)_{29}$ '3:29'. In a recent paper by Kalogirou et al. [4], the $A2/m$ space group was identified as giving a better structure. The '3:29', like the '2:17' and '1:12' structures, is derived from the hexagonal $CaCu_5$ structure and is formed by the replacement of Ca atoms by an Fe–Fe dumb-bell. In relation to rare-earth–iron–transition metal alloy systems, the Ca corresponds to the rare-earth atoms and the Cu to transition metal atoms. This replacement procedure can be represented by the following expression $R_{1-\delta}(2T)_\delta T_5 \rightarrow RT_y$ where δ is the fraction of Ca atoms replaced by an Fe–Fe dumb-bell. For the '3:29' $\delta = 2/5$ [2], and for the '2:17' and '1:12', δ is 1/3 and 1/2 respectively. The '3:29' is an intermediate phase and can be represented by the following equation: $R_3(Fe,Ti)_{29} = R_2(Fe,Ti)_{17} + R(Fe,Ti)_{12}$.

The '3:29' phase is now known to form in ternary systems other than that of Nd–Fe–Ti, and has been reported to exist for R–Fe–Ti (R = Y [5], Ce [6], Pr

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[7], Sm [8], Gd [9] and Tb [10]), R–Fe–V (R = Y, Nd, Sm, Gd [11] and Dy [12]), Nd–Fe–M (M = Cr, Mn [13], Re [14], Mo [4] and W [15]) and R–Fe–Mn (R = Ce, Nd and Sm [13]) systems.

The $R_3(Fe,Ti)_{29}$ compounds, like their $R(Fe,Ti)_{12}$ and $R_2(Fe,Ti)_{17}$ counterparts, can be interstitially modified with nitrogen [16–18] and carbon [19], with increases observed in the magnetic ordering temperature, anisotropy field and saturation magnetisation.

Here, we report microstructural characterisation by backscattered electron (BSE) imaging and energy dispersive X-ray microanalysis (EDS), powder X-ray data refinement, thermogravimetric analysis (TGA) and Mössbauer spectroscopy of an alloy having a nominal composition of $Dy_3Fe_{27.5}Ti_{1.4}$, and having the $Nd_3(Fe,Ti)_{29}$-type compound as the majority phase.

2. Experimental procedure

An alloy with a composition of $Dy_3Fe_{27.5}Ti_{1.4}$ was prepared from Dy, Fe and Ti of greater than 99.9% purity by argon-arc melting, and then annealing in a sealed quartz tube under an argon atmosphere at 960°C for 7 days. Microstructural characterisation was carried out using a Jeol 5400LV scanning electron microscope equipped with an EDS system for quantitative analysis, and a backscattered electron detector for imaging and phase contrast analysis. The sample was etched in a 4% solution of nitric acid in alcohol (Nital) to generate topological contrast. Structural characterisation of the alloy was made with a Philips X-ray diffractometer (Co Kα radiation) and the structure refined using a modified Rietveld profile analysis program [20]. Curie temperatures were determined by using a Perkin–Elmer TGA, modified by a permanent magnet to function as a Faraday balance. ^{57}Fe Mössbauer spectroscopy was carried out using a constant acceleration, transmission spectrometer with a ^{57}CoRh source and calibrated with an α-Fe foil.

3. Results and discussion

A combination of scanning electron microscopy utilising BSE imaging and EDS, and powder XRD of a $Dy_3Fe_{27.5}Ti_{1.4}$ alloy annealed at 960°C for 7 days has revealed the existence of a novel ternary phase with a nominal composition of $Dy_3(Fe,Ti)_{29}$ and having the monoclinic $Nd_3(Fe,Ti)_{29}$-type structure. Fig. 1 shows a BSE micrograph of the annealed alloy after etching. EDS analysis of the majority phase using a LINK software package yields an apparent Dy:Fe:Ti ratio of 8.3:87.0:4.7 which corresponds to the presence of the $Dy_3(Fe,Ti)_{29}$ compound. The second phase, which is approximately 15% of the total, has an apparent Dy:Fe:Ti ratio of 7.2:86.2:6.6, and is the tetragonal $Dy(Fe,Ti)_{12}$ phase. Owing to the very strong overlap which exists between the Dy L and Fe K series lines, the compositional ratios require further correction. Table 1 shows the apparent and normalised data, where the normalised data was determined with reference to a single phase sample of Dy_2Fe_{17}, which had been prepared with negligible weight loss during arc-melting and annealing.

Fig. 1. BSE micrograph of $Dy_3Fe_{27.5}Ti_{1.4}$ after etching (majority phase—$Dy_3(Fe,Ti)_{29}$, rise—$Dy(Fe,Ti)_{12}$).

XRD analysis shows that the main phase present in the as-cast sample has the hexagonal Th_2Ni_{17}-type structure. Annealing the sample for a period of 7 days at 960°C results in the formation of $Dy_3(Fe,Ti)_{29}$ with the monoclinic $Nd_3(Fe,Ti)_{29}$-type structure as the majority phase. In our sample there is approximately 85% of the $Dy_3(Fe,Ti)_{29}$ compound and 15% of the $Dy(Fe,Ti)_{12}$ phase.

Two Rietveld refinements have been carried out on our powder XRD data, the first assuming the original $P2_1/c$ space group assignment reported by Li et al. [2], and the second using the $A2/m$ space group suggested by Kalogirou et al. [4]. The $A2/m$ space group is a minimal non-isomorphic supergroup of type II of the $P2_1/c$ space group, and was reported, by Kalogirou et al. [4], to give a better structural description of the monoclinic '3:29' structure. Figs. 2 and 3 show the observed and calculated diffraction patterns for both the $P2_1/c$ and $A2/m$ space groups respectively. Table 2 lists the lattice parameters obtained from the Rietveld refinement for both structural assignments. The resultant R values obtained from the fitting procedure

Table 1
Apparent and normalised EDS data for $Dy_3(Fe,Ti)_{29}$

		Apparent (at.%)	Normalised (at.%)
$Dy_3(Fe,Ti)_{29}$	Dy	8.3	9.6
	Fe	87.0	85.7
	Ti	4.7	4.7

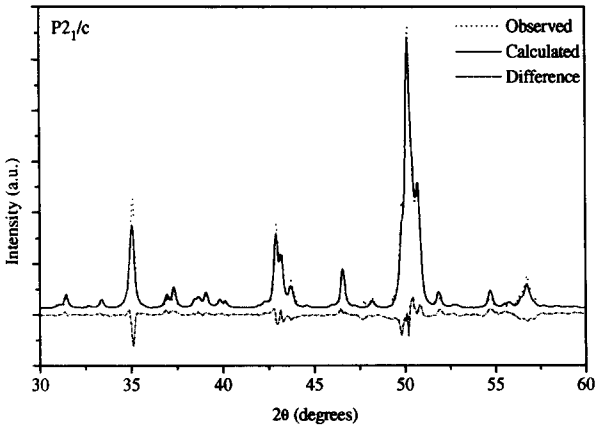

Fig. 2. Observed and calculated diffraction spectra for the $P2_1/c$ space group.

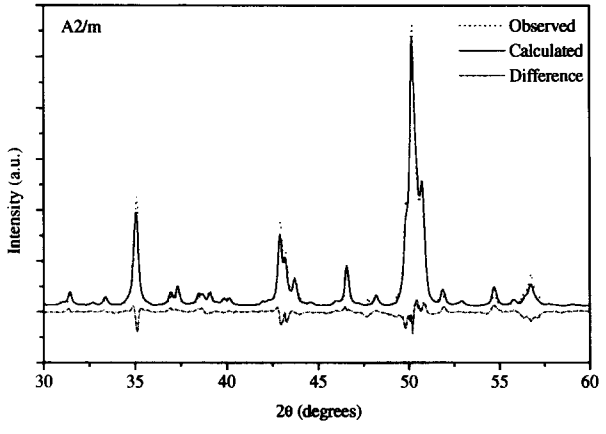

Fig. 3. Observed and calculated diffraction spectra for the $A2/m$ space group.

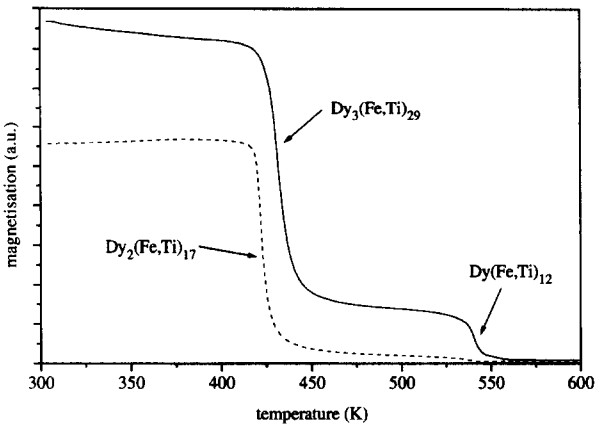

Fig. 4. TGA trace for the $Dy_3Fe_{27.5}Ti_{1.4}$ ($Dy_3(Fe,Ti)_{29}$ and $Dy(Fe,Ti)_{12}$) annealed alloy and $Dy_2(Fe,Ti)_{17}$.

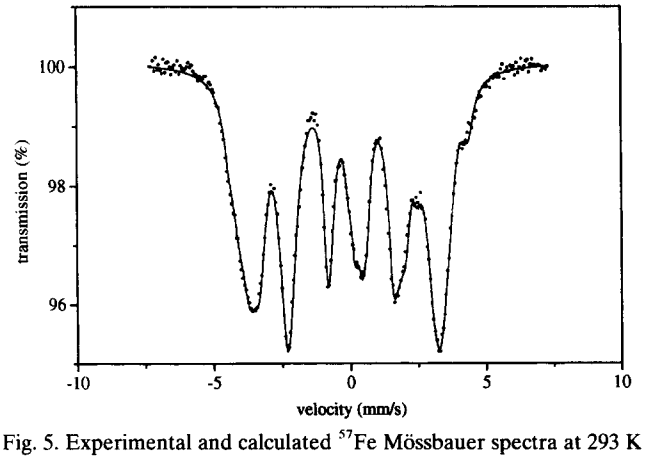

Fig. 5. Experimental and calculated ^{57}Fe Mössbauer spectra at 293 K (dots—observed, solid line—calculated).

show that the $A2/m$ space group better describes the '3:29' structure.

Curie temperatures were measured in a Perkin–Elmer TGA modified by addition of a permanent magnet, to function as a Faraday balance. Fig. 4 shows the TGA trace for the $Dy_3Fe_{27.5}Ti_{1.4}$ annealed alloy. Two events have been observed: the first corresponds to the presence of the $Dy_3(Fe,Ti)_{29}$ phase, which has a Curie temperature of 438 K; the second occurs at 544 K and corresponds to the magnetic ordering temperature of the $Dy(Fe,Ti)_{12}$ phase. A TGA analysis of a $Dy_2(Fe,Ti)_{17}$ sample (Fig. 4) shows that this phase has a magnetic ordering temperature of 426 K, clearly distinguishing it from the $Dy_3(Fe,Ti)_{29}$ phase. The presence of two thermal events in the TGA trace corresponding to the '3:29' and '1:12' phases is in agreement with scanning electron microscopy and EDS analyses.

Table 2
Refined structural data of the monoclinic lattice using the $P2_1/c$ and $A2/m$ space groups

Space group	a (Å)	b (Å)	c (Å)	β (deg)	R (%)
$P2_1/c$	10.5759	8.4962	9.6704	97.0472	10.4
A2/m	10.5759	8.4958	9.6697	97.0416	9.8

The ^{57}Fe Mössbauer spectrum is shown in Fig. 5. Owing to the complexity of the structure, and hence the large number of Fe sites (11) in the monoclinic $R_3(Fe,M)_{29}$ structure and the effects of site occupancy by the 3d transition element atoms, only an average hyperfine field could be determined for $Dy_3(Fe,Ti)_{29}$. In order to generate the theoretical fit, four magnetically-split sextets with variable line widths were employed. The deduced ^{57}Fe average hyperfine field from the fitting procedure is 19.9(2) T at 293 K. This corresponds to an average Fe magnetic moment of 1.3 μ_B.

4. Conclusion

In conclusion, we have prepared an alloy with a nominal composition of $Dy_3Fe_{27.5}Ti_{1.4}$ which contains the novel ternary phase $Dy_3(Fe,Ti)_{29}$. Structural refine-

ment of powder XRD data, using the $P2_1/c$ and $A2/m$ space groups, demonstrates that the novel phase has the monoclinic $Nd_3(Fe,Ti)_{29}$-type structure. The $A2/m$ space group provides a better structural description, with an R value of 9.8%, whereas for the $P2_1/c$ assignment, an R value of 10.4% is achieved. The magnetic ordering temperature of the new phase is 438 K. ^{57}Fe Mössbauer spectroscopy yields an average hyperfine field of 19.9(2) T at 293 K, which corresponds to an average Fe magnetic moment of 1.3 μ_B. The identification of the '3:29' phase in the DyFeTi system further expands the series of rare-earth–iron–transition element systems for which this phase exists.

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References

[1] S.J. Collocott, R.K. Day, J.B. Dunlop and R.L. Davis, in *Proc. 7th Int. Symp. on Magnetic Anisotropy and Coercivity in Rare-Earth Transition Metal Alloys, Canberra, Australia, 1992*, p. 447.

[2] H.-S. Li, J.M. Cadogan, R.L. Davis, A. Margarian and J.B. Dunlop, *Solid State Commun., 90* (1994) 487.

[3] Z. Hu and W.B. Yelon, *Solid State Commun., 91* (1994) 223.

[4] O. Kalogirou, V. Psycharis, L. Saettas and D. Niarchos, *J. Magn. Magn. Mater., 146* (1995) 335.

[5] H.-S. Li, D. Courtois, J.M. Cadogan, B.-P. Hu and W.-S. Zhan, *Proc. IEEE Int. Magnetics Conf. (Intermag 95), San Antonio, TX, USA, 1995.*

[6] A. Margarian, J.B. Dunlop and S.J. Collocott, unpublished results, 1994.

[7] H.-S. Li, Suharyana, J.M. Cadogan, G.J. Bowden, J.-M. Xu, S.X. Douand and H.K. Liu, *J. Appl. Phys., 75* (1994) 7210.

[8] A. Margarian, J.B. Dunlop and S.J. Collocott, *Rare-Earth Magnets Workshop (abstract), Wagga Wagga, NSW, Australia, 1994*, p. 27.

[9] J.-M. Xiu, H.-S. Li, J.M. Cadogan, S.X. Dou and H.K. Liu, *J. Phys.: Condens. Matter*, in press.

[10] M.R. Ibarra, L. Morellon, J. Blasco, L. Pareti, P.A. Algarabel, J. Garcia, F. Albertini and A. Paoluzzi, *J. Phys.: Condens. Matter, 6* (1994) L717.

[11] Ye.V. Shcherbakova, G.V. Ivanova, A.S. Yermolenko, Ye.V. Belozerov and V.S. Gaviko, *J. Alloys Comp., 182* (1992) 199.

[12] D. Courtois, H.-S. Li and J.M. Cadogan, *Proc. IEEE Int. Magnetics Conf. (Intermag 95), San Antonio, TX, USA, 1995.*

[13] C.D. Fuerst, F.E. Pinkerton and J.F. Herbst, *J. Magn. Magn. Mater., 129* (1994) L115.

[14] N. Scheepers, A. Margarian and J.B. Dunlop, in preparation.

[15] A. Margarian, J.B. Dunlop, J.M. Cadogan and H.-S. Li, in preparation.

[16] D.H. Ryan, J.M. Cadogan, A. Margarian and J.B. Dunlop, *J. Appl. Phys., 76* (1994) 6150.

[17] A. Margarian, J.B. Dunlop, S.J. Collocott, H.-S. Li, J.M. Cadogan and R.L. Davis, *Proc. 8th Int. Symp. on Magnetic Anisotropy and Coercivity in Rare-Earth Transition Metal Alloys, Birmingham, UK, 1994*, p. 353.

[18] O. Kalogirou, V. Psycharis, M. Gjoka and D. Niarchos, *J. Magn. Magn. Mater., 147* (1995) L7.

[19] B.-P. Hu, G.-C. Li, Y.-Z. Wang, B. Nasunjilegal, N. Tang, F.-M. Yang, H.-S. Li and J.M. Cadogan, *J. Phys.: Condens. Matter, 6* (1994) L595.

[20] C.J. Howard and R.J. Hill, *J. Appl. Crystallogr., 18* (1985) 173