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Hydrogenation of Sm_2Fe_{17}

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Abstract

The characteristics of the reaction between Sm_2Fe_{17} and H_2 have been studied by means of isochorothermal analysis, X-ray diffraction and thermomagnetic analysis. Sm_2Fe_{17} begins to absorb hydrogen at about 185 °C. At 250 °C the hydrogen content reaches the maximum value of 2.4 atoms of hydrogen per mole of Sm_2Fe_{17}. Subsequent cooling to room temperature causes an increase in the hydrogen concentration up to the value of 5 H atoms per mole of Sm_2Fe_{17}. Above 250 °C the Sm_2Fe_{17} hydride begins to desorb hydrogen and its composition becomes $Sm_2Fe_{17}H_{0.1}$ at about 500 °C. The Sm_2Fe_{17} hydride desorbs and absorbs hydrogen reversibly in the temperature range between 25 and 500 °C. At about 510 °C the hydride begins to decompose into Sm hydride and α-Fe. The decomposition reaction is accompanied by massive hydrogen absorption. The Sm_2Fe_{17} hydride has the rhombohedral crystal structure (the same as the parent compound) with a 3.4% expanded lattice with parameters $a = 8.667$ Å and $c = 12.520$ Å. The stresses introduced by the lattice expansion cause crack formation along the Sm_2Fe_{17} grain boundaries and the samples become friable. The Curie temperature and saturation magnetization are 280 °C and 159 e.m.u. g^{-1} for $Sm_2Fe_{17}H_5$ as compared with 135 °C and 116 e.m.u. g^{-1} for Sm_2Fe_{17}. For both Sm_2Fe_{17} and Sm_2Fe_{17} hydride the easy direction of magnetization is perpendicular to the c direction in the rhombohedral structure.

1. Introduction

The discovery of a new magnetic material, the Sm_2Fe_{17} nitride [1], has triggered renewed interest in the Sm–Fe intermetallic compounds in general. Permanent magnets based on the Sm_2Fe_{17} nitride have already been prepared by several methods such as mechanical alloying (MA) [2, 3], rapid solidification [4, 5], conventional powder metallurgy [3, 6, 7] and hydrogen treatment, hydrogenation decomposition desorption recombination (HDDR) [8, 9]. All these methods involve two major steps: (a) the formation of the Sm_2Fe_{17} phase (preferably in a microcrystalline form) and (b) the nitrogenation of the Sm_2Fe_{17} in N_2 or ammonia to form the interstitial Sm_2Fe_{17} nitride which is responsible for the hard magnetic properties.

Many studies have been published on the Sm_2Fe_{17} nitrides, concerning mainly the nitrogenation kinetics [10, 11] and substitutions [1, 12–17] of Sm or Fe by other rare earth or transition metals respectively. The reaction of the Sm–Fe alloys with hydrogen is very important for the HDDR, powder metallurgy and nitrogenation (in ammonia or a mixture of N_2+H_2) processes. The hydrogenation reactions of the Sm, $SmFe_2$ and $SmFe_3$ phases were reported previously by the present authors in refs. 18–20 respectively. The present study concludes the series of studies conducted by the present authors regarding the hydrogenation of the Sm–Fe intermetallic compounds (including Sm), by focusing specifically on the characteristics of the reaction between the Sm_2Fe_{17} phase and hydrogen. It includes information about the phase transformations occurring during hydrogenation as a function of temperature and the magnetic properties of the Sm_2Fe_{17} hydride. Some aspects of the reaction between Sm_2Fe_{17} and hydrogen were also reported by Xiang-Zhong *et al.* [21].

2. Experimental details

The Sm_2Fe_{17} alloy was prepared by arc melting the constituent elements (purity better than 99.9 wt.%) in a pure argon gas atmosphere. During melting, 5 wt.% excess of Sm was added to account for the Sm loss due to vaporization. The as-prepared Sm_2Fe_{17} alloy was heat treated at 1000–1200 °C for about 1 week in order to dissolve the primary α-Fe and produce an Sm_2Fe_{17} single-phase alloy. The purity of the H_2 gas used for hydrogenation was higher than 99.999 vol.%.

The constant-volume reactor (isochorothermal analyser or ITA [18–20, 22]) which was used in the present study is similar to the thermopiezic analyser (TPA) used by other researchers (*e.g.* Coey *et al.* [10]) for the study of gas–solid reactions. The volume of the ITA

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was about 2.3 cm^3 and only about 5% of the total volume was heated. The Sm_2Fe_{17} samples, weighing about 10 mg, were placed in a quartz tube (ITA) and heated with a precisely controlled programmable furnace capable of reaching a temperature of 1000 °C. The pressure was measured with a pressure sensor capable of detecting pressure differences of about 100 Pa. The temperature was measured to an accuracy of ± 1 °C. The pressure *vs.* temperature data were collected in a computer and analysed by taking into consideration the pressure variations due to the thermal effects (heated volume). By utilizing the ideal gas law, the data were transformed and plotted in terms of the number of atoms of gas absorbed by the solid or desorbed from the solid as a function of temperature. The ideal gas law was considered to be a good approximation because of the relatively low pressure and high temperature conditions (0–125 kPa and 20–1000 °C) applied during the experiments. ITA isochores were obtained for the "$Sm_2Fe_{17}+H_2$" system in the temperature range between 20 and 950 °C.

Phase analysis was performed by thermomagnetic analysis (TMA) and powder X-ray diffraction (XRD). Magnetization experiments were performed using a vibrating sample magnetometer (VSM) at 25 °C in a maximum applied field of 15 kOe. TMA was performed in a Faraday balance in the temperature range between 25 and 900 °C and in a magnetic field of about 1 kOe. The samples used in the Faraday balance were sealed in a quartz tube of known volume under argon or hydrogen gas, depending on the scope of the experiment. Powder XRD patterns were obtained under ambient conditions using a Philips automated diffractometer with Cu Kα radiation monochromated with a graphite single crystal. XRD patterns were obtained for both randomly oriented and magnetically aligned powders.

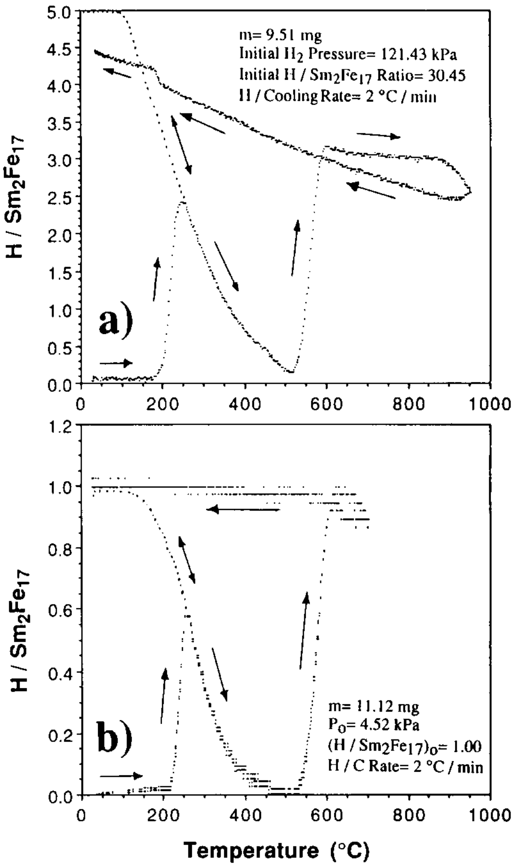

Fig. 1. ITA traces for the "$Sm_2Fe_{17}+H_2$" system obtained under different initial conditions: (a) $(H/Sm_2Fe_{17})_0=30.45$, $P_0=121.43$ kPa; (b) $(H/Sm_2Fe_{17})_0=1.00$, $P_0=4.52$ kPa.

3. Results and discussion

3.1. Hydrogen absorption–desorption–decomposition

3.1.1. Isochorothermal analysis (ITA)

The ITA isochore trace for the "$Sm_2Fe_{17}+H_2$" system is shown in Fig. 1(a). Interstitial hydrogen absorption begins at about 185 °C. The hydrogen concentration reaches the value of 2.4 H atoms per mole of Sm_2Fe_{17} at a temperature of 250 °C. Subsequently, hydrogen is desorbed gradually up to a temperature of 510 °C, where the low hydrogen concentration Sm_2Fe_{17} hydride decomposes into Sm hydride and α-Fe. The decomposition reaction is accompanied by massive hydrogen absorption according to the reaction

$$Sm_2Fe_{17}H_\delta+(2+x-\delta/2)H_2 \longrightarrow 2SmH_{2+x}+17\alpha\text{-}Fe$$

($\delta\approx0.1$ and $-0.3\leq x\leq0.6$). Further heating causes a partial loss of hydrogen from the Sm hydride. Subsequent cooling causes reabsorption of hydrogen by the Sm hydride which is more profound at about 190 °C. This behaviour of the Sm hydride was reported previously by the present authors in a study of the "$Sm+H_2$" system [18].

On cooling from 500 °C, the Sm_2Fe_{17} compound reabsorbs hydrogen reversibly (Fig. 1). The room temperature hydrogen concentration is 5 H atoms per mole of Sm_2Fe_{17}. Temperature-cycling experiments between 500 and 25 °C showed that hydrogen desorption and absorption are completely reversible in this temperature range.

When the ITA experiment (Fig. 1(b)) was conducted under a low initial hydrogen pressure ($P_0=4.52$ kPa and $H/Sm_2Fe_{17}=1.00$), the reaction characteristics were similar to those obtained under higher pressures (Fig. 1(a)). In this case the maximum amount of hydrogen absorbed at 250 °C was 0.6 H/Sm_2Fe_{17}, as expected because of the low hydrogen pressure. Above 510 °C the entire amount of hydrogen is absorbed (1H/Sm_2Fe_{17}), causing the decomposition of the majority of Sm_2Fe_{17} into Sm hydride and α-Fe. After decomposition and under the hydrogen concentration of 1H/Sm_2Fe_{17}, $0.25Sm_2Fe_{17}$ should be decomposed into $0.5SmH_2+(17/4)\alpha$-Fe, with the rest of the $0.75Sm_2Fe_{17}$ remaining unaffected. The XRD pattern for this sample suggested that much more Sm_2Fe_{17} phase was decomposed, implying that the presence of a relatively small amount of hydrogen inside the structure causes its destabilization and destruction, forming α-Fe, Sm hydride and Sm. If hydrogen is readily available under the conditions of the experiment, Sm will react instantly to form Sm hydride. Therefore a small amount of hydrogen has a rather catastrophic effect on the Sm_2Fe_{17} structure. The same behaviour was observed during the decomposition of $SmFe_3$ hydride [20].

The maximum interstitial hydrogen concentration in the Sm_2Fe_{17} hydride was found to be 5H/Sm_2Fe_{17} (Fig. 2). This was obtained by heat treating the Sm_2Fe_{17} powder inside the TMA apparatus under hydrogen at 230 °C for 12 h and then cooling at a rate of 2 °C min^{-1} to room temperature. The same hydrogen content (4.8–5.0) was reported in the case of R_2F_{17} hydrides (R≡Ce, Pr, Nd) [23–26]. Three of the five H atoms completely occupy the 9*e* octahedral (distorted) sites. The other two H atoms partially (one-third) occupy the 18*g* tetrahedral (Sm_2Fe_2) sites. The 3*a* dodecahedral sites (between the Fe dumb-bell atoms) do not accommodate any H atoms [26].

The desorption of hydrogen was examined by obtaining the ITA trace for the $Sm_2Fe_{17}H_5$ compound (Fig. 2) under initial vacuum conditions as shown in Fig. 3. The hydride begins to desorb hydrogen at about 100 °C and up to 510 °C, where the decomposition reaction takes place to form Sm hydride and α-Fe. At temperatures higher than 725 °C (and under the existing low hydrogen pressure) the Sm hydride begins to desorb hydrogen, leading to its dissociation ($Sm+H_2$) and the subsequent partial recombination [9] of elemental Sm and α-Fe to form Sm_2Fe_{17}. Subsequent cooling (to about 850 °C) causes the decomposition of Sm_2Fe_{17} (a large portion of it), which was formed during recombination at higher temperatures, into Sm hydride and α-Fe.

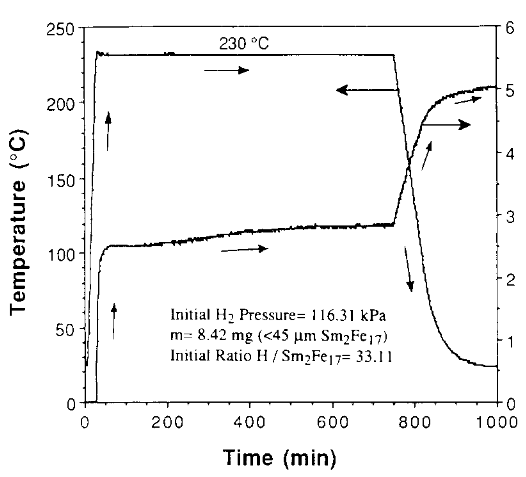

Fig. 2. ITA trace for the "$Sm_2Fe_{17}+H_2$" system obtained by isothermal heat treatment under hydrogen (P_0 = 116.31 kPa) at 230 °C for 12 h and then cooling to 25 °C. The final hydride has the composition $Sm_2Fe_{17}H_{5.0}$.

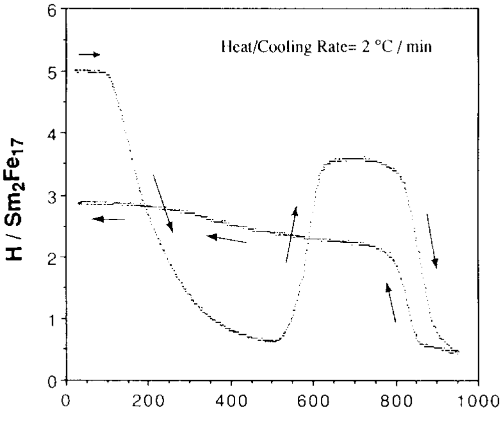

Fig. 3. ITA trace for $Sm_2Fe_{17}H_{5.0}$ obtained under initial vacuum conditions (m = 8.42 mg).

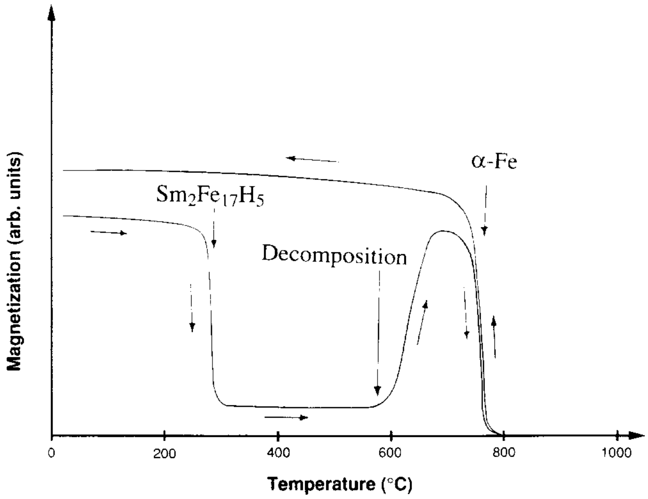

Fig. 4. TMA trace for $Sm_2Fe_{17}H_{5.0}$ sealed in a quartz tube under 0.9 atm argon gas pressure.

3.1.2. *Thermomagnetic analysis (TMA)*

The TMA trace of an $Sm_2Fe_{17}H_5$ sample sealed in a small quartz tube under 0.9 atm argon gas is shown in Fig. 4. The Curie temperature is about 280 °C. In fact, the actual Curie temperature may be higher because of the partial loss of hydrogen occurring in this temperature range. The sharp increase in the magnetization initiated at about 575 °C is due to the decomposition of the hydride into Sm hydride and α-Fe, which are retained after cooling to room temperature.

The TMA trace of an Sm_2Fe_{17} sample sealed in a small quartz tube under 0.9 atm hydrogen gas is shown in Fig. 5. The Curie temperature of the Sm_2Fe_{17} phase

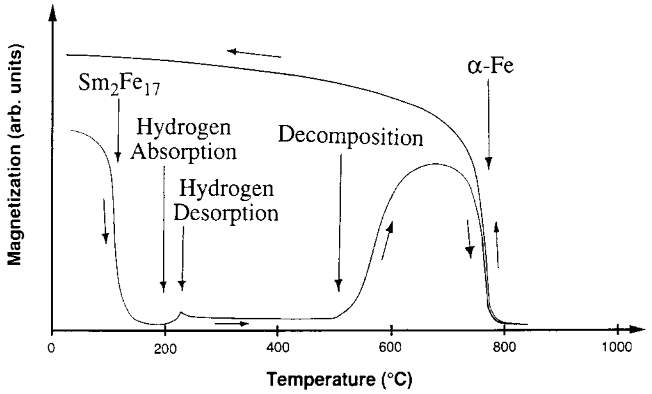

Fig. 5. TMA trace for Sm_2Fe_{17} sealed in a quartz tube under 0.9 atm hydrogen gas pressure.

is about 135 °C. At a temperature of about 200 °C the magnetization begins to increase and shortly afterwards to decrease again. This is due to the hydrogen absorption–desorption reactions occurring in that temperature range, as was observed previously in the ITA experiment shown in Fig. 1. The Curie temperature of the Sm_2Fe_{17} hydride is higher than that of Sm_2Fe_{17} as shown above (Fig. 4). The decomposition of the Sm_2Fe_{17} hydride begins at about 510 °C, as indicated by the sharp increase in the magnetization.

3.1.3. X-ray diffraction (XRD)

Figure 6 shows the XRD patterns for the starting Sm_2Fe_{17} alloy (Fig. 6(a)) and for the same alloy hydrogenated at 250 °C (Fig. 6(c)) and 600 °C (Fig. 6(e)). Hydrogenation at 250 °C (Fig. 6(c)) causes the formation of Sm_2Fe_{17} hydride with lattice parameters $a = 8.667$ Å and $c = 12.520$ Å. This corresponds to a 3.4% expansion of the rhombohedral unit cell. The stresses introduced by the lattice expansion cause crack formation along the Sm_2Fe_{17} grain boundaries and the samples become friable, but decrepitation does not occur. The sample hydrogenated at 600 °C (Fig. 6(e)) contains Sm hydride and α-Fe arising from the decomposition reaction. The broad Bragg peak of the Sm hydride is due to the non-uniform composition of the hydride [18] (SmH_{2+x}, $x = 0$–0.6) as well as to the microcrystallinity of the hydride (this is also true for the α-Fe Bragg peak).

3.2. Magnetic properties

XRD patterns obtained for random powder samples and for powder samples aligned in a magnetic field showed that for both Sm_2Fe_{17} (Figs. 6(a) and 6(b)) and Sm_2Fe_{17} hydride (Figs. 6(c) and 6(d)) the easy direction of magnetization lies in the basal plane. The room temperature magnetization obtained at 15 kOe for the Sm_2Fe_{17} hydride is 159 e.m.u. g^{-1}, compared with 116 e.m.u. g^{-1} for the parent compound. Their corresponding Curie temperatures are 280 and 135 °C respectively. The increase in the magnetization and Curie temperature is attributed to the increase in the Fe–Fe interatomic distances resulting in the minimization of the negative Fe–Fe exchange interactions [25].

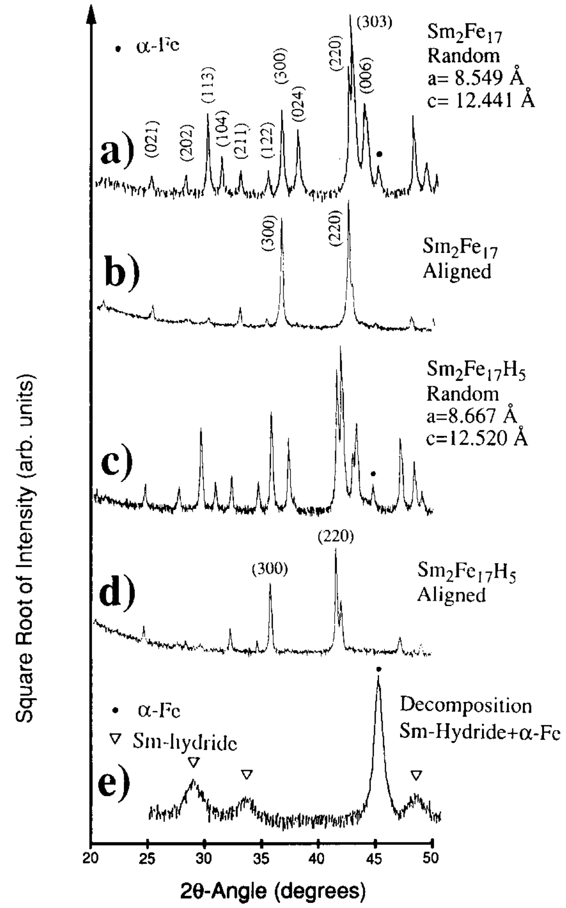

Fig. 6. XRD patterns: (a) random Sm_2Fe_{17} alloy powder; (b) aligned Sm_2Fe_{17} alloy powder; (c) random $Sm_2Fe_{17}H_5$ powder (Sm_2Fe_{17} hydrogenated at 250 °C); (d) aligned $Sm_2Fe_{17}H_5$ powder; (e) Sm_2Fe_{17} hydrogenated at 600 °C (decomposed).

4. Summary

Sm_2Fe_{17} begins to absorb hydrogen at about 185 °C and reaches a hydrogen content of 2.4H/Sm_2Fe_{17} at 250 °C. Subsequent cooling to room temperature causes an increase in the hydrogen concentration to 5 H atoms per mole of Sm_2Fe_{17}. Above 250 °C the Sm_2Fe_{17} hydride begins to desorb hydrogen up to 510 °C, where the hydride begins to decompose into Sm hydride and α-Fe. The decomposition reaction is accompanied by massive hydrogen absorption. The Sm_2Fe_{17} hydride has the rhombohedral crystal structure (the same as the parent compound) with a 3.4% expanded lattice with parameters $a = 8.667$ Å and $c = 12.520$ Å. The stresses introduced by the lattice expansion cause crack formation along the Sm_2Fe_{17} grain boundaries and the samples become friable. The Curie temperature and saturation magnetization are 280 °C and 159 e.m.u. g^{-1} for $Sm_2Fe_{17}H_5$ as compared with 135 °C and 116 e.m.u. g^{-1} for Sm_2Fe_{17}. For both Sm_2Fe_{17} and Sm_2Fe_{17} hydride, the easy direction of magnetization is perpendicular to the *c* direction in the rhombohedral structure.

References

1 J. M. D. Coey, H. Sun and Y. Otani, A new family of rare earth iron nitrides, in S. G. Sankar (ed.), *Proc. Sixth Int. Symp. on Magnetic Anisotropy and Coercivity in Rare Earth–Transition Metal Alloys, Pittsburgh, PA, October 1990,* Carnegie Mellon University, Pittsburgh, PA, 1990, p. 36.

2 K. Schnitzke, L. Schultz, J. Wecker and M. Katter, *Appl. Phys. Lett., 57* (1990) 2853.

3 M. Endoh, M. Iwata and M. Tokunaga, *J. Appl. Phys., 70* (1991) 6030.

4 M. Katter, J. Wecker and L. Schultz, *J. Appl. Phys., 70* (1991) 3188.

5 C. N. Christodoulou and T. Takeshita, *J. Alloys Comp.,* in press.

6 J. M. D. Coey and H. Sun, *J. Magn. Magn. Mater., 87* (1990) L251.

7 M. Q. Huang, L. Y. Zhang, B. M. Ma, Y. Zheng, J. M. Elbicki, W. E. Wallace and S. G. Sankar, *J. Appl. Phys., 70* (1991) 6027.

8 H. Nakamura, K. Kurihara, T. Tatsuki, S. Sugimoto, M. Okada and M. Homma, Variation of magnetic properties of $Sm_2Fe_{17}N_x$ alloys by hydrogen treatment, *Dig. 15th Ann. Conf. on Magnetics in Japan, Ibaraki, October 1991,* Magnetic Society of Japan, Ibaraki, Japan, 1991, p. 379 (in Japanese).

9 C. N. Christodoulou and T. Takeshita, *J. Alloys Comp.,* in press.

10 J. M. D. Coey, J. F. Lawler, H. Sun and J. E. M. Allan, *J. Appl. Phys., 69* (1991) 3007.

11 T. Mukai and T. Fujimoto, *J. Magn. Magn. Mater., 103* (1992) 165.

12 M. Q. Huang, B. M. Ma, W. E. Wallace and S. G. Sankar, Magnetic properties and structure of nitrogenated $R_2(Fe, Co)_{17}$ intermetallic compounds, in S. G. Sankar (ed.), *Proc. Sixth Int. Symp. on Magnetic Anisotropy and Coercivity in Rare Earth–Transition Metal Alloys, Pittsburgh, PA, October 1990,* Carnegie Mellon University, Pittsburgh, PA, 1990, p. 204.

13 L. Y. Zhang, Y. Zheng and W. E. Wallace, Magnetization and PCIs of nitrogenated $R_2(Fe, Co)_{17}$ systems, in S. G. Sankar (ed.), *Proc. Sixth Int. Symp. on Magnetic Anisotropy and Coercivity in Rare Earth–Transition Metal Alloys, Pittsburgh, PA, October 1990,* Carnegie Mellon University, Pittsburgh, PA, 1990, p. 219.

14 K. H. J. Buschow, R. Coehoorn, D. B. de Mooij, K. de Waard and T. H. Jacobs, *J. Magn. Magn. Mater., 92* (1990) L35.

15 J. M. D. Coey, H. Sun and D. P. F. Hurley, *J. Magn. Magn. Mater., 101* (1991) 310.

16 M. Q. Huang, Y. Zheng, K. Miller, J. M. Elbicki and S. G. Sankar, *J. Appl. Phys., 70* (1991) 6024.

17 D. P. F. Hurley and J. M. D. Coey, *J. Magn. Magn. Mater., 99* (1991) 229.

18 C. N. Christodoulou and T. Takeshita, *J. Alloys Comp., 190* (1992) 99.

19 C. N. Christodoulou and T. Takeshita, *J. Alloys Comp.,* in press.

20 C. N. Christodoulou and T. Takeshita, *J. Alloys Comp., 191* (1993) 279.

21 W. Xiang-Zhong, K. Donnelly, J. M. D. Coey, B. Chevalier, J. Etourneau and T. Berlureau, *J. Mater. Sci., 23* (1988) 329.

22 C. N. Christodoulou and T. Takeshita, *J. Alloys Comp., 190* (1992) 41.

23 B. Rupp and G. Wiesinger, *J. Magn. Magn. Mater., 71* (1988) 269.

24 O. Isnard, S. Miraglia, J. L. Soubeyroux, D. Fruchart and A. Stergiou, *J. Less-Common Met., 162* (1990) 273.

25 O. Isnard, S. Miraglia, D. Fruchart and J. Deportes, *J. Magn. Magn. Mater., 103* (1992) 157.

26 O. Isnard, S. Miraglia, J. L. Soubeyroux and D. Fruchart, *Solid State Commun., 81* (1992) 13.