Plasma nitrogenation of Pr_2Fe_{17} and Sm_2Fe_{17}

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The effect of plasma nitrogenation on the structural and magnetic properties of Pr_2Fe_{17} and Sm_2Fe_{17} compounds was investigated by Mössbauer spectroscopy, thermomagnetic measurements, optical metallography, and electronic microprobe analysis. Samples were prepared starting from Pr_2Fe_{17} and Sm_2Fe_{17} commercial powders with 20 μm granulometry, submitted to nitrogenation treatment at 400 °C in 10 Torr atmosphere of 80%H_2–20%N_2 during periods up to 8 h. Our results show the formation of $R_2Fe_{17}N_3$ and metallic Fe and indicate the existence of two other phases. The Mössbauer parameters of the latter are characterized by magnetic hyperfine fields (peak values) of 21 (24) and 3 (4) T and isomer shifts of 0.17 and 0.24 (0.24 and 0.29) mm/s for Pr (Sm). Their magnetic-phase transitions were determined to be close to 250 and 90 °C. Our results suggest that these 2:17 phases present stoichiometries close to $R_2Fe_{17}N_8$ and $R_2Fe_{17}N_{11}$, respectively. © *2000 American Institute of Physics.* [S0021-8979(00)21908-7]

INTRODUCTION

Since the discovery in the early 1990s that the addition of interstitial elements as hydrogen, carbon, and mainly nitrogen in R_2Fe_{17} compounds (R=rare earth) can enhance their magnetic properties enormously,[1,2] there is intense activity in this research field.[1–7] Usually, during nitrogenation, the N content is less than 3 atoms per formula unit. Iryiama *et al.*[4] and Wei *et al.*[5] have investigated $Sm_2Fe_{17}N_x$ obtained by diffusion in NH_3+H_2 atmospheres, with $x<6$ and $x<8$, respectively.

In this work, we report on the structural and magnetic properties of R_2Fe_{17} (R=Pr and Sm) alloys after plasma nitrogenation in a mixed H_2-N_2 atmosphere. The nitrogen-induced changes on the structural and magnetic properties of Pr_2Fe_{17} and Sm_2Fe_{17} powders were investigated by x-ray diffraction (XRD); ^{57}Fe Mössbauer spectroscopy, thermomagnetic analysis (TMA), optical metallography, and electronic microprobe analysis.

EXPERIMENT

The samples were obtained starting from Pr_2Fe_{17} and Sm_2Fe_{17} powders. Pr_2Fe_{17} alloy was prepared by arc melting in argon followed by heat treatment at 1000 °C during 10 days, and commercial Sm_2Fe_{17} (Goldschmidt) has been used. The powders with particle size smaller than 20 μm were nitrogenated at 400 °C under a 10 Torr atmosphere of 80 vol% H_2–20 vol% N_2 in a glow-discharge plasma reactor over periods ranging from 4 to 8 h. After nitrogenation, the $Pr_2Fe_{17}(Sm_2Fe_{17})+N$ samples were characterized by XRD with Cu $K\alpha$ radiation, by ^{57}Fe Mössbauer spectroscopy, thermomagnetic analysis, and by electronic microprobe analysis. Room-temperature Mössbauer spectra have been obtained by transmission on a constant acceleration transducer with a ^{57}Co/Rh source. The NORMOS least-squares-fit program was employed to calculate the spectral hyperfine parameters. In the microprobe analysis, compositional analysis were obtained by wavelength-dispersive x-ray analysis.

RESULTS AND DISCUSSION

Typical x-ray diffraction patterns resulting from the applied nitrogenation process are shown in Fig. 1 for a Sm_2Fe_{17} sample before (a) and after (b) nitrogenation at 400 °C over 8 h, treatment that induces a clear loss of crystallinity of the 2:17 phase and the formation of α-Fe, characterized in the Fig. 1(b) by the intense (101) peak at $2\theta=44°$. Besides α-Fe, the large background and the absence of the diffraction lines corresponding to the 2:17 phase are interpreted as indications of a significant amount of a 2:17 amorphous phase with increased N content, since similar amorphization has

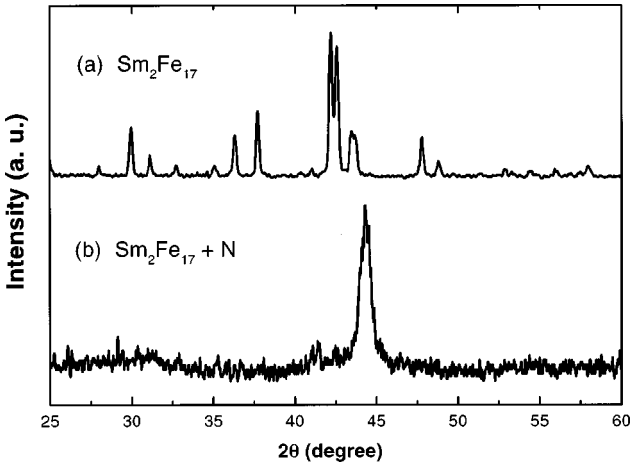

FIG. 1. X-ray diffraction patterns of Sm_2Fe_{17} before (a) and after (b) plasma nitrogenation at 400 °C during 8 h.

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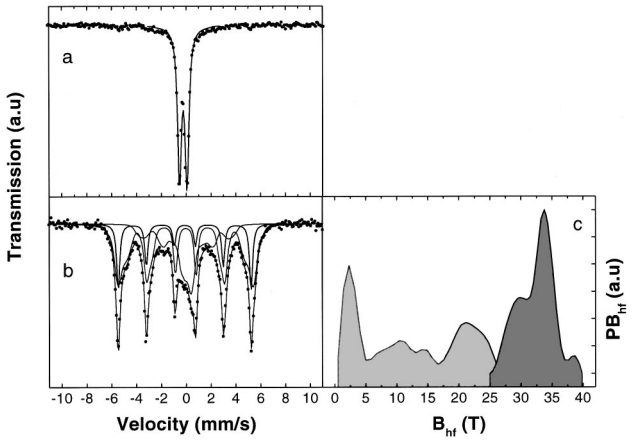

FIG. 2. Room-temperature Mössbauer spectra of Pr_2Fe_{17} powder before (a) and after (b) plasma nitrogenation at 400 ° C during 8 h. After nitrogenation, the spectrum is fitted to α-Fe (sextet) plus two hyperfine field distributions, shown in (c).

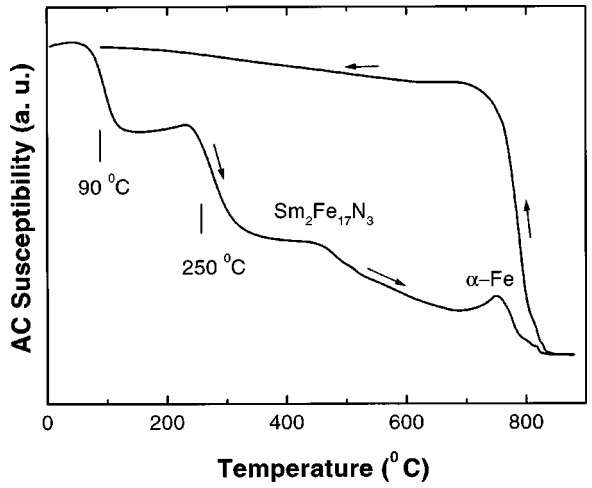

FIG. 4. TMA traces for Sm_2Fe_{17} powder after plasma nitrogenation at 400 °C during 8 h.

been observed by other authors for $x>6$.[3–5] The existence of 2:17+N amorphous phases is supported by our Mössbauer results, as discussed below.

Due to the amorphous character of the samples, Mössbauer spectroscopy allows better characterization of the evolution of the Fe phases induced by the nitrogenation process. Room-temperature Mössbauer spectra of Pr_2Fe_{17} and Sm_2Fe_{17} compounds before and after nitrogenation at 400 °C for 8 h are shown in Figs. 2 and 3. Pure Pr_2Fe_{17} presents a characteristic paramagnetic doublet with an isomer shift of -0.16 mm/s and quadrupole splitting of 0.22 mm/s [Fig. 2(a)] and Sm_2Fe_{17} is characterized by a magnetic spectrum with an average hyperfine field of 21.8 T and isomer shift of -0.15 mm/s [Fig. 3(a)].[6] Figures 2(b) and 3(b) show the spectra for Pr_2Fe_{17}+N and Sm_2Fe_{17}+N, respectively. Both spectra were fitted to a crystalline sextet corresponding to metallic Fe (up to 19%) plus two hyperfine field distributions: one distribution for high hyperfine fields (25–50 T) and a low-field distribution (1–30 T), shown in Figs. 2(c) and 3(c) in gray and light gray, respectively. The high-field distribution [gray areas in Figs. 2(c) and 3(c)] have hyperfine parameters characteristic for $Pr_2Fe_{17}N_3$ and the $Sm_2Fe_{17}N_3$ phases, respectively ($B_{hf}=32.1$ T, $\delta=-0.04$ mm/s for Pr and $B_{hf}=33.4$ T, $\delta=-0.06$ mm/s for Sm).[6] The low-field distributions account for the broad central area of the spectra, as shown in Figs. 2(c) and 3(c) (light-gray areas). These low-field distributions are characterized by isomer shifts of 0.17 (0.24) and 0.24 (0.29) mm/s and at least two maxima, centered at 21 (24) and 3 (4) T for Pr_2Fe_{17} (Sm_2Fe_{17}).

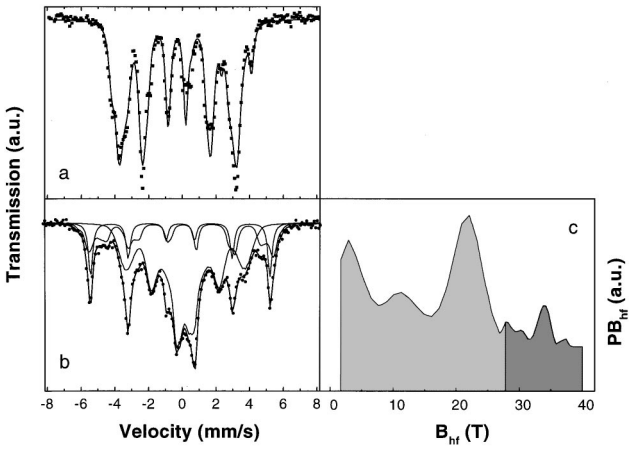

FIG. 3. As in Fig. 2, for Sm_2Fe_{17}.

The presence of the two peaks with hyperfine parameters differing very much from those presented by pure 2:17 and 2:17 phases with three nitrogen atoms per formula unit[6] are interpreted as an indication of the existence of at least two other magnetic phases in our samples. This hypothesis is reinforced by the TMA results, as illustrated in the Fig. 4 for a Sm_2Fe_{17} sample after plasma nitrogenation. In Fig. 4, we observe four magnetic transitions at 770, 480, 250, and 90 °C. The transition at 770 °C corresponds to α-Fe and that at 480 °C corresponds to $Sm_2Fe_{17}N_3$.[1]

With the intention of identifying the remaining phases, optical microscopy and electronic microprobe analyses were applied. The microstructure of Sm_2Fe_{17}+N, as illustrated by the micrography in Fig. 5, allows the identification of three different regions in the grains: (i) a light-gray central region, involved by (ii) a dark-gray ring and (iii) a dark boundary. Electronic microprobe compositional analysis results in a stoichiometry close to $R_2Fe_{17}N_8$ for region (i) and a higher nitrogen concentration (11%) for region (ii), and suggests that the dark grain boundaries are related to oxide layers. By microprobe analysis, it was not possible to identify a region with stoichiometry close to $R_2Fe_{17}N_3$. As the original proportion of metals is 2:17, we will refer to the phase in region (ii) as $R_2Fe_{17}N_{11}$.

Considering that the results from Iriyama *et al.* for $R_2Fe_{17}N_x$, with $x>3$, indicate the monotonic decrease of the Curie temperature with N content,[4] we could suppose that the magnetic transitions observed by TMA at 250 and 90 °C would correspond to $R_2Fe_{17}N_8$ and $R_2Fe_{17}N_{11}$, respectively. Taking that supposition into account, for Sm_2Fe_{17}+N the behavior of T_C vs nitrogen content ($x>3$) could be described as shown in Fig. 6, with a linear decrease of $\sim$50 °C/N atom in the 2:17 matrix. In this way, back to our

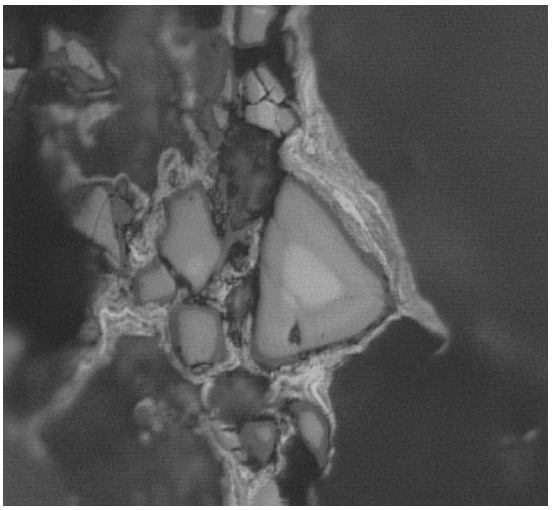

FIG. 5. Metallography of a Sm_2Fe_{17} sample after plasma nitrogenation at 400 °C during 8 h.

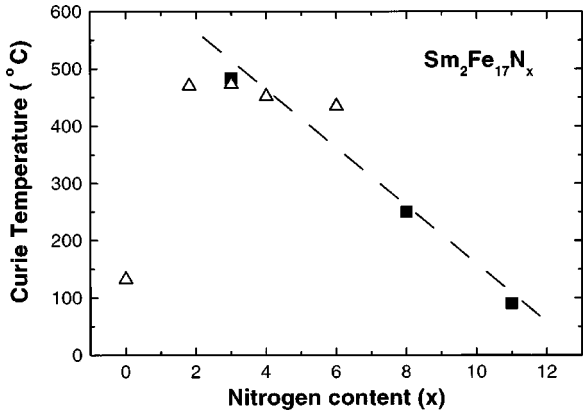

FIG. 6. Magnetic transition temperature vs nitrogen content for $Sm_2Fe_{17}N_x$. Open circles are results from Iriyama *et al.* (Ref. 4) and full squares are our results for a sample submitted to plasma nitrogenation at 400 °C during 8 h.

Mössbauer results, the different peaks at the low-field magnetic hyperfine field distributions could be attributed to R:Fe:N phases with 2:17:8 and 2:17:11 stoichiometries. Although it has not been possible to identify by electronic microprobe analysis a region with stoichiometry close to $R_2Fe_{17}N_3$, from our results we can affirm that this phase is formed in the very central part of the grains.

CONCLUSIONS

We have investigated the effect of plasma nitrogenation on the structural and magnetic properties of Pr_2Fe_{17} and Sm_2Fe_{17} compounds. Nitrogenation at 400 °C in 10 Torr atmosphere of $80\%H_2-20\%N_2$ during periods up to 8 h induces the formation of $R_2Fe_{17}N_3$ and metallic Fe and of two other phases with magnetic transition temperatures near 90 and 250 °C. Our results suggest that these 2:17 phases present stoichiometries close to $R_2Fe_{17}N_{11}$ and $R_2Fe_{17}N_8$, respectively.

ACKNOWLEDGMENTS

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