X-ray structural studies of nitrogen diffusion in Dy_2Fe_{17}

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The reaction between N_2 and Dy_2Fe_{17} has been studied by thermopiezic analysis on 20–25 μm sized powders in the temperature range 400–500 °C. Partially nitrided powders were analyzed using CuK_α x-ray diffraction and thermomagnetic techniques. Both high angle x-ray and thermomagnetic data show only the presence of Dy_2Fe_{17} and $Dy_2Fe_{17}N_{3-\delta}$ ($\delta<0.3$) with no evidence of intermediate compositions. The results of the x-ray diffraction experiments at several Bragg peaks were simulated using a two phase model structure: a Dy_2Fe_{17} core with a $Dy_2Fe_{17}N_3$ surface layer. The results show that at low temperatures the nitride layer is too thin to account for all of the nitrogen absorbed by the sample, indicating that a significant amount of the nitrogen diffused into the core of the particles, presumably along grain boundaries.

During a gas–solid reaction, nitrogen diffuses into R_2Fe_{17} (R=rare earth), occupying interstitial sites and expanding the lattice without changing the crystal structure. The enhancement of the magnetic properties was observed[1] as a result of interstitial nitrogen diffusion in R_2Fe_{17}. Neutron powder diffraction[2] showed that the R_2Fe_{17} and $R_2Fe_{17}N_3$ phases are in equilibrium during the reaction. However, it was observed[3,4] that a continuous solid solution $R_2Fe_{17}N_x$ ($0<x<3$) is formed on annealing partially nitrided powders. In this study we use x-ray diffraction and thermomagnetic techniques to characterize nitrogen diffusion in the 2-17 structure. Nitrogen diffusion in the 2-17 structure typically occurs above 350 °C, and significant diffusion through extended defects such as grain boundaries at 400 °C has been observed using metallography.[5]

The polycrystalline Dy_2Fe_{17} alloy was prepared by induction melting of appropriate amounts of Dy and Fe, followed by vacuum annealing at 1173 K for two weeks. Induction melting ensures homogeneity of alloys and mass loss was below 0.03% during preparation. The homogenized ingot was ground and sieved to select powder sizes between 20 and 25 μm. The powder size was confirmed by scanning electron microscopy. Nitrogen diffusion was performed in a thermopiezic analyzer (TPA) at a starting pressure of 1 bar and temperatures ranging from 400 °C (590 min) to 500 °C (25 min) to obtain $Dy_2Fe_{17}N_{0.85}$. The amount of nitrogen diffused into the sample was obtained directly from the gas pressure change in the TPA. Structural analyses on Dy_2Fe_{17}, before and after the gas–solid reaction, were carried out using CuK_α radiation on an automated Nicolet–Stöe powder diffractometer with a graphite monochromator in the diffracted beam. Thermomagnetic analyses were done using a Perkin–Elmer thermogravimetric analyzer (TGA) in a small field gradient.

The x-ray diffraction pattern of $Dy_2Fe_{17}N_{0.85}$ is shown in Fig. 1. As a consequence of nitriding, a new phase was formed with the same structure as Dy_2Fe_{17} but with the Bragg peaks shifted towards lower angles indicating an expansion of the unit cell. This shift is shown more clearly in Fig. 2, where the (300) peaks of $Dy_2Fe_{17}N_{0.85}$ (top) are compared with those (bottom) of pure Dy_2Fe_{17} (N_0) and $Dy_2Fe_{17}N_3$ (N_3). $Dy_2Fe_{17}N_{0.85}$ clearly contains both $Dy_2Fe_{17}N_3$ and unreacted Dy_2Fe_{17}. The position of the Dy_2Fe_{17} peak is shifted towards lower angles, due to the expansion of the unreacted core, while that of $Dy_2Fe_{17}N_3$ is shifted slightly towards higher angles. Careful examination of the (332) Dy_2Fe_{17} and $Dy_2Fe_{17}N_3$ diffraction peaks (inset of Fig. 1), which are well separated, shows no evidence of the existence of an intermediate composition phase. Using TGA two distinct Curie temperatures, $T_{c1}=128$ °C and $T_{c2}=445$ °C are detected as shown in Fig. 3. T_{c1} is 28 °C higher than the Curie temperature of Dy_2Fe_{17} and T_{c2} is 5 °C lower than the Curie temperature of $Dy_2Fe_{17}N_3$. The x-ray and the TGA data are thus in agreement, as T_c changes with the lattice expansion of Dy_2Fe_{17}. Even if the observed experimental data only show the existence of Dy_2Fe_{17} and $Dy_2Fe_{17}N_3$, they are not at equilibrium at 500 °C. After subsequent annealing for 60 h at 480 °C, a uniform $Dy_2Fe_{17}N_{0.85}$ solid solution was obtained. Further work is in progress to study this equilibrium phase. Because $Dy_2Fe_{17}N_3$ and Dy_2Fe_{17} are not in equilibrium, we tried to estimate the amount of the undetected intermediate phase (in the interface between $Dy_2Fe_{17}N_3$ and Dy_2Fe_{17}) by comparing the x-ray patterns of crushed $Dy_2Fe_{17}N_{0.85}$, shown in Fig. 2(b), with

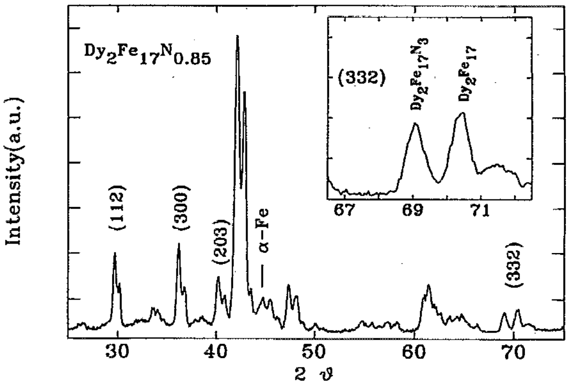

FIG. 1. The x-ray diffraction pattern of $Dy_2Fe_{17}N_{0.85}$ for nitrogen diffused at 500 °C for approximately 25 min. Inset: (332) peak of $Dy_2Fe_{17}N_{0.85}$.

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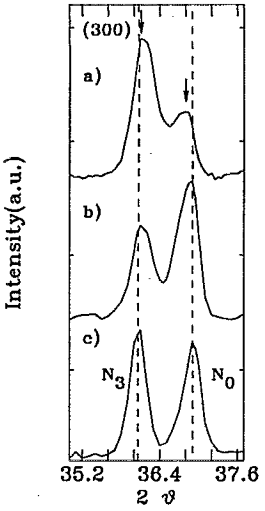

FIG. 2. (a) The (300) diffraction peak of $Dy_2Fe_{17}N_{0.85}$ (powder sizes between 20 and 25 μm). (b) The diffraction peak of the subsequently crushed $Dy_2Fe_{17}N_{0.85}$. (c) The (300) peak of a mixture of pure Dy_2Fe_{17} and $Dy_2Fe_{17}N_3$ powders in the ratio 1:1.

those (bottom of Fig. 2) of pure Dy_2Fe_{17} (N_0) and $Dy_2Fe_{17}N_3$ (N_3). Note that for the crushed $Dy_2Fe_{17}N_{0.85}$ powder the x-ray peaks are mostly relaxed to the unshifted positions. Fitting shows that the possible amount of the intermediate phase is much lower than the amount of the $Dy_2Fe_{17}N_3$ phase.

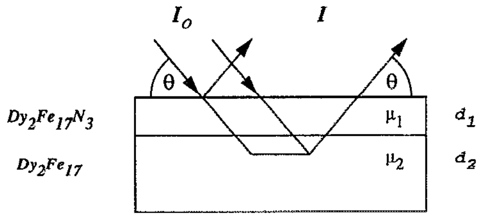

FIG. 4. Two layer model structure used to calculate x-ray diffraction patterns.

Nitrogen distribution can be estimated from the ratio of the intensities of the diffraction peaks by using a simple model where the core is nitrogen-free and the surface layer is fully nitrided as shown schematically in Fig. 4. Estimating the volume fractions is complicated because the $Dy_2Fe_{17}N_3$ phase coats the Dy_2Fe_{17} phase and so attenuates the x-ray scattering. In a multilayered system the intensity of the reflected beam from the ith layer can be expressed as

$$I_i=I_0 e^{-\Sigma_{j=1}^{i-1}(2d_j\mu_j/\sin\theta)}\int_0^{d_i} e^{-2x\mu_i/\sin\theta}\,dx\int dS, \qquad (1)$$

where I_0 and θ are the intensity and angle of the incident beam, d_i and μ_i are the thickness and absorption coefficient of the ith layer, respectively, and S is the surface area illuminated by the beam. The term $e^{-\Sigma_{j=1}^{i-1}(2d_j\mu_j/\sin\theta)}$ comes from the attenuation of the x-ray beam from the top $(i-1)$ layers. For the two layer model, the intensity ratio becomes

$$I_1/I_2=(\mu_2/\mu_1)(e^{2d_1\mu_1/\sin\theta}-1), \qquad (2)$$

where we have neglected the term $e^{-2d_2\mu_2/\sin\theta}$ as $d_2\approx 20$ μm and $\mu_2=1.577$ μm^{-1}.

The relative intensities (I_1,I_2) were estimated by a simultaneous fitting of the measured (112), (300), and (203) Bragg peaks to Eq. (1) where each Bragg peak is a combination of two Gaussians with position p_i and width w_i $(i=1,2)$, representing the contributions from $Dy_2Fe_{17}N_3$ and Dy_2Fe_{17}. The widths, w_1 and w_2, are adjusted during the fitting. We note that this model assumes that the nitrogen diffuses uniformly through the bulk of the material. Figure 5 shows the CuK_α x-ray diffraction patterns of $Dy_2Fe_{17}N_{0.85}$ samples nitrided at 500 °C. The solid lines in Fig. 5 are the fits to the experimental data and the dotted lines are the contributions of Dy_2Fe_{17} and $Dy_2Fe_{17}N_3$ calculated from the model. Assuming that the average particle has a rectangular shape with the dimensions $20\times15\times10$ μm^3 (this particle shape is an approximate representation deduced from scanning electron microscope photographs) we obtain, using the calculated thicknesses of the layers, that for nitrogen diffusion at 500 °C approximately 90% of the nitrogen can be accounted for by the intensity of the fully nitrided peak. This shows that almost the entire amount of nitrogen is in the surface layer (the penetration of the CuK_α in Dy_2Fe_{17} is restricted to approximately 1–2 μm). To observe the nitrogen

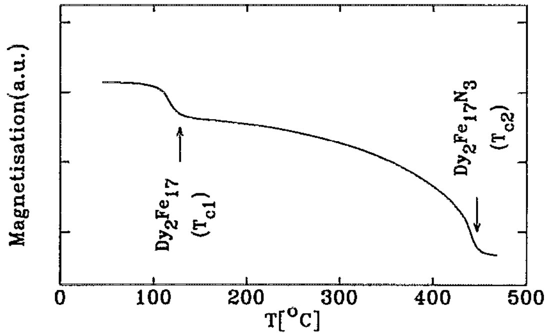

FIG. 3. Thermogravitometric analyses of $Dy_2Fe_{17}N_{0.85}$. T_{c1} correspond to the Curie temperature of the Dy_2Fe_{17} and T_{c2} to Curie temperature of the $Dy_2Fe_{17}N_3$ phase.

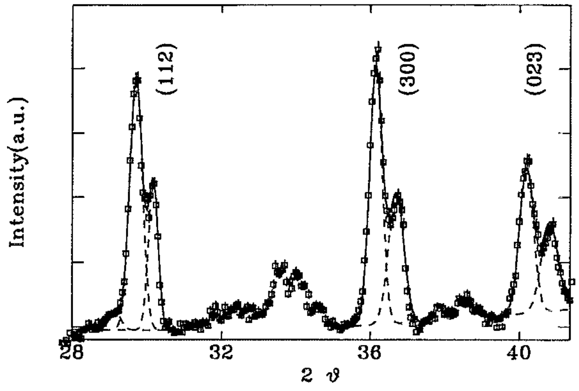

FIG. 5. Simultaneous fitting of (112), (300), and (023) peaks using a two layer model structure. The solid lines are contributions of Dy_2Fe_{17} and $Dy_2Fe_{17}N_3$ calculated from the model.

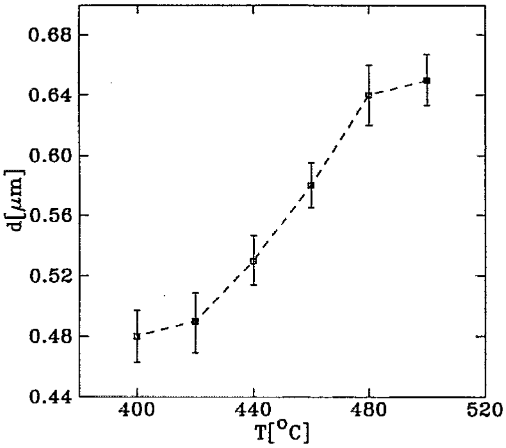

FIG. 6. Effect of reaction temperature on the apparent $Dy_2Fe_{17}N_3$ layer thickness derived from fits to the x-ray diffraction patterns. All samples have the same nominal nitrogen content.

distribution at different temperatures we introduced the same amount of nitrogen (a bulk average of 0.85 atoms per unit formula) to 20–25 μm sized powders at temperatures between 400 and 500 °C.

The values for the thicknesses of the nitrided layer versus the nitriding temperature is shown in Fig. 6. Despite the fact that all of the nitrided samples have the same nominal composition, the $Dy_2Fe_{17}N_3$ surface layer is clearly thinner in the samples prepared at lower temperatures. In the absence of any evidence for the formation of an intermediate composition nitride phase, we attribute the apparent nitrogen deficit to the formation of the nitride phase at depths within the particles beyond the penetration range of the CuK_α radiation (≈1 μm). For this to happen, the nitrogen must find more rapid diffusion paths than bulk diffusion allows, presumably along extended defects such as grain boundaries. Above 480 °C, the two layer model accounts for over 90% of the absorbed nitrogen, and we conclude that for these temperatures nitrogen transport is dominated by bulk diffusion.

In conclusion, using x-ray diffraction and a thermomagnetic technique only Dy_2Fe_{17} and $Dy_2Fe_{17}N_3$ phases were observed. The thickness of the nitrogen layer was obtained by fitting x-ray diffraction peaks with a two phase model structure: a $Dy_2Fe_{17}N_3$ surface layer and a Dy_2Fe_{17} core. Significant nitrogen diffusion through extended defects such as grain boundaries was observed at temperatures below 480 °C.

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