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Diffusion patterns of nitrogen in the $Fe_{17}Nd_2$ compound as a function of temperature

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Abstract

Nitrogen diffusion patterns were obtained for the compound $Fe_{17}Nd_2$ at temperatures of 400, 500 and 575 °C. The formation of a nitrogen solid solution was not observed, and the fully nitrided phase precipitated from the phase free from nitrogen. At 400 °C the shell–core diffusion structure was not observed, and diffusion occurred preferentially through extended defects such as grain and phase boundaries and dislocations. At higher temperatures, the bulk diffusion coefficient was large enough for bulk diffusion to compete with the faster diffusion through defects, so that the shell–core structure was observed. For all temperatures colour differences were observed in the fully nitrided phase, indicating fluctuations in nitrogen concentration. For higher temperatures, precipitation of NdN was observed.

1. Introduction

The discovery that the 17:2 phases of the Fe–rare earth (Fe–RE) systems can absorb large amounts of nitrogen, with a remarkably large increase in their Curie temperatures and that, for the samarium case, uniaxial anisotropy appears on nitrogen uptake [1] has triggered a series of investigations on the effects of nitrogen on the magnetic properties of these compounds [2, 3]. However, little work has been carried out on the diffusion mechanism itself [4]. The existing work tends to support the concept of a continuous solid solution of nitrogen in the compound, with the Curie temperature varying as the nitrogen concentration varies. This also seems to be supported by X-ray diffraction measurements, which show a continuous variation in the diffraction line positions as a function of temperature.

In previous work, we have performed several experiments to investigate these ideas, and the first results have already been reported [5, 6]. Samples of the $Fe_{17}Nd_2$ phase were prepared containing various amounts of nitrogen atoms per formula unit at 400 °C, and they were analysed using metallography, X-ray diffraction, electron probe microanalysis (EPMA) and thermomagnetic analysis (TMA). The results showed that the diffusion process can be described as the precipitation of a nitrogen-saturated phase in the body of pure $Fe_{17}Nd_2$, and that the main diffusion mechanism is via extended defects, such as grain and phase boundaries or dislocations. The simultaneous presence of the two phases was confirmed by all the experimental techniques used in the sample analyses. The TMA signals showed a significant broadening of the transition of the non-nitrided part of the sample, and a small broadening for the saturated part. This effect is discussed at length in this paper. There was also an apparent broadening and continuous displacement of the X-ray diffraction peaks, but this can be simply ascribed to the superposition of the diffraction lines of the two phases present in the sample when the pattern is carefully examined [6].

The purpose of this work is to compare the diffusion patterns for the $Fe_{17}Nd_2$ phase taken at different temperatures, since it is expected that a higher absorption temperature will change the patterns observed at 400 °C. Experiments were also performed to study a possible mechanism leading to the observed broadening of the TMA signals.

2. Experimental details

The starting materials for alloy preparation were 99.99% Fe and 99.9% Nd, both from Johnson Matthey. The stoichiometric samples were melted at least four times in an arc furnace under an argon atmosphere, being turned after each melting for better homogenization. The samples were wrapped in tantalum foil,

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encapsulated in quartz ampoules under high purity argon and heat treated at 1100 °C for 10 days. Before the nitriding treatment, a piece of each sample was metallographically analysed.

The nitriding treatments were performed in a Sieverts apparatus. The samples were crushed, milled in a miniature planetary ball mill using a chromium steel bowl and WC balls (from Fritsch) under *n*-heptane to avoid oxidation, and sieved prior to treatment. Only grains smaller than 75 μm were placed in the Sieverts reactor, with the temperature maintained within 1% of the desired absorption value. The sample temperature was continuously monitored by a type K thermocouple located inside the reactor. Absorptions were performed at 400, 500 and 575 °C (the highest stable temperature achievable in our apparatus). The procedure used to prepare the samples of $Fe_{17}Nd_2N_x$ with $x=0.5$, 1.0, 1.5, 2.0 and the saturation value for each temperature (see Table 1) was as follows. Nitrogen gas (purity, better than 99.999%) was admitted to the reactor chamber at pressures such that, after the absorption was completed, the final pressure was around 1 Torr for samples with $x \leqslant 1.5$. For samples with $x \geqslant 1.5$ the final pressure was increased up to 700 Torr (Table 1). The amount of gas absorbed was calculated with an accuracy better than 1% and pressures were measured with a membrane gauge (MKS).

The nitrided samples were also analysed using metallography, TMA, X-ray diffraction and EPMA. The metallographic preparation of the samples and the TMA apparatus, are described in ref. 6.

3. Results and discussion

For each temperature we prepared a sequence of samples with varying nominal nitrogen contents. At each temperature the same pattern was observed: for *x* values lower than the saturation value, the particles of the nitrided samples consisted of a mixture of two phases, one corresponding to the pure 17:2 phase and the other to the saturated phase. This observation is confirmed by X-ray diffraction measurements as well as by TMA. Figure 1 shows the TMA signals for the representative samples at different nitrogen absorption temperatures. The signal for the pure phase broadens as the nitrogen concentration increases. This may be interpreted as an increase in the solid solution of nitrogen in the pure phase. However, it should also be noted that, as shown by the metallographs, the two phases coexist in the same particle (see subsequent figures). As the saturated phase presents a greater volume than the pure phase, it is expected that they exert mutual tension, and this may be the cause of the observed broadening.

A portion of the pure phase was submitted to different ball-milling periods under *n*-heptane in a planetary ball mill. This imparts deformation energy to the powder, reproducing the tensioned state encountered in the particles of the partially nitrided powders. After each

TABLE 1. Nitrogen absorption times and final pressures for the $Fe_{17}Nd_2$ compound at 400, 500 and 575 °C. x_{sat} is 2.1, 2.3 and 1.85 for 400, 500 and 575 °C respectively

$x_0 \rightarrow x_1$	Absorption temperature					
	400 °C		500 °C		575 °C	
	Time (h)	Final pressure (Torr)	Time (h)	Final pressure (Torr)	Time (h)	Final pressure (Torr)
$0 \rightarrow 0.5$	1.0	16.3	2.0	0.35	0.5	0.20
$0.5 \rightarrow 1.0$	1.5	5.30	3.0	0.30	3.0	0.70
$1.0 \rightarrow 1.5$	3.0	3.50	3.0	0.35	2.0	2.20
$1.5 \rightarrow 2.0$	12.0	1.00	12.0	1.00	12.0[a]	700.0
$2.0 \rightarrow x_{sat}$	16.0	370.0	24.0	620.0	–	–

[a]These values are for $x=1.5$ to $x=1.85$.

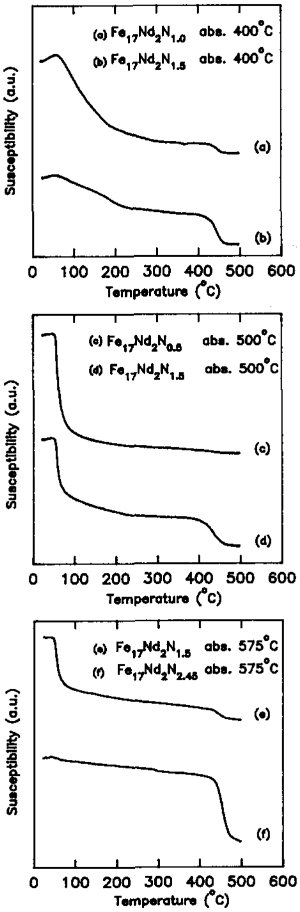

Fig. 1. TMA signals for the $Fe_{17}Nd_2$ compound for different nitrogen absorption temperatures.

milling period, the sample was run in the TMA apparatus. Figure 2 shows the resulting curves. An accentuated broadening of the transition of the pure 17:2 phase is observed until the signal disappears, when the sample is totally amorphous as revealed by X-ray diffraction. This clearly shows that the observed broadening in the TMA signals from the nitrided powders is due to the state of stress established by the precipitation of the saturated phase in the pure phase.

The observed diffusion pattern at 400 °C, described in detail in ref. 6, presents the following features. The diffusion proceeds preferentially through extended defects such as phase and grain boundaries, dislocations and dislocation arrays. The expected shell–core model for the diffusion pattern is not observed. The bulk diffusion coefficient is very small compared with the short circuit diffusion coefficients, so that diffusion only takes place through these easy pathways. Thus particles crossed by layers of nitrided regions are observed, where it is apparent that the nitrogen diffuses into the particle along one such path and then bulk diffusion occurs perpendicularly to this path inside the particle. The results of this mechanism can be seen in Fig. 3. It is also observed that the nitrided regions present different colours, suggesting that they are not homogeneous, possibly due to an extended solid solution in the nitrided phase. Another feature is the appearance of striae in the more nitrogen-rich samples. Our interpretation is that the striae correspond to paths of fast diffusion, which are differentiated from the bulk of the nitrided region due to a greater nitrogen content. For the saturated sample, the particles are not totally made up of the nitrided phase.

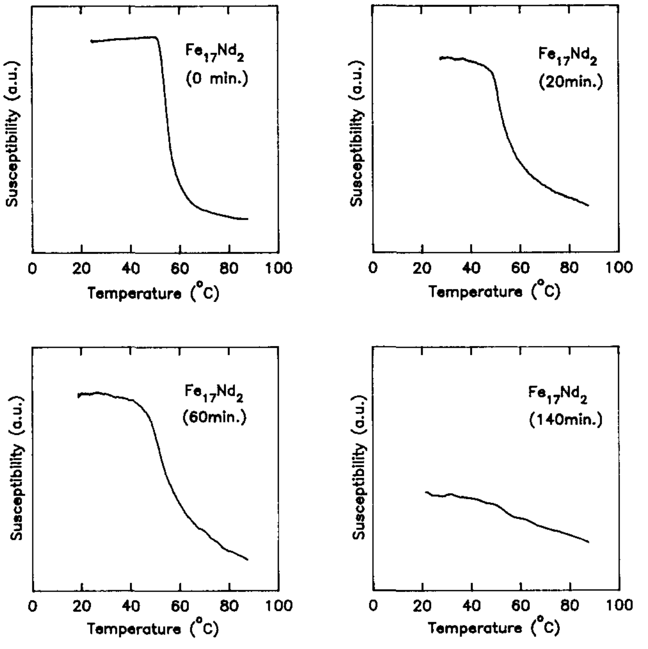

Fig. 2. TMA signals for the $Fe_{17}Nd_2$ compound for different milling times in a planetary ball mill under *n*-heptane.

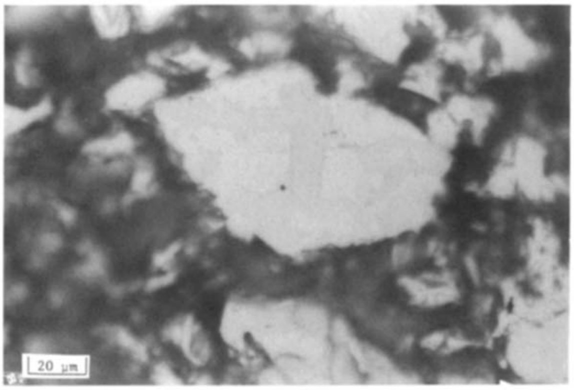

Fig. 3. Micrograph of the $Fe_{17}Nd_2N_{1.5}$ sample (nitrogen absorption temperature of 400 °C).

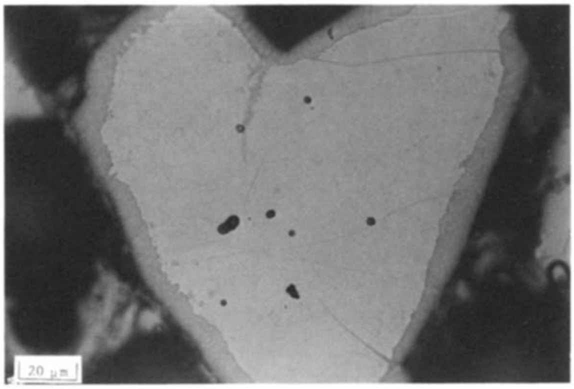

Fig. 4. Micrograph of the $Fe_{17}Nd_2N_{1.0}$ sample (nitrogen absorption temperature of 500 °C).

The observed diffusion patterns at 500 °C present some distinguishing features from the 400 °C patterns. The bulk diffusion coefficient becomes large enough so that bulk diffusion can compete with the diffusion mechanism along the extended defects. Figure 4, where $x = 1.0$, shows this clearly. The formation of a substantial nitrided layer is observed at the surface of the particles, and fast diffusion occurs along grain boundaries. This is observed for all nitrogen concentrations at this temperature. Three other features are observed in this series of samples. The first is that, at large nitrogen concentrations, black precipitates appear (probably NdN) along the grain boundaries (Figs. 5 and 6). The second feature involves the appearance of a second nitrided layer at the exterior of the particles for large nitrogen concentrations (Figs. 5 and 6). This layer exhibits a slightly darker colour than the interior region, and at 500 °C no precipitates are observed at the boundary with the inner region. We believe that this feature corresponds to a different nitriding stage. Experiments are under way to determine if this hypothesis is correct. The nitrided regions at 500 °C again exhibit

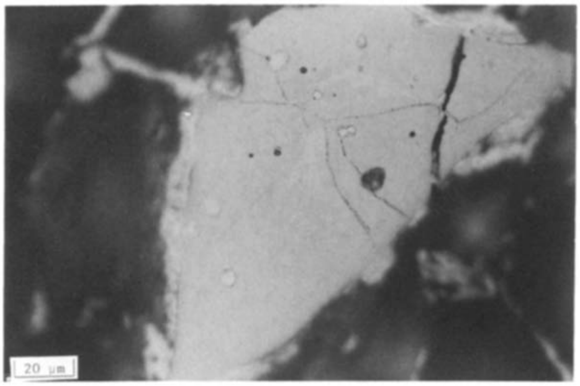

Fig. 5. Micrograph of the $Fe_{17}Nd_2N_{2.0}$ sample (nitrogen absorption temperature of 500 °C).

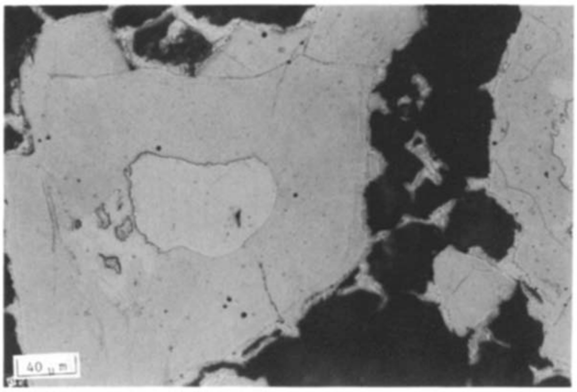

Fig. 6. Micrograph of the $Fe_{17}Nd_2N_{2.0}$ sample (nitrogen absorption temperature of 500 °C) showing a partially nitrided particle.

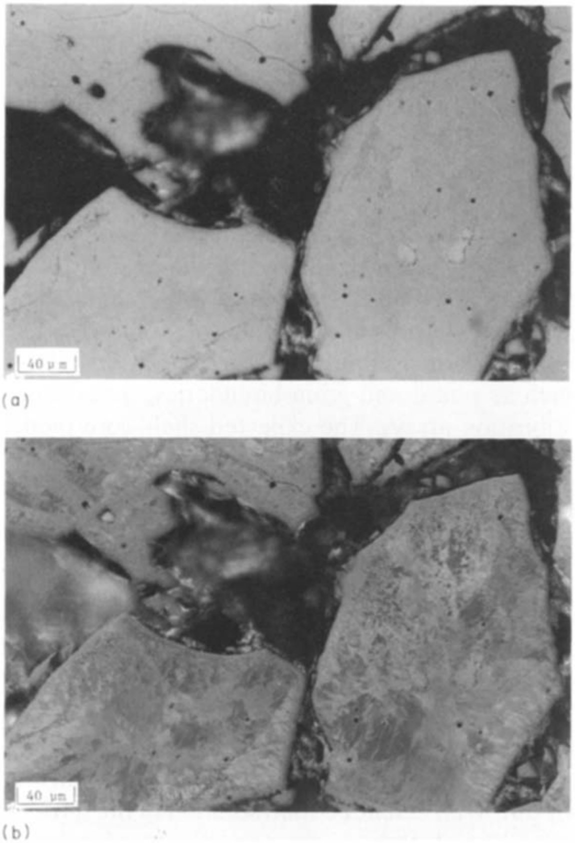

Fig. 7. Micrograph of the $Fe_{17}Nd_2N_{2.3}$ sample (nitrogen absorption temperature of 500 °C): (a) normal illumination ; (b) polarized light illumination.

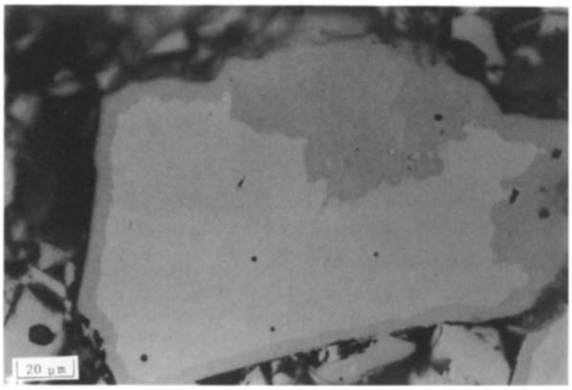

Fig. 8. Micrograph of the $Fe_{17}Nd_2N_{0.5}$ sample (nitrogen absorption temperature 575 °C).

different colours, implying the existence of a range of solid solutions in the nitrided phase. The third feature is that the nitrided particles show larger optical activities (observed when the particles are examined under polarized light in the optical microscope, Figs. 7(a) and 7(b)). Some regions of the particle show large changes in the colour of the polarized light. This is not only indicative of nitrogen concentration differences, but also differences in optical activity since the regions change colour on rotation of the microscope stage. It seems that nitrogen uptake introduces, at this temperature, greater anisotropy, leading to enhanced optical activity of the nitrided phase. It is also observed that, for the saturated sample, the particles are uniformly nitrided, in contrast with the 400 °C case.

The diffusion patterns observed for the 575 °C samples are similar to those described for the 500 °C case. The bulk diffusion coefficient is greater and diffusion proceeds more rapidly. The two diffusion mechanisms operate simultaneously, with the bulk diffusion being an important part of the pattern. Figure 8 shows a particle for the $x=0.5$ sample. The formation of the shell–core structure and fast diffusion along striae are observed. The nitriding of the particles is not uniform, with totally nitrided particles adjacent to partially nitrided particles, as shown in Fig. 9 for $x=1.0$. Two diffusion fronts and the abundant precipitation of NdN along and near grain boundaries (Fig. 10) are also observed. The frontier of the two diffusion fronts is also a locus for NdN precipitates. As for the 500 °C case, the saturated sample is uniformly nitrided.

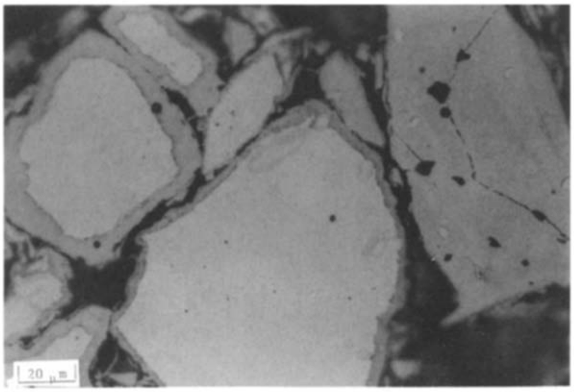

Fig. 9. Micrograph of the $Fe_{17}Nd_2N_{1.0}$ sample (nitrogen absorption temperature of 575 °C).

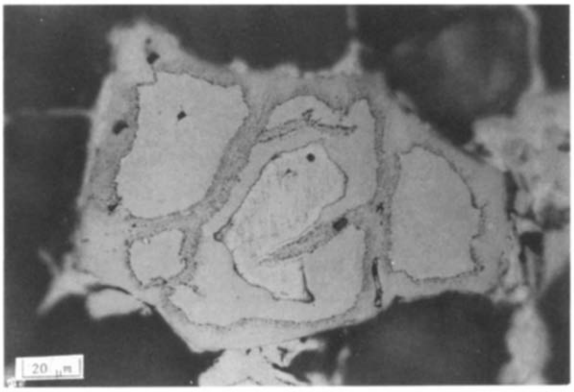

Fig. 10. Micrograph of the $Fe_{17}Nd_2N_{1.5}$ sample (nitrogen absorption temperature of 575 °C).

4. Conclusions

The following conclusions can be drawn from this study.

(1) Broadening of the magnetic transitions observed in the TMA signals most probably originates from the state of stress established in the particles due to the coexistence of the pure and nitrided phases, since the latter has a specific volume 6%–7% greater than the former [1].

(2) The bulk diffusion coefficient at 500 and 575 °C is large enough to promote bulk diffusion, which competes with the faster diffusion mechanism along extended defects, so that for these temperatures the shell–core diffusion structure is observed.

(3) For the 500 °C samples, the diffusion pattern for large x shows the appearance of NdN precipitates along grain boundaries. This also happens at 575 °C, but the precipitates extend to the neighbourhood of the grain boundaries.

(4) For the 500 °C samples at large x, there is a second diffusion front, presenting a different colour from the nitrided region in the interior of the particle. This is also observed for the 575 °C samples, but the frontier of the two regions also presents NdN precipitates.

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