

# Phase characterization of $\text{Fe}_{17}\text{Nd}_2\text{N}_x$ samples with different nitrogen contents

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## Abstract

Samples of  $\text{Fe}_{17}\text{Nd}_2\text{N}_x$  have been prepared for  $x=0.0, 0.5, 1.0, 1.5, 2.0$  and  $2.1$  nitrogen atoms per formula unit, at  $400^\circ\text{C}$ . They were analysed by metallography, thermomagnetic analysis, electron microprobe and X-ray diffraction. The measurements showed that all the samples contained the phase  $\text{Fe}_{17}\text{Nd}_2$ , free of nitrogen, together with the  $\text{Fe}_{17}\text{Nd}_2\text{N}_{2.3}$  saturated phase.

## 1. Introduction

Since the pioneering work of Coey and Sun [1] on the nitridation of the  $\text{Fe}_{17}\text{R}_2$  phases, several articles have been published on the production and characterization of these new phases, and on their magnetic properties [2–5]. In the case of samarium, several studies indicate that this phase is a promising material for the preparation of good permanent magnets [2, 5]. Not much is found in the literature about the nitridation process itself. The usual procedure normally yields the powdered saturated phase that is difficult to analyse. In attempts to obtain nitrided samples of several 17:2 phases, we became interested in the nitridation process, and this work presents our first results from this line of research.

## 2. Experimental procedure

We report here the results for the neodymium case. Samples were taken from a master alloy with 17:2 stoichiometry, prepared from starting materials of at least 99.9% purity, and melted in an arc furnace under argon atmosphere. This master alloy was wrapped in tantalum foil, encapsulated in an argon-filled quartz ampoule and heat treated at  $1100^\circ\text{C}$  for 10 days. After that, pieces of the master alloy were crushed in an iron mortar and milled in a planetary ball mill. The

resulting powder was sieved, and for the nitridation experiments only the powder below  $75\ \mu\text{m}$  was used.

The nitridation of the powder was carried out in a Sieverts apparatus. The reactor was heated to  $400^\circ\text{C}$ , with a type K thermocouple measuring the temperature of the sample inside the reactor. The temperature was controlled to  $\pm 4^\circ\text{C}$ . We used high purity nitrogen with initial pressures such that, after the absorption of the gas by the sample, the resulting concentrations were 0.5, 1.0, 1.5, 2.0 and 2.1 nitrogen atoms per formula unit. The Sieverts apparatus allows concentration measurements with accuracy of 1% or better.

The samples were characterized by optical metallography, scanning electron microscopy (SEM) and electron microprobe measurements of chemical composition, thermomagnetic analysis (TMA) and X-ray powder diffraction. TMA measurements were performed inductively with a low applied field (about 2 Oe) at 5 kHz. X-ray diffractograms were obtained with a Philips PW 1140 diffractometer system, using vanadium-filtered  $\text{Cr K}\alpha$  radiation ( $\lambda = 2.291\ \text{\AA}$ ) generated at 40 kV and 25 mA.

## 3. Results and discussion

The metallographic examination of the powders showed that the powder grains contained two phases, one light yellow corresponding to the  $\text{Fe}_{17}\text{Nd}_2$  phase without nitrogen, and a light grey phase corresponding to the saturated  $\text{Fe}_{17}\text{Nd}_2\text{N}_{2.3}$ . They contain also a white phase corresponding to pure iron, remaining from the peritectic formation of the  $\text{Fe}_{17}\text{Nd}_2$  phase (Fig. 1). This analysis is semiquantitatively confirmed by the SEM

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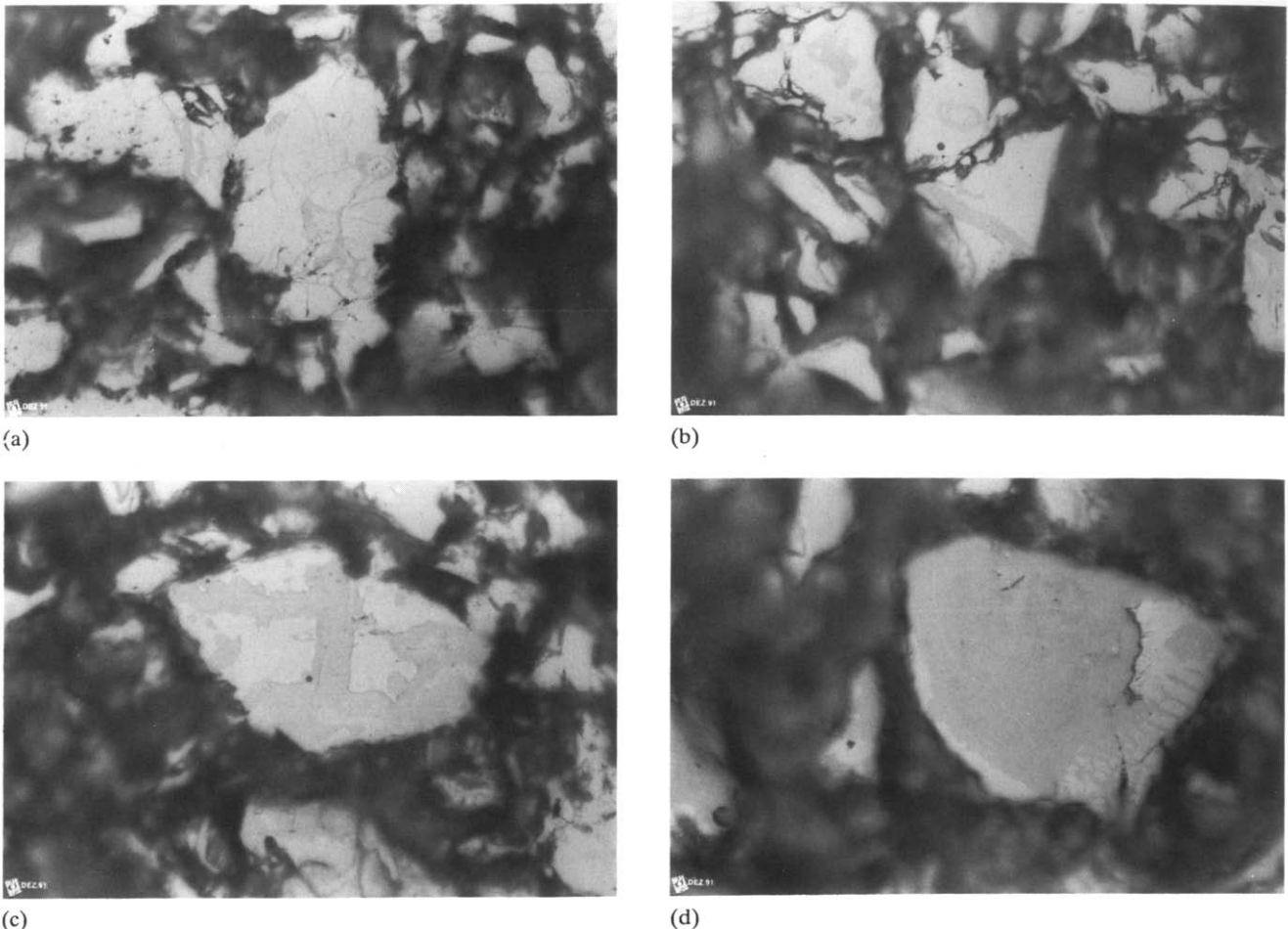


Fig. 1. Optical micrographs of  $Fe_{17}Nd_2$  samples heat treated at 1100 °C with different nitrogen contents: (a)  $Fe_{17}Nd_2N_{0.5}$ ; (b)  $Fe_{17}Nd_2N_{1.0}$ ; (c)  $Fe_{17}Nd_2N_{1.5}$ ; (d)  $Fe_{17}Nd_2N_{2.1}$ . (a), (b), (c) 1 cm = 20  $\mu\text{m}$ , (d) 1 cm = 13  $\mu\text{m}$ .

analysis and electron microprobe measurements. For the low nitrogen content samples, the grains in general contain a small amount of the grey phase (Fig. 1(a)), although it can be observed that rare grains can be heavily nitrated. As the nitrogen concentration increases, the grains become more heavily nitrated, but still display the two-phase feature (Figs. 1(b) and 1(c)). Even for the fully nitrated sample, with  $x=2.1$ , most grains reveal the presence of the pure  $Fe_{17}Nd_2$  phase (Fig. 1(d)). The expression “fully nitrated” means, under the conditions of the experiment, that the sample has absorbed the maximum amount of nitrogen. We think that this maximum nitrogen amount is not the same as that determined at higher temperatures (2.3 nitrogen atoms per formula unit [1, 2]), because in our samples the pure phase is surrounded by the nitrated phase (Fig. 1(d)). Furthermore, as described below, the TMA signal is always the same for the nitrated phase, and coincides with the reported  $T_c$  for the  $Fe_{17}Nd_2N_{2.3}$  phase.

The samples were also thermomagnetically analysed. The thermograms exhibit two signals, one at 54 °C and the other at 460 °C, corresponding to the presence of the two phases (Fig. 2). It was observed, as well, that, as the nitrogen concentration increases, the signal corresponding to the pure phase decreases, while that corresponding to the saturated phase increases (Fig. 2). These features are fully consistent with the metallographic and SEM observations. It was observed also that, as the nitrogen concentration increases, the signal corresponding to the pure phase broadens. At first sight, and considering only the TMA signal, one is led to interpret this as a continuously varying Curie temperature as a result of different nitrogen contents. This interpretation is inconsistent with the metallographic and SEM observations and with the fact that the TMA signal always presents a well-defined signal corresponding to the saturated phase at 460 °C. We have indications that this broadening is caused by the stresses and strains induced in the pure phase by the volume dilatation corresponding to the nitrogen up-

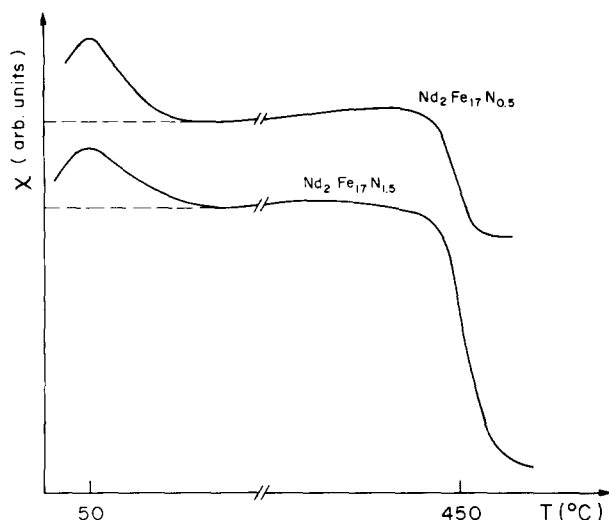


Fig. 2. Thermomagnetic signal of nitrated  $Fe_{17}Nd_2$  samples. The peak around  $50^\circ C$  corresponds to the pure  $Fe_{17}Nd_2$  and the step-like transition around  $450^\circ C$  corresponds to the fully nitrated  $Fe_{17}Nd_2N_{2.3}$  phase.

take or by the fact that under high nitrogen charges a dilution of the pure phase occurs. This kind of experiment is being finished and results will be published elsewhere.

The samples were also analysed by X-rays using  $Cr K\alpha$  radiation. A first run was carried out at a  $2^\circ \text{ min}^{-1}$  for all the samples, and the resulting diffractograms are depicted in Fig. 3. It is clear that for the pure and the saturated 17:2 phases the diffraction peaks are sharp and well defined, while for the intermediate nitrogen concentrations the lines are broad and not so well defined. In all the diffractograms we observe the presence of pure iron, in agreement with the metallographic and SEM analyses. If one interprets the broad lines corresponding to the intermediate nitrogen concentrations as belonging to one single phase, then it is easy to conclude that there is a continuous variation in the interplanar distances, or, which amounts to the same thing, a continuous variation in the lattice parameters. Of course, this is in contradiction to the former metallographic, SEM and TMA observations. For this reason, we decided to have a closer look at the intermediate diffraction patterns. We changed the collimating slit of the goniometer to 0.5 mm in order to obtain sharper lines, and ran the samples at a  $2\theta$  scanning rate of  $0.25^\circ \text{ min}^{-1}$ , concentrating on the region of the most intense reflections, the 220 and 303 reflections. Figure 4 shows the resulting diffraction scans for the  $x=0.5$  and  $x=1.0$  samples. It is clear from this figure that the resulting patterns can be interpreted as the superposition of the lines from the pure and the saturated phases. In particular, it should be noted that, as the sample goes from  $x=0.5$  to  $x=1.0$ , there is a significant change in

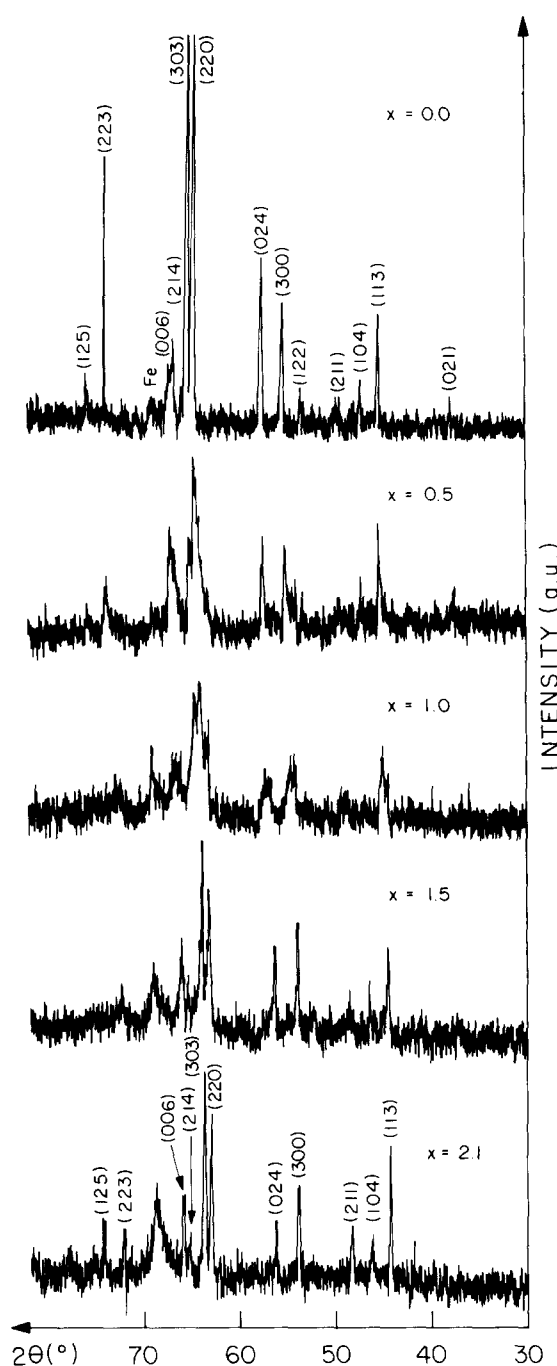


Fig. 3. X-ray diffractograms for the nitrated  $Fe_{17}Nd_2$  samples ( $Cr K\alpha$  radiation;  $2\theta$  scanning rate,  $2^\circ \text{ min}^{-1}$ ).

the relative intensities of the two sets of peaks, corresponding to the change in the relative amounts of the two phases present in the samples, as revealed by the other analytical techniques.

It is clear then that the analyses from the different techniques are in good agreement. Thus the nitridation process occurs by the precipitation of the saturated phase from the pure phase, without the formation of a solid solution, as could be inferred from a superficial analysis of the TMA and X-ray results.

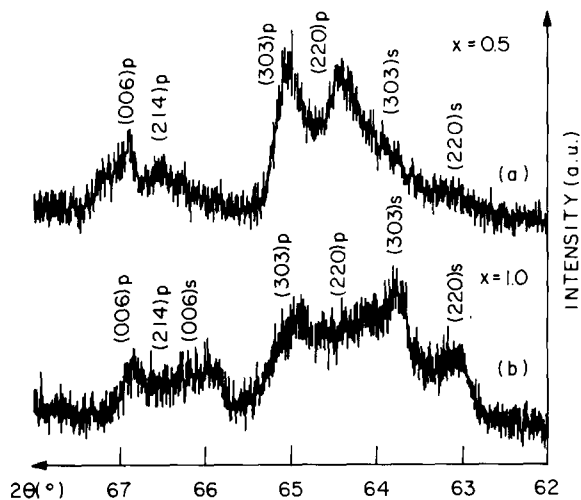


Fig. 4. X-ray diffractograms for the  $x=0.5$  and  $x=1.0$   $Fe_{17}Nd_2N_x$  samples (Cr  $K\alpha$  radiation;  $2\theta$  scanning rate,  $0.25^\circ \text{ min}^{-1}$ ).

#### 4. Conclusions

(1) Metallographic and SEM analyses reveal the presence of two phases, for all the studied nitrogen concentrations.

(2) TMA also indicates two phases, but a broadening of the first transition. This broadening can be caused by stresses or by dilution. The TMA signal for the nitrated phase presents little or no broadening, and the transition temperature coincides with the value reported for the  $Fe_{17}Nd_2N_{2.3}$  phase.

(3) X-ray diffraction, at a closer inspection, also supports the two-phase view.

(4) All together, the nitridation process occurs by precipitation of a saturated phase from a pure phase, without formation of a solid solution.

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