Journal of Alloys and Compounds 253–254 (1997) 140–143

The hydrogenation–disproportionation–desorption–recombination process of $Nd_2Fe_{14}B$ studied by in-situ neutron diffraction and thermomagnetic measurements

S. Liesert*, D. Fruchart, P de Rango, J.L. Soubeyroux

Laboratoire de Cristallographie du CNRS, associé à l'Université J. Fourier, 166X, 38042 Grenoble France

Abstract

The hydrogenation–disproportionation–desorption–recombination behaviour of Nd–Fe–B alloys has been studied by in-situ powder neutron diffraction and thermomagnetic measurements performed under hydrogen gas. Decomposition temperatures have been determined in order to obtain partial or complete reactions. Intermediate phases have been observed. The recombination process is complete if performed at 860°C for 20 min. The rate of iron present after recombination is temperature dependent.

Keywords: HDDR; Neutron diffraction; Nd–Fe–B

1. Introduction

The hydrogenation–disproportionation–desorption–recombination (HDDR) process is a new route for the production of coercive Nd–Fe–B powder for bonded magnet applications [1,2]. Many investigations using microstructural analysis [3–6] and in-situ measurements [7,8] were carried out to explain the mechanisms involved in this process. According to McGuiness et al. [3] and Takeshita and Nakayama [9], the $Nd_2Fe_{14}B$ phase disproportionates after a heating treatment above 600°C under one bar hydrogen pressure, following the reaction (1):

$$Nd_2Fe_{14}B + (2 \pm x)H_2 \rightarrow 2NdH_{2\pm x} + \alpha - Fe + Fe_2B \qquad (1)$$

Subsequent vacuum heat treatment removes hydrogen from the sample and simultaneously causes a recombination reaction (2) to form the $Nd_2Fe_{14}B$ compound:

$$2NdH_{2\pm x} + \alpha - Fe + Fe_2B \rightarrow Nd_2Fe_{14}B + (2 \pm x)H_2 \qquad (2)$$

The recombination process leads to the formation of very fine grains of $Nd_2Fe_{14}B$. The size of these grains is comparable with the critical size for single domain particles of $Nd_2Fe_{14}B$, which explains the high coercivity of the powder. The present investigation was undertaken in order to study the different compounds involved during the HDDR operations, by means of thermomagnetic measurements and in-situ neutron diffraction experiments, in order to get a better understanding of the Nd–Fe–B powders HDDR processes.

2. Experimental details

The compound of chemical composition $Nd_{32}Dy_{1.5}Fe_{65}Nb_{0.5}B_1$ was prepared by induction melting under argon atmosphere and pulverised into a fine powder by combination of hydrogen decrepitation and jet milling.

The magnetic measurements were done using a home made thermomagnetic balance allowing the magnetic characteristics of a sample to be recorded under gas reaction. The sample is placed in an autoclave under a constant gas flow and a temperature range from 25°C to 700°C. The magnetic interaction between the compound and a permanent magnet attached to the torque was weighed and then plotted versus temperature or time.

The in-situ neutron diffraction experiments were performed using the D1B diffractometer of the Institut Laue Langevin in Grenoble, France. The sample was placed in a quartz tube connected to a pressure controlled gas line during the HDDR process (gas pressure 70 kPa, secondary vacuum, temperature range 25–1000°C). A multicounter allows diffraction diagrams to be recorded during the

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*Corresponding author.

0925-8388/97/$17.00
PII S0925-8388(96)02975-1

reaction every 5 min on a 80° angular range. Data reduction was done using the cyclic Fullprof program [10].

3. Results and discussion

3.1. Investigation of the disproportionation of the $Nd_2Fe_{14}B$ phase by hydrogen

3.1.1. Thermomagnetic measurements

The magnetisation of a $Nd_2Fe_{14}B$ powder has been measured during a disproportionation reaction (Fig. 1). The sample was exposed to flowing hydrogen at constant pressure (100 kPa) and the temperature was monitored up to 630°C. During the heating (5 C° min^{-1}), a first increase in the magnetisation can be observed between 110°C and 190°C (step 1 to 2), due to the hydrogen absorption and the $Nd_2Fe_{14}BH_x$ formation. The Curie temperature of the $Nd_2Fe_{14}BH_x$ phase is seen clearly at 340°C (step 3). Above 600°C, the increase in the magnetisation corresponds to the formation of α-Fe during the decomposition of the $Nd_2Fe_{14}B$ phase. This disproportionation takes place mainly during the plateau temperature (Tp = 630°C) (step 4) fixed at one hour in our experiment. A complete disproportionation is achieved when the duration at Tp is long enough. However, if the sample is cooled before the end of this process, the resulting sample is a mixture of disproportionated and non-disproportionated particles. Moreover, an increase in the magnetisation corresponding to the Curie temperature of the $Nd_2Fe_{14}B$ hydrogenated phase can again be observed in that last case during cooling (step 5).

Many records have been performed at different temperatures in order to evaluate the rate of disproportionation. A quantitative information on this rate can be obtained by comparing the drops of magnetisation at the Curie temperature before (step 3, height b) and after (step 5, height a) the disproportionation reaction, calculated with the formula $\frac{b-a}{b}$ and plotted versus the plateau temperature (Fig. 2). A complete decomposition was obtained after one hour at Tp = 665°C.

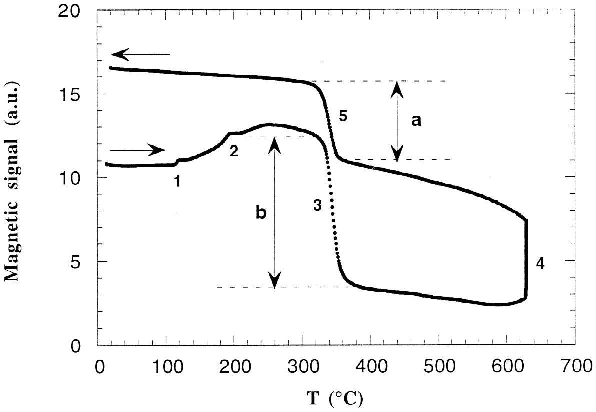

Fig. 1. Thermomagnetic measurement performed under a 100 kPa hydrogen gas flow: (1, 2) hydrogen absorption and hydride formation; (3) Curie temperature of the $Nd_2Fe_{14}B$ phase before the decomposition reaction; (4) hold temperature of 720°C for 1 h; (5) Curie temperature of the $Nd_2Fe_{14}B$ phase after the decomposition reaction.

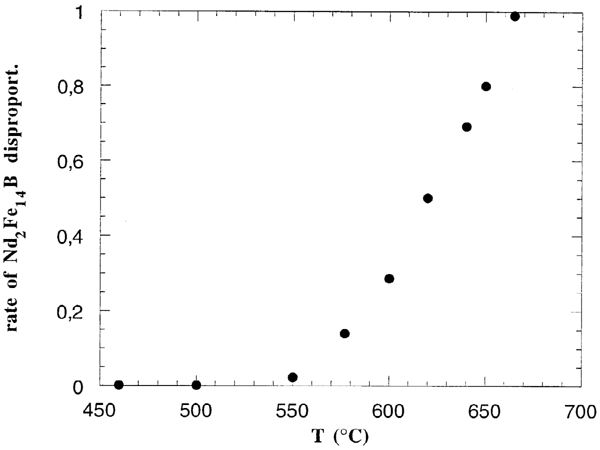

Fig. 2. Decomposition rate of $Nd_2Fe_{14}B$ measured from the thermomagnetic experiments with one hour hold time at different temperatures.

3.1.2. Neutron diffraction analysis

The decomposition of the sample by hydrogen under a pressure of 70 kPa was followed at 720°C, 680°C and 660°C. Fig. 3 shows the diffraction angle (2Θ) plotted versus the neutron counts intensity and the time of the in-situ neutron diffraction experiment at 720°C with a hold time of one hour. In the first diagram at $t = 0$ the reflection peaks correspond to the $Nd_2Fe_{14}B$ alloy only. The cell

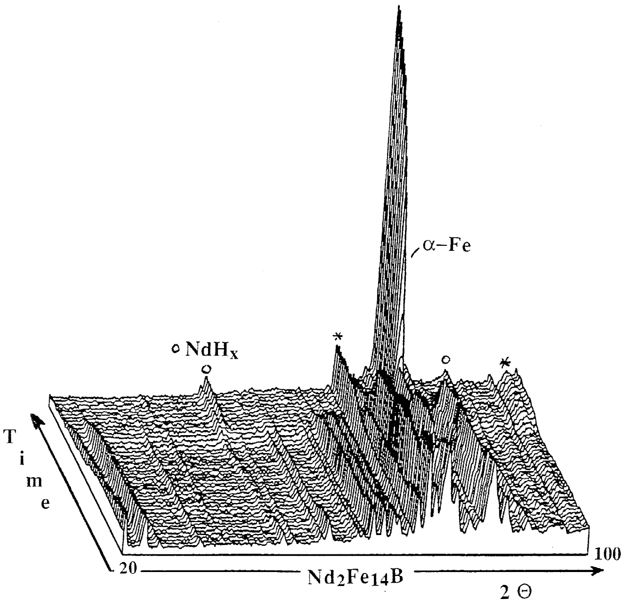

Fig. 3. Thermodiffractogram recorded at 2.52 Å by powder neutron diffraction, hydrogenation and decomposition processes performed under a 70 kPa hydrogen gas pressure (extra lines from the furnace are marked with *).

parameters determined are $a=8.823(2)$ Å and $c=12.215(3)$ Å. With increasing temperature, starting at $T=580$°C, the $Nd_2Fe_{14}B$ phase disappears and the reflection peaks of the α-Fe phase become visible. At the end of the hold temperature at 720°C, only α-Fe and $NdH_{(2\pm x)}$ phases are observed by diffraction. The decomposition of $Nd_2Fe_{14}B$ seems to be achieved. No boron containing phases have been detected, in particular the Fe_2B phase proposed in Eq. (1). The cell parameters of the $Nd_2Fe_{14}BH_x$ and α-Fe phases have been determined during heating and at the hold temperature. A cell parameter increase of the $Nd_2Fe_{14}B$ phase in the a and c directions, starting at 180°C, is observed [Fig. 4(a and b)], corresponding to the formation of the $Nd_2Fe_{14}BH_x$ phase. The maximum increase of the cell parameters is achieved at 210°C with $a=8.844(2)$ Å and $c=12.274(3)$ Å. By continuation of the heating (up to 350°C), we observe a decrease of the a and c parameters corresponding to a release of hydrogen by the hydride. Above 350°C, the a and c parameters increase again as a result of thermal expansion. This behaviour was only followed up to 720°C where the $Nd_2Fe_{14}B$ phase disappears.

In Fig. 5 we have drawn the scale factors (SF) of each phase, determined from the structure refinement. They are proportional to the amount of each phase present in the neutron diagram. The SF value for $Nd_2Fe_{14}B$ decreases at the beginning of the reaction with increasing temperature. During that period no α-Fe is detected by diffraction. It corresponds to the formation of the hydride. During the hold time at 720°C, the SF of $Nd_2Fe_{14}B$ decreases quickly. At the same time the diffraction peaks of α-Fe can be observed and increase simultaneously with the decreasing amount of $Nd_2Fe_{14}B$. We have performed several experiments at different decomposition temperatures. As expected, we have observed that the rate of decomposition increases as the temperature increases.

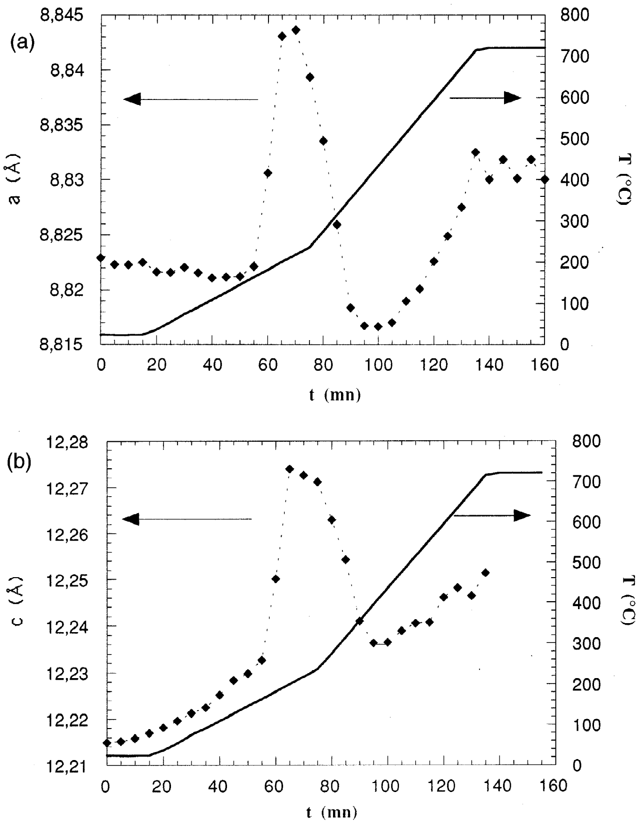

Fig. 4. Unit cell parameters of the $Nd_2Fe_{14}BH_x$ phase recorded between 25°C and 720°C during the hydrogenation and decomposition processes performed under a 70 kPa hydrogen gas pressure.

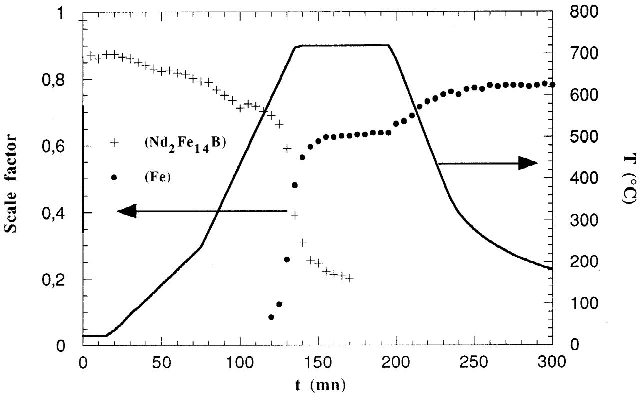

Fig. 5. Powder diffraction scale factors of the $Nd_2Fe_{14}BH_x$ and α-Fe phases measured during the hydrogenation and decomposition processes.

3.2. Investigation of the recombination of the $Nd_2Fe_{14}B$ phase under vacuum

Fig. 6 shows the diffraction diagrams of the in-situ neutron diffraction during the recombination at 860°C. During this reaction the cell parameters of the $Nd_2Fe_{14}B$ and α-Fe phases follow the thermal expansion without any anomaly. The cell parameters at the end of the reaction ($a=8.798(2)$ Å and $c=12.090(3)$ Å) are slightly smaller than the ones of the starting material (hydrogenated by the

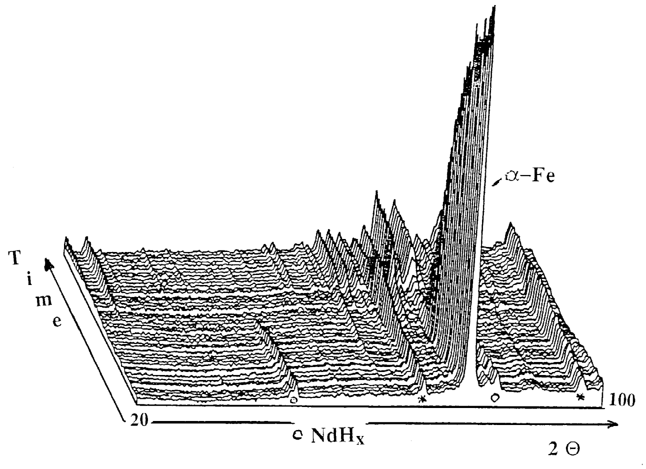

Fig. 6. Thermodiffractogram recorded at 2.52 Å by powder neutron diffraction, recombination process performed under vacuum.

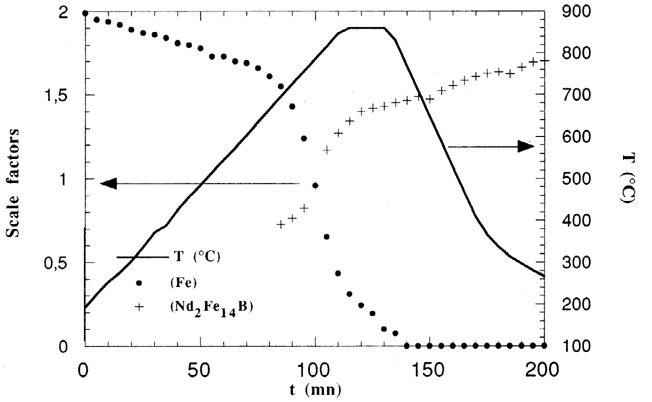

Fig. 7. Powder diffraction scale factors of the $Nd_2Fe_{14}BH_x$ and α-Fe phases measured during the recombination process performed under vacuum.

decrepitation process used to pulverise the initial ingot) and close to those of $Nd_2Fe_{14}B$ without hydrogen.

Fig. 7 reports the SF of the two phases as previously described. By increasing the temperature to 720°C the amount of α-Fe, as detected from the diffraction peaks, decreases rapidly. Before the hold temperature of 860°C is reached no diffraction peak of $Nd_2Fe_{14}B$ can be observed over short periods. This phenomena was only observed at high recombination temperatures (≥860°C) and after complete decomposition of the $Nd_2Fe_{14}B$ phase. Moreover we have performed several recombination processes at different temperatures (860°C, 810°C and 765°C). It was noticed that the kinetics of the recombination reaction, estimated from the disappearance of the α-Fe phase during reaction was the same for all three temperatures (Fig. 8).

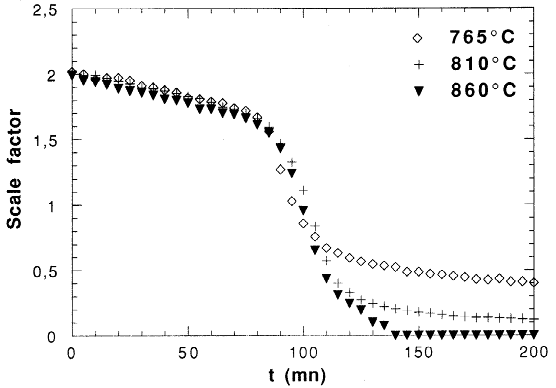

Fig. 8. Powder diffraction scale factors of the α-Fe phase measured during the recombination process performed under vacuum at various temperatures.

4. Conclusions

It has been observed by thermomagnetic measurements that it was possible to monitor the rate of disproportionation of the $Nd_2Fe_{14}B$ phase under hydrogen gas flow. For a one hour decomposition time, a suitable temperature for complete decomposition of the alloy is 670°C. From neutron diffraction experiments we have observed that the decomposition products are cubic α-Fe, and cubic NdH_x. As no boron compounds diffract, it seems that they should be amorphous or very finely divided in agreement with Ref. [5]. The $Nd_2Fe_{14}BH_x$ phase formed at low temperature releases the hydrogen prior to decomposition, so that it is certainly possible to decompose the alloy when introducing the hydrogen at a temperature higher than the hydride absorption temperature.

The recombination process at 860°C is complete after 20 min and does not show any α-Fe in the final product. Using recombination temperatures lower than 860°C, α-Fe had been detected in the final product. The amount of α-Fe left after reaction did not depend on the reaction time but only on temperature.

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