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HDDR process of Nd–Fe–B with an excess of intergranular Nd-rich phase under magnetic field

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Abstract

High coercive isotropic Nd–Fe–B powders can be obtained using the hydrogenation–disproportionation–desorption–recombination (HDDR) process. In order to produce anisotropic coercive powders, a static magnetic field of 7 T has been applied during the recombination stage, using an Nd–Fe–B alloy, with an excess of intergranular Nd/Cu eutectic. In parallel, the behaviour of the Nd/Cu eutectic has been studied by in-situ neutron diffraction experiments: under hydrogen, the Nd/Cu eutectic is solid in all temperature ranges, but under vacuum, hydrogen desorbs and the Nd/Cu becomes liquid. To induce a rotation of the magnetic $Nd_2Fe_{14}B$ crystallites, it is necessary to reach a pronounced desorption of hydrogen. Hence, we have been able to produce anisotropic Nd–Fe–B material under a magnetic field by increasing the holding time during the recombination stage of the HDDR process. © 1997 Elsevier Science S.A.

1. Introduction

Modern hard magnetic materials are based on rare earth (R)/transition metal (T) systems. The combination of these elements in alloys or in interstitial stabilised intermetallics (B,C,N...) allows the maximisation of intrinsic and extrinsic properties, such as:

- a high degree of magnetisation and a high Curie temperature due to a high T atom density; consequently a large induction is obtained from an anisotropic magnet;
- a high magneto-crystalline anisotropy from the contribution of the R crystal electric field; as a result, a large coercivity can be developed from an appropriate microstructure.

Nowadays, manufacturers are increasingly interested in the production of coercive and anisotropic $Nd_2Fe_{14}B$ powders for bonded magnets. In these powders, the coercive forces are directly related to the microstructure: to avoid the propagation of the wall domains, the size of the elementary crystallites and that of the free particles must be controlled as well as the composition and the repartition of the minor intergranular Nd-rich phases. Furthermore, if the grains are textured, i.e. with crystallites essentially oriented along a common direction, the inductive force of the resulting magnet is doubled.

Highly coercive powders are obtained by the Hydrogenation–Recombination–Disproportionation–Recombination (HDDR) route. This process, first reported by Takeshita et al. [1], consists in disproportionation of the starting alloy under a hydrogen atmosphere above 600°C, according to the reaction (1):

$$Nd_2Fe_{14}B + xH_2 \rightarrow 2NdH_x + \alpha\text{-}Fe + Fe_2B \qquad (1)$$

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followed by recombination to form an improved microstructure after desorption using vacuum heat treatment at around 850°C, according to the reaction (2):

$$2NdH_x + \alpha\text{-Fe} + Fe_2B \rightarrow Nd_2Fe_{14}B + xH_2 \quad (2)$$

Large coercive forces have been obtained thanks to the well controlled homogeneous microstructure developed after dehydrogenation and recombination. The powders are essentially isotropic, but an oriented growth of the elementary crystallites can be induced via epitaxy mechanisms due to elemental additives (Zr, Ga, Nb,...) [2]. Using in-situ thermomagnetic measurements, we have demonstrated that a similar mechanism can be achieved by a controlled but incomplete disproportionation reaction starting with textured precursor [3]. The non-disproportionate Nd–Fe–B fine grains act as nucleation centres during the recombination step.

The control of the texture by solidification in a magnetic field, successfully applied to the high T_c superconductor $YBa_2Cu_3O_7$ [4] and more recently to the Sm_2Co_{17}-type magnets [5], suggests evidence of new possibilities for the development of anisotropic magnetic powders. In the present study, we have performed the HDDR process under a static magnetic field to investigate the possibility of inducing anisotropic crystallisation of the $Nd_2Fe_{14}B$ nuclei during the recombination step.

2. Experimental

Three compositions have been studied: a composition of magnet manufacturer $Nd_{32}Dy_{1.5}Fe_{65}Nb_{0.5}B_1$, a composition corresponding to a large amount of intergranular eutectic (50 wt% $Nd_{32}Fe_{60.5}Co_{5.2}B_{1.3}$ in $Nd_{70}Cu_{30}$ eutectic) and a pure $Nd_{70}Cu_{30}$ eutectic. The starting alloys were prepared by induction melting under pure argon atmosphere.

The HDDR process has been performed in a dedicated furnace designed and developed to allow the application either of a high magnetic field (up to 8 T) or of a high field gradient. The temperature ranges from RT to 1200°C, gas pressure and vacuum level are strictly controlled by dedicated sensors. The cryogenic device, including a superconducting magnet, is described in de Rango et al. [4]. The successive heat treatments of the process are illustrated in Fig. 1. All the samples have been submitted to the same disproportionation treatment, i.e. 1-h plateau at 720°C under 70 kPa hydrogen pressure. A complete recombination is achieved when the t time spent at the temperature plateau T is long enough. Both these parameters have been varied throughout our study.

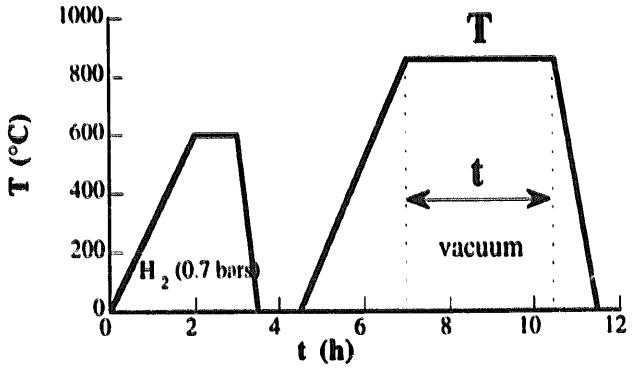

Fig. 1. Description of the HDDR process.

The in-situ neutron diffraction experiments were performed using the D1B diffractometer of the Institut Laue Langevin in Grenoble. The sample was placed in a stainless steel tube connected to a pressure controlled gas line (deuterium pressure 40 kPa, secondary vacuum, temperature range 25–1000°C). The multi-counter allows diffraction diagrams to be recorded during the reaction every 5 min on a 80° angular range.

The magnetic properties of the sample were measured at room temperature in a dc extraction type magnetometer.

The microstructural investigations were carried out by X-Ray fluorescence analysis using a Kevex EDX probe attached to a JEOL Scanning Electron Microscope.

3. Results and discussion

3.1. Preliminary results

A first series of experiments has been performed on

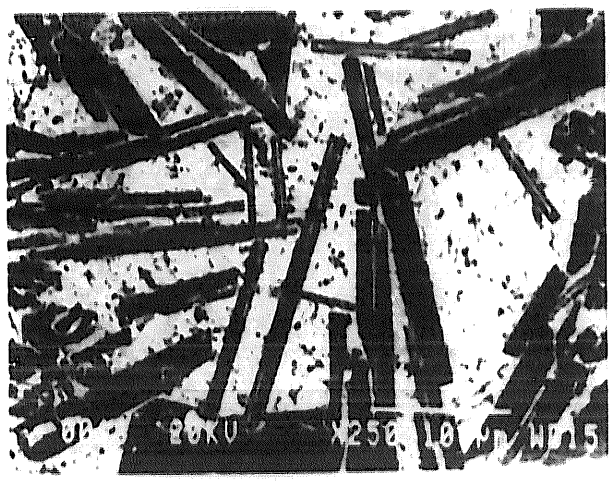

Fig. 2. Back-scattered electron image observed on a polished face of the starting alloy containing the Nd/Cu eutectic, at magnification of 250 ×. The platelets (in black) are dispersed in the Nd/Cu eutectic (in grey). Some pure neodymium metal is visible (in white) around the Nd/Cu eutectic.

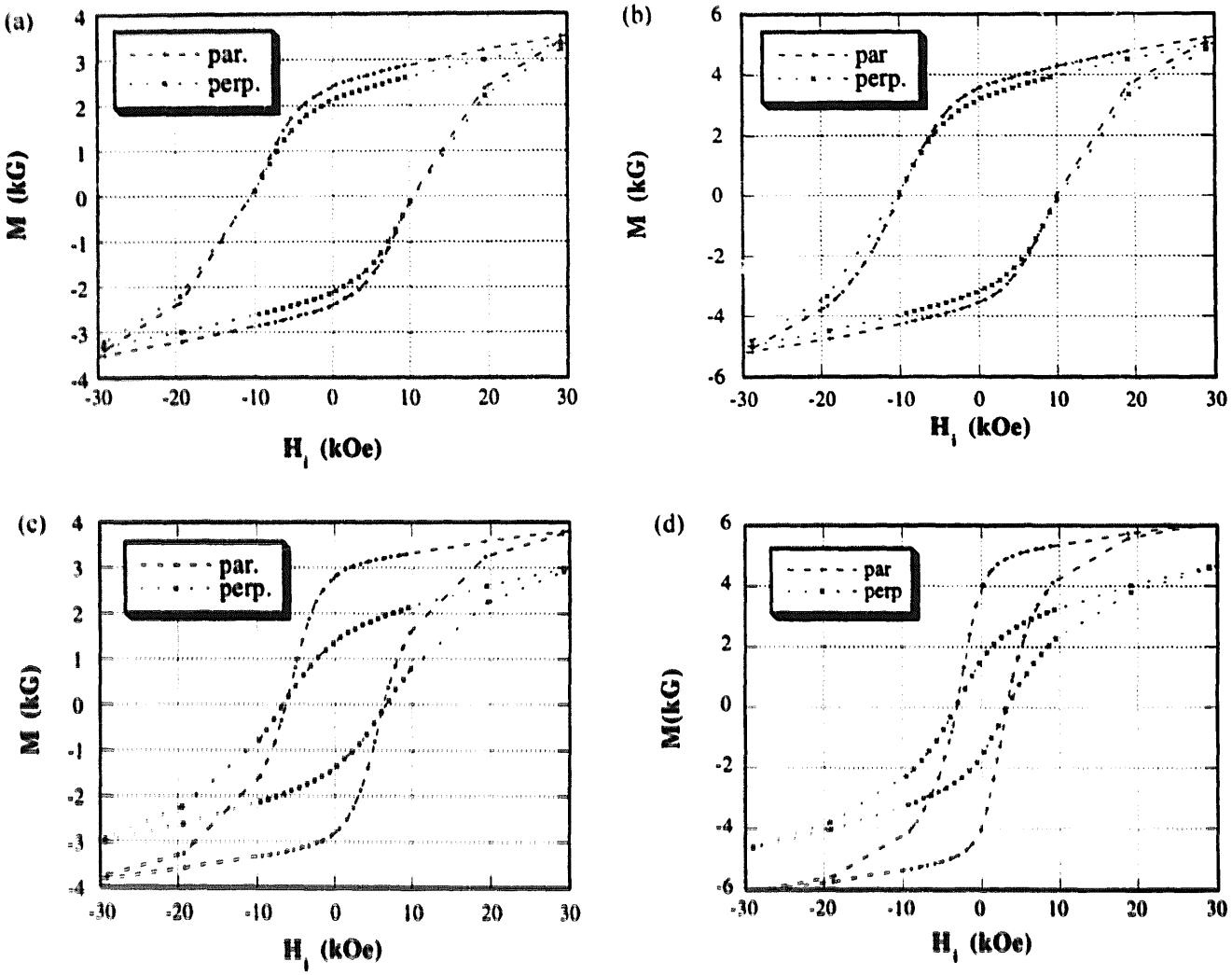

Fig. 3. Magnetisation cycles measured after applying the HDDR process under a magnetic field of 7 T on the alloys containing the Nd/Cu eutectic. The samples correspond to increasing recombination times at $T = 900°C$ (Fig. 3a = 1 h; Fig. 3b = 4 h; Fig. 3c = 6 h and Fig. 3d = 10 h). They are cut with a cubic shape and the measured magnetic field has been applied parallel to and perpendicularly to the direction of the magnetic field used during the HDDR process.

the 'magnet composition' ($Nd_{32}Dy_{1.5}Fe_{65}Nb_{0.5}B_1$). We have applied a static magnetic field or a field gradient during the previously optimised HDDR process ($T = 860°C$; $t = 20$ min for the recombination stage). No significant anisotropic growth was developed at such high temperature. It seems that in the paramagnetic state, the magneto-crystalline anisotropy is too weak to induce a directional ordering effect.

Nevertheless, it has been shown that the anisotropy of susceptibility of $Nd_2Fe_{14}B$ in the paramagnetic state persists along the c-axis direction and is large enough to allow orientation of $Nd_2Fe_{14}B$ single-crystal grains with the c-axis parallel to the applied field direction, for temperatures up to 1100°C [6]. This behaviour has been observed when $Nd_2Fe_{14}B$ crystallites are diluted in a Nd/Cu eutectic having a melting temperature (520°C) lower than that of the $Nd_2Fe_{14}B$ phase.

3.2. Application of the HDDR process with an excess of Nd / Cu eutectic

In order to induce both anisotropy and coercivity, we have again applied a magnetic field during the HDDR process using a Nd–Fe–B alloy with an excess of intergranular Nd/Cu eutectic (50% wt. Nd/Cu; 50% wt. $Nd_2Fe_{14}B$). The microstructure of the starting alloy consists in $Nd_2Fe_{14}B$ platelets of approximately 100 μm in length and 10 μm in width, randomly oriented in the Nd/Cu eutectic (Fig. 2). The minor phase which appears in white in the Nd/Cu eutectic is some pure neodymium.

Four samples have been HDDR-processed, applying systematically the treatment described in Fig. 1. The recombination temperature T has been fixed at 900°C and the time t has been varied ($t = 1$ h for sample A; $t = 4$ h for B; $t = 6$ h for C and $t = 10$ h for

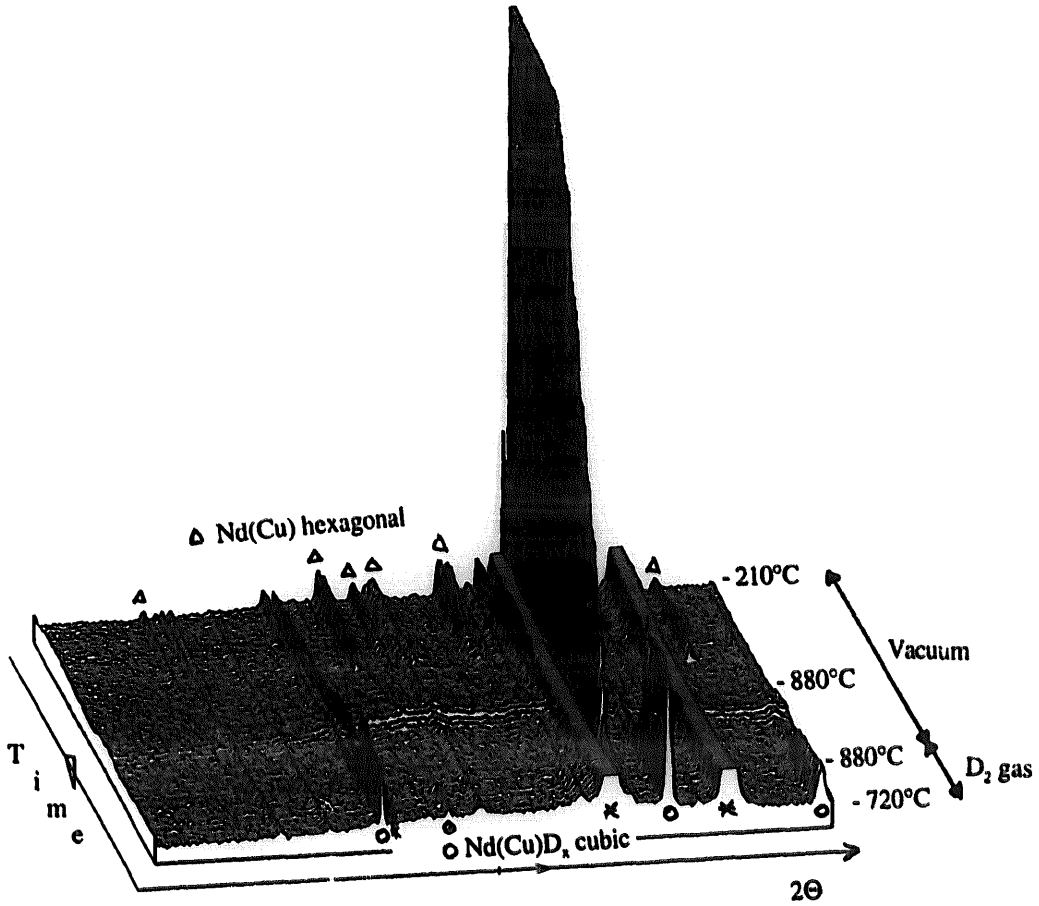

Fig. 4. Thermodiffractogram recorded at 2.52 Å by powder neutron diffraction. First, data are performed under a 40-kPa deuterium gas pressure, then under vacuum (extra lines from the sample holder are marked with an asterisk *).

D). A 7 T magnetic field has been applied all along the recombination step (from room temperature to the end of the process).

The evolution of the hydrogen desorption has been followed by recording the pressure. When the desorption is achieved the pressure quickly decreases to $10^{-3}/10^{-4}$ kPa. X-ray diffraction analysis performed just before and after the end of the desorption indicate that the end of the desorption coincides with the complete recombination of the $Nd_2Fe_{14}B$ phase. For a typical $Nd_2Fe_{14}B$ magnet composition, the recombination at 900°C is achieved after approx. 20 min.

Using an excess of Nd/Cu eutectic in the alloys, the hydrogen desorption at 900°C appears to be much longer: it is only achieved after 5 h. Nevertheless, magnetic measurements performed on samples A and B (partially desorbed) indicate a high coercivity H_c = 10 kOe (Figs. 3a,b). Magnetic properties of the $Nd_2Fe_{14}B$-hydride have been studied in detail [7]. No coercive forces can be developed as some hydrogen remains in the $Nd_2Fe_{14}B$ phase. These results suggest that only the Nd/Cu eutectic is hydrogenated in samples A and B.

On the contrary, a large magnetic anisotropy is obtained on samples C and D, for which a complete hydrogen desorption is achieved (Figs. 3c,d). In the ferromagnetic state, the $Nd_2Fe_{14}B$ compound is axial and the easy axis is c. As the enhancement of the inductive forces is obtained when applying the measured magnetic field parallel to the direction of the magnetic field applied during the recombination step of the HDDR process, the results are consistent with an orientation of the c-axis of the crystallites along the applied magnetic field. Nevertheless, if the coercivity remains high before the complete desorption of the Nd/Cu eutectic, it markedly decreases when the time spent at 900°C after the complete desorption increases (H_c = 7kOe for sample C and only 3 kOe for sample D).

The behaviour of the Nd/Cu eutectic under deuterium gas has been studied by in-situ neutron diffraction experiments (Fig. 4). These experiments revealed that, under hydrogen, the Nd/Cu intergranular phase is solid and forms a cubic Nd/Cu deuteride (up to 880°C), so that the rotation of the $Nd_2Fe_{14}B$ crystallites is avoided. Under vacuum, the deuteride outgas forms a liquid phase after approximately 1 h in those conditions. During the slow cooling, the composition of the eutectic varies with the rise of the lines of the copper metal. Under 700°C

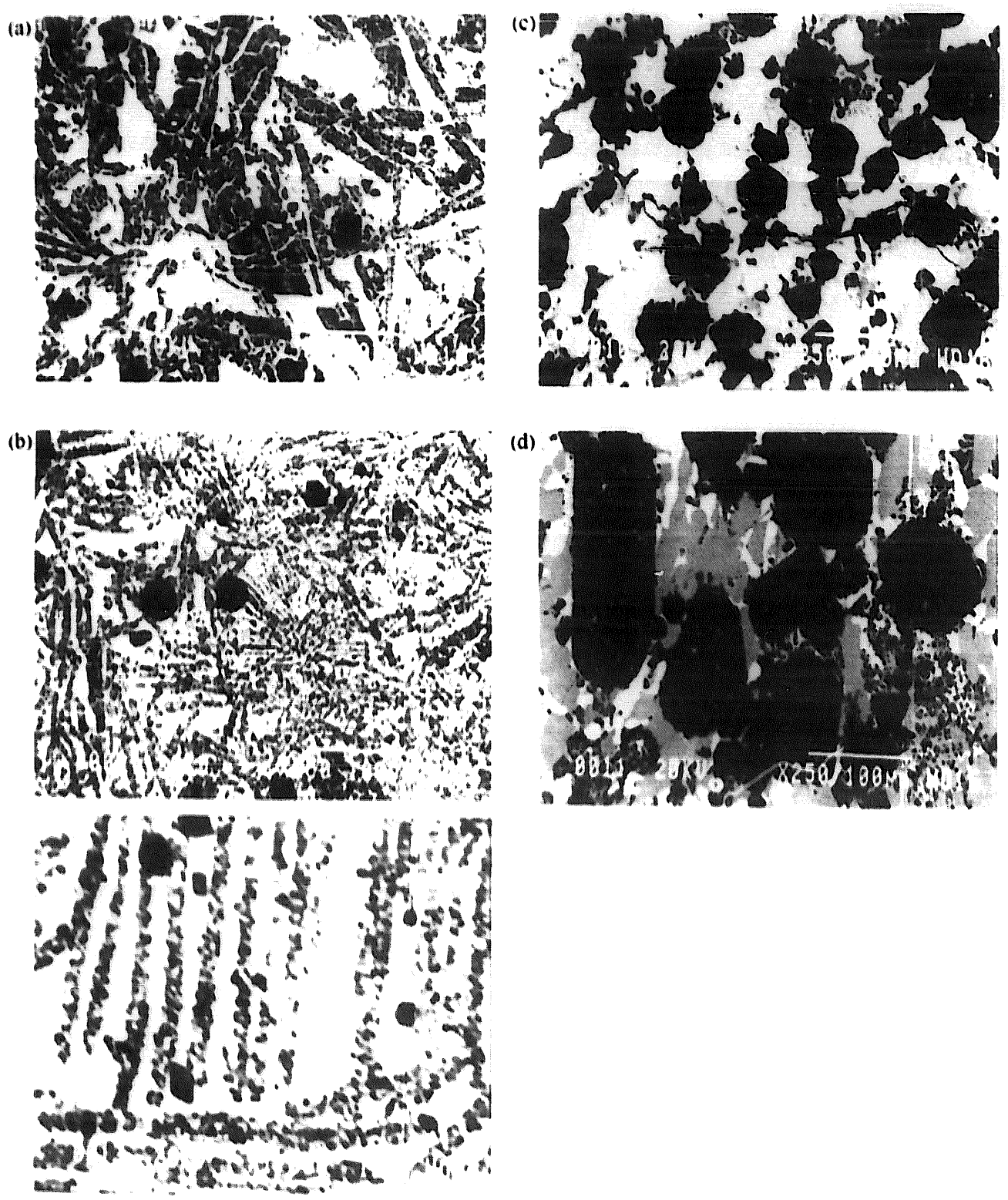

Fig. 5. Back-scattered electron images observed after applying the HDDR process under a magnetic field of 7 T on the alloys containing the Nd/Cu eutectic. The samples correspond to increasing recombination times at $T = 900°C$ (Fig. 5a = 1 h; Fig. 5b = 4 h; Fig. 5c = 6 h and Fig. 5d = 10 h). They are cut along the direction of the applied field (vertical on the micrographs). Magnification is 250 × except for the lower Fig. 5b which is 1000 ×.

the new eutectic composition solidifies and shows lines of an hexagonal phase, down to room temperature. To induce rotation of the magnetic $Nd_2Fe_{14}B$ crystallites in the presence of a liquid it is necessary to reach a pronounced desorption of hydrogen. Hence, we have been able to produce anisotropic Nd–Fe–B powders under magnetic field by increasing the holding time during the recombination reaction of the HDDR process.

The microstructure observed on samples A, B, C

and D are shown in Fig. 5a–d, respectively. Partially desorbed samples A and B present a very similar microstructure: the large $Nd_2Fe_{14}B$ platelets are converted into submicron grains and the Nd-rich phase has diffused into the disproportioned area, as expected for HDDR processed materials (lower Fig. 5b). Nevertheless, the print of the platelets present in the starting alloy is perfectly visible.

On the contrary, samples C and D present a typical microstructure of a large crystal growth of $Nd_2Fe_{14}B$ particles in a liquid eutectic, which is responsible for the decrease in coercive forces. One hour after the complete hydrogen desorption (sample C), the size of the $Nd_2Fe_{14}B$ crystallites is approximately 50 μm and the particles which are free to rotate in the liquid eutectic tend to align with each other in order to minimise the dipolar energy (the direction of the applied magnetic field corresponds to the up-down arrows on the micrographs). Five hours after the complete desorption (sample D), the growth of the $Nd_2Fe_{14}B$ crystallites has been enhanced and the platelets align their axes parallel to the magnetic field.

4. Conclusion

Both experiments performed for texturation of $Nd_2Fe_{14}B$ in a Nd/Cu eutectic and neutron diffraction study have revealed that under hydrogen gas, the Nd/Cu intergranular phase forms a solid material up to 900°C. To induce rotation of the $Nd_2Fe_{14}B$ crystallites during the recombination stage of the HDDR process, it is necessary to reach a pronounced desorption level of hydrogen. By increasing the holding time during the recombination stage of the HDDR process, we were able to produce anisotropic and coercive materials.

An excess of Nd/Cu eutectic has been introduced to ease the rotation of the crystallites in the liquid, but it is expected that the orientation of the recombined crystallites would be possible within a lower quantity of the intergranular phase.

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