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Magnetic anisotropy induced in $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$ by Hf additions

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Abstract

Remanence, coercivity and maximum energy product $(BH)_{\text{max}}$ of $\text{Nd}_{16}\text{Fe}_{76-x}\text{Hf}_x\text{B}_8$ ($x = 0, 0.1, 0.2$) magnets processed under different hydrogenation-disproportionation-desorption-recombination (HDDR) conditions, were studied. Vibrating sample magnetometry results showed that Hf-doped materials develop an important degree of anisotropy, especially for the case of solid-HDDR treatments at 800°C and 850°C, with the largest effect at 850°C. Maximum values of remanence and coercivity were observed for Hf-added samples S-HD at 850°C, and 900°C, respectively. The highest $(BH)_{\text{max}}$ value was also observed in S-HD 900°C Hf-added samples. These results are discussed in terms of the expected microstructure of the intermediate HD and final HDDR processed powders. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nd–Fe–B hard magnets; HDDR process; Magnetic anisotropy

Elements such as Hf and Zr have been reported to enhance the permanent magnet properties of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based alloys submitted to hydrogenation-disproportionation-desorption-recombination (HDDR) cycle [1,2].

Due to reported results [3,4], which reveal some effect of disproportionation temperature and the presence of additives on the development of anisotropy, we investigated the impact that small additions of Hf produce in powders and cold-pressed magnets of the ternary system under solid and conventional HDDR processing.

Ingot alloys with nominal composition $\text{Nd}_{16}\text{Fe}_{76-x}\text{Hf}_x\text{B}_8$ ($x = 0, 0.1, 0.2$) were homogenised for 67 h at 1050°C under vacuum and crushed into fine powder ($< 150 \mu\text{m}$), prior to the HDDR experiments.

Two types of HD experiments were made: S-HD (solid HD) and C-HD (conventional HD). In the first case, the powders were heated in vacuum to temperatures of 800°C, 850°C or 900°C, and then hydrogen was supplied at a constant pressure of 0.95 bar for 100 min. In the second one, the hydrogen supply was performed at RT and then after 1 h the samples were heated at 800°C, 850°C or 900°C for 100 min under a constant H_2 pressure of 0.95 bar.

For recombination, the selected temperature was always 850°C and the hydrogen pressure was lowered to 0.1 bar. The powder was held under these conditions for 30 min, followed by a final desorption stage of 5 min under continuous pumping and then the samples were rapidly cooled to RT.

To know the phases present in the final powders, they were characterised by XRD and ME experiments. Magnetic properties of the recombined samples were studied by VSM with a maximum

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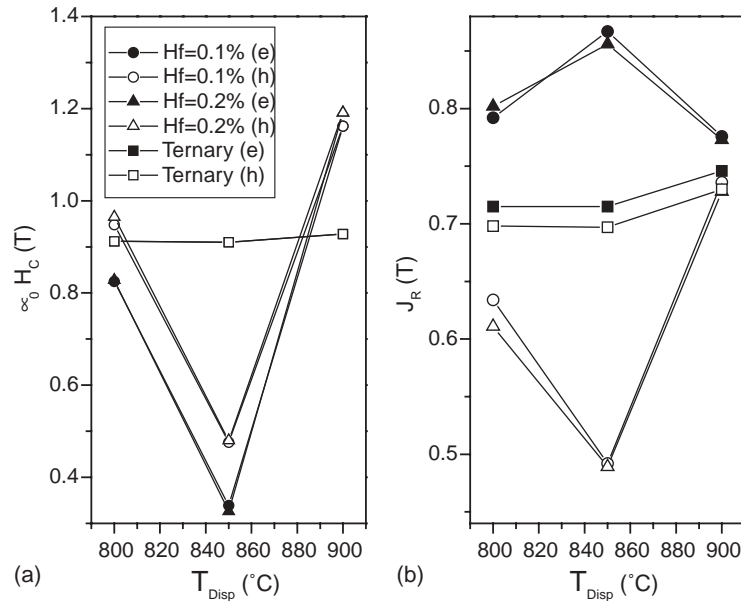


Fig. 1. (a) Coercivity ($\mu_0 H_c$) determined from VSM measurements in easy-axis (e) and hard-axis (h) directions of S-HDDR magnets, as a function of disproportionation temperatures. The symbols corresponding to ternary alloys superimpose within the scale of the graph. (b) Idem for remnant polarisation (J_R).

field of 8 T at room temperature. Prior to the VSM measurements the powders were cold compacted and aligned in a magnetic field of 2 T. This field produces remanence values of the order of 90% of those obtained under saturation conditions.

Fig. 1 shows remanence and coercivity under easy and hard directions, obtained from ternary, Hf 0.1% and Hf 0.2% added samples, S-HDDR at disproportionation temperatures of 800°C, 850°C and 900°C. The Hf samples show higher anisotropy than ternary ones, this property being more pronounced for the 850°C samples and much weaker for the one disproportionated at 900°C.

The samples that develop anisotropy show at the same time higher remanence and lower coercivity as compared to the ternary ones, probably due to a stronger collaborative interaction between aligned single domain grains.

Fig. 2 shows the easy axis demagnetization curves of Hf 0.1% samples. The smooth hysteresis loops of the S-HDDR samples disproportionated at 900°C are the characteristic response of an almost non-textured, single component system.

The same shape is observed for the conventional treatments.

For the disproportionation at 850°C the system develops an important remanence while coercivity reduces drastically. The polarisation decreases from 0.865 to 0 T within 0.34 T just after reversion of the magnetic field $\mu_0 H$, probably due to the already mentioned development of texture and to the magnetic interactions among neighbouring crystallites.

The hysteresis loops of S-HDDR Hf-added samples disproportionated at 800°C (see Fig. 2) suggest the coexistence of more than one component. However, neither ME nor XRD measurement indicate the presence of a magnetic phase besides the $\text{Nd}_2\text{Fe}_{14}\text{B}$ one. This behaviour may be due to the simultaneous presence of textured and non-textured regions in the material and/or of grains of different sizes. This mixture would give rise to the superposition of the responses from one component with relatively high remanence and low coercivity (textured region) and another with low remanence and high coercivity (non-textured region).

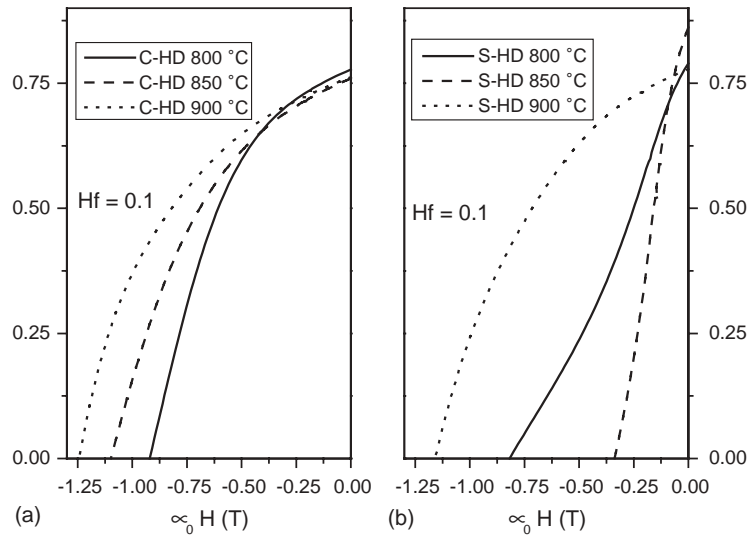


Fig. 2. Second quadrant of major hysteresis loop measured in magnets produced from powders with $x = 0.1$, conventional and solid treated at disproportionation temperatures as are indicated.

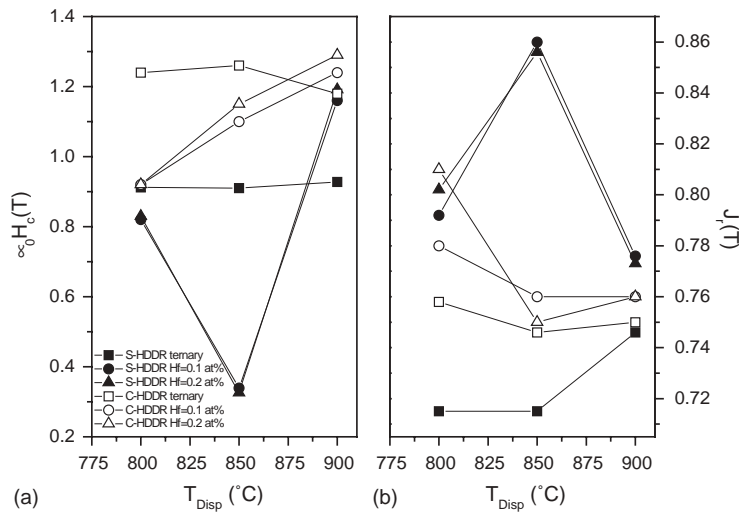


Fig. 3. (a) Coercivity ($\mu_0 H_c$) determined from VSM measurements in easy-axis direction, as a function of disproportionation temperatures. (b) Idem for remnant polarisation (J_R).

Therefore, the observed anisotropic properties are tentatively ascribed to a particular microstructure which develops preferentially in S-HDDR Hf-added samples disproportionated at 800–850 °C. In effect, previous works [5,6] report that the amount of $t\text{-Fe}_3\text{B}$, an intermediate phase considered responsible for texture, has a smooth max-

imum at disproportionation temperatures of 800 °C and 850 °C. The relative $t\text{-Fe}_3\text{B}/\text{Fe}_2\text{B}$ abundance changes approximately from 2 at 800–850 °C to 1 at 900 °C. On the other hand, Hf additions would reduce the disproportionation rate, such as Zr additions do [7]. It was found [5] that disproportionation velocity in Hf 0.08 at%

added samples is maximum in the range 800–850°C but decreases significantly at 900°C. It is expected that a slower rate will favour a coarser disproportionated microstructure and from that a coarser recombined one. This would also imply thicker Nd-rich interphases and less coupling between grains.

These two facts, texture and microstructure scale, compete in the determination of the resulting remanence and coercivity values.

Figs. 3(a) and (b) show the easy-axis remanences and coercivities, respectively, as a function of the disproportionation temperature for solid and conventional treatments. It can be seen that remanence is higher in Hf-containing samples than in ternary ones, for every type of disproportionation treatments. The higher remanences were obtained for the S-HDDR at 850°C.

The coercivities of C-HDDR samples are higher than those of the S-HDDR ones, in all cases. Those of the S-HDDR ternary samples are almost constant but a slight decrease is observed at 900°C in the conventional ones. In the case of Hf-added samples submitted to conventional treatment, coercivity increases steadily with disproportionation temperature. This gives rise to the highest coercivity (of all samples studied here) for the C-HDDR process at 900°C. At this temperature the highest energy product (97.5 kJ/m³) was observed for Hf-added samples, disregarding the type of disproportionation process.

In summary, the ternary samples do not depart much from isotropic behaviour, while the Hf-doped ones exhibit a significant degree of anisotropy, especially treated under S-HDDR conditions. Hf-included samples have higher re-

manences than the ternary ones with the maximum for S-HD at 850°C. Remanence and coercivity values are highly dependent on the disproportionation temperature. The highest energy product (97.5 kJ/m³) was observed for Hf-added samples disproportionated at 900°C.

These results are tentatively explained in terms of microstructural properties. Larger grains separated by thicker Nd-rich interphase would lead to less intergranular coupling and higher coercivity. Hf additions lead to the highest coercivity at 900°C, probably due to the ability of this element to slow down the disproportionation rates in that temperature range. This impurity has a beneficial effect on remanence at lower temperatures (800–850°C). This may be connected to the observation that maximum production of the intermediate phase *t*-Fe₃B occurs in this temperature range, this phase was associated with the development.

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