ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 892–896

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

An improved HDDR treatment for the production of anisotropic Nd–Fe–B ternary powders

S. Sugimoto*, N. Koike, D. Book, T. Kagotani, M. Okada, K. Inomata, M. Homma

Department of Materials Science, Graduate School of Engineering, Tohoku University, Aoba-yama 02, Sendai 980-8579, Japan

Abstract

The magnetic properties of $Nd_{12.2}Fe_{81.8}B_{6.0}$ alloys processed using a new HDDR (hydrogenation disproportionation desorption recombination) treatment were investigated. This newly proposed HDDR treatment is a combination of heat treatments at hydrogen pressures close to the recombination pressure of the $Nd_2Fe_{14}B$ compound, in both the disproportionation and recombination stages. In other words, this new treatment is a combination of the l-HD (heating in a low H_2 pressure during the hydrogenation disproportionation stage), and s-DR (heating in Ar or in a relatively high pressure of hydrogen, at the start of recombination) treatments. In this investigation, the influence of the s-DR conditions on the magnetic properties of anisotropic Nd–Fe–B HDDR-treated powders, were investigated. It was found that an s-DR treatment in which the hydrogen pressure was decreased in steps from 0.1 MPa to 0.5 kPa, enhanced the remanence (1.45 T) and anisotropy (Br/Js=0.94). The rate at which the hydrogen pressure decreases to 6 kPa during s-DR is also considered to be an important factor in obtaining both a high remanence and a high coercivity. In addition, the coercivity was found to increase after an s-DR treatment in which the temperature was decreased in a step by step manner. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nd–Fe–B; HDDR; Anisotropy; Disproportionation; Recombination; Hydrogen pressure

1. Introduction

The hydrogenation, disproportionation, desorption, and recombination (HDDR) phenomena in Nd–Fe–B alloys [1,2] occur after a heat treatment in hydrogen, and a subsequent heat treatment under vacuum. Nd–Fe–B powders produced by utilizing the HDDR phenomena are useful for the production of high performance anisotropic bonded magnets [3]. While it has been shown that the addition of Co, Ga, Zr or Nb can induce magnetic anisotropy in HDDR-treated magnets [3], an investigation of hydrogen absorption and desorption characteristics [4], and resistivity measurements during HDDR phenomena [5] in our previous works suggested that the main effect of additives is to alter the HDDR conditions. In addition, the authors have shown that anisotropic powders can be prepared from the ternary alloy, by raising the vacuum treatment temperature to higher than 800°C [6]. These results show that not only additives, but also the treatment conditions are important in obtaining anisotropic powder. However, the most suitable HDDR treatment conditions for the enhancement of magnetic anisotropy have not yet been established, because the mechanism for the inducement of anisotropic during HDDR is still not understood.

Recently, a study into the effect of HDDR conditions on the ternary alloy was carried out, and the temperature dependence of the recombination pressure of the $Nd_2Fe_{14}B$ compound was clarified, as shown in Fig. 1 [7–9]. The pressure–temperature plot can be divided into three regions (I–III): (I) the $Nd_2Fe_{14}B$ compound is stable, (II) the disproportionated mixture is stable, and (III) although the disproportionated mixture is more stable, the $Nd_2Fe_{14}B$ compound (or its hydride) exists because of unfavorable kinetics at these low temperatures. Using this result, the necessary HDDR treatment conditions for the production of high performance anisotropic ternary alloy powders were established. The newly proposed HDDR treatment was a combination of heat treatments, at hydrogen pressures close to the recombination pressure of the $Nd_2Fe_{14}B$ compound, in both the disproportionation and recombination stages. Namely, the combination of l-HD (heating in a low H_2 pressure during the hydrogenation disproportionation stage), and s-DR (heating in Ar or in hydrogen with a certain pressure for 10 min, at the start of the recombination) treatments. High remanences of 1.3–

---

*Corresponding author.

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01503-1

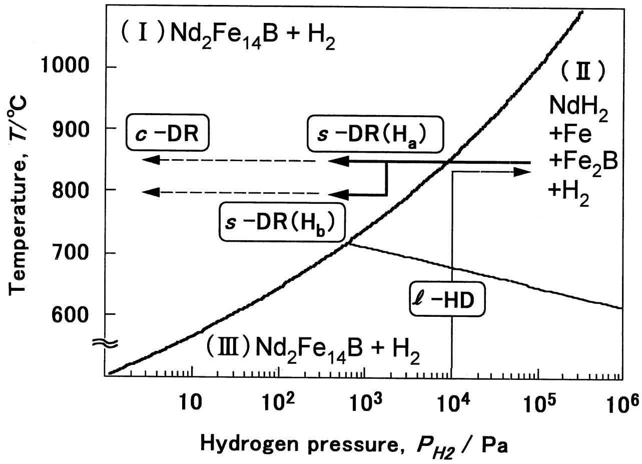

Fig. 1. The hydrogen pressure–temperature curve of the recombination reaction of the $Nd_2Fe_{14}B$ compound, the dissociation of NdH_2 and the starting disproportionation reaction during heating.

1.4 T for the new HDDR-treated ternary powders, prove that the additives are not necessary to obtain anisotropic HDDR powder.

However, the coercivity of the new HDDR-treated powders were lower than those of conventional HDDR-treated powders. This may be explained by excess grain growth occurring during the recombination stage, due to the longer treatment time used for s-DR. In addition, the effect of the recombination stage using the s-DR treatment on the enhancement of magnetic properties, is not been yet clear. Therefore, the purpose of this study is to investigate the influence of the s-DR conditions on the magnetic properties of anisotropic Nd–Fe–B HDDR-treated powders.

2. Experimental procedures

The compositions of the studied alloys were $Nd_{12.2}Fe_{81.8}B_{6.0}$. The alloys were induction melted using high purity elements and ferroalloys, under an Ar atmosphere, and were then homogenized at 1150°C for 50 h. The HDDR treatment was carried out on hydrogen decrepitated ingots (mass of the samples was around 10 g) and the schematic illustration of heat treatment patterns for the HDDR are shown in Fig. 2. For the disproportionation stage, the l-HD treatment (heating in a low H_2 pressure followed hydrogenation disproportionation) were used. The samples were heated under a certain pressure of hydrogen ($P_{\mathrm{H2\text{-}HEAT}}$) at a rate of 400°C/h up to 850°C, exposed to a mixture of hydrogen and Ar ($P_{\mathrm{H2\text{-}HD}}$) for 1 h, and then exposed to 0.1 MPa of hydrogen for a further 1 or 2 h. The relationship between hydrogen pressure and temperature during l-HD is indicated by an arrow in Fig. 1.

For the recombination stage, the s-DR treatment was carried out before the usual evacuation treatment (c-DR), using a rotary pump. In this investigation, heat treatments in hydrogen with a constant pressure (0.5–8 kPa) were used for the s-DR treatment and their conditions were

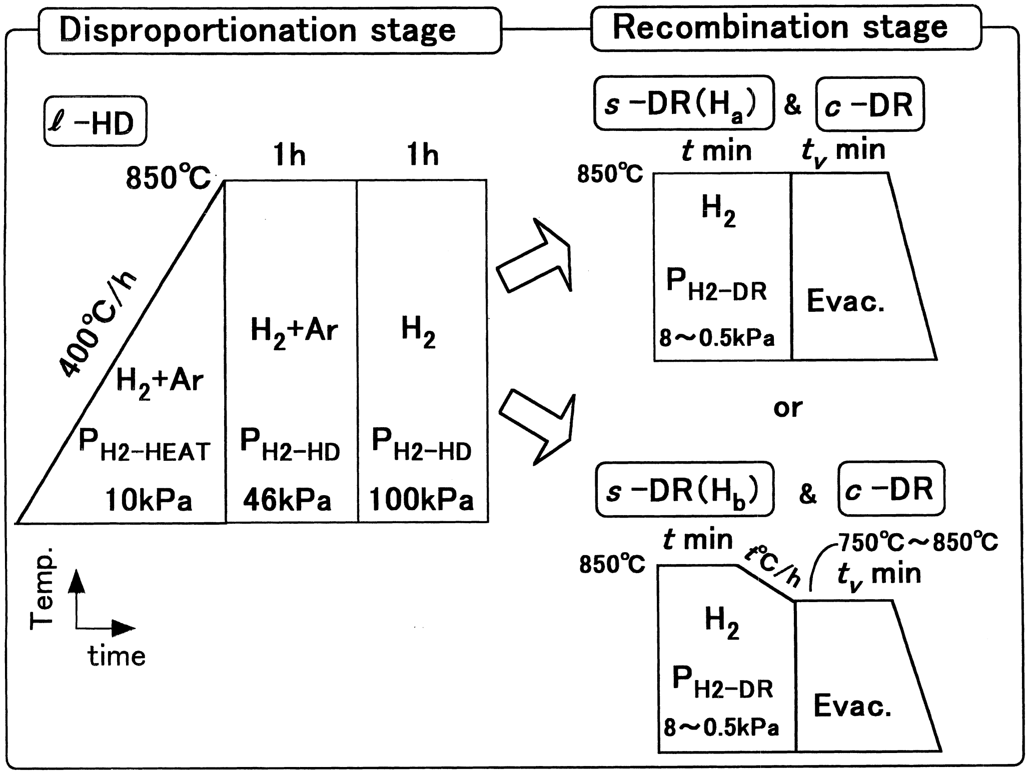

Fig. 2. Schematic diagram showing the different HDDR treatments used in this study.

varied, as shown in Fig. 2. Two different types of s-DR treatments were adopted, in which the samples were: (a) s-DR treated at the same temperature as the l-HD treatment in hydrogen, and the pressure was decreased step by step from 8 to 0.5 kPa, and (b) the samples were heated at temperatures in the range 750–850°C and hydrogen pressure was decreased in steps from 8 to 0.5 kPa. These processing routes are shown in Fig. 1 as s-DR(H_a) and s-DR(H_b). However, the c-DR treatment time (t_v) was not fixed, but rather the pressure of the rotary pump was monitored, and when the recombination reaction was observed to finish, the samples were rapidly cooled.

HDDR treated ingots were ground into powders of <63 μm by milling. Fifty-mg samples of these powders were mixed with molten paraffin in a cylindrical case (internal diameter, 6 mm; internal height, 3 mm), and the paraffin was allowed to solidify in a magnetic field of 960 kA m^{-1} which was applied parallel to the bottom of the case. The magnetic properties were measured using a vibrating sample magnetometer (VSM) with a maximum applied field of 1.2 MA m^{-1}, after applying a pulsed field of 6.4 MA m^{-1} to the sample. The density of the homogenized ingots, and a demagnetizing factor of 0.12 which was determined by measuring the as-homogenized powder, were used for the VSM measurements.

3. Results and discussion

Fig. 3 shows the variation of magnetic properties of $Nd_{12.2}Fe_{81.8}B_{6.0}$ samples HDDR treated at 850°C by changing the hydrogen pressure and treatment time during the s-DR treatment. The magnetic properties did not so change much with respect to the s-DR treatment time, however, they were greatly effected by the hydrogen pressure. The samples s-DR treated at lower hydrogen pressures exhibited higher coercivities; however, higher remanences were obtained for the samples treated at higher hydrogen pressures. It can be said that anisotropic powder was obtained in samples s-DR treated at a hydrogen pressure close to the recombination pressure of the $Nd_2Fe_{14}B$ compound. In particular, the samples s-DR treated at 6 kPa for ≥5 min, exhibited the highest remanences of about 1.4 T. Fig. 4 shows magnetic properties of the samples s-DR treated at 850°C by changing the hydrogen pressure in the order: 6, 1 and 0.5 kPa, with respect to the total treatment time of s-DR. The highest remanence of 1.45 T was obtained under these conditions: 6 kPa for 5 min, 1 kPa for 5 min and 0.5 kPa for 10 min. As far as we aware, this remanence is the highest reported value for a HDDR treated Nd–Fe–B powders (with or without additions). However, the coercivity value of 0.46 MA m^{-1} is half that of samples s-DR treated in an Ar atmosphere (s-DR(Ar)), which was reported in our previous paper [8], or c-DR treated.

In order to clarify the difference in the s-DR treatment using hydrogen (s-DR(H)) and Ar gas (s-DR(Ar)), the hydrogen pressure during both the s-DR treatments was monitored, and the result in the case of s-DR(Ar) is shown in Fig. 5. This shows that the hydrogen pressure steadily decreased to 6 kPa within 5 min and then the pressure

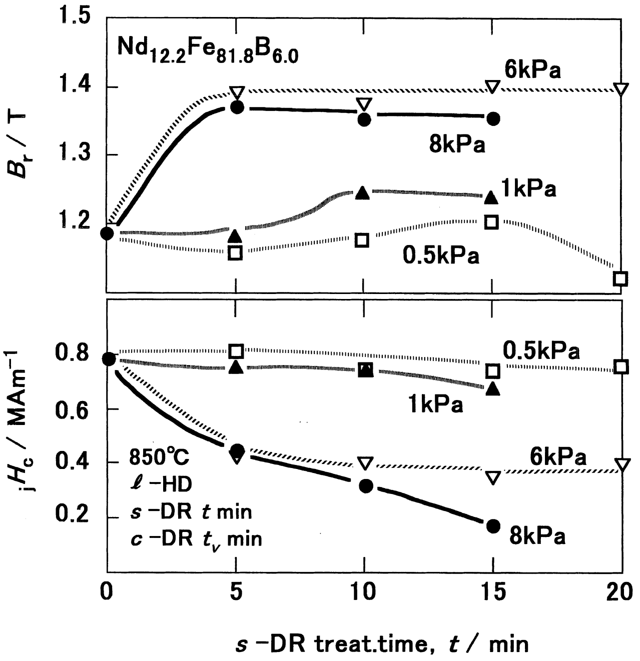

Fig. 3. Variation of magnetic properties of $Nd_{12.2}Fe_{81.8}B_{6.0}$ samples HDDR treated at 850°C by changing the hydrogen pressure and treatment time during s-DR treatment.

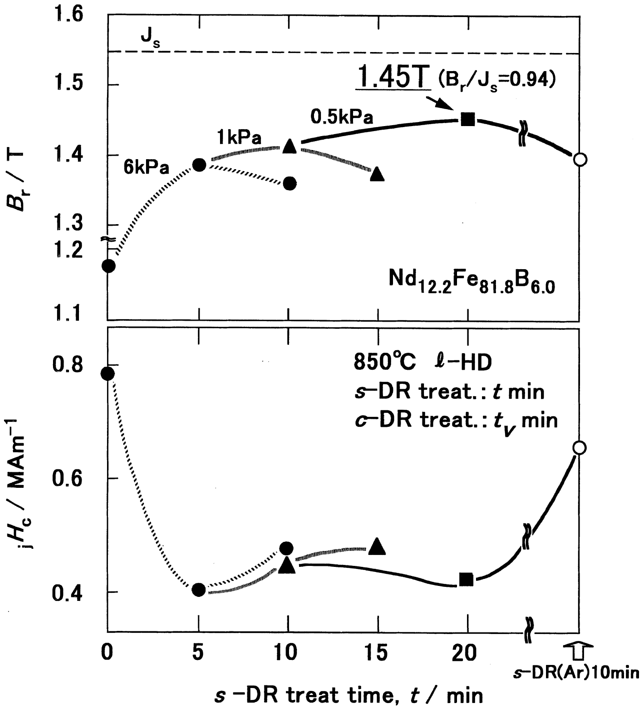

Fig. 4. Magnetic properties of samples s-DR treated at 850°C by changing the hydrogen pressure in the order of 6, 1 and 0.5 kPa, with respect to the total s-DR treatment time.

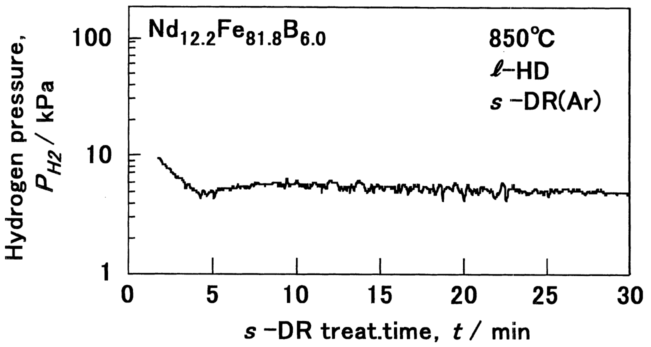

Fig. 5. Hydrogen pressure during the s-DR(Ar) treatment.

remained constant. However, using the s-DR(H) treatment, the hydrogen pressure decreased to the target pressure within several seconds. Judging from the difference of the magnetic properties between the s-DR(Ar)- and s-DR(H)-treated powders, it can be said that the rate at which the hydrogen pressure decreases at the start of the s-DR(H) treatment is also an important factor for obtaining both higher remanence and coercivity. Therefore, samples were prepared using a new s-DR(H) treatment, in which the hydrogen pressure decreased to 6 kPa for 5 min after the l-HD treatment, and was then held at this pressure for a certain number of minutes, and their magnetic properties were measured. Fig. 6 shows their demagnetization curves in comparison with the s-DR(Ar) sample. The sample which was not held at 6 kPa, exhibited a high coercivity but a low remanence. The s-DR(H) treated sample held at 6 kPa for 2 min, exhibited a remanence of 1.39 T and a coercivity of 0.6 MA m^{-1}, which were equivalent to those of the s-DR(Ar) treated sample. From these results, it can be concluded that the rate at which the hydrogen pressure decreases during s-DR(H) is an important factor for obtaining good magnetic properties.

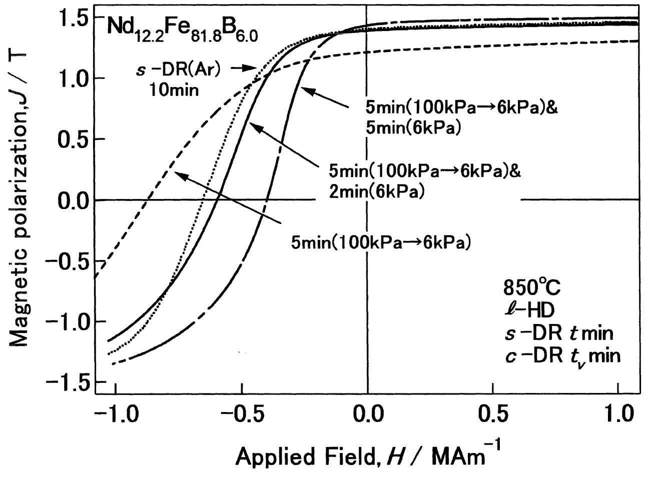

Fig. 6. Demagnetization curves of samples prepared using a new s-DR treatment, in which the hydrogen pressure decreased to 6 kPa within 5 min after the l-HD treatment, and was then held at this pressure for a certain number of minutes (0, 2, and 5 min), compared with that of the s-DR(Ar) treated sample.

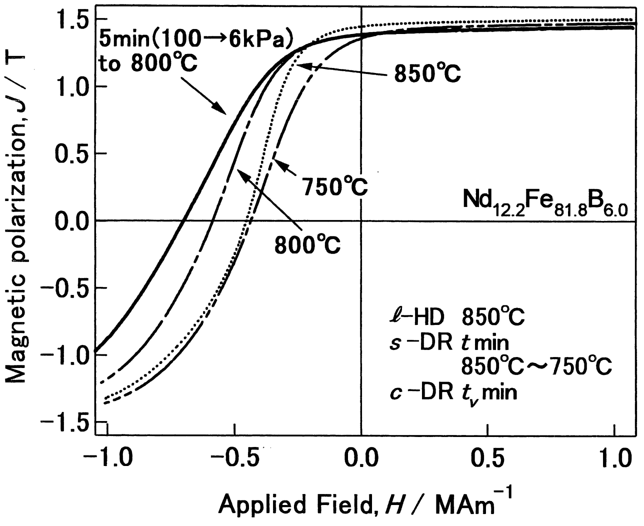

Fig. 7. Demagnetization curves of samples: (i) heat-treated at 850°C in 6 kPa of hydrogen for 5 min, step-cooled to 750–800°C and decreasing the hydrogen pressure to 0.5 kPa, and then c-DR treated; (ii) treated by an s-DR treatment, in which the hydrogen pressure decreased to 6 kPa within 5 min after the l-HD treatment, step-cooled to 800°C with decreasing hydrogen pressure to 0.5 kPa, and then c-DR treated.

Next, the effect of decreasing the temperature during s-DR(H) treatment was investigated. First of all, after the l-HD treatment, the samples were heat-treated at 850°C in 6 kPa of hydrogen for 5 min, step-cooled to 750–800°C, decreasing the hydrogen pressure to 0.5 kPa, and then c-DR treated. The demagnetization curves of these samples are shown in Fig. 7. The sample step-cooled to 750°C did not have good magnetic properties. These poor magnetic properties were due to the treatment temperature not being high enough to allow the complete desorption of hydrogen during the recombination reaction. The samples step-cooled to 800°C exhibited a higher coercivity (0.59 MA m^{-1}) than those treated at 850°C. Fig. 7 also shows the demagnetization curve of the sample, which was s-DR(H) treated at 850°C in hydrogen decreasing pressure from 0.1 MPa to 6 kPa for 5 min, step-cooled to 800°C, and then c-DR treated. This sample exhibited good magnetic properties with high remanence of 1.39 T and high coercivity of 6.7 MA m^{-1}. It can be concluded the decrease of treatment temperature during the s-DR treatment is effective for increasing coercivity. This may be because grain growth is restricted during the recombination stage.

Acknowledgements

The authors would like to thank Mr. H. Murai and for his assistance in many experiments. This work has been supported in part by a Grant-in-Aid for Scientific Research on Priority Areas A of 'New Protium Function' and No 11875145, from the Ministry of Education, Science, Sports and Culture of Japan.

References

[1] T. Takeshita, R. Nakayama, Proc. 10th Int. Workshop on R.E. Magnets & Their Applications, Kyoto, 1989, Vol. I, p. 551.

[2] P.J. McGuiness, X.J. Zhang, X.J. Yin, I.R. Harris, J. Less-Common Met. 158 (1990) 359.

[3] T. Takeshita, R. Nakayama, in: Proc. 12th Int. Workshop on R.E. Magnets & Their Applications, Canberra, 1992, p. 670.

[4] H. Nakamura, S. Sugimoto, T. Tanaka, M. Okada, M. Homma, J. Alloys Comp. 222 (1995) 136.

[5] S. Sugimoto, O. Gutfleisch, I.R. Harris, J. Alloys Comp. 260 (1997) 284.

[6] H. Nakamura, R. Suefuji, S. Sugimoto, M. Okada, M. Homma, J. Appl. Phys. 76 (1994) 6828.

[7] H. Nakamura, K. Kato, D. Book, S. Sugimoto, M. Okada, M. Homma, in: Proc. 15th Int. Workshop on R.E. Magnets & Their Applications, Dresden, 1998, p. 507.

[8] S. Sugimoto, H. Nakamura, K. Kato, D. Book, T. Kagotani, M. Okada, M. Homma, J. Alloys Comp. 293–295 (1999) 862.

[9] H. Nakamura, K. Kato, D. Book, S. Sugimoto, M. Okada, M. Homma, IEEE Trans. Magn. 35 (1999) 3274.