Texture Study in HDDR-treated Nd-Fe-B-type Particles

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Effects of the disproportionating hydrogen pressure and alloy composition on the texture in the HDDR-treated Nd-Fe-B particles were examined using the $Nd_{12.6}Fe_{81.4}B_6$ and $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloys. Disproportionation kinetics of the $Nd_2Fe_{14}B$ phase in the Nd-Fe-B alloy was retarded significantly by the addition of Co, Ga and Zr. The retarded disproportionation kinetics of the $Nd_2Fe_{14}B$ phase ensured a wider processing window in terms of disproportionating hydrogen pressure for achieving a texture in the HDDR-treated Nd-Fe-B alloy particles.

Key words : Nd-Fe-B particle, HDDR, texture

1. Introduction

A Nd-Fe-B-type annealed alloy ingot exhibits a negligible coercivity because of the huge grain size of the $Nd_2Fe_{14}B$ main magnetic phase in the alloy. A hydrogen treatment, known as HDDR process, can readily concert this coarse grained and no coercivity Nd-Fe-B-type ingot material into a powder with fine grain structure, thus ensuring high coercivity [1, 2]. The HDDR process is, therefore, effectively used as a means of producing highly coercive Nd-Fe-B-type magnetic powder directly from the annealed ingot material. More importantly, it has been known that a combination of alloy modification and precise control of HDDR variables leads to an anisotropic powder in which the newly recombined fine grains have a texture by keeping their crystallographic orientation parallel to that of their mother grain [3-7]. In this anisotropic HDDR process the addition of alloying element(s) and HDDR variables are believed to play a key role in achieving the texture [7]. In the present study, the Nd-Fe-B-type alloys were HDDR-treated, and the effects of alloy composition and disproportionating hydrogen pressure on the texture in the HDDR particle were investigated.

2. Expermentals

Two types of starting alloys of $Nd_{12.6}Fe_{81.4}B_6$ and

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$Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ were prepared by an induction melting of the high purity component elements. The cast alloy ingots were homogenized at 1070 °C for 72 hrs (under Ar gas) and crushed into pieces (0.5~1.0 mm). The crushed pieces were, then, hydrogenated at 350 °C for 60 min under hydrogen pressure of 1.0 kgf/cm^2. Subsequently, the hydrogenated material was continuously heated up to 820 °C and hold for 60 min under various hydrogen pressures (0.1~1.0 kgf/cm^2) to cause a disproportionation. Desorption and recombination of the disproportionated material was carried out at 820 °C for 45 min under vacuum atmosphere. The texture in the HDDR-treated particle was examined by a magnetic way. The HDDR-treated particles were placed in a disc-shaped sample holder and aligned by applying 10 kOe DC field along the diameter direction, and then fixed with a paraffin wax. Demagnetisation curves were measured along the direction parallel and perpendicular to the aligning direction using a VSM with a maximum field of 15 kOe after a pre-magnetizing with 6 T pulsing field. On the VSM measurement a self-demagnetising field in the specimen was not corrected. It is noted that as the measurement was performed along the diameter direction in the disc-shaped sample the demagnetising factors along the parallel and perpendicular direction are identical. The texture in the HDDR-treated particle was evaluated by a degree of alignment (DoA) of the particles, which is defined by $(Mr(//) - Mr(\perp))/Mr(//) \times 100$ (%), where, $Mr(//)$ and $Mr(\perp)$ are the remanence along the direction parallel and perpendicular to the aligning direction in the aligned

specimen, respectively.

3. Results and Discussion

Fig. 1 shows the demagnetization curves of the $Nd_{12.6}Fe_{81.4}B_6$ and $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloys HDDR-treated with disproportionating hydrogen pressure of 1 kgf/cm². It can be seen that both the HDDR-treated alloy powders showed a reasonably high coercivity. This indicates that the alloys were well disproportionated and recombined into fine grains. It can also be seen that both the HDDR-treated alloy powders showed an isotropic nature regardless of the alloy composition. This result indicates that with the HDDR variables used in the present work, the alloys were fully disproportionated and during the recombination the newly formed grains had their crystallographic orientation in random manner, thus no texture was achieved in each particle.

However, it should be noted that the texture in the HDDR-treated particle may be closely related to the disproportionation step, in particular the hydrogen pressure [7]. In an attempt to see the effect of the disproportionating hydrogen pressure on the texture in the HDDR-treated particles both the alloys were HDDR-treated with various disproportionating hydrogen pressures. Fig. 2 shows the dependence of coercivity and particle alignment of the HDDR-treated $Nd_{12.6}Fe_{81.4}B_6$ and $Nd_{12.6}Fe_{68.7}B_6$-$Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloy powders on the disproportionating

Fig. 2. Dependence of the coercivity and particle alignment of the HDDR-treated (a) $Nd_{12.6}Fe_{81.4}B_6$ and (b) $Nd_{12.6}Fe_{68.7}B_6$-$Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloys powder on the disproportionating hydrogen pressure.

hydrogen pressure. The coercivity values in Fig. 2 are obtained from the measurement along the direction parallel to the aligning direction. It seems that the $Nd_{12.6}Fe_{81.4}B_6$ alloy disproportioned with lower hydrogen pressure (0.1 kgf/cm²) showed an appreciable coercivity and some degree of alignment. The appreciable coercivity indicates that the material was properly disproportionated (see Fig. 3(a)) and recombined. It is noted that the particle alignment in this material indicates that during the recombination the newly recombined grains have their crystallographic orientation somewhat parallel to that of
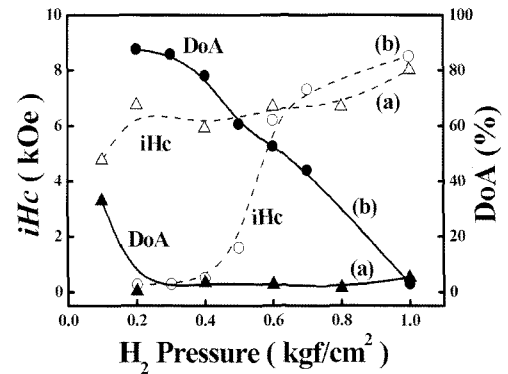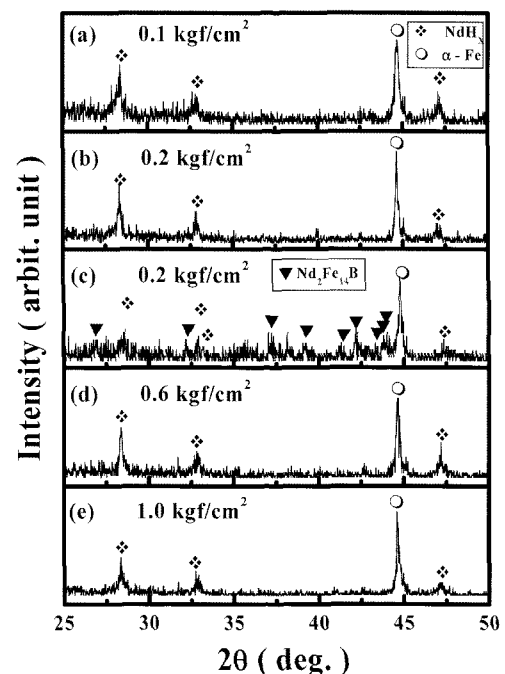

Fig. 1. Demagnetization curves of the (a) $Nd_{12.6}Fe_{81.4}B_6$ and (b) $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloys HDDR-treated with disproportionating hydrogen pressure of 1 kgf/cm².

Fig. 3. XRD patterns of the (a, b) $Nd_{12.6}Fe_{81.4}B_6$, and (c, d, e) $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloys disproportionated with various hydrogen pressures.
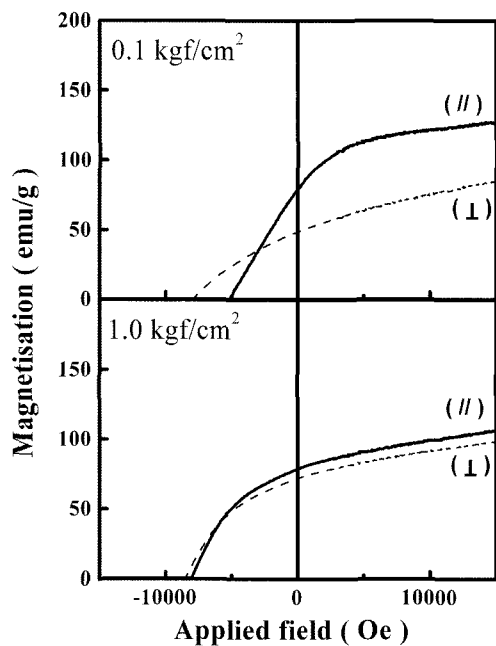
Fig. 4. Demagnetization curves of the ternary $Nd_{12.6}Fe_{81.4}B_6$ alloy HDDR-treated with various disproportionating hydrogen pressures.

Fig. 5. Demagnetization curves of the $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}$-$Ga_{1.0}Zr_{0.1}$ alloy HDDR-treated with various disproportionating hydrogen pressures.

their mother grain, thus having a texture to some extent in each particle after the HDDR. The $Nd_{12.6}Fe_{81.4}B_6$ alloy disproportioned with hydrogen pressure over 0.2 kgf/cm² still exhibited high coercivity, but virtually no alignment was achieved. With the hydrogen over 0.2 kgf/cm² the alloy may have been over-disproportionated (see Fig. 3(b)), and during the recombination the newly formed grains may, however, have their crystallograpphic orientation in random manner, thus no texture was achieved in each particle and no alignment could be obtained. Fig. 4 shows the demagnetization curves of the ternary $Nd_{12.6}Fe_{81.4}B_6$ alloy HDDR-treated with various disproportionating hydrogen pressures.

Meanwhile, the $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloy HDDR-treated with lower disproportionating hydrogen pressure (below 0.4 kgf/cm²) showed a negligible coercivity, but unexpectedly the degree of alignment of this powder appeared to be very high. The good particle alignment in this material may be due to an incomplete HDDR. With the lower hydrogen pressure the alloy may be partially disproportionated (see Fig. 3(c)) and the undisproportionated part in each particle may remain intact in large grain. This undisproportionated part will be decrepitated into small single grain particles after the HDDR. These small single grain particles will be aligned perfectly under a magnetic field. Therefore, it becomes apparent that the particle alignment in this material may be due to an incomplete HDDR rather than to the texture
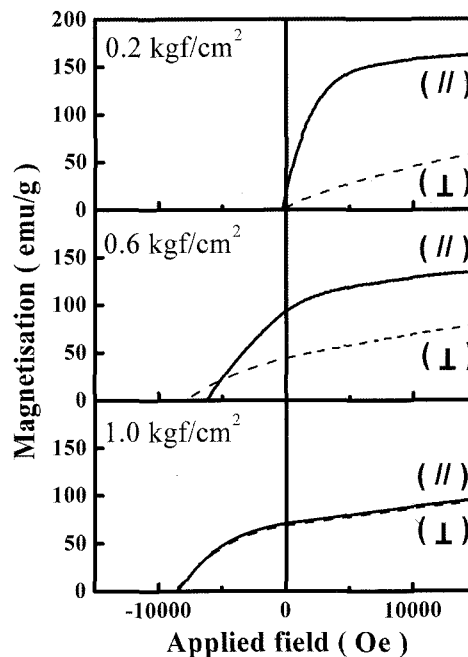
in the particles. The incomplete HDDR associated with a poor disproportionation is evidenced by the lower coercivity of this material. The $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloy disproportioned with moderate hydrogen pressure (0.5~0.7 kgf/cm²) shows a good particle alignment together with considerably high coercivity. The high coercivity indicates that the material was properly disproportionated (see Fig. 3(d)) and recombined. Most importantly, the good particle alignment in this material indicates that the recombined grains have a texture. For the $Nd_{12.6}Fe_{68.7}B_6$-$Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloy disproportioned with higher hydrogen pressure (1.0 kgf/cm²) a considerably high coercivity was achieved. However, the particle alignment was negligible and the powder was virtually isotropic. This indicates that although the material was fully disproportionated (see Fig. 3(e)) and recombined the recombined fine grains oriented randomly and the particles had no texture. Demagnetization curves of the $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}$-$Zr_{0.1}$ alloy HDDR-treated with various disproportionating hydrogen pressures are shown in Fig. 5.

The above results seem to suggest that the texture formation in the HDDR-treated Nd-Fe-B particles is significantly influenced by the alloy composition and disproportionating hydrogen pressure. For the ternary $Nd_{12.6}Fe_{81.4}B_6$ alloy the texture can only be achieved by very low disproportionating hydrogen pressure, and for the $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloy by a moderate and
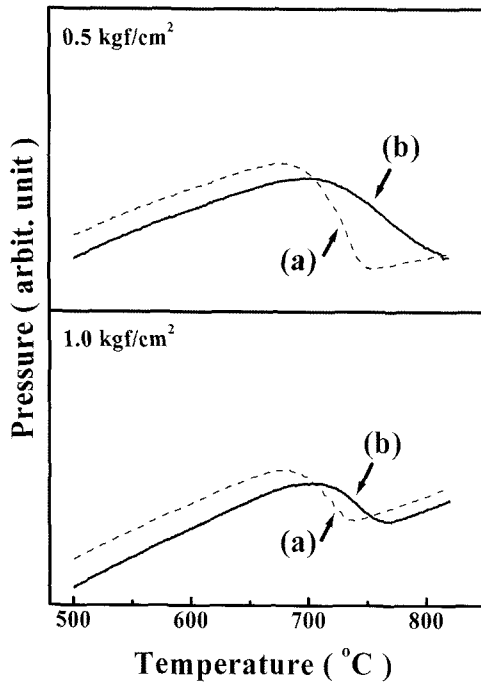
Fig. 6. TPA tracings of the pre-hydrogenated (a) $Nd_{12.6}Fe_{81.4}B_6$ and (b) $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloys under different hydrogen pressures.

more or less wide range of disproportionating hydrogen pressure. It is thought that the texture formation in the HDDR-treated Nd-Fe-B particles may be closely related to the hydrogen sensitivity of the alloys, in particular of the $Nd_2Fe_{14}B$ magnetic phase in the alloys. The hydrogen sensitivity of the $Nd_{12.6}Fe_{81.4}B_6$ and $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}$-$Ga_{1.0}Zr_{0.1}$ alloys was examined by a thermopiezic analysis (TPA). In the TPA a pre-hydrogenated alloy powder was placed in a closed system filled with hydrogen. The change of hydrogen pressure in the reaction chamber was monitored in the course of heating. As can be seen in Fig. 6, the hydrogen pressure in the reaction chamber decreased abruptly at around 700 °C, and this was due to the hydrogen absorption for the disproportionation. It can be seen that under the hydrogen pressure of 1 kgf/cm^2 the ternary $Nd_{12.6}Fe_{81.4}B_6$ alloy started to be disproportionated from 690 °C and it completed at 730 °C. Meanwhile, the $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloy appeared to be disproportionated from around 710 °C and the reaction was accomplished at around 760 °C. This result indicates that the $Nd_2Fe_{14}B$ magnetic phase in the $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}$-$Ga_{1.0}Zr_{0.1}$ alloy was stabilized by the addition of the alloying elements against the hydrogen atmosphere [8-11]. The stabilization of the $Nd_2Fe_{14}B$ magnetic phase by the additives is more obvious under a lower hydrogen pressure (0.5 kgf/cm^2) as can be seen in Fig. 6. For the

ternary $Nd_{12.6}Fe_{81.4}B_6$ alloy the disproportionation kinetics of the $Nd_2Fe_{14}B$ phase is high and even the low hydrogen pressure may lead to an over-disproportionation of the magnetic phase. Thus, the newly recombined fine grains may have random orientation irrelevant to their mother grain's orientation, and no texture was achieved in each particle after HDDR. In the $Nd_{12.6}Fe_{81.4}B_6$ alloy a texture was achieved only with very low hydrogen pressure where the disproportionation kinetics of $Nd_2Fe_{14}B$ phase was significantly retarded. On the other hand, for the $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloy the disproportionation kinetics of the $Nd_2Fe_{14}B$ phase is retarded significantly by the stabilization due to the Co, Ga and Zr addition. Therefore, the $Nd_2Fe_{14}B$ phase in the $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}$-$Zr_{0.1}$ alloy could not be disproportionated under lower hydrogen pressure and a proper disproportionation could occur under a moderate hydrogen pressure. The retarded disproportionation kinetics may lead to an optimum disproportionation, and ensuring that during the recombination the newly recombined grains still remember their mother grain's crystallographic orientation, thus having a texture in each particle after the HDDR. Of course, even for the $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloy a high disproportionation kinetics under higher hydrogen pressure may cause an over-disproportionation of the $Nd_2Fe_{14}B$ magnetic phase. In this material the newly recombined grains can not remember their mother grain's crystallographic orientation any longer, thus no texture can be achieved in each particle after the HDDR as verified in Fig. 2.

4. Conclusion

Disproportionation kinetics of the $Nd_2Fe_{14}B$ phase in Nd-Fe-B alloy was retarded significantly by the addition of Co, Ga and Zr. The retarded disproportionation kinetics of the $Nd_2Fe_{14}B$ phase ensured a wider processing window for achieving a texture in the HDDR-treated Nd-Fe-B alloy particles. For the ternary $Nd_{12.6}Fe_{81.4}B_6$ alloy with higher disproportionation kinetics of the $Nd_2Fe_{14}B$ phase a texture in the HDDR-treated particles was achieved only by very low disproportionating hydrogen pressure. For the $Nd_{12.6}Fe_{68.7}B_6Co_{11.0}Ga_{1.0}Zr_{0.1}$ alloy with retarded disproportionation kinetics of the $Nd_2Fe_{14}B$ phase a texture was achieved in a wider processing window in terms of disproportionating hydrogen pressure.

Acknowledgement

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