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Preparation of $Nd_2Fe_{14}B$ Single Domain Particles from Nd-Fe-B Alloy Ingot Using a Combination of HDDR and Mechanical Milling

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This study examined the feasibility of the combining HDDR-process (hydrogenation, disproportionation, desorption and recombination) with mechanical milling to prepare single domain $Nd_2Fe_{14}B$ particles from a Nd-Fe-B alloy ingot. The $Nd_{15}Fe_{77}B_8$ alloy was HDDR-treated and then subjected to a roller-milling. In the HDDR-treated $Nd_{15}Fe_{77}B_8$ alloy, very small $Nd_2Fe_{14}B$ grains comparable to their critical single domain size (0.3 μm) were observed. These fine individual grains were separated successfully along the grain boundaries by a roller-milling. The separated $Nd_2Fe_{14}B$ grains were found to be single domain particles. These results suggest that single domain particles of the $Nd_2Fe_{14}B$ phase can be prepared from a Nd-Fe-B ingot alloy by combining a HDDR-process with mechanical milling.

Keywords : Nd-Fe-B alloy, $Nd_2Fe_{14}B$ compound, single domain particle, HDDR-process

1. Introduction

Nd-Fe-B-type magnetic materials are widely used in the industry on account of their high permanent magnetic performance [1, 2]. This high performance is attributed to the basic magnetic phase of $Nd_2Fe_{14}B$. This magnetic compound exhibits outstanding intrinsic magnetic properties, such as; high saturation magnetisation [3], high magnetocrystalline anisotropy [4], and a reasonably high ordering temperature [3]. Single domain particles of this phase are required for studies into permanent magnetic materials. There has been considerable research aimed at preparing fine particles of the $Nd_2Fe_{14}B$ phase [5-10]. However, most studies focused on preparing particles consisting of fine multi-grains rather than fine single grain particles. There are few reports on the preparation of $Nd_2Fe_{14}B$ single domain particles.

The HDDR-process (hydrogenation, disproportionation, desorption, and recombination) employing a hydrogen treatment is well established as an effective means of producing a fine grain-structured Nd-Fe-B powder [11, 12]. The HDDR-process can easily convert a coarse grain-structured Nd-Fe-B bulk material to particles with a fine grain structure. In an optimally HDDR-treated Nd-Fe-B powder the size of the recombined $Nd_2Fe_{14}B$ grains is comparable to the single domain size (~0.3 μm [13]). Therefore, perfect single domain particles can be prepared if the finely recombined grains in the HDDR-treated Nd-Fe-B material can be separated successfully. This study reports the preparation of single domain particles of $Nd_2Fe_{14}B$ from a Nd-Fe-B alloy ingot by combining a HDDR-process with mechanical milling.

2. Experimentals

The $Nd_{15}Fe_{77}B_8$ starting alloy was prepared by an induction melting of high purity constituent elements. The cast alloy ingot was homogenized at 1070°C for 72 h (under Ar gas) and crushed into coarse granules (0.5-1.0 mm). The granules were, then, hydrogenated at 350°C for 60 min under 1.0 kgf/cm^2 hydrogen. Subsequently, the hydrogenated powder was disproportionated at 820°C for 45 min under the same hydrogen pressure. Desorption and recombination was carried out at 820°C for 30 min under a vacuum. The HDDR-treated material was roller-milled to produce single domain particles. The morphology of the particles was observed by HRSEM. For magnetic characterisation, the particles were aligned by applying a 10 kOe DC field, and the aligned particles

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were fixed with wax. The magnetic properties of the particles were measured using a vibrating sample magnetometer with a maximum field of 12 kOe after pre-magnetizing with a 60 kOe pulsing field. The likelihood of a single domain particle was evaluated from the degree of alignment (DoA), along with the microstructural observations. The DoA was defined by the ratio, $M_{(//)10}/M_{(\perp)10}$, where, $M_{(//)10}$ and $M_{(\perp)10}$ are the magnetisation at 10 kOe in the first quadrant demagnetisation curve along the directions parallel and perpendicular to the aligning direction, respectively.

3. Results and Discussion

Fig. 1 shows the microstructure of the annealed $Nd_{15}Fe_{77}B_8$ alloy ingot. The $Nd_2Fe_{14}B$ grains in the annealed $Nd_{15}Fe_{77}B_8$ alloy ingot have a large grain size of opproximately 100-200 μm. It was expected that simple prolonged mechanical milling of an annealed ingot with a large grain structure would lead to a very fine powder with a particle size down to the critical single domain size ($d_c \cong 0.3$ μm) of $Nd_2Fe_{14}B$. The annealed ingot was roller-milled for up to 24 h, and the morphology of the milled powder was examined. As shown in Fig. 2, it appears that the particle size of the milled powder ranged from sub-μm to 3 μm after 12 hrs milling. No further particle size reduction was achieved up to 24 h. This suggests that simple prolonged mechanical milling of an annealed ingot is not a suitable means of preparing fine $Nd_2Fe_{14}B$ particles with a size comparable to the critical single domain size (d_c) of the compound.

It is desirable to have a Nd-Fe-B material with a fine

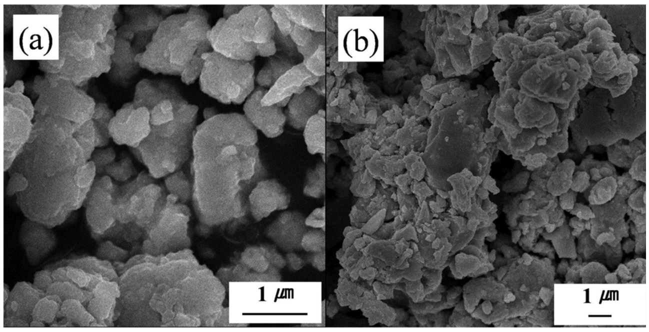

Fig. 2. HRSEM images showing the particle morphology of the $Nd_{15}Fe_{77}B_8$ alloy roller-milled for (a) 12 and (b) 24 h.

$Nd_2Fe_{14}B$ grain structure comparable to the single domain size (~0.3 μm [12]). Perfect single domain particles of $Nd_2Fe_{14}B$ can be prepared if the fine grains in the Nd-Fe-B material can be separated successfully along the grain boundaries. The HDDR-process can be used as an effective means of converting a coarse grain-structured Nd-Fe-B material into a fine grain-structured material [10, 11]. In an attempt to obtain a fine grain-structured Nd-Fe-B material, a HDDR-treatment was applied to the annealed $Nd_{15}Fe_{77}B_8$ alloy ingot. The microstructure of the HDDR-treated material was examined by observing the morphology of the fractured surface of the material after brief crushing. As shown in Fig. 3, the recombined $Nd_2Fe_{14}B$ grains in the HDDR-treated material have a very fine microstructure with a grain size of approximately 0.3 μm. It is expected, then, that the perfect single domain particles can be prepared if the fine grains in the HDDR-treated material are separated successfully along the grain boundary. The HDDR-treated material was subsequently milled

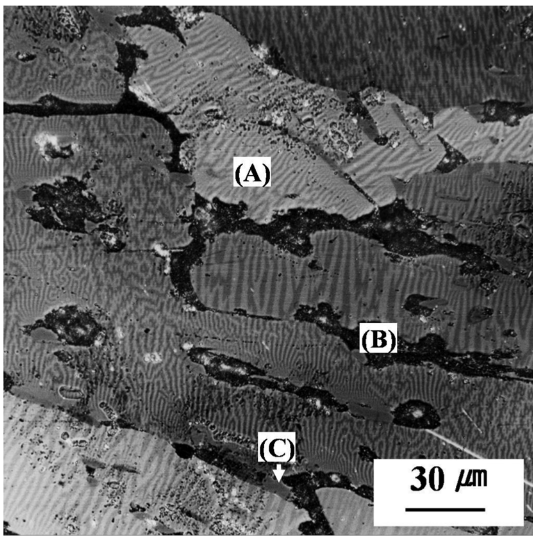

Fig. 1. Microstructure of the annealed $Nd_{15}Fe_{77}B_8$ alloy ingot. (A) $Nd_2Fe_{14}B$. (B) Nd-rich. (C) $Nd_{1+x}Fe_4B_4$.

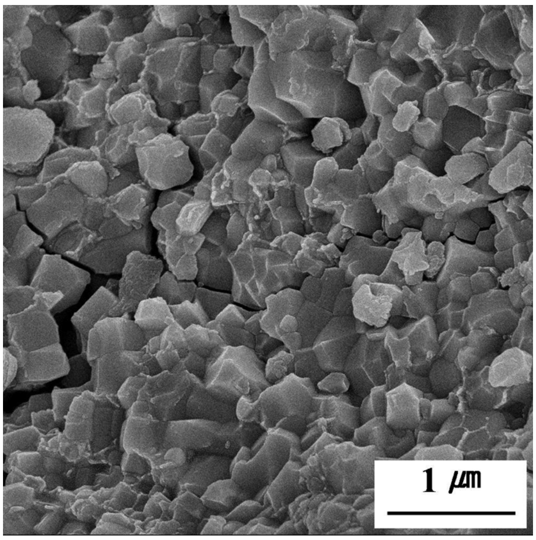

Fig. 3. The grain structure of the $Nd_2Fe_{14}B$ phase in the HDDR-treated $Nd_{15}Fe_{77}B_8$ alloy.

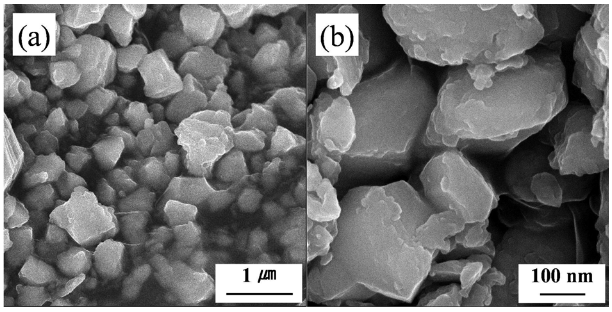

Fig. 4. HRSEM photographs showing the morphology of the particles obtained from the $Nd_{15}Fe_{77}B_8$ alloy HDDR-treated and subsequently roller-milled for 12 h. (a) general view (b) close observation.

for 12 h using a roller mill. As shown in Fig. 4, the HDDR-treated material was milled into a powder with a particle size approximately 0.3 μm, which is the critical single domain size of the $Nd_2Fe_{14}B$ compound. Here, it is important to confirm that these 0.3 μm particles are single grains. These particles cannot be classified as single domain particles if they consist of multi-grains.

The likelihood that the HDDR-treated and milled particles are single domain particles was confirmed by measuring the magnetic alignment of the particles. The HDDR-treated and roller-milled particles were aligned by applying a DC magnetic field, and the demagnetisation curves were measured along the directions parallel and perpendicular to the aligning direction. As shown in Fig. 5, the magnetisation along the parallel direction was much higher than along the perpendicular direction, highlighting the good magnetic alignment with a DoA of approximately 2.24. This suggests that the HDDR-treated and roller milled particles are well aligned in such a way that the easy magnetisation axis (*c*-axis) of the $Nd_2Fe_{14}B$ particles orients parallel to the aligning field. The good alignment can be achieved because the particles are probably in single grain form. The particles cannot be aligned if they are in multi-grain form. Therefore, the fine grains in the HDDR-treated material had been separated successfully along the grain boundaries by milling, and the obtained particles were single domain particles. Here, it will be interesting to compare the magnetic alignment of these single domain particles with that of coarse $Nd_2Fe_{14}B$ single grain particles, which show virtually perfect alignment under an applied magnetic field. The coarse single grain particles were prepared simply by roller-milling a $Nd_{15}Fe_{77}B_8$ alloy ingot for 12 h. As shown earlier, the $Nd_2Fe_{14}B$ grain size in the starting alloy ingot was approximately 100-200 μm (Fig. 1), and the particle size after roller-milling ranged from sub-μm to 3 μm (Fig. 2(a)). It is almost certain that the particles in this milled powder were single grains. These coarse single grain particles showed a virtually perfect alignment under an applied magnetic field. The obtained coarse single grain particles were aligned in a similar manner, and the demagnetisation curves along the different directions were measured. As shown in Fig. 6, the coarse single grain particles showed good magnetic alignment as expected and exhibited a DoA of approximately 2.19, which is similar to that (2.24) of the particles obtained from the HDDR-treatment and milling. This result also shows that the HDDR-treated and roller milled particles are probably in single grain form.

The possibility that the 0.3 μm particles of the HDDR-treated and roller milled powder are multi-grains, where the individual grains have parallel crystallographic orientation, cannot be excluded. A particle can also be aligned perfectly under a magnetic field if it consists of multi grains with the individual grains in a parallel orientation. The likelihood that the 0.3 μm particles of the HDDR-

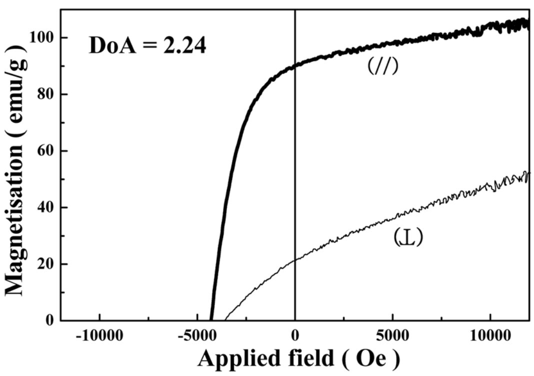

Fig. 5. Demagnetisation curves measured along the directions parallel and perpendicular to the aligning direction for the $Nd_2Fe_{14}B$ particles obtained from the HDDR-treated and roller-milled (12 h) $Nd_{15}Fe_{77}B_8$ alloy ingot.

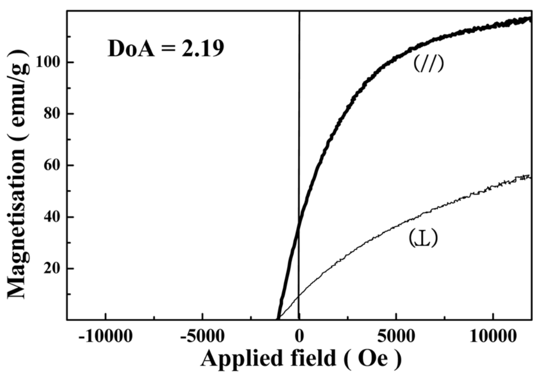

Fig. 6. Demagnetisation curves measured along the directions parallel and perpendicular to the aligning direction for the coarse $Nd_2Fe_{14}B$ single grain particles obtained from roller-milled (12 h) $Nd_{15}Fe_{77}B_8$ alloy ingot.

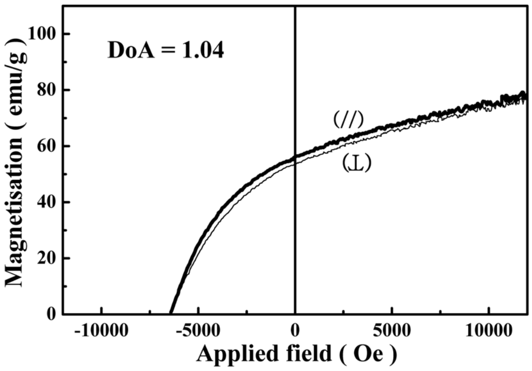

Fig. 7. Demagnetisation curves measured along the directions parallel and perpendicular to the aligning direction for the HDDR-treated and briefly milled $Nd_{15}Fe_{77}B_8$ alloy powder.

treated and roller milled powder are multigrain particles with a parallel crystallographic orientation is closely related to whether the fine grains in HDDR-treated material have texture. It is possible that the 0.3 μm particles would be in multigrain form if the HDDR-treated material has a $Nd_2Fe_{14}B$ grain texture and mechanical milling causes fractures in a trans-granular crack mode. The presence of $Nd_2Fe_{14}B$ grain texture in the HDDR-treated material was also examined by measuring the magnetic alignment. The HDDR-treated material was milled briefly for 2 min using a mortar and pestle. The resulting powder had a particle size of approximately 20-30 μm to ensure that the particle was a multi-grain particle. The particles were aligned under a magnetic field, and the demagnetisation curves along the different directions were measured. As shown in Fig. 7, the demagnetisation curves along the two different directions were similar, showing no alignment with DoA $\cong$ 1. This indicates that the fine $Nd_2Fe_{14}B$ grains in the HDDR-treated material are randomly oriented and have no texture. Therefore, the 0.3 μm particles of the HDDR-treated and roller milled powder are not in multi-grain form with the individual grains in a parallel crystallographic orientation. These results suggest that single domain particles of $Nd_2Fe_{14}B$ can be prepared from a Nd-Fe-B alloy ingot by combining a HDDR-process with mechanical milling.

4. Conclusion

In the HDDR-treated $Nd_{15}Fe_{77}B_8$ alloy the $Nd_2Fe_{14}B$ grains were reconstructed with very fine size comparable to the critical single domain size (0.3 μm). These fine individual grains were separated successfully along the grain boundary by roller-milling, and the separated $Nd_2Fe_{14}B$ grains were found to be single domain particles. This suggests that single domain particles of the $Nd_2Fe_{14}B$ phase can be prepared from a Nd-Fe-B ingot alloy using a combination of a HDDR-process and mechanical milling.

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