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# Study of the Enhancement of Magnetic Properties of NdFeB Materials Fabricated by Modified HDDR Process

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**The HDDR (Hydrogenation-Disproportionation-Desorption-Recombination) process is a special method to produce anisotropic NdFeB powders for bonded magnet. The effect of the modified HDDR process on magnetic properties of $Nd_2Fe_{14}B$-based magnet with several composition $Nd_{11.2}Fe_{66.5-x}Co_{15.4}B_{6.8}Zr_{0.1}Ga_x$ (x = 0~1.0) and that of microelement Ga, disproportional temperature and annealing temperature on $_jH_c$, grain size were investigated in order to produce anisotropic powder with high magnetic properties. It was found that modified HDDR process is very effective to enhance magnetic properties and to fine grain size. The addition of Ga could change disproportionation character remarkably of the alloy and could improve magnetic properties of magnet powder. Increasing annealing temperature induces significant grain growth. And grain size produced by modified HDDR process is significantly smaller than those produced by conventional HDDR process.**

**Key words :** $Nd_2Fe_{14}B$, Modified HDDR process, Magnet powder, Grain size, Coercivity

## 1. Introduction

The HDDR [1-3] (Hydrogenation-Disproportionation-Desorption-Recombination) process is well established as a special method to produce high anisotropic powder, which can be used for the production of $Nd_2Fe_{14}B$-based bonded magnet. The HDDR process can be interpreted as follows: The $Nd_2Fe_{14}B$ phase disproportionates into $NdH_{(2\pm x)}$, $\alpha$-Fe and $Fe_2B$ three phase during a heat treatment in hydrogen up to temperatures range from 650 to 900 °C [4]. During evacuation of the system, hydrogen desorbs, and the disproportionated mixture of Nd, $\alpha$-Fe and $Fe_2B$ recombines forming submicron grains of $Nd_2Fe_{14}B$ with an average grain size of about 0.3 $\mu$m [5]. While Takeshita [5] and some authors thought that the addition of Co, Zr and Ga is necessary to produce anistropic NdFeB permanent magnet powder, Nakamura [6] and other authors have shown that anistropic powders can be prepared from the pure ternary alloy by adjusting the treatment conditions. This shows that not only additives, but also the treatment conditions are important in obtaining anisotropic powder.

In this work, two different techniques, the conventional HDDR process and the modified HDDR process (i.e., low vacuum dehydrogen treatment was appended between HD stage and high vacuum dehydrogen stage) have been used in order to illustrate the influence of microelement Ga on $_jH_c$, grain size and disproporational temperature of $Nd_2Fe_{14}B$-based anistropic magnet powder, and that of modified HDDR process on magnetic properties of $Nd_2Fe_{14}B$-based magnet powder with several compositions.

## 2. Experimental Procedures

The compositions of the studied alloys were $Nd_{11.2}Fe_{66.5}Co_{15.4}B_{6.8}Zr_{0.1}$ (1# alloy), $Nd_{11.2}Fe_{66.4}Co_{15.4}B_{6.8}Zr_{0.1}Ga_{0.1}$ (2# alloy), $Nd_{11.2}Fe_{66.2}Co_{15.4}B_{6.8}Zr_{0.1}Ga_{0.3}$ (3# alloy), $Nd_{11.2}Fe_{66.0}Co_{15.4}B_{6.8}Zr_{0.1}Ga_{0.5}$ (4# alloy) and $Nd_{11.2}Fe_{65.5}Co_{15.4}B_{6.8}Zr_{0.1}Ga_{1.0}$ (5# alloy). The alloys were induction melted using high purity elements and ferroalloys. To eliminate the $\alpha$-Fe dendritic crystal, these alloys were homogenized at 1100 °C for 20 h in an Ar atmosphere, and then were quenched to room temperature in the water. The as-cast materials were crushed and then were put into vacuum anneal furnace, and the hydrogen pressure of $1.5 \times 10^5$ Pa was introduced. Modified HDDR has been carried out at 750~850 °C. For disproportionation, the material was heated to 830 °C and the powder was held for 1~4 h. For Desorption and Recombination,

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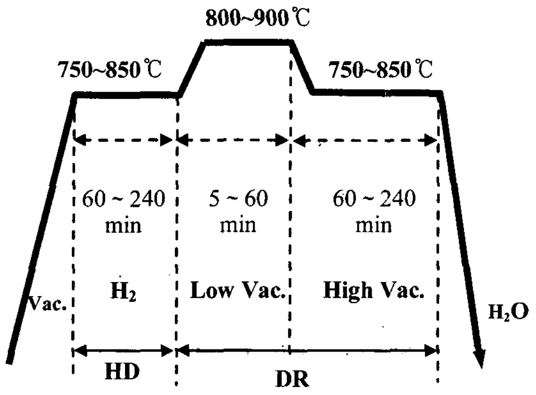


**Fig. 1.** Schematic diagram of modified HDDR process.

the material was held for 5~60 min at 800~900 °c in low vacuum, and then was held for 1~4 h at 750~850 °C in high vacuum, finally quenched with water to room temperature. Fig. 1 shows that modified HDDR process. The magnetic properties of all samples were measured using a PM32 high field pulse magnetometer with a maximum applied field of 6 T at room temperature. A theoretical density of 7.6 g/cm$^3$ was assumed for the materials. Structure of 4# HD alloy was investigated by X-ray diffraction (XRD) with Cu-K$\alpha$ radiation. Grain size was estimated from the XRD patterns using the Williamson and Hall method [7].

## 3. Results and Discussion

Published work [6] recently suggests that there are close relationship between magnetic properties of HDDR NdFeB material and desorption hydrogen partial pressure. And the perfect magnetic properties will be obtained with slow dehydrogen treatment. Fig. 2 shows relationship of low vacuum treatment time on $B_r$ and $_jH_c$ of 4# alloy. For modified HDDR, temperature of producing the magnet powder was 830 °C throughout the whole process. $B_r$ and

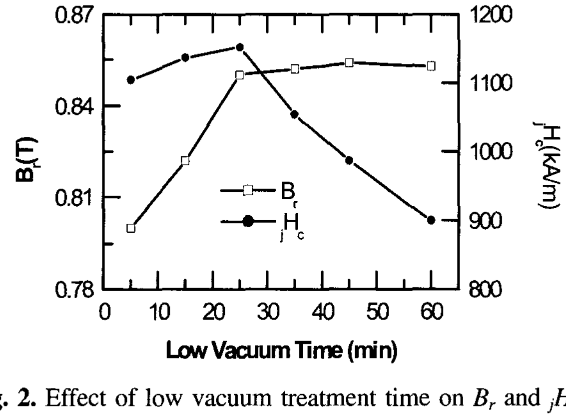


**Fig. 2.** Effect of low vacuum treatment time on $B_r$ and $_jH_c$ of 4# alloy.

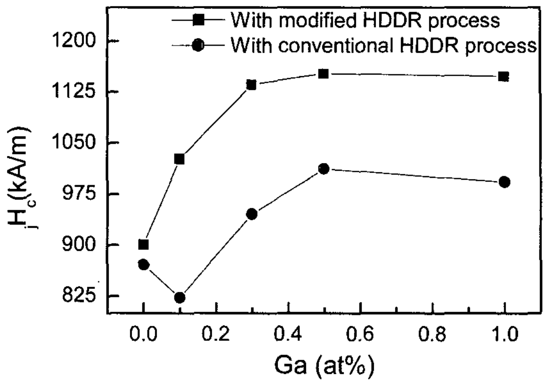


**Fig. 3.** Effect of Ga addition on $_jH_c$ of $Nd_{11.2}F_{66.5-x}Co_{15.4}B_{6.8}Zr_{0.1}Ga_x$ alloy.

$_jH_c$ of the powder depend on low vacuum treatment time closely. $B_r$ increases with low vacuum treatment time. On the other hand, $_jH_c$ increases first, and then decreases dramatically with low vacuum treatment time. These results show that the optimum low vacuum treatment time is about 25 min for 4# alloy. It is propitious to form and grow up for anistropic $Nd_2Fe_{14}B$ "memory cell" in thermodynamics because of slow dehydrogen. When desorption hydrogen partial pressure is low especially in critical, and it is also propitious to meliorate magnetic properties of NdFeB material. Slow dehydrogen cannot perform in thermodynamics when desorption hydrogen partial pressure is high, so magnetic properties of NdFeB material is bad.

Fig. 3 shows that the effect of Ga addition on $_jH_c$ of $Nd_{11.2}Fe_{66.5-x}Co_{15.4}B_{6.8}Zr_{0.1}Ga_x$ (x = 0~1.0) alloy in modified HDDR process and conventional HDDR process. The addition of Ga can improve magnetic properties of NdFeB material as observed. The modified HDDR process results in a much fine magnetic properties compared to those of the conventional HDDR process. There is a large difference in magnetic properties even between 2# alloy of low Ga additive and 1# alloy of without Ga additive. The additive of Ga make coercivity increase from 901 kA/m without Ga additive to 1152 kA/m with 0.5 at% Ga. The magnetic properties of magnet powder fabricated by conventional HDDR process obviously vary with microelement Ga additive. This additive can increase anisotropic field and decrease saturation magnetization, so $_jH_c$ increases.

Fig. 4 shows the effect of Ga additive on main phase grain size of $Nd_{11.2}Fe_{66.5-x}Co_{15.4}B_{6.8}Zr_{0.1}Ga_x$ (x = 0~1.0) alloy in modified HDDR process and conventional HDDR process. Average grain size of main phase of magnet powder produced by modified HDDR process decreases dramatically with increase of element Ga, which changes

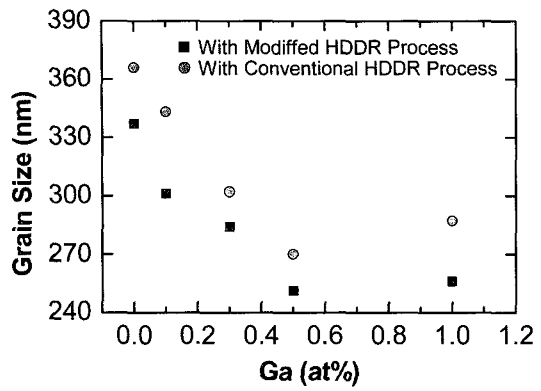


**Fig. 4.** Effect of Ga additive on main phase grain size of $Nd_{11.2}Fe_{66.5-x}Co_{15.4}B_{6.8}Zr_{0.1}Ga_x$ alloy.

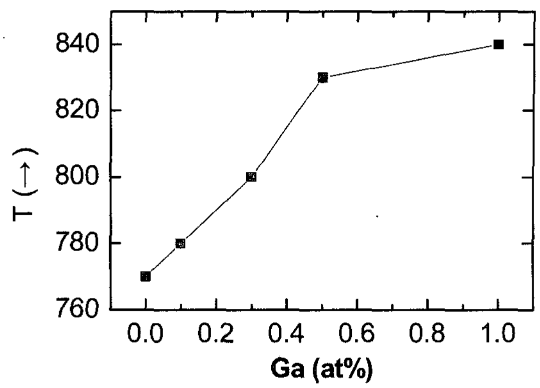


**Fig. 6.** Relationship of Ga additive to disproportionation temperature of $Nd_{11.2}Fe_{66.5-x}Co_{15.4}B_{6.8}Zr_{0.1}Ga_x$ (x = 0~1.0) alloy.

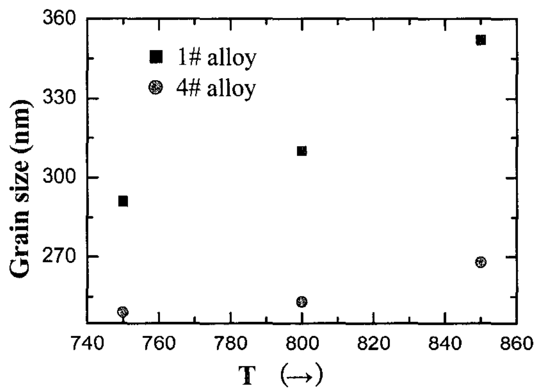


**Fig. 5.** Effect of annealing temperature on grain size of 1# and 4# alloy.

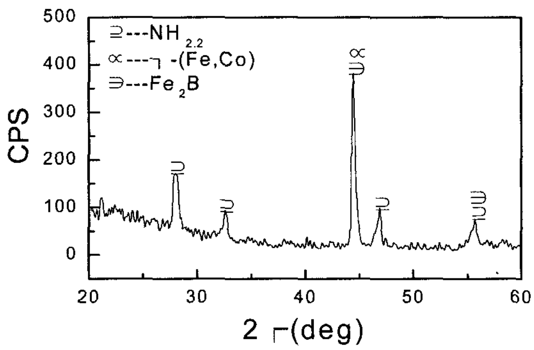


**Fig. 7.** X-ray diffraction patterns of 4# alloy HD stage.

from 337 nm without Ga additive to 251 nm with 0.5 at% Ga and 256 nm with 1.0 at% Ga. There are same disciplinarian between modified HDDR process and conventional HDDR process, but average grain size of the former is less than that of the latter. Fig. 3 and Fig. 4 shows that average grain size fined can increase magnetic properties of NdFeB alloy. Fig. 5 shows the effect of annealing temperature on average grain size of annealed powders in modified HDDR process. With increasing annealing temperature, grain growth is observed in 1# and 4# alloy, very markedly at temperature 850 °C. In these two cases, the without Ga-containing alloy exhibit a suppressed grain growth. After annealing at 750 °C, 1# and 4# alloy exhibit average grain size of 291 nm and 249 nm, respectively. And these increase to 352 and 268 nm after annealing at 850 °C, respectively.

Fig. 6 shows relationship of Ga additive to disproportional temperature of $Nd_{11.2}Fe_{66.5-x}Co_{15.4}B_{6.8}Zr_{0.1}Ga_x$ (x = 0~1.0) alloy. The disproportional temperature of these alloys increases with increase of Ga. It is 770 °C for 1# alloy, and 840 °C for 5# alloy. These indicate that Ga additive can change disproportionation character remarkably of the alloy and improve disproportional temperature. Fig. 7 shows XRD pattern of the disproportionated 4# alloy at 830 °C, showing the products of HD process: $NdH_2$, $\alpha$-(Fe,Co) and $Fe_2B$. Ga additive slackens $Nd_2(Fe,Co)_{14}BH_x$ decomposed into disproportional phase. Bushow [8] thought that the addition of Co, Ga and Zr stabilizes $Nd_2Fe_{14}B$ phase in hydrogen atmosphere and our works agree with it.

## 4. Conclusions

These investigations have shown that modified HDDR process is very effective to enhance magnetic properties of the powder and to fine grain size of main phase. $B_r$ and $_iH_c$ of the powder depend on low vacuum treatment time and the optimized low vacuum treatment time is 25 min. The modified HDDR process results in refined grain size and high $_iH_c$ compared to these of the conventional HDDR. The addition of Ga improves $_iH_c$ and reduces the grain size of the magnet powder, and changes the disproportionation character remarkably of the alloy and improves disproportional temperature. Significant grain growth can be observed with increasing annealing temperature.

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