Effect of DyH$_x$ addition on the magnetic properties and microstructure of Nd$_{14.1}$Co$_{1.34}$Cu$_{0.04}$Fe$_{68}$B$_{5.84}$ magnets

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Abstract. The sintered Nd$_{14.1}$Co$_{1.34}$Cu$_{0.04}$Fe$_{68}$B$_{5.84}$ permanent magnets with DyH$_x$ addition have been prepared by powder-blending technique. The magnetic properties and microstructures of the magnets were investigated. It was found that Dy element is enriched in the intergranular phase, being evenly distributed throughout the grain boundary and improving the orientation of magnets as a lubricant, and 1.2% to 2% DyH$_x$ additions are proved to be very effective in improving the permanent magnetic properties of Nd$_{14.1}$Co$_{1.34}$Cu$_{0.04}$Fe$_{68}$B$_{5.84}$ magnets. Further analysis revealed that the increase of coercivity and slight decrease of remanence due to DyH$_x$ addition can be attributed to the reduction of the primary phase volume, formation of the (NdDy)-rich phase and grain refinement of the main phase.

1. Introduction

The production and application of Nd-Fe-B magnets has an incredible growth in recent years. The development of material, process of production, exploration of higher quality of magnets and ultimate upper limits for permanent magnet properties are paid more and more attention to. It was reported that the energy product of Nd-Fe-B reached high up to 59.6MGOe[1]. Nd-Fe-B magnets with excellent properties, especially high-coercivity, are extensively applied to the field of permanent magnet motors. It was well known that the addition of heavy rare-earth element content in Nd-Fe-B system can be very effective to enhance the magnetocrystalline anisotropy field of 2:14:1 phase and thus high coercivity. However, based on the dramatically high cost of magnets, it is very important to develop highly coercive Nd-Fe-B magnets with low cost.

It is well known that the coercivity is strongly dependent on the microstructure of sintered Nd-Fe-B. The distribution of liquid phase as a thin layer separating the grains of the hard magnetic phase is considered a unique microstructure feature that brings significant enhancement in $H_c$. Besides, the sintering behaviour of sintered Nd-Fe-B magnets can be effectively improved by introducing the liquid phase. Many elements have been tried to modify the composition of grain boundary. However, these additives improve the coercivity at the expense of other magnetic properties such as $B_r$[2-4]. Dy or Tb is known to cause the significant improvement in $H_c$, which is attributed to the better distribution of the Nd-rich intergranular phase with the solubility of the additive element in it.

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However, because J_s of Dy_2Fe_14B and Tb_2Fe_14B compounds only equals to about half of the Nd_2Fe_14B's, the addition of Dy or Tb will lead to a sharp decline of J_s, thus resulting in the decrease of Br and (BH)_{max}. The perfect structure of this way is the heavy rear-earth distributing uniformly in the grain boundaries, and not substituting into the Nd sites of the main phase. Although researchers have attempted to achieve this structure for a long time, no way has been developed in efficiently condensing the heavy rear-earth near the grain boundaries [5, 6].

Our recent results show that the intergranular addition of metal hydrides is helpful in improving the coercivity without significant reduction of other properties (Br, α). In this paper, the Nd_{14.1}Co_{1.34}Cu_{0.04}Fe_{5.84}B_{5.84} magnets with different contents of DyH_x additives were prepared by means of the powder blending technique, and their structures, magnetic properties and magnetic orientation were investigated.

2. Experiment
The original alloy with nominal composition of Nd_{14.1}Co_{1.34}Cu_{0.04}Fe_{5.84}B_{5.84} (at %) is prepared by the strip casting (SC) technique, using the 99.9 wt% Nd, Co, Cu, Fe, and FeB alloy with 22.74 wt% B content as raw materials. The alloy strips are crushed into coarse powders with particle size about 10-100μm by HD technique. In the nitrogen atmosphere, the hydrogen powders are grinded into powders with an average particle size of 3.38μm through the jet milling. The different proportions of DyH_x (x=1-3) powders with the average size of 1.8μm are mixed, compacted under a magnetic field of 1800kA/m and isostatically pressed at 300MPa. The green compacts are sintered at 1040-1060°C for 2h in vacuum followed by gas quenching and then tempered at 900 and 500°C, respectively, for 2h.

The magnetic properties are measured using a magnetic measurement device NIM-500C. The microstructure investigations of the as-cast and homogenized samples are carried out using Hitachi TM-1000 Scanning Electron Microscope and Hitachi 4800 Field Emission Scanning Electron Microscope (FE-SEM). The grain orientation degree of sintered magnets is studied by Bruker D8 Advance Diffractometer X-ray diffraction (XRD) with Cu Kα radiation.

3. Results and discussion
The sintering function and the gas pressure character in vacuum sinter process are shown in figure 1. It can be seen that large amounts of gas are released in the low temperature stage of 300 - 800°C, attributing to the release of hydrogen from the alloy. The gas pressure peaks have been associated with hydrogen desorbing from the main phase and the intergranular phase with DyH_x addition, same as desorption stage in HD process [7]. Besides, the sintering environment keeps high vacuum in the sintering temperature. And the residual hydrogen content of magnets after the sinter process was less than 60ppm. Thus, this powder blending technique with DyH_x addition can effectively avoid the deterioration in the magnetic properties of the final magnets owing to the residual hydrogen, and ensure the Dy element diffusing uniformly in the grain boundary.

![Figure 1](image-url)
The magnetic properties of the sintered magnets, with different proportions of DyHₓ powder, are shown in figure 2. It can be seen that, with the increase of DyHₓ, the coercivity increases and the remanence as well as the energy product decreases monotonously. When the addition of DyHₓ is between 1.2-2 wt%, the DyHₓ additives result in a considerable increase of \( H_{\text{c}} \), without significant reduction of \( B_{r} \) and \( (BH)_{\text{max}} \). When the DyHₓ additions are added up to more than 2 wt%, the remanence together with the magnetic energy product is dramatically reduced.

![Figure 2. Variation of magnetic properties as a function of DyHₓ additions](image)

The SEM images of the magnets with 0.2 wt% and 3 wt% DyHₓ additions are shown respectively in figure 3(a) and 3(b). The result indicates that a very uniform Dy distribution along the grain boundary is observed in the magnet with 0.2 wt% DyHₓ addition, as presented in figure 3(a). However, there exist some large pieces of agglomerate phase accompanied by some grains of main phase in the magnets with 3 wt% DyHₓ additions, in accordance to the observation of X M Li et al. [8] where the excess RE-rich phase reunion in the grain boundary cross-corner and an appropriate amount of RE-rich phase can be better diffuse to the grain boundary precipitates.

![Figure 3. Microstructures of magnets, with 0.2%wt DyHₓ additions (a) and 3%wt DyHₓ additions (b) (image)]

Figure 4 shows the EDX results of the areas of grain boundary and grain for magnet with 2 wt% DyHₓ additives. It is seen that the additive Dy element presents in the grain boundaries, and no Dy is found in main grains. According to Ref. [9], Dy element can increase the coercivity and decrease both the remanence and the energy product due to a higher magnetic crystalline anisotropy and lower saturation magnetic polarization of Dy₂Fe₁₄B. Here, the Dy element is only distributed in grain boundaries and thus the magnetocrystalline anisotropy field of 2:14:1 grain surface is increased. This
prevents the nucleation of magnetization reversal domain and effectively improves the coercivity, similar to that observed by F Vial et al. [10]. At the same time, Dy has not entered the main phase grains and the Nd$_2$Fe$_{14}$B phase accordingly keeps its high saturation magnetization, so the values of Br and (BH)$_{\text{max}}$ should not decrease.

The preferred orientation or crystallographic alignment of final magnets has been studied by the x-ray diffraction. Endoh et al. [11] indicated that the crystal alignment degree of the anisotropic sintered Nd-Fe-B magnet can be qualitative described by (006) and (105) diffraction peak intensity ratio $A = I(006)/I(005)$. The increasing relative intensity of the (006) and (105) peaks reveals the improvement of the degree of crystal alignment. Figure 5 shows the x-ray diffraction patterns of the sintered magnets, with various proportions of the DyH$_x$ additions. The result demonstrates that the orientation of magnets is obviously improved with increasing the content of DyH$_x$ additives, which can be attributed to the addition of DyH$_x$ that plays a role as a grain boundary lubricant at the initial stage of pressing process and the easy c-axis of the powders that is aligned more easily with the increase of intergranular additions.
From the above results, it is clear that the intergranular additions do not enter into the interior of grains, but distribute in the grain boundaries as an intergranular lubricant. According to the viewpoint of Y Matsuura[1], the intrinsic coercivity of Nd-Fe-B sintered magnet decreased with the improvement of grain orientation. When more than 1.2 wt % DyH₃ powders are added in the magnets, the uptrend of the coercivity slows down due to the improvement of grain alignment. The hard magnetic phase is diluted by the intergranular additions, leading to the slight decrease of both remanence and maximum energy product.

4. Conclusions

The addition of DyH₃ powder is an effective way to enhance the coercivity of Nd-Fe-B type magnets with the slight decrease of remanence. When entering the intergranular phase, the Dy element is evenly distributed throughout the grain boundary, eventually forming (NdDy)-rich phase and refining the grain of main phase. The coercivity of Nd-Fe-B magnets can be enhanced by the addition of DyH₃ in the form of the fine powder before the sintering process. The coercivity significantly increases with the increasing of the DyH₃ addition. Besides, the intergranular addition as a grain boundary lubricant forming at the initial stage of pressing process induces the easy c-axis of the grains more easily aligned and thus almost keeps the remanence constant.

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