The preparation of sintered NdFeB magnet with high-coercivity and high temperature-stability

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Abstract. The NdFeB magnets with high intrinsic coercivity have been produced by using the conventional powder metallurgy method (including SC, HD and JM) of sintered NdFeB magnets. The effects of grain boundary phases on the microstructure and magnetic properties of as-sintered and annealed magnets have been tried to investigate. Also the Curie temperature of the magnets was studied. By adopting suitable component ratio of some heavy rare-earth atoms and some micro-quantity additives, we have prepared high-coercivity sintered NdFeB magnets with magnetic properties of $H_c=36.3\text{kOe}$, $B_r=11.7\text{kGs}$ and $(BH)_{max}=34.0\text{MGOe}$. The temperature coefficient of residual magnetic flux of the magnets (between 20 and 200°C) is $-0.113\%/\text{°C}$, while the temperature coefficient of intrinsic coercivity $-0.355\%/\text{°C}$. The Curie temperature of the magnets is about 342°C.

1. Introduction
NdFeB magnets have been employed into various applications because of their excellent magnetic properties, since they were discovered by Sagawa [1]. In recent years, there is a trend of permanent magnet motors replacing traditional motors, because they have high efficiency and can run on lower energy. The NdFeB magnets with excellent properties have extended the applications in the field of motors such as Hybrid Electric Vehicles and Electric Vehicles. Therefore, the sintered NdFeB magnets with high coercivity have much appeal for the scientists and engineers. In order to attain high coercivity of sintered NdFeB magnets, various methods have been employed. The intrinsic coercivity can be obviously increased by adding heavy rare-earth elements [2-3]. The elements Al and Cu with a low melting point mainly affect the wetting behavior of the RE-rich phase, and can modify the boundaries phase. Subsequently, they can increase the intrinsic coercivity [4-5]. At the same time, permanent magnet motors often work at high temperature, even to 200°C. So there is a requirement of high temperature-stability for the sintered NdFeB magnets to ensure high efficiency of the motors. By adding Co atoms, the high Curie temperature and high temperature-stability of the magnets can be obtained [6-7]. In this paper, we adopted suitable component ratio of heavy rare-earth elements and some micro-quantity additives, and adjusted optimized processing parameters. The sintered NdFeB magnets with high-coercivity and relatively high temperature-stability have been produced eventually.
2. Experimental

The alloy with nominal composition of Nd$_{1.13}$Fe$_{8.67}$Tb$_{0.61}$Dy$_{0.61}$Co$_{1.12}$Zr$_{0.14}$Al$_{0.49}$Cu$_{0.24}$B$_{6.07}$ (at.%) was produced by the strip casting (SC) technique from industrial grade raw materials with purity above 99.5%. The strips were employed in hydrogen decrepitation (HD) into coarse fragile particles. These coarse particles were then sent into jet milling (JM) procedure under a N$_2$ gas flow. The dry powder was compacted of 14 mm diameter and 15 mm height with the alignment made with the maximum 2 T magnetic field. This was followed by a cold isostatic pressing under a pressure of 300 MPa. The compacts were sintered in the vacuum of $10^{-3}$ Pa at the temperature of 1060-1090°C for 2-4 hours. The magnets were then rapidly quenched from the sintering temperature to room temperature under an over pressure of argon gas. Two step heat treatments were employed on the sintered magnets under the same vacuum of sintering procedure. A post heat treatment was made at 800-900°C for 2 h, including rapidly quench to the room temperature under the gas atmosphere of argon. And the low temperature annealing was made at 480-550°C for 2 h, followed by the same quenching techniques of the post heat treatment.

The microstructure of SC strips was observed by scanning electron microscope (TM-1000). And the size distribution of powder attained by JM was measured by laser diffraction particle size analyzer. The magnetic properties of the magnets at room temperature were measured with physical properties measurement system (PPMS) (Quantum Design Model-9). And the demagnetization curves at high temperature were measured after full magnetization under a pulsed magnetic field of 3 T, using the B-H measuring instrument.

In order to correlate the intrinsic coercivity with annealing processing and the microstructure of the boundary phase, the high-resolution field emission gun-scanning electron microscopy (FEG-SEM) was applied. All the test samples were prepared using as-sintered and two steps heat treatment. And the microstructure was investigated on cross sections perpendicular to the alignment direction.

The curves of magnetization depended on temperature for the sintered magnets were measured by VSM (Lakeshores 7410) with the magnetizing field of 1000Oe with temperature zone from room temperature (298K) to 1273 K.

3. Results and discussion

Figure 1(a) and 1(b) show the microstructure of the strips made at 500X and 10kX magnification, respectively.

![Figure 1](image)

**Figure 1.** The microscopy pictures of the SC strip with v(wheel speed)=1.7m/s.

Figure 1(a) indicates that a high uniform columnar grain of matrix phase has formed through the strips with the thickness between 0.2 and 0.3mm. From Figure 1(b), it can be seen that the matrix phases (RE$_2$Fe$_{14}$B) with the thickness between 4 and 6µm were obviously separated by the grain
boundaries of RE-rich phases with the thickness of 0.3-0.5µm. No alpha iron phase can be observed from the microstructure of SC strips. After procedures of strip casting and hydrogen decrepitation, the attained coarse particles were then sent into jet milling procedure. The average size of the powder produced by JM is about 3.60µm.

In order to verify whether the alpha iron is absent in the sintered magnets or not, we employed VSM to measure the magnetization of sintered NdFeB magnets dependent on temperature at the magnetic field H=1000Oe and under increasing temperature from 25-980°C applied on them. Also the Curie temperature of the magnet was easily obtained.

Figure 2 shows the curves of magnetization and dM/dT depended on temperature. The Curie temperature of the sintered magnet reaches a higher value of about 342°C than that of Nd2Fe14B (312°C). The additive cobalt atoms can enter the matrix phase to substitute for iron, and formed additional RE2(Fe, Co)14B during sintering process. The Curie temperature of cobalt (1403K) is higher than that of iron (1043K). Thereby, the Curie temperature can increase by about 11°C per at% cobalt, reported by R. S. Mottram et al. [6]. And additive Tb (or Dy) atoms are able to partially substitute into Nd sites in the matrix phase and form (Nd, Tb)2Fe14B (or (Nd, Dy)2Fe14B), which can also increase the Curie temperature of the magnets. The Curie temperature of the magnets can increase by about 30°C under the effect of the additive atoms substituting.

One can find a peak in M-T curve from 600-800°C, as shown in Figure 2. It indicates that some soft magnetic phase (α-Fe) may exist in the sintered NdFeB magnets. That may attribute to alpha iron dendrites in SC strips which attained under not optimized conditions. The soft magnetic phase plays a negative role on the intrinsic coercivity as well as the magnetic energy product [8]. Therefore, the sintered NdFeB magnets have some potential in both intrinsic coercivity and energy product when the strip casting technique has been improved.

The density of sintered NdFeB magnets is roughly 7.57 g/cm³. The magnetic properties were measured to investigate the influence of the annealing conditions on the coercivity of the demagnetizing loops. Also the demagnetization curves measured at difference temperature (room temperature, 100°C, 200°C) were conducted to investigate the temperature coefficient of residual magnetic flux α(BC) and intrinsic coercivity β(Hc).

Figure 3 shows the demagnetizing loops of as-sintered state and as-annealed state. We employed the vacuum sintering parameter of 2h at 1085°C, post heat treatment of 2h at 875°C, and dual heat treatment of 2h at 875°C and 2h at 515°C. The intrinsic coercivity increases from 28.2kOe to 33.1kOe after post annealing. And it exceeds 36kOe after dual heat treatment. The high coercivity of the
as-sintered magnets is attributed to the effects of Dy and Tb addition on the anisotropy field of the matrix phase of magnets. At the same time, the heavy rare-earth elements can be able to enter the grain boundaries, which may increase the nucleation field of sintered magnet and then make the intrinsic coercivity increase.

Figure 3. The demagnetization curves of the sintered magnets. a) as-sintered; b) post heat treatment; c) dual heat treatment.

Figure 4. The demagnetization curves of the magnets with dual heat treatment. a) room temperature; b) 100°C; c) 200°C.

Figure 4 shows the demagnetizing curves measured at difference temperature for the magnet annealed at both high and low temperature. Both the residual magnetic flux $B_r$ and intrinsic coercivity $H_c$ decrease with the temperature of circumstance increasing. According to Figure 4, the temperature coefficient of residual magnetic flux $\alpha(B_r)$ (20-200°C) is calculated as -0.113%/°C while the one of coercivity $\beta(H_c)$ -0.355%/°C.

The low temperature coefficients display a high temperature-stability of sintered magnets. And this may be due to the effect of temperature compensation for residual magnetic flux and magnetocrystalline anisotropy field for coercivity. The low temperature coefficient of $B_r$ may due to the effect of temperature compensation of heavy rare-earth elements as Tb and Dy. The compounds containing heavy rare-earth (Tb and Dy) have the positive temperature coefficient zone of $B_r$, in comparison to the compounds containing light rare-earth elements, such as Nd and Pr, with negative temperature coefficient zone [9]. Thereby, Tb (or Dy) atoms partially substituting into Nd sites could be able to compensate the negative coefficient of Nd$_2$Fe$_{14}$B, which result the lower temperature coefficient of residual magnetic flux. By adding the heavy rare-earth elements, the magnetocrystalline anisotropy field can be increased, which may result a slight decrease in coercivity with the temperature outside increasing in a certain extent of temperature. Because of all the reasons above, the temperature coefficient of coercivity may become to get lower. With the low temperature coefficient of $B_r$ and $H_c$, the temperature-stability of the sintered NdFeB magnets can be enhanced.

Trying to study the effect of annealing processing on the enhancement of magnetic properties, the microstructure of the sintered magnets was analyzed by FEG-SEM, which is a possible technique to detect the morphology of grain boundaries affected by heat treatment.

Figure 5 shows FEG-SEM images of sintered magnet made at 30KX magnification. Figure 5(a) corresponds to the as-sintered sample, in which the interfaces between grains seem not well defined and relatively discontinuous. Figure 5(b) corresponds to the sample after dual heat treatment at same magnification. The grain boundary phase of annealed sample looks more defined, continuous and clean compared to the as-sintered state. The annealing processing may modify the grain boundaries of the magnets into well defined, continuous and clean interfaces, which may result the increasing of intrinsic coercivity. Besides the change of morphology of grain boundaries, the diffusion and distribution of the elements affected by heat treatment may be another factor on coercivity.
There are some visible white inclusions in the RE$_2$Fe$_{14}$B phase, which is similar to the results reported by F. Vial et al [10]. The EDX shows that the visible spherical inclusions in the RE$_2$Fe$_{14}$B phase are RE-rich inclusions. These probably correspond to liquid of RE-rich caught in matrix phase during the re-crystallization processing.

4. Conclusions
Through appropriate processing conditions of traditional powder metallurgy of sintered NdFeB magnets, the magnet with high intrinsic coercivity was produced. After optimized heat treatment, the magnet with the nominal composition of Nd$_{11.13}$Fe$_{89}$Tb$_{2.67}$Dy$_{0.61}$Co$_{1.12}$Zr$_{0.14}$Al$_{0.49}$Cu$_{0.24}$B$_{6.07}$ (at.%) reached high coercivity with the value of 36.3kOe, which the energy product was 34MGOe. The temperature coefficients of residual magnetic flux and intrinsic coercivity (20-200°C) were about -0.113%/°C and -0.355%/°C, respectively.

The relation between the magnetic properties, especially the intrinsic coercivity, and heat treatment applied on the magnets of as-sintered state had been investigated. The analysis of microstructure of the magnet indicates that the intrinsic coercivity may be closely related to the morphology of grain boundary phases. The FEG-SEM technique may provide a method to detect the change of morphology of grain boundaries affected by heat treatment.

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