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Effects of intergranular phase and structure defect on the coercivity for the HDDR Nd–Fe–B bonded magnet

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Abstract. Based on the specific microstructure of HDDR (hydrogenation, disproportionation, desorption, recombination) grains, that the bivariate model concerning the anisotropy constant K_1' and exchange integral A_1' in defect region, which was put forward. Subsequently, the dependence of magnet coercivity on the intergranular phase thickness d and structure defect thickness r_0 was studied. The results showed that the coercivity, H_c, increases with increasing d, for the r_0, the anisotropy constant $K_1(0)$ and exchange integral constant $A_1(0)$ at the grain surface taking different values. While $K_1(0)$ and $A_1(0)$ are fixed, H_c enhances with increasing r_0 for the same d. On the contrary, for the fixed r_0 and d, H_c decreases with increasing $K_1(0)$ or $A_1(0)$. The calculated coercivity is in good agreement with experimental results given by others when d takes 1 nm, r_0 is in the rang of 2–5 nm, $A_1(0)$ and $K_1(0)$ change in the range of (0.6–0.7) of A_1 and K_1, respectively.

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Key words: bonded magnet, bivariate model, microstructure, coercivity

1 Introduction

For the Nd–Fe–B magnet, the magnetic structure parameters will be influenced by the structure defect at the grain boundary. Thus, the crystalline anisotropy constant K_1' the exchange integral constant A_1' and magnetization M_s' in the defect regions of grains are all different from their respective values in the inner part of grains. Usually, three parameters may all vary, and their respective variation laws are different from each other. Most investigators only considered the variation of magnetic structure parameter K_1', which is the main factor influencing the coercivity of magnet, and the other magnetic parameters (A_1',M_s') takes the normal values in the inner part of a grain, respectively. Kronmüller *et al.* [1–3] described

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the anisotropy of defect region by using $K_1' = K_1(\infty) - \Delta K / ch^2(r/r_0)$, where $K_1(\infty)$ is the first crystalline anisotropy constant, ΔK is the reduction anisotropy, r_0 is the defect thickness, and r is the distance to the grain surface. Gao *et al.* [4] used $K_1' = K_1(1-\exp[-(r/r_0)^2])$ to describe the anisotropy of defect region, where K_1' and K_1 are the anisotropy constant in the inner and boundary parts of a grain, respectively. Both of them investigated the magnetization reversal process and coercivity mechanism of sintered magnet. Liu *et al.* [5] investigated the demagnetization process and coercivity mechanism of HDDR (hydrogenation, disproportionation, desorption, recombination) Nd–Fe–B magnet, by adopting the negative index variation law to describe the anisotropy variation of defect region. Factually, due to the appearance of composition fluctuation and structure defect at the grain boundary, which leads to both crystalline anisotropy constant K_1' and exchange integral constant A_1' may different from their respective values in the inner part of a grain [6]. Theoretically, in order to build an actually simple model describing the microstructures at the grain boundary for the HDDR magnetic powders, then we proposed a bivariate model considering the crystalline anisotropy constant K_1' and exchange integral constant A_1' at the grain boundary region, and further studied the effects of intergranular phase thickness and structure defect thickness on the anisotropy and coercivity of HDDR Nd–Fe–B magnet.

2 Double variable model

The HDDR magnetic powder grain is about $0.2 \sim 0.3$ μm in diameter [7, 8], which is close to the size of a single magnetic domain of $Nd_2Fe_{14}B$ phase, such unique microstructure is between nanocrystalline magnet and sintered magnet. Liu *et al.* [5] considered that the grain boundary anisotropy was simultaneously influenced by the structure defect and exchange-coupling interaction. In this paper, proposed that the HDDR grain is a cubic grain with the edge of 0.3 μm, where the length of exchange-coupling is lex and structure defect thickness is r_0. (Supposed $r_0 > lex/2$, as shown in Fig. 1). And proposed that the intergranular phase is a non-magnetic phase, which distributes homogeneously around the grains. Due to small size of intergranular phase, thus, its thickness d is always smaller than both lex and $2r_0$. The presence of intergranular phase not only weakens the exchange-coupling interaction, but also reduces the region of structure defect at the grain boundary, which leads to the length of exchange-coupling interaction and structure defect thickness reduce from $lex/2$ to $(lex-d)/2$ and from r_0 to $(r_0 - d/2)$, respectively. Based on the different region influenced by the exchange-coupling interaction and structure defect, a grain can be divided the three parts. The center of intergranular phase is chosen as the origin of the coordinate of r. When $d/2 < r < (lex-d)/2$, the anisotropy is simultaneously influenced by the exchange-coupling interaction and structure defect. It is affected by the structure defect alone for $(lex-d)/2 < r < (r_0 - d/2)$. While $r > r_0$, it is not influenced by exchange-coupling interaction and structure defect, and is equal to the K_1 (the normal magnetocrystalline anisotropy constant in the inner part of a grain). Liu *et al.* [5] described the anisotropic variation of defect region by using the variation law of negative index square of r. Han *et al.* [9] pointed out that the variation of

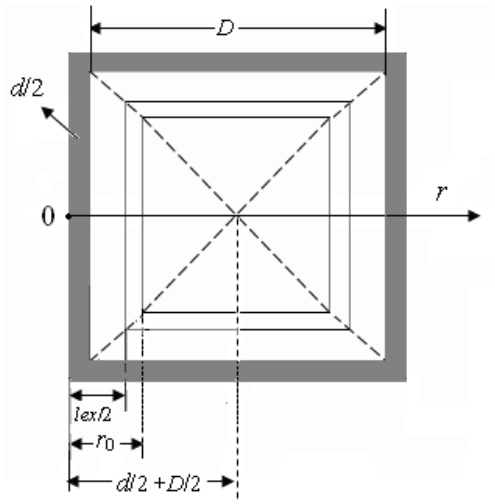

Figure 1: Sketch of a grain divided into three parts with different anisotropies in the case of $D/2>r0>lex/2$.

$K_1(2r/lex)3/2$ is similar to that of $K_1(1-\exp[-(2r/lex)2])$. For convenience, we used the form of $(2r/lex)3/2$ to describe the variations of $K_1(r)$. ($K_1(r)$ is the anisotropy of defect region). Due to the effect of structure defect of grain surface, the anisotropy constant $K_1(0)$ and exchange integral constant $A_1(0)$ at the grain boundary vary in the range of $(0\sim K_1)$ and $(0\sim A_1)$, respectively (K_1 and A_1 are normal values in the inner part of a grain). For simplicity, assumed that the variation law of A_1' is the same with that of K_1', and their variation laws can be expressed by Eqs. (1), (3) and Eqs. (2), (4), respectively.

When $r_0 \le lex/2$,

$$K_1'(r)=\begin{cases} 0, & 0\le r\le \frac{d}{2}, \\ K_1-\Delta K\left(1-\frac{2\left(r-\frac{d}{2}\right)^2}{\left(r_0-\frac{d}{2}\right)(lex-d)}\right)^{\frac{3}{2}}, & \frac{d}{2}<r<r_0, \\ K_1-\Delta K\left(1-\frac{2\left(r-\frac{d}{2}\right)^2}{(lex-d)}\right)^{\frac{3}{2}}, & r_0\le r\le \frac{lex}{2}, \end{cases} \tag{1}$$

$$A_1'(r)=\begin{cases} 0, & 0\le r\le \frac{d}{2}, \\ A_1-\Delta A\left(1-\frac{2\left(r-\frac{d}{2}\right)^2}{\left(r_0-\frac{d}{2}\right)(lex-d)}\right)^{\frac{3}{2}}, & \frac{d}{2}<r<r_0, \\ A_1-\Delta A\left(1-\frac{2\left(r-\frac{d}{2}\right)^2}{(lex-d)}\right)^{\frac{3}{2}}, & r_0\le r\le \frac{lex}{2}, \end{cases} \tag{2}$$

and when $r_0 > lex/2$,

$$K_1'(r) = \begin{cases} 0, & 0 \le r \le \frac{d}{2}, \\ K_1 - \Delta K\left(1 - \frac{2\left(r-\frac{d}{2}\right)^2}{\left(r_0-\frac{d}{2}\right)(lex-d)}\right)^{\frac{3}{2}}, & \frac{d}{2} < r < \frac{lex}{2}, \\ K_1 - \Delta K\left(1 - \frac{r-\frac{d}{2}}{r_0-\frac{d}{2}}\right)^{\frac{3}{2}}, & \frac{lex}{2} \le r \le r_0, \end{cases} \tag{3}$$

$$K_1'(r) = \begin{cases} 0, & 0 \le r \le \frac{d}{2}, \\ A_1 - \Delta A\left(1 - \frac{2\left(r-\frac{d}{2}\right)^2}{\left(r_0-\frac{d}{2}\right)(lex-d)}\right)^{\frac{3}{2}}, & \frac{d}{2} < r < \frac{lex}{2}, \\ A_1 - \Delta A\left(1 - \frac{r-\frac{d}{2}}{r_0-\frac{d}{2}}\right)^{\frac{3}{2}}, & \frac{lex}{2} \le r \le r_0, \end{cases} \tag{4}$$

where r is the distance along coordination to the center of intergranular phase, $\Delta K = K_1 - K_1(0)$, $\Delta A = A_1 - A_1(0)$.

3 Coercivity of HDDR Nd–Fe–B bonded magnet

Kronmüller *et al.* [1] regarded the grain boundary as the plane defect pinning the domain wall. Supposed the grain boundary defect is made up atom layers of n, the distance between the adjacent layers is d, and each inter-layer with the same magnetic property, then the coercivity is expressed as follows

$$H_c = \frac{2K_1\pi r_0}{3\sqrt{3}J_S\delta_B'}\left(\frac{A_1}{A_1'} - \frac{K_1'}{K_1}\right) - N_{eff}M_S, \tag{5}$$

where A_1, A_1' and K_1, K_1' are the integral constants and anisotropy constants in the inner and boundary parts of a grain, respectively. $\delta_B' = \pi\sqrt{\pi/K_1}$ is the domain wall thickness. M_S and J_S are saturation magnetization and magnetic polarization intensity, respectively. r_0 and N_{eff} are defect thickness and effective demagnetizing factor, respectively.

For the HDDR Nd–Fe–B magnetic powders, except that the grain boundary defect may become the center position pinning the domain wall. Yue *et al.* [10] considered that the rich-Nd intergranular phase can also be regarded as the plane defect to hinder the domain wall movement. Thus, r_0 in the Eq. (5) should be rewritten as $d/2$ and thickness of anisotropy uneven regions, which is denoted by $\overline{r_0}$. Exchange integral constant is usually taken as $A = A'$, and K_1' takes the fixed value less than K_1 [1]. Based on our anisotropy model, Both A_1' and K_1' continuously change in the range of $(0 \sim A_1)$ and $(0 \sim K_1)$, respectively. For convenience, we use the average value of exchange integral constant and anisotropy constant $\langle A_1' \rangle$ and $\langle K_1' \rangle$ in uneven regions for the intergranular phase and anisotropy, to replace A_1' and K_1' regarded as

the fixed values in the Eq. (5), respectively. Consequently, Eq. (5) can be rewritten to be

$$H_c = \frac{2K_1\pi\overline{r_0}}{3\sqrt{3}J_S\delta_B'}\left(\frac{A_1}{\langle A_1'\rangle}-\frac{\langle K_1'\rangle}{K_1}\right)-N_{eff}M_S. \tag{6}$$

Due to the intergranular phase being non-magnetic phase, both the exchange integral constant and anisotropy constant are zero in the intergranular phase region. Then, $\langle A_1\rangle$ and $\langle K_1\rangle$ are mainly affected by the anisotropy of uneven regions, where $\langle A_1\rangle$ and $\langle K_1\rangle$ can be described as follows, respectively

$$\langle A_1'\rangle = \begin{cases} \frac{2}{lex}\left(\int_{\frac{d}{2}}^{r_0}\left(A_1-\Delta A\left(1-\frac{2(r-\frac{d}{2})^2}{(r_0-\frac{d}{2})(lex-d)}\right)^{\frac{3}{2}}\right)dr+\int_{r_0}^{\frac{lex}{2}}\left(A_1-\Delta A\left(1-\frac{2(r-\frac{d}{2})}{lex-d}\right)^{\frac{3}{2}}\right)dr\right), & r_0\le\frac{lex}{2}, \\ \frac{1}{r_0}\left(\int_{\frac{d}{2}}^{\frac{lex}{2}}\left(A_1-\Delta A\left(1-\frac{2(r-\frac{d}{2})^2}{(r_0-\frac{d}{2})(lex-d)}\right)^{\frac{3}{2}}\right)dr+\int_{\frac{lex}{2}}^{r_0}\left(A_1-\Delta A\left(1-\frac{(r-\frac{d}{2})}{r_0-\frac{d}{2}}\right)^{\frac{3}{2}}\right)dr\right), & \frac{lex}{2}<r_0, \end{cases} \tag{7}$$

$$\langle K_1'\rangle = \begin{cases} \frac{2}{lex}\left(\int_{\frac{d}{2}}^{r_0}\left(K_1-\Delta K\left(1-\frac{2(r-\frac{d}{2})^2}{(r_0-\frac{d}{2})(lex-d)}\right)^{\frac{3}{2}}\right)dr+\int_{r_0}^{\frac{lex}{2}}\left(K_1-\Delta K\left(1-\frac{2(r-\frac{d}{2})}{lex-d}\right)^{\frac{3}{2}}\right)dr\right), & r_0\le\frac{lex}{2}, \\ \frac{1}{r_0}\left(\int_{\frac{d}{2}}^{\frac{lex}{2}}\left(K_1-\Delta K\left(1-\frac{2(r-\frac{d}{2})^2}{(r_0-\frac{d}{2})(lex-d)}\right)^{\frac{3}{2}}\right)dr+\int_{\frac{lex}{2}}^{r_0}\left(K_1-\Delta K\left(1-\frac{(r-\frac{d}{2})}{r_0-\frac{d}{2}}\right)^{\frac{3}{2}}\right)dr\right), & \frac{lex}{2}<r_0, \end{cases} \tag{8}$$

Taking the intrinsic magnetic parameters of $Nd_2Fe_{14}B$: $K_1 = 4.3$ MJ/m^3, $A_1 = 7.7\times 10^{-12}$ J/m, $M_s = 1280$ kA/m [11], $J_s = 1.61$T [4], $lex = 4.2$ nm [12], $\delta_B = 4.2$ nm, N_{eff} taking 0.6 for the grain dimension of about (0.2∼0.3 νm) [13]. Based on the above equations and data, the average anisotropy at the grain boundary and coercivity can be calculated for r_0 and d ranging from 0 to 4 nm and from 0 to 3 nm, respectively, for the HDDR Nd–Fe–B bonded magnet.

4 Results and discussion

Fig. 2 shows the variations of anisotropy, $K_1'(r)$, at the grain boundary with r, when the grain defect thickness r_0 takes value of 3nm, surface anisotropy constant $K_1(0)$ and intergranular phase thickness d take different values. The results indicate that $K_1'(r)$ decreases rapidly with r after a slow decrease to r of 2.1 nm for different values of $K_1(0)$ and d. This is due to that both the structure defect and exchange coupling interaction make the anisotropy $K_1(r)$ decrease. And the anisotropy $K_1(r)$ is affected alone by the structure defect when r ranges between 2.1 nm and r_0. For r ranging from $d/2$ to 2.1 nm, The anisotropy $K_1(r)$ is simultaneously influenced by the structure defect and exchange coupling interaction. It is also owing to that $K_1'(r)$ influenced by one factor interaction decrease more slowly than it influenced by two factor interactions. Thus, $K_1'(r)$ decreases rapidly with r after a slow decrease to r of 2.1 nm. It can be also seen that the variation rate increases with increasing d for the $K_1'(r)$, when $K_1(0)$ takes fixed value. This is attributed to that the variable quantity $(K_1'K_1(0))$ is fixed for the $K_1'(r)$ in the anisotropic unevenly regions, the variation interval decreases with increasing d. For the fixed d, the variation rate decreases with increasing

$K_1(0)$ for the $K_1'(r)$. This is due to that the variation interval $[r_0-d/2,r_0]$ is fixed for the $K_1'(r)$ in anisotropic inhomogeneously regions, the variation quantity $(K_1-K_1(0))$ decreases with increasing $K_1(0)$ for the $K_1'(r)$.

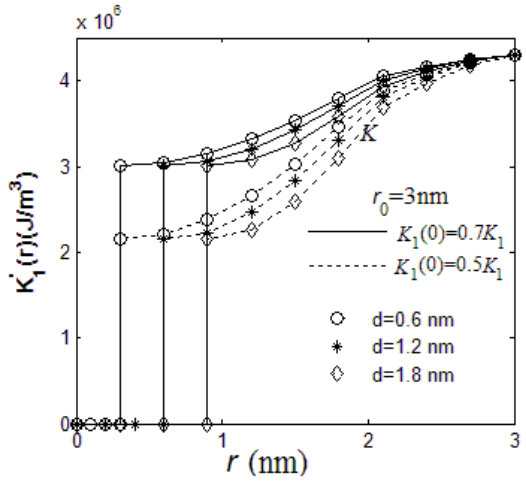

Figure 2: Variations of anisotropy, $K_1'(r)$, at grain boundary with r for fixed value r_0 and different values of $K_1(0)$ and d.

For $K_1(0)$ and r_0 taking different values, the effect of intergranular phase thickness d on the average anisotropy $\langle K_1'\rangle$ at the grain boundary is shown in the Fig. 3. The data show that $\langle K_1'\rangle$ decreases with increasing d, such variation discipline does not change owing to $K_1(0)$ and r_0 taking different values. This is attributed to that with increasing non-magnetic phase thickness, such variation rate of which $K_1'(r)$ with r, increases (as shown in Fig. 2). Fig. 3 also shows that for the fixed $K_1(0)$ and d, $\langle K_1'\rangle$ reduces with decreasing r_0. This is owing to that the variation quantity $(K_1-K_1(0))$ is fixed in anisotropy uneven regions, with decreasing r_0, the variation interval $[r_0-d/2,r_0]$ for the $K_1'(r)$ declines, which leads to the variation rate of $K_1'(r)$ with r gradually enhances, therefore, $\langle K_1'\rangle$ decreases. For the fixed r_0 and d, $\langle K_1'\rangle$ increases with increasing $K_1(0)$. This is due to that the variation interval $[r0-d/2,r0]$ is fixed, with increasing $K_1(0)$, the variation quantity $(K_1-K_1(0))$ reduces for the $K_1'(r)$. Thus, the variation rate of $K_1'(r)$ with r decreases, which causes $\langle K_1'\rangle$ increase.

Fig. 4 indicates that the dependence of coercivity H_c on the intergranular phase thickness d for $K_1(0)$, $A_1(0)$ and r_0 taking different values, respectively. It can be seen that H_c increases with increasing d for different values of $K_1(0)$, $A_1(0)$ and r_0. This is due to that with increasing d, the intergranular phase region that the domain wall walks through increases, therefore, the domain wall is pinned more sharply, the critical field of irreversible domain wall displacement is bigger, and thus the coercivity is higher. When $K_1(0)$ and $A_1(0)$ are fixed, the coercivity H_c enhances with increasing r_0 for the same value of d. This is attributed to that with increasing r_0, the defect region that the domain wall displacement goes through

increases for the fixed value of d, thus the domain wall is pinned more sharply, the critical field of irreversible domain wall displacement is bigger, and thus the coercivity is also higher. The data also show that for the fixed values of r_0 and d, the coercivity H_c enhances with decreasing $K_1(0)$ or $A_1(0)$. This is due to that the smaller $K_1(0)$ or $A_1(0)$, the variation rate of domain wall energy density or the perturbation of exchange coupling is bigger, thus the coercivity is higher. And the coercivity influenced by $A_1(0)$ ranging in $(0.5\sim0.7)$ A_1 changes more obviously than that influenced by $K_1(0)$ ranging in $(0.5\sim0.7)$ K_1. This result is consistent with that of Kronmüller *et al.* [1] pointing out the pinning that perturbation causes is bigger than that the exchange coupling generates.

Usually, the HDDR Nd–Fe–B magnet are prepared by the experiment with the intergranular phase of about 1nm in thickness [7], and their coercivity fluctuate between 700 kA/m and 1210 kA/m [8, 14, 15]. Based on the above analysis, the bigger of grain defect thickness r_0 and intergranular phase thickness d are, and the smaller of exchange integral constant $A_1(0)$ and anisotropy constant $K_1(0)$ are, the higher of coercivity is. But the bigger r_0 and d, and the smaller $A_1(0)$ and $K_1(0)$ will lead to the remanence reduce quickly, which will hinder the improvement of magnetic energy integral. Above analysis also indicated that the calculated coercivity is in good agreement with experimental results given by others when d takes 1 nm, r_0 is in the rang of (2∼5) nm, $A_1(0)$ and $K_1(0)$ change in the range of (0.6∼0.7) of A_1 and K_1, respectively. Therefore, it is necessary to have a strict control that the intergranular phase is about 1 nm in thickness, the defect thickness is equivalent to the domain wall thickness, and the exchange integral constant $A_1(0)$ and anisotropy constant $K_1(0)$ varies in the range of (0.6∼0.7) of A_1 and K_1, respectively, by reasonably adjusting the alloy's composition and technical process. Thus, the coercivity of magnet can be improved, in addition, the remanence will not reduce quickly. Thereby, the HDDR NdFeB magnet with high performance can be obtained.

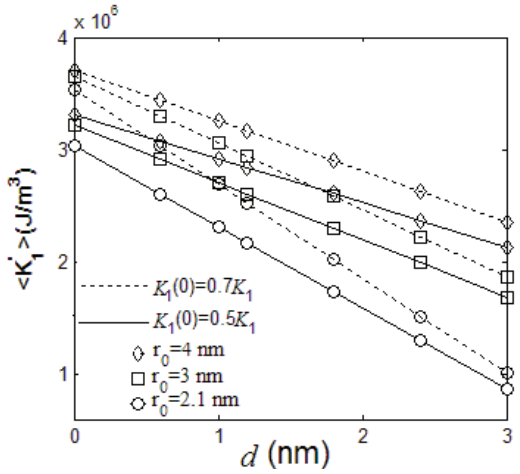

Figure 3: Dependence of average anisotropy $\langle K_1' \rangle$ on d for different values of $K_1(0)$ and r_0.

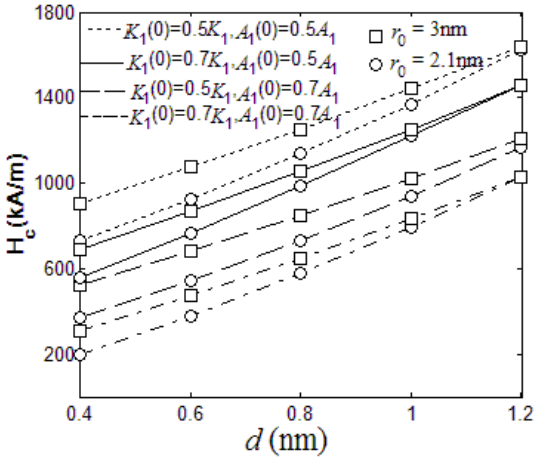

Figure 4: Variations of coercivity H_c with d for different values of $K_1(0)$, $A_1(0)$ and r_0.

5 Conclusion

Based on the unique microstructure of HDDR Nd–Fe–B magnetic powder grains, that the bivariate model concerning the anisotropy constant K_1' and exchange integral A_1' in defect region, which was put forward. The effects of intergranular phase thickness d and structure defect thickness r_0 on the coercivity of magnet were studied. The results showed that the average anisotropy $\langle K_1' \rangle$ decreases with increasing d when the anisotropy constant $K_1(0)$ at the grain surface and defect thickness r_0 take different values. When $K_1(0)$ and d are fixed, $\langle K_1' \rangle$ reduces with decreasing r_0. But for the fixed r_0 and d, $\langle K_1' \rangle$ enhances as $K_1(0)$ increases. For the coercivity, H_c, which increases with d increasing when $A_1(0)$, $K_1(0)$ and r_0 take different values. For $K_1(0)$ and $A_1(0)$ taking the fixed values, H_c enhances as r_0 increases for the same d. But for the fixed r_0 and d, H_c decreases with increasing $K_1(0)$ or $A_1(0)$. The calculated coercivity is in good agreement with experimental results given by others when d takes 1 nm, r_0 is in the rang of (2∼5) nm, $A_1(0)$ and $K_1(0)$ change in the range of (0.6∼0.7) of A_1 and K_1, respectively. Therefore, it is necessary to have a strict control that the intergranular phase is about 1 nm in the thickness, the defect thickness is equivalent to the domain wall thickness, and its exchange integral constant $A_1(0)$ and anisotropy constant $K_1(0)$ varies in the range of (0.6∼0.7) of A_1 and K_1, respectively, by reasonably adjusting the alloy's composition and technical process. Thus, the coercivity of magnet can be improved, in addition, the remanence will not reduce quickly. Thereby, the HDDR NdFeB magnet with high performance can be obtained.

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