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Micromagnetic simulation of the influence of grain boundary on cerium substituted Nd-Fe-B magnets

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A three-dimensional finite element model was performed to study the magnetization reversal of $(Ce_xNd_{1-x})_2Fe_{14}B$ nanocomposite permanent magnets. The influences of volume fraction, width and performance parameters of the grain boundary (GB) composition on the coercivity were analyzed by the method of micromagnetic simulation. The calculation results indicate that the structure and chemistry of GB phase play important roles in $Nd_2Fe_{14}B$-based magnets. An abnormal increase in the value of coercivity is found to be connected with the GB phase, approximately when the percentage of doped cerium is between 20% and 30%. While the coercivity decreases directly with the increase in cerium content instead of being abnormal when there is no GB phase in magnets at all or the value of magnetocrystalline anisotropy or exchange integral is too large. [http://dx.doi.org/10.1063/1.4972803]

I. INTRODUCTION

Since the advent of Nd-Fe-B magnets in 1980s,[1] it has become the most widely used rare earth permanent magnets, which is the key material for lots of equipments such as computer peripherals, vibratory motors, loudspeakers and so on.[2] However, due to the high price and short supply of neodymium (Nd), many researchers have attempted to substitute Nd by using the low cost rare earth metals.[3,4] Among all the rare earth elements, cerium (Ce) is the most abundant metallic element and its price is less than a third of Nd. As already shown by experimental investigations, the magnetic properties do not decrease monotonously with the increase of Ce proportion. Pathak *et al.* discovered the relatively high coercivity with 20%-30% Ce-substituted in $(Nd_{1-x}Ce_x)_2Fe_{14}B$ melt-spun ribbons.[5] Pei *et al.* also found an anomaly in coercivity at x = 0.24 in $[(Nd_4Pr)_{1-x}Ce_x]_{27}Fe_{72}B$ melt-spun powders.[6]

Because the magnetic properties of $Nd_2Fe_{14}B$-based magnets are extremely sensitive to their microstructures, especially the grain boundaries, understanding the microstructure-coercivity relationship is essential for developing high-performance magnets. Besides, since the Curie temperature, crystallization temperature and spin-reorientation temperature, which are affected by the main phases, decreases gradually with the increase of Ce proportion in $(Nd_{1-x}Ce_x)_2Fe_{14}B$, the unusual phenomenon of coercivity is more likely caused by grain boundaries rather than the main phases.[7,8] However, there are few reports or details about the structure change of Nd-Fe-B magnets with Ce substitution. In this article, the influences of microstructural and magnetic parameters of GB phase on magnets were studied by micromagnetism finite element method. The results agree with the experimental ones that there is an abnormal increase in the value of coercivity under certain conditions. By controlling the volume fraction and the performance parameters of GB phase, it is able to understand the magnetization reversal mechanism of dual main phases permanent magnets.

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II. SIMULATION METHOD

A. Theoretical background

Numerical method is an effective way to investigate the relationship between the macroscopic properties and the microstructures of modern permanent magnet materials.[9,10] The systematic study of magnetization state is based on the static micromagnetic theory.[11] The total magnetic Gibbs free energy (E_{tot}) consists of Zeeman energy (E_{ext}), magnetocrystalline anisotropy energy (E_{ani}), exchange energy (E_{exc}) and demagnetization energy (E_d):

$$E_{tot} = E_{ext} + E_{ani} + E_{exc} + E_d, \tag{1}$$

$$E_{tot} = \int \left\{ A \left[(\nabla \mathbf{m_x})^2 + \left(\nabla \mathbf{m_y}\right)^2 + (\nabla \mathbf{m_z})^2 \right] - K_1 \mathbf{m_z}^2 - \frac{1}{2}\mu_0 \mathbf{M} \cdot \mathbf{H_d} - \mu_0 \mathbf{M} \cdot \mathbf{H_{ext}} \right\} dV. \tag{2}$$

Where A is exchange constant, K_1 is anisotropy constant and V is total volume of magnetic material. A stable equilibrium state of magnetization distribution can be obtained by minimizing the total Gibbs free energy with respect to the direction cosines of the spontaneous polarization:

$$\mathbf{m} \times \mathbf{H_{eff}} = 0, \tag{3}$$

where $\mathbf{H_{eff}} = \frac{2A}{M_S}\nabla^2\mathbf{m} + \mu_0\mathbf{H_d} + \mu_0\mathbf{H_{ext}} - \frac{1}{M_S}\frac{\partial w_{ani}}{\partial \mathbf{m}}$, μ_0 is permeability of vacuum and w_{ani} is energy associated with magnetocrystalline anisotropy. Eq. (3) is the Brown equation, which describes the magnetic polarization parallel to the effective field.

B. Simulation model

The simulation was performed using the parallel finite element micromagnetics package Magpar and a more detailed description of this simulation method has been given in Ref. 12. Modeling and finite element mesh generation were achieved by a three-dimensional finite element grid generator Gmsh.[13]

The microstructure of the Ce substituted Nd-Fe-B magnet was created by the Voronoi tessellation. The intergranular layers were created by shrinking every grain with respect to its Voronoi generating point, which is called the GB phase. Fig. 1 shows the grain structure of $(Ce_xNd_{1-x})_2Fe_{14}B$ nanocrystalline magnet with nonideal grain boundaries. The model size is 200×200×200 nm^3 containing 100 irregularly shaped grains. The material parameters used for the calculation at room temperature are as follow:[14,15] for $Nd_2Fe_{14}B$, the anisotropy constant K_1 = 4.3 MJ/m^3, the saturation magnetization Js = 1.61 T, and the exchange integral A = 7.7 PJ/m; for $Ce_2Fe_{14}B$, K_1 = 1.5 MJ/m^3, Js = 1.17 T, and A = 5 PJ/m. The parameters of GB phase will be given in response to the different situations below.

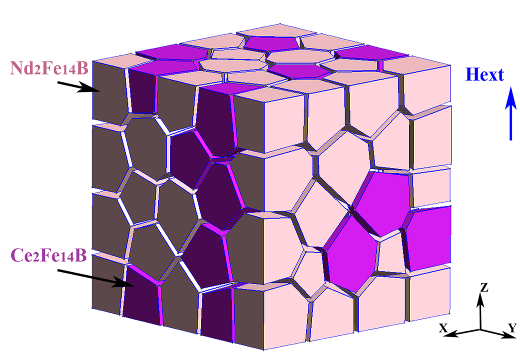

FIG. 1. The microstructure of the Ce substituted Nd-Fe-B magnet created by the Voronoi tessellation. The model consists of 100 irregular grains separated by GB phase. The $Nd_2Fe_{14}B$ grains are painted pink and $Ce_2Fe_{14}B$ grains are purple. The volume fraction of $Ce_2Fe_{14}B$ shown in this figure is 25%.

III. RESULTS AND DISCUSSION

A. Effect of the volume fraction (width) of GB phase

The simulations show that the structure and components strongly affect the magnetic properties. When the volume fraction of GB phase is 0%, 14%, 27% and 38%, the corresponding width is about 0 nm, 2 nm, 4 nm and 6 nm, respectively. The GB phase was considered an amorphous soft material characterized by $K_1 = 0$ MJ/m^3, A = 6.0 PJ/m and Js = 0.16 T. As illustrated in Fig. 2(a), the average magnetization, which is weighted by element volume, decreases with Ce substitution. The reason for the reduction could be correspondent to the soft phase exists in the space between the magnetic particles. Fig. 2(b) shows that a little additive amount of $Ce_2Fe_{14}B$ results in a dramatic drop of coercivity. It proves that the coercivity is abnormally sensitive to the Ce content, probably because the nucleation feature and mechanism are different. The ideal coherent rotation model according to Stoner and Wohlfahrt are replaced by decoupled model.[16] When the grains are contacted without any GB phases, the coercivity directly reduces with the increase of Ce addition. However, if the GB phase exists, the coercivity decreases firstly and then rises. After a peak at x = 0.25, the coercivity decreases gradually. It might be the distribution of the GB phase between the grains that led to the phase separation, which influence the nucleation of reversed domain and coercivity. A phase segregation phenomenon was predicted by Maxwell construction that a stable partially ordered phase emerges when x = 0.25 in $(Nd_{1-x}Ce_x)_2Fe_{14}B$, which is likely to be related to the abnormality.[17] Similar result was reported in Ref. 5. The coercivity is abnormally dependent on the soft phase content around 20%-30%Ce doped and it might be related to the grain boundaries, phase separation and intergranular rare earth-rich phases.

In ferromagnetic materials demagnetization processes are mainly determined by long range magnetostatic interaction and the exchange coupling interaction of neighboring grains, which sensitively depend on microstructural properties. Fig. 3 presents magnetization reversal pattern of two different

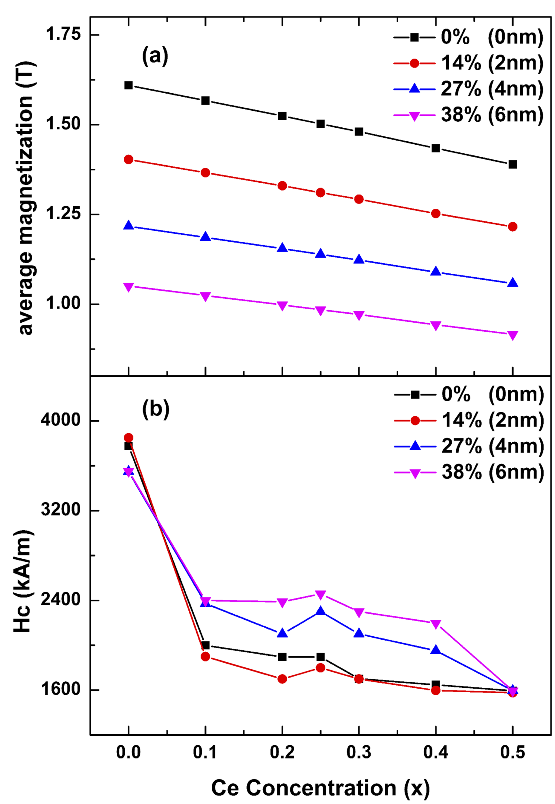

FIG. 2. The dependence of (a) average magnetization and (b) coercivity (Hc) on the Ce concentration with various volume fraction of GB phase.

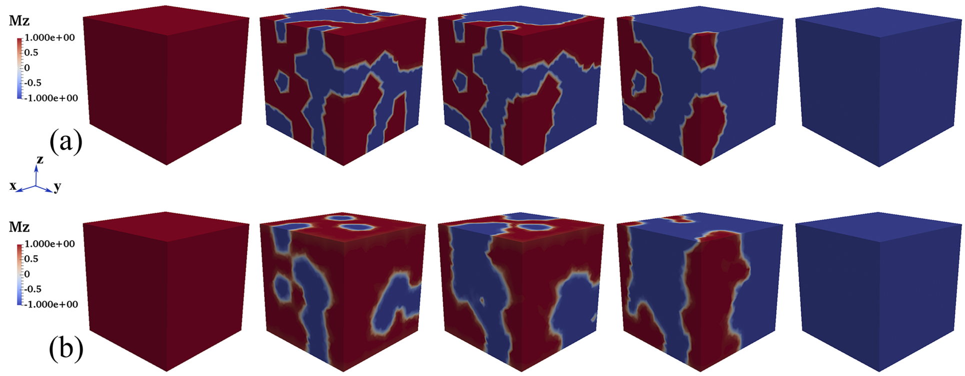

FIG. 3. Magnetization reversal patterns of $(Ce_xNd_{1-x})_2Fe_{14}B$ magnets in surface view for two different types of intergranular phase: (a) without any GB phase, (b) with 27% GB phase. The ratio for the percentage of hard phase and soft phase is 1:3 in each model.

simulation models in surface view. One has no GB phase (Fig. 3(a)) and the other has 38% GB phase (Fig. 3(b)), while the ratio for the percentage of $Nd_2Fe_{14}B$ and $Ce_2Fe_{14}B$ is 1:3 in each model. Mz is the z components of magnetization, which represents the magnetization state. The initial magnetization state (in the +z direction) is shown in red, and the reversed state (in the -z direction) is shown in blue.

At the beginning of the reversal processes, the reversed magnetic domains start to nucleate at the soft phase illustrated by the vector plots of the magnetization distributions. When the reverse domain expands to GB phase from $Ce_2Fe_{14}B$ grains, the GB phase play an important part of pinning to enhance the coercivity. And then the entire magnets reversed gradually. The features such as crystal structure, microchemistry, magnetic state or structural defects determine the performance of NdFeB-based magnets.[18] The above magnetization reversal patterns indicate that the main process for determining coercivity is the pinning of the reverse domains at grain boundaries.

B. Effect of the performance parameters of GB phase

The coercivity is dependent not only on the microstructure, but also on the intrinsic magnetic properties of GB phase. With a fixed volume fraction of GB phase, the exchange and anisotropy constants varies from their initial values. This setting allows one to investigate systematically the influence of material parameters of GB phase on demagnetization processes. As a result of Fig. 4(a), the curve of coercivity gradually rises with the decreasing of exchange constants due to the decoupling of GB phase. Obviously, owing to long range magnetostatic interactions decreasing with the exchange constants, the exchange coupling effected between the soft and hard phase is suppressed. Fig. 4(b) shows that the magnetization distribution is mainly determined by exchange interactions instead of the easy axes as the anisotropy constant of GB phase reduces. The smaller the anisotropy constants is, the more easily the external field can rotate the intergranular magnetic moments. Therefore, exchange coupling of GB phase is of crucial importance in double main phases system, which leads to a reduce of the coercive field.

In the figures above, different changes of coercivity are created by the variation of exchange and anisotropy constants. The coercivity generally rises with the reduction of the intergranular exchange interaction, and the effect of magnetocrystalline anisotropy is opposite. Whereas, the unusual phenomenon of coercivity both disappear when the value of magnetocrystalline anisotropy or exchange integral is too large. The abnormal dependence of coercivity is likely related to the physical properties and chemical composition of intergranular phase.[19] There are some experimentals which partially support this notion. The substitution of Ce into $Nd_2Fe_{14}B$ may seriously destroy the magnetocrystalline anisotropy at the grain boundaries and then decrease the nucleation field.[20] Huang *et al*[21] also found that the Ce element lowers the eutectic reaction temperature and improves the wetting characteristics in the sinter process. The GB phase becomes thicker since more liquid phase surround the

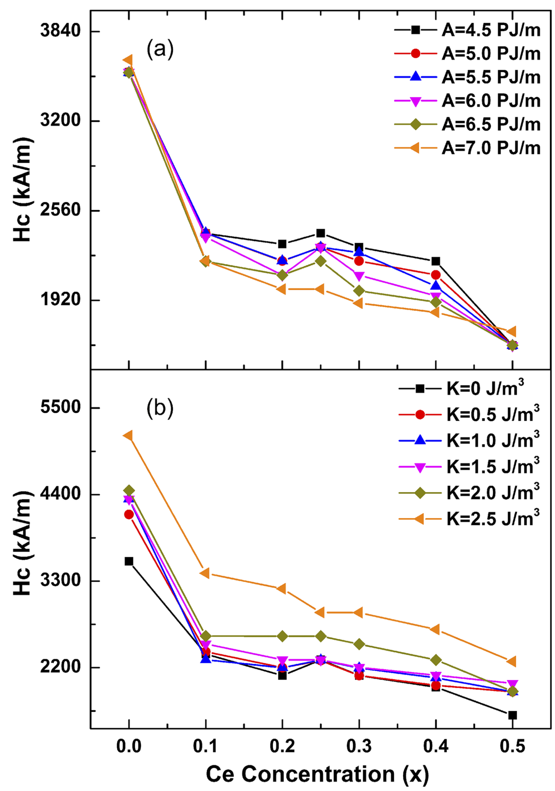

FIG. 4. The dependence of coercivity on the Ce Concentration for different exchange integral (A) and magnetocrystalline anisotropy constant (K) of GB phase. The volume fraction of GB phase used here is 27%.

hard phase, which would enhance the coercivity by reducing the interfacial bond strength, providing a partial compensation for the loss of coercivity caused by the soft phase.

IV. CONCLUSION

By building the model of random distribution of two phase grains, this paper presents a treatment of the correlation between the GB phase and the magnetic properties. It is proved that the chemistry and crystal structure of the boundary phases play a decisive role for the abnormalities of coercivity in Nd-Ce-Fe-B magnets. As a result of the existence of GB phase, the coercivity is relatively high with an appropriate Ce concentration, approximately when the replacement of Nd by Ce is 20% to 30%. While the phenomenon becomes less significant or even disappeares when there is no GB phase or exchange and anisotropy constants of GB phase are too large. The simulation results indicate that the GB phase is one of the reasons why there is an abnormal increase in the value of coercivity. The investigation for multiple particles configurations emphasizes the important role of GB phases for the enhancement of coercivity, which will promote the composition design and manufacture in preparing high abundant rare earth magnets. It is also expected that these investigations could serve as a reference for the research of sustainable nanoscaled permanent magnets.

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