Research Article

2D Simulation of Nd₂Fe₁₄B/ α -Fe Nanocomposite Magnets with Random Grain Distributions Generated by a Monte Carlo Procedure

Nguyen Xuan Truong, Nguyen Trung Hieu, Vu Hong Ky, and Nguyen Van Vuong

Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Ha Noi 10000, Vietnam

Correspondence should be addressed to Nguyen Van Vuong, vuongnv@ims.vast.ac.vn

Received 17 May 2012; Accepted 1 July 2012

Academic Editor: Yi Du

Copyright © 2012 Nguyen Xuan Truong et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The magnetic properties of Nd₂Fe₁₄B/ α -Fe nanocomposite magnets consisting of two nanostructured hard and soft magnetic grains assemblies were simulated for 2D case with random grain distributions generated by a Monte Carlo procedure. The effect of the soft phase volume fraction on the remanence B_r , coercivity H_c , squareness γ , and maximum energy product $(BH)_{\max}$ has been simulated for the case of Nd₂Fe₁₄B/ α -Fe nanocomposite magnets. The simulation results showed that, for the best case, the $(BH)_{\max}$ can be gained up only a several tens of percentage of the origin hard magnetic phase, but not about hundred as theoretically predicted value. The main reason of this discrepancy is due to the fact that the microstructure of real nanocomposite magnets with their random feature is deviated from the modeled microstructure required for implementing the exchange coupling interaction between hard and soft magnetic grains. The hard magnetic shell/soft magnetic core nanostructure and the magnetic field assisted melt-spinning technique seem to be prospective for future high-performance nanocomposite magnets.

1. Introduction

The preparation of nanocomposite magnets containing simultaneously both soft and hard magnetic phases is an advanced technology that can enhance maximum energy product $(BH)_{\max}$ twice and thus keeps further the tendency of the permanent magnet development which was going on over last 30 years.

In principle, for the case of nanocomposite magnets, by choosing the soft magnetic phase which has the saturation magnetization, J_s^s , higher than that of the matrix of the hard magnetic phase, J_s^h , the higher total saturation magnetization, J_s , can be achieved. Besides, for this nanocomposite magnet, the related magnetic moment reversal mechanism, which can provide the total magnetic remanence value, B_r , larger than that of the pure hard magnetic phase, B_r^h , should be taken in to account. Thus, the suitable nanostructured microstructure of the nanocomposite magnet consisting of the soft and hard magnetic phases can be obtained by controlling the magnet microstructure with regards to the

related moment reversal mechanism. In this ideal case, the coercivity H_c of the nanocomposite magnet can be remained while the maximum energy product $(BH)_{\max}$ can be enhanced up to the upper limit of $(B_r)^2/4\mu_0$.

The theory for one dimension case [1] has explained this enhancement by accounting the hardening process of fine soft magnetic particles that occurred under the exchange coupling of hard magnetic grains. This theory requires the soft magnetic grain size to be less than the critical value $\delta_{\text{cm}} = \pi(A_m/2K_h)^{1/2}$, where A_m is the soft magnetic phase exchange energy, and K_h is the hard magnetic phase anisotropy energy with $A_m = 10^{-11}$ J/m and $K_h = 2.10^6$ J/m³, respectively, for α -Fe and Nd₂Fe₁₄B.

Numerous theoretical works [2–5] have shown the ability of obtaining a large value of $(BH)_{\max}$ for modeled regular nanostructured configurations. However, up to date, the experimental studies reported that the $(BH)_{\max}$ value is still less than 200 kJ/m³ [6–20].

This paper presents 2D simulation of Nd₂Fe₁₄B/ α -Fe nanocomposite magnets by using Monte Carlo method. The

FIGURE 1: (a) The soft magnetic grains (red) are randomly distributed in the hard magnetic phase matrix (white). (b) Some sets of closed three and more soft magnetic grains (yellow) will be replaced by the one new grain with the area conservation rule. The blue parts are the parts of the soft magnetic particles hardened under the exchange coupling interactions.

TABLE 1: Magnetic parameters of hard grains, soft grains, and soft grains which are hardened under the exchange coupling interactions.

Type of grains	Saturation magnetization J_s (T)	Remanent magnetization J_r (T)	Coercivity iH_c (kA/m)	Coercivity bH_c (kA/m)	Squareness γ	Energy product $(BH)_{\max}$ (kJ/m ³)
Parts of hard magnetic grains	1.61	1.3	960	880	0.92	300
Parts of soft magnetic grains	2.15	1.978	0.0	0.0	—	0.0
Parts of soft magnetic grains which are hardened under the exchange coupling interaction	1.61	1.3	960	880	0.92	300

simulation results allow to find out the answer how difficult to prepare the high quality nanocomposite magnets. The paper also suggests the way to get high quality hard/soft magnetic two-phase nanostructure by using an external magnetic field to assist the formation of this structure.

2. 2D Simulation Algorithm

Considering the case of which the soft magnetic α -Fe grains are randomly dispersed into a two-dimensional (2D) magnet with sizes a , b of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase as presented in Figure 1. The number of the soft magnetic grains is suggested to be large enough to apply Gaussian function to their grain size distribution.

The simulation algorithm is as follows.

- (i) Using the special random number generator with Gaussian statistics [21] to “spray” the assembly of the soft magnetic α -Fe grains (with the mentioned Gaussian distribution function) and the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix to build up $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha$ -Fe nanocomposite microstructure.
- (ii) Inspecting all the soft magnetic grains. If three or more grains are placed closely with one another on the given distance ε , then they will be replaced by bigger grains with the effective diameter defined by the area conservation.
- (iii) The Monte Carlo probability bin of the hardening process of the soft magnetic grains is chosen on the basics of the Kneller-Hawig criterion [1]. It was

suggested that the exchange coupling interaction of the hard phase is expanded into the soft phase keeping continuously on the distance of order of the hard magnetic phase domain wall width δ_{cm} .

- (iv) In the common case, there are three kinds of grains: the origin hard magnetic grains, the original soft magnetic grains, and the hardened soft grains. Correspondingly, we have three types of the magnetization loops: the origin hard phase loop $J^h(H)$, the origin soft phase loop $J^s(H)$, and the loop $J^{hs}(H)$ of the parts of soft grains which are hardened under the exchange coupling with the hard grains. The loop $J^h(H)$ of $\text{Nd}_2\text{Fe}_{14}\text{B}$ is chosen with properties consequently observed in practice: $J_s^h = 1.61$ T, $J_r^h = 1.3$ T, $iH_c^h = 960$ kA/m, $bH_c^h = 880$ kA/m, squareness $\gamma = 0.92$, and $(BH)_{\max} = 300$ kJ/m³. The loop of hardened grains $J^{hs}(H)$ is suggested to have the intrinsic coercivity iH_c^h and the squareness γ like those of the hard magnetic phase. The remanence of the soft phase $J_r^s = \gamma J_s^s$ with $J_s^s = 2.15$ T is selected for the case of α -Fe. For clarity, the main magnetic properties of these three parts of grains are listed in the Table 1.

The total loop of the 2D nanocomposite magnet is then calculated by averaging all the loops with weighted factors of the volume fractions of three kinds mentioned above.

We present below the simulating results with $a = 80\delta_{\text{cm}}$, $b = 40\delta_{\text{cm}}$ and ε was taken to be equal $0.3\delta_{\text{cm}}$ with $\delta_{\text{cm}} = 5$ nm.

FIGURE 2: (a) The magnetization loops J^{hs} of the magnet (sky-blue) and J^h of the origin hard phase $Nd_2Fe_{14}B$ (red); (b) the demagnetization curves $J(H)$ (sky-blue), $B(H)$ (blue), and $(BH)_{max}$ curve (red) of the $Nd_2Fe_{14}B/\alpha$ -Fe magnet.

3. Results and Discussion

3.1. Exchange Coupling Nature. Simulation data proved the significant enhancement in magnetic properties of nanocomposite magnets in the case that a large total volume fraction of the magnets is occupied by the fine soft magnetic grains. The typical example is shown in Figures 2(a) and 2(b). In this case, the soft phase volume fraction is 33%, 700 α -Fe grains with the averaged particle size of 6.75 nm, and the half-width, σ , of the Gaussian distribution is 0.5.

The magnetization loop presented in Figure 2(a) shows the conventional single phase behavior, which corresponds to the fully hardening of all soft grains. The demagnetization curve together with the $(BH)_{max}$ versus the external magnetic field curve is shown in Figure 2(b). This magnet has the remanence $J_r = 1.46$ T and $(BH)_{max} = 370$ kJ/m³ that was enhanced by 12 and 23%, respectively, in comparison with ones of pure $Nd_2Fe_{14}B$ hard phase.

3.2. Effects of the Soft Magnetic Phase Volume Fraction on Magnetic Properties of the Nanocomposite Magnet. The dependence of magnetic properties on the soft magnetic phase volume fraction ξ is crucial for nanocomposite magnets. It is worthy to note that ξ is the function of two variables, the number and sizes of grains. For the same value of ξ , the number of grains and grain sizes can be different thus lead to the different option of implementing the Kneller-Hawig criterion, and thus lead to the dispersion of the magnetic properties of different samples prepared by different routes but with the same soft phase volume fraction. This behavior was observed in our simulation results.

The ξ -dependent magnetic properties are presented on Figure 3, and it shows clearly their complicated feature which can be summarized as follows.

- (1) A large dispersion of $(BH)_{max}$ is observed for $\xi > 20\%$. This phenomenon might be caused mainly by the dispersion of J_r (up to 10% of its maximum

FIGURE 3: The simulated dependence of $(BH)_{max}$ on the soft phase volume fraction ξ .

value), the dispersion of bH_c (7%), and the dispersion of iH_c (small, within 1% only).

- (2) The optimal value of ξ for the given simulated magnet is about 50%. For $\xi > 50\%$, all of the magnetic performances became worse.
- (3) For $\xi < 50\%$, the dashed curve presented in Figure 3 corresponds to the upper limit of the enhancements of the magnetic properties. So, for the given magnet, $(BH)_{max}$ can be gained up only 30% at $\xi = 50\%$.

3.3. The Dependence of Magnetic Properties on the Grain Size. Based on the Kneller-Hawig theory, it is clear that the quality of nanocomposite magnets depends mainly on the two parameters of the soft magnetic phase: volume fraction and grain size. The volume fraction must be large enough to increase the remanence, and the grain sizes must be small enough for strengthening the hardening process.

FIGURE 4: The effect of the soft phase grain size on (a) coercivity iH_c , (b) remanence J_r , and (c) $(BH)_{\max}$.

Figure 4 shows the dependence of the magnetic properties on the grain size D . The value of 40% of ξ was kept constant during the simulation, the other input data are the same as those mentioned in Section 3.1. It is interesting to note that, for the given configuration of the magnet, the intrinsic coercivity iH_c is nearly independent on the soft magnetic grain size. In contrast, the remanence J_r and the maximum energy product $(BH)_{\max}$ reach maximum values for $D < 2\delta_{\text{cm}}$ ($=10$ nm in this case) and linear dependent on the grain size in the range $D > 2\delta_{\text{cm}}$ (from 10 to 16 nm) with the slopes of -0.026 T/nm and -18.6 kJ/m³/nm, respectively.

4. The Hard Magnetic Shell/Soft Magnetic Core Nanostructure

The large dispersion observed in Figure 3 belongs to the random behavior of the distribution of soft magnetic grains

in the hard magnetic phase matrix which can form a large soft phase cluster. This effect is described in the second step of the given algorithm. In practice, the effect of increasing in randomness on soft magnetic grain size is closely related to interdiffusion of Fe/Co in the ball-milled Nd-Fe-B/ α -Fe or Sm-Co/ α -Fe systems. In melt-spun ribbons, this effect is raised up due to the splitting of the CCT (Continuous Cooling Transformation) curves of the soft and hard magnetic phases. In hot compacted nanocomposite magnets, this effect also relates to the soft phase interdiffusion process.

The effect of soft phase cluster formation disturbs the Kneller-Hawig criterion and diminishes the exchange coupling, making the nanocomposite magnet become a mixture of hard and soft phases with poor magnetic properties. To avoid this effect, one can use the nanocomposite structure of hard shell/soft core. In this configuration, the soft phase is confined inside the hard shell and the soft cluster cannot be formed. Moreover, under the protection of hard shell, instead

FIGURE 5: The $M(T)$ curve of the nanocomposite ribbon sample with the hard shell/soft core nanostructure. The sample was demagnetized thermally. The measuring magnetic field was 40 kA/m. The temperature was cycled between the room temperature and 600°C.

of being subjected to the external magnetic field, the soft core magnetization follows the magnetization of hard shell which allows keeping the coercivity of magnets at high values.

A technology which provides the hard magnetic shell/soft magnetic core is the magnetic field assisted melt-spinning technique [22]. For Nd-Fe-B/ α -Fe system, during the field assisted melt-spinning process, the α -Fe seeds are formed initially on the wheel surface, the hard magnetic Nd-Fe-B grains are then grown on the seed along the (001) direction and perpendicular to the ribbon free surface. As mentioned in [22], the magnetic field increases the energy inside the volume of seeds and thus decreases the critical size of seeds and, consequently, the average grain size.

In our experimental work, the hard magnetic shell/soft magnetic core nanostructure is realized by melt-spinning the alloy $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8 + 40 \text{ wt.}\% \text{ Fe}_{65}\text{Co}_{35}$ with an external magnetic field, $H_{\text{ex}} = 0.32 \text{ T}$. The dependence of the magnetization on temperature was measured in the magnetic field of 40 kA/m from T_{room} to 600°C and vice versa and is presented in Figure 5. During the heating stage, the hard magnetic shell protects the soft magnetic core from the external magnetic field and the magnetization of sample is increased gradually, reaching the maximum value at the Curie temperature of the Co-containing hard magnetic phase. After reaching 400°C, the hard magnetic shell is degraded totally and as a result, only the bare soft magnetic core is left but the magnetization is kept at the value around $2 \text{ A}\cdot\text{m}^2/\text{kg}$, then increased continuously and reached the saturation when T is reaching the T_c of the soft magnetic phase. By cooling from 600°C, the magnetization that existed inside the bare soft magnetic phase is increased normally until 395°C where the hard magnetic shell restores its own hard magnetic properties.

This hard magnetic shell/soft magnetic core realizes a good exchange coupling interaction that keeps the remanence about of 0.99 T, $iH_c \sim 675 \text{ kA/m}$, and $(BH)_{\text{max}} \sim 140 \text{ kJ/m}^3$ for the ribbon melt-spun at the speed of 30 m/s. The loops of prepared ribbons melt-spun at

different wheel speeds are presented in Figure 6(a). The hysteresis curve of optimal sample at $v = 30 \text{ m/s}$ is smooth, indicating the existence of an exchange coupling between the hard and soft magnetic phases. This obtained $(BH)_{\text{max}}$ value of 140 kJ/m^3 of our work is an encouraging result and approached to that reported by other research groups [6–20] while using a rather simple preparation method.

The simple calculation in the framework of the model of spherical soft core covered entirely by the hard shell showed that the upper limit of the volume fraction of the soft phase is about 60%. The thickness of the hard magnetic shell in this case reaches about 2 nm, the size of the superparamagnetic state for $\text{Nd}_2\text{Fe}_{14}\text{B}$. This value, 60%, is greater than the limit 50% mentioned above for the case of random distribution of hard and soft grains. Thus, it is quite reasonable to expect that the optimized magnetic field assisted melt spinning method is promising to prepare high performance nanocomposite magnets.

5. Conclusion

The magnetic properties of nanocomposite magnets have been simulated with random grain distributions generated by a Monte Carlo procedure. The simulation results for the case of $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ showed the ability of enhancing the magnetic performance of magnet. However, the enhancement is not crucial as predicted theoretically. For the tested magnet configuration, the maximum energy product $(BH)_{\text{max}}$ can be enhanced only by about 30% of the value of the origin $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase. The upper limit of $\alpha\text{-Fe}$ phase volume fraction is found to be about 50%, and beyond this value the $(BH)_{\text{max}}$ decreases abruptly. At the fixed values of the $\alpha\text{-Fe}$, the magnetic properties exhibit a large dispersion depending on the soft magnetic cluster formation. For further increase of $(BH)_{\text{max}}$ of nanocomposite magnets, it is suggested to use the hard shell/soft core nanostructure. This nanocomposite configuration with large

FIGURE 6: (a) The loops of the nanocomposite ribbons melt-spun at different wheel speeds, $v = 20, 25, 30$ m/s. (b) The $M(H)$ and $B(H)$ and $(BH)_{\max}$ of the high performance ribbon melt-spun at the optimal wheel speed 30 m/s.

soft phase volume fraction is suggested to be prepared by means of the magnetic field assisted melt-spinning technique.

Acknowledgment

This research is supported by Vietnam's National Foundation for Science and Technology Development (NAFOSTED), code: 103.02-2010.05.

References

- [1] E. F. Kneller and R. Hawig, "The exchange-spring magnet: a new material principle for permanent magnets," *IEEE Transactions on Magnetics*, vol. 27, no. 4, pp. 3588–3600, 1991.
- [2] R. Skomski and J. M. D. Coey, "Giant energy product in nanostructured two-phase magnets," *Physical Review B*, vol. 48, no. 21, pp. 15812–15816, 1993.
- [3] T. Schrefl and J. Fidler, "Modelling of exchange-spring permanent magnets," *Journal of Magnetism and Magnetic Materials*, vol. 177–181, no. 2, pp. 970–975, 1998.
- [4] H. Fukunaga and H. Nakamura, "Computer simulation of magnetic properties of anisotropic nanocomposite magnets," *IEEE Transactions on Magnetics*, vol. 36, no. 5, pp. 3285–3287, 2000.
- [5] J. Fidler, T. Schrefl, W. Scholz, D. Suess, R. Dittrich, and M. Kirschner, "Micromagnetic modelling and magnetization processes," *Journal of Magnetism and Magnetic Materials*, vol. 272–276, pp. 641–646, 2004.
- [6] Z. Chen, Y. Zhang, G. C. Hadjipanayis, Q. Chen, and B. Ma, "Effect of wheel speed and subsequent annealing on the microstructure and magnetic properties of nanocomposite $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ magnets," *Journal of Magnetism and Magnetic Materials*, vol. 206, no. 1, pp. 8–16, 1999.
- [7] G. Mendoza-Suárez, J. I. Escalante-García, J. López-Cuevas, G. Vargas-Gutiérrez, H. Mancha-Molinari, and J. Mendez-Nonell, "Effect of roll speed on the magnetic properties of nanocomposite PrFeB magnets prepared by melt-spinning," *Journal of Magnetism and Magnetic Materials*, vol. 206, no. 1, pp. 37–44, 1999.
- [8] A. Melsheimer, M. Seeger, and H. Kronmüller, "Influence of Co substitution in exchange coupled NdFeB nanocrystalline permanent magnets," *Journal of Magnetism and Magnetic Materials*, vol. 202, no. 2, pp. 458–464, 1999.
- [9] C. J. Yang and E. B. Park, "Enhancement of magnetic properties of $\text{Fe}_3\text{B}/\text{Nd}_2\text{Fe}_{14}\text{B}$ magnet by the addition of Co," *IEEE Transactions on Magnetics*, vol. 35, no. 5, pp. 3328–3330, 1999.
- [10] W.-Y. Zhang, S.-Y. Zhang, A.-R. Yan, H.-W. Zhang, and B.-G. Shen, "Effect of the substitution of Pr for Nd on microstructure and magnetic properties of nanocomposite $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ magnets," *Journal of Magnetism and Magnetic Materials*, vol. 225, no. 3, pp. 389–393, 2001.
- [11] A. Arai, H. Kato, and K. Akioka, "High-energy isotropic resin bonded magnets produced from $(\text{Nd,Dy})\text{-(Fe,Co)-B}$ nanocomposite alloys," *IEEE Transactions on Magnetics*, vol. 37, no. 4, pp. 2555–2557, 2001.
- [12] L. Shandong, D. Yaodong, B. X. Gu, T. Zongjun, and D. Youwei, "Effect of amorphous grain boundaries on the magnetic properties of B-rich nanocomposite permanent magnets," *Journal of Alloys and Compounds*, vol. 339, no. 1–2, pp. 202–206, 2002.
- [13] M. Daniil, Y. Zhang, H. Okumura, G. C. Hadjipanayis, and D. J. Sellmyer, "Effect of grain growth inhibitors on the hysteresis properties of $\text{Nd}_{10}\text{Fe}_{82}\text{C}_6\text{B}_2$ melt-spun alloys," *IEEE Transactions on Magnetics*, vol. 38, no. 5, pp. 2973–2975, 2002.

- [14] Y. Sen, S. Xiaoping, and D. Youwei, "Exchange coupled $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanocomposite magnets with fine $\alpha\text{-Fe}$ grains," *Microelectronic Engineering*, vol. 66, no. 1–4, pp. 121–127, 2003.
- [15] D. N. Brown, Z. Chen, P. Guschl, and P. Campbell, "Developments with melt spun RE-Fe-B powder for bonded magnets," *Journal of Magnetism and Magnetic Materials*, vol. 303, no. 2, pp. e371–e374, 2006.
- [16] W. Chen, X. Zhao, J. J. Hu et al., "Refinement of the microstructure and enhancement of the magnetic properties in $\alpha\text{-Fe}/(\text{Nd,Dy})_2\text{Fe}_{14}\text{B}$ nanocomposite using the two-step annealing technique," *Journal of Magnetism and Magnetic Materials*, vol. 306, no. 1, pp. 51–54, 2006.
- [17] Z. Q. Jin, H. Okumura, Y. Zhang, H. L. Wang, J. S. Muoz, and G. C. Hadjipanayis, "Microstructure refinement and significant improvements of magnetic properties in $\text{Pr}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanocomposites," *Journal of Magnetism and Magnetic Materials*, vol. 248, no. 2, pp. 216–222, 2002.
- [18] D. Sultana, M. Marinescu, Y. Zhang, and G. C. Hadjipanayis, "Isotropic nanocomposite Pr-Fe-Co-B ribbons with $(\text{BH})_{\text{max}} > 20 \text{ MGOe}$," *Physica B*, vol. 384, no. 1–2, pp. 306–309, 2006.
- [19] Z. W. Liu and H. A. Davies, "The practical limits for enhancing magnetic property combinations for bulk nanocrystalline NdFeB alloys through Pr, Co and Dy substitutions," *Journal of Magnetism and Magnetic Materials*, vol. 313, no. 2, pp. 337–341, 2007.
- [20] X.-R. Zeng, H. C. Sheng, J. Z. Zou, and S. H. Xie, "New crystallographic textures of $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanocomposite materials prepared by controlled melt spinning," *Materials Science Forum*, vol. 654–656, pp. 1170–1173, 2010.
- [21] N. V. Vuong, N. V. Khanh, and D. M. Thuy, "Simulation of the energy product $(\text{BH})_{\text{max}}$ of Nd-Fe-B anisotropic bonded magnets," *Physica B*, vol. 327, no. 2–4, pp. 349–351, 2003.
- [22] N. V. Vuong, C. Rong, Y. Ding, and J. Ping Liu, "Effect of magnetic fields on melt-spun $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based ribbons," *Journal of Applied Physics*, vol. 111, no. 7, pp. 07A731–1–07A731–3, 2012.