JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 5, May 2007, p. 1474 - 1477

Nanocomposite (Nd, Dy)$_2$Fe$_{14}$B/α-Fe magnetic materials coupled by exchange interactions

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The structural and magnetic properties of $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$/α-Fe nanocomposite obtained by mechanical milling and subsequent annealing have been investigated. The structural evolution of the sample was followed versus the milling and annealing conditions by X-ray diffraction. The width of the diffraction peaks of the magnetic phase was found to increase with milling time and the peaks almost disappeared after 12 hours of milling. The characteristic diffraction peaks of the $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ phase are restored during subsequent heat treatment. The coercive field, remanent magnetization and the degree of the exchange coupling between the hard magnetic gains and the soft grains are dependent on the milling time and the annealing conditions. The exchange coupling between the soft magnetic α-Fe, and the hard magnetic $(Nd,Dy)_2Fe_{14}B$-type phase is analysed.

(Received November 14, 2006; accepted April 12, 2007)

Keywords: Nanocomposite magnetic materials, $(Nd, Dy)_2Fe_{14}B$/α-Fe, Exchange interactions

1. Introduction

Nanocomposite exchange-enhanced hard magnetic $Nd_2Fe_{14}B$/α-Fe alloys have been intensively studied since their first experimental and theoretical description [1-3]. The understanding of the exchange coupling [1] leads to new ways of developing hard magnetic materials with enhanced properties. Combining the high coercivity of the hard magnetic materials with the high magnetization of the soft ones leads to a new categories of magnets with a large value of the stored energy. Skomski and Coey [4] first predicted that a giant energy product $(BH)_{max}$ of 1MJ/m^3 might be attainable in oriented exchange coupled $Sm_2Fe_{17}N_3/Fe_{65}Co_{35}$ nanocomposites. Similarly, a potential $(BH)_{max}$ of 720 kJ/m^3 was predicted in $Nd_2Fe_{14}B$/α-Fe nanocomposite [5]. These values are about twice that of commercially available anisotropic permanent magnets (~ 400 kJ/m^3). The $(BH)_{max}$ of 150-175 kJ/m^3 were found in Nd-Fe-B/α-Fe [6] and respectively $Pr_9Nd_3DyFe_{72}Co_8B_{6.9}Zr_{0.1}$ [7] nanocomposites. The grain sizes of the soft and hard magnetic phases constitute an important structural factor that critically influences the magnetic properties of the nanocomposite magnets. Of particular importance is that the average grain size of soft magnetic phase in the nanocomposites has to be sufficiently small to ensure the exchange interactions between neighbouring grains [8]. It is expected that the optimum nanostructure should be made of uniformly distributed soft and hard magnetic grains. Because of the short range feature of the exchange-coupling interaction between nanograins, the soft magnetic α-Fe grains should be small enough, approximately twice the domain wall width of the hard magnetic phase [1,9-10]. In order to promote an optimum ferromagnetic exchange coupling between hard and soft magnetic phase, the corresponding soft/hard mean grain size in $Nd_2Fe_{14}B$/α-Fe composite, should ideally be of 10 nm for the soft phase and 20 nm for the hard phase [3,8,11-13]. The intergranular exchange interaction leads to the enhancement of the remanence, J_R, to well above the Stoner–Wohlfarth value of $0.5J_S$, but with reduced intrinsic coercivity Hc. Until now, two types of compositions of $Nd_2Fe_{14}B$-based nanocomposite magnets have been widely studied. One is $Nd_2Fe_{14}B/Fe_3B$ and the other is $Nd_2Fe_{14}B$/α-Fe [14–16]. One of the drawbacks of α-Fe, $Fe_3B/Nd_2Fe_{14}B$ nanocomposite is the low coercivity and energy product who are still impeding the application of these materials [12–16]. There is a close relationship between the coercivity and the microstructure [19-20]. However, in practice it is not an easy job to appropriately control the grain size of nanocomposite magnets during preparation. One of the more effective ways to optimize the nanostructure and magnetic properties (especially the coercivity) of nanocomposite magnets is by adjusting the composition [21]. For the $Nd_2Fe_{14}B$ phase, it has been shown that substitution of Dy for Nd increases the anisotropy field [22-24]. According to the measurement of Hirosawa et *al*. [25], the room temperature anisotropy field monotonically increases from 67 kOe for $Nd_2Fe_{14}B$ to 150 kOe for $Dy_2Fe_{14}B$. The main advantage of increasing the anisotropy consists is the extension of the single domain limit for the alloy, thus minimizing the degrading effects of physical defects such as large or misshapen grains [24]. This improvement of the coercivity is accompanied by the decrease of the saturation magnetisation as a consequence of the antiparallel coupling between Fe and Dy moments. For the exchange spring magnets, the lower saturation magnetisation of the hard magnetic phase could be compensated by a better coupling between the soft and the hard magnetic phases which could results in a strong coercivity.

Mainly, the exchange spring magnets could be obtained by: thin layers deposition, rapid quenching and mechanical milling. This study is a part of our researches on the nanocomposite materials obtained by mechanical milling. The coercivity and the remanence were found to be dependent upon the process conditions and they could be improved by adjusting the milling and/or heat treatment conditions (time and temperature) [26,27].

In the present study, we proceed to a systematic study of the exchange coupling which is induced by mixing a hard magnetic phase, $(Nd,Dy)_2Fe_{14}B$, and a soft magnetic phase, α-Fe, through mechanical milling. Our aim is to obtain exchange coupled crystallites of these two phases, without chemical reaction between the starting magnetic phases.

2. Experimental

The alloy with the nominal composition of $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ was prepared by arc melting under argon atmosphere. The ingots were remelted at least four times to promote homogeneity. The purities of all the constituent elements are better than 99.9%. An excess amount (about 1 wt%) of Nd was added in order to compensate for the weight loss during the preparation (melting and milling). The ingot was crushed into small pieces and it was subsequently mechanically milled for 2 hours in a high energy planetary mill under argon atmosphere. The $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ powder thus obtained was mixed with an iron powder (grain size bellow 40 μm) in a ratio of 78 wt % $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$/ 22 wt % α-Fe. The mixture was mechanically milled under argon atmosphere using the above-mentioned high-energy planetary mill. Several milling times were used ranging from 4 hours up to 12 hours. In order to investigate the influence of the heat treatment on the evolution of the exchange coupling between the hard and soft phases, the samples of milled powder were sealed in evacuated silica tubes and heated at temperature between 450 and 800°C for different times. For the nanocrystalline samples, in order to avoid the recrystallisation, the chosen annealing temperature must be smaller than the recrystallisation temperature of the phases involved in the samples.

X-ray diffraction (XRD) was carried out with Cu K_α radiation on a Bruker diffractometer and with a Siemens D500 powder diffractometer with the $K_{\alpha 1}$ radiation of copper (λ = 0.15406 nm). The intensities were measured from 2θ = 20° to 85°. The magnetic ordering temperatures were determined with a Faraday type balance at heating and cooling rates of 5K per minute. The sample was sealed under vacuum in a small silica tube in order to prevent the oxidation of the sample during heating. The magnetisation curves were recorded between 4K and room temperature by the extraction method in a continuous magnetic field of up to 10 T [28].

3. Results and discussion

XRD patterns of $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B/\alpha$-Fe milled for 4, 6, 8 and 12 hours are presented in Figure 1. The X-ray pattern for 2 hours milled $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ sample is also shown for comparison. As a consequence of the induced internal stresses and decrease of the crystallites size, after two hours of milling of $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ the width of the diffraction peaks increases and the high angle peaks become progressively undetectable. For the $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B/\alpha$-Fe composite

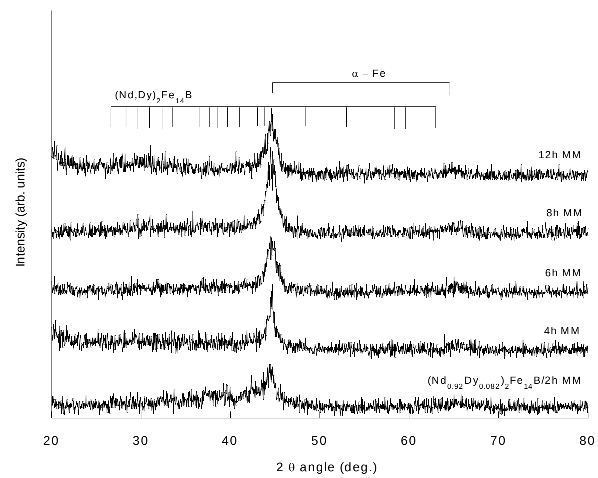

Fig. 1. X-ray diffraction patterns of the $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B/\alpha$-Fe composite sample milled from 4 to 12 hours in comparison to that of $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ milled for 2 hours.

samples, the Bragg peaks corresponding to $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ and α-Fe phases are broadened by milling but no additional peaks are observed. The small crystallite sizes and the large microstrains for long milling times given by severe plastic deformation are accompanied by a high degree of structural disorder [29, 30]. The nanocrystallites mean size of both the soft and the hard magnetic phases, calculated from Full-Width-at-Half-Maximum - FWHM of the diffraction peaks according to Scherrer's formula [31], are estimated to be inferior of 30 nm for the samples milled 6 hours or more. This work is in progress. With the milling time the mean size of the *a*-Fe nanocrystallites decrease to a mean value of about 9 nm after 12 hours milling, which is similar to the results of the previous studies [32,33].

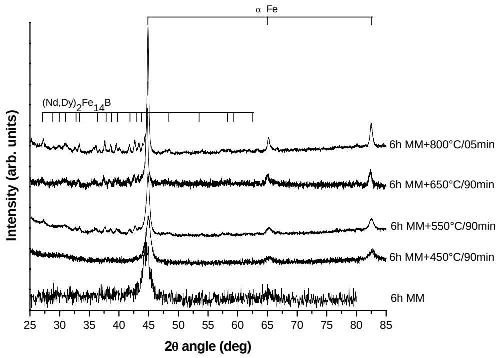

Fig. 2. X-ray diffraction patterns of the $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B/\alpha$-Fe composite sample milled for 6 hours and annealed for the indicated time and temperature.

The heat treatment is very efficient in the refinement of the structure (Fig. 2). Progressive developments of the $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ characteristic peaks were observed by annealing; narrowing of the peaks and increase in their intensity is observed. For the annealing temperatures which are smaller than the recrystallisation temperature, the sharper peaks of the X-ray diffraction patterns can be attributed to a decrease in the internal stresses. A similar behaviour was obtained for all milling times. It is very clear that the annealing temperature is more important than the annealing time in this structural evolution. Additionally, note that, even after 12 hours of milling, the X-ray patterns of all annealed samples show the presence of both starting phases: $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ and α-Fe. This behaviour proves that the milling and annealing do not change the nature of the phases present in the studied samples. The annealing at 800 °C for a short time (5 minutes) show rather narrow peaks which prove that this temperature is higher that the recrystallisation temperature for $Nd_2Fe_{14}B$ phase.

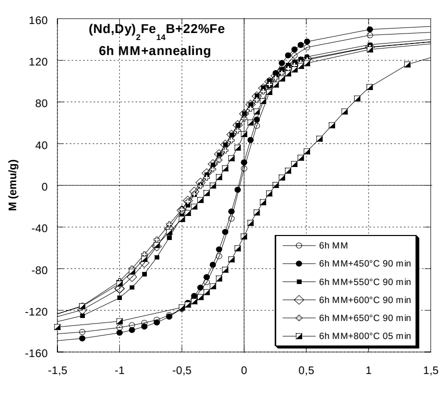

Fig. 3. Room temperature hysteresis cycles recorded for the $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B/\alpha$-Fe composite samples milled for 6 hours and annealed from 450 to 800 °C.

The isothermal magnetisation curves recorded at room temperature for $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B/\alpha$-Fe samples milled for 6 hours and annealed from 450 to 800°C are plotted in Figure 3. The $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ hard phase milled for 2 hours has a magnetisation of about 140 emu/g under a field of 10 T.

By milling the hard $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B$ phase with the Fe soft magnetic phase for 6 hours, an enhancement of the saturation magnetisation is observed up to about 155 emu/g for as milled samples. After a heat treatment of the 6h milled $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B/\alpha$-Fe sample in the temperature range 450 - 800 °C, the saturation magnetisation increased up to 163 emu/g for an annealing temperature of T_a = 550°C. The same evolution is observed for the remanence and the coercivity. Fig. 4 shows the evolution of the saturation magnetisation, remanence and the coercivity vs. annealing temperature for the 6 hours milled samples. Higher annealing temperature induce a slow decreasing of the magnetic properties for the sample annealed at 800°C for 5 min. This evolution can be correlated with the structure evolution. From X-Ray diffraction we can observe that for 5 minutes annealing at 800°C rather narrow peaks were observed (Fig. 2). The room temperature hysteresis cycles show a decrease of the both remanence and the coercivity by about 30%, for the same sample, (Fig. 3). This evolution of both, structural and magnetic properties indicates that the 800 °C annealing temperature could be higher than the recrystallisation temperature. At this temperature some recrystallisations take place and the exchange coupling between crystallites becomes poorer and consequently a decoupling between the hard and the soft magnetic phases appears.

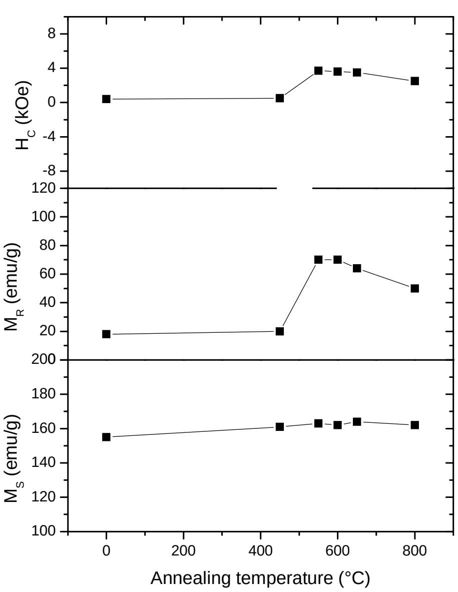

Fig. 4. The evolution of the magnetization (measured at 10T), the remanent magnetisation and the coercivity of the 6 hours mechanically milled $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B/\alpha$-Fe powder samples vs. the annealing temperature.

4. Conclusions

Mechanical milling has been applied in order to obtain $(Nd_{0.92}Dy_{0.08})_2Fe_{14}B/\alpha$-Fe magnetic nanocomposite. The influence of the milling and annealing conditions on the structural and magnetic behaviour of the as milled powder has been studied. The coercivity and the remanence are very sensitive to the synthesis process and can be improved by adjusting the milling and/or annealing conditions. This behaviour was connected to the strength of the exchange coupling between the hard and the soft magnetic nanocrystallites. Heat treatments from 450 °C to 650 °C on the powder milled for 6 hours in a planetary mill refine the structure and increase both the remanence and the coercivity. The optimum values were obtained for a heat treatment at temperatures between 550 °C and 600 °C for 1.5 hours. Consequently a good exchange coupling between the $(Nd,Dy)_2Fe_{14}B$ hard magnetic phase and the α-Fe soft magnetic phase was obtained in nanocomposite samples. The coercivity and the remanence decrease for the nanocomposite samples annealed at temperatures higher than 650 °C. This evolution shows that at these temperatures some recrystallisation starts and also chemical reaction between the two phases may occur, whereas the exchange coupling becomes poorer. Future thermal analysis (DTA or DSC measurements) are necessary for a better understanding of this behaviour. Further investigations are in progress in order to improve the magnetic properties of this nanocomposite. Special attention will be done to the chemical composition, structure and microstructure of the starting mixed powders.

References

[1] E. Kneller, R. Hawig, IEEE Trans. Magn. **27**, 3588 (1991).
[2] A. Manaf, R. A. Buckley, H. A. Davies, J. Magn. Magn. Mater. **128**, 302 (1993).
[3] I. Bétancourt, H. A. Davies, Appl. Phys. Lett. **87**, 162516 (2005).
[4] R. Skomski, J. M. D. Coey, Phys. Rev. B **48**, 15812 (1993).
[5] T. Lieneweber, H. Kronmuller J. Magn. Magn. Mater. **176**, 145 (1997).
[6] V. Neu, L. Schultz, J. Appl. Phys. 90, 1540 (2001)
[7] O. Gutfleisch, A. Bollero, A. Handstein, D. Hinz, A. Kirchner, A. Yan, K.-H. Muller, L. Schultz, J. Magn. Magn. Mater. **242-245**, 1277 (2002).
[8] R. Fischer, T. Schrefl, H. Kronmuler, J. Fidler, J. Magn. Magn. Mater. **153**, 35 (1996).
[9] T. Schrefl, H. Kronmuler, J. Fidler, Phys. Rev. B **49**, 6100 (1994).
[10] B. Z. Cui, X. K. Sun, W. Liu, Z. D. Zhang, D. Y. Geng, X. G. Zhao, J. Phys. D **33**, 338-344 (2000).
[11] X. Y. Zhang, Y. Guang, J. W. Zhang, Appl. Phys. Lett. **80**, 1996 (2002).
[12] H. W. Zhang, S. Y. Zhang, B. G. Shen, J. Appl. Phys. **85**, 4660 (1999).
[13] P. G. McCormick, W. F. Miao, P. A. I. Smith, J. Ding, R. Street, J. Appl. Phys. **83**, 6256 (1998).
[14] S. Hirosawa, H. Kanekiyo, IEEE Trans. Magn. **29**, 2863 (1993).
[15] Y.H. Gao, J.H. Zhu, Y.Q. Wang, E.B. Park, C.J. Yang, J. Magn. Magn. Mater. **191**, 146 (1999).
[16] Y.Q. Wu, D. Ping, B.S. Murty, H. Kanekiyo, S. Hirosawa, K. Hono, Scripta Mater. **45**(3), 355 (2001).
[17] L. Withanawasam, G.C. Hadjipanayis, J. Appl. Phys. **76**, 7065 (1994).
[18] J.M. Yao, T.S. Chin, S.K. Chen, J. Appl. Phys. **76**, 7071 (1994).
[19] T. Schrefl, R. Fischer, J. Fidler, H. Kronmuller, J. Appl. Phys. **76**, 7053 (1994).
[20] J. Bauer, M. Seeger, A. Zern, H. Kronmuller, J. Appl. Phys. **80**, 1667 (1996).
[21] A. M. Gabay, Y. Zhang, G. C. Hadjipanayis, J. Magn. Magn. Mater. **238**, 226-232 (2002).
[22] M. Sagawa, S. Hirosawa, K. Tokuhara, H. Yamamoto, S. Fujimura, Y. Tsubokawa, R. Shimizu, J. Appl. Phys. **61,** 3559 (1987).
[23] Z. Liu, H. A. Davies, J. Magn. Magn. Mater. **290-291**, 1230-1233 (2005).
[24] B. E. Meacham, D. J. Branagan, J. E. Shield J. Magn. Magn. Mater. **277**, 123 (2004).
[25] S. Hirosawa, Y. Matsuura, H. Yamamoto, S. Fujimura, M. Sagawa, H. Yamauchi, J. Appl. Phys. **59**, 873 (1986).
[26] V. Pop, O. Isnard, I. Chicinaş, D. Givord, J. M. Le Breton, J. Optoelectron. Adv. Mater. **8**, 494 (2006).
[27] V. Pop, O. Isnard, I. Chicinas, D. Givord, Proc. of Euro PM2005 Congress, 2-5 Oct., Prague, **1**, 487 (2005).
[28] A. Barlet, J. C. Genna, P. Lethuillir, Cryogenics **31**, 801 (1991).
[29] K. Kumar, J. Appl. Phys. **63**, R13 (1988).
[30] Z. Chen, X. Meng-Burany, G. C. Hadjipanayis, Appl. Phys. Lett. **75**, 3165 (1999).
[31] P. Scherrer, Göt. Nachr. **2**, 98 (1918).
[32] C. You et al. J. Magn. Magn. Mater. **268**, 403-409 (2004).
[33] W. F. Miao, J. Ding, P. G. McCormick, R. Street, J. Phys. D: Appl. Phys. **29**, 2371 (1996).

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