

Coercivity of Near Single Domain Size Nd₂Fe₁₄B-type Particles

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The coercivity of near single domain size Nd₂Fe₁₄B-type particles prepared by ball milling of HDDR-treated Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2} alloy was investigated. The feasibility of a surface nitrogenation for improving the coercivity stability of the fine Nd₂Fe₁₄B-type particles was also studied. The near single domain size Nd₂Fe₁₄B-type particles had a high coercivity of over 9 kOe. However, the coercivity radically deteriorated as the temperature increased in air (< 2 kOe at 200 °C). This coercivity reduction was attributed to the soft magnetic phases, α-Fe and Fe₃B, which formed on the surface of the fine particle due to oxidation. Surface nitrogenation of the fine particles significantly improved the stability of their coercivity. The improvement in coercivity stability was attributed to the formation of a thin nitrogenated layer on the surface of the fine Nd₂Fe₁₄B-type particles, which enhanced the anisotropy field and gave improved resistance to oxidation (dissociation).

Keywords : Nd₂Fe₁₄B, single domain size particle, oxidation, coercivity, nitrogenation

1. Introduction

The high performance of the Nd-Fe-B-type magnets has been attributed to the superior magnetic properties of the matrix Nd₂Fe₁₄B magnetic crystal in the magnet [1, 2]. Due to these superior magnetic properties, Nd₂Fe₁₄B-type fine particles have increasingly found new applications, such as in high performance micro-magnets. Since the Nd₂Fe₁₄B compound contains a high content of the rare earth metal Nd, which has a high affinity with oxygen, it is particularly prone to oxidation [3-6]. What's worse is that the fine Nd₂Fe₁₄B-type particles have an extremely large specific surface area. Due to their high oxygen-affinity and large specific surface area, the fine Nd₂Fe₁₄B-type particles can be easily oxidized in service, hence radically losing coercivity. While a bulk sintered Nd-Fe-B magnet is usually surface-coated with a highly oxidation-resistant metal, such as Ni or Al, for the prevention of oxidation, this surface coating technique is not applicable to fine particles. The oxidation issue is a major limitation of fine Nd₂Fe₁₄B-type particles for high performance applications. In this study, the coercivity of fine Nd₂Fe₁₄B-type particles of near single domain size was investigated. The effect of oxidation on the coercivity of the fine

particles was examined. The feasibility of surface nitrogenation of the fine Nd₂Fe₁₄B-type particles for improving the oxidation resistance and the stability of coercivity was also studied.

2. Experimental Work

Fine Nd₂Fe₁₄B-type particles with a near single domain size were prepared by the ball milling (4 hr in cyclohexane) of HDDR-treated Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2} alloy. Details of the HDDR treatment and ball milling of the HDDR-treated alloy can be found elsewhere [7-9]. The particle morphology of the HDDR-treated alloy powder, before and after, ball milling was observed by SEM (Fig. 1). The Nd₂Fe₁₄B-type particles prepared by ball milling of the HDDR-treated alloy had a particle size near that of a single domain ($d_c \approx 0.3 \mu\text{m}$). The prepared fine particles were heated in air or a vacuum, and the variation of coercivity was measured by VSM. Magnetic phase analysis of the oxidation product of the particles was carried out by TMA (350 Oe, 7 °C/min, Ar). The surface of the fine particles was nitrogenated in a pure nitrogen gas ($P_{\text{N}_2} = 1 \text{ kg/cm}^2$) at 450 °C for 3 hr. These nitrogenated fine particles were heated in air or in a vacuum, and their coercivity variation was compared with those of the particles without nitrogenation. The long-term stability of the coercivity of the fine particles with/without nitro-

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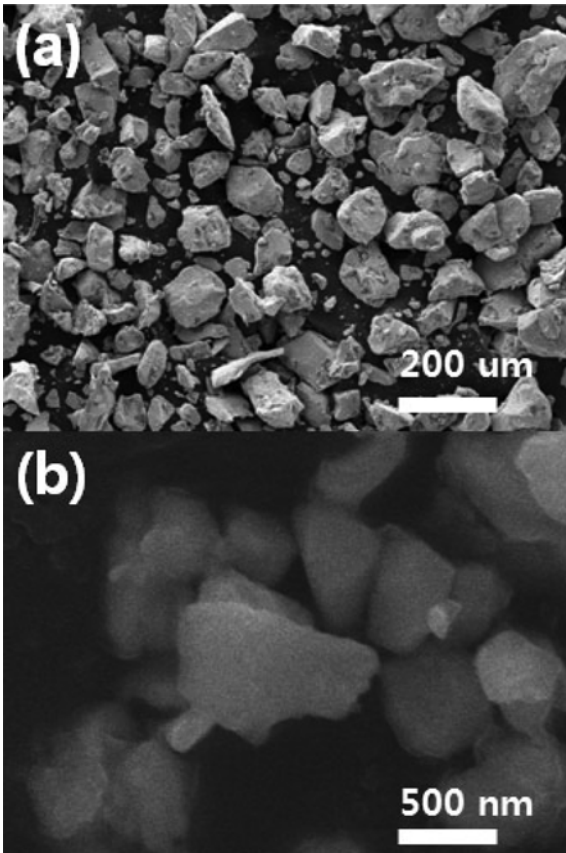


Fig. 1. SEM photos showing the particle morphology of the HDDR-treated alloy powder (a) before and (b) after the ball milling.

generation was examined at room temperature in air (relative humidity = 75%). The oxidation kinetics of the fine particles with/without nitrogenation was studied by TGA in air.

3. Results and Discussion

Fig. 2 shows the demagnetization curves of the HDDR-treated alloy powder before and after the ball milling. Although the high coercivity (approximately 13.5 kOe) of the HDDR-treated alloy was deteriorated somewhat by ball milling, the ball-milled fine $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type particles with a near single domain size still had a considerably high coercivity exceeding 9 kOe. The near single domain size $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type particles were heated in air or vacuum, the variation of coercivity is shown in Fig. 3. Also included in Fig. 3 is the variation of coercivity in the surface-nitrogenated fine $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type particles. Discussion about the coercivity variation of the surface-nitrogenated particles will be made afterwards. It appears that the coercivity of the as-ball-milled powder heated in air was radically reduced as the temperature increased [(a) in Fig.

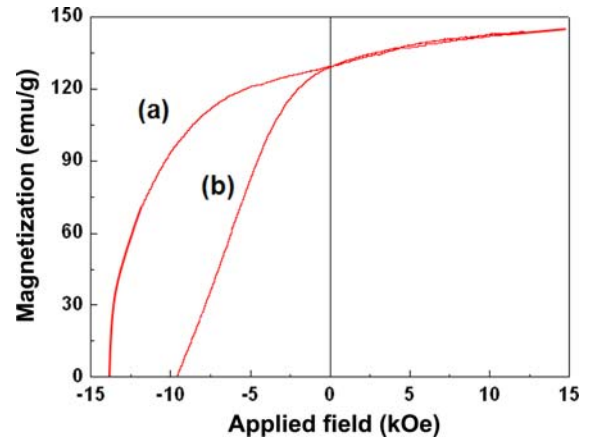


Fig. 2. (Color online) Demagnetization curves of the HDDR-treated alloy powder (a) before and (b) after the ball milling.

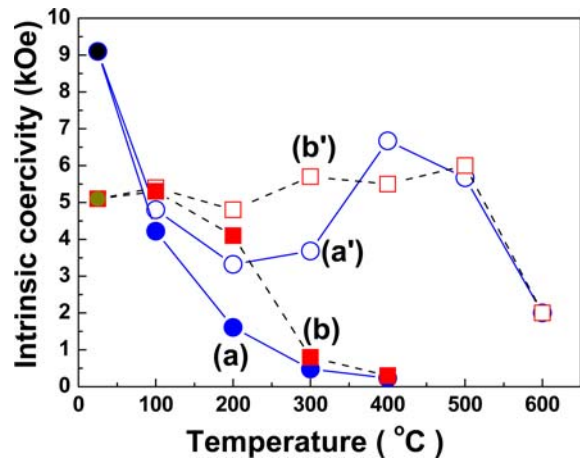


Fig. 3. (Color online) Variations of coercivity of the fine $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type particles. As-ball-milled particles heated in (a) air or (a') vacuum. Surface-nitrogenated particles heated in (b) air or (b') vacuum.

3]. Obviously, this radical coercivity deterioration is attributed to oxidation. Oxidation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound has been known to occur through a dissociation of the phase into a mixture of dissociated phases [3, 4, 6]. The radical coercivity deterioration may be related closely with the phase constitution in the oxidation product. In particular, the presence of magnetic phases in the oxidation product may heavily influence the coercivity. The fine $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type particles were fully oxidized at 400 °C for 3 hr in air, the magnetic phase analysis of these particles was performed by TMA. Fig. 4 shows the TMA results, and it can be seen that there are two magnetic transitions at approximately 550 °C and 770 °C, corresponding to the Curie temperature of the meta-stable Fe_3B and $\alpha\text{-Fe}$ phases, respectively. The radical coercivity reduction may, therefore, be attributed to the presence of the soft mag-

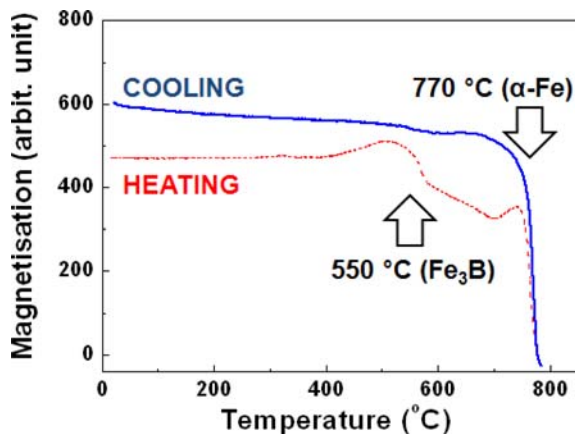


Fig. 4. (Color online) TMA results of the fine $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type particles oxidized at 400°C for 3 hr.

netic phases, $\alpha\text{-Fe}$ and Fe_3B . The magnetic soft phases ($\alpha\text{-Fe}$, Fe_3B) at the surface of the fine $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles facilitate the nucleation of the reverse domain in a demagnetising field, hence reducing the coercivity radically (Fig. 5). Coercivity of the as-ball-milled powder was also reduced up to a temperature of 200°C when heated in vacuum, and then increased, peaking at around 400°C [(a') in Fig. 3]. The coercivity reduction up to 200°C may have been caused by the slight oxidation due to an imperfect vacuum (2×10^{-5} mbar), and the coercivity recovery at an elevated temperature may be attributed to the removal of the internal strain (stress), which was introduced during the mechanical ball milling.

The radical coercivity reduction of the fine $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles may severely limit their application. As this reduction is caused by the dissociation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type phase, which is initiated at the particle surface, a surface passivation may be beneficial for improving the stability of the coercivity. It has been suggested that nitrogenation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type phase could affect its oxidation resistance, but there is still debate over the benefit of nitrogenation for improving the oxidation resistance of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.^{10,11} In an attempt to investigate the feasibility of surface nitrogenation for improving the oxidation resistance and stability of the coercivity of the fine $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type particles, the fine particles were surface-nitrogenated. The surface-nitrogenated fine particles were heated, in air or in a vacuum, and the variation of coercivity was measured, as shown in Fig. 3 [(b), (b') in Fig. 3]. It appears that the high coercivity of the as-ball-milled fine $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type particles was reduced significantly by nitrogenation from around 9 kOe to around 5 kOe [(b) in Fig. 3]. This coercivity deterioration may be attributed to slight oxidation during nitrogenation. Although the nitrogenation was carried out in a vacuum (2×10^{-5} mbar), the

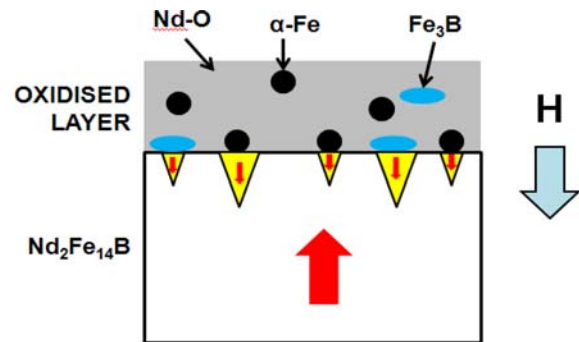


Fig. 5. (Color online) Schematic showing the nucleation of reverse domain in demagnetising field by the soft magnetic phases of $\alpha\text{-Fe}$ and Fe_3B formed by oxidation.

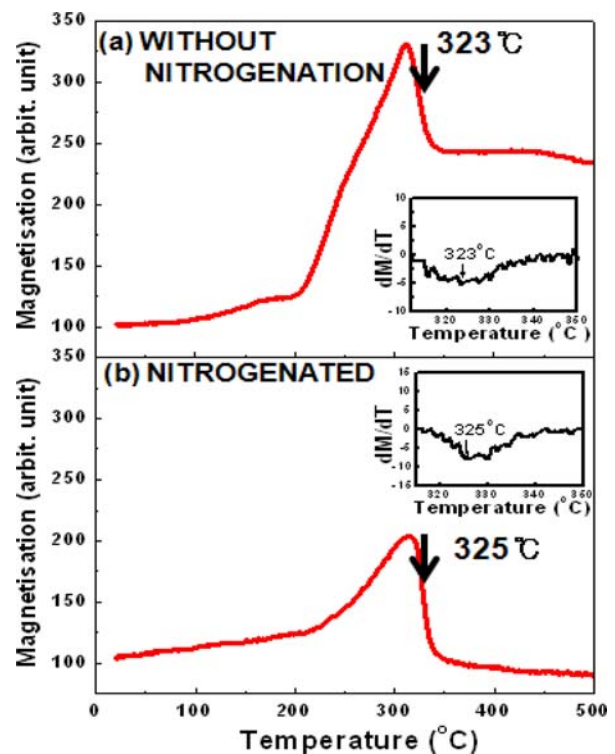


Fig. 6. (Color online) TMA results for the fine $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type particles (a) before and (b) after the nitrogenation.

vacuum was not perfect and the remaining oxygen may have caused slight oxidation. It is interesting, however, that the coercivity of the nitrogenated fine particles is consistently higher than that of the as-ball-milled particles without nitrogenation, in particular in the temperature range from 100°C to 200°C [(b) in Fig. 3]. The nitrogenation may probably have formed a thin nitrogenated layer only on the surface of the particle, and most of the inner body remains intact. This was verified by TMA for the fine particles before and after the nitrogenation, and the results were shown in Fig. 6. The insets in Fig. 6

show the dM/dT vs. T curves for the temperature range around the Curie temperature for determining the precise Curie temperature. It appears that Curie temperatures of the Nd₂Fe₁₄B-type phase in both particles are not significantly different. It is known that a nitrogenation causes a significant Curie temperature increase of the Nd₂Fe₁₄B-type phase [11, 12]. The almost identical Curie temperature of the fine particles before and after the nitrogenation indicates that the core of particle has not been nitrogenated, and only very thin surface of the particle has been nitrogenated. The improved stability of coercivity caused by the nitrogenation in the temperature range from 100 °C to 200 °C can, therefore, be explained in this way. First, the anisotropy field of the thin outer shell of Nd₂Fe₁₄B-type phase was enhanced by the nitrogenation, and this may account for the improvement of coercivity stability. It has been known that nitrogenation of the Nd₂Fe₁₄B-type phase caused an enhancement of the anisotropy field of the phase [11]. The enhanced anisotropy field may suppress the nucleation of reverse domain in demagnetising field at the surface of the particle, hence improving the stability of coercivity. Secondly, the nitrogenation may suppress the oxidation of the thin outer shell of the Nd₂Fe₁₄B-type particle, preventing formation of the soft magnetic phases of Fe₃B and α -Fe. Likelihood of suppressing the oxidation (dissociation) of the Nd₂Fe₁₄B-type particle surface by the nitrogenation was examined by TGA, and the results were shown in Fig. 7. As can be seen, the nitrogenated fine particles exhibits slightly slow oxidation kinetics with respect to the particles without nitrogenation. The improved oxidation resistance of the surface by the nitrogenation may also contribute to the improvement of coercivity stability. The slight coercivity recovery caused by heating in vacuum at an elevated temperature for the nitrogenated particles [(b') in Fig. 3]

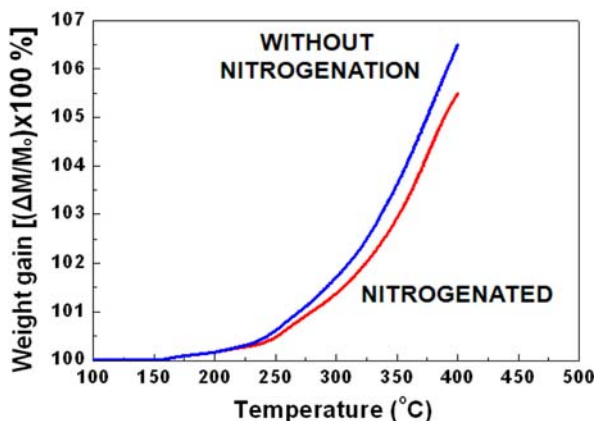


Fig. 7. (Color online) TGA results for the fine Nd₂Fe₁₄B-type particles with/without the nitrogenation.

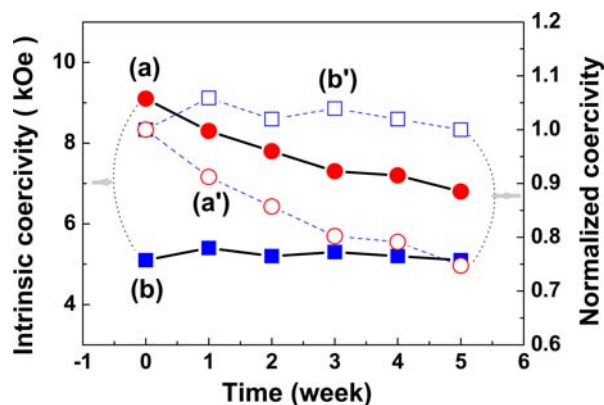


Fig. 8. (Color online) Variation of coercivity and its normalized value for the fine Nd₂Fe₁₄B-type particles exposed to air (75% relative humidity) at room temperature. (a) and (a') for as-ball-milled particles, (b) and (b') for surface-nitrogenated particles.

may again be attributed to the removal of internal strain (stress).

Feasibility of the surface nitrogenation for improving the long-term coercivity stability of the fine Nd₂Fe₁₄B-type particles was also investigated. Coercivity variation of the fine particles with/without surface nitrogenation for long period of time at room temperature was examined, and the results were shown in Fig. 8. Although the coercivity value of the nitrogenated particles appeared to be lower than that of the as-ball-milled particles, the coercivity of the nitrogenated particles was more stable with respect to that of the as-ball-milled particles. The coercivity of the nitrogenated particles exhibited virtually no deterioration over the long period of exposing time (5 weeks).

4. Conclusion

Near single domain size Nd₂Fe₁₄B-type particles prepared by ball milling of HDDR-treated Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2} alloy had high coercivity over 9 kOe. However, the coercivity was radically deteriorated as the temperature increased in air (< 2 kOe at 200 °C). This radical coercivity reduction was attributed to the soft magnetic phases, α -Fe and Fe₃B, which formed on the surface of the fine particles due to the oxidation. Surface nitrogenation of the fine particles significantly improved the stability of coercivity in air in the temperature range from 100 °C to 200 °C. Long-term coercivity stability of the fine Nd₂Fe₁₄B-type particles was also improved by the surface nitrogenation. The improvement of coercivity stability was attributed to the formation of thin nitrogenated layer on the surface of the fine Nd₂Fe₁₄B-type particle, which had

an enhanced anisotropy field and an improved resistance to the oxidation (dissociation).

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References

- [1] J. J. Croat, J. F. Herbst, R. W. Lee, and F. E. Pinkerton, *J. Appl. Phys.* **55**, 2078 (1984).
- [2] M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, and Y. Matsuura, *J. Appl. Phys.* **55**, 2083 (1984).
- [3] Y. Li, H. E. Evans, I. R. Harris, and I. P. Jones, *Oxidation of Metals* **59**, 167 (2003).
- [4] I. Skulj, H. E. Evans, and I. R. Harris, *J. Mater. Sci.* **43**, 1324 (2008).
- [5] Y. C. Yang, X. D. Zhang, L. S. Kong, Q. Pan, Y. T. Hou, S. Huang, L. Yang, and S. L. Ge, *J. Less-Common Metals* **170**, 37 (1991).
- [6] H. W. Kwon and J. H. Yu, *J. Kor. Mag. Soc.* **22**, 85 (2012).
- [7] T. Takeshita and R. Nakayama, *Proc. 10th Int'l. Workshop on RE Magnets and Their Applications*, 551 (1989).
- [8] P. J. McGuinness, X. J. Zhang, X. J. Yin, and I. R. Harris, *J. Less-Common Metals* **158**, 379 (1990).
- [9] J. I. Lee, H. W. Kwon, and Y. S. Kang, *J. Magnetism* **13**, 102 (2008).
- [10] A. S. Kim, F. E. Camp, and E. J. Dulis, *IEEE Trans. Magn.* **26**, 1936 (1991).
- [11] T. S. Chin, H. J. Bai, K. D. Lin, F. D. King, and S. J. Heh, *J. Appl. Phys.* **70**, 6600 (1991).
- [12] X. D. Zhang, Q. Pan, S. L. Ge, Y. C. Yang, J. L. Yang, Y. F. Ding, B. S. Zhang, C. T. Ye, and L. Jin, *Solid State Commun.* **83**, 231 (1992).