Effect of sintering conditions on the magnetic and microstructural properties of Nd–Fe–B sintered magnets doped with DyF₃ powders

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The microstructural and magnetic property changes of DyF₃-doped (Nd_{26.06}, Dy_{6.51})–Fe_{bal}–B_{0.97}–M_{2.39} (wt. %) ($M = \text{Cu, Al, Co, and Nb}$) sintered magnets as functions of the sintering conditions were studied. The sintering conditions for the optimum core-shell microstructure were determined. When the magnets were sintered at 1050 °C for 4 h, a coercivity of 35.1 kOe was obtained without sacrificing the remanence. When the magnets were doped with DyF₃, the formation of the RE-rich phase (Nd–Dy–O) was effectively suppressed and, hence, saving the Dy. In addition, the formation of a cubic-NdOF triple-junction phase (TJP) improves the interface uniformity and enhances the coercivity. © 2012 American Institute of Physics. [doi:10.1063/1.3672246]

I. INTRODUCTION

In recent years, Nd–Fe–B sintered magnets have played an important role in various applications, such as the motors in hybrid vehicles, because of their high-energy production. It is well known that the addition of Dy is an effective way to increase the coercivity in Nd–Fe–B magnets, because the Dy₂Fe₁₄B phase and (Nd, Dy)₂Fe₁₄B phase have a higher anisotropy field than the Nd₂Fe₁₄B phase. However, there are several problems, such as high costs and limited reserves of Dy, and the reduction of the remanence caused by the antiferromagnetic coupling between the Dy and Fe atoms.^{1–4} The structure and chemistry of the grain-boundary phase play a key role in increasing the coercivity of Nd–Fe–B sintered magnets. Recently, it has been reported that the Dy distribution along the grain-boundary phase, the so-called core-shell microstructure, could effectively enhance the coercivity without sacrificing the remanence and saving the Dy content.^{2–7} The addition of rare-earth fluorides, such as NdF₃ and DyF₃, to Nd–Fe–B sintered magnets improves the magnetic properties.^{7,8} In our previous research, we confirmed the increased coercivity and the reduction of the RE-rich phase (Nd–Dy–O) in DyF₃-doped magnets.⁹ However, the remanence was decreased because the Dy atoms were distributed evenly in the main phase grains when the magnets were sintered at 1070 °C for 4 h, which is not the optimized sintering condition for the core-shell microstructure. There is a lack of previous studies on the structure – chemistry – magnetic properties of rare-earth fluoride-doped Nd–Fe–B sintered magnets.

In this study, we investigated the relationship between the microstructural and magnetic property changes and the diffusional behavior of Nd–Fe–B sintered magnets doped with DyF₃ powder as a function of the sintering temperature and time.

II. EXPERIMENTAL PROCEDURE

Nd_{60.1}–Dy_{6.51}–Fe_{bal}–B_{0.97}–M_{2.39} (wt. %) ($M = \text{Cu, Al, Co, and Nb}$) was prepared by the powder metallurgical method. The powder was mixed with DyF₃ powder (2.4 wt. %). 2.4 wt. % DyF₃ doping yielded a total of 8.1 wt. % of Dy after sintering. The magnets were sintered at 1050, 1060, and 1070 °C for 4 h. The sintering time was varied from 2 to 4 h at 1070 °C. After sintering, the samples were post-sintering annealed (PSA) at 850 °C for 2 h (first PSA), annealed at 500 °C for 2 h (second PSA), and then annealed again at 530 °C for 2 h (third PSA). The microstructural studies were carried out using scanning electron microscopy (SEM, JXA-8500 F) and high-resolution transmission electron microscopy (HRTEM, FEI Tecnai F20). The volume fraction of RE-rich phases was measured by the image analyzer (UTHSCSA Image Tool). The area fraction of the RE-rich phase is determined by the image analyzer and this could be converted into the volume fraction. The studies of the phase composition and elemental distribution were carried out using electron probe micro-analysis (EPMA) and wavelength dispersive x-ray spectroscopy (WDS, JXA-8500 F). The thin-foil specimens for the HRTEM observations were prepared using an ion-milling system.

III. RESULTS AND DISCUSSION

Figure 1 shows the magnetic properties of the Nd–Fe–B sintered magnets doped with DyF₃ powder as a function of the sintering temperature. The coercivity of the DyF₃-doped magnet increased as the sintering temperature decreased. However, the remanences of the magnets did not change appreciably as the sintering temperature decreased. When the magnets were sintered at 1050 °C for 4 h, a coercivity of 35.1 kOe was obtained without sacrificing the remanence. The coercivity of the un-doped magnet (8.1 wt. % of Dy content) sintered at 1070 °C for 4 h was 33.6 kOe. Therefore, the DyF₃ doping is undoubtedly effective for improving the coercivity and saving the Dy content.

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FIG. 1. Magnetic property changes of the DyF_3 -doped magnets as a function of the sintering temperature.

Figure 2 shows the EPMA mapping images of the DyF_3 -doped magnets as a function of the sintering conditions. In the SEM backscattered secondary electron (BSE) images, two kinds of triple-junction phase (TJP) can be found in the microstructure. WDS analysis indicated that one is Cu-rich TJP, which consists of Nd, Cu, Co, and O (brighter contrast) and the other one is NdOF TJP, which consists of Nd, O, and F (darker contrast). In our previous research, the Dy atoms were distributed uniformly in the main phase grains when the DyF_3 -doped magnets were sintered at 1070 °C for 4 h [Fig. 2(c)].⁹ However, when the magnets were sintered at 1050 °C for 4 h, a core-shell microstructure was developed, as shown in Fig. 2(a). When the DyF_3 -doped magnets were sintered at 1070 °C for 2 h, a core-shell microstructure was also developed (not shown here). The core-shell microstructure could be optimized by adjusting the sintering temperature and time. This core-shell microstructure could effectively enhance the coercivity without sacrificing the remanence and saving the Dy content, as shown in Fig. 1.

Figure 3 shows the volume fraction changes of the RE-rich phase (Nd–Dy–O) in the DyF_3 -doped Nd–Fe–B sintered

FIG. 3. The volume fraction changes of the RE-rich phase in the DyF_3 -doped magnets as a function of the sintering temperature.

magnets as a function of the sintering temperature. The RE-rich phase and Cu-rich TJP co-existed in the un-doped magnets.¹⁰ The RE-rich phase does not enhance the coercivity, but only consumes Dy. Therefore, it should be reduced to save the Dy content. The volume fraction of the RE-rich phase was about 3.1% in the un-doped magnet. However, when the magnets were doped with DyF_3 powder, the volume fraction of the RE-rich phase was markedly reduced to less than 0.5%, as shown in Fig. 3. Therefore, the DyF_3 doping enables a uniform distribution of Dy to be obtained in the magnet and reduces the useless consumption of the Dy.

Figures 4(a) and 4(b) show the HRTEM image and fast Fourier transform (FFT) image of the Nd–O–F TJP in the DyF_3 -doped magnet sintered at 1060 °C for 4h, respectively. According to the FFT image analysis, the crystal structure of the Nd–O–F TJP is cubic NdOF. This phase is in complete agreement with the stoichiometric cubic-NdOF phase. The measured d spacings of the (111) and (200) planes for the cubic-NdOF phase are 0.324 and 0.2797 nm (0.323 and 0.2795 nm for JCPDS), respectively, as shown in Fig. 4(b). The cubic-NdOF phase in the DyF_3 -doped magnet is similar to the C-type Nd_2O_3 phase, which is usually obtained during

FIG. 2. (Color online) The EPMA mapping images of the DyF_3 doped magnets as a function of the sintering conditions. Sintered at (a) 1050 °C, (b) 1060 °C, and (c) 1070 °C for 4 h.

FIG. 4. HRTEM images and fast Fourier transform (FFT) image of the DyF_3 -doped magnets sintered at 1060°C for 4 h.

the second PSA. The formation of a C-type Nd_2O_3 can be derived from the fluorite-type NdO_2 phase. If $1/4$ of the oxygen atoms of NdO_2 are removed, C- Nd_2O_3 can be obtained.¹¹

The activation energies for the decomposition of rare-earth fluorides (REF) tend to decrease with increasing atomic number of the rare earths in REF_3 .¹² The decomposition of Dy in DyF_3 occurs relatively easily, as reported previous study.⁹ The decomposed Dy diffused into the main phase and the remaining F probably preferentially reacts with Nd, allowing the cubic-NdOF phase to be formed. The suppression of the RE-rich phase (Nd-Dy-O) formation by the DyF_3 doping, as shown in Fig. 3, is speculated to be caused by the formation of cubic-NdOF phase.

It was reported that the formation of the C-type Nd_2O_3 TJP and the grain-boundary phase (GBP) in the un-doped magnet after PSA was the major factor for increasing the coercivity.^{10,13} The lattice misfits between the C- Nd_2O_3 and the Nd-Fe-B main phase are quite small, and this reduced lattice mismatch undoubtedly improved the interface uniformity and magnetic properties of the magnet after the second PSA. The formation of the cubic-NdOF phase in the DyF_3 -doped magnet plays a similar role to that of the C-type Nd-rich phase in the un-doped magnet in terms of the coercivity enhancement. The (111) plane of the cubic NdOF, which is tilted at an angle of 22° , is connected to the (110) plane of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase at the cubic-NdOF || $\text{Nd}_2\text{Fe}_{14}\text{B}$ interface (not shown here). The lattice mismatch between the cubic-NdOF and the $\text{Nd}_2\text{Fe}_{14}\text{B}$ is 2.62%, which is smaller than that between the C- Nd_2O_3 and the $\text{Nd}_2\text{Fe}_{14}\text{B}$ in the un-doped magnet (3.11%).¹³

IV. CONCLUSIONS

The magnetic and microstructural properties of DyF_3 -doped Nd-Fe-B-sintered magnets were investigated as a function of the sintering conditions. When the DyF_3 -doped magnets were sintered at 1050°C for 4 h, an optimum core-shell microstructure and a coercivity of 35.1 kOe could be obtained without sacrificing the remanence. The effects of the DyF_3 -powder doping on the microstructure of the Nd-Fe-B sintered magnet are: first, a core-shell microstructure was able to be developed by adjusting the sintering temperature and time; second, the reduction of the RE-rich phase formation effectively promoted the distribution of Dy in the main phase; and third, the formation of cubic-NdOF phase in the interface reduced the misfit strain.

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