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Coercivity Enhancement in Nd-Fe-B-type Hot-pressed Magnet by RF_3 doping

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I. INTRODUCTION

Having been used as an essential part in the traction motor and generator of the HEV, EV and wind turbine, the Nd-Fe-B-type magnet is exposed to harsh condition of high operating temperature. Ordinary standard Nd-Fe-B-type magnet cannot function properly at the elevated operating temperature because of its insufficient magnetic properties. Smart technique for enhancing coercivity with avoiding the problems is the grain boundary diffusion (GBD) technique. The GBD technique has also been applied to the hot-pressed or die-upset magnet as a means of enhancing coercivity, and various rare earth fluorides (RF_3) have been investigated as a source of rare earth dopant into the flakes. In this study, the coercivity enhancement in Nd-Fe-B-type hot-pressed magnet by RF_3 doping were investigated.

II. EXPERIMENTALS

Commercial melt-spun flakes (MQU-F : $Nd_{13.6}Fe_{73.6}Co_{6.6}Ga_{0.6}B_{5.6}$) supplied by the Magnequench (Molycorp) were mixed with 1.6 wt% RF_3 (R = La, Ce, Pr, Nd, Dy) and then hot-pressed at the temperature ranging from 610 °C to 810 °C in a vacuum to prepare fully dense hot-pressed magnet. Magnetic characterization was performed using SQUID (max. field = 5 T) and VSM. Microstructure observation and element distribution analysis was performed by SEM equipped with energy dispersive X-ray analysis (EDX). Decomposition of RF_3 salt was examined by TGA (thermogravimetric analysis) in Ar gas.

III. RESULTS AND DISCUSSION

Fig. 1 shows the effect of RF_3-doping on the coercivity of hot-pressed $Nd_{13.6}Fe_{73.6}Co_{6.6}Ga_{0.6}B_{5.6}$ magnet pressed at different temperatures. Significant coercivity enhancement was achieved in the hot-pressed magnet doped with RF_3 (R = Dy, Nd, Pr) with respect to the un-doped magnet, and the most profound coercivity enhancement was achieved in the DyF_3-doped magnet hot-pressed at 735 °C. NdF_3- and PrF_3-doping were also beneficial for enhancing coercivity. For the magnets doped with light rare-earth elements using RF_3 (R = La, Ce), while the LaF_3-doping appeared to be some beneficial in the magnet hot-pressed below 700 °C the CeF_3-doping exhibited no coercivity enhancement. Coercivity of the magnet hot-pressed at high temperature of 810 °C was radically reduced regardless of the doping. Fig. 2 shows the BSE and elemental mapping images of some elements in the RF_3-doped magnet hot-pressed at 735 °C. The Fe atoms in the $Nd_2Fe_{14}B$ phase of the flakes are believed almost certainly not to have migrated actively during the hot-pressing, the estimation of initial width of the added RF_3 by the width of dark Fe-free region between the flakes. For the DyF_3-doped magnet, as can be seen clearly in Fig. 2(a), the initial 5 μm width of added DyF_3 (see Fe image) was reduced down to 1.5 μm (see BSE and Dy images) after the hot-pressing. It was found that the Dy diffusion-out region in the initial DyF_3 region was back-filled with the replaced Nd atoms from neighboring flake (see Nd image in Fig. 2(a)). Although the thickness of the Dy-substituted region near the flake boundary could not be estimated in the BSE and elemental mapping images in Fig. 2(a) the thickness was believed to be a few μm thick. This thickness was inferred by the analogy with the observation of PrF_3-doped magnet in Fig. 2(b). Unlike the BSE image of the DyF_3-doped magnet the BSE image of the PrF_3-doped magnet clearly showed the Pr-substituted region (dark bands) around the added PrF_3 band. As the diffusion characteristics of dopant Dy into the flake was considered to be similar to that of the dopant Pr the thickness estimation of the Dy-substituted region near the flake boundary in the DyF_3-doped magnet by the analogy with the case of PrF_3-doped magnet was more or less reasonable. Although the diffusion of dopant Nd into the flake could not be examined by means of BSE and elemental mapping because the dopant rare earth in this NdF_3-doped magnet was the same element as the rare earth in the flakes, it was almost certainly believed that significant self-diffusion of the doped Nd into the neighboring flakes has occurred. Therefore, the significant coercivity enhancement by NdF_3-doping was thought to be not to do with the change of anisotropy field of the $Nd_2Fe_{14}B$ matrix grains. In this region the $Nd_2Fe_{14}B$ phase grain boundaries may have been restructured by the self-diffusion of dopant Nd. PrF_3-doping was also beneficial to enhance coercivity. As can be seen in the BSE and elemental mapping images of Pr and Nd of the Pr-doped magnet shown in Fig. 2(b) the Nd atoms existed even in the region initially occupied only by the added PrF_3. This indicated clearly that Pr and Nd atoms have inter-diffused actively, and the substitution of some Nd by the doped Pr in the region along the flake boundaries may have occurred during the hot-pressing. The Pr-substituted region near the added PrF_3 was observed clearly as dark bands (~ 4 μm thick) as can be seen in the BSE image in Fig. 2(b). For the magnets doped with light rare-earth elements using RF_3 (R = La, Ce), the LaF_3-doping slightly enhanced coercivity in the magnet hot-pressed below 700 °C. As can be seen in Fig. 2(c), it seemed that active diffusion of the dopant La has not occurred in the LaF_3-doped magnet hot-pressed up to 735 °C. The $Nd_2Fe_{14}B$ grain boundaries near the flake surface then would have been restructured slightly, and this may have slightly enhanced coercivity. The CeF_3-doping showed no influence on the coercivity in the magnet hot-pressed up to 700 °C but caused radical coercivity reduction in the magnet hot-pressed above 735 °C. As can be seen in Fig. 2(d), diffusion of the doped Ce into the neighboring flakes has occurred actively in the magnet hot-pressed at 735 °C. The Ce substitution may have reduced the anisotropy field of the $Nd_2Fe_{14}B$-type grains in the region near the surface of the flakes. The radical coercivity reduction in the LaF_3- and CeF_3-doped magnets hot-pressed at high temperature of 810 °C may be attributed to the reduced anisotropy field of the $Nd_2Fe_{14}B$-type grains by the light rare earth substitution in the region near the flake surface.

IV. CONCLUSION

In the RF_3 (R = La, Ce, Pr, Nd, Dy)-doped magnet hot-pressed at modest temperature (735 °C) the dopant Ce, Pr, Nd and Dy actively substituted Nd in the region near the flake surface to form thin shell in the flake. RF_3 (R = Dy, Nd, Pr)-doping achieved significant coercivity enhancement and it was attributed to the enhanced anisotropy field of the $Nd_2Fe_{14}B$-type grains (for Dy-, Pr-doping) and grain boundary restructuring (for Nd-doping) in the shell. The most profound coercivity enhancement as high as 5 kOe was achieved in the DyF_3-doped magnet. Doping with the light rare-earth elements using RF_3 (R = La, Ce) led to poor coercivity enhancement with respect to the RF_3 (R = Dy, Nd, Pr)-doping.

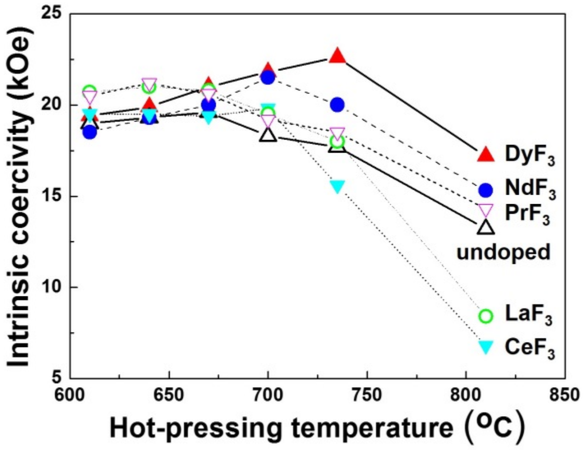

Fig. 1. Effect of RF_3 doping on the coercivity of hot-pressed magnet pressed at different temperatures.

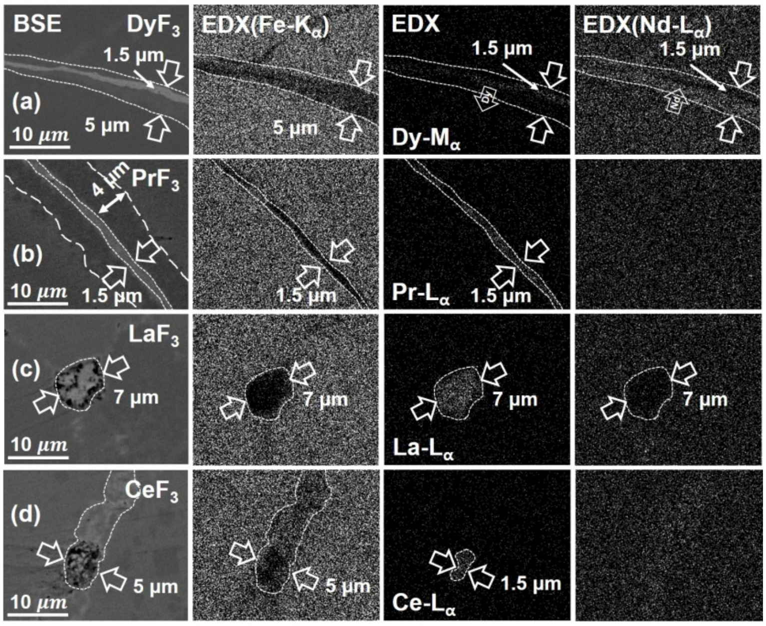

Fig. 2. BSE and elemental mapping of the RF_3 (R = Dy, Pr, La, Ce)-doped magnets hot-pressed at 735 °C