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Properties improvement and structural optimization of sintered NdFeB magnets by non-rare earth compound grain boundary diffusion

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ABSTRACT

Grain boundary diffusion using rare earth (RE)-containing compounds has recently become an effective approach for improving the coercivity and reducing the heavy RE content in sintered NdFeB magnets. Here we report the enhancement of magnetic properties and corrosion resistance of NdFeB magnets by a non-RE compound diffusion process. The Dy-free sintered NdFeB magnets were coated with an MgO layer by magnetron sputtering, followed by solid diffusion heat treatment. With the successful diffusion of MgO into the magnet, the coercivity increasing from 1094 to 1170 kA/m and the maximum energy product increasing from 240 to 261 kJ/m^3, together with the enhanced temperature stability and corrosion resistance, have been demonstrated. The underlying mechanisms for these enhancements have been analyzed. Microstructural investigations show that MgO entered mainly into the intergranular regions and modified the composition and structure of the grain boundary phase. The intergranular Nd–O–Fe–Mg phases observed in the MgO diffused magnet contribute to the improved performance. The current non-RE compound grain boundary diffusion process has significance in further minimizing the use of rare earth (RE).

1. Introduction

Sintered NdFeB rare earth (RE) magnets with excellent permanent magnetic properties at room temperature have found a wide range of applications [1]. In order to meet the needs of the applications for the traction motors of hybrid electric vehicles and wind generators, many recent efforts have been put towards improving both their magnetic properties and thermal stability [2–4]. The properties of the magnets are dependent not only on the intrinsic magnetic properties of the main hard magnetic phase ($RE_2Fe_{14}B$), but also on the characteristics, volume fraction, and distribution of the intergranular phases [5]. It is possible to improve the properties of the NdFeB magnets by modifying the microstructure and compositions of both the main phase and intergranular structures. Enhancing the intrinsic coercivity H_{cj} has currently been achieved by the partial substitution of Dy for Nd in commercial NdFeB sintered magnets and the anisotropy field of the hard phase has been enhanced by the formation of $(Nd,Dy)_2Fe_{14}B$ phase [6]. However, this coercivity enhancement by Dy substitution can only be achieved at the expense of the maximum energy product, $(BH)_{max}$, due to the reduction in magnetization M_s because of the antiferromagnetic coupling of Dy atoms with Fe atoms in the $(Nd,Dy)_2Fe_{14}B$ lattice. Moreover, the scarcity of Dy resources has motivated extensive research into the enhancement of coercivity while minimizing Dy usage. In recent years, a new method named grain boundary diffusion process (GBDP) has been reported [7], in which Dy can be enriched along the grain boundaries of the NdFeB magnet and not enter into the hard magnetic phase. This process involves coating the Dy oxide or fluoride powders on the surface of the powders or magnets followed by diffusion heat treatment. As a result, the coercivity of the magnet was enhanced significantly without a considerable reduction in remanence. Except Dy diffusion, other RE compounds, like Nd–Cu [8], Pr–Cu [9] and Dy–Ni [10], have also been proposed as the diffusion agents for grain boundary diffusion process and proved to be successful. However, the previous reports suggest that a RE containing compound is necessary for such diffusion process. Up to now, there is no report on the grain boundary diffusion using non-rare earth compound.

The insufficient corrosion resistance is another major problem limiting the applications of NdFeB magnets. The low corrosion resistance of sintered NdFeB magnets is attributed to the presence of Nd-rich phases, which have more negative electrochemical potential than the $Nd_2Fe_{14}B$ matrix [11]. Previous works have proved that the addition of alloying elements such as Al, Cu, Mg and Nb can modify the Nd-rich phase to improve the corrosion resistance of sintered NdFeB magnets [12–14]. However, the element addition is likely associated with the reduced magnetic performance of the magnet. The reason is that one or several intrinsic magnetic properties will be impaired when these elements are dissolved in the matrix $Nd_2Fe_{14}B$ type phase. For example, Cu is a good candidate for enhancing the corrosion resistance of NdFeB magnets due to its high standard electrode potential. However, the

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non-ferromagnetic Cu added by direct alloying approach will enter the matrix phase ($Nd_2Fe_{14}B$) besides and deteriorate the magnetic performance. Therefore, in order to obtain a balanced performance of NdFeB-type magnet, it is important to control the distribution of the alloying elements in the magnets. Ideally, the added element should stay only at the intergranular regions [15].

In this work, we propose a grain boundary solid diffusion process for sintered NdFeB magnets using a non-rare earth compound of MgO. The NdFeB magnet was coated with an MgO layer by magnetron sputtering followed by diffusion heat treatment. Our results demonstrated that MgO optimized the grain boundaries of the magnets and effectively improved the magnetic properties and corrosion resistance.

2. Experimental

A commercial sintered NdFeB magnet without Dy addition (JingYueSanHuan Co., China) was used as the starting material, which was cut into cylinder shape with a size of $\Phi = 2 \times 4$ mm^3 (Fig. 1 inset). The top surfaces of samples were coated with an MgO layer by magnetron sputtering deposition for 20–40 min with MgO target. The sputtering chamber was evacuated to a base pressure of 1.9×10^{-4} Pa. Argon was used as the sputtering gas. During sputtering, the sputtering gas pressure, the gas flow rate, and the RF power were maintained at 0.7 Pa, 24 sccm, and 120 W, respectively. The subsequent solid diffusion process was carried out in a vacuum furnace at the elevated temperatures ranging 600–900 °C for 120 min. The whole process for the experiments is schematically shown in Fig. 1.

The treated magnets were cut by wire-electrode cutting and fully magnetized with a pulsed magnetic field of 8 T along the easy axis of the magnets for magnetic property analysis. The magnetic properties were tested by a physical property measurement system (PPMS-9, Quantum Design Co.). The microstructure was observed by field emission scanning electric micrograph (SEM, Nano430, FEI Co.) and transmission electron microscopy (TEM, JEM-1200EX). The Energy Dispersive Spectroscopy (EDS) was used to analyze the element distributions of Nd, Mg, Fe, etc. The polarization curve was measured by electrochemical workstation (Metrohm AUTOLAB PGSTAT 30) in 3 wt.% NaCl solution in a scan rate of 0.002 V/s. Pt with standard potential +0.47 V is used as the reference electrode.

3. Results and discussions

MgO treated magnets were obtained by the process of deposition and diffusion shown in Fig. 1. The diffusion process was carried out at 900 °C for 1 h in vacuum with subsequent heat treatment at 600 °C for 1 h. For comparison, the magnet without MgO coating was also heat treated at same condition, which we called simple heat treatment here.

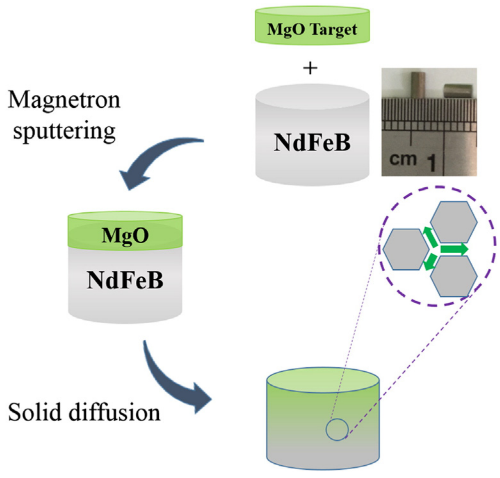

Fig. 1. The schematic of the MgO deposition solid diffusion process.

3.1. Room temperature magnetic properties

Fig. 2 shows the demagnetization curves at 300 K for the sintered NdFeB magnets before and after MgO diffusion treatment. The enhancement of coercivity (H_{cj}) and remanence (J_r) are evident after MgO solid diffusion treatment. The coercivity was enhanced from 1094 to 1170 kA/m and the remanence increased slightly from 1.19 to 1.20 T at 300 K. The $(BH)_{max}$ of the initial magnet and the diffusion processed magnet are calculated to be 240 and 261 kJ/m^3, respectively. However, as shown in Fig. 2, the magnetic properties of the magnet without MgO addition were deteriorated after simple heat treatment. The result indicates that the enhancement of coercivity is mainly due to the diffusion of MgO but not the heat treatment itself. The degraded magnetic properties of simply treated magnet are due to the change of grain boundary phase layer [16].

To verify the diffusion of the MgO, Fig. 3 shows the variations of the coercivity and remanence with the height for the diffusion treated sample after cutting from the top with different heights. One should remember that the MgO was coated on the top surface of the magnet. It is clear that the J_r has almost no change at different parts. However, the H_{cj} increases with the increasing height, indicating that the part of the magnet close to the MgO coating has higher coercivity than those far from the coating. The results thus demonstrate that MgO has successfully diffused into the magnet. The increase of the coercivity is mainly due to the modifications of the grain boundary microstructure and composition after MgO treatment.

3.2. Temperature stability

The magnetic properties at 300 K and 393 K for the sintered NdFeB magnets before and after MgO diffusion processes are shown in Table 1. As expected, the coercivity and remanence decrease with the increasing temperature due to the temperature dependences of magnetization and anisotropy field. At both 300 K and a high temperature of 393 K, the diffusion treated sample has higher magnetic properties than the untreated sample. The temperature stability of permanent magnets in the temperature range of T_0–T can be evaluated by the temperature coefficient of remanence (α) and temperature coefficient of coercivity (β), defined as [13]

$$\alpha = [J_r(T) - J_r(T_0)]/[J_r(T_0)(T - T_0)] \times 100\% \quad (1)$$

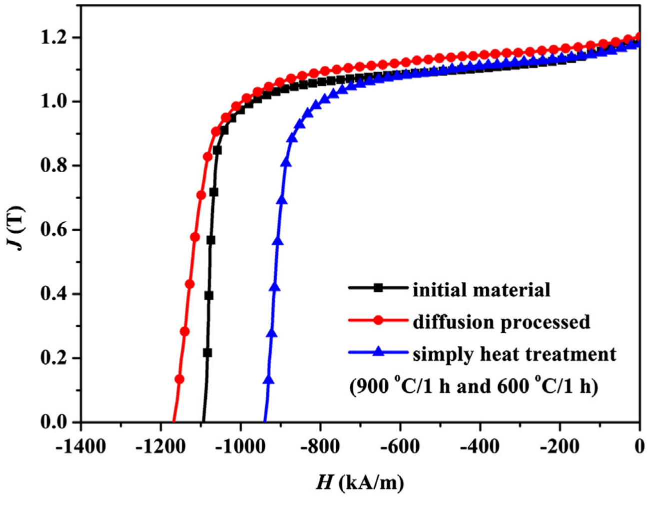

Fig. 2. The demagnetization curves for the initial sintered NdFeB magnet, heat treated NdFeB magnet (900 °C/1 h + 600 °C/1 h), and MgO diffusion processed magnet.