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ARTICLE

Influence of Spray Coating Deposition on Magnetic Properties and Microstructure of Grain Boundary Diffusion Nd-Fe-B Magnets

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Abstract: A novel method of spray coating deposition (SCD) was proposed to deposit TbF₃ powder solution uniformly onto the surface of Nd-Fe-B magnets, and then the Tb element was introduced into the magnets through the grain boundary diffusion process (GBDP). Nd-Fe-B magnets with thickness up to 5 mm were treated with this method (SCD+GBDP). The effects of mass gain ratio (*w*) of TbF₃ coatings, diffusion time and the diffusion temperature on the microstructure and magnetic properties of the sintered magnets were investigated. The samples were diffused at 940 °C for 10 h and then annealed at 480 °C for 5 h. Results show that when the TbF₃ mass gain ratio increases from 0% to 0.8%, the coercivity of the magnets increases from 1201 to 1930 kA/m and the remanence is only decreased by 0.01 T. With increasing the mass gain ratio of TbF₃, the coercivity of the magnets increases firstly and then decreases obviously. SEM results show that the (Nd, Tb)₂Fe₁₄B core-shell phases can be formed by Tb which replaces the Nd in the boundary region among Nd₂Fe₁₄B grains. The improved decoupling effect by the continuous grain boundary phase and the higher magnetocrystalline anisotropy of the core-shell phase plays a positive role in the coercivity enhancement. The distribution and concentration of core-shell phase have a close influence on the coercivity. When the TbF₃ mass gain ratio is more than 2.4%, the grain boundary diffusion is obviously enhanced in the region close to the magnet surface. The SEM image of the element shows that the more Tb enters the inside of the grain, the higher the Tb concentration in the core than in the shell. Furthermore, the formation of a large amount of Nd-F/Nd-O-F phase causes the grain boundary phase not being as continuous as that of the sample with *w*=0.8%, which may be the main reason for the decrease in coercivity.

Key words: sintered Nd-Fe-B magnets; spray coating deposition; grain boundary diffusion process (GBDP); magnetic properties

By virtue of its excellent magnetic performance, sintered Nd-Fe-B magnets have been widely used in various applications such as wind power generation, electric vehicles, hybrid electric vehicles, energy-efficient appliances and consumer electronics^[1]. Electric vehicles and hybrid electric vehicles which require magnets to work for a long time at high temperatures between 120 °C to 150 °C, which puts forward strict request for magnets to have good temperature stability. The conventional method is adding heavy rare earth

(HRE) elements in the process of melting. The substitution of Dy/Tb for Nd is helpful to enhance the magnetocrystalline anisotropy field. However, it is at the sacrifice of remanence because of the antiferromagnetic coupling between HRE and Fe in the (Nd, Dy/Tb)₂Fe₁₄B phase^[2]. In order to improve the temperature stability and reduce the material cost without significantly reducing the remanence, grain boundary diffusion (GBDP) process has been researched to improve the coercivity and the temperature coefficient of magnets^[3,4].

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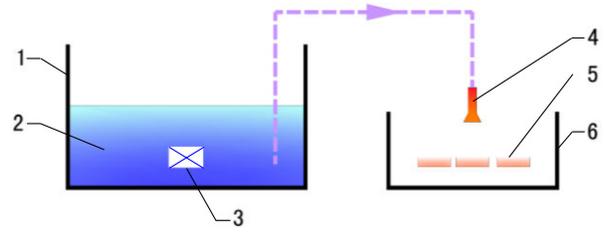
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Currently, one of the most advanced technologies is the GBDP, which can enhance the coercivity of magnets without significant reducing the remanence. The surface of Nd-Fe-B sintered magnets is coated with HRE elements in the form of oxides, fluorides, hydrides, pure metal or alloys. These HRE elements are diffused and allocated at the magnet grain boundaries and then enter the outer regions of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, which leads to the core-shell microstructure after the heat treatment process^[5,6]. It is a promising method of the core-shell microstructure that can significantly increase the coercivity without the cost of decreasing remanence and also dramatically reduce the amount of HRE elements required for sintered magnets. Common coating techniques include dip coating^[7-9], electrophoretic deposition^[10,11], magnetron sputtering^[12,13] and vapor deposition^[14,15]. The main difference among these processes is the method by which the HRE elements are coated on the surfaces of the magnets. The new method of SCD we proposed has not been reported publicly, which is a fire-new means with higher efficiency and cost performance at the same time.

In the present work, a new method of SCD to deposit TbF_3 powder solution uniformly onto the surface of magnets was proposed, by which the TbF_3 can be more uniformly distributed on the surface of the magnets and the content of TbF_3 can also be easily controlled by adjusting the spaying speed. We investigated influences of the TbF_3 mass gain ratio, diffusion temperature and time on the properties and microstructure of the magnets. The reason why the coercivity of TbF_3 coating increased firstly and then decreased with the increase of coating mass ratio was explained from the microstructure.

1 Experiment

Sintered Nd-Fe-B magnets with nominal compositions of $(\text{Pr}, \text{Nd})_{30.2}(\text{Cu}, \text{Co}, \text{Zr}, \text{Ga})_{1.6}\text{Fe}_{\text{bal}}\text{B}_{0.95}$ (wt%) were prepared by conventional powder metallurgical process. The green blocks were sintered at 1060 °C for 6 h, then annealed at 900 °C for 3 h, and further annealed at 480 °C for 5 h in a vacuum sintering furnace. The as-sintered magnets were then used in the subsequent experiments without any post-sintering heat treatment. The sintered blocks were cut into pieces with a cuboid shape of 20 mm×10 mm×5 mm (along the *c*-axis) by slicing cutting. After mixing the TbF_3 powder and ethanol solvent uniformly in a certain proportion, the TbF_3 powder was deposited on two surfaces perpendicular to the *c*-axis of the magnets by SCD method. The mass gain ratio (*w*) of the TbF_3 coatings to the magnet was 0%~3.2% ($w = (w_2 - w_1) / w_1 \times 100\%$, where w_2 is mass of coated TbF_3 of magnet, w_1 is original mass of magnet). Fig. 1 is the schematic diagram of the spray coating process. TbF_3 powder was mixed with ethanol in an ultrasonic vibrator and sprayed through a high-speed gas flow device, so as to be sprayed uniformly on the surface of sintered magnets. The magnets were removed from the dispersion and immediately dried with hot air. The magnets with TbF_3 coating were diffused at 880~960 °C for 1~20 h and subsequently annealed at 480 °C for 5 h. Magnetic



1-solution tank, 2- TbF_3 solution, 3-ultrasonic vibrator, 4-spray nozzle, 5-sintered magnets, 6-recovery tank

Fig.1 Schematic diagram of the spray coating deposition process

properties were measured at 20~150 °C by the permanent magnet measurement device (NIM-2000, National Institute of Metrology, China). The microstructure and composition of the samples were analyzed with the scanning electron microscopy (SEM, AMCS, Sigma 500, ZEISS) in the back-scattered electron (BSE) mode.

2 Results and Discussion

Fig.2a shows the room temperature demagnetization curves for SCD-coated magnets with different mass ratios of TbF_3 coating after GBDP treatment under optimum conditions (diffused at 940 °C for 10 h and then annealed at 480 °C for 5 h). The coercivities of the diffused magnets with $w=0.4\%$,

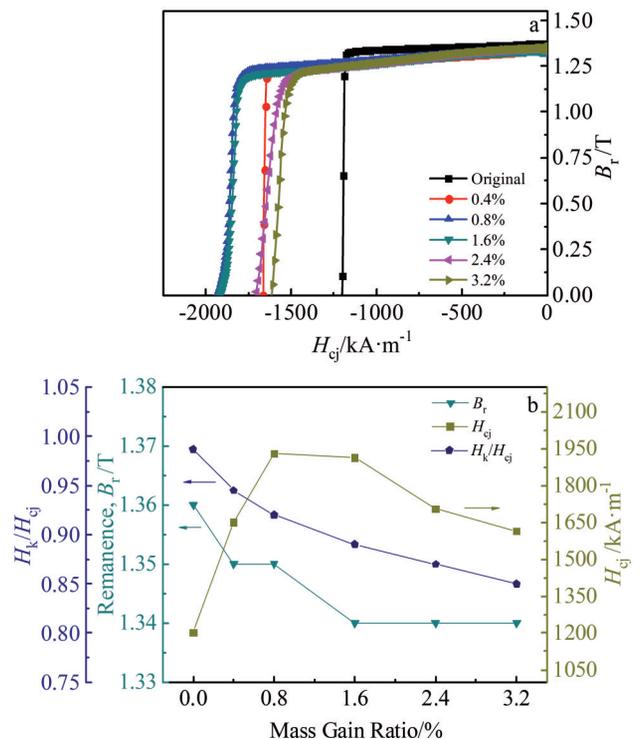


Fig.2 Demagnetization curves for SCD-coated magnets with different mass gain ratios of TbF_3 coating after optimum GBDP condition treatment (diffused at 940 °C for 10 h and then annealed at 480 °C for 5 h) (a); magnetic properties of TbF_3 SCD-coated magnets with different mass gain ratios of TbF_3 coating (b)

0.8%, 1.6%, 2.4%, 3.2% are 1650, 1930, 1913, 1705 and 1613 kA/m, which are increased by 449, 729, 712, 504 and 412 kA/m compared to that of the original magnets (1201 kA/m), respectively. Coercivity of magnet with TbF_3 coating increases significantly compared with that of the original sample. But the coercivity rises at first, and then decreases while the TbF_3 mass gain ratio of coating increases. Fig. 2b shows the magnetic properties for TbF_3 SCD-coated magnets with different mass gain ratios of TbF_3 coating which were diffused at 940 °C for 10 h and then annealed at 480 °C for 5 h. It is obvious that the magnets with TbF_3 coating have a remarkable coercivity (H_{cj}) enhancement. However, the remanence (B_r) and squareness (H_c/H_{cj}) are reduced slightly at the same time. On the one hand, the anti-ferromagnetic coupling between Tb and Fe atoms decreases the overall remanence. On the other hand, the squareness of the magnets decreases with the increase of the coating rate. The poor squareness is due to the non-uniform distribution of the diffusion sources in the magnet, as there are a large number of diffusion sources close to the surface area, but the microstructure in the center is similar to that of the sample before diffusion. Thus, the reason for the degradation of squareness of the demagnetization curve is the difference in the reversal field between the surface and center part which is caused by the uneven formation of HRE-rich shell^[16]. Compared with the original magnet, the coercivity of magnet increases from 1201 kA/m to 1930 kA/m with mass gain ratio of TbF_3 coating of 0%~0.8%. The coercivity remains stable at about 1900 kA/m with a mass gain ratio of TbF_3 coatings of 0.8%~1.6%. But the coercivity decreases with further increase of the TbF_3 above 2.4%. In particular, when the mass gain ratio reaches to 3.2%, the coercivity is the lowest in the coated samples. These results show that the most optimum mass gain ratio is 0.8%. It indicates that the coercivity of the TbF_3 SCD-coated magnets can be efficiently enhanced without significant decrease of remanence within a certain range of mass gain ratio of TbF_3 by the SCD method, and the way of SCD+GBDP is appropriate for preparing magnets with high coercivity.

Fig. 3a shows the coercivity change of TbF_3 SCD-coated sintered Nd-Fe-B magnets (A1~A6) with mass gain ratio of TbF_3 of 0.8% against the diffusion temperature. It can be unambiguously seen that the trend of coercivity change for different samples is basically the same when the diffusion temperature changes from 880 °C to 960 °C. The samples treated at 940 °C for 10 h may acquire the maximum coercivity. The diffusion of Tb into magnets depends on the diffusion temperature strongly. The TbF_3 powder can be decomposed sufficiently with the aid of a relatively high temperature. Then more Tb may diffuse into the Nd-Fe-B magnets, which can contribute to a higher coercivity. As the diffusion temperature increases higher than 940 °C, the magnetic properties begin to deteriorate. Diffusion temperature exceeding 940 °C will cause formation of more C-Nd₂O₃ phases^[17]. In addition, a relatively high diffusion temperature can result in growth of the main phase grain, the decrease of Nd-rich phase, and hole formation in the magnet, causing

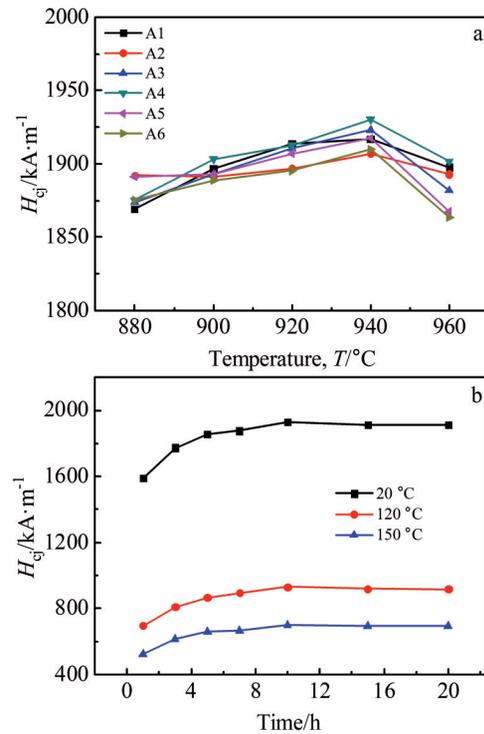
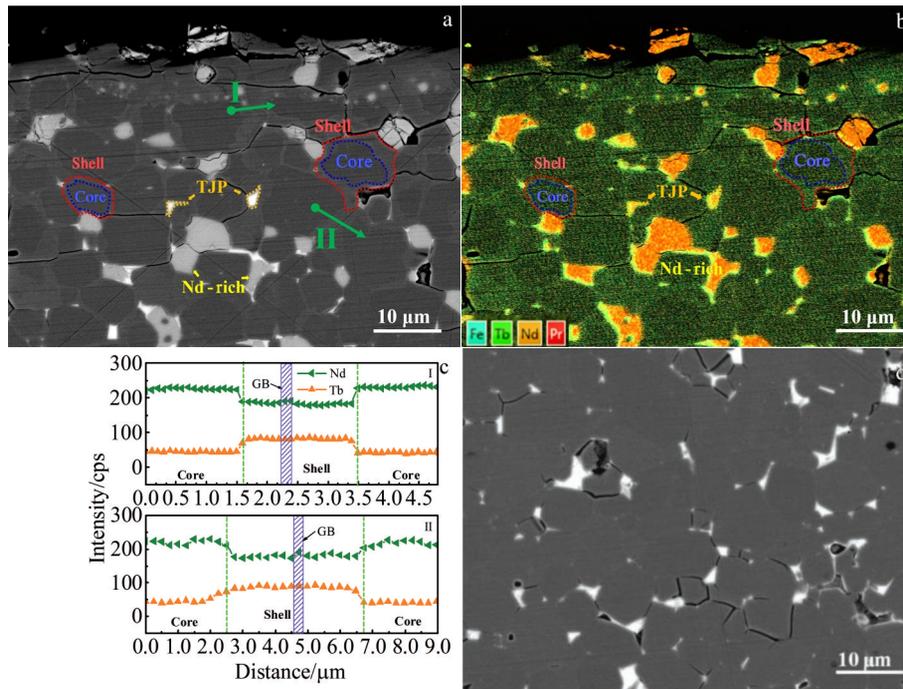


Fig.3 Coercivity of TbF_3 SCD-coated sintered Nd-Fe-B magnets (A1~A6) with mass gain ratio of TbF_3 of 0.8% as a function of diffusion temperature (a) and diffusion time (b)

a coercivity reduction^[18]. Fig. 3b shows the coercivity of samples with the mass gain ratio of TbF_3 of 0.8% at different diffusion time. It takes about 10 h for coercivity to reach the optimum for magnets with a thickness of 5 mm. Since the grain growth area restrains Tb diffusion, the coercivity does not change obviously, but tends to be stable with the further increase of diffusion time. Therefore, 10 h shall be the most appropriate diffusion time for TbF_3 SCD-coated sintered Nd-Fe-B magnet.

Microstructures of the optimal sample (the mass gain ratio of 0.8%) were analyzed, so as to study the enhancement of coercivity by SEM-BSE images, EDS elemental map and line concentration profile for Tb/Nd at the depth of 20 μm from the surface of the samples, as shown in Fig. 4a~4c. For comparison, the BSE image taken at the depth of 500 μm is also shown in Fig.4d. A mass of core-shell structures (red and blue dashed area) form obviously, with a depth of about 20 μm from the surface of SCD-coating sample in Fig.4a. Tb-rich shells are imaged with bright gray in the BSE images while the dark gray parts represent the core. The main phase of sintered Nd₂Fe₁₄B magnet is shown in the dark gray area, while the white area represents the triple junction phases (TJP), Nd-rich grain boundary phases (GBP) and Nd-O/Nd-O-F phases. Light gray parts are distributed outside of dark gray parts, indicating that Tb is diffused into Nd₂Fe₁₄B grain and core-shell structure is formed. Fig.4c shows the concentration curves (scanned along the green line in Fig.4a) of Nd, Tb in the core-shell structure. The Tb-concentration decreases



0

Fig.4 BSE image (a), EDS mapping at a depth of 50 μm from the sample surface (b), EDS line scan profile of Tb and Nd across the shell (c), and BSE image taken at the depth of 500 μm (d)

gradually from the core/shell interface to the grain boundary at which Tb concentration shows a spike. Through the grain boundary phase, Tb element diffuses into the main phase, replacing Nd and formation of $(\text{Nd}, \text{Tb})_2\text{Fe}_{14}\text{B}$ phase, which can make the magnetocrystalline anisotropy field H_A of the main phase increase significantly and enhance the coercivity of the magnet, resulting in substantial changes of Tb and Nd concentration at the interface between two grains. Fig. 4d shows the BSE image taken at the depth of 500 μm, the Tb-rich shell is not clearly observed at the depth of 500 μm by the SEM. It shows that the diffusion of Tb along grain boundaries becomes weaker and weaker with the increase of depth. The coercivity can be efficiently enhanced with a small amount of Tb element using SCD method and TbF_3 SCD-coated GBDP is suitable for producing high coercivity magnets.

To better understand the dependence of microstructure of the SCD-coated sample on mass gain ratio of TbF_3 , the cross-sectional SEM-BSE images 500 μm to surface of the samples are shown in Fig. 5a~5e. In all SCD-coated samples diffused with TbF_3 , the typical Tb-rich shell structure can be observed in the region near the surface (indicated with red arrow) clearly but the Tb-rich shell is not clearly observed at the original sample (Fig. 5a). Since the concentration gradient of Tb is caused by the diffusion of Tb from the surface of the Nd-Fe-B magnet to the center, a large number of core-shell structures appear at a distance of 50 μm from the surface of the sample. When the depth increases beyond 200 μm, the core-shell structure almost fades away, and the grain boundary phase becomes discontinuous at the same time. The nucleation of reverse magnetic domains in the grains may be prevented

by the relatively high magnetocrystalline anisotropy of the core-shell phase in the outer region of the crystal grain, which is beneficial to the coercivity enhancement. The Tb-rich core-shell structure near the surface of the magnet sample with $w=0.8\%$ is clearly visible in the backscattered image as a gray reaction phase surrounding the dark $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, which is well developed and shown in Fig. 5b. Tb core-shell thickness increases and grain area of the main phase decreases near the surface of the magnet sample with $w=3.2\%$. A thick Tb-rich shell is observed in TbF_3 -SCD magnets because the diffusivity of Tb into the main phase increases. It is well known that the grain boundary phase is the main channel for the Tb diffusion. However, the Tb element is coated on the surface of the magnet, so the concentration gradient of Tb near the surface is very high, which may increase the volume diffusion of the Tb element, resulting in the formation of a thick Tb diffusion layer near the surface of the magnet^[19]. Since most of Tb elements are consumed by volume diffusion near the surface of the magnets, Tb element cannot diffuse deeper into the magnet, then the grain boundary diffusion depth of Tb element is decreased and the grains with the formation of Tb-enriched core-shell structure are limited^[20]. This may be the main reason for the coercivity decrease as the TbF_3 coating increases.

The Tb, Nd and F concentration variation versus distance from the surface of the TbF_3 SCD-coated magnets is shown in Fig. 6. The Tb and F concentration gradient occurs upon diffusion from the surface to the magnet. Tb and F concentrations of samples with mass gain ratio of TbF_3 of 3.2% are significantly higher than those of samples with low

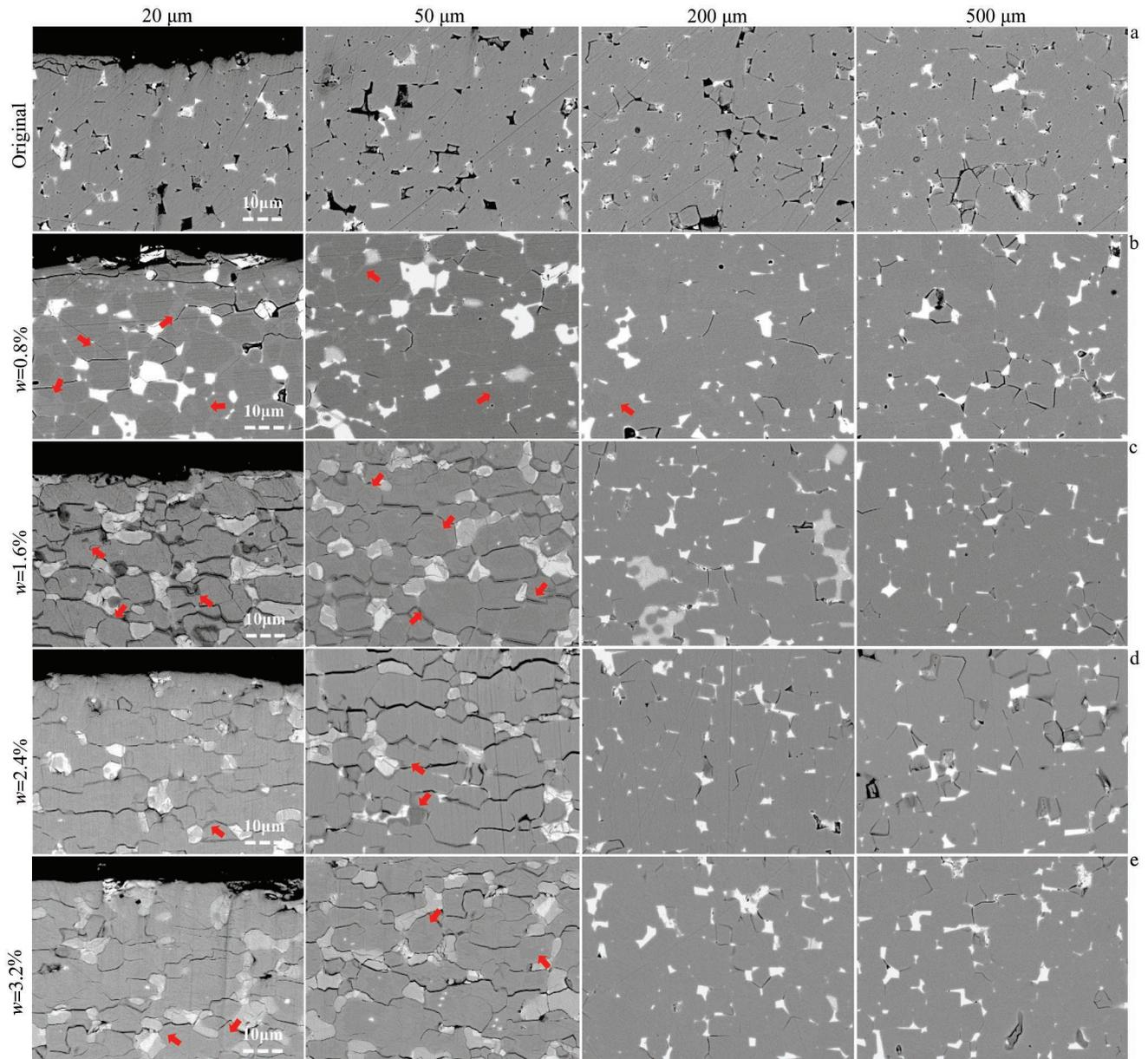


Fig.5 SEM-BSE microstructures of original sample (a) and samples with different mass gain ratios of TbF_3 coatings (b~e) at different diffusion depths

mass gain ratio of TbF_3 (0.8%) at about 50 μm depth from the surface. The Tb and F concentrations of the samples tend to be identical when the depth is greater than 200 μm . The results show that the diffusion depth of Tb along grain boundaries is less affected by the Tb concentration at the surface. The variation of Nd concentration is opposite to that of Tb and F, which indicates that in the diffusion process, molten Nd and solid-state Tb diffuse reciprocally, driven by chemical potential gradient, and finally reach the chemical potential equilibrium state, and some Nd elements precipitate out onto the surface of the magnet. Nd concentration decreases from 27.0wt% to 25.5wt% when the mass gain ratio increases from 0.8% to 3.2% at depth of 50 μm , and a large amount of Tb and F are enriched on the surface where Nd-F/Nd-O-F forms with Nd-rich phases; the reduction of Nd-rich hinders the further

diffusion of Tb along grain boundaries^[21]. Thus, the high magnetic anisotropy of Tb-rich core-shell structure and the reduction of continuous grain boundary phase lead to a decrease in coercivity. It indicates that the HRE element contents on the magnet surface shall not be so high during the grain boundary diffusion process. The materials will be wasted with lower coercivity if the coating contents are too high.

To further verify the distribution of Tb and Nd in core-shell structures formed by different coating ratios, and the influence of Tb core-shell formed by the Nd-O-F phase, Fig.7 shows the SEM-BSE images of the samples with $w=1.6\%$ and $w=3.2\%$ at the depth of 50 μm . The histogram of Tb and Nd content scanned at top right corner of the SEM-BSE image through the corresponding region spots (spot 3, 4, 6, 7) and the data

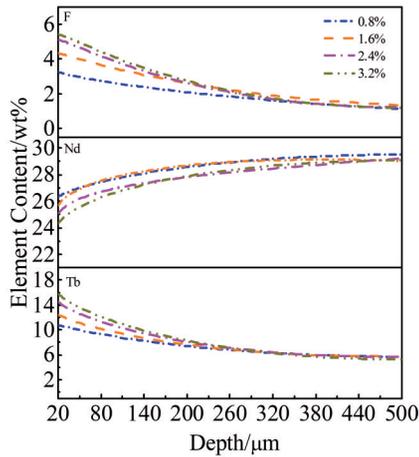


Fig.6 Tb, Nd and F concentration variation versus distance from the surface of the TbF_3 /SCD-coated magnets with different mass gain ratio of TbF_3 coatings

are shown in Table 1. It can be seen that Tb concentration at core (6.33wt% and 6.69wt%) is lower than that at shell (14.97wt% and 15.18wt%) when the mass gain ratio is 1.6%. On the contrary, Tb concentration at core (17.17wt% and 16.44wt%) is higher than that at shell (7.11wt% and 6.67wt%) when the mass gain ratio is 3.2%. In addition, Tb concentration with $w=1.6\%$ is 14.97 wt% and 15.18 wt%, higher than that with $w=3.2\%$ (7.11wt% and 6.67wt%). It shows that more Tb goes into the crystal grains when the Tb content on the surface of the magnet increases. The diffusivity of Tb into the main phase of the $w=3.2\%$ magnet increases compared to that of $w=1.6\%$ magnet, as shown in Table 1. EDS mapping of Nd, Tb, F and O obtained from the same region of SEM-BSE images is displayed at the right. When the TbF_3 mass gain ratio of coating is greater than 1.6%, F is obviously concentrated in the same region as Nd does. Nd-rich phase is the main channel for Tb to diffuse into the

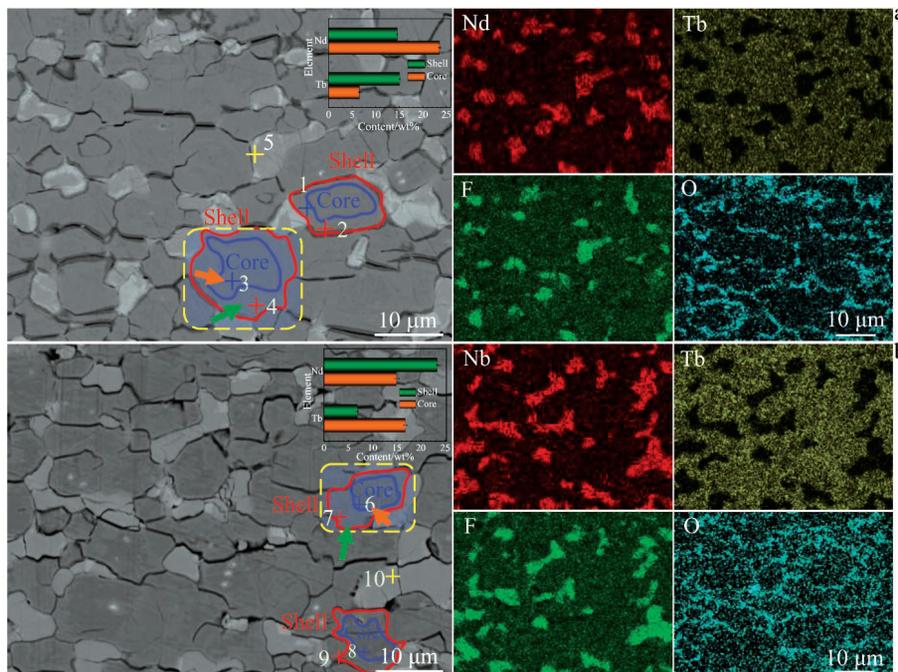


Fig.7 SEM-BSE images and EDS mappings of samples with $w=1.6\%$ (a) and $w=3.2\%$ (b) at the depth of 50 μm (histograms of Tb and Nd content are scanned at top right corner of the SEM-BSE image through the corresponding region spot 3, 4, 6, 7)

magnet. When F- and Nd-rich phases gather together, Nd-F/Nd-O-F phase will be formed, resulting in discontinuous liquid Nd-rich phase, and the channel of Tb diffusion is blocked and the tendency of diffusion along the grain is enhanced^[21]. EDS mapping of Tb shows that more Tb enters inside the grains and the core-shell structure becomes less obvious. Tb spectrum is consistent with the results of the spot scan in Table 1. The RE-rich phase typically has a curved interface, whereas the Nd-O-F phase has planar interfaces. Coherent or semi-coherent interfaces between the magnet's main phase and the Nd-O-F phase can be formed but incoherent interfaces between the main phase and the RE-rich phase exist because the surface energy of the RE-rich phase is

much larger than that of the Nd-O-F phase^[22]. In the surface region, most Tb elements are distributed in the matrix of the grains of $w=3.2\%$ magnet. The concentration differences of Tb at the interface between the grain boundary phase and the matrix phase reduce the magnitude of the magnetic anisotropy field and suppress nucleation of a reverse domain, which gives drop to the coercivity enhancement. This is consistent with our study.

3 Conclusions

1) When the TbF_3 mass gain ratio increases from 0% to 0.8 %, the coercivity of the magnets increases from 1201 kA/m to 1930 kA/m and the remanence is only decreased by

Table 1 EDS results of selected spots 1~10 marked in Fig.7a and Fig.7b (wt%)

Element	Fig.7a					Fig.7b				
	Core-1	Shell-2	Core-3	Shell-4	Re-rich-5	Core-6	Shell-7	Core-8	Shell-9	Re-rich-10
C	5.89	6.46	6.42	6.42	-	7.47	5.33	5.14	5.14	-
O	1.35	1.43	1.26	1.43	8.57	3.68	1.40	1.45	1.34	4.51
F	0.90	1.02	1.19	1.38	9.05	3.20	1.09	1.02	1.07	17.07
Fe	61.77	61.52	61.18	59.97	3.33	52.95	61.93	61.55	62.15	1.31
Nd	23.76	14.59	23.25	14.50	76.37	15.53	23.15	14.40	23.64	75.02
Tb	6.33	14.97	6.69	15.18	2.69	17.17	7.11	16.44	6.67	2.10

about 0.01 T.

2) With the increase of grain boundary F concentration, the Nd-F/Nd-O-F phases formed in Nd-rich grain boundary phase become discontinuous. In addition, with the increase of TbF₃ mass gain ratio, the diffusion of Tb atoms into the main phase via volume diffusion may increase relatively. Therefore, more Tb diffuses into the matrix grains, resulting in the concentration of Tb inside the grains much higher than that at the grain boundaries, and the coercivity of the magnet is reduced.

3) Compared with the dip-coating method, TbF₃ can be distributed more uniformly on the surface of the magnets and the content of TbF₃ can also be controlled easily by spray coating deposition method. Compared with magnetron sputtering, this method has higher efficiency and lower cost.

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雾化喷涂沉积对晶界扩散Nd-Fe-B磁性能和微观结构的影响

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摘 要: 提出了一种新的雾化喷涂沉积 (SCD) 方法, 在Nd-Fe-B磁体表面均匀沉积TbF₃粉末, 同时通过晶界扩散过程 (GBDP) 将Tb元素引入到磁体中。用这种方法 (SCD+GBDP) 处理厚度达5 mm的钕铁硼磁体。研究了TbF₃涂层增重比、扩散时间和扩散温度对烧结磁体组织和磁性能的影响。样品扩散温度和时间为940 °C和10 h, 退火温度和时间为480 °C和5 h。TbF₃增重比 (w) 从0%增加到0.8%时, 磁体的矫顽力从1201 kA/m提高到1930 kA/m, 剩磁下降约0.01 T。研究发现, 随着TbF₃增重比的增加, 磁体的矫顽力先增大后减小。SEM结果表明, 在Nd₂Fe₁₄B晶粒边界区域, Tb取代Nd形成(Nd, Tb)₂Fe₁₄B核壳相。晶界相和核壳相中较高的磁晶各向异性对矫顽力的增强有积极的促进作用。核壳相的分布和浓度对矫顽力有密切的影响。当TbF₃增重比大于2.4%时, 靠近磁体表面区域的晶界扩散明显增强。元素的SEM图像显示, 进入磁体的Tb越多, 晶核内的Tb浓度就越高。此外, 大量Nd-F/Nd-O-F相的形成导致晶界相不像 $w=0.8%$ 时的样品那样连续, 这可能是导致矫顽力下降的主要原因。

关键词: 烧结钕铁硼磁体; 雾化喷涂; 晶界扩散; 磁性能

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