Grain Boundary Diffusion Sources

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Definition

Grain boundary diffusion process provides a promising way to enhance coercivity for Nd-Fe-B permanent magnets with a tiny consumption of critical rare earth resources. By this method, during a diffusion heat treatment, diffusion sources infiltrate from magnet surface into interior of magnet through melting grain boundary phases. Nowadays, 3 generations of grain boundary diffusion sources haven been developed, i.e., heavy rare earth based, light rare earth based, and non-rare earth based sources.

1. Grain Boundary Diffusion for Nd-Fe-B Magnets

Nd-Fe-B permanent magnets have been widely used in various fields including conventional electric motors, renewable energy, and mobile communication industries [1][2][3]. The total world production of sintered Nd-Fe-B magnets in 2019 was 1.9 × 10^5 tons, and the demand of Nd-Fe-B magnets is constantly increasing due to the large employment of electric motors and generators in the near future [4]. The magnets in the motors and generators should operate at temperatures greater than 150 °C [3], but the Nd-Fe-B magnets without the addition of heavy rare earth (HRE) elements have insufficient coercivity (H_{cj}) to withstand the demagnetization field at high such temperatures because the hard magnetic $Nd_2Fe_{14}B$ (2:14:1 phase) compound has a low Curie point (T_c) of ~312 °C, and its anisotropy field (H_A) decreases drastically with the increasing temperature [5][6]. A conventional route for fabricating high-coercive Nd-Fe-B magnets is adding the HRE elements of Dy and Tb during smelting. However, it results in a large consumption of expensive HRE resource and a sacrifice of remanence (J_r).

The grain boundary diffusion (GBD) process for the Nd-Fe-B magnets, which was firstly proposed in 2005, provides the best route to enhance the H_{cj} with less consumption of HRE [7][8]. By this way, HRE infiltrates from the surface to the interior of the magnets during a diffusion heat treatment, mainly strengthening the surface of Nd 2Fe 14B grains by forming $(Nd,HRE)_2Fe_{14}B$ structured shells. With the coercivity increment of 560 kA/m, the amount of Dy introduced by GBD is only 10% of that added by the conventional route [8]. Up to now, GBD has attracted much interest from both industry and academic, and it has become an important approach for the industry to fabricate cheap yet strong products. Now, most commercial Nd-Fe-B magnets with H_{cj} > 1600 kA /m (SH grade) are fabricated by GBD [9]. Their maximum working temperatures can be greater than 150 °C.

2. Typical Grain Boundary Diffusion Sources

The HRE-based compound is regarded as the first generation of diffusion source. To get rid of the dependence of HRE, in 2010, a diffusion alloy of Nd-Cu without any HRE element was demonstrated effective for coercivity enhancement, which started the research and development (R&D) of the second generation of sources based on light rare earth (LRE) elements [10]. Subsequently, in 2015, a cost-effective diffusion source of MgO was proposed [11]. It gave an idea that the non-rare earth (non-RE) compound or alloy can be used to modify the grain boundary (GB) phase as the next generation of diffusion source.

Among the three types of GBD sources, the HRE-based one can directly enhance the H_{cj} by increasing the H_A of 2:14:1 phase, and has been industrialized. Generally, a two-step diffusion heat treatment is needed for commercial sintered magnets. During the first step GBD, the heating temperature range is generally selected at 800 to 1000 °C to ensure that the melting GB phase provides effective diffusion channels for HRE atoms. At this stage, the surface of $Nd_2Fe_{14}B$ grains also melts due to the eutectic reaction of Nd-$Nd_2Fe_{14}B$ system at ~685 °C [12], which is lower than the temperature of the first step GBD. In this case, HRE atoms substitute Nd atoms in the 2:14:1 lattice at the surface of the 2:14:1 grain, forming $(Nd,HRE)_2Fe_{14}B$ shells around the hard magnetic grains [13][14]. The temperature of the second step GBD is usually selected between 400 to 600 °C to modify the distribution of GB phase, i.e., facilitating the formation of continuous GB layers for magnetic decoupling. The reported HRE-based diffusion sources can enhance the H_{cj} by > 900 kA/m for the magnets with a thickness of <5 mm. The effective HRE containing GBD sources mainly include fluorides, hydrides, and metals/alloys [15][16][17][18][19][20][21][22][23][24].

The LRE-based alloys with low melting points can form thick and continuous GB layers, effectively isolating the hard magnetic grains for decoupling. The GBD conditions of LRE sources are similar to those of the HRE sources, i.e., using a two-step heat treatment process. At present, the effective LRE-based diffusion sources mainly include Pr- and Nd-based low-melting alloys [25][26][27][28][29][30][31]. The coercivity increment caused by Pr-Al-Cu reaches 700 kA/m and ~500 kA/m for 2 mm- and 10 mm-thick magnets, respectively [28]. In addition to the Pr- and Nd-based diffusion alloys, high-abundance La- and Ce-based alloys have been also studied as diffusion sources recently [29][30][31]. However, their caused coercivity enhancement is still marginal. Some recent researches demonstrated that the non-RE elements have positive effects on microstructure modification, i.e., wetting the GB phase and reducing the defects at 2:14:1grain/GB interfaces [11][31][32][33][34]. Therefore, various non-RE metals, alloys, and compounds have been selected as the diffusion sources. The diffusion of ZnO can lead to a coercivity enhancement of 205 kA/m in a 4-mm thick magnet [32]. So far, although the coercivity enhancement by the non-RE diffusion (<250 kA/m) is still much lower than that by the RE diffusion, the non-RE GBD is expected to improve the corrosion resistance and mechanical properties of the magnets.

3. Coating Methods for Diffusion Sources

In addition to the component of the diffusion sources, the development of their coating methods are quite important for the industry. Since the Nd-Fe-B products are mainly fabricated under customization, different diffusion sources and coating methods can be employed to meet the specific applications.

Compared with the investigations of diffusion sources, the studies about how the sources can be deposited onto the magnets are relatively insufficient. However, this issue is quite critical for the industry. With the development of GBD process, more and more coating techniques have been employed for coating the diffusion sources. At present, the coating methods for GBD sources can be mainly classified into three types: adhesive coating, electrodeposition, and vapor deposition.

Among the mentioned coating methods, the vapor deposition has an overwhelming advantage regarding environmental protection. Meanwhile, it can precisely control the consumption of GBD sources, which is beneficial for saving the critical RE resources and improving the stability of the product. However, owing to the necessary vacuum environment and the relatively low deposition rate, the production efficiency is lower than those of the adhesive coating and the electrodeposition. Furthermore, the vapor deposition still exhibits high costs from equipment and processing. Therefore, this approach applies to small quantities of products.

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Keywords

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