Journal of Magnetism and Magnetic Materials 355 (2014) 131–135

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Coercivity enhancement of NdFeB sintered magnets by low melting point $Dy_{32.5}Fe_{62}Cu_{5.5}$ alloy modification

Liping Liang, Tianyu Ma*, Pei Zhang, Jiaying Jin, Mi Yan*

Department of Materials Science and Engineering, State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 12 May 2013
Received in revised form
3 November 2013
Available online 4 December 2013

Keywords:
Low melting point alloy
Intergranular addition
Sintered NdFeB magnet
Coercivity

ABSTRACT

To improve coercivity without sacrificing other magnetic performance of NdFeB sintered magnets, a low melting point $Dy_{32.5}Fe_{62}Cu_{5.5}$ alloy was introduced as an intergranular additive. Magnetic properties and microstructure of the magnets with different $Dy_{32.5}Fe_{62}Cu_{5.5}$ contents were studied. At the optimum addition of 3 wt%, coercivity H_{cj} was enhanced from 12.7 to 15.2 kOe, the maximum magnetic energy product $(BH)_{max}$ was simultaneously increased from 46.6 to 47.8 MG Oe, accompanied by a slight reduction in remanence B_r. Further investigation on microstructure and grain boundary composition indicated that the enhanced H_{cj} and $(BH)_{max}$ could be attributed to the refined and uniform 2:14:1 phase grains, continuous grain boundaries and a $(Nd,Dy)_2Fe_{14}B$ hardening shell surrounding the 2:14:1 phase grains.

1. Introduction

Due to excellent magnetic properties, NdFeB sintered magnets have been widely applied in sensors, motors, generators and so on [1]. However, the poor thermal stability limits their applications in high-temperature environments, such as the hybrid electric vehicles and wind driven generators [2]. In order to solve this problem, high coercivity NdFeB magnets are required.

The coercivity H_{cj} of NdFeB sintered magnets is dominated by the nucleation of the reverse domain, generally, at the surface region of the 2:14:1 phase grains with reduced magnetic anisotropy field H_a. The surface H_a depends, on one hand, on the intrinsic H_a value of the $R_2Fe_{14}B$ phase and, on the other hand, on the microstructure defects in the surface [3]. Many efforts have been carried out to enhance the surface H_a of NdFeB sintered magnets. Direct alloying with heavy rare-earth element Dy or Tb is well known to enhance the H_a by partially replacing Nd in the 2:14:1 phase lattice [4–6]. Inevitably, B_r significantly decreases due to the anti-ferromagnetic coupling between Fe and Dy or Tb [7]. Besides, both Dy and Tb are expensive and scarce resources, direct alloying causes very high material cost. Therefore, producing high coercivity NdFeB magnets with less heavy rare-earth content is of strategic interest. Instead of direct alloying, formation of a $(Nd,R)_2Fe_{14}B$ (R=Tb or Dy) hardening shell surrounding the 2:14:1 phase grains can enlarge the reduced H_a in the surface region to enhance H_{cj} effectively without B_r dilution [8–10]. Nakamura et al. used grain boundary diffusion (GBD) method and enhanced H_{cj} obviously by forming a Dy-containing layer surrounding the 2:14:1 phase grains [11]. However, this process is limited to thin sheet-like magnets with a thickness less than 5 mm. For bulk magnets, Yue et al. enhanced the H_{cj} by doping Tb and Dy nanoparticles to form $(Nd,Tb/Dy)_2Fe_{14}B$ shells [12]. In comparison with the micro-sized particles doping, both preparation of nanoparticles and homogenous mixture of nanoparticles with the micro-sized NdFeB powders are still difficult for mass production. Besides, the H_{cj} can also be further enhanced by refining 2:14:1 phase grains and modifying the grain boundaries microstructure. Kim et al. reported that the enhanced H_{cj} without B_r reduction could be reached by uniform matrix grains and continuous grain boundaries [13,14]. Therefore, to fabricate high coercivity NdFeB sintered magnets for mass production, adding suitable micro-sized Dy-containing alloy to form hardening shell and modified microstructure could be a distinct way.

For this approach, the additives should have good wettability with the matrix phase for densification and structural homogenization. Lemke et al. reported that a small addition of Cu (less than 0.2 at%) improved the wettability between matrix phase and grain boundary to obtain uniform grain and continuous grain boundary [15,16]. Our group has also developed low melting point AlCu and NdFeCu alloys to densify the magnets and homogenize the distribution of intergranular phase [14–17]. In this work, we designed a low melting point $Dy_{32.5}Fe_{62}Cu_{5.5}$ (at%) alloy to form the hardening shell and homogenous microstructure to enhance the H_{cj}. Good magnetic performance with H_{cj}=15.2 kOe, $(BH)_{max}$=47.8 MG Oe, B_r=1.35 T have been achieved in NdFeB magnets doped with 3 wt% $Dy_{32.5}Fe_{62}Cu_{5.5}$ alloy.

2. Experimental

The starting materials with composition of $(Pr,Nd)_{13.05}Dy_{0.12}Fe_{bal}Al_{0.25}Nb_{0.07}B_{5.7}$ (at%) were prepared by induction melting and subsequent strip casting. The casting thin flakes were pulverized

* Corresponding authors. Tel.: +86 571 8795 2730; fax: +86 571 8795 2366.
E-mail addresses: maty@zju.edu.cn (T. Ma), mse_yanmi@zju.edu.cn (M. Yan).

0304-8853/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jmmm.2013.11.007

to powders with an average size of 3.7 μm by hydrogen decrepitating and jet-milling process. The adding alloy $Dy_{32.5}Fe_{62}Cu_{5.5}$ was prepared by arc melting under the protection of high purity argon atmosphere. Then the ingot was mechanically crushed and refined to ~1.5 μm by ball milling with isopropanol as protection medium. These two kinds of micro-sized powders were blended homogeneously by ball milling for 2 h, followed by aligning under a magnetic field of 1.6 T and compacting under a pressure of 200 MPa. The amount of aiding alloy powders was ranged from 1 to 4 wt%. The green compacts were sintered for 3 h at 1084 °C and subjected subsequently to a two-step annealing treatment, which were conducted for 2 h at 890 °C and for 3 h at 520 °C.

The magnetic density was determined by the Archimedes method. Melting point of $Dy_{32.5}Fe_{62}Cu_{5.5}$ was evaluated by analyzing the differential scanning calorimetry (DSC) curves, which was measured by heating the specimen at 10 K/min. Magnetic properties were measured using an AMT-4 magnetic measurement device. The microstructure and composition of the grain boundary were analyzed by a field emission scanning electron microscopy equipped with an energy dispersive X-ray spectroscopy.

3. Results and discussion

Fig. 1 shows the magnetic properties for magnets doped with different amounts of $Dy_{32.5}Fe_{62}Cu_{5.5}$ powders. As expected, H_{cj} increases from 12.7 to 15.2 kOe by 20% as the $Dy_{32.5}Fe_{62}Cu_{5.5}$ amount increases from 0 to 3 wt%. Continuous increasing the amount to 4 wt%, H_{cj} can be further increased to 15.5 kOe. However, B_r and $(BH)_{max}$ will decrease rapidly when the adding amount is over 3 wt%. Therefore, the optimum adding amount of $Dy_{32.5}Fe_{62}Cu_{5.5}$ is 3 wt%. At this doping level, in addition to the enhanced H_{cj}, $(BH)_{max}$ of the magnet could also be improved from 46.6 to 47.8 MG Oe.

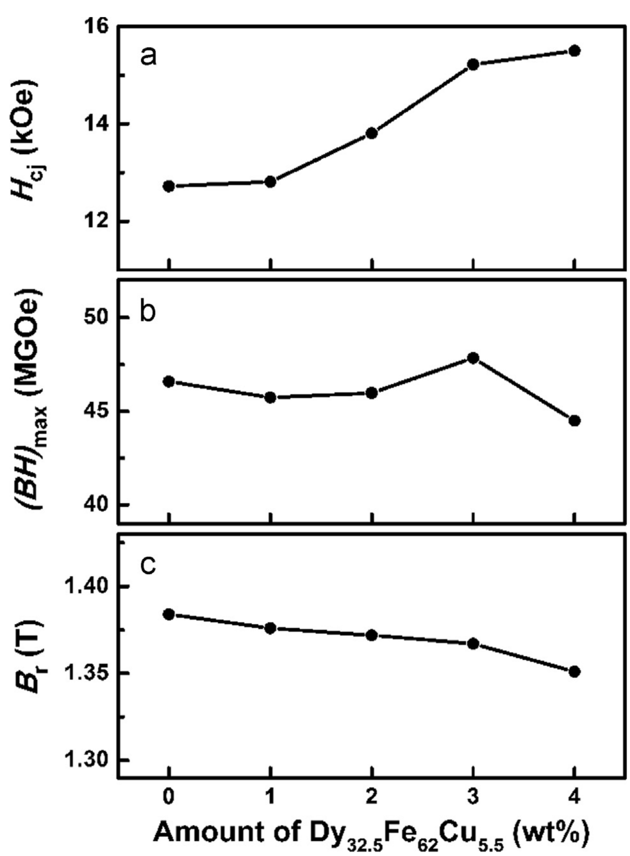

Fig. 1. Magnetic properties of $(Pr,Nd)_{13.05}Dy_{0.12}Fe_{bal}Al_{0.25}Nb_{0.07}B_{5.7}$ sintered magnets as a function of the amount of $Dy_{32.5}Fe_{62}Cu_{5.5}$ addition.

SEM images of the starting magnet and the ones with different amounts of $Dy_{32.5}Fe_{62}Cu_{5.5}$ addition are shown in Fig. 2. The dark gray region corresponds to the 2:14:1 phase and the bright region surrounding the 2:14:1 phase grains corresponds to the Nd-rich phase. For the starting magnet, as shown in Fig. 2a, there is no continuous grain boundary layer between two ferromagnetic 2:14:1 phase grains, which means that the neighboring ferromagnetic grains are not isolated well. Additionally, the triple junctions are almost round-shaped, indicating that the wettability between the 2:14:1 phase and the intergranular phase is poor. Besides, the 2:14:1 phase grains are not uniform, where the grain size is ranging from 8–15 μm. As $Dy_{32.5}Fe_{62}Cu_{5.5}$ is doped, distributions of the intergranular phase and 2:14:1 phase grain size are optimized, as shown in Fig. 2b–e. In comparison with the starting magnet, grain boundary layer between the neighboring matrix phases becomes thicker and continuous. At 3 wt% addition, smooth and continuous grain boundaries form, as shown in Fig. 2d. Grain size of the 2:14:1 phase becomes more uniform for the $Dy_{32.5}Fe_{62}Cu_{5.5}$ doped ones, locating in a much narrower scope from 5 to 8 μm. Meanwhile, in comparison with the starting magnet, there are two different contrasts in the triple junctions for the doped ones. One exists as a regular white contrast (which is marked by red arrow in Fig. 2b) and the other exists as a gray contrast (which is marked by white arrow in Fig. 2b) in corners of the triple junctions. It indicates that two different types of Nd-rich phases tend to exist in the doped magnets [18]. With formation of the gray Nd-rich phase, the triple junctions turn from round-shaped into strip-like. It can be inferred that the wettability of the magnets is improved. As a result, the magnetic density could be increased, as reflected by Fig. 3. The magnetic density increases continuously from 7.55 to 7.58 g/cm^3 with the increase of $Dy_{32.5}Fe_{62}Cu_{5.5}$ amount from 1 to 4 wt%.

DSC curve of the as-prepared $Dy_{32.5}Fe_{62}Cu_{5.5}$ alloy is shown in Fig. 4, where point “A” indicates that its melting point is approximately 394.5 °C. It should be noted that it is far below the melting point of Nd-rich phase (655 °C) and the sintering temperature (1084 °C) in the present work. Fig. 5 schematically illustrates the effect of the low melting point additive $Dy_{32.5}Fe_{62}Cu_{5.5}$ on the sintering process. The NdFeB green compacts consist of NdFeB particles (large green region), low melting point $Dy_{32.5}Fe_{62}Cu_{5.5}$ alloy powders (blue dots) and Nd-rich phases (dark green regions), as shown in Fig. 5a. Generally, after hydrogen decrepitating and jet-milling process, Nd-rich phases exist in three types, which are the precipitates inside the matrix phase grains, the intergranular phases attaching to their surfaces and the ones isolated from the matrix phase powder. During the liquid-phase sintering process, the $Dy_{32.5}Fe_{62}Cu_{5.5}$ powders were first melted at 394.5 °C. The liquid flowed and permeated into the interspace between NdFeB and Nd-rich phases solid particles. As the flowing of the liquid, rearrangement of solid particles and preliminary densification of the magnet occurred under capillary pressure of the liquid phase, as illustrated in Fig. 5b. Meanwhile, Dy atoms began to diffuse towards the surface region of $Nd_2Fe_{14}B$ from the $Dy_{32.5}Fe_{62}Cu_{5.5}$ liquid phase. At 655 °C, due to the eutectic reaction, the Nd-rich phase liquid formed at the $Nd_2Fe_{14}B$ grain boundaries. Then the system might be considered consisting of two main components, i.e. the solid $Nd_2Fe_{14}B$ particles and the mixed liquid of $Dy_{32.5}Fe_{62}Cu_{5.5}$ and Nd-rich phase. During the following sintering process, the angles and sharp corners of $Nd_2Fe_{14}B$ particles dissolved and removed in the flowing liquid. Due to the driving force of the capillary pressure of the mixed liquid between solid $Nd_2Fe_{14}B$ particles, further densification occurred. The two stages of liquid flowing and particles rearrangement results in smooth and continuous grain boundaries surrounding the $Nd_2Fe_{14}B$ grains,