Acta Materialia 128 (2017) 22-30

Contents lists available at ScienceDirect

Acta Materialia

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



Effects of REFe₂ on microstructure and magnetic properties of Nd-Ce-Fe-B sintered magnets

Yujing Zhang ^a, Tianyu Ma ^{a, *}, Jiaying Jin ^a, Jiangtao Li ^a, Chen Wu ^a, Baogen Shen ^b, Mi Yan ^{a, *}

^a State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Key Laboratory of Novel Materials for Information Technology of Zhejiang Province, Zhejiang University, Hangzhou 310027, China

^b State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history: Received 25 October 2016 Accepted 1 February 2017 Available online 1 February 2017

Keywords: Nd-Fe-B Highly abundant rare earth Microstructure Magnetic properties

ABSTRACT

Ce substitution level in Nd-Fe-B magnets has been significantly increased via the binary main phase (BMP) approach, i.e. sintering the mixture of Ce-free and Ce-containing RE₂Fe₁₄B (RE, rare earth) powders. REFe₂ phase that forms in the high Ce-containing Nd-Ce-Fe-B magnets has been considered to be harmful to magnetic performance due to its soft magnetism. In this work, we found that REFe₂ phase with lower melting point than the 2:14:1 phase plays positive role on optimizing the microstructure and retaining magnetic performance of the Nd-Ce-Fe-B BMP magnets. The wettability of 2:14:1 phase can be improved by sintering above the melting point of REFe₂ phase, which promotes densification of the magnet and the formation of continuous and smooth grain boundary (GB) phases. This contributes to the weakened short-range exchange coupling between adjacent grains, hence ensures superior magnetic performance of BMP magnets to the single main phase (SMP) ones with the same average composition. As a result, magnetic properties of $B_r = 12.4$ kG, $H_{cj} = 9.0$ kOe and $(BH)_{max} = 36.7$ MGOe can be obtained even when 45 wt % Ce substitutes for Nd in the BMP magnets.

© 2017 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Incorporation of Ce, the most abundant and cheapest rare earth (RE) element, into the Nd₂Fe₁₄B-type sintered magnets has drawn considerable interest recently from an economic point of view [1–10]. Although Nd can be substituted by Ce in the tetragonal Nd₂Fe₁₄B phase, inferior intrinsic magnetic properties of Ce₂Fe₁₄B compound (saturation magnetic polarization J_s , anisotropy field H_A , and Curie temperature T_C for Ce₂Fe₁₄B are 11.7 kG, 26 kOe, 151 °C, respectively) to Nd₂Fe₁₄B ($J_s = 16.0$ kG, $H_A = 73$ kOe, and $T_C = 312$ °C) [11] pose a big challenge to fabricate high-performance Nd-Ce-Fe-B magnets with high Ce substitution. Early studies have shown that homogeneous Ce substitution for Nd in the 2:14:1 phase lattice deteriorates the magnetic properties degrade drastically with B_r of 13.2 kG, H_{Cj} of 10.2 kOe and (BH)_{max} of 40 MGOe with only 5 wt % Ce substitution for Nd [14]. Recently, the addition of Ce has

http://dx.doi.org/10.1016/j.actamat.2017.02.002

been pushed to a higher level with much weakened magnetic dilution effect by the binary main phase (BMP) approach, i.e. sintering the mixture of Ce-free and Ce-containing powders with both compositions close to the stoichiometric 2:14:1 [7–9]. Magnetic properties of (*BH*)_{max} = 43.3 MGOe, B_r = 13.6 kG, and H_{cj} = 9.26 kOe have been obtained when 30 wt % of Nd is replaced by Ce in the (Nd_{0.7}Ce_{0.3})₃₀(Fe,M)_{bal}B₁ sintered magnets [7]. Consequently, the BMP approach is appealing for developing permanent magnets with high Ce content and low cost.

Analogous to the magnets fabricated by the conventional single main phase (SMP) approach, the BMP magnets are also composed of 2:14:1 matrix phase and intergranular RE-rich phase [7–9]. While the BMP magnets show distinctly difference of elemental distributions compared with the SMP ones. The inter-diffusions of RE atoms between the Ce-free and Ce-containing components result in inhomogeneous elemental distributions either within an individual grain or across grains, forming a multi-main-phase microstructure [9]. Such composition fluctuation results in localized intrinsic magnetic properties of BMP magnets. Consequently, three types of magnetic interactions exist, i) short-range exchange coupling within an individual grain, ii) long-range magnetostatic





Acta MATERIALIA

^{*} Corresponding author. E-mail addresses: maty@zju.edu.cn (T. Ma), mse_yanmi@zju.edu.cn (M. Yan).

^{1359-6454/© 2017} Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

interactions across isolated grains with different mean Ce contents, and iii) short-range exchange coupling between adjacent grains that are not well isolated by intergranular RE-rich phase. The first type of magnetic interaction, as discussed in our recent work [9], is beneficial to retain the remanence. The second type plays an essential role on the achievement of superior coercivity to the SMP magnet with the same average composition as the magnetically "harder" Ce-lean grains tend to impede the propagation of reversed domains from the adjacent magnetically "softer" Ce-rich grains. The third type is usually undesired in the conventional SMP magnets as it deteriorates the coercivity [15,16], but how does it affect the coercivity of BMP magnets remains a fundamental question. It is important because one can enhance greatly the coercivity by forming nonferromagnetic grain boundary (GB) layers through incorporating intergranular additives like that for the SMP magnets [17-20].

In addition, to further improve the substitution level of Ce in the final BMP magnets, the Ce content in the initial Ce-rich component should be designed as high as possible. While high Ce content may result in the formation of additional phases in the Ce-rich component, and their contents and distributions strongly affect the macroscopic magnetic properties, especially the coercivity. An early work by Herbst et al. [3] has shown that the melt-spun $Ce_{17}Fe_{78}B_6$ alloy contains up to 12 wt % CeFe2 in addition to the Ce2Fe14B matrix phase. Other studies have also shown that REFe₂ phase forms when Ce content in Nd-Ce-Fe-B exceeds the critical values, for instance, 32 at. % in La2.50Ce4.72Pr1.55Nd5.65Dy0.29Cu0.09Al0.10Nb0.09Co0.74-B_{6.09}Fe_{bal} (at.%) alloy [8] and 24 wt % in (Di_{0.76}Ce_{0.24})_{27.5-} Dy₃Al_{0.1}Cu_{0.1}Fe_{bal}B₁ (wt. %) alloy [21]. Consequently, it has been considered that the REFe₂ phase inevitably forms in the Nd-Ce-Fe-B component with high Ce content. Its existence has been thought to be harmful to magnetic performance of the magnets because of its lower intrinsic magnetic parameters than the 2:14:1 phase. CeFe₂ is paramagnetic at room temperature and magnetically soft even below its $T_{\rm C}$ [22]. Considering that the CeFe₂ has a lower melting point (925 °C) than that of the sintering temperature for 2:14:1 magnets [8,23], it is inspiring to understand how the REFe₂ phase affect the liquid-phase sintering process and the microstructure of the final BMP magnets. If it works like the low melting point alloys of Nd-Cu, Pr-Cu, Dy-Fe, Al-Cu etc. in the intergranular region for Nd-Fe-B magnets [24–28], the exchange coupling between adjacent grains could be significantly weakened due to the improved wettability of main phase and the formation of continuous and smooth RE-rich GB phases. The correlation between microstructure and coercivity of BMP magnets can then be well understood.

In this work, a Ce-free component and a Ce-containing component (Ce in the total RE is 50 wt %) that contains REFe₂ phase are designed to fabricate the BMP magnets. The distribution of REFe₂ phase and its influences on both microstructure and magnetic properties of the magnets have been investigated.

2. Experimental

A Ce-containing component $[(Pr,Nd)_{0.5}Ce_{0.5}]_{30.5}Fe_{bal}M_{1.0}B_{1.0}$, M = Al, Cu, Ga, Zr, in wt. %) (hereafter named as Ce-50) and a Ce-free component $(Pr,Nd)_{30.5}Fe_{bal}M_{1.0}B_{1.0}$ (hereafter named as Ce-0) have been designed. Each component was subjected to induction melting, strip-casting, hydrogen decrepitation and jet milling. Mean particle size of the final powders is $3.0-3.5 \ \mu m$. After blending the powders of Ce-50 and Ce-0 with the mass ratios of 54: 46, 72: 28 and 90: 10, green compacts with nominal composition of $[(Pr,Nd)_{0.73}Ce_{0.27}]_{30.5}Fe_{bal}M_{1.0}B_{1.0}$, $[(Pr,Nd)_{0.64}Ce_{0.36}]_{30.5}Fe$ $balM_{1.0}B_{1.0}$, and $[(Pr,Nd)_{0.55}Ce_{0.45}]_{30.5}Fe_{bal}M_{1.0}B_{1.0}$ (hereafter named as Ce-27, Ce-36 and Ce-45, respectively) were obtained under a compressive pressure of 5.5 MPa in a perpendicular magnetic field of 1.5 T followed by isostatic pressing under ~200 MPa. Final magnets were prepared by sintering at 1030 °C for 4 h, followed by a two-step annealing treatment at 890–920 °C for 2 h and 460–520 °C for 4.5 h. For comparison, Ce-27 SMP magnets with the nominal composition of $[(Pr,Nd)_{0.73}Ce_{0.27}]_{30.5}$ Fe_{bal}M_{1.0}B_{1.0} were also prepared using the same procedures.

To identify the phase constituents, step-scanned X-ray diffraction (XRD) was performed on the powder samples for the Ce-50 component, Ce-27 SMP, Ce-27 BMP and Ce-45 BMP magnets. Rietveld refinements of the XRD patterns were carried out by a Rietica software [29]. To determine the melting point of constituting phases in the Ce-50 component, differential scanning calorimetry (DSC) curve was obtained upon heating to 1200 °C at 10 °C/ min under Ar flow using a differential thermal analysis device (DTA, Netzsch 449F3 Jupiter). Demagnetization curves of the sintered magnets were measured using an AMT-4 magnetometer at room temperature. Density (ρ) of the magnet was determined according to the Archimedes principle. Micro-morphology observations of the polished sample surfaces were carried out using a Hitachi S-3400I scanning electron microscopy (SEM). Elemental distribution mappings were obtained using a JXA 8230 WD spectrometer. Specimen for transmission electron microscope (TEM) observation was prepared utilizing the standard techniques of grinding, dimpling and argon ion-beam thinning. Ion-beam thinning was carried out on both sides of the specimen at an inclination angle of 8° for the ionbeam with respect to the specimen surface. TEM characterization was performed using a JEOL-2100F microscope equipped with a GATAN CCD slow scan camera. The magnetic domain structure was observed using JEOL2100F L-TEM (Fresnel method).

3. Results and discussion

Magnetic measurements show that the Nd-Ce-Fe-B BMP magnets have superior performance to the SMP ones at the same average composition. Fig. 1 shows the room temperature demagnetization curves of the Ce-0, Ce-27 SMP, Ce-27 BMP, Ce-36 BMP and Ce-45 BMP magnets. The derived coercivity H_{cj} , remanence B_{r} , energy product (*BH*)_{max} and squareness factor H_k/H_{cj} are summarized in Table 1. Compared to the Ce-free (Ce-0) magnet with H_{cj} of 13.8 kOe, B_r of 14.1 kG and (*BH*)_{max} of 48.7 MGOe, the magnetic properties of Ce-27 SMP magnet deteriorate drastically to H_{cj} of



Fig. 1. Room temperature demagnetization curves for the Ce-0 and Ce-27 magnets prepared by single main phase (SMP) approach, the Ce-27, Ce-36 and Ce-45 magnets prepared by binary main phase (BMP) approach.

Table 1

Nominal composition, room temperature coercivity (H_{cj}), energy product ((BH)_{max}), remanence (B_r), squareness factor (H_k/H_{cj}) and density (ρ) for the Ce-0, Ce-27, Ce-36, Ce-45 sintered magnets prepared by different approaches.

Magnet	Composition (wt. %)	Approach	H _{cj} (kOe)	$B_{\rm r}({\rm kG})$	$(BH)_{\max}$ (MGOe)	$H_{\rm k}/H_{\rm cj}$ (%)	ρ (g/cm ³)
Ce-0	$(Pr,Nd)_{30.5}Fe_{bal}M_{1.0}B_{1.0}$	SMP	13.8	14.1	48.7	97.4	7.55
Ce-27	[(Pr,Nd) _{0.73} Ce _{0.27}] _{30.5} Fe _{bal} M _{1.0} B _{1.0}	SMP	10.4	12.8	39.0	94.3	7.56
Ce-27	[(Pr,Nd) _{0.73} Ce _{0.27}] _{30.5} Fe _{bal} M _{1.0} B _{1.0}	BMP	11.4	13.0	41.1	97.7	7.57
Ce-36	[(Pr,Nd) _{0.64} Ce _{0.36}] _{30.5} Fe _{bal} M _{1.0} B _{1.0}	BMP	10.3	12.7	38.8	96.4	7.57
Ce-45	$[(Pr,Nd)_{0.55}Ce_{0.45}]_{30.5} Fe_{bal}M_{1.0}B_{1.0}$	BMP	9.0	12.4	36.7	94.2	7.57

10.4 kOe, B_r of 12.8 kG and $(BH)_{max}$ of 39.0 MGOe. It is due to the magnetic dilution effect that Ce substituting for Nd in the 2:14:1 phase lattice decreases the intrinsic magnetic properties [30]. The BMP approach, however, is effective to weaken the magnetic dilution effect. With the same average composition, the Ce-27 BMP magnet shows better magnetic properties of $H_{cj} = 11.4$ kOe, $B_r = 13.0$ kG, and $(BH)_{max} = 41.1$ MGOe than the SMP one. As the Ce content is increased to 36 wt %, magnetic properties of the Ce-36 BMP magnet are comparable to the Ce-27 SMP one. When the Ce content is further increased to 45 wt % (the Ce-45 BMP magnet), preferable magnetic performance of $B_r = 12.4$ kG, $H_{cj} = 9.0$ kOe and $(BH)_{max} = 36.7$ MGOe can be obtained.

The superior magnetic performance of the BMP magnet is ascribed to the chemical heterogeneity of the main phase, where Ce and Pr/Nd are distributed inhomogeneously either within an individual grain or across grains. As shown by the elemental mapping analysis in Fig. 2, the Ce-45 BMP magnet in which the mass ratio of Ce-50 to Ce-0 component is 9:1, exhibits obvious chemical heterogeneity within the matrix phase grains, where both Ce-lean and Ce-rich grains can be distinguished. Due to the initial chemical gradient between the Ce-50 and Ce-0 components, RE atoms interdiffused during liquid-phase sintering and post annealing. The local chemistry for an individual grain of the 2:14:1 matrix phase can be roughly clarified into two types, i) Ce concentration gradually decreases from the GB towards a Pr/Nd-rich grain core (close to the initial Ce-0 component) and ii) Pr/Nd concentrations gradually decrease from the GB towards a Ce-rich core (close to the initial Ce-50 component). Additionally, these two types of grains are randomly distributed within the whole magnet, i.e. the mean Cecontent inside 2:14:1 matrix phase grains is inhomogeneous. Consequently, the resultant long-range magnetostatic interactions among the 2:14:1 phase grains result in single-phase like demagnetization behaviors [9], as no apparent kink or step is observed in the demagnetization curves in Fig. 1. All the BMP magnets possess high squareness factors with $H_k/H_{ci} > 94\%$.

More importantly, the distributions of RE elements in the intergranular regions are also inhomogeneous. As indicated by arrows with different colors, some local triple junctions (white arrows) consist mainly of Pr/Nd/Ce (>70 wt %) and a small amount of Fe (~20 wt %), and others (black arrows) contain ~50 wt % Pr/Nd/Ce and ~40 wt % Fe. The former ones are the conventional RE-enriched phases, which are commonly observed in Ce-free magnets [31–33]. The latter ones, however, are usually unavailable within the Ce-free magnets, which are completely different from the triple junctions composed mainly of REs or oxygen with much lower Fe content. The atomic ratio of RE to Fe in such regions was evaluated to be ~1:2, which is in good agreement with the stoichiometric composition of REFe₂ phase. To clarify whether they are REFe₂ phase or not, TEM characterizations were carried out, as shown in Figs. 3 and 4.

Fig. 3a shows a low magnification bright field image (BFI) of the Ce-45 BMP magnet. Grain 1 and grain 2 with larger size are the 2:14:1 matrix phase, as identified by the SAED patterns in Fig. 3b and c, taken along the [001] and [211] zone axes, respectively.

Crystal structure of the triple junction region has also been identified by SAED patterns using a smaller aperture as indicated by the red dashed circle. The SAED patterns in Fig. 3d and e were taken from RE-rich triple junction region with two different orientations which can be indexed as a diamond cubic structure with zone axes of [211] and [321], respectively. The *d*-spacings for the planes $(1\overline{11})$ and $(0\overline{2}2)$ in Fig. 3d are 0.422 nm and 0.261 nm with the calculated lattice parameter of a = 0.737 nm which agrees well with REFe₂ phase (Table 2). Besides, the obtained *d*-spacing of $d_{(1\overline{33})} = 0.168$ nm is also consistent with the REFe₂ phase (Fig. 3e). TEM characterizations conducted for another region of the Ce-45 BMP magnet are also shown in Fig. 4. The BFI picture (Fig. 4a) shows two matrix phase grains and a typical triple junction region. The SAED patterns (Fig. 4b and c) of the triple junction region are also obtained with two orientations. Again, it is proved to be the cubic REFe₂ phase with zone axes of [211] and [310], respectively. Furthermore, the REFe₂ phase and 2:14:1 matrix phase grains are well combined with smooth interface as shown in Fig. 4d and e.

The above characterizations confirm the existence of REFe₂ phase in the intergranular regions in BMP magnets, being consistent with the EPMA results in Fig. 2. The following questions then arise, how does the REFe₂ phase form and how does it affect the microstructure and the magnetic properties of BMP magnets? To answer these questions, we have investigated the phase constituents and the microstructural evolutions as follows.

Firstly, we investigated the initial phase constituents of the Ce-50 component powders by Rietveld XRD analysis, as shown in Fig. 5. The strongest reflections correspond to the 2:14:1 tetragonal phase (space group P4₂/mnm). Further refinement reveals that the REFe₂ phase (space group $Fd\overline{3}m$) and a small amount of RE-rich phase (space group P6₃/mmc) coexist with the 2:14:1 matrix phase. The lattice parameters and mass fraction for each phase are listed in Table 2. Besides the overlapped reflections, the individual ones (111), (022) and (113) at the Bragg angles 2θ of 21.0°, 34.6° and 40.8° correspond to the REFe₂ phase. The mass fraction of REFe₂ phase was evaluated to be 6.85 wt %, which is lower than the ternary Ce-Fe-B system [3]. The lattice parameter of REFe₂ phase is a = 0.7346 nm, which is consistent with the calculated value from SAED patterns. In addition, the calculated lattice parameters of 2:14:1 phase (a = 0.8788 nm, and c = 1.2182 nm as in Table 2) are slightly smaller than the reported data for Nd₂Fe₁₄B (a = 0.880 nm and c = 1.220 nm) since the Ce₂Fe₁₄B possesses smaller lattice parameters (a = 0.876 nm and c = 1.211 nm) than those of the Nd₂Fe₁₄B [11]. It also confirms that Ce substitutes for partial Pr/Nd in the 2:14:1 phase.

After sintering and post annealing, the REFe₂ phase is inherited from the Ce-50 component to the BMP magnets. In Fig. 6a and b, the step-scanned XRD patterns for the Ce-45 and Ce-27 BMP magnets in powder form shows that (111), (022) and (113) reflections of the REFe₂ phase still exist in addition to the matrix 2:14:1 tetragonal phase, as indicated by the " \bigtriangledown " symbols. The typical diffraction reflections of REFe₂ phase show higher intensity in the Ce-45 magnet due to the increased Ce-50 component. Considering that both Ce-27 BMP and Ce-45 BMP magnets were prepared by the Ce-



Fig. 2. (a) Back-scattered SEM image and the corresponding elemental concentration distribution mappings of (b) Fe, (c) Ce, (d) Nd and (e) Pr. The brighter contrast in (a) is the RErich phase, and the darker contrast reflects the 2:14:1 matrix phase. The white dashed lines illustrate the GBs and are guide for eyes. The black arrows in (b) and (c) indicate the Ce concentrated RE-rich triple junctions with relatively higher Fe content, while the white arrows indicate Pr/Nd/Ce concentrated RE-rich triple junctions with lower Fe content.

free component and the Ce-50 component with initial mass ratio of 46: 54 and 10: 90, the mass fraction of REFe₂ phase in Ce-27 BMP and Ce-45 BMP magnets should be 3.70 wt % and 6.17 wt %. The calculated mass fraction of REFe₂ phase from Fig. 6a and b (2.27 wt % and 5.60 wt %) are slightly smaller than the initial values. It suggests that partial REFe₂ phase reacts with the RE-rich phase during sintering and post annealing. For comparison, such representative diffraction reflections were not detected in the Ce-27 SMP magnet (Fig. 6c), indicating that the REFe₂ phase is absent or its amount is too small to be detected by XRD.

Role of REFe₂ phase on the microstructure of BMP magnets has also been investigated. Fig. 7 shows the DSC curve of the Ce-50 component upon heating to 1200 °C at 10 °C/min. Two obvious endothermic peaks are observed. The endothermic reaction at 1142 °C corresponds to the melting of the 2:14:1 matrix phase. Considering that the alloy contains 50 wt % of Ce in the total RE content, the melting point of 2:14:1 phase is decreased compared to Nd₂Fe₁₄B (1155 °C) [34]. The other endothermic reaction at 978 °C can be attributed to the melting of REFe₂ phase which has a higher melting point than CeFe₂ (925 °C) [8,23]. As the sintering temperature of 1030 °C is much higher than the melting point of the REFe₂ phase, REFe₂ phase melts during high-temperature sintering, which provides additional liquid phase in addition to the conventional RE-rich phase.

 $Nd_2Fe_{14}B$ -type sintered magnets possess a liquid phase sintering process and the wettability between the matrix 2:14:1 phase and liquid phase plays an important role on the microstructure and magnetic properties [35]. The volume fraction of liquid phase strongly affects the sintering process, which is essential for densification of the magnet. As schematically described for the SMP magnets (Fig. 8a), the RE-rich phase primarily melts upon heating, flows and penetrates into the interspace of the 2:14:1 phase particles by further sintering, leading to rearrangement and displacement of matrix particles due to capillary suction. Finally, dense sintered magnets can be obtained. For the BMP magnets (Fig. 8b), the RE-rich phase can also gradually wet the 2:14:1 phase grains similarly. However, the additional REFe₂ phase melts and increases the volume fraction of the liquid phase, which is beneficial to enlarge the direct contact areas between liquid GB phase and the 2:14:1 grains during the high-temperature sintering. Better wettability contributes to magnet densification as well as the formation of continuous GB phase. Consequently, high density could be obtained for the BMP magnets (Table 1).

Fig. 9 shows the back-scattered SEM images for the Ce-27 SMP, Ce-27 BMP, Ce-36 BMP and Ce-45 BMP magnets. The Ce-27 SMP magnet possesses discontinuous GBs which means the neighboring ferromagnetic grains are not well isolated (Fig. 9a). Note that, for the BMP magnets, the higher Ce content, the larger volume fraction of the REFe₂ phase. Fig. 9b–d shows obvious change of the GBs in the BMP magnets. In comparison with the Ce-27 SMP magnet, continuous intergranular RE-rich phases are formed in the Ce-27 BMP magnet with the same average composition (Fig. 9b). As the



Fig. 3. TEM characterizations for the Ce-45 BMP magnet. (a) Bright field image taken along the [001] zone axis of grain 1 (G1). (b) SAED pattern taken in the region of grain 1. (c) SAED pattern taken in the region of grain 2 (G2). (d) and (e) SAED patterns taken in the region indicated by red dashed circle in (a) by tilting it to different zone axes, revealing a cubic structure (space group Fd3m). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Ce amount increases, the contrast of intergranular phases becomes clearer and more continuous, isolating well the 2:14:1 phase grains (Fig. 9c and d). It is clear that the increased $REFe_2$ phase promotes the formation of continuous intergranular phases along the GBs.

Thin GB layer is observed for the Ce-27 SMP magnet (Fig. 10a), which appears discontinuous in the back-scattered SEM image. Such thin GB phase is not sufficient to isolate adjacent grains, which is one important reason for its low coercivity. For the BMP magnet, the GB layer is much thicker (~23.5 nm, Fig. 10b). It is beneficial to isolate neighboring 2:14: 1 phase grains and to decouple them during magnetization reversal. Fig. 11 shows the L-TEM images (Fresnel mode). Since the samples were prepared with the *c*-axis in plane, the opposite magnetizations produce the dark and bright contrasts at the magnetic domain walls. These images were observed with the sample in zero magnetic field. For the Ce-27 SMP sample (Fig. 11a), the configuration shows that the triple junction



Fig. 4. TEM characterizations for another typical region of the Ce-45 BMP magnet. (a) Bright field image taken along the [211] zone axis of REFe₂ phase (triple junction). (b) and (c) are SAED patterns for the triple junction region as indicated by the red dashed circle in (a) along two different zone axes. (d) and (e) are TEM images with a high magnification taken from the regions indicated by the red squares I and II in (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with three 2:14:1 hard magnetic grains isolated by the thin intergranular phase. Note that the domain walls are continuous across the GBs (indicated by the red dashed rectangle), which indicates short-range exchange coupling between adjacent hard magnetic grains. Such kind of continuous domain walls are quite common in the Ce-27 SMP sample, but are rare in the Ce-45 BMP magnet. The L-TEM image of the Ce-45 BMP sample (Fig. 11b) shows that the magnetic domains are interrupted by the thick GB phase. The discontinuous magnetic domain walls suggest the magnetic decoupling of the adjacent grains. The magnetization reversal will not be cascaded across the GBs even if nucleation occurs at the weakest point in the bulk magnet, as each 2:14:1 grain is magnetically decoupled. Thus, the unique structural and chemical feature of the GB phase in Ce-substituted BMP magnets may also

ble 2	
ace group, crystal structure, lattice parameters and mass fraction of the phases in the Ce-50 component evaluated by Rietveld analysis (Fig.	<mark>5</mark>).

Phase	Space group	Structure	Lattice parameters (nm)	Mass fraction (%)
RE ₂ Fe ₁₄ B	P4 ₂ /mnm	Tetragonal	a = 0.8788; c = 1.2182	89.49
REFe ₂	Fd 3 m	Cubic	a = 0.7346	6.85
RE-rich	P6 ₃ /mmc	Hexagonal	a = 0.3828; c = 0.6737	3.66
Refine profile $R_{\rm p} = 4.69$, $R_{\rm w} =$	= 5.96, $R_{ m exp} =$ 2.57, $\chi^2 =$ 5.40			

play an important role on enhanced coercivity.

The above results demonstrate that REFe₂ phase exerts important effects on the microstructure of Nd-Ce-Fe-B sintered magnets by changing the distribution of the GB phase. It may lead to important consequences. Firstly, it brings new insights into the demagnetization mechanism of BMP magnets. The superior magnetic performance of the BMP magnets to the SMP ones has been attributed to the chemical heterogeneity of the matrix phase [9]. An



Fig. 5. XRD pattern for the Ce-50 component in powder form. The black dots show the observed experimental data and the red full line represents the calculated fits to the experimental data. Green line shows the difference between the fitted and observed results. The Bragg positions of $RE_2Fe_{14}B$, $REFe_2$ and RE-rich phases are indicated by the short vertical bars in blue, red and olive, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. XRD patterns for the powder samples of (a) Ce-45 BMP, (b) Ce-27 BMP and (c) Ce-27 SMP sintered magnets. The black dots show the observed experimental data and the red full line represents the calculated fits to the experimental data. Green line shows the difference between the fitted and observed results. The Bragg positions of RE₂Fe₁₄B, REFe₂ and RE-rich phases are indicated by vertical bars in blue, red and olive, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

individual grain has locally different Ce and Pr/Nd concentration, which means the local regions have different intrinsic magnetic properties accordingly. The exchange coupling between Ce-lean local region (magnetically harder) and the Ce-rich region (magnetically softer) inside an individual grain is beneficial to the magnetic properties, especially for retaining B_r and $(BH)_{max}$. In addition, the magnetization reversals. Once reverse domains nucleate in deteriorated regions (close to the GB), the neighboring regions/grains with higher H_A impedes its quick immigration.



Fig. 7. DSC curve for the Ce-50 component upon heating to 1200 °C at 10 °C/min.



Fig. 8. Schematic illustrations for the evolution of microstructure for (a) SMP and (b) BMP magnets during sintering.



Fig. 9. Back-scattered SEM images of the magnets. (a) Ce-27 SMP, (b) Ce-27 BMP, Ce-36 (c) BMP and (d) Ce-45 BMP. The dark contrast corresponds to 2:14:1 matrix phase and the bright contrast corresponds to the RE-rich intergranular phases, respectively.

Consequently, it takes a relatively long progress to achieve complete domain reversals within the whole magnet, producing a larger coercivity than the SMP magnets. The present work further reveals that the weakened exchange coupling effect between adjacent grains is also essential to obtain a higher coercivity, like that for the SMP magnets, as supported by the direct evidence of magnetic isolation (L-TEM characterizations in Fig. 11b). This implies a feasible principal to further enhance the coercivity of BMP magnets, via forming continuous GB phase (thicker than the exchange length $L_{\rm ex}$) surrounding each matrix phase grain to decouple them.

Secondly, the existence of REFe₂ phase helps to optimize the microstructure of BMP magnets. Previous literature [8] has also revealed the existence of minor REFe₂ phase as independent grains in the high-Ce containing Nd-Ce-Fe-B magnets. Since the CeFe₂ is paramagnetic at room temperature (Curie temperature T_C of 227 K [36]), its existence decreases the remanence of Nd-Ce-Fe-B magnets. Although the T_C of present REFe₂ phase (containing Pr and Nd) could be different from CeFe₂, it is usually deemed as a soft magnet below T_C , being harmful to the hard magnetism. Its existence, however, is beneficial to optimize the microstructure and hence to enhance the coercivity. As revealed in Fig. 7, the melting point of



Fig. 10. TEM images for the GBs between adjacent RE₂Fe₁₄B matrix phase grains. (a) Ce-27 SMP and (b) Ce-45 BMP magnets.



Fig. 11. L-TEM Fresnel images of (a) Ce-27 SMP and (b) Ce-45 BMP magnets with the *c*-axis in plane and observed in the zero applied magnetic field. Red dashed rectangles in (a) and (b) highlight the domain walls. Blue rectangle in (a) indicates the magnetic domain across three different grains. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

REFe₂ phase is lower than that of the 2:14:1 phase. Sintering above its melting point enlarges the volume fraction of liquid phase and promotes the formation of continuous GB phases (Figs. 9 and 10), which in turn weakens the exchange coupling effect between adjacent hard magnetic grains. In addition, it is spontaneously formed in the initial Ce-containing component, which facilitates the improvement of wettability between GBs and matrix phase without the need of incorporating extra low-melting-point intergranular additives.

Finally, our work suggests that the Ce substitution level in Nd-Ce-Fe-B permanent magnets can be further increased. Taking advantage of the BMP approach, the Ce content in the final magnet

can be raised by increasing its content in the Ce-containing component. Although the volume fraction of REFe₂ phase increases with raised Ce content, which may deteriorate the remanence, the benefits it brings to the coercivity enhancement can balance the degradation of energy product. Despite the deteriorated intrinsic magnetic properties of the Ce-rich magnets, the BMP approach allows us to fabricate Ce-based permanent magnets with magnetic properties fulfilling the large gap between hard ferrites and current commercial Nd-Fe-B magnets [37]. In the present work, even when 45 wt % Nd is substituted by Ce, preferable energy product (*BH*)_{max} of 36.7 MGOe can still be obtained for the BMP magnet.

4. Conclusions

Effects of the REFe₂ phase on microstructure and magnetic properties of Ce-substituted Nd-Ce-Fe-B sintered magnets prepared by BMP approach have been investigated.

- 1) The REFe₂ phase forms spontaneously in the initial Ce-50 component and inherits into the final BMP magnets. The REFe₂ phase is mainly located in the intergranular regions, which distinctly differs from the conventional RE-rich phases in the Nd-Fe-B sintered magnets.
- 2) REFe₂ phase melts during sintering due to its lower melting point than the matrix 2:14:1 phase, which enlarges the volume fraction of the liquid phase. It improves the wettability of matrix phase grains and promotes the formation of continuous grain boundary phases.
- 3) The formation of continuous grain boundary layers is beneficial to isolate the adjacent matrix grains, i.e. to weaken the shortrange exchange coupling between them, which is also an important reason for retained coercivity for the BMP magnets in addition to the long-range magnetostatic interactions among grains with different mean compositions.
- 4) The positive role played of the REFe₂ phase on microstructure suggests that Ce substitution level in Nd-Ce-Fe-B sintered magnets can be further increased, enabling the fabrication of low-cost rare earth permanent magnets with magnetic properties fulfilling the gap between hard ferrites and commercial Nd-Fe-B magnets.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 51571176, 51590881 and 51622104), the National Key Research and Development Program of China (No. 2016YFB0700902) and the Key Research and Development Program of Zhejiang Province (No. 2016C01G2010561).

References

- O. Gutfleisch, M.A. Willard, E. Brück, C.H. Chen, S.G. Sankar, J.P. Liu, Magnetic materials and devices for the 21st century: stronger, lighter, and more energy efficient, Adv. Mater. 23 (2011) 821–842.
- [2] A.K. Pathak, M. Khan, K.A. Gschneidner Jr., R.W. McCallum, L. Zhou, K. Sun, K.W. Dennis, C. Zhou, F.E. Pinkerton, M.J. Kramer, V.K. Pecharsky, Cerium: an unlikely replacement of Dysprosium in high performance Nd-Fe-B permanent magnets, Adv. Mater. 27 (2015) 2663–2667.
- [3] J.F. Herbst, M.S. Meyer, F.E. Pinkerton, Magnetic hardening of Ce₂Fe₁₄B, J. Appl. Phys. 111 (2012) 07A718.
- [4] A.K. Pathak, M. Khan, K.A. Gschneidner Jr., R.W. McCallum, L. Zhou, K. Sun, M.J. Kramer, V.K. Pecharsky, Magnetic properties of bulk, and rapidly solidified nanostructured (Nd_{1-x}Ce_x)₂Fe_{14-y}Co_yB ribbons, Acta Mater. 103 (2016) 211–216.
- [5] A. Alam, M. Khan, R.W. McCallum, D.D. Johnson, Site-preference and valency for rare-earth sites in (R-Ce)₂Fe₁₄B magnets, Appl. Phys. Lett. 102 (2013) 042402.
- [6] A. Alam, D.D. Johnson, Mixed valency and site-preference chemistry for

cerium and its compounds: a predictive density-functional theory study, Phys. Rev. B 89 (2014) 235126.

- [7] M.G. Zhu, W. Li, J.D. Wang, L.Y. Zheng, Y.F. Li, K. Zhang, H.B. Feng, T. Liu, Influence of Ce content on the rectangularity of demagnetization curves and magnetic properties of Re-Fe-B magnets sintered by double main phase alloy method, IEEE Trans. Magn. 50 (2014) 1000104.
- [8] E. Niu, Z.A. Chen, G.A. Chen, Y.G. Zhao, J. Zhang, X.L. Rao, B.P. Hu, Z.X. Wang, Achievement of high coercivity in sintered R-Fe-B magnets based on mischmetal by dual alloy method, J. Appl. Phys. 115 (2014) 113912.
- [9] J.Y. Jin, T.Y. Ma, Y.J. Zhang, G.H. Bai, M. Yan, Chemically inhomogeneous RE-Fe-B permanent magnets with high figure of merit: solution to global rare earth criticality, Sci. Rep. 6 (2016) 32200.
- [10] J.Y. Jin, Y.J. Zhang, G.H. Bai, Z.Y. Qian, C. Wu, T.Y. Ma, B.G. Shen, M. Yan, Manipulating Ce valence in RE₂Fe₁₄B tetragonal compounds by La-Ce Codoing: resultant crystallographic and magnetic anomaly, Sci. Rep. 6 (2016) 30194.
- [11] J.F. Herbst, R₂Fe₁₄B materials: intrinsic properties and technological aspects, Rev. Mod. Phys. 63 (1991) 819–898.
- [12] E.B. Boltich, E. Oswald, M.Q. Huang, S. Hirosawa, W.E. Wallace, E. Burzo, Magnetic characteristics of R₂Fe₁₄B systems prepared with high purity rare earths (R = Ce, Pr, Dy, and Er), J. Appl. Phys. 57 (1985) 4106–4108.
- [13] S.X. Zhou, Y.G. Wang, Investigations of magnetic properties and microstructure of 40Cedidymium-Fe-B based magnets, J. Appl. Phys. 75 (1994) 6268–6270.
- [14] M. Okada, S. Sugimoto, C. Ishizaka, T. Tanaka, M. Homma, Didymium-Fe-B sintered permanent magnets, J. Appl. Phys. 57 (1985) 4146–4148.
- [15] T.G. Woodcock, Y. Zhang, G. Hrkac, G. Ciuta, N.M. Dempsey, T. Schrefl, O. Gutfleisch, D. Givord, Understanding the microstructure and coercivity of high performance NdFeB-based magnets, Scr. Mater. 67 (2012) 536–541.
- [16] K. Hono, H. Sepehri-Amin, Strategy for high-coercivity Nd-Fe-B magnets, Scr. Mater. 67 (2012) 530–535.
- [17] W.F. Li, T. Ohkubo, K. Hono, Effect of post-sintering annealing on the coercivity and microstructure of Nd-Fe-B permanent magnets, Acta Mater. 57 (2009) 1337–1346.
- [18] Y.J. Zhang, T.Y. Ma, X.L. Liu, P. Liu, J.Y. Jin, J.D. Zou, M. Yan, Coercivity enhancement of Nd-Fe-B sintered magnets with intergranular adding (Pr,Dy,Cu)-H_x powders, J. Magn. Magn. Mater. 399 (2016) 159–163.
- [19] T.T. Sasaki, T. Ohkubo, Y. Takada, T. Sato, A. Kato, Y. Kaneko, K. Hono, Formation of non-ferromagnetic grain boundary phase in a Ga-doped Nd-rich Nd-Fe-B sintered magnet, Scr. Mater. 113 (2016) 218–221.
- [20] H. Sepehri-Amin, T. Ohkubo, K. Hono, The mechanism of coercivity enhancement by the grain boundary diffusion process of Nd-Fe-B sintered magnets, Acta Mater. 61 (2013) 1982–1990.
- [21] C.J. Yan, S. Guo, R.J. Chen, J. Liu, D. Lee, A.R. Yan, Effect of Ce on the magnetic properties and microstructure of sintered Didymium-Fe-B magnets, IEEE Trans. Magn. 50 (2014) 2102605.
- [22] K.H.J. Buschow, Intermetallic compounds of rare-earth and 3d transition metals, Rep. Prog. Phys. 40 (1977) 1179–1256.

- [23] A.V. Morozkin, YuD. Seropegin, A.V. Gribanov, J.M. Barakatova, Analysis of the melting temperatures of RT₂ compounds (MgCu₂ structure) (R = Rare Earth, T = Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) and RT₂X₂ compounds (R = La, Ce, Sm, Er; T = Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Pt; X = Si, Ge), J. Alloys Compd. 256 (1997) 175–191.
- [24] T.G. Woodcock, Q.M. Ramasse, G. Hrkac, T. Shoji, M. Yano, A. Kato, O. Gutfleisch, Atomic-scale features of phase boundaries in hot deformed Nd-Fe-Co-B-Ga magnets infiltrated with a Nd-Cu eutectic liquid, Acta Mater. 77 (2014) 111–124.
- [25] H. Sepehri-Amin, T. Ohkubo, S. Nagashima, M. Yano, T. Shoji, A. Kato, T. Schrefl, K. Hono, High-coercivity ultrafine-grained anisotropic Nd-Fe-B magnets processed by hot deformation and the Nd-Cu grain boundary diffusion process, Acta Mater. 61 (2013) 6622–6634.
- [26] H. Sepehri-Amin, L.H. Liu, T. Ohkubo, M. Yano, T. Shoji, A. Kato, T. Schrefl, K. Hono, Microstructure and temperature dependent of coercivity of hotdeformed Nd-Fe-B magnets diffusion processed with Pr-Cu alloy, Acta Mater. 99 (2015) 297–306.
- [27] L.P. Liang, T.Y. Ma, P. Zhang, M. Yan, Effects of Dy_{71.5}Fe_{28.5} intergranular addition on the microstructure and the corrosion resistance of Nd-Fe-B sintered magnets, J. Magn. Magn. Mater. 384 (2015) 133–137.
- [28] J.J. Ni, T.Y. Ma, Y.R. Wu, M. Yan, Effect of post-sintering annealing on microstructure and coercivity of Al₈₅Cu₁₅-added Nd-Fe-B sintered magnets, J. Magn. Magn. Mater. 322 (2010) 3710–3713.
- [29] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, J. Appl. Cryst. 2 (1969) 65–71.
- [30] Z. Li, W.Q. Liu, S.S. Zha, Y.Q. Li, Y.Q. Wang, D.T. Zhang, M. Yue, J.X. Zhang, X.L. Huang, Effects of Ce substitution on the microstructures and intrinsic magnetic properties of Nd-Fe-B alloy, J. Magn. Magn. Mater. 393 (2015) 551–554.
- [31] T.T. Sasaki, T. Ohkubo, K. Hono, Structure and chemical compositions of the grain boundary phase in Nd-Fe-B sintered magnets, Acta Mater. 115 (2016) 269–277.
- [32] W.J. Mo, L.T. Zhang, Q.Z. Liu, A.D. Shan, J.S. Wu, M. Komuro, Dependence of the crystal structure of the Nd-rich phase on oxygen in an Nd-Fe-B sintered magnet, Scr. Mater. 59 (2008) 179–182.
- [33] T.H. Kim, S.R. Lee, H.J. Kim, M.W. Lee, T.S. Jang, Simultaneous application of Dy-X (X = F or H) powder doping and dip-coating processes to Nd-Fe-B sintered magnets, Acta Mater. 93 (2015) 95–104.
- [34] Y. Kaneko, N. Ishigaki, Recent developments of high-performance NEOMAX magnets, J. Mater. Eng. Perform. 3 (1994) 228–233.
- [35] B.B. Straumal, Yu. O. Kucheev, I.L. Yatskovskaya, I.V. Mogilnikova, G. Schütz, A.N. Nekrasov, B. Baretzky, Grain boundary wetting in the NdFeB-based hard magnetic alloys, J. Mater. Sci. 47 (2012) 8352–8359.
- [36] X. Zhang, N. Ali, Effects of Co and Y substitution on magnetic properties of CeFe₂, J. Appl. Phys. 75 (1994) 7128–7130.
- [37] J.M.D. Coey, Permanent magnets: plugging the gap, Scr. Mater 67 (2012) 524–529.