Effect of different grain boundary diffusion alloys on magnetic properties of Dy-free sintered NdFeB magnet

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Dy-free sintered magnets were fabricated by blending Neo powder with different grain boundary diffusion alloy powders. Cu, CeAl and CeAlCu have a negative effect on H_{cj} of magnets, while PrAlCu and AlCuGa have a positive effect. The PrAlCu-added magnet achieves the best magnetic properties among all magnets with the additions of different diffusion alloys. With increasing PrAlCu from 0-10 wt.%, H_{cj} of the magnets gradually increases from the original 14.5 kOe to 19.2 kOe. The magnet with 7.5 wt.% PrAlCu obtains a H_{cj} of 18 kOe and $(BH)_{max}$ of 39.1 MGOe. It is found that Pr and Cu in PrAlCu alloy is mainly distributed at grain boundary and triple junctions, leading to a reduced coupling among grains, thus an enhanced H_{cj}. The grain boundary engineering by adding an appropriate alloy is an effective method to improve H_{cj} of Dy-free NdFeB magnets.

***Index Terms*—Grain boundary engineering, Magnetic properties, Microstructure, diffusion alloy, Sintered NdFeB magnets.**

I. Introduction

EFFICIENT high power density electric drive motors require permanent magnets with high energy product, good thermal stability, and less critical elements. Nd-Fe-B-based sintered magnets are the most popular magnet used in traction motor and power generator applications [1, 2]. However, Nd-Fe-B-based magnets without heavy rare earth elements (HREEs) have reduced performance when the operating temperature is above 80°C, which is also the minimum operating temperature for most of the EV traction motors. HREEs, such as Dy and Tb, are added to the magnets to enhance coercivity and improve the performance at elevated temperatures [3, 4]. Adding more HREEs extends the operating temperature further. At 200 °C, the amount of required Dy in traditional sintered Neo magnets would exceed 10 wt.%. Unfortunately, HREEs are subject to near-term supply risk and have been considered as the most critical material since 2011's rare earth crisis [5]. Consequently, the development of Dy-lean or free Nd-Fe-B magnets capable of high temperature operation became a great interest to the EV industry and to the magnetic materials community.

It has been established that the coercivity mechanism in Nd-Fe-B-based magnets is controlled by the nucleation of reversal domains at local grain surfaces with defects [6, 7]. Coercivity is sensitive to grain size, chemistry of grain boundary phases (GBPs), and how the GBP is distributed. To date, several approaches have been investigated to develop Dy-lean or free Nd-Fe-B magnets. One promising approach is grain size reduction. Magnetic domain reversal occurs by nucleation in the magnetically isolated grains. With smaller grains, both the defect density in the surface region [8-12] and the average reverse circularity are lowered, leading to coercivity enhancement [12]. Another approach is bulk magnet surface modification through grain boundary diffusion of low melting point metals (Ga, Cu, Al) or rare earth oxide/compounds (Dy_2O_3, DyF_3) from magnet's outer surface to the grain boundary network, resulting in an enhanced magnetic isolation between grains. For example, Dy compounds are diffused from outer magnet surfaces along grain boundaries to form a Dy-rich layer on individual 2:14:1 phase grain to enhance coercivity. The addition of low melting point metals at grain boundaries also can reduce the defects on the surface of grains and weaken the magnetic coupling between 2:14:1 grains [13–15]. In our previous work, magnets fabricated by blending Pr-Cu eutectic alloy powders with Dy-free NdFeB feedstock powders were studied [16]. H_{cj} of the magnets significantly increases after adding Pr-Cu alloy. In this work, more GB modification alloys including Cu, CeAl, CeAlCu, PrAlCu, AlCuGa are extendedly investigated. The effects of these alloys on microstructure and magnetic properties of the sintered magnets are studied. Among these alloys, PrAlCu is the most effective on enhancement of H_{cj}. The microstructure and roles of these alloys, especially for PrAlCu in the GB modifiers-added magnets are analysed and discussed.

II. Experimental Details

The starting magnet material is commercial Dy-free NdFeB hydrogen decrepitated (HD) coarse alloy powder with a nominal composition of $Nd_{24.05}Pr_{7.68}Ga_{0.18}Cu_{0.15}Co_{1.02}B_{0.93}Fe_{bal}$ (in wt.%). $Ce_{96.7}Al_{3.3}$, $Ce_{89.3}Al_{4.9}Cu_{5.8}$, $Pr_{89.3}Al_{5.8}Cu_{4.9}$ (in wt.%) alloys were arc-melted, melt-spun at 20 m/s, and then ball-milled into powders with a particle size less than 75 µm. The particle size of commercial Cu powder is ~15 µm. The HD Neo powders were mixed with one of the alloy powders at a ratio from 0.5 to 10 wt.%. The mixtures were ball-milled into a fine powder with an average particle size of 3.5 µm. The fine powder samples in a rubber die were magnetically aligned by a 9 T pulse field and then cold isostatic pressed under a pressure of 500 MPa. The obtained green compacts were sintered at 1050-1090°C for 1 to 5 h. The samples were post sinter annealed at 900°C for 0.5 h, 580°C for 2 h, and 480°C for 5 h. Magnetic properties of magnets were measured by a closed-loop hysteresisgraph tracer with a maximum field of 2 T. Microstructures and compositions of magnets were examined using an FEI Teneo field-emission scanning electron microscope (FE-SEM) equipped with an Oxford Aztec energy dispersive detector (EDS) and a Titan Themis scanning transmission electron microscope (STEM) with Super X EDS detector.

III. Results and Discussion

Grain boundary diffusion (GBD) requires that GBD alloys have lower melting points and better wettability with the matrix 2:14:1 grain, and don't have a considerable reaction with the matrix phase. At sintering temperature, the alloys might partially react with the localized matrix grains, but they can be separated out and finally form new and non-magnetic grain boundary phases with the original RE-rich phase at lower annealing temperatures. Moreover, the alloys are inexpensive and are able to be easily comminuted into fine powder. In the studies in this paper, non-rare earth (RE)-containing Cu and AlCuGa were selected. In RE-containing alloys, CeAl and CeAlCu without a critical REE, and PrAlCu were studied. These alloys are at or close to their eutectic compositions, and their melting-points are below 600°C except for pure Cu. The lower melting points enable the alloys to diffuse at grain boundary regions during sintering and subsequent annealing. The magnetic properties of the sintered magnets fabricated by blending Neo powder with different GBD alloys and the amounts added are listed in Table I. The demagnetization curves of the magnets with an optimal addition amount for each alloy based on their magnetic properties are shown in Fig. 1. For comparison, the nonadditive magnet (original) as a base line and the magnets with PrCu addition [16] are also included in Table I and Fig. 1. It is seen from Table I and Fig. 1 that PrCu, PrAlCu and AlCuGa (up to 1.5%) have a positive effect on H_{cj} of the magnets, while Cu, CeAl and CeAlCu have a negative effect. Among all these GBD alloys, PrAlCu stands out in enhancement of H_{cj}.

TABLE I
Magnetic Properties of Magnets with different GBD alloy additions

Additive	wt %	M_S (kGs)	Br (kGs)	H_{cj} (kOe)	$(BH)_{max}$ (MGOe)
None	N/A	14.1	13.9	14.5	45.3
Cu	0.5	13.5	11.6	13.4	40.7
	0.1	13.4	11.5	7.5	38.2
CeAl	7.5	12.2	11.8	13.3	34.3
CeAlCu	5.0	12.3	11.8	13.7	33.9
	7.5	11.9	11.4	12.7	30.5
PrCu	5.0	13.2	13.0	16.6	39.5
	7.5	12.3	12.2	18.6	35.0
	10.0	11.4	11.2	18.8	28.4
PrAlCu	3.0	13.7	13.6	16.4	46.5
	5.0	13.1	13.0	17.1	42.0
	7.5	12.7	12.6	18.0	39.1
	10	12.3	12.2	19.2	37.2
AlCuGa	0.5	12.7	12.1	16.6	32.5
	1.5	12.3	11.9	16.5	32.4
	3.0	11.5	11.4	7.6	30.4

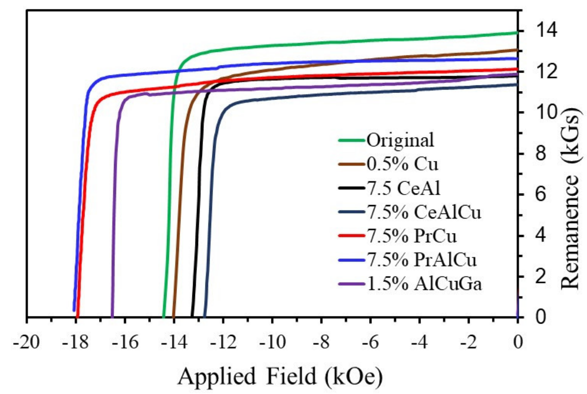

Fig. 1. Demagnetization curves of the sintered magnets with different GBD alloys.

Fig. 2 shows the demagnetization curves of the magnets with different additions of PrAlCu alloys. With increasing PrAlCu contents from 0 to 7.5 wt.%, H_{cj} increases from 14.5 to 18.0 kOe, while Br and $(BH)_{max}$ decrease from 13.9 to 12.6 kGs and 45.3 to 39.1.0 MGOe, respectively. When PrAlCu is increased to 10 wt.%, H_{cj} is increased to 19.2 kOe, but Br and $(BH)_{max}$ are reduced to 12.2 kGs and 37.2 MGOe, respectively. These results show an excessive addition of PrAlCu slightly improves H_{cj} but also leads to reduction of $(BH)_{max}$ due to the dilution of magnetic phase.

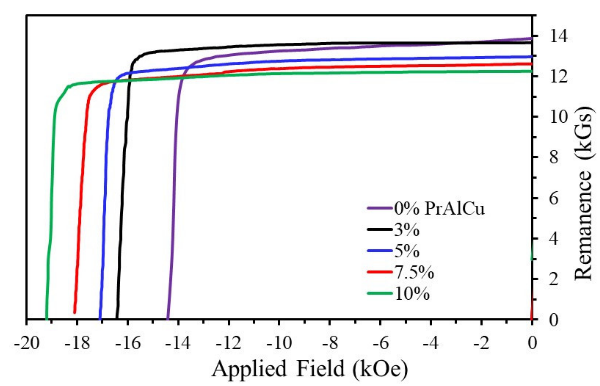

Fig. 2. Demagnetization curves of the sintered magnets with different additions of PrAlCu alloy.

The microstructures of the sintered magnets with additions of 7.5 wt% CeAl and CeAlCu, 1.5 and 3 wt% AlCuGa, and 0.5 wt% Cu are shown in Fig. 3. In the CeAl or CeAlCu-added magnets (Fig. 3a and 3b), the grains appear to be rounded, well surrounded by a continuous gain boundary (GB) and their triple junction (TJ) phases. In the AlCuGa-added magnets, a much thinner GB&TJ phase is formed. The amount of GB&TJ phase increases with increasing the addition amount of AlCuGa from 1.5 to 3 wt% (Fig. 3c and d) as expected. However, additional GB&TJ phases do not extend along the GB regions, instead they tend to aggregate at the TJ areas. Similarly, the GB&TJ phase in the Cu-added magnet mainly aggregates at the TJ areas (Fig. 3e). In fact, two different phases in the GB &TJ areas are formed as shown in the enlarged figure of a TJ region in Fig. 3e, which are labeled as grey and white. These results indicate that the GB & TJ phase formed by non-RE containing GB modification alloys not only have a poor wettability on the $Nd_2Fe_{14}B$ grain surface compared to the RE-containing ones, but also can possibly result in forming other secondary phases.

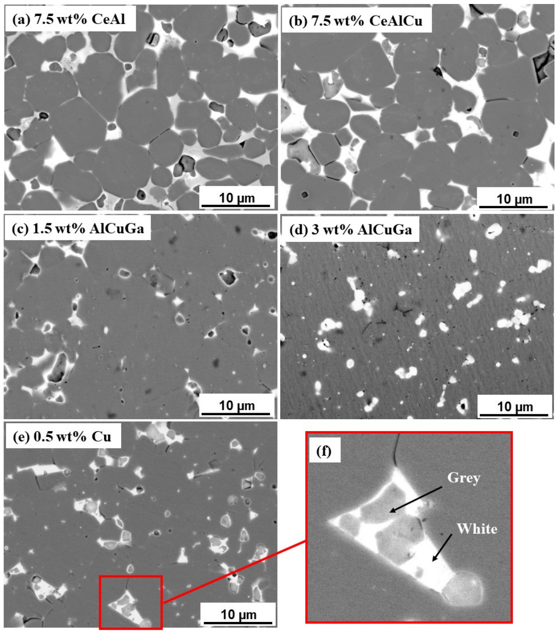

Fig. 3. SEM BSE images of the sintered magnets with different GBD alloys, 7.5 wt% CeAl (a), 7.5 wt% CeAlCu (b), 1.5 wt% AlCuGa (c), 3 wt% AlCuGa (d), and 0.5 wt% Cu (d), respectively. Fig. 3f shows the enlarged image of a selected TJ region in Fig. 3e.

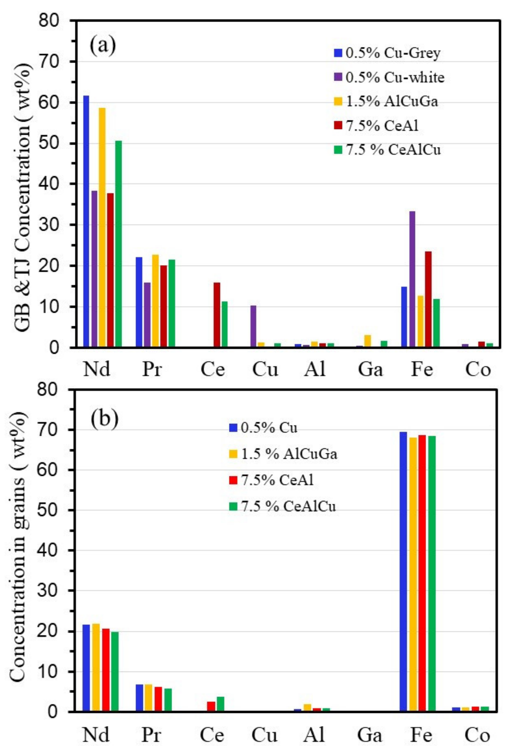

Fig. 4. EDS concentration profiles at the GB &TJ regions (a) and in the matrix grains (b) of the sintered magnets with additions of Cu, CeAl, CeAlCu and AlCuGa.

EDS concentration profiles in the matrix grain and at GB &TJ regions of the magnets with additions of Cu, CeAl, CeAlCu and AlCuGa, respectively, are shown in Fig. 4a and 4b. The GB & TJ regions are primarily comprised of varying amounts of Nd, Pr, Ce-rich phases (in the case of the magnets with addition of CeAl or CeAlCu), intermediate amounts of Fe, and minor amounts of Cu, Al, Ga and Co. In the 0.5 wt% Cu-added magnets, the grey phase in the GB &TJ region (see the enlarge area in Fig. 3e) is Nd-rich, while the brighter phase is Cu-rich, indicating that it is difficult to form a new and uniform RE-rich GB phase by adding only pure Cu to the originally existing RE-rich phase during sintering and subsequent annealing processes. As a result, these GB & TJ phases are not beneficial to improving H_{cj}. It is not surprised that the gains are the 2:14:1 phase constituted by Fe, REEs and minor amount of Al and Co (Fig.4b).

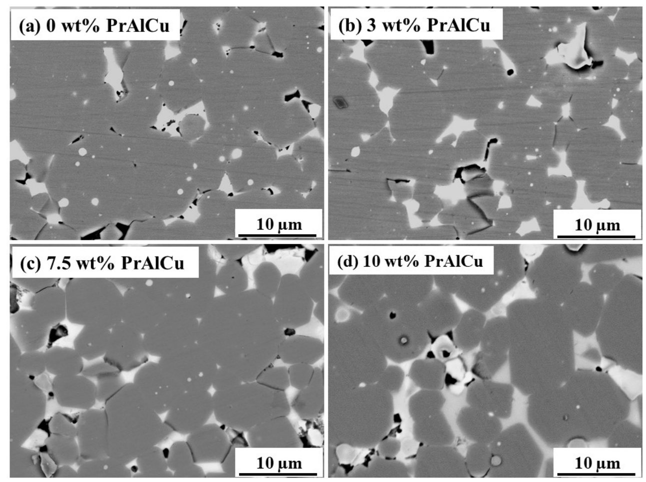

Fig. 5. SEM BSE images of the sintered magnets with different addition of PrAlCu alloys, 0 wt% (a), 3 wt% (b), 7.5 wt% (c), and 10 wt% (d), respectively.

As is known from Table I, and Fig. 1 and 2, the addition of PrAlCu can effectively improve H_{cj}. SEM images (Fig. 5) show the microstructures of magnets with varying PrAlCu additions. With increasing PrAlCu content, the average grain size varies slightly from 3.1 to 3.5 μm, which is not statistically significant. However, the percentage of GB &TJ phases considerably increases from 7.1 to 17.8 vol% as listed in Table II. EDS composition profiles at the GB & TJ regions are shown in Fig. 6. The GB & TJ regions are rich in Cu, Pr, and Nd. The concentrations of Cu and Pr increase while that of Fe decreases with increasing of PrAlCu addition. The increase of GB&TJ regions with Cu and Pr-rich and Fe-poor forms a thicker and non-magnetic phase, which results in a reduced coupling among grains, and thus enhancing H_{cj}.

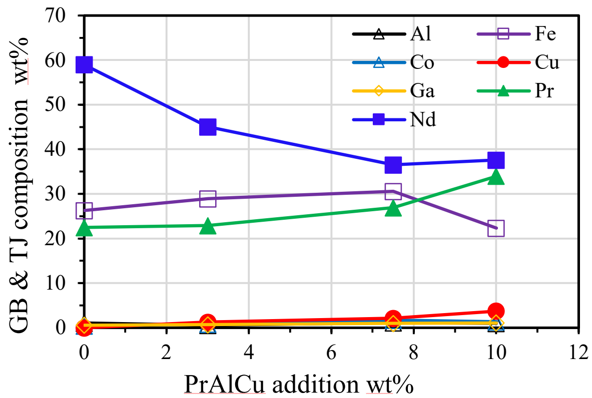

Fig. 6. EDS composition profiles at GB & TJ regions for magnets with different PrAlCu additions

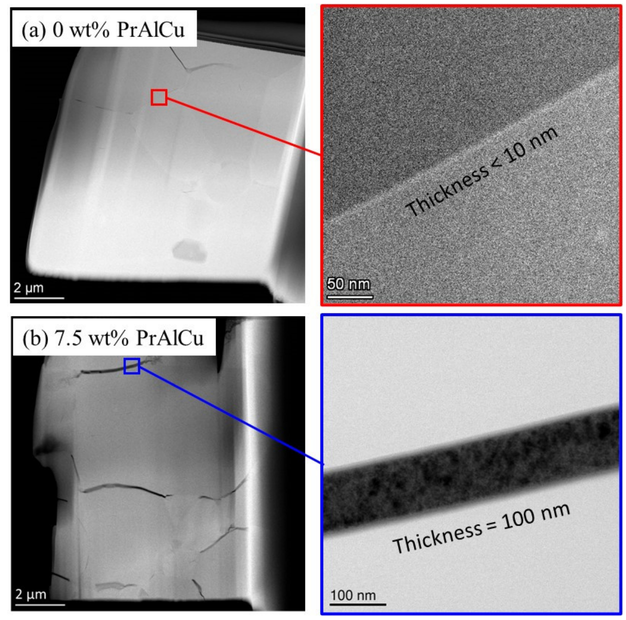

Fig. 7. STEM images showing the microstructures of the sintered magnets with additions of PrAlCu, 0 wt% (a), and 7.5 wt% (b), respectively. A GB region selected in each sample is further enlarged, shown in the right figures. The composition profiles across GB were analyzed by EDS.

STEM was used to study the details of the GB microstructure and their composition profiles. STEM images of the magnets with 0 and 7.5 wt% PrAlCu addition are shown in Fig. 7. One GB region is selected in each sample for further analysis. The composition profiles across GB were analyzed by EDS. The EDS composition profiles across the GBs are shown in Fig. 8. The STEM images in Fig. 7a shows that the GB thickness of the magnet without addition of PrAlCu is less than 10 nm, and there is no obvious composition variation across the GB (Fig. 8a), indicating that the GB phase is non-continuous or too thin to provide strong decoupling between grains in this GB region. In contrast, the GB of the magnet with 7.5 wt% PrAlCu exceeds 100 nm (Fig.7b). The EDS results in Fig.8b shows that Pr/Nd and Cu are rich, and Fe is depleted at the GB. In addition, Oxygen at the GB is also high, indicating that the RE-rich GB phase is easily oxidized. At this time, it is not clear if the higher Oxygen content came from the original magnet samples, or the RE-rich GB phase was partially oxidized during the preparation of the STEM sample. The results of the microstructures further confirm the formation of thicker and continuous GB with Pr/Nd and Cu-rich is important to improve H_{cj}. Fig 9 shows the effect of PrAlCu addition on the GB & TJ phase percentage in the magnets. With increasing the addition amount of PrAlCu alloy, the percentage of the GB &TJ phase increases, and thus H_{cj} increases as well.

TABLE II
PHASE DISTRIBUTION OF MAGNETS WITH DIFFERENT PRALCU ADDITIONS

PrAlCu wt%	Matrix vol%	GB&TJ vol%
0	92.9	7.1
3.0	90.6	9.4
7.5	84.1	15.9
10.0	82.2	17.8

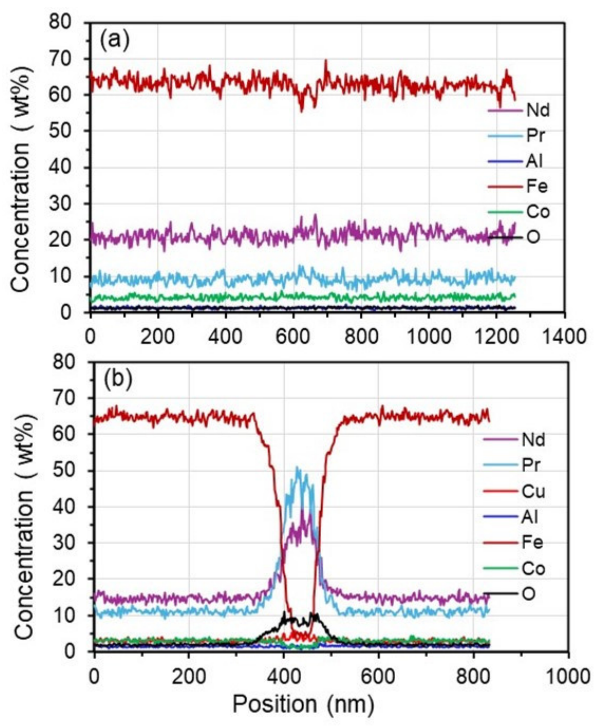

Fig. 8. EDS composition profiles across GB in the enlarged figures in Fig. 7 for the magnet without addition of PrAlCu (a), and with 7.5 wt% PrAlCu addition (b), respectively.

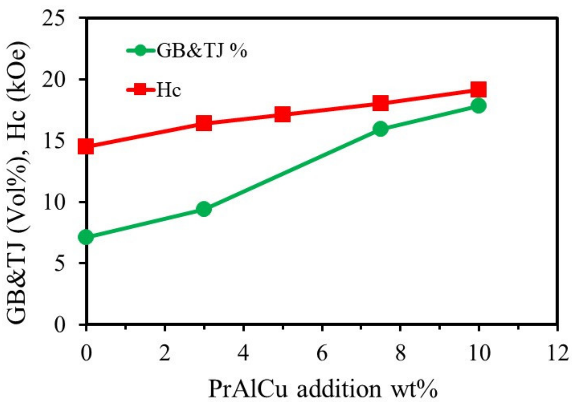

Fig. 9. H_{cj} and GB &TJ phase percentage as a function of the addition amount of PrAlCu in the magnets.

As described above, non-RE containing Cu and AlCuGa alloys have lower wettability with the matrix grains, resulting in non-continuous GB phases. The matrix grains appear to be more irregular in shape compared to those of the magnet samples using RE containing alloys. In the Cu-added magnets, we observed two distinct GB &TJ phases. We speculate that these different GB &TJ phases are the reason why the Cu-added magnets have a low H_{cj} due to the poor wettability, resulting in thinner GB regions. The eutectic alloy based on Al-Cu-Ga has superior magnetic properties compared to magnets sintered with only Cu additions. In the 1.5 wt% AlCuGa-added magnet, a thinner GB &TJ phase (Fig.3c) with Nd, Pr, Al, Cu, Ga-rich and Fe-depleted is formed (Fig. 4a). If AlCuGa is further increased to 3 wt %, the formed GB & TJ phase prefers to aggregate at TJ regions instead of uniformly spreading across the GB and TJ areas, which leads to significant reduction of H_{cj}. RE-containing eutectic alloys have a better wettability and promote the formation of more rounded 2-14-1 matrix grains with fewer asperities which can be sources of reversal domains. The RE-containing alloys easily form an accommodating and continuous RE-phase at GB &TJ regions, which well isolates the round shaped grains (Fig.3a and 3b, Fig.5). Such microstructure features are ideal for improving H_{cj}. However, unlike PrCu or PrAlCu, the addition of CeAl or CeAlCu in magnets didn't improve H_{cj} as expected. Based on these observations, we speculate that addition of RE-containing alloys can be effective in increasing coercivity in magnets only if they contain REE matching the one in the 2:14:1 matrix. For example, Pr in PrAlCu matches with Nd/Pr in $(Nd, Pr)_2Fe_{14}B$, while Ce in CeAl or CeAlCu doesn't match with Nd/Pr in $(Nd, Pr)_2Fe_{14}B$ phase. Therefore, although the Ce-containing GB modifier helps to form an ideal microstructure, it cannot obviously improve the H_{cj} of the Nd/Pr-based magnets. The underlying mechanism is waiting to be further studied and revealed.

In summary, blending Dy-free Neo powder with an appropriate GBD modification alloy powder before sintering is an effective method for grain boundary engineering and improving H_{cj}. Among the studied GBD alloys, Cu, CeAl and CeAlCu have a negative effect on H_{cj} of magnets, while PrAlCu (up to 10 wt.%) and AlCuGa (up to 1.5 wt.%) have a positive effect. PrAlCu alloy stands out in enhancement of H_{cj}. The Pr and Cu in PrAlCu are mainly distributed at Nd-rich GB & TJ regions, leading to a reduced coupling between grains and thus enhanced H_{cj}. With increasing PrCu from 0-10 wt.%, H_{cj} gradually increases from the original 14.5 kOe to 19.2 kOe, accompanied by a $(BH)_{max}$ of 45.3 to 37.2 MGOe. The addition of PrAlCu significantly improve H_{cj} but only slightly reduces $(BH)_{max}$.

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