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Limitations in the grain boundary processing of the recycled HDDR Nd-Fe-B system

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Abstract

Fully dense spark plasma sintered recycled and fresh HDDR Nd-Fe-B nanocrystalline bulk magnets are processed by surface grain boundary diffusion (GBD) treatment to further augment the coercivity and investigate the underlying diffusion mechanism. The fully dense SPS processed HDDR based magnets were placed in a crucible with varying the eutectic alloys Pr₆₈Cu₃₂ and Dy₇₀Cu₃₀ from 2 – 20 wt.% as direct diffusion source above the ternary transition temperature for GBD processing followed by secondary annealing. The changes in mass gain was analysed and weighted against the magnetic properties. For the recycled magnet, the coercivity (H_{Ci}) values obtained after optimal GBDP yielded ~ 60% higher than the starting recycled HDDR powder and 17.5% higher than the SPS-ed processed magnets. The fresh MF-15P HDDR Nd-Fe-B based magnets gained 25 – 36% higher coercivities with Pr-Cu GBDP. The FEG-SEM investigation provided insight on the diffusion depth and EDXS analysis indicated the changes in matrix and intergranular phase composition within the diffusion zone. The mechanism of surface to grain boundary diffusion and the limitations to thorough grain boundary diffusion in the HDDR Nd-Fe-B based bulk magnets are detailed in this study.

32 1 Introduction

33 The Nd-Fe-B based rare-earth permanent magnets (REPMs) possess great significance for
34 microelectronics, data storage, electric motors and medical devices (Gutfleisch, 2000). The grain size
35 refinement has been theorized to improve the coercivity (H_C), i.e. resistance to demagnetization in
36 REPMs (Sugimoto, 2011). The hydrogenation-disproportionation-desorption-recombination (HDDR)
37 is a well-established and greener route for developing anisotropic ultrafine grains (~400 nm) with
38 preferential easy-axis orientation (Sheridan et al., 2016). The overall surge in production volume and
39 application demand has necessitated the utilization of recycled REPMs into the industrial feedstocks
40 (Binnemans et al., 2018; Reimer et al., 2018). The effectiveness of hydrogen gas towards decrepitating
41 (HD) and disproportionation (HDDR) of the end-of-life rare-earth (RE) scrap has convincing been
42 proven in previous studies (Zakotnik et al., 2008; 2009; Hono and Sepehri-Amin, 2012; Li et al.,
43 2014; Sheridan et al., 2014; Horikawa et al., 2015; Walton et al., 2015). Contrary to the theoretical
44 models, the HDDR Nd-Fe-B system lacks high coercivity as a translation of high magnetocrystalline
45 anisotropy ($\mu_0 H_a$) ~ 7.2 T because of crystal structure inhomogeneities, grain morphology, surface
46 defects, oxidation, nonferromagnetic grain boundaries and localized exchange interactions at the grain
47 interfaces, which restrict their usability (Liu et al., 2009; Zheng and Zhao, 2009; Liu,
48 2012; Balasubramanian et al., 2014; Kwon et al., 2014). Therefore, rather confining the potential
49 application of the recycled HDDR Nd-Fe-B powders to polymer bonded magnets only (Liu,
50 2012; Périgo et al., 2012; Kimiabeigi et al., 2018; Li et al., 2018), we have recently demonstrated Spark
51 Plasma Sintering (SPS) as a convenient method to practically fabricate bulk magnets with magnetic
52 properties at par with the end-of-life sintered magnets (Ikram et al., 2019a; Ikram et al., 2019b; Ikram
53 et al., 2020) or commercial grade HDDR Nd-Fe-B powder (Takagi et al., 2015). Several researchers
54 have further explored the possibilities of improving the coercivity in the HDDR Nd-Fe-B system, with
55 alloying additions (Barbosa et al., 2004; Han et al., 2009; Sepehri-Amin et al., 2010a; Morimoto et al.,
56 2012; Morimoto et al., 2016), by mechanical milling (Gang et al., 2006; Güth et al., 2012; Nakamura et
57 al., 2013; Pal et al., 2013; Nakamura et al., 2015) and via tailoring the disproportionation-desorption-
58 recombination parameters (Luo et al., 2011; Cha et al., 2014; Sheridan et al., 2014; Wan et al.,
59 2014; Horikawa et al., 2015; Kim et al., 2016; Szymański et al., 2016; Lixandru et al., 2017; Yamazaki et
60 al., 2017).

61 More pragmatic approach has been the application of grain boundary diffusion (GBD) treatment on
62 the HDDR Nd-Fe-B powders (Sepehri-Amin et al., 2010b; Wan et al., 2014; Song et al., 2019). In case
63 of the bulk magnets obtained via hot-pressing the HDDR Nd-Fe-B powder Song et al. (Song et al.,
64 2019) achieved $\mu_0 H_C = 1.55$ T ($H_{Ci} = 1230$ kA/m) by eutectic Pr-Cu GBD treatment. Another versatile
65 method applied to the bulk sintered magnets from the HDDR Nd-Fe-B powder has demonstrated that
66 by doping with the rare-earth (RE) fluoride (DyF_3) and controlled heat treatment, an improvement of
67 up to 70% in coercivity (H_{Ci}) can be accomplished (Ikram et al., 2019c). As compared to the sintered
68 magnets from microcrystalline jet-milled powders and the nanocrystalline hot-deformed melt-spun
69 ribbons, the GBD process has not been extensively researched on the HDDR Nd-Fe-B system.
70 Moreover, a step ahead, very limited published data is available on the bulk HDDR Nd-Fe-B magnets,
71 let aside GBD processing. [When comparing the existing scientific reports, the underlying mechanism](#)
72 [of diffusion has been not interpreted either for the HDDR Nd-Fe-B system \(Sepehri-Amin et al.,](#)

73 2010b;Wan et al., 2014), and sparsely interlinked with hot deformed nanocrystalline and sintered Nd-
74 Fe-B magnets (Liu et al., 2016;Tang et al., 2016;Liu et al., 2017;Nakamura, 2018). Citing the GBDP
75 of the HDDR Nd-Fe-B powder, the loose powder particles have a remarkably higher surface area as
76 compared to bulk sintered magnets and therefore, the suggested improvement in coercivity is only due
77 to the widening of intergranular boundaries along the Nd₂Fe₁₄B grains which would effectively
78 decouple the grains with a higher concentration of non-ferromagnetic elements in this spacer phase (Li
79 et al., 2009;Sepehri-Amin et al., 2010a). Accordingly, the diffusion mechanism is relatively
80 straightforward for the loose HDDR powder particles undergoing GBD treatment, such that the liquid
81 phase engulfs all the particles when 5 – 30 wt. % RE-rich alloys are added and the short-range diffusion
82 causes widening of grain boundary regions within individual particles (Sepehri-Amin et al.,
83 2010b;Wan et al., 2014). On the contrary, when compacted to full density, the diffusion mechanism in
84 the HDDR Nd-Fe-B system is not the same as the loose powder particles and must vary with the GBD
85 processing parameters. The previous report on the hot deformed HDDR Nd-Fe-B bulk magnets does
86 not compliment on the diffusion mechanism either and relates more to the improvement in magnetic
87 properties after GBDP with hyper-eutectic Pr₈₂Cu₁₈ alloy (Song et al., 2019). The recycled HDDR
88 powder when compacted with SPS contains particle boundaries within which the RE-rich phase is non-
89 uniformly distributed before annealing. The RE-rich phase gets transported from the interparticle
90 region to the grain boundaries during the annealing and as a result, the coercivity reportedly increased
91 (Ikram et al., 2019b). This non-uniform distribution of Nd-rich phase in the particle boundaries
92 happened under intense uniaxial pressure in the SPS such that liquid phase was squeezed out of grain
93 boundaries to the interparticle junctions, and as a result, the coercivity dropped because of localized
94 exchange interactions within the adjoining Nd₂Fe₁₄B grains. During annealing, this liquid phase is
95 partially transported back towards the grain boundaries surrounding ~400 nm sized Nd₂Fe₁₄B matrix
96 grains from these interparticle boundaries, as the system is equilibrated. When evaluated based on
97 particle size, we were able to distinguish that for the smaller particle (< 100 μm) there is a loss in total
98 grain boundary area which also consequently resulted in a higher degree of oxidation as the liquid
99 phase was squeezed out to the particle boundaries during SPS, where the bulk of hcp-Nd₂O₃ phase
100 transformation took place (Ikram et al., 2019a). The capillary transport was theorized and confirmed
101 during the local doping and grain boundary engineering of bulk HDDR Nd-Fe-B magnets with DyF₃
102 nanoparticles (Ikram et al., 2019c).

103 Evidently the insufficient understanding of the demagnetization (or coercivity) mechanism, the
104 obvious effect of RE-rich interfaces – the grain boundaries as well as the surface diffusion kinetics in
105 the HDDR Nd-Fe-B system potentially constrain their commercial applicability (Zhao and Wang,
106 2006;Li et al., 2008;Gopalan et al., 2009;Li et al., 2009;Suresh et al., 2009;Zheng and Zhao,
107 2009;Sepehri-Amin et al., 2010b;Sugimoto, 2011).

108 The rudimentary aim of this scientific briefing is to highlight the potential challenges in grain boundary
109 diffusion processing (GBDP) of the recycled HDDR Nd-Fe-B based fully dense bulk magnets in
110 comparison to the commercial (Aichi MF-15P) HDDR powder with respect to the magnetic properties
111 evolution after the GBD treatment with Pr-Cu and Dy-Cu eutectic alloys. In case of direct diffusion
112 source and surface GBDP, the uniform and thorough dispersal of the RE-rich liquid phase to the grain
113 boundaries under enhanced capillary transport was observed to be constricted in the bulk HDDR Nd-

114 Fe-B magnets and this phenomenon has not been previously identified or reported elsewhere.
115 Moreover, the diffusion depth after the thermal treatments and the effect of processing temperatures
116 have been investigated in this report. This research also highlights the surface diffusion mechanism in
117 the recycled HDDR Nd-Fe-B system from direct diffusion source, which has not been previously
118 reported and interlink has been devised from the context of mass gain with the different GBDP
119 parameters. The fundamental challenge regarding the diffusion depth limitations in the HDDR Nd-Fe-
120 B bulk magnets has been investigated and proposed due to partial capillary diffusion confined due to
121 the presence of complex intergranular oxides with the aid of SEM and EDXS analysis. Apart from the
122 complicated diffusion mechanism in the HDDR Nd-Fe-B bulk magnets, the asymmetrical
123 transformation of $(\text{Pr,Nd})_2\text{Fe}_{14}\text{B}$ phase facets along with the interconnected Pr-Cu rich liquid phase
124 and the $(\text{Pr,Nd})_x\text{CuO}_y$ complexes at the intergranular junction have been suggested in correlation with
125 the different GBDP parameters.

126 2 Contribution to the Field Statement

127 The majority of work on GBDP of Nd-Fe-B system accounts to sintered magnets from the
128 microcrystalline powders and the nanocrystalline melt-spun ribbons, either in form of milled powder
129 or hot-deformed magnets. On the contrary, citable literature on the Hydrogenation-Disproportionation-
130 Desorption-Recombination (HDDR) Nd-Fe-B system is scarce such that these two nanocrystalline Nd-
131 Fe-B systems are radically different and the diffusion treatment mechanism is relatively sparsely
132 understood for the HDDR system. Importantly, the direct magnet recycling philosophy utilizes
133 processing magnetic scrap with hydrogen, like in hydrogen decrepitation (HD) or HDDR, with latter
134 technique extensively applicable for producing anisotropic ≤ 400 nm nanostructured $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains
135 and high coercivity bonded magnets. The GBDP on the HDDR powders have been reported (Sepehri-
136 Amin et al., 2010b; Wan et al., 2014) citing coercivity improvement but without the explanation of the
137 diffusion mechanism in comparison to the sintered magnets or the nanocrystalline melt-spun ribbons.
138 A recent study suggested application of Pr-Cu low melting alloy to HDDR powder treated with hot
139 deformation, improving the coercivity from 1065 kA/m to 1232 kA/m (Song et al., 2019). However,
140 the bulk diffusion depths and the mechanism of the particle to grain boundary diffusion were still
141 lacking.

142 The concurrent research work addresses the diffusion mechanism in the recycled HDDR Nd-Fe-B
143 system, which has never been reported before. The details are presented in the context of mass gain
144 with diffusion processing parameters and the diffusion depth limitations in the system due to limited
145 capillary channelling and presence of complex intergranular oxides with the aid of SEM and EDXS
146 analysis. Beyond the complications of constricted diffusion depth in the dense HDDR Nd-Fe-B bulk
147 magnets, the asymmetrical formation of $(\text{Pr,Nd})_2\text{Fe}_{14}\text{B}$ phase along the facets rich with Pr-Cu
148 containing liquid phase and $(\text{Pr,Nd})_x\text{CuO}_y$ phase transformation at the intergranular junction under
149 different processing conditions have been identified. The magnetic properties as a comparison were
150 also analysed after the diffusion treatment on the commercial HDDR Nd-Fe-B based bulk magnets,
151 which resulted in $\sim 25\%$ coercivity gain whereas the reprocessed magnets yielded $\sim 60\%$ higher
152 coercivity over the starting recycled HDDR powder. This brief report also indicates further action plans

153 for the future on GBDP of the HDDR Nd-Fe-B system to tackle the limitations in diffusion depth and
154 augment the coercivity beyond the current state of the art values.

155 3 Materials and Methods

156 The cylindrical/disk-shaped bulk SPS reprocessed magnets of diameter 9.5 mm and height 3 mm were
157 prepared from the recycled HDDR Nd-Fe-B powder of nominal atomic composition:
158 $\text{Nd}_{13.4}\text{Dy}_{0.67}\text{Fe}_{78.6}\text{B}_{6.19}\text{Nb}_{0.43}\text{Al}_{0.72}$ (and in the mass ratio: $\text{Nd}_{29.46}\text{Dy}_{1.66}\text{Fe}_{66.94}\text{B}_{1.02}\text{Nb}_{0.65}\text{Al}_{0.30}$). The
159 HDDR processing on the end-of-life magnets with this composition has been well documented by
160 Sheridan et al. (Sheridan et al., 2012; Sheridan et al., 2014). Sequentially, the fabrication of bulk
161 sintered magnets from the recycled HDDR Nd-Fe-B powder has also been thoroughly elaborated
162 previously by Ikram et al. (Ikram et al., 2019a; Ikram et al., 2019b), including the physical properties
163 like density (7.57 g/cm^3), oxygen content (4800 ppm) and anisotropic powder particles in a wide
164 distribution from 30 – 700 μm (average size $\sim 220 \mu\text{m}$). As a comparison, the commercial grade Aichi's
165 Magfine MF-15P HDDR Nd-Fe-B anisotropic powder (Aichi-ken, Japan), with average particle size
166 120 μm in a narrow size distribution was also consolidated with the similar SPS processing conditions
167 (Ikram et al., 2020) to replicate the GBD effect on fresh material. The binary eutectic $\text{Pr}_{68}\text{Cu}_{32}$ and
168 $\text{Dy}_{70}\text{Cu}_{30}$ alloy ribbons were prepared through arc-melting 10g of elements in stoichiometric
169 compositions (MAM-1 Arc Melter, Edmund Bühler, Bodelshausen, Germany). The Pr-Cu and Dy-Cu
170 alloys were homogenized by 5 arc-melting passes and cooled to room temperature before grindings off
171 the surfaces with 500 grit SiC papers. This was followed by vacuum induction melting ($> 10^{-4}$ mbar)
172 and subsequent melt spinning on a 200 mm copper wheel with rotational velocity of 30 m/s in argon
173 atmosphere (MSP-10 SC Melt Spinner, Edmund Bühler, Bodelshausen, Germany). The alloy ribbons
174 (several mm thickness, without further comminution) were placed within a ceramic crucible as direct
175 diffusion source on the top and bottom of surface cleaned bulk magnets (thermally annealed at $750 \text{ }^\circ\text{C}$
176 for 1h) (Ikram et al., 2019a). The loaded crucible was placed in a horizontal tube furnace (Carbolite
177 Gero Limited, Hope Valley, UK) for the GBD processing in high vacuum ($> 10^{-5}$ mbar) with a heating
178 rate of $50 \text{ }^\circ\text{C}/\text{min}$. The GBD treatment was performed at $900 \text{ }^\circ\text{C}$ for 3 h with secondary annealing at
179 $500 \text{ }^\circ\text{C}$ for additional 3 h in the same tube furnace setup (vacuum and heating rate), which is above the
180 ternary transition temperature (Ikram et al., 2019b) to accelerate the surface diffusivity. The magnetic
181 measurements on bulk GBDP samples were performed at room temperature on a permeameter
182 (Magnet-Physik Dr. Steingroever, Cologne, Germany) with demagnetizing fields up to 2 T. For further
183 characterization, the samples were thermally demagnetized at $400 \text{ }^\circ\text{C}$ for 15 min in the tube furnace
184 (vacuum $> 10^{-5}$ mbar). Samples were sliced into half by low speed diamond saw at 300 rpm and fluxed
185 with isopropanol (IsoMet™ Precision Cutter, Buehler, IL, USA). Later, these demagnetized GBDP
186 samples were grinded by 500, 1000 and 2400 grit size SiC papers. Successively, the polishing was
187 done with $0.25 \mu\text{m}$ diamond paste slurry on a velvet cloth at 200 rpm. The microstructural investigation
188 was accomplished with JEOL 7600F (Field Emission Scanning Electron Microscope – JEOL Ltd,
189 Tokyo, Japan) with an electron energy dispersive X-ray spectroscopy (EDXS) analyzer and a 20 mm^2
190 Oxford INCA 350 detector (Oxford Instruments, High Wycombe, UK) for compositional/elemental
191 analysis, performed at 20 keV accelerating voltage.

192 4 Results and Discussion

193 The recycled and fresh Magfine MF-15 HDDR Nd-Fe-B magnets were developed by SPS sintering
 194 operation at 750 °C with holding time of 1 minute, and further complemented by thermal treatment at
 195 750 °C for 1 h. The magnetic properties of HDDR powder and annealed bulk magnets were measured
 196 prior to the GBD treatment with eutectic Pr-Cu and Dy-Cu alloy ribbons and summarized in Table 1
 197 (Ikram et al., 2019b).

198

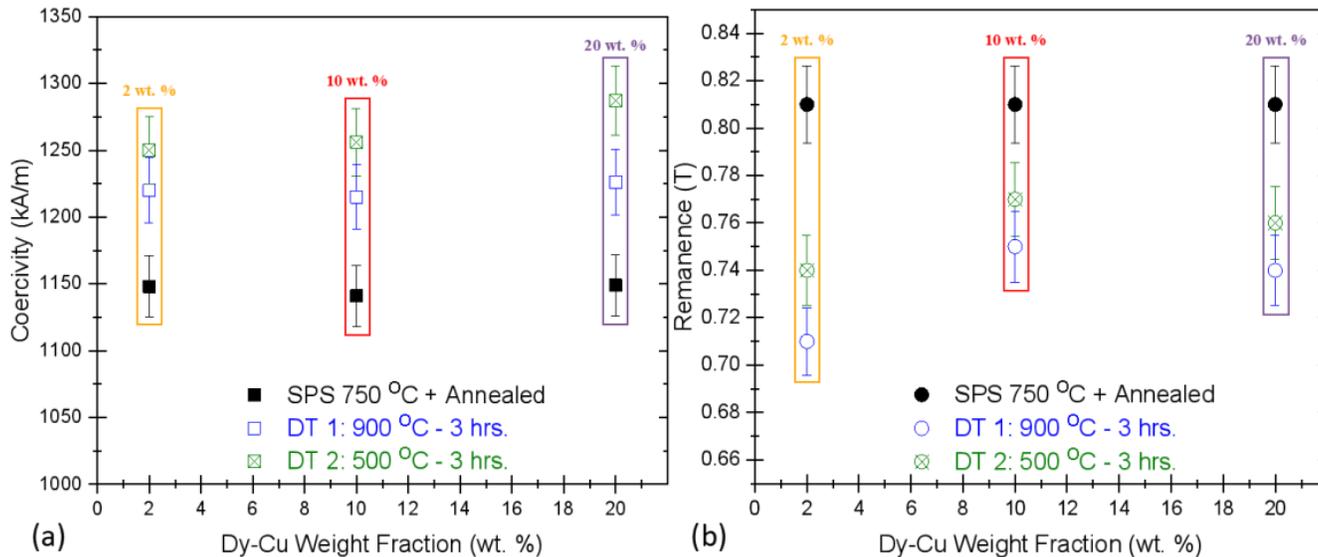
Table 1: Magnetic properties of HDDR Nd-Fe-B magnets prior to Pr-Cu and Dy-Cu GBDP.				
Material Class	Coercivity H_{Ci} (kA/m)	Remanence B_r (T)	BH_{max} (kJ/m³)	M_r/M_S Ratio
End-of-Life (EOL) Scrap Magnet	1170	1.19	250	0.74
Recycled HDDR Nd-Fe-B Powder (RP)	830	0.9	124	0.56
Optimally SPS-ed & Annealed Recycled Magnets (RMs)	1150 – 1170	0.79 – 0.83	112 – 120	0.52
Fresh Magfine MF-15P HDDR Nd-Fe-B Powder (MFP)	1020 - 1130	1.27 – 1.32	270 – 310	> 0.81
Optimally SPS-ed & Annealed Fresh MF-15P Magnets (MFMs), see 3.3	960 – 970	1.06 – 1.07	196 – 200	0.67

199

200 4.1 Dy-Cu Grain Boundary Diffusion Treatment

201 The grain boundary diffusion (GBD) treatment parameters were contemplated from a similar study on
 202 Nd-Fe-B melt-spun ribbons by Bao et al. (Tang et al., 2016) in which Dy₇₀Cu₃₀ and Pr₆₈Cu₃₂ were
 203 utilized. The starting bulk magnets had a relative density > 99 % after the thermal treatment, therefore
 204 they can be classified as fully dense magnets before GBDP. The eutectic melting point for Dy₇₀Cu₃₀
 205 was reported as 790 °C. In order to promote eutectic alloy ribbons fluidity and uniform melting on the
 206 surfaces of bulk magnets, the primary GBDP temperature was retained at 900 °C for 3 h. Secondary
 207 annealing at 500 °C for 3 h was opted to relax the thermal strains formed in the bulk magnets during
 208 GBDP. The mass gain (up to 3 digits precision) was analyzed to overview how much the molten species
 209 have diffused into the magnets after GBDP. The starting magnets ranged from 2.600 – 2.800 g in
 210 nominal masses after the initial grinding was performed to remove carbon layer off the SPS-ed
 211 specimen. The actual mass gain in reprocessed magnets (RMs) was as follows: for 2 wt. % sample

212 approx. 0.019 g (1.94 %), 10 wt. % sample approx. 0.068 g (2.57 %) and 20 wt. % sample approx.
 213 0.0911 g (3.25 %).



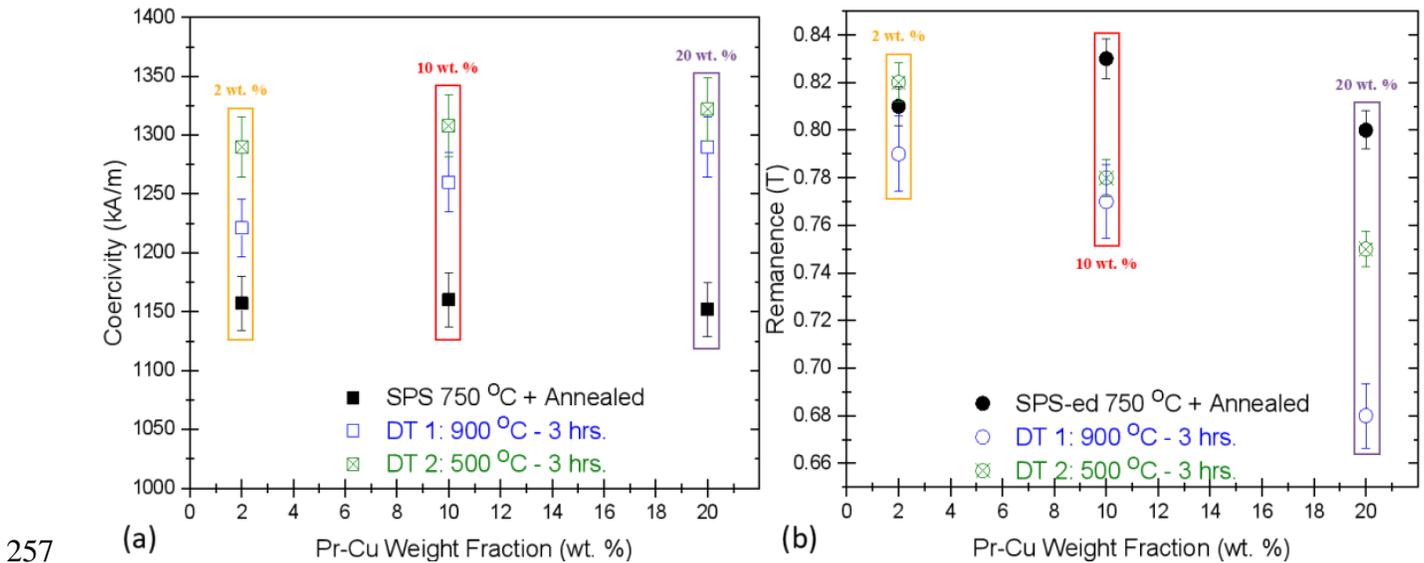
214 (a) dependence of coercivity (H_{Ci}) and (b) remanence (B_r) with different weight fractions of
 215 eutectic $Dy_{70}Cu_{30}$ alloys during the 2 stages of GBD treatment. Plots legend: yellow 2 wt. %, red 10
 216 wt. % and purple 20 wt. % Dy-Cu as the diffusion source on bulk SPS reprocessed magnets (RMs).
 217

218 The augmentation of the magnetic properties is clearly illustrated in Figure 1. The coercivity (H_{Ci}) of
 219 the starting bulk magnets (1148 kA/m) increased to a modest value of 1220 kA/m with 2.wt. % Dy-Cu
 220 eutectic alloy addition at the first stage of GBDP and slightly more to 1250 kA/m after secondary
 221 annealing at 500 °C. In case of 10 wt. % Dy-Cu alloy added as the diffusion source, H_{Ci} increased from
 222 1141 kA/m to 1216 kA/m at 900 °C and finally to 1257 kA/m with the secondary annealing. For 20
 223 wt. % there was a subsequent increase in coercivity from 1149 kA/m to 1226 kA/m (at 900 °C) and
 224 1287 kA/m (at 500 °C), as shown in Figure 1(a). Whereas the remanence (B_r) of the starting bulk
 225 magnets prior to GBDP was uniformly 0.81 T and it consistently dropped more for primary diffusion
 226 processing at 900 °C with a minor recovery after secondary annealing at 500 °C. Earlier investigation
 227 on hot-deformed HDDR Nd-Fe-B magnets suggested that the thermal treatment above the ternary
 228 transformation point introduces higher degree of alignment (texturing) and the subsequent relaxation
 229 in processing strains introduced by grain boundary phase (Ikram et al., 2020). This factor may be at
 230 play here such that the RE-enriched liquid phase at 900 °C realigns the HDDR particles slightly, since
 231 the melt-flows preferentially along the c-axis, resulting in a minor improvement in remanence after
 232 annealing (Ikram et al., 2019b). The overall the drop in the B_r due to a higher weight fraction of Dy-
 233 Cu alloy after the GBD treatment has been reported due to the antiferromagnetic coupling introduced
 234 by partial substitution of Nd with the Dy atoms (Seelam et al., 2014) at the surface of the
 235 nanocrystalline $Nd_2Fe_{14}B$ matrix grains during the primary diffusion treatment at elevated
 236 temperatures, above the binary eutectic 790 °C for $Dy_{70}Cu_{30}$ and ternary transition temperature of Nd-
 237 Fe-B alloys (665 °C) (Tang et al., 2016; Ikram et al., 2019c). This 20 wt. % addition of Dy-Cu eutectic
 238 ribbons caused approximately 55% improvement in H_{Ci} over the starting recycled HDDR Nd-Fe-B
 239 powder and 12% better demagnetization resistance over the optimally SPS reprocessed bulk magnets.

240 Comparing the gain in masses after GBDP, the surface of RMs still contained brazed and non-diffused
 241 species on the top and bottom, so the surface was grinded to the original height of the bulk magnet for
 242 magnetic measurements. This partial mass gain, besides very slight decline in the B_r (< 0.1 T) for the
 243 diffusing Dy indicates that the Dy-Cu alloy ribbons did not melt properly under the 900 °C GBDP
 244 conditions, owing to their high eutectic temperature which caused very limited H_{Ci} improvement in
 245 RMs.

246 **4.2 Pr-Cu Grain Boundary Diffusion Treatment**

247 The eutectic melting regime for $Pr_{68}Cu_{32}$ based melt-spun ribbons was identified at 472 °C, in which
 248 the authors also suggested Pr-Cu alloys were found more effective than Dy-Cu system to augment the
 249 coercivity, without conversely affecting the remanent magnetization (Tang et al., 2016). The change
 250 in relative density was insignificant after the GBDP of reprocessed magnets (RMs) and values were
 251 consistently higher than 7.56 g/cm³ after primary diffusion treatment and secondary annealing. The
 252 actual mass gain in Pr-Cu GBDP reprocessed magnets (RMs) was higher as compared to the Dy-Cu
 253 based RMs, with measurements detailed as follows: for 2 wt. % sample approx. 0.055 g (2 %), 10 wt.
 254 % sample approx. 0.105 g (3.87 %) and 20 wt. % sample approx. 0.138 g (4.96 %). Apparently the Pr-
 255 Cu alloy diffused from the surface in 2 wt. % condition, the brazed species were still present in 10 and
 256 20 wt. % RM samples which were finely grinded to the preceding dimensions.



257 (a) 258 Figure 2: Shows the variation of (a) coercivity (H_{Ci}) and (b) remanence (B_r) after GBD treatment with
 259 different wt. % $Pr_{68}Cu_{32}$ alloy ribbons. Plots legend: yellow 2 wt. %, red 10 wt. % and purple 20 wt. %
 260 Pr-Cu as the diffusion source on bulk HDDR Nd-Fe-B SPS-ed magnets (RM).

261 The magnetic properties prior to and after the GBDP are illustrated in Figure 2, indicating a more
 262 profound effect of Pr-Cu alloy in improving the coercivity without appreciable reduction in the
 263 remanent magnetization. For 2 wt. % Pr-Cu ribbons, a minor improvement in $H_{Ci} = 1221$ kA/m was
 264 observed (RM $H_{Ci} = 1157$ kA/m) during primary diffusion which further increased to 1283 kA/m after
 265 annealing, as shown in Figure 2 (a). This value corresponds to similar H_{Ci} improvement as possible

266 with 20 wt. % Dy-Cu alloy (actual 3.25 % mass gain). The B_r improved slightly to 0.82 T over the
267 original starting RM (0.8 T) after 2 wt. % GBDP, which indicates Pr diffusion is overall more efficient
268 in augmenting the H_{Ci} without negatively impacting the B_r as in case of Dy diffusion. The B_r dropped
269 slightly to 0.78 T (10 wt.%) and 0.75 T (20 wt. %) Pr-Cu GBDP, as shown in Figure 2 (b) indicating
270 the dilution of the hard-magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase with the non-ferromagnetic species diffusing inwards
271 from the surface (Liu et al., 2016; Seelam et al., 2016; Tang et al., 2016; Zhang et al., 2016; Liu et al.,
272 2017). Consequently, with more mass gained by 10 and 20 wt. % Pr-Cu samples, it is plausible that
273 the remanent magnetization is expected to get reduced since these eutectic alloys are compensating and
274 becoming part of the intergranular phase, making it richer with the REEs content. With more
275 intergranular phase and unchanged volume fraction of the ferromagnetic phases, we can expect the
276 improvement in coercivity but only at the cost of a slight reduction in remanence (Sugimoto, 2011).
277 However, the toll on remanence with the addition of Pr-Cu alloys is comparatively less prominent as
278 the Dy-Cu system, since the antiferromagnetic coupling of substituting the Dy atoms in the hard-
279 ferromagnetic phases causes a more noticeable drop in the net magnetization (Tang et al., 2016), which
280 is apparent from Figure 1. Comparatively the H_{Ci} improved from 1160 kA/m (RMs) to 1260 kA/m
281 (900 °C GBDP) and 1308 kA/m (after secondary annealing) for 10 wt. % Pr-Cu diffusion processing
282 (3.87% mass increase). Likewise, utilizing 20 wt. % (4.96% actual mass gain) Pr-Cu alloy ribbons as
283 the direct diffusion source resulted in H_{Ci} enhancement to 1290 kA/m (just after primary diffusion
284 treatment – 900 °C) and subsequently to 1322 kA/m with additional annealing (at 500 °C), as disclosed
285 in Figure 2 (a). This approx. 5% mass gain with Pr-Cu diffusion treatment suggests 15% higher
286 coercivity over the starting RM and 59.3% over the original recycled HDDR Nd-Fe-B powder (RP).
287 These attained values are slightly better than the recently reported H_{Ci} improvement by Pr-Cu diffusion
288 processing of the hot deformed magnets to 1232 kA/m from the fresh HDDR Nd-Fe-B powders, with
289 starting H_{Ci} = 1065 kA/m (Song et al., 2019).

290 The microstructural analysis was performed on 2 wt. % Pr-Cu diffusion processed RM after secondary
291 annealing, using the backscattered electron imaging as shown in Figure 3. For the sake of comparison,
292 the recycled HDDR powder (RP) and the reprocessed magnet (RM) prior to the GBDP with Pr-Cu
293 alloys are also shown in Figure 3 (A) and (B) respectively. Fractography of the HDDR powder particles
294 will most inevitably reveal microstructure similar to Figure 3 (A), i.e. 3D network of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains
295 with preferred orientation along the easy-axis (c-axis) in each particle. The disproportionation of
296 microcrystalline $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix in the EOL magnets spreads uniformly at elevated temperatures to a
297 reaction mixture of NdH_2 , $\alpha\text{-Fe}$ and Fe_2B throughout the whole particle, such that the vacuum
298 desorption of H_2 and recombination reaction creates a transcending continuous 3D network of
299 submicron sized $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains within each HDDR particle (Sugimoto, 2011). As reported
300 previously, the recycled HDDR Nd-Fe-B powder contains a high oxygen content (~5000 ppm) and
301 therefore formation of additional oxide phases (fcc- NdO_x and cubic/hcp Nd_2O_3 – depending on oxygen
302 concentration/up-take) reduces the overall amount of Nd-rich phase present within the system below
303 13.4 at. % (Ikram et al., 2019a; Ikram et al., 2020). The SPS reprocessed magnet (Figure 3b), has been
304 developed with microstructure optimally retained conceivably as close as possible to the starting
305 recycled powder and enhanced magnetic properties followed by annealing. The anticipated changes
306 with GBD treatment are illustrated in Figure 3 (C – F) for 2 wt. % Pr-Cu surface diffusion after the
307 primary and secondary annealing. This specimen was also selected for the reason that nearly all the Pr-

308 Cu alloy apparently diffused inside the magnet indicated by 2% weight gain. [The BSE images indicates](#)
309 [different zones of diffusion \(bright phase indicates rare-earth rich phases\) detailed in Figure 3 \(C\).](#) The
310 diffusion depth illustrated in this image is clearly limited as the Pr-Cu-rich species were located in near
311 surface regions, ranging up to approximately 250 μm from the surface. The possible origin of extended
312 diffusion zone must be associated with the primary GBD treatment at 900 $^{\circ}\text{C}$, such that it is anticipated
313 that time and concentration dependent diffusion happened with the liquification of aggregate RE-phase
314 above the ternary transition temperature (665 $^{\circ}\text{C}$), which enhanced the diffusion depth to $\sim 600 \mu\text{m}$
315 from the surface. This lack of diffusion depth beyond $\sim 600 \mu\text{m}$ can be assumed because of high surface
316 tension caused by the eutectic melt-pool, which requires multiple micron sized channels to diffuse
317 through the surface regions; besides time and concentration gradient limitations at the surface. As
318 previously demonstrated, the HDDR Nd-Fe-B system is very much unlike the melt-spun ribbon flakes
319 and the sintered magnets with several micron sized grains having thicker grain boundary channels,
320 such that the RE-rich melt is transported thermodynamically by grain boundary channels. In this
321 HDDR Nd-Fe-B system, the diffusive transport happens via inwards capillary suction along very thin
322 grain boundary channels of $\sim 3 \text{ nm}$ thickness (Ikram et al., 2019c). This complicates the diffusivity and
323 the prodigious surface tension caused by a high mass fraction of eutectic species in nearly dense
324 magnets require a greater number of surface perforations to penetrate inwards. Thinner channels in the
325 HDDR Nd-Fe-B surges the required capillary forces for diffusivity towards the grain boundaries
326 connecting the nanocrystalline grains. The perforations in the conventional sintered magnets from
327 microcrystalline precursors are considerably thicker to promote grain boundary diffusion. The HDDR
328 particle size is $\sim 220 \mu\text{m}$, whereas in the sintered magnets the particle size is around 5 – 10 μm , which
329 indicates numerous grain boundary channels in the sintered magnets as compared to the particle
330 boundaries accessible at the surface of HDDR Nd-Fe-B based magnets. The nanoscopic grain boundary
331 channels connected to the particle boundaries in the HDDR Nd-Fe-B system are much thinner than the
332 sintered magnets, in which diffusion is controlled by concentration gradient (Seelam et al., 2014; Tang
333 et al., 2016). The first hindrance for the RE-rich liquid phase are the surface channels to diffuse the
334 liquid phase along the particle boundaries, which in turn distribute this liquid phase along the grain
335 boundaries under capillary diffusion (Ikram et al., 2019c). Hence the effective particle boundary
336 surface area in the HDDR Nd-Fe-B system is considerably lower than the sintered magnets, which is
337 required to accelerate the diffusion from the surface region under capillary forces and so the diffusion
338 depth is lower than 1 mm. [Another factor to account for the partial diffusivity is related to preferential](#)
339 [flow kinetics with the magnetization easy axis \(c-axis\) in the HDDR Nd-Fe-B system \(Ikram et al.,](#)
340 [2020\).](#) In case of GBD processing of bulk magnets, the powder particles are joined up with interparticle
341 boundaries, such that for these regions oriented with (parallel to) the easy axis (c-axis) will tend to
342 preferentially allow capillary diffusion in to the grain boundary channels adjoining the ultrafine
343 $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains within the diffusion (Figure 3D) and extended zones (Figure 3E), in the vicinity of
344 Pr-Cu rich pools at the intergranular junctions. The presence of darker features 100 – 200 μm in size
345 from Figure 3 (C) are merely powder particles misoriented during the SPS reprocessing under applied
346 pressures (Ikram et al., 2019b).

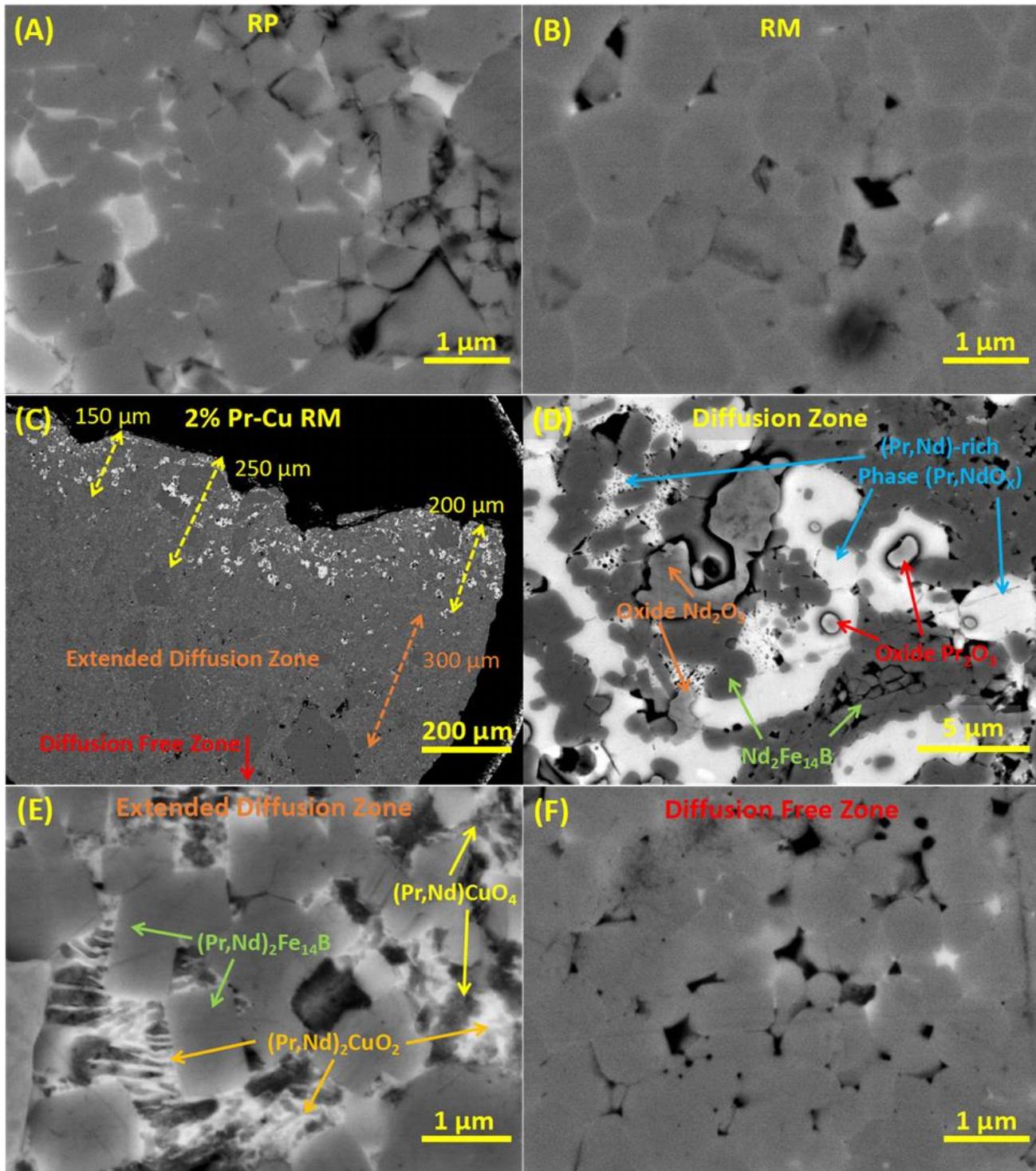
347 The Pr-Cu diffusion treatment has already been reported that the Pr-rich liquid/intergranular phase
348 induces strains in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase which may also lead to strain-induced transformation of
349 Nd_2O_3 above ternary point facilitated by Cu segregation (Sepehri-Amin et al., 2015). Therefore, the

350 secondary annealing at 500 °C helps in relaxing the microstructure with reduced defect density by
351 smoothening the grain boundaries and reprecipitated $(\text{Pr,Nd})_2\text{Fe}_{14}\text{B}$ surfaces from the RE-enriched
352 melt, which is beneficial for the improvement in the magnetic properties. Close-up image of diffusion
353 zone is shown in Figure 3 (D), which indicates the various phases randomly distributed within the
354 microstructure and quantified in Table 2. This region is concentrated with Pr-rich phases, with a high-
355 volume fraction of bright regions corresponding to $(\text{Pr,Nd})\text{O}_x$ type species intercalated at the HDDR
356 particle boundaries and the $\text{Nd}_2\text{Fe}_{14}\text{B}$ intergranular regions. In the near surface regions up to extended
357 diffusion zone and close to the Pr-rich phase, the stoichiometric composition of the matrix phase
358 resembled $(\text{Pr,Nd})_2\text{Fe}_{14}\text{B}$ (Morimoto et al., 2016). The surface of 2:14:1 grains partially melt during
359 GBDP above ternary transition temperature in equilibrium with RE-rich phase, such that enrichment
360 of facet region causes reprecipitation and asymmetrical solidification of shell structure at the interface
361 (in case of HREEs) (Seelam et al., 2014). Previously it has been suggested that the grains facets in
362 contact with (Nd,Pr) -rich liquid phase transformed to $(\text{Pr,Nd})_2\text{Fe}_{14}\text{B}$ due to Nd depletion but did not
363 completely form the Pr-type shell structure over the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (Sepehri-Amin et al., 2015). The
364 EDXS results provide evidence for this transformation of nanocrystalline matrix grains during GBDP,
365 such that the surfaces connected to the Pr-enriched liquid phase partially substitute Nd with Pr to form
366 $(\text{Pr,Nd})_2\text{Fe}_{14}\text{B}$ facets and depleted Nd becomes part of liquid phase. In the diffusion region, the Pr-rich
367 phase was analyzed with a nominal composition of $(\text{Pr,Nd})\text{O}_2$, besides the presence of slightly greyish
368 $\text{Pr}_2\text{O}_3/\text{Nd}_2\text{O}_3$ oxide phase which is formed due to excessive availability of oxygen within the
369 microstructure. Overall, the distribution of Pr, Nd, Cu and O at the intergranular channels with matrix
370 phase and the particle boundaries is non-uniform and varies inconsistently with the diffusion depth.
371 Furthermore it can also be hypothesized that the secondary annealing may not have contributed
372 significantly in increasing the diffusion depth of RE-rich species, since the Pr-Cu alloy should have
373 transformed to different phases as indicated in Figure 3 (D) above the ternary transition temperature
374 during the primary GBDP.

375 The miscibility of eutectic species in the Nd-rich intergranular phase is significantly higher and
376 therefore, for the surface species to be propelled inside, rate of mass transport (diffusivity) is limited
377 by concentration gradient which is also limited by time. Hence during the primary GBD treatment, it
378 is anticipated that the diffusivity limits the penetration of melt to near surface regions only (up to 500
379 – 600 μm). Since the primary GBDP occurs above the ternary eutectic point (665 °C), so the Nd-rich
380 phase is in liquid state with nanocrystalline $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Nd}_{1+\epsilon}\text{Fe}_4\text{B}_4$ phases (Ikram et al., 2019b).
381 Now the influx and dissolution of Pr-Cu will be limited by the concentration gradient of liquid phase
382 along the HDDR particle boundaries before capillary infusion along the nanocrystalline grains. Initially
383 Pr and Cu in the RE-rich melt become part of aggregate liquid phase at the particle boundaries making
384 it enriched with the rare-earth species. As the capillary diffusion begins, Cu remains segregated within
385 the liquid phase while Pr substitutes partially on the facets in contact with RE-rich liquid phase (Song
386 et al., 2019). This capillary diffusion from the surface to particle boundaries and finally to grain
387 boundaries is both time and concentration dependent, although considerably slow as compared to the
388 localized diffusion previously devised by DyF_3 doping of the HDDR Nd-Fe-B system (Ikram et al.,
389 2019c). The diffusion zone, shown in Figure 3 (D) also indicates the presence of secondary phases like
390 Nd_2O_3 at the intergranular junctions restrict the capillary flow of liquid phase, either by limiting the
391 liquidus phase to localized regions only and/or scavenging the rare earth elements to form more dhcp-

Limitations in the grain boundary processing of the recycled HDDR Nd-Fe-B system

392 RE₂O₃ type phases (Ikram et al., 2019b). Since EDXS indicates a more common distribution of Nd₂O₃
393 phase as compared to Pr₂O₃, which implies that Pr preferably interacts more with the surface facets of
394 adjacent Nd₂Fe₁₄B grains or remain associated within the grain boundary channels. The segregation of
395 Cu in the intergranular region has been observed to rearrange the Nd atoms during annealing at 500
396 °C, resulting into transformation of hcp-Nd₂O₃ oxide to cubic-Nd₂O₃ phase (Kim et al., 2014; Song et
397 al., 2019). This suggests that Cu segregation induced changes to the hcp-Nd₂O₃ phase at the
398 intergranular region favors the transformation to cubic type crystal structure, which releases the strain
399 introduced by hcp-Nd₂O₃ phase due to their significantly higher mismatch with the (Pr,Nd)₂Fe₁₄B
400 matrix grains (Ikram et al., 2019a). Furthermore, the transformation of cubic-Nd₂O₃ phase originates
401 from the oxidation of metallic Nd and cubic-PrO₂ type phase stabilized by Cu at the intergranular
402 junctions (Song et al., 2019). Additionally, the RE-rich phase has been identified within the diffusion
403 zone in RE-O_x form, suggesting the bright region is composed of (Pr,Nd)O_x phase. The more lamellar
404 form factor indicates NdO₂/NdO type phase in the vicinity to (Pr,Nd)₂Fe₁₄B matrix, while the
405 continuous white region suggests combined NdO₂ and (Pr,Nd)O₂ phase. More elaborate analytical
406 analysis with the transmission electron microscopy to understand the capillary diffusion limiting
407 factors at the 2 – 3 nm scale of grain boundaries is recommended, since the FEG-SEM in terms of
408 EDXS resolution can precisely classify only the intergranular junctions and particle boundaries of size
409 ≥ 0.5 μm and distinguishing different crystal structures was not possible with the existing setup.



410

411 Figure 3: BSE-SEM analysis, high magnification image of (A) bonded recycled HDDR Nd-Fe-B
 412 powder (RP) and (B) optimally SPS-ed HDDR Nd-Fe-B bulk magnet (RM) prior to GBDP; (C)
 413 micrograph of 2 wt. % Pr-Cu GBDP specimen indicating diffusion zones after secondary annealing,
 414 (D) close-up image of diffusion zone with different phases quantified in Table 2, (E) the diffusion zone
 415 extension due to secondary annealing showing the distribution of Pr-Cu-rich phase at the intergranular

416 regions, and (F) diffusion free zone which mimics the microstructure of original RM due to limited
 417 diffusion depth of Pr-Cu alloys in HDDR Nd-Fe-B system.

418

Table 2: FEG-SEM EDXS quantification of different phases in the 2 wt. % Pr-Cu GBD processed recycled HDDR Nd-Fe-B bulk magnets.							
Phases	Nd (at. %)	Pr (at. %)	Dy (at. %)	Fe (at. %)	O (at. %)	Al (at. %)	Cu (at. %)
Nd₂Fe₁₄B	13.1	2.2	-	80.7	-	1.1	2.9
(Pr,Nd)₂Fe₁₄B	4.2	9.3	-	85.6	-	0.9	-
(Pr,Nd)-rich Phase (Pr,Nd)_xO_x/(Pr,Nd)O₂	7.5	19.5	-	1.5	71.5	-	-
Pr₂O₃ / Nd₂O₃	10.4	15.4	-	10.5	63.7	-	-
(Nd, Pr)₂CuO₂	20.1	13.4	2.1	14.8	30.9	-	18.7
(Pr,Nd)_xCuO₄	9.1	13.0	-	3.0	51.4	-	23.5
RE₂CuO₂	23.7	16.5	3.3	10.7	32.6	-	13.2
<p><i>*Oxford Instruments INCA 350 EDXS 20 mm² detector Point ID analysis system at 20 kV and XPP matrix corrections with quantitative error for light elements in standard deviation (S.D) ~ 0.085 and for combined elements S.D ~ 0.055. Quant and Profile optimization applied for normalized Point ID analysis with >10k cps during all individual quantitative measurements. All individual measurements except the last three were repeated twice and average at. % values are reported in this study.</i></p>							

419

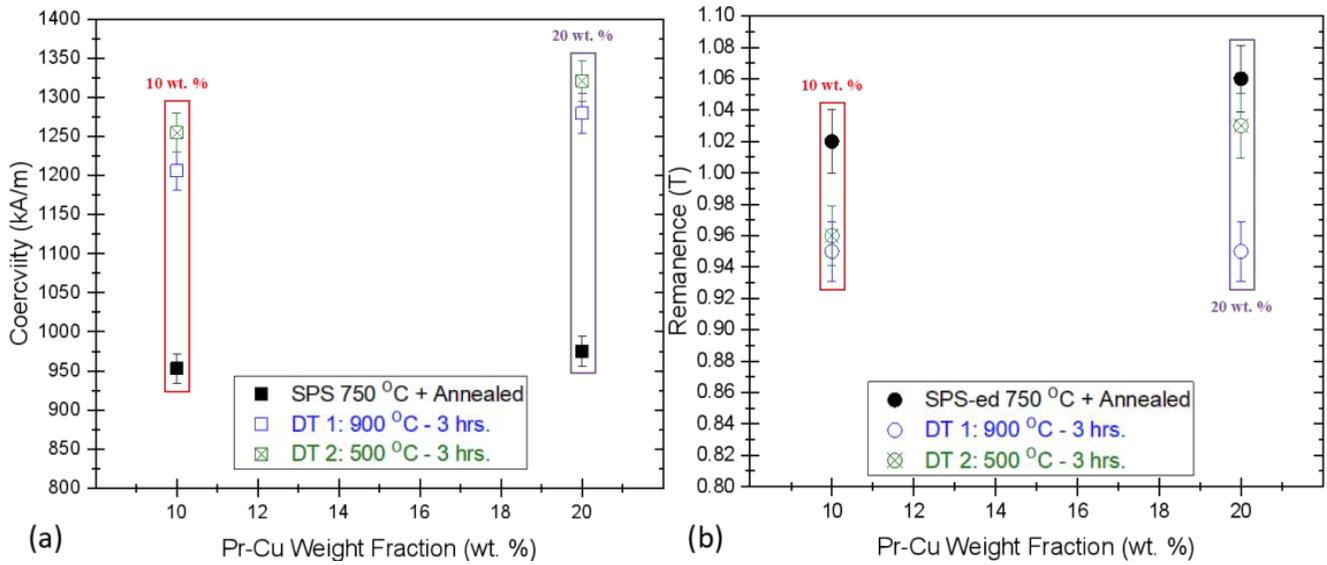
420 It is anticipated that the secondary annealing above the Pr-Cu binary eutectic point 472 °C only resulted
 421 in re-melting and redistribution of localized Pr-Cu phase from the particle and intergranular boundaries.
 422 It is speculated based on EDXS results that although Cu remains segregated within the liquid phase, Pr
 423 and Nd switch positions asymmetrically, such that per this matrix facets substitution implies liquid
 424 phase becoming richer with Nd instead of Pr. The melting point of eutectic Nd-Cu alloy is 520 °C
 425 (Sepehri-Amin et al., 2010b), indicating limited capillary flow distance and redistribution of Nd-rich
 426 species. However, this temperature is effective in releasing the thermal processing strains within the

427 magnets, which subsequently resulted into an improvement of the coercivity as well as the remanent
428 magnetization (Ikram et al., 2019b).

429 The lamellar structure of intergranular phase is rich with Cu and rare-earth elements illustrated in
430 Figure 3 (E), corresponds to RE_2CuO_2 (Wilson et al., 2006) with brighter contrast, while a darker tone
431 RE_xCuO_4 phase (cuprate with long-range magnetic order) was also identified within this extended
432 region (Weber et al., 2010) as the RE-rich phase was diffused inwards. The bright lamellar
433 $(\text{Nd,Pr})_2\text{CuO}_2$ is widely distributed within the $\sim 600 \mu\text{m}$ diffusion zone indicating conversion of the
434 primary Nd-rich phase NdO_x to $(\text{Pr,Nd})\text{O}_2$ phase, which is a thermodynamic transformation
435 precipitated by Cu at the intergranular junctions and the grain boundaries (Song et al., 2019). This
436 region in the extended diffusion zone, shown in Figure 3 (E) and supplementary image (C) illustrates
437 the RE-rich region containing complex cuprates [the darker $(\text{Pr,Nd})\text{CuO}_4$ and grayish lamellar
438 $(\text{Pr,Nd})_2\text{CuO}_2$ phase] are of size 300 – 500 nm, co-existing with $(\text{Pr,Nd})\text{O}_x$ phase. The magnetic
439 exchange effects originating from $(\text{Nd,Pr})\text{CuO}_4$ at the intergranular regions are out of scope for
440 concurrent study. In the vicinity, Pr from the melt also partially substitutes Nd in the hard-
441 ferromagnetic matrix by transforming to $(\text{Pr,Nd})_2\text{Fe}_{14}\text{B}$ phase (Sepehri-Amin et al., 2015; Tang et al.,
442 2016). Previous literature reported the segregation of Cu and transition metals (Fe, Co) at the
443 intergranular phase along the interface with $(\text{Pr,Nd})_2\text{Fe}_{14}\text{B}$ nanocrystalline grains (Sepehri-Amin et al.,
444 2015), which apparently is also true for the HDDR Nd-Fe-B system; however, this type of analysis is
445 beyond the scope of utilized FEG-SEM and EDXS technique. The region beyond the diffusion zone
446 shown in Figure 3 (F) primarily consisted of microstructure similar to that of the bulk sintered magnet
447 prior to GBDP, with exception of very limited Nd-rich phase redistribution in sparse regions only. This
448 suggests that the overall diffusion depth of eutectic Pr-Cu alloys from the surface is limited to ~ 600
449 μm in the HDDR Nd-Fe-B based bulk magnets, prioritizing the requirement of localized grain
450 boundary engineering instead of surface diffusion treatments.

451 4.3 Magfine MF-15P Grain Boundary Diffusion Treatment

452 The commercial grade MF-15P type HDDR Nd-Fe-B has been sparsely used in research but has been
453 popular for the bonded magnet applications due to suitable magnetic properties at room temperature
454 and up to 100°C (Takagi et al., 2015). In order to compare the effectiveness of Pr-Cu diffusion
455 treatment, the MFMs were produced with similar SPS and GBD processing conditions. The optimally
456 SPS-ed and annealed MFMs have starting $H_{Ci} = 968 \text{ kA/m}$, $B_r = 1.07 \text{ T}$, $BH_{max} = 198 \text{ kJ/m}^3$ and 99%
457 relative density. In this case with MFMs, 10 and 20 wt. % of Pr-Cu alloy ribbons were added to the
458 crucible to achieve optimal diffusion treatment results to compare with GBDP MRs, as shown in Figure
459 4. The GBDP with 10 wt. % Pr-Cu alloy ribbons improved the H_{Ci} to 1206 kA/m (at primary diffusion
460 treatment) and 1255 kA/m (secondary annealing). The B_r reduced slightly to 0.96 T for 4.11% mass
461 gain (0.113 g), as plotted in Figure 4 (b). Similarly, according to Figure 4(b), the MFM sample diffusion
462 treated with 20 wt. % Pr-Cu alloy gained mass by 0.171 g (6.37 %), which resulted in H_{Ci} boosted to
463 1269 kA/m (at 900°C) and consequently, after 500°C annealing to 1313 kA/m with $B_r = 1.04 \text{ T}$. This
464 resistance to demagnetization i.e. coercivity is approx. 35.6% better than optimally SPS processed
465 MFMs and a modest 11.3% better than the previously reported (Takagi et al., 2015).



466

467 Figure 4: Illustrates the deviations in (a) coercivity (H_{Ci}) and (b) remanence (B_r) with GBD treatment
 468 for different wt. % $\text{Pr}_{68}\text{Cu}_{32}$ alloy ribbons. Plots legend: red 10 wt. % and purple 20 wt. % Pr-Cu as the
 469 diffusion source on fresh HDDR Nd-Fe-B SPS-ed magnets (MFM).

470

Table 3: Magnetic properties of HDDR Nd-Fe-B bulk magnets after Pr-Cu and Dy-Cu GBDP.

	Diffusion Source Alloy Weight Fraction	Coercivity H_{Ci} (kA/m)	Remanence B_r (T)	BH_{max} (kJ/m ³)	Actual Mass Gain (%)
Dy₇₀Cu₃₀ + Recycled Magnet (MR)	0 wt. %	1148	0.81	115	-
	2 wt. %	1250	0.74	90	1.94
	10 wt. %	1256	0.78	105	2.57
	20 wt. %	1287	0.77	104	3.25
Pr₆₈Cu₃₂ + Recycled Magnet (MR)	0 wt. %	1160	0.83	120	-
	2 wt. %	1283	0.82	116	2.00
	10 wt. %	1308	0.78	107	3.87

	20 wt. %	1322	0.75	100	4.96
Pr₆₈Cu₃₂ + Fresh Magnet (MFM)	0 wt. %	969	1.07	198	-
	10 wt. %	1255	0.96	127	4.11
	20 wt. %	1313	1.04	190	6.37

471

472 Figure 3 (C – F) confirms gradient microstructure of the Pr-Cu GBDP HDDR Nd-Fe-B magnet with
473 surface regions experiencing magnetic hardening as compared to the inner segment. The magnetic
474 properties of the bulk HDDR Nd-Fe-B magnets after GBDP with the eutectic Dy-Cu and Pr-Cu alloys
475 are organized in Table 3. The results indicate that although the GBDP of the eutectic alloy ribbons is
476 limited in mass gain and diffusion depth to near surface regions (~600 μm for Pr-Cu alloy) in the
477 HDDR system, the Dy-Cu alloys are comparatively less effective in improving the coercivity as
478 compared to Pr-Cu alloys, besides a more significant impact on the magnetization reduction ($B_r < 0.1$
479 T) in case of former type alloys due to the HREEs and unreacted Dy at the boundary interfaces adds
480 up to the reduction in B_r as well as H_{Ci} . Henceforth, the Dy-Cu alloys will always cause reduction in
481 the B_r for the diffusing Dy implying that the Dy-Cu alloy ribbons did not achieve adequate liquefaction
482 as the Pr-Cu ribbons under the 900 °C GBDP conditions, owing to their high eutectic temperature
483 which caused very limited H_{Ci} improvement in RMs. The improvement achieved with eutectic Pr-Cu
484 alloys is approx. 60 % in H_{Ci} as compared to Dy-Cu alloys at 55 % in the recycled HDDR Nd-Fe-B
485 system. This effect of Pr-Cu alloys excelling Dy-Cu has been previously identified in the commercial
486 grade sintered magnets treated with same composition of eutectic alloys diffusion processed at 900 °C
487 for 4 h, suggested the lower melting Pr-Cu alloy registered approx. 240 kA/m higher H_{Ci} over Dy-Cu
488 alloy, although the latter alloy developed core-shell structures (Tang et al., 2016). The secondary
489 annealing is responsible for the relaxation of thermal stresses and reformation of grain facets, such that
490 the grain boundary distribution is more uniform among the grains after the secondary annealing. As a
491 matter of fact, the diffusing Dy-rich species via surface GBDP were found less effective as compared
492 to the HREEs original added to the composition because of unreacted Dy at the interface and
493 inhomogeneous core-shell formation, which in turn increases the coercivity $\mu_0 H_C > 2$ T (Zhang et al.,
494 2016). Similarly, the Pr-Cu alloy ribbons enhanced the H_{Ci} without negligible impact on the B_r of the
495 fresh MF-15P HDDR Nd-Fe-B system by 25% over the starting HDDR powder (MFP) and pre-GBDP
496 bulk magnet (MFM) by 36% approximately. Evidently for the HDDR Nd-Fe-B system, the observed
497 mass gain associated with Dy-Cu alloy is lower for all weight fractions as compared to Pr-Cu alloys
498 confirming the thermally controlled concentration gradient effect here. This suggests that the eutectic
499 Dy-Cu system may be more effective for the HDDR Nd-Fe-B powders instead of the bulk magnets
500 subsequently due to rapid and uniform short-range diffusion over loose powder with a high surface
501 area at these GBDP conditions. In case of the HDDR powders, there may not be a requirement to
502 facilitate short-range diffusion from the particle interfaces, so GBDP HDDR powder with Dy-Cu alloys
503 can later be compacted with SPS and annealed as a general suggestion for the future work. A pragmatic

504 recommendation for future research would also be to mill-down the eutectic alloy ribbons to reduce
505 the surface tension associated effects which limit the capillary diffusion and redistribution of RE-rich
506 species under concentration gradients. Another alternative is to uniformly mix the finely milled alloy
507 ribbons with the rare-earth-lean recycled HDDR Nd-Fe-B powder and subsequently sinter them with
508 the SPS at even lower temperatures, such that overall processing steps are considerably reduced.
509 Utilization of hyper-eutectic rare-earth rich alloys instead also has effectively served the purpose in the
510 sintered and hot deformed magnets (Sepehri-Amin et al., 2015;Liu et al., 2016;Tang et al., 2016;Zhang
511 et al., 2016;Liu et al., 2017).

512 5 Conclusions

513 The HDDR Nd-Fe-B based bulk magnets were grain boundary diffusion (GBD) treated with the
514 eutectic alloy ribbons of Pr-Cu and Dy-Cu in the range of 900 °C. The variation in magnetic properties
515 was studied with respect to different weight fractions of Pr-Cu and Dy-Cu alloy ribbons placed on top
516 and bottom of the bulk magnets for thermal processing. The GBDP resulted in improvement of the
517 coercivity of the HDDR Nd-Fe-B systems, bulk magnets made from both fresh and recycled materials.
518 The high temperature Dy-Cu eutectic was found less efficient as compared to low melting Pr-Cu binary
519 eutectic during the scheme of primary processing at 900 °C and secondary annealing at 500 °C resulted
520 in overall improvement H_{Ci} by 60% at 1322 kA/m as compared to 830 kA/m for the recycled powder.
521 Correspondingly, the fresh MF-15P HDDR Nd-Fe-B based bulk magnets gained up to 36%
522 improvement in H_{Ci} without a substantial decrease in B_r , proving the suitability of GBDP with binary
523 eutectic alloys. Therefore, the transport of liquid phase from the surface to the particle boundaries is
524 postulated to occur under the effect of concentration gradient which is controlled by temperature and
525 interparticle phase chemistry, whereas further from the particles to the grain boundaries is activated by
526 capillary transport. On the contrary, the mass gain was lower than total diffusing species. It was further
527 observed with SEM analysis that the diffusion treatment is limited in achieving thorough surface
528 penetration, primarily because of reduced capillary forces from high weight fraction of molten species
529 creating surface tension and lack of excessive particle boundaries in fully dense magnets. The matrix
530 adjacent to the diffusion zone up to ~600 μm constitutes of $(\text{Pr,Nd})_2\text{Fe}_{14}\text{B}$ nanocrystalline grains with
531 RE-rich $(\text{Pr,Nd})\text{O}_2$ and the secondary phases: lamellar Nd_2CuO_2 and $(\text{Nd,Pr})\text{CuO}_4$ at the intergranular
532 regions. The region beyond the diffusion zone is similar to the bulk magnets prior to the GBD
533 treatment. Nonetheless, the retention of magnetization (B_r) after GBDP indicate limited surface
534 diffusivity for the mass gain is still effective in revitalizing the coercivity and the bulk magnets have
535 gradient microstructure with magnetic hardening of the surface regions. Convincingly, this report also
536 suggests that eutectic $\text{Dy}_{70}\text{Cu}_{30}$ is not an optimal alloy for GBDP of the HDDR Nd-Fe-B bulk magnets
537 because of the requirement for very high processing temperatures to activate the mass diffusion. The
538 effectiveness of eutectic Dy-Cu alloy's is substantially slower than Pr-Cu alloys based on mass and
539 coercivity gain, thus limiting its GBDP applicability to HDDR Nd-Fe-B powders only, since
540 processing above 900 °C may deteriorate the magnetic properties due to unnecessary abnormal grain
541 coarsening.

542 6 Conflict of Interest

543 The authors declare that this research was performed in the absence of any commercial or financial
544 relationships that could be interpreted as a potential conflict of interest.

545 **7 Author Contributions**

546 Conceptualization, A.I.; methodology, A.I.; software, A.I.; validation, A.I. and M. A.; formal analysis,
547 A.I.; investigation, A.I.; resources, M.A., R.S. and A.W.; data curation, A.I.; writing—original draft
548 preparation, A.I.; writing—review and editing, A.I., M.A. and F.P.; visualization, A.I.; supervision,
549 S.K., A.W., K.Ž.R and F.P.; project administration, K.Ž.R., S.K. and A.W.; funding acquisition, S.K.,
550 A.W. and K.Ž.R.

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