

REPROCESSING OF RECYCLED Nd-Fe-B
AND Sm-Co-BASED MAGNETS WITH
CONTEMPORARY SINTERING TECHNIQUE

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Doctoral Dissertation
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Doctoral Dissertation

PONOVNA PREDELAVA RECIKLIRANIH MAGNETOV NA OSNOVI Nd-Fe-B IN Sm-Co S SODOBNO TEHNIKO SINTRANJA

Doktorska disertacija

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To my *beloved family* back home who were dearly missed, my
determined wife and the *home like no other Pakistan*.

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Abstract

The rare-earth-based permanent magnets (REPM) are vital for modern electrical appliances and green energy technologies which has created a massive supply-demand frontier for the industries. Usually high thermal stability and resistance to demagnetization comes with the addition of heavy rare earth elements (HREEs) like Dy and Tb in $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type permanent magnets, which has the highest energy products (BH_{max}) per unit volume. The addition of HREEs to Nd-Fe-B permanent magnets has strong implications on natural abundance, costs as well as the reduction in magnetization (and BH_{max}) due to the antiferromagnetic coupling of the magnetic moments of the HREE atoms with that of iron. Since the 2011 rare earth (RE) crisis, which caused the prices of raw material (especially Nd, Dy, Tb) to surge by 700%; the global REPM producers are looking for supply chain and economic sustainability to fulfill this commercial demand. On the contrary, the scientific front has been looking to explore a new class of permanent magnets without the costly rare earth elements or try to develop the methods to recycle the end-of-life (EOL) REPMs. The former has not been very successful since the past decade or so, whereby the later route has shown high potential in commercial up-scaling if the processing parameters are controlled to preserve and control the microstructure. Direct reusage or direct/indirect recycling of EOL magnets is an area of interest for the researchers as well as the magnet producers. Slight modification of chemical composition towards rare earth rich compositions has helped developed REPMs with better magnetic properties than the starting EOLs, but the higher costs due to the addition of rare earth rich compositions to the existing systems may be a problem.

The hydrogen-based recycling route of REPM is an economically feasible and clean method due to its very low environmental footprint compared to pyro- and hydrometallurgical recycling methods. Normally the rejected waste in REPM production goes up to 25%, which is huge considering the aggregate global magnet production. This rejected scrap or EOL waste magnets can be processed by hydrogen-based recycling methods like: hydrogen decrepitation (HD) used for Nd-Fe-B and Sm-Co or hydrogenation–disproportionation–desorption–recombination (HDDR) used for Nd-Fe-B to develop magnetic powder can either be sintered by conventional powder metallurgical routes or readymade to assorted shapes in the form of plastic bonded magnets. The HD treatment facilitates the intergranular cracking in EOL Nd-Fe-B magnets due to formation of NdH_x (causing volume expansion) and this friable non-magnetic powder can be further jet-milled to 3 – 5 μm size, magnetically aligned and sintered to final shape. The chemical composition can be easily modified by blending fine RE-rich alloy powder/dopant (DyF_3) with the HD-treated recycled powder to achieve the desirable level of magnetic properties.

Identically the HDDR reprocessing has the additional benefit since it can develop anisotropic nanocrystalline grains in the size range of ~ 400 nm for achieving higher coercivities than the microcrystalline counterparts. The HDDR-treated recycled powders can be formed to shape by mixing them with the polymeric binders or sintered by rapid

consolidation techniques like hot deformation or spark plasma sintering (SPS) to bulk magnets. Normally these nanocrystalline powders cannot be conventionally sintered, as higher temperatures for prolonged periods would result in exaggerated grain coarsening and the coercivity will decline severely. Therefore, rapid compaction by SPS is an alternate method in magnet recycling to achieve the magnetic properties at par with the commercial grade or fresh HD/HDDR powder. The SPS process is very rapid and heating rates can be controlled to prevent the deterioration to the microstructure, which in turn preserves the magnetic properties of the original powder and fully dense magnets can be formed in a matter of minutes at lower sintering temperatures than those in conventional sintering. Simultaneous application of pressure in the SPS is beneficial for achieving full densification and ramping it rapidly (> 100 MPa) and is beneficial in the texture in the Nd-Fe-B nanocrystalline material by hot forging (deformation).

Within this thesis two different kinds of recycled magnetic powders HD-treated SmCo_5 and HDDR Nd-Fe-B, were investigated by consolidation with the SPS. In the former case the SPS temperature range was identified around $900 - 950$ °C with holding time of $1 - 5$ minutes and 100 MPa pressure in 0.2 mbar Ar pressure for achieving > 97 % densification. The resultant magnetic properties of isotropic SPS-ed SmCo_5 magnets ($H_{\text{Ci}} > 2000$ kA/m & $B_r = 0.47$ T) were slightly better than the vacuum-sintered magnets due to better microstructural control (optimal distribution of Sm-rich Sm_2Co_7 phase in the SmCo_5 matrix) achieved with the SPS. As compared to the commercial grade material, the finer HD-treated recycled powder had a tighter grain size control ($4 - 20$ μm), which resulted in nearly full density and room temperature $H_{\text{Ci}} > 2000$ kA/m and better thermal stability at 180 °C.

Similarly, the recycled HDDR Nd-Fe-B powder was optimally SPS-ed at $750 - 800$ °C (approx. 30 % lower sintering temperature) for 1 minute and 100 MPa to reach $H_{\text{Ci}} \sim 1200$ kA/m which was slightly better than the fresh HDDR powder MF-15P (1180 kA/m). The starting HDDR powder with $\text{Nd}_{13.4}\text{Dy}_{0.6}\text{Fe}_{78.6}\text{B}_{6.1}\text{Nb}_{0.4}\text{Al}_{0.7}$ composition had the $H_{\text{Ci}} = 830$ kA/m. The effect of post SPS thermal treatments was thoroughly investigated for the recycled HDDR powder and with HR-SEM and EDXS it was confirmed the redistribution of Nd-rich grain boundary phase is important for achieving higher coercivities after the SPS fabrication. These optimally SPS-ed magnets were hot deformed at 750 °C by varying the hot deformation pressure to 100 and 150 MPa in WC + Co cermet dies to induce texture in the isotropic bulk magnets. As compared to the starting HDDR powder with $B_r = 0.9$ T, the resultant improvement after 150 MPa hot deformation in B_r was ~ 1.01 T ($BH_{\text{max}} = 180$ kJ/m³) with 55% height reduction of the sample.

It is important to consider that hydrogen-based recycling is effective only if the protective coating on EOL magnets is non present or ruptured for decrepitation to occur. In secondary recycling, these coatings are removed from the fragmented powder with an average particle size less than 100 μm by mechanically crushing the magnets. On the contrary, the HDDR powder is prone to excessive oxidation if the reduction in average particle size is too significant. But this critical particle size range has not been identified previously, which also restrained the commercial scale up. The in-depth studies were performed to verify the relationship of HDDR powder particle size with the oxygen content, sinterability and the magnetic properties. The particle fractions from 700 μm to < 50 μm were individually tested for the oxygen content, the magnetic properties and the sinterability. It was evaluated that particles sized below 100 μm took up twice the oxygen (> 7000 ppm) and as a result, the overall Nd-rich phase declined due to excessive Nd_2O_3 formation. This resulted in poor sinterability and severe degradation of the magnetic

properties ($H_{Ci} < 200$ kA/m). Therefore, it was suggested to limit sizing down the HDDR powder particles not less than the 100 μ m range for achieving optimal magnetic properties.

Lastly the improvement in H_{Ci} of the recycled HDDR Nd-Fe-B powder was realized by blending it with DyF_3 in varying weight fractions from 1 – 5 %. The blends were compacted at 750 °C for 1 minute and 100 MPa. These magnets were subjected to vacuum thermal treatments at 600 – 900 °C for 1 – 6 hours. The optimal thermal treatment condition: 750 °C for 1 hour for 2 wt. % DyF_3 resulted in $H_{Ci} \sim 1410$ kA/m which is approx. 70% higher than the starting HDDR powder. This doping technique developed uniform a $(Dy,Nd)_2Fe_{14}B$ core-shell structure throughout the sample due to localized Dy diffusion and solution reprecipitation upon solidification below the ternary eutectic temperature 665 °C. Excessive DyF_3 content ≥ 5 wt. %, prolonged thermal treatment (≥ 3 hours) and higher temperatures (900 °C) deteriorated the magnetic properties due to the decomposition of core-shell structure and formation of complex Nd-Fe-F-type intermetallic phases besides the excess of unreacted, non-ferromagnetic DyF_4 & NdF_4 phases.

Povzetek

Trajni magneti na osnovi elementov redkih zemelj (RE) in prehodnih kovin (TM), kot npr. Nd-Fe-B in Sm-Co, so bistveni sestavni deli sodobnih električnih in elektronskih naprav ter bistveni v zelenih energetskih tehnologijah. Visoko toplotno stabilnost in odpornost na razmagnetenje v trajnih magnetih tipa Nd₂Fe₁₄B dosežemo z dodatkom težkih redkih zemelj, kot sta Dy in Tb. Dodajanje Dy in Tb v Nd-Fe-B trajne magnetne pa ima močne negativne posledice na izčrpavanje naravnih rudnih virov ter s tem posledično dviguje proizvodne stroške. Od t. i. "krize redkih zemelj" leta 2011, zaradi katere so se cene surovin (RE= Nd, Dy, Tb) zvišale kar za 700 %, svetovni proizvajalci trajnih magnetov iščejo dobavno verigo, ki bi vodila v gospodarsko trajnost. Znanstvena srenja se je izziva lotila z dveh plati, in sicer si po eni strani prizadeva raziskati novo vrsto trajnih magnetov brez dragih redkih zemelj ali poskusiti razviti metode za recikliranje že izrabljenih trajnih magnetov na osnovi slednjih. Prvi cilj na žalost ni bil izpolnjen v meri, ki bi vodila v komercializacijo, je pa reciklaža pokazala velik tržni potencial. Neposredno/ponovno ali neposredno/posredno recikliranje odsluženih magnetov je področje, ki je zanimivo tako za raziskovalce kot za proizvajalce magnetov. Majhna sprememba v kemijski sestavi, kjer se dodaja redke zemlje v obliki hidridov, je pomagala razviti trajne magnetne z boljšimi magnetnimi lastnostmi, kot so jih imeli začetni magneti, vendar je bila ta izboljšava ponovno povezana z višjimi stroški zaradi dodatka RE.

Reciklirna pot magnetov RETM, predvsem Nd-Fe-B, ki temelji na vodiku, je zaradi svojega nizkega okoljskega vpliva bolj ekonomsko izvedljiva in čistejša od piro- in hidrometalurških metod recikliranja. Običajno zavrženi odpadki v proizvodnji trajnih magnetov doprinesejo kar 25 %, kar je veliko glede na skupno proizvodnjo. Dekrepitacija v vodiku olajša razpokavanje trajnih magnetov zaradi nastajanja NdH_x (povzroča povečanje volumna). Tak krhki nemagnetni prah se lahko nadalje melje do velikosti 3–5 µm, magnetno poravnava in sintra do končne oblike. Kemično sestavo lahko zlahka spreminjamo z mešanjem finega prahu/dodatka zlitine, bogate z redkimi zemljami, z recikliranim prahom, obdelanim z vodikom, da dosežemo želene magnetne lastnosti.

Prav tako ima ponovna predelava s postopkom hidriranja, disproporcionacije, desorpcije in rekombinacije (HDDR) korist, saj lahko razvija anizotropna nanokristalna zrna v velikostnem razponu do ~ 400 nm. Ti prahovi so superiorni za doseganje višjih koercitivnosti kot mikrokristalinični. Reciklirani prah, obdelan s HDDR, se lahko oblikuje z mešanjem s polimernimi vezivi ali sintranjem s hitrimi konsolidacijskimi tehnikami, kot je vroča deformacija ali sintranje s plazmo (SPS). Običajno teh nanokristaliničnih prahov ni mogoče konvencionalno sintrati, saj bi višje temperature in daljši časi obdelave povzročili pretirano rast zrn in koercitivnost bi se močno zmanjšala. Zato je hitro zgoščevanje s SPS alternativna metoda pri recikliranju magnetov, da se dosežejo visoke koercitivnosti tako svežih kot z vodikom obdelanih prahov sistemov REPM. Proces SPS je zelo hiter, hitrosti segrevanja pa se lahko nadzorujejo, da se prepreči poslabšanje mikrostrukture, kar ohranja magnetne lastnosti prvotnega prahu ter omogoča sintezo popolnoma gostih magnetov, ki

se lahko sintetizirajo v nekaj minutah in pri nižjih temperaturah sintranja kot običajno. Istočasna uporaba tlaka v SPS je koristna za doseganje popolne zgostitve in hitro naraščanje slednjega (> 100 MPa) lahko inducira teksturo v materialu s procesom vročega kovanja oz. vroče deformacije.

Dve različni vrsti recikliranih magnetnih prahov, in sicer v vodiku dekrepitiran SmCo_5 in s HDDR obdelan Nd-Fe-B, sta bili raziskani z vidika zgoščevanja in sintranja s SPS-om. V prvem primeru je bilo optimalno temperaturno območje SPS ugotovljeno med $900\text{--}950$ °C z zadrževalnim časom 1–5 minut in tlakom 100 MPa v tlaku 0,2 mbar Ar, s čimer smo dosegli zgoščevanja > 97 %. Končne magnetne lastnosti izotropnih magnetov SmCo_5 po SPSu ($H_{\text{Ci}} > 2000$ kA/m & $B_r = 0,47$ T) so bile zaradi boljšega mikrostrukturnega nadzora nekoliko boljše od vakuumsko sintranih komercialnih magnetov (optimalna porazdelitev Sm-bogate faze Sm_2Co_7 v matrici SmCo_5). V primerjavi z materialom komercialne kakovosti je bil reciklirani prah SmCo_5 obdelan z dekrepitacijo, imel ožjo porazdelitev velikosti zrn ($4\text{--}20$ μm), kar je imelo za posledico visoko gostoto blizu teoretične $H_{\text{Ci}} > 2000$ kA/m, izmerjeno pri sobni T, ter boljšo termično stabilnost pri 180 °C.

Podobno se je obnašal tudi reciklirani prah Nd-Fe-B, obdelan s HDDR in optimalno posintran s SPS pri $750\text{--}800$ °C (približno 30% nižja temperatura sintranja kot komercialna) v 1 minuti pri 100 MPa. Dosežene koercitivnosti so bile $H_{\text{Ci}} \sim 1200$ kA / m, kar je bilo nekoliko boljše kot v primeru SPS procesiranih komercialnih svežih prahov HDDR MF-15P (1180 kA/m). Začetni prah HDDR s sestavo $\text{Nd}_{13.4}\text{Dy}_{0.6}\text{Fe}_{78.6}\text{B}_{6.1}\text{Nb}_{0.4}\text{Al}_{0.7}$ je imel koercitivnost $H_{\text{Ci}} = 830$ kA/m. Učinek naknadne toplotne obdelave po SPS, smo temeljito preiskali, s HR-SEM in EDXS. Ugotovili smo, da je s termično obdelavo povzročena prerazporeditev z Nd-bogate faze med zrnji pomembna za doseganje višjih koercitivnosti po obdelavi v SPS. Slednji optimizirani magneti s SPS so bili tudi deformirani pri 750 °C s ciljem, da bi inducirali teksturo, kar smo storili s spreminjanjem tlaka med SPS ter tako povzročili vročo deformacijo oz. vroče kovanje. Uporabljeni tlaki med SPS-om so bili med 100 in 150 MPa uporabili pa smo modele na osnovi WC + C. Posledično smo izboljšali B_r na ~ 1.01 T ($BH_{\text{max}} = 180$ kJ/m³) pri 55% zmanjšanje višine pri 150 MPa.

Pomembno dejstvo je tudi, da je recikliranje na osnovi vodika učinkovito samo, če zaščitna prevleka na izrabljenih magnetih ni prisotna ali je razpokana. Pri sekundarnem recikliranju se te prevleke odstranijo iz razdrobljenih prahov s povprečno velikostjo delcev manj kot 100 μm z mehanskim drobljenjem. Nasprotno pa je prah HDDR nagnjen k prekomerni oksidaciji, če so delci majhni. Vendar pa ta kritična velikost delcev še ni bila identificirana, kar je omejilo tudi komercialni obseg. Izvedli smo poglobljene študije, kjer smo preverjali razmerje velikosti prašnih delcev HDDR z vsebnostjo kisika ter določili vpliv slednjih na sinterabilnost in končne magnetne lastnosti. Frakcije delcev od 700 μm do < 50 μm so bile posamično testirane na vsebnost kisika, magnetne lastnosti in sinterabilnost. Ocenjeno je bilo, da so delci, manjši od 100 μm , navzeli dvakrat več kisika (> 7000 ppm), zaradi česar se je celotna vsebnost z Nd-bogate faze zmanjšala zaradi prekomerne tvorbe Nd_2O_3 . To je povzročilo slabo sintranje in hudo poslabšanje magnetnih lastnosti ($H_{\text{Ci}} < 200$ kA/m). Zato je bilo predlagano, da se prašni delci HDDR zmanjšajo na > 100 μm za doseganje optimalnih magnetnih lastnosti.

Nazadnje je bilo izboljšanje H_{Ci} recikliranega prahu HDDR Nd-Fe-B realizirano z mešanjem slednjega z DyF_3 v različnih masnih deležih od 1 do 5 %. Mešanice so bile kompaktirane s SPS pri 750 °C 1 minuto pri tlaku 100 MPa. Ti magneti so bili podvrženi

naknadni vakuumski termični obdelavi pri 600–900 °C 1–6 ur. Optimalna termična obdelava s SPS pri 750 °C za 1 uro z dodatkom 2 mas. % DyF_3 je povzročila porast na $H_{\text{Ci}} \sim 1410 \text{ kA/m}$, kar je za pribl. 70 % višje od začetnega prahu HDDR. Ta tehnika dopiranja je rezultirala v enotni mikrostrukturi $(\text{Dy}, \text{Nd})_2\text{Fe}_{14}\text{B}$ v obliki jedra in lupine v celotnem vzorcu zaradi lokalizirane difuzije Dy pod ternarno evtektično temperaturo 665 °C. Prekomerna vsebnost DyF_3 v količini ≥ 5 mas. % in dolgotrajna toplotna obdelava (3 ure) na višjih temperaturah (900 °C) so poslabšali magnetne lastnosti zaradi razgradnje strukture jedra in lupine ter nastajanja kompleksnih intermetalnih faz Nd-Fe-F poleg še presežka nezreagiranih, ne-feromagnetnih faz DyF_4 in NdF_4 .

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Abbreviations

bcc	...	Body Centered Cubic
BSE	...	Backscattered Electrons
DSC	...	Differential Scanning Calorimetry
EDXS	...	Energy Dispersive X-ray Spectroscopy
EPD	...	Electrophoretic Deposition
ECS	...	Electric Current Sintering
fcc	...	Face Centered Cubic
FAST	...	Field Assisted Sintering Technique
FE-SEM	...	Field Emission Scanning Electron Microscopy
GBD	...	Grain Boundary Diffusion
GBDP	...	Grain Boundary Diffusion Process
GBE	...	Grain Boundary Engineering
GBM	...	Grain Boundary Modification
hcp	...	Hexagonal Close Pack
HD	...	Hydrogen Decrepitation
HDDR	...	Hydrogenation Disproportionation Desorption Recombination
HREE	...	Heavy Rare Earth Element
ICP-AES	...	Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	...	Inductively Coupled Plasma Mass Spectroscopy
LREE	...	Light Rare Earth Elements
MFM	...	Magnetic Force Microscopy
MR	...	Magnetization Reversal
MRI	...	Magnetic Resonance Imaging
MSR	...	Melt Spun Ribbons
PECS	...	Pulsed Electric Current Sintering
PM	...	Permanent Magnets
SEM	...	Scanning Electron Microscope
RE	...	Rare Earth
REPM	...	Rare Earth Permanent Magnets
SCA	...	Strip Cast Alloys
SPS	...	Spark Plasma Sintering
TEM	...	Transmission Electron Microscopy
TG-DSC	...	Thermogravimetric Differential Scanning Calorimetry
VCM	...	Voice Coil Motor
VSM	...	Vibrating Sample Magnetometer
XRD	...	X-Ray Diffraction

Symbols

B	...	Magnetic Field Induction	T
B_r	...	Remanent Magnetization (Remanence)	T
BH_{max}	...	Maximum Energy Product	kJ/m ³
e⁻	...	Electron	
q	...	Electric Charge	C
E_a	...	Crystal Anisotropy Energy	J
E_f	...	Fermi Level	eV
h	...	Planck's Constant	Js
K_i	...	Anisotropy Constant	J/m ³
M	...	Magnetization	T
M_r	...	Remanent Magnetization	T
M_s	...	Saturation Magnetization	T
v	...	Velocity	m/s
r	...	Radius	M
m	...	Mass of Electron	kg
H	...	Applied/External Magnetic Field	A/m
H_A	...	Anisotropy Field	A/m
H_{CI}	...	Intrinsic Coercivity	A/m
H_C	...	Coercivity	A/m
H_d	...	Demagnetizing Field	A/m
I	...	Electric Current	A
J	...	Polarization	T
J_r	...	Remanent Polarization	T
J_s	...	Saturation Polarization	T
l_{ex}	...	Exchange Length	m
N_d	...	Demagnetizing Factor	-
N_{eff}	...	Effective Demagnetizing Factor	-
mm	...	Millimeter	
μm	...	Micrometer	
nm	...	Nanometer	
μ	...	Magnetic Permeability	H/m
μ₀	...	Magnetic Permeability of Free Space	
α	...	Absolute Temperature Coefficient of Remanence	%/ °C
β	...	Absolute Temperature Coefficient of Intrinsic Coercivity	%/ °C
μ	...	Magnetic Moment	Nm/T
ρ	...	Density	g/cm ³
P	...	Pressure	Pa
P	...	Electric Power	W
R	...	Electrical Resistance	Ω

t	...	Time	s
T	...	Temperature	°C
T_c	...	Curie Temperature	°C
Q	...	Heat	J
Φ	...	Magnetic Flux	Wb
χ	...	Magnetic Susceptibility	-

Preface

This **first chapter** in this dissertation outlined the theme of research on rare-earth permanent magnets (and taking into consideration their present state-of-the-art magnetic properties, processing routes, economic and technological importance).

Chapter 2 introduces the basic concepts of magnetism which are important in the sense of atomic structure, chemical composition and microstructure. The effective parameters and magnetic properties mentioned in Chapter 1 are linked to the explanation provided in this chapter. The definition of sintering and the important mechanisms are also given in Chapter 2. The contemporary consolidation technique of Spark Plasma sintering is also explained in this chapter.

Chapter 3 describes the different rare-earth-based magnetic materials in terms of their crystal structure, phase diagrams, microstructure, processing routes, literature overview of research work and applications. The recyclability and criticality of rare-earth permanent magnets is also briefed in Chapter 3, which defines the hypothesis of this research dissertation.

Chapter 4 cites the aims of the project and the hypotheses for the research work in this dissertation. The project hypotheses are connected with the results in the form of publications included in Chapters 6, 7, 8.

Chapter 5 gives details on the ‘Materials and Methods’, outlining the source of the recycled Nd-Fe-B and SmCo₅ powders; and all the equipment used in the sintered magnet development and various characterization tools (ranging from microstructure to the magnetic properties).

Chapter 6 presents the result on the SPS reprocessing of recycled HDDR Nd-Fe-B powder from EOL magnets. The resultant coercivities achieved by optimal SPS reprocessing of the recycled HDDR Nd-Fe-B powder are at par with the commercial grade HDDR powder MF15P.

Chapter 7 sheds light on the dependence of the magnetic properties and sinterability of the recycled HDDR powders on the particle size and oxygen content. The pros and cons of primary and secondary recycling are explained in this work. This research work can also serve as a guideline for industrial upscaling of the magnet recycling and controlled processing.

Chapter 8 illustrates the effectiveness of doping the HDDR Nd-Fe-B powders with DyF₃. The results presented in this chapter are state of the art for the recycled HDDR Nd-Fe-B powder in terms of the coercivity achievement due to characteristic Nd₂Fe₁₄B – (Dy,Nd)₂Fe₁₄B core – shell formation.

Chapter 9 is related to the hot pressing and hot deformation experiments on the recycled HDDR Nd-Fe-B powder for developing anisotropic sintered magnets with $B_r \sim 1$ T.

Chapter 10 presents the SPS reprocessing results of HD recycled SmCo_5 powders in comparison to the fresh sintered magnets (at RT and high temperature $\sim 180^\circ\text{C}$).

The important conclusions from this joint study on the recycling and reprocessing of the nanocrystalline Nd-Fe-B and HD treated SmCo_5 are given in **Chapter 11**.

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Chapter 1

Introduction

A compass needle placed on a solid surface will oscillate and align towards the north, signifies the magnetism in the needle originating from the earth's magnetic field [1]. Magnetism is characteristic in the materials that can experience alignment with the external field and generate their own magnetic field response within a specific volume of space. Depending on their response to the external field, the magnets can either be magnetically soft or hard. Usually soft magnets behave as magnets only in the presence of an external magnetic field and demagnetize easily like iron (Fe). Whereas the materials that can indefinitely create their own persistent magnetic field once they are magnetized are called permanent magnet (*PMs*) [2]. The permanent magnets can be considered as energy storage devices and the magnetic energy remains confined until demagnetized thermally or by large reverse magnetic fields [1]. The practical applications of permanent magnets in the modern world are numerous, ranging from: electric motors, wind turbine generators, medical resonance imaging (MRI), intelligent sensors, automatic switches, microelectronics, hard disk drives' voice coil motors (VCM), magnetic levitation tracks, toys, loudspeakers, military, aerospace, fusion devices, green energy technologies, microwave and automotive equipment [1-3]. The factors which contribute to the commercial success of rare-earth permanent magnets include: high maximum energy product (BH_{max}), high magnetization after the removal of external magnetic field – remanence (B_r), superior resistance to demagnetization – intrinsic coercivity (H_{ci}), high service temperature, low magnetization changes with temperature, excellent environmental stability, corrosion resistance, mechanical integrity, manufacturing flexibility and costs (raw materials, availability, fabrication and tooling) [3, 4].

After the advent of electricity, first electromagnet made by Hans Oersted in 1820 paved the way for magnetizing the materials without mechanically rubbing the lodestone [1]. In 1967, K. Strnat et al. [5, 6] discovered SmCo_5 -based permanent magnets having hexagonal CaCu_5 -type crystal structure with $P6/mmm$ space group. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type permanent magnets developed by M. Sagawa et al. [7] in 1984 were based on powder metallurgy route. In the same year, J. J. Croat et al. [8] utilized melt spinning technology to prepare alloy ribbons of rare-earth borides (Pr-Fe-B and Nd-Fe-B). The Nd-Fe-B and Sm-Co-based permanent magnets are commercially the strongest available and most widely used permanent magnets and their demand is ever-growing because of the high energy confined within a smaller volume, i.e. maximum energy product (BH_{max}) [9-12]

In order to compliment the understanding, the magnetic properties are elucidated in [Chapter 2 Basics of Magnetism in Magnetic Materials](#). The magnetic properties of REPMs

independent of microstructure are designated as [intrinsic properties](#) (see [2.2](#) for explanation) which includes [Saturation Magnetization \(\$M_s\$ \)](#), [Curie Temperature \(\$T_c\$ \)](#) and the [Magnetocrystalline Anisotropy \(MCA, i.e. \$\mu_0 H_a\$ \)](#). These properties are on atomic scale and are related to the magnetic moments of an atom and involve the quantum phenomena of exchange, crystal field interactions and spin orbit coupling [[1](#), [13](#)]. The M_s can simply be defined as the vector sum of the magnetic moments aligned in the direction of the applied field. T_c is the transition temperature above which ferromagnetic ordering of the magnetic moments is lost. The MCA is an inclination of the magnetic moments to magnetize easily in a certain crystallographic direction [[1](#)].

The microstructure of REPMs governs their magnetic output, i.e. [extrinsic properties](#) (see [2.3](#)). The mechanisms for demagnetization are strongly influenced by the microstructure. In thermal demagnetization when the magnet is heated above its Curie Temperature (T_c), the magnetic ordering (remanent magnetization) is lost due to paramagnetic transformation of the magnetic moments [[13](#)]. For improving thermal resistance to demagnetization and increasing the T_c , a fraction of Nd atoms is substituted with HREEs (Dy, Tb) and some of Fe atoms can be replaced with Co in the system. Due to the low price of raw materials, Nd-Fe-B magnets rapidly substituted the Sm-Co-based permanent magnets for high performance room temperature applications. For demagnetization with reverse fields, the mechanisms can either be pinning or nucleation type. The sintered Sm-Co magnets are pinning type, such that the growth of inverse domains is restricted by pinning the existing domains movement at the defects, inclusions or grain boundaries. The sintered Nd-Fe-B magnets with micron sized multi-domain grains are based on the nucleation type, so the nucleation of reverse domains is controlled by reinforcing the grains' surface with HREE and by smooth continuous grain boundaries, which effectively decouple the grains and so the reverse domain propagation is hindered [[12](#)].

The excellent magnetic properties of these rare earth based permanent magnets (REPM) originate from their microstructure, which is strongly dependent on the nominal chemical composition and respective manufacturing routes via powder metallurgy [[14](#)]. The Nd-Fe-B magnets can be commercially developed by a variety of established routes, e.g. powder metallurgy and sintering for anisotropic high $BH_{\max}$ sintered magnets or by melt-spinning or HDDR processing to develop nanocrystalline powders for (isotropic or anisotropic) plastic bonded magnets. For high performance applications at temperatures less than 100 °C, the preferred choice are anisotropic sintered Nd-Fe-B-based PMs prepared by vacuum sintering of single crystalline micron-sized jet-milled powders, as shown in Figure 1. Similarly the nanocrystalline powders can also be hot pressed and hot deformed to develop anisotropic bulk magnets suited for microelectronic applications [[3](#)]. The Nd-Fe-B magnets based on the stoichiometric compositions have saturation magnetization (M_s) $\sim$ 1.6 T, Curie Temperature (T_c , above which ferromagnet become paramagnet) $\sim$ 312 °C, remanent magnetization after switching off the external field, i.e. $B_r \sim$ 1.48 T, magnetocrystalline anisotropy ($\mu_0 H_a$) = 7.2 T and anisotropy constant (K_I) $\sim$ 5×10^6 J/m³ (from [Stoner Wohlfarth](#) relation for coercivity, i.e. resistance to demagnetization: $H_c = 2$

$K_i / \mu_0 M_s$) [3, 13]. In order to facilitate the understanding, the reader is kindly referred to the explanation of these magnetic parameters (T_C , H_{Ci} , M_S , B_r , H_a and K_1) in Chapter 2 detailing the [intrinsic](#) and [microstructure dependent magnetic properties](#).

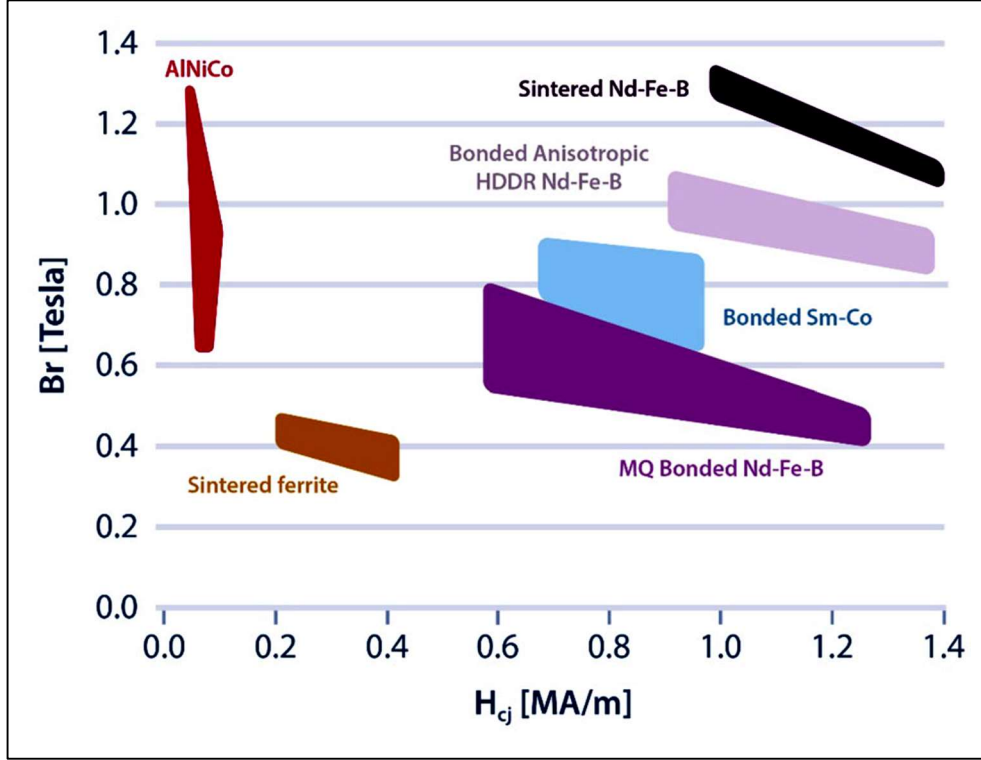


Figure 1: The magnetic properties comparison of different Nd-Fe-B, Sm-Co and ceramic magnets [11].

Whereas the SmCo_5 magnets have very high $\mu_0 H_a = 28 \text{ T}$, $M_S \sim 1.1 \text{ T}$ and importantly a twofold higher Curie Temperature (T_C) than Nd-Fe-B to resist the thermal demagnetization, which allows operability up to 550°C [3, 15, 16]. The Sm-Co magnets are comparatively more brittle than Nd-Fe-B counterparts and may require overlay coatings to resist mechanical shock and failure. The sintered Nd-Fe-B magnets have higher $BH_{\max}$ (440 kJ/m^3) than the Sm-Co counterparts (200 kJ/m^3), serving as a figure of merit for engineering applications indicating higher remanent magnetization (B_r) and the magnetic energy confined per volume, as shown in Figure 2 [11, 13]. The Nd-Fe-B magnets are more susceptible to thermal fluctuations and environmental degradation (corrosion) as compared to AlNiCo and Sm-Co-based PMs, which limits their usability at elevated temperatures and harsh conditions. Therefore, the Nd-Fe-B magnets require protective coatings to prevent them from oxidation or environmental degradation.

More importantly, the resistance to demagnetization i.e. coercivity ([refer to 2.3.2](#)) of the Nd-Fe-B type PMs is strongly dependent on making chemical compositions rich with the heavy rare-earth elements (*HREE*) like terbium (*Tb*), dysprosium (*Dy*). The coercivity is strongly related to the characteristic microstructure and how the magnet processing was done. These HRE elements substitute Nd from the hard phase grains ($\text{Nd}_2\text{Fe}_{14}\text{B}$) to form

$\text{H}_2\text{Fe}_{14}\text{B}$ (where $\text{H} = \text{Tb}, \text{Dy}, \text{Ho}$) grains with a relatively higher magnetocrystalline anisotropy and intrinsic coercivities [3, 9, 12]. With up to 5 wt. % Dy added to Nd-Fe-B magnets significantly enhance their maximum operating temperature to 200 °C, as indicated in Figure 2 [11]. The disadvantage of this HREE addition in the Nd-Fe-B magnets is the reduction in saturation magnetization (M_s), remanence (B_r) and the BH_{max} , due to antiferromagnetic coupling of the magnetic moments of HREE atoms with that of the Fe atoms [17]. So, the magnet selection criterion of high performance REPM can strictly be based on the end user requirement and the operational environment.

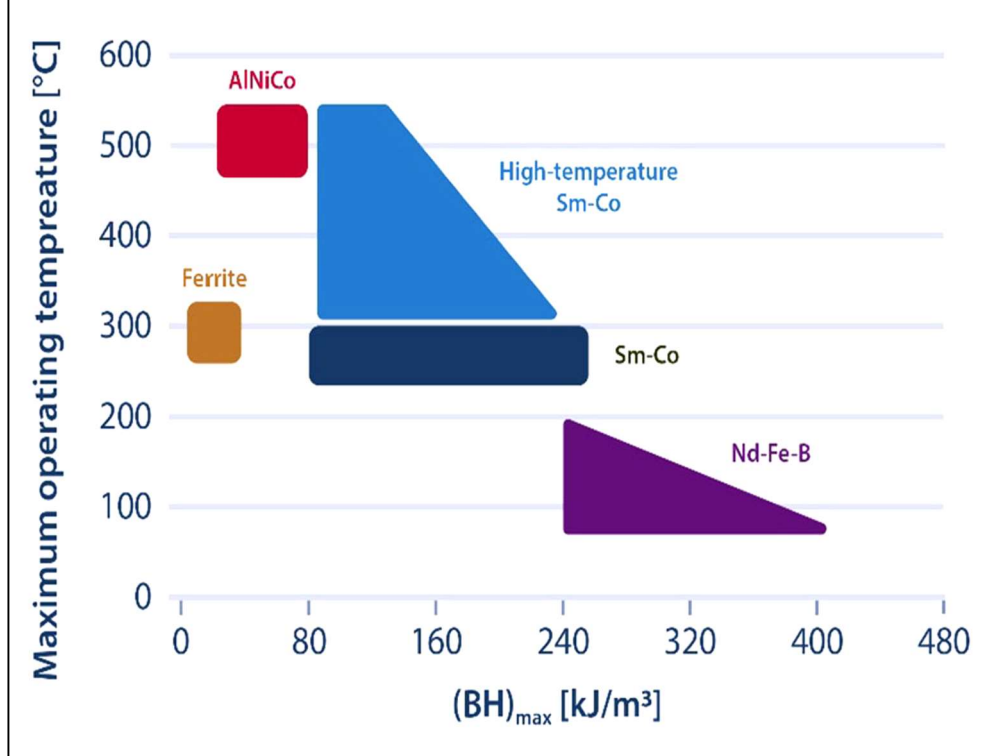


Figure 2: Comparison of Nd-Fe-B and Sm-Co magnets in terms of maximum operating temperature and maximum energy product (BH_{max}) [11].

Rare-earth permanent magnets (REPM) with very high energy product allow the conservation of rare-earth elements and the miniaturization of appliances, because the smaller magnets become more efficient in generating strong persistent magnetic fields. The demand for high performance PMs has been forecast to rise exponentially due to an increase in the production of REPMs, as well as the machines and appliances which utilize these efficient PMs. It is approximated that if 1 kg of Nd based magnets are used in the electric cars approx. 150,000 tons of Nd magnets will be required by 2040 in the traction motors alone. The Nd-Fe-B magnets suitable for electric motor applications require thermal stability, whereas they have a relatively lower Curie temperature (310 °C) and coercivity (H_{Ci}) degrades severely due to the thermal stresses. The experimental coercivity reached in the sintered Nd-Fe-B is only 15% approx. of the anisotropy field (7800 kA/m), which is also substantially lower than experimental models. The coercivity required for resisting the room temperature demagnetization is ~ 2400 kA/m in the sintered Nd-Fe-B magnets, which is technologically not possible without the addition of HREE [3]. Therefore these

permanent magnets are considered as a backbone for the future of renewable energy and green technologies for reducing the CO₂ emissions, which is deteriorating the global warming phenomena [3, 16]. But the HRE elements are significantly less abundant, costly in production (refining) and overall much more expensive to utilize. For this same reason the European Commission has classified rare-earths elements as the most critical raw materials for green technologies and renewable energy since the rare-earth crisis of 2011, as shown in Figure 3, when the prices of REEs rose exponentially to 700 % due to geopolitical strategic interests [9-11].

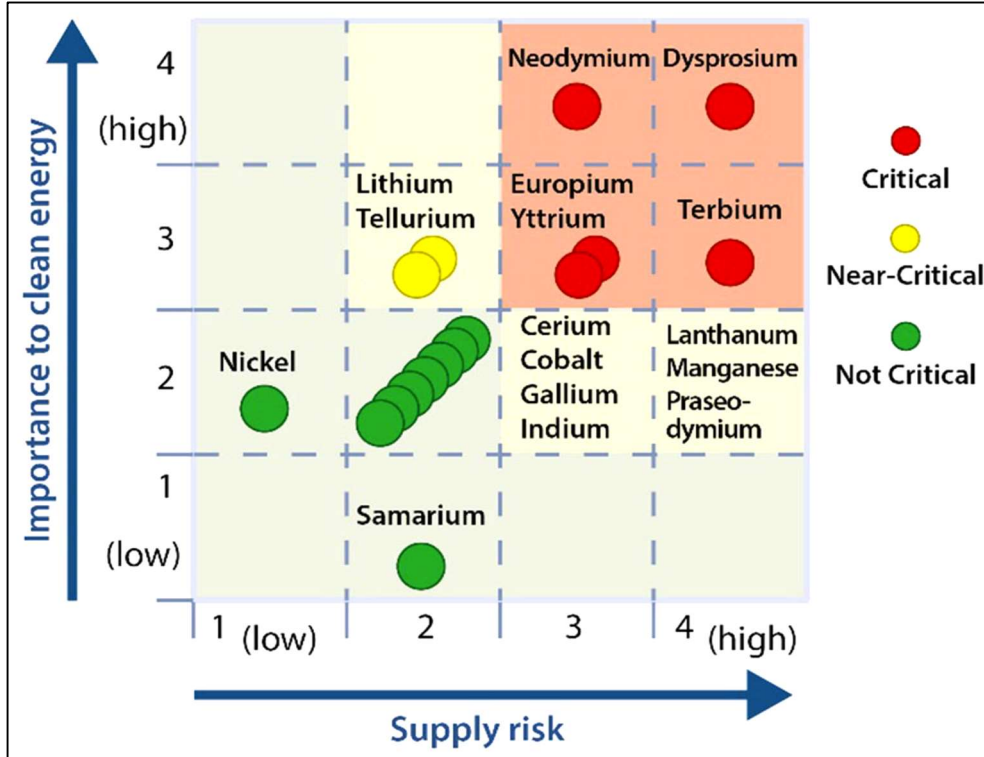


Figure 3: The criticality matrix for mid-term (2015 – 2025), with Nd, Dy, Tb, Eu and Yb classified as the most critical raw materials in terms of supply risk vs socioeconomic – technological importance [11].

Taking in to consideration the excellent performance of high energy product magnets, they represent a significantly large and rapidly growing market in terms of consumption volume and economic aspects. The Nd-Fe-B PMs dominate the market by > 95 % as compared to other permanent magnets [11]. The sintered REPMs are thus indispensable for their applicability in the high-tech global market today. The Nd-Fe-B permanent magnets have the best energy product to cost ratio, therefore the necessity for developing Dy-lean Nd-Fe-B permanent magnets are strongly in demand and technologically significant. Since the REE are considered as the most critical raw materials in the European Commission report, so in order to satisfy this ever-growing demand, there is an urge to develop high performance magnets without REEs and/or take the material recycling in to consideration [10, 11, 18-21]. Ever since the 2011 RE crisis, the industrial demand has advocated the development high performance heavy/light rare-earth free permanent

magnets. In order to reduce the heavy/light rare-earth elements consumption, the grain size reduction and control of grain boundary structure in the sintered magnets has been reported to improve the resistance to demagnetization i.e. higher coercivity, that would enable high H_{Ci} even without the HREs additions. With the rare-earth (RE) elements' supply chain geopolitically constricted, and due to very high costs of REEs refining and magnet production whereby an up-surging requirement of permanent magnets in hybrid/full electric vehicles and microelectronics necessitate the sustainable control of the REE circular economy [10, 11].

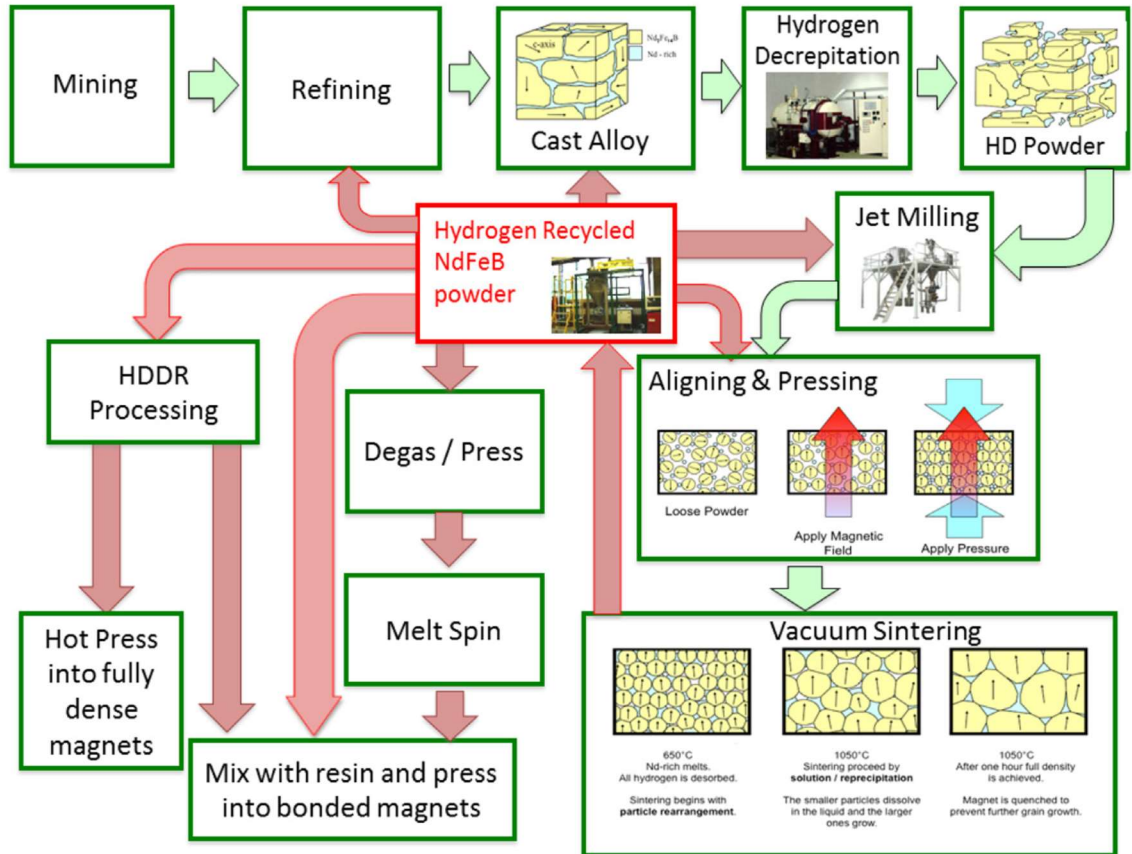


Figure 4: Schematic of rare-earth magnet production, with the green arrow describing the primary processing routes for manufacturing a sintered Nd-Fe-B magnet and red arrows pointing to recycling the possibilities from the sintered magnets, courtesy of A. Walton et al. [19]

The utilization of magnetic scrap, industrial wastes and end-of-life (EOL) magnets holds great scientific and economic potential to meet this overgrowing demand of RE permanent magnets especially in renewable and green energy technologies. Scrap magnets, if properly collected and systematically separated from the waste stream, can be suitably recycled with the hydrogen-based routes. Hydrogen decrepitation (HD) helps recover and break down the EOL RE-based magnets to fully non-magnetized powder, which can be separated from the protective coatings and other waste residues [19]. The researchers are therefore keen to introduce the direct and indirect recycling of REPMs in to the production stream. Several recycling techniques have been adopted to recycle the rare-earth elements as well

as the scrap/EOL magnets via: hydrometallurgical, pyro-metallurgical, direct reusage and indirect recycling approaches [22-30].

The flowchart of primary magnet production and systematic recycling approach is illustrated in Figure 4 [19]. The hydrogen-based recycling routes (red arrows) indicate after the HD treatment, the magnetic powder becomes friable (easier to mill down in size) and therefore this powder can be conventionally sintered again after jet milling. The magnetic powder can also be degassed and melt-spun to make isotropic ribbons for bonded magnet applications. The advantage of direct recycling and reusage methods based on hydrogen-based reprocessing have a smaller environmental footprint as compared to the conventional hydro & pyrometallurgical methods which are energy intensive and require plenty of highly corrosive chemical mediums. Therefore, the hydrogen-based methods offer a more economical and energy efficient route to obtain pulverized and demagnetized powder from the end-of-life (EOL) magnets [23, 25, 26].

Up to now the modified two-stage hydrogenation method, i.e. Hydrogenation Disproportionation Desorption Recombination (HDDR) has been utilized only for anisotropic plastic bonded Nd-Fe-B magnets only. The benefit of HDDR process includes the development of c-axis alignment (magnetization improvement) and nanocrystallinity of Nd-Fe-B grains (coercivity improvement) in the individual powder particles, therefore the bonded magnets have better magnetic properties than micron-sized powder counterparts and/or isotropic magnets [2, 31-33].

Due to the availability of 25 – 30% rejection from the industrial production and global RE-scrap in the form of EOL or discarded appliances, there is a massive supply chain which can be developed in view of magnet recycling. The hydrogen-based recycling processes can also be upscaled to cater for a wide variety of permanent magnets from diverse scrap types. This provides a wideset opportunity to the researchers to improve on the recycling techniques for the rare-earth permanent magnets, such that either they can be directly reused or recycled to form micro or nanocrystalline powders, which can be conveniently processed to sintered or bonded magnets. The industrial upscaling can be considered if the resultant magnets from scrap are effectively as good as the commercial counterparts. Therefore, the commercial suitability of aforementioned hydrogen-based routes becomes more viable because the primary recycling costs are lower than the pyro- or hydrometallurgical waste processing. If the recycled powder becomes good enough to be included into the primary processing stream with the available technologies and setup, then the recycling approach can be considered as a massive success. This idea is discussed thoroughly in this dissertation from a technological perspective, how lab-grown magnets can become available for the consumer market and effectively compete with their fresh counterparts.

Chapter 2

Basic Principles of Magnetism in Magnetic Materials & the Science of Sintering

This chapter provides a brief explanation of the science of magnetism, concepts behind the terminology and a definition of magnetic materials in terms of their structure and magnetic properties. The second part details the Nd-Fe-B- and Sm-Co-based permanent magnets, as well as the contemporary powder metallurgy techniques applied for developing the alloys, magnetic powders and sintered magnets.

2.1 Magnetism Basics

The magnetic field is generated by an electrical charge in motion, which can be due to the current passing through a copper coil i.e. electromagnetism or by the spin and orbital moments (m) of electrons (e) in an atom. When these magnetic moments coordinate in parallel, ferromagnetic domains are formed which are separated by thin regions called domain walls [1].

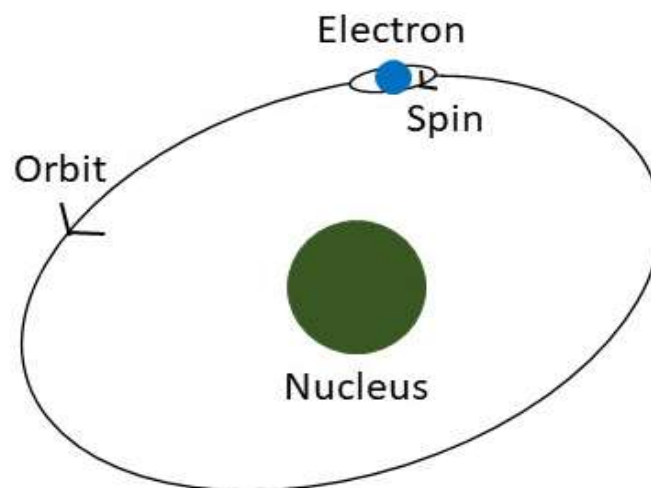


Figure 5: The origin of magnetism due to spin of electron and orbital motion around the nucleus, adapted after [34].

The magnetization ($\mathbf{M}$) on the atomistic scale can be derived from the electrons' spin moments around its axes and the orbital moments around the nucleus, as shown in Figure 5. The magnetization is therefore the sum of all the magnetic moments ($\mathbf{m}$) per unit volume on the atomic scale ($\mathbf{M} = \frac{1}{V} \sum_i^n \mathbf{m}$) [13]. The magnetization is measured in ampere/meter (A/m) or tesla (T) in SI system [1]. Although the effect of the magnetic moments of the nuclear spin is negligible, magnetism is from the two contributions of the angular momentum of electrons, i.e. spin ($\pm \frac{1}{2} \hbar$) where $\hbar$ is the Planck's constant divided by 2π and the orbital moment given by Bohr magneton: $\mu_B = \frac{e\hbar}{2m_e}$. The magnetic moment due to orbital angular momentum in the first Bohr's orbit is equal to the spin magnetic moment and it is represented by the Bohr magneton (μ_B) [13, 34].

In the absence of applied field, if an atom has a net zero spin magnetic moments and a weak contribution of the orbital moments, then the material is termed diamagnetic. The diamagnetic materials exhibit an antiparallel magnetization $\mathbf{M}$ with respect to the direction of the applied field $\mathbf{H}$. For a non-zero vector sum of spin magnetic moments, the material can either be paramagnetic, ferrimagnetic, antiferromagnetic and ferromagnetic [1, 13]. The magnetic moment due to electronic spin is equal to one Bohr magnetron. The spin quantum number (s) is given by $m_s = \pm \frac{1}{2}$, which means there are only two possible angular momentum states and the spin angular momentum is two folds effective in generating magnetic moment as compared to orbital angular momentum [13].

The magnetic field induction ($\mathbf{B}$) measured in SI system in *tesla* (T) incorporates the net magnetization ($\mathbf{M}$) originating from the orbital and spin moments within a material plus an external magnetizing field $\mathbf{H}$ in the following relationship:

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) \quad (\text{Eq. 2.1})$$

The value of permeability of free space (μ_0) = $4\pi \times 10^{-7} \text{ N/A}^2$. The magnetic induction is the number of magnetic force lines per cm^2 (gauss or G) generated by a material placed in an external field. In the free space, $\mathbf{M} = 0$ and the relationship is simplified to $\mathbf{B} = \mu_0 \mathbf{H}$. For the comparison of units, one tesla is equivalent to 795775 A/m (or 1 T = 800 kA/m approx.). The $\mathbf{B}$, $\mathbf{H}$ and $\mathbf{M}$ are vectors and the quantity $\mathbf{B} - \mathbf{H} = 4\pi \mathbf{M}$ represents the saturation value [34]. In engineering terminology, the relationship is modified as:

$$\mathbf{B} = (\mu_0 \mathbf{H}) + \mathbf{J} \quad (\text{Eq. 2.2})$$

Here $\mathbf{J} = \mu_0 \mathbf{M}$ and termed as *magnetic polarization*, i.e. the intensity of magnetization. It is also measured in tesla (SI units).

2.1.1 Magnetic Susceptibility and Magnetic Permeability

The physical quantity which describes the magnetic response of a material in an external magnetic field is called **magnetic susceptibility** (χ) and the magnetic behavior is characterized with the following equation:

$$\mathbf{M} = \chi \mathbf{H} \quad (\text{Eq. 2.3})$$

Since susceptibility is the ratio of magnetic moments per unit volume (magnetization) to the external magnetic field, the unit for both $\mathbf{M}$ and $\mathbf{H}$ is A/m, therefore χ is considered a dimensionless quantity. In an isotropic material, when magnetized, the magnetic moments align parallel to the applied field $\mathbf{H}$. For the aligned single crystals, magnetic susceptibility may vary in different crystallographic directions, therefore the tensor relationship (sum of vectors) with three independent components in the Cartesian coordinates (x, y) is: $M_x = \chi_{xy} H_y$ [1, 13].

From Eq. (2.1), the susceptibility can be written as:

$$\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) = \mu_0 (1 + \chi) \mathbf{H} = \mu \mathbf{H} \quad (\text{Eq. 2.4})$$

From Eq. (2.4) the expression $(1 + \chi)$ is the *relative permeability* of the material and μ_0 is the vacuum permeability. The magnetic susceptibility (χ) and permeability (μ) can be related by formula:

$$\mu = \mu_0 (1 + \chi) \quad (\text{Eq. 2.5})$$

The magnetic permeability ($\mu = \mathbf{B}/\mathbf{H}$) measures the degree of magnetic induction possible within an external magnetic field, as given in Eq. (2.4).

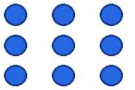
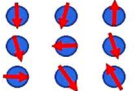
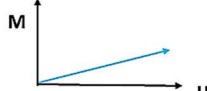
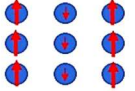
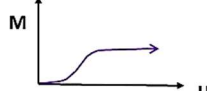
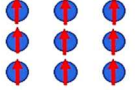
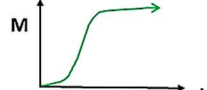
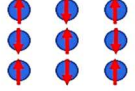
Material Type	Atomic Structure	Magnetic Behavior	Characteristics	Examples
Diamagnetism			Atoms have no net spin magnetic moments & weak orbital moments, which align antiparallel with H; Negative Susceptibility $\chi < 0$	Inert gases, H ₂ , N ₂ , metals: Au, Cu, Hg, non-metals: B, Si, P, H ₂ O, Organics
Paramagnetism			Atoms have randomly oriented magnetic moments; Susceptibility $\chi > 0 > 1$	Al, O ₂ , NO, transition and rare earth metals, their salts and oxides.
Ferrimagnetism			Oppositely aligned magnetic moments of different magnitude in the crystal sublattices; Positive susceptibility $\chi > 1$	Magnetite Fe ₃ O ₄ , mixed oxides of Fe and ferrites (Sr)
Ferromagnetism			Atoms have aligned parallel magnetic moments; Massive susceptibility $\chi > 1$ below T _c	Transition metals: Fe, Co, Ni, MnBi, REEs 64 $\leq Z \leq 69$, TM alloys (Sm-Co, Nd-Fe-B)
Antiferromagnetism			Atoms have aligned anti-parallel magnetic moments; Small susceptibility $\chi > 1$	Transition metals: Mn, Cr etc. and compounds: MnS, CoO, NiO, Cr ₂ O ₃ .

Figure 6: Summary of structure and magnetic behavior of different classes of magnetic materials, adapted from Ref [1].

Figure 6 shows, if the value of magnetic susceptibility $\chi > 0$, then the material is considered as para-, ferri-, ferri- or antiferromagnetic, such that the magnetic induction is possible under an applied field. Whereby for the negative susceptibility value i.e. $\chi < 0$, the material is diamagnetic in nature such that the materials are repulsed by the field and the magnetic induction is in the opposite direction to H [1]. The magnetic permeability of the para- or ferromagnetic material is a degree of order higher than at vacuum and of diamagnetic materials. Likewise, during the initial magnetization, the degree of polarization in the ferromagnetic materials is several orders of magnitude higher than paramagnetic materials.

2.1.2 Classification of Magnetic Materials

As explained in Figure 6, based on the magnetic susceptibility and atomic structure, the magnetic materials can be classified into five different categories:

2.1.2.1 Diamagnetism

The atoms in the diamagnetic materials have net zero spin magnetic moments without an external magnetic field. When an applied field is switched on, the magnetization is produced in the direction opposite to the field and the moments align in reverse direction. The magnetic susceptibility of diamagnetic material is negative and independent of temperature [1].

2.1.2.2 Paramagnetism

The sum of magnetic moments in paramagnetic materials in the absence of external field is zero and they are randomly oriented due to thermal agitation. Under an external magnetic field, the paramagnetic materials experience field orientation of the magnetic moments, so a relatively small magnetization effect is induced. With an increase in temperature, the thermal agitation diminishes the magnetization effect and the magnetic moments in the material will switch to random directions, therefore the susceptibility is small and positive. Pierre Curie proposed that the susceptibility of the paramagnetic materials varies inversely with the temperature, as given by Curie Weiss Law:

$$\chi = \frac{C}{T - \theta}$$

Eq. 2.6

Here C is the Curie constant per gram of the material and θ is the temperature constant. This law suggests that the magnetic moments do interact with each other and this coordination can be defined as an internal molecular field (H_m). The molecular field intensity defined in Eq. (2.7) is directly proportional to magnetization (M).

$$H_m = \gamma M$$

Eq. 2.7

Here γ is the molecular field constant, so the total field (H_t) according to Eq. (2.8) on a magnet is the sum of applied and molecular magnetic fields:

$$H_t = H + H_m$$

Eq. 2.8

The molecular field is considered proportional to the magnetization induced in a material from the alignment of magnetic moments. A positive θ value explains that the molecular field is reinforcing to align the magnetic moments parallel to the applied field which contributes to higher magnetic susceptibility like in ferromagnetic and ferrimagnetic materials. For the negative θ value, the molecular field is opposite to the applied field, therefore the net effect of the magnetic moments is reduced and susceptibility is lower, i.e. paramagnets. The magnetic susceptibility range for the paramagnets is of the order 10^{-4} [1].

2.1.2.3 Ferrimagnetism

Two unequal oppositely oriented magnetic lattices constitute a ferrimagnet e.g. hexagonal ferrite. The magnetic structure in a ferrimagnet is composed of more than one magnetic sublattices (ionic sites A and B) separated by oxygen anions. The magnetic moments within the particular sublattices are ordered ferromagnetically, whereas the coupling between the adjacent magnetic moments A and B is anti-ferromagnetic. They exhibit non-zero magnetization ($\mathbf{M}_A \neq -\mathbf{M}_B$ and $\mathbf{M} > \mathbf{0}$) due to the difference in the magnitudes of the magnetic moments A and B, therefore, the exchange interactions mediated by oxygen anions result into anti-parallel ordering of the spins between the sublattices A and B [13]. In spite of a different magnetic ordering than in the ferromagnets, the ferrimagnets are characterized by a hysteresis loop (coercivity, remanence) and Curie Temperature effects. The magnetic susceptibility of ferrimagnets is in the range of $50 - 10^4$ [1].

2.1.2.4 Antiferromagnetism

Two equal but oppositely directed magnetic lattices constitute an antiferromagnet. The magnetic moments in the antiferromagnets align with their adjacent atoms in the anti-parallel direction, e.g. in a sequence if one magnetic moment points upwards, then the neighboring moment in will be in the downward direction. This order will continue throughout the lattice, such that these magnets have a net zero magnetization ($\mathbf{M}_A = -\mathbf{M}_B = \mathbf{0}$) and a small susceptibility. When heated above a certain temperature, called **Neel Temperature** (T_N), they will lose anti-parallel alignment and become paramagnetic [13]. These magnets follow modified Curie Weiss law with a negative value of temperature coefficient at $T > T_N$:

$$\chi = \frac{C}{T - (-\theta)} = \frac{C}{T + \Phi} \quad \text{Eq. 2.9}$$

Here θ and Φ are temperature constants. In the antiferromagnets, the applied field acts to align the magnetic moments of ions, whereby the molecular field causes misalignment in opposite directions. Therefore, the susceptibility is smaller ($\chi \sim 10^{-5} - 10^{-3}$) and slightly larger than paramagnets (which have zero molecular field) [1].

2.1.2.5 Ferromagnetism

This kind of magnetism is possible because of parallel alignment of the magnetic moments of the interacting atoms arranged in the lattice. The classical explanation of ferromagnetism by Weiss in 1907 postulated: (1) spontaneous magnetization and (2) domains from coordination of magnetic moments; and suggested that the molecular field in the ferromagnets (coordination of magnetic moments) is sufficient to saturate the magnetization in the direction of applied field. These regions of parallel alignment were termed as magnetic domains. The movement of domains measures the ferromagnetic strength of materials in terms of saturation magnetization (i.e. magnitude of M when the domains are aligned) in an applied field. When the ferromagnetic materials are heated, the magnetic moments begin to lose their parallel alignment due to thermal agitations, which reduces the saturation magnetization and they eventually become paramagnetic above the T_c . So from Curie-Weiss law in Eq. (2.19), when θ is positive, the γ is also positive and both molecular field (H_m) and magnetization (M) are parallel to each other and the external magnetic field [1].

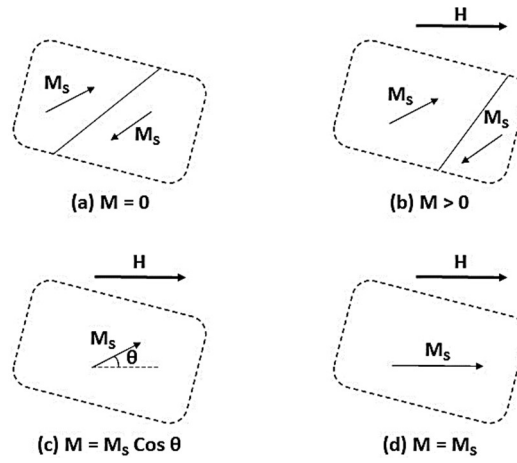


Figure 7: The magnetization process in the domains of a ferromagnet under an applied external magnetic field, adapted from [1].

Figure 7 shows the magnetization process in the interacting domains of a ferromagnet based on Weiss's postulates. When no external field is applied, the two ferromagnetic domains of equal magnetic moments aligned in the opposite directions contribute to net zero magnetization. When the external magnetic field (H) is applied, the magnetization and susceptibility become positive and the domains start to incline towards the direction of magnetic field with relation $M = M_s \cos \theta$. When all the coordinating magnet moments (domains) gain the alignment in the direction of the applied field, the net magnetization reaches the values of saturation magnetization.

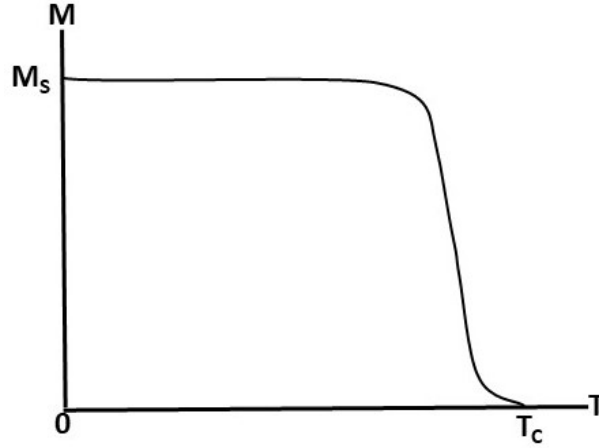


Figure 8: The effect of saturation magnetization of ferromagnet with the temperature, adapted from [35].

The ferromagnetic effect is prominent only below the Curie temperature, which leads to demagnetization of the magnet due to paramagnetic transformation. At zero kelvin and high enough external fields, the magnetic dipoles perfectly align with the applied field in a ferromagnetic material, reaching saturation magnetization which decreases as the thermal distortions increase with temperature, as plotted in Figure 8 [35].

The quantum mechanics principles of ferromagnetism are defined by Heisenberg's model originating from the exchange interactions among the parallel magnetic moments adjacent to each other. The Weiss theory does not present the details about the origin of molecular field and exchange field interactions. The exchange interactions are responsible for developing parallel spin moments ($\mathbf{S}_i$ and $\mathbf{S}_j$) for two sites i and j . The exchange interaction can be explained by Heisenberg's theory, for these two sites, having the spin angular momentum $S_i\hbar/2\pi$ and $S_j\hbar/2\pi$ respectively, then the exchange energy can be expressed as:

$$E_{ex} = -2 J_{ex} S_i S_j = -2 J S_i S_j \cos \phi \quad \text{Eq. 2.10}$$

Here $\mathbf{J}_{ex}$ is the exchange integral and Φ is the angle between the electronic spins. If the exchange integral is positive, the spins are parallel ($\cos \Phi = 1$) and the exchange energy is in a minimum state, indicating a strong ferromagnetic effect. The negative values of $\mathbf{J}_{ex}$ indicate antiparallel spins and $\mathbf{E}_{ex}$ is maximum ($\cos \Phi = -1$).

If each ferromagnetic atom has n number of nearest neighbors and all atoms have the same spin S , then the exchange energy between an atom and surrounding neighbors (parallel spin) is given by:

$$E_{ex} = n(-2 J_{ex} S^2) \quad \text{Eq. 2.11}$$

For the atom, the magnetic moments (μ_H) of the atoms aligned with the molecular field ($\mathbf{H}_m$), the potential energy equivalent to exchange energy is related as:

$$E_p = -\mu_H H_m \quad \text{Eq. 2.12}$$

The energy minimization in Eq. (2.12) explains the parallel alignment of magnetic moments with the applied magnetic field. Combining these two Eq. (2.11) and (2.12), we get:

$$H_m = \frac{2n J_{ex} S^2}{\mu_H}$$

Eq. 2.13

Therefore, the exchange interactions are primarily dependent on the interatomic distances and the spin moments from the molecular field for developing the ferromagnetic behavior. The exchange interactions are nonetheless independent of crystallinity and/or other geometric factors. The co-deposited Co-Au thin film alloy developed in 1965 was the first example of amorphous ferromagnetic material. The ferromagnets have the susceptibility in the range of $50 - 10^5$ [1].

2.1.2.5.1 Magnetic Domains

The orbital and spin moments of electrons in a crystal lattice cause the magnetization, such that the parallel coordination and orientation of the magnetic moments is responsible for forming up the **magnetic domains** below the T_C . These domains are separated by thin interfaces called the **domain walls**. A single domain system will create a demagnetizing field outside which will store large magnetostatic energy. The formation of magnetic domains by division and rotation forms a closed loop system with zero demagnetizing field as the magnetostatic energy of the system is minimized. The magnetic domains are different for different magnetic materials, for Nd-Fe-B the domains are approx. 300 nm in size. Without an external magnetic field, these domains are randomly oriented within the magnet. After the application of an external magnetic field, these domains acquire a parallel alignment with the applied field direction. The Weiss's theory postulated that the domains are randomly aligned, even though the magnetic moments are ordered in specific crystallographic directions. When all the magnetic moments are oriented with the applied field, the material reaches the state of saturation magnetization.

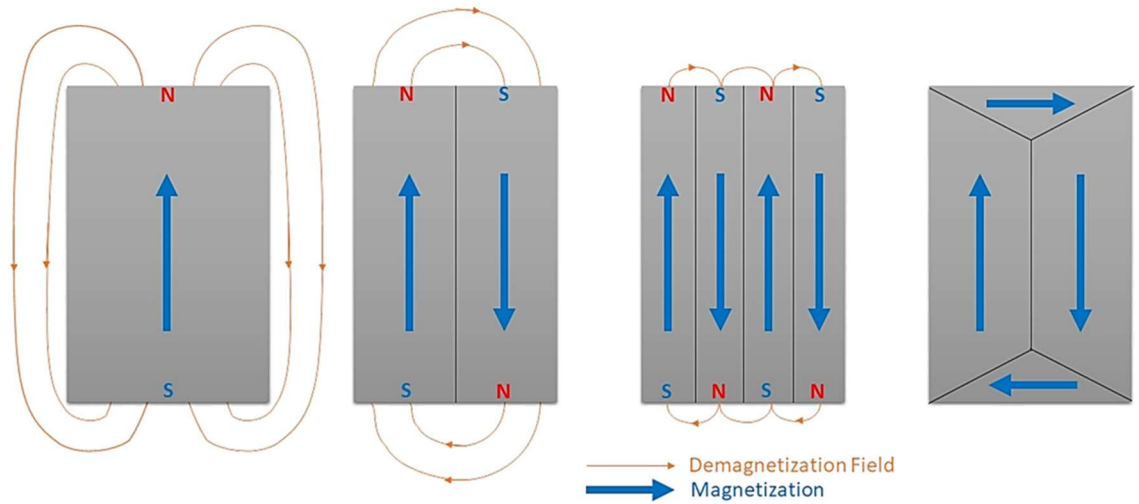


Figure 9: mechanism of splitting the magnetization into domains for minimizing the internal energy, adaptation from B. D. Cullity [1].

Below T_C , the fragmentation of parallel magnetic moments to domains is fundamentally due to lowering the magnetostatic exchange energy, as shown in Figure 9. Each domain uniformly points to a certain direction in agreement with the magnetocrystalline anisotropy. The direction of magnetization vector changes at the domain walls by rotation from one easy axis to another [13]. *Micromagnetics* is the study of the magnetic domains and the interface phenomena. In para- and diamagnetic materials, the magnetic moments

align as a response to the applied field but the spontaneous magnetization is not possible, therefore they do not have a domain structure. The exchange interactions, which create the magnetization, force the domains to have parallel alignment across the domain walls and the exchange energy is minimized. If the magnetic dipoles rotate from 180° out of plane to in plane at the domain wall interface, then it is termed as *Bloch wall*, as illustrated in Figure 10 (a). The exchange energy (E_{ex}) tries to widen up the domain walls, so that the angle between the spins becomes smaller. Whereas the anisotropy energy (E_a) works to thin the domain walls by reducing the overall spins pointing in the non-easy directions. The minimized total energy favoring the formation of domain walls is the sum of exchange and anisotropy energies [1, 34].

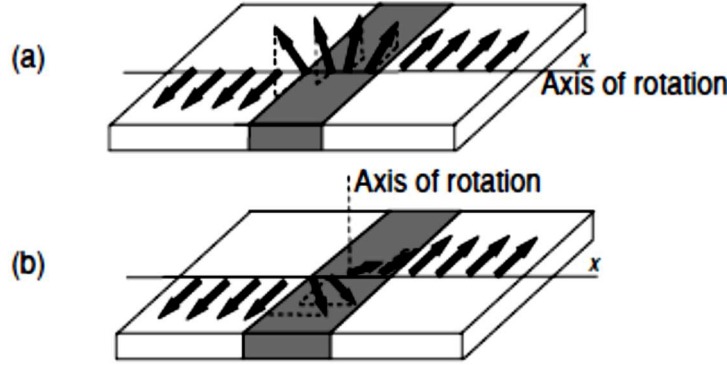


Figure 10: (a) out of plane 180° Bloch wall with antiparallel magnetic domains and (b) the gradual in plane transition of magnetic dipoles at the Neel's wall, courtesy of J. M. D Coey et al. [13].

For two domains in an antiparallel arrangement, the equilibrium Bloch wall width is given as:

$$\delta_w = \pi \left(\frac{A}{2K} \right)^{\frac{1}{2}} \quad \text{Eq. 2.14}$$

Where A is the exchange stiffness constant and K is the anisotropy constant. The domain wall width is proportional to the exchange length given by: $l_{ex} = (A/K)^{1/2}$. Substituting the values of $A = 10^{11} \text{ J/m}$ and $K \sim 2 \times 10^6 \text{ J/m}^3$ for hard magnetic phase, we can compute the domain wall width $\delta_w \sim 6 \text{ nm}$ for the permanent magnets. The energy of 180° Bloch wall is given as: $\gamma_B = 4 (AK)^{1/2}$. The critical single domain size (d_{crit}) is approximated as:

$$d_{crit} \sim \frac{\mu_0 \left(\frac{A}{K} \right)^{\frac{1}{2}}}{J_s^2} \quad \text{Eq. 2.15}$$

The d_{crit} is equivalent to the size of the largest isolated spherical crystallite, in which the energy of forming a domain wall is higher than the gain in the magnetostatic energy. In the Nd-Fe-B system, the d_{crit} falls in the range of 200-300 nm for the single domain

grains. The Bloch walls will not form in a system with all the crystallites of the size of d_{crit} as the parallel alignment due to the exchange interactions will require very high demagnetizing fields to coherently rotate the magnetic moments away from the easy axis. So, if the crystallite will exceed the critical size limit, the domains will split up and each domain will have strength of parallel magnetic moments equal to M_s . If the crystallite size is less than critical size, then the M_s is uniformly parallel throughout [1].

In the Neel wall, the rotation dipole moments at the interface are in-plane with the magnetization of neighboring domains, as shown in Figure 10 (b). This kind of domain wall has higher energy than Bloch wall because the thinner wall width incorporates the stray field due to magnetization divergence [13].

2.1.2.5.1.1 Domain Wall Motion

The motion of domain walls due to an applied field is observed to be discontinuous and kinky; this phenomenon is termed the Barkhausen effect, as indicated in Figure 11 (by arbitrary division to explain the domain wall motion). In M-H plots, this is defined due to sudden discontinuous change in magnetization towards the saturation point. The domain wall motion is significant in a discontinuous manner up to the knee of the magnetization curve. Above this point and up to saturation, the domain walls rotate with the applied field as taking the alignment of the domains' magnetization vector. At the point of domain wall rotation, the energy must be supplied against the anisotropy field, so a large external field is requisite to induce a small increase in M.

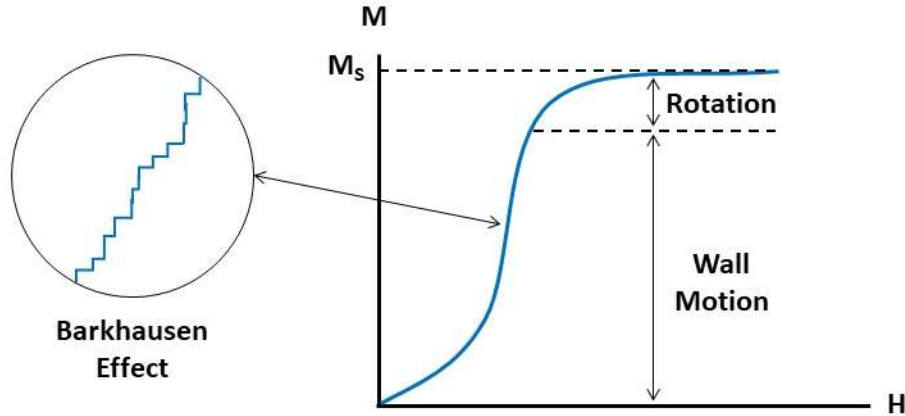


Figure 11: The Barkhausen effect in the magnetization process due to the domain wall motion below the onset of saturation magnetization, modified from [1].

2.1.2.5.1.2 Hindrance to Domain Wall Motion

The hindrance to domain wall motion is possible by the inhomogeneities like inclusions, secondary phases, grain boundaries, defects and residual microstress. The inhomogeneities may have different magnetization or can be nonmagnetic, therefore, in order to minimize the system's magnetostatic energy the domain wall may adjoin with these inhomogeneities, so that the wall energy will be spread over a larger area [13].

The residual stresses can generate the effects like dislocations and magnetostriction, which will in turn reduce the domain wall energy and hence hinder the domain wall mobility.

2.2 Intrinsic Properties of Magnetic Materials

The atomic scale equilibrium magnetic properties of REPMs which are independent of the microstructure and processing routes are termed as intrinsic magnetic properties including: **Saturation Magnetization (M_s)**, **Curie Temperature (T_c)** and the **Magnetocrystalline Anisotropy ($\mu_o H_a$)**. These properties are related to the chemical structure and composition, the magnetic moments of the atoms (spin and orbital) and involve quantum phenomena of exchange, crystal field interactions and spin orbit coupling [1, 13].

2.2.1 Saturation Magnetization

The Saturation Magnetization (M_s) of a magnet is defined as the maximum magnetization in a material due to complete parallel alignment of the magnetic moments with the applied field, which cannot exceed further with an increasing H. It can also be explained as the maximum magnetization exerted by a ferromagnet to its surroundings [13]. The saturation magnetization strongly depends on the temperature (from Figure 8) and tends to reduce as the thermal distortions increase (Brownian motion). It is also affected with the changes in the crystal structure of the magnet, the degree of order and alignment of the magnets moments, and the presence of non-magnetic elements [1]. The magnetization process to saturation point is explained in Figure 7.

2.2.2 Curie Temperature

As explained by the Curie-Weiss law from Eq. (2.6), the thermal demagnetization above the Curie Temperature (T_c) causes the atoms to lose their parallel ordering of the magnetic moments and become paramagnetic. Below T_c , the magnetic moments are aligned parallel to the direction of applied field in ferri-, ferro- and antiferromagnetic materials. The magnitude of magnetization is finite without an external field but goes to zero above T_c [1]. The Curie temperature can be altered by making **composite materials** (with chemical bonding), **reduction in lattice size** (due to fluctuations in electronic spin and lattice changes), **pressure** (volume decrease as a result of pressure on crystal lattice and vibrations disrupt magnetic order) and **orbital ordering** (more delocalized electrons in the same plane of crystal lattice will enhance the exchange interactions and the strength of magnetic moments), [13, 34].

According to modified Curie-Weiss law:

$$\chi = \frac{C}{T - T_c}$$

Eq. 2.16

The magnetic susceptibility is inversely proportional to the Curie Temperature and a ferromagnet will be saturated to M_s when $T < T_c$.

Weiss calculated T_c in an expression:

$$T_C = \frac{C\lambda}{\mu_0}$$

Eq. 2.17

Here λ is the Weiss's Molecular Field Constant, C is the Weiss's material constant and μ_0 is the permeability of free space. The relationship of exchange integral with the T_C is given by Brillouin function for magnetization of sublattices by defining z as interatomic neighbor and S for spin quantum number:

$$T_C = \frac{2 z J_{ex} S (S + 1)}{3k_B}$$

Eq. 2.18

So k_B is the Boltzmann's constant in Eq. (2.18) and this relation explains that for more neighbors with spin coupling interactions, the ferromagnetic exchange interactions are positively coordinating below the Curie temperature [1].

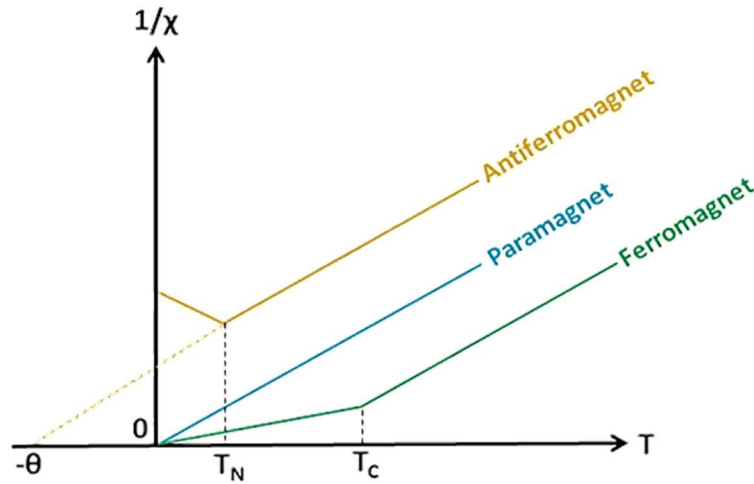


Figure 12: Temperature dependence of the magnetic susceptibility of para, ferro and antiferromagnets, adapted from [34].

Figure 12 shows the comparison of the temperature dependence of magnetic susceptibility in para, ferro- and antiferromagnets. The susceptibility of ferromagnets decline sharply after the T_C and for the antiferromagnets it reaches maximum value at Neel's temperature, and declines sharply as the temperature increases further above the critical temperatures [1, 34].

2.2.3 Magnetic Anisotropy

The dependence of the magnetic properties on the direction of measurement is related to anisotropy, which can be of three different types and strongly influence the shape of the hysteresis loop.

1. Magnetocrystalline anisotropy (or simply crystal anisotropy),
2. Shape anisotropy
3. Stress anisotropy

4. Induced Anisotropy

Only the magnetocrystalline anisotropy is an intrinsic property of a magnet, the rest are either extrinsic or induced.

2.2.3.1 Magnetocrystalline Anisotropy

The magnetocrystalline anisotropy (MCA) can be explained as the tendency of orientating the magnetic moments (i.e. magnetization) in a certain preferred crystallographic direction called the easy axis. The spin-orbital coupling of electrons in the subshell of 3d transition metals and 4f rare-earth elements is preferential along this easy axis, which promotes high magnetocrystalline anisotropy. Due to this, the preferential magnetization by an applied field may require less energy than for the hard axis (the unfavorable crystalline magnetization direction). Materials with large magnetocrystalline anisotropy magnetize more spontaneously along the easy axis and require very large external fields to rotate the directional alignment in other axes or during demagnetization. To change the magnetization vector away from the easy crystalline direction requires very high demagnetizing fields as the magnetic dipoles are coupled with the crystal field. Whereas the magnets with multiple easy axes require relatively less external field strength to demagnetize them [1]. This enhancement of demagnetization strength causes an improvement in the coercivity. The origin of MCA is related to the spin-orbital coupling and magnetic dipole interactions in the crystal field [13]. The easy axes of magnetization are essentially the directions of spontaneous magnetization in the demagnetized state. For instance, the easy axes for bcc Fe is (010) direction, so the net magnetization reaching M_s with the applied field in this easy axis is an order of magnitude higher than (001) or (100) directions as shown in Figure 13 (a).

The exchange energy between the neighboring spins is isotropic and does not depend on the direction of spin axes w.r.t. the crystal lattice, so spin-spin coupling is not a contributing factor for MCA. The electronic spins are also coupled to the orbital momentum of electrons and under the influence of an external magnetic field, the orbitals reorient and the spin moments align accordingly. On the contrary, the electronic orbitals are also strongly coupled to the crystalline lattice, therefore resist disorientation against the easy axis. The strength of spin-orbital-lattice coupling interactions is given in Figure 13 (b) and proves dominant lattice-orbital coupling is the mechanism for high magnetocrystalline anisotropy. Hence the MCA is postulated as the energy required to overcome the spin-orbital coupling in the preferred crystal field.

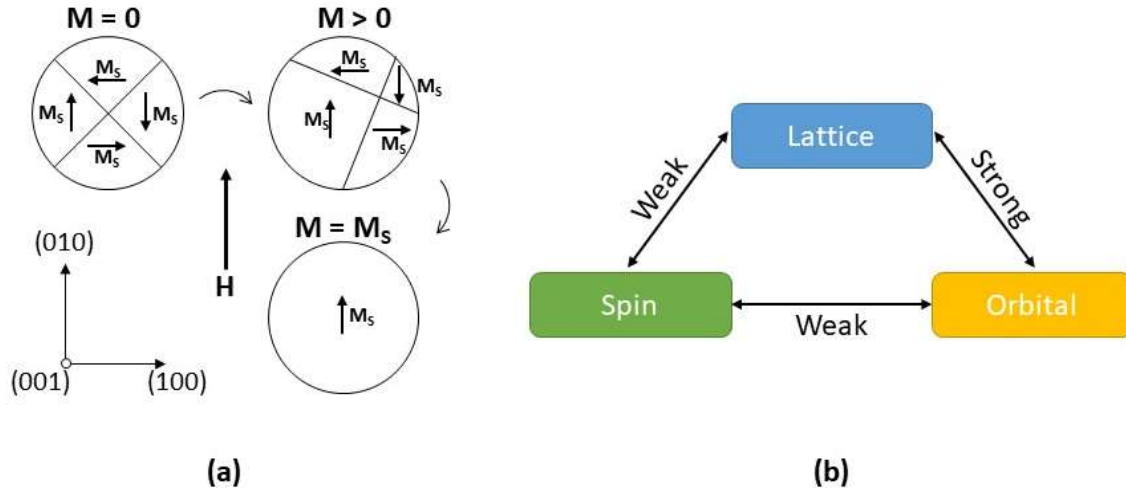


Figure 13: (a) shows the schematics of magnetic moments alignment in the easy (010) direction for Fe single crystals and (b) the interaction strength of spin-orbital-lattice coupling, [1].

For example, in the Nd-Fe-B PMs, the easy axis of magnetization is along the tetragonal c-axis of the hard phase as shown in Figure 14 (a). The magnetic moments in Nd-Fe-B can take one of the two directions along the easy-axis of tetragonal crystal structure (parallel and antiparallel). For the hexagonal type SmCo₅ permanent magnets, the easy axis is also along the c-axis (0001) direction and the hard axis is in (10 $\bar{1}$ 0) direction. Figure 14 (b) shows the easy/hard axis of SmCo₅ PMs and the magnetization plot in these respective directions, indicating the magnetization reaches M_s value at very low applied fields in the c-axis and vice versa. The REPMs exhibiting this mechanism have very high magnetocrystalline anisotropies and therefore the resistance to demagnetization, i.e. coercivities are high as well.

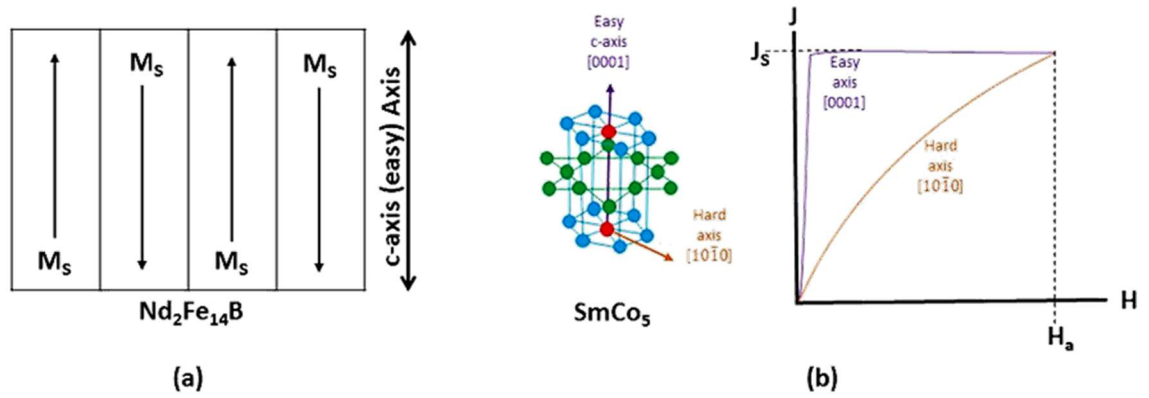


Figure 14: (a) shows the easy magnetization axis of Nd-Fe-B and (b) for hexagonal SmCo₅ magnets, the c-(easy) axis has very high magnetocrystalline anisotropy, sourced from https://www.softmagneticallloy.com/about_magnetic_materials.htm.

To alter the direction of magnetization vector away from easy axis, a significantly larger external field is requisite and the energy stored in the crystallites to work against the anisotropy force is called crystal anisotropy energy (E_a), measured in J/m³ (SI Units). It can be expressed in the form of series and depends on the single angle θ between the M_s vector and the easy axis (c-axis for tetragonal Nd₂Fe₁₄B and hexagonal SmCo₅), given by Eq. (2.19). Anisotropy can be described as uniaxial for the crystals with only one easy axis, as shown in Figure 14 (a) for Nd-Fe-B, the magnetization can either point upwards or downwards.

$$E_a = K_0 + K_1 \sin^2 \theta + K_2 \sin^4 \theta + \dots \quad \text{Eq. 2.19}$$

Here K_0 , K_1 and K_2 are the temperature dependent anisotropy constants of the material with SI Units J/m³. The constant K_0 is independent of the angle, so it is ignored while the constants above second order are not needed as the term K_2 is relatively small (possibly it can also be neglected). Therefore, from Eq. (2.19), when K_1 and K_2 are positive, the anisotropy energy will be minimal when the magnetization vector is directed towards the easy axis (i.e. $\theta = 0$) [1] and can be denoted as:

$$E_a = K_1 \sin^2 \theta \quad \text{Eq. 2.20}$$

In case of $M = M_s \cos(\theta)$, the magnetic potential energy can be written as:

$$E_p = -M_s H \cos(\theta) \quad \text{Eq. 2.21}$$

For minimal energy conditions, $\cos 0 = 1$ (i.e. M_s parallel to easy axis), so Eq. (2.19) and Eq. (2.21) can be combined as:

$$H = \frac{2K_1}{M_s} \left(\frac{M}{M_s} \right) + \frac{4K_2}{M_s} \left(\frac{M}{M_s} \right)^3 \quad \text{Eq. 2.22}$$

With the magnetization equals saturation ($M/M_s = 1$) in the easy axis, the Eq. (2.22) can be simplified as:

$$H = \frac{2K_1 + 4K_2}{M_s} \quad \text{Eq. 2.23}$$

So, when the K_2 is taken as zero, then the magnetization curve is a straight line and the saturating external magnetic field in the SI units (cgs units as a multiple of μ_0) can be expressed as:

$$H = \frac{2K_1}{\mu_0 M_s} \quad \text{Eq. 2.24}$$

For the case of Eq. (2.24) in a uniaxial crystal, the saturating field is equal to the anisotropy field H_a , which is the magnetic field trying to retain the magnetization parallel to the easy axis [1].

2.2.3.2 Shape Anisotropy and the Demagnetizing Factor

The shape anisotropy is not an intrinsic property as it is very much microstructure dependent. The changes to the grain shape and aspect ratio will alter the shape anisotropy. The extent of magnetization due to an external field for a perfectly spherical ferromagnetic particle would be the same in any direction [13]. For the non-spherical particles, the magnetization is easier in the longer direction (of higher aspect ratio) than the short axis. In isotropic polycrystalline materials, the grains do not exhibit the preferred orientation, therefore, the applied field can magnetize it uniformly in any direction. The magnetization is preferred along the easy axis but the demagnetizing field (H_d), which acts to oppose the magnetization, is weaker in the longer axis as it behaves like easy axis of uniaxial crystal. The demagnetization field will be much stronger in the shorter axis (i.e. normal to the easy axis) [1]. According to the Weiss theory, the alignment of ferromagnetic moments in to localized regions of magnetization, called the domains is responsible for the energy minimization. If the long axis c shrinks to dimensions equal to short axis a , then the shape anisotropy constant K_s can be explained as:

$$K_s = \frac{1}{2} \mu_0 (N_a - N_c) M^2 = \frac{1}{2} \mu_0 \Delta N M^2 \quad \text{Eq. 2.25}$$

Here $\mathbf{N}$ is the shape demagnetizing factor in c and a direction and $\mathbf{M}$ is magnetization. So as the $\mathbf{N}_a$ becomes equal to $\mathbf{N}_c$, then the $\mathbf{K}_s = \mathbf{0}$, which means that the shape anisotropy will disappear. Therefore, the strength of shape anisotropy is proportional to the aspect ratio c/a for ($N_a = N_c$) determination and the degree of magnetization [1, 13].

Similarly, the inhomogeneities in the crystal structure as well as the surface imperfections are apparently the local sites for initiating demagnetization. The defects like irregularly shaped grains, non-ferromagnetic inclusions, soft magnetic phases, grain boundaries, surface or geometric defects, etc. become the sites for local nucleation fields H_N (regions favoring magnetization reversal). These defects reduce the coercivity to:

$$H_{ci} = \alpha H_a - N_{eff} M_s \quad \text{Eq. 2.26}$$

Here H_a is the anisotropy field, the Kronmuller's factor $\alpha \sim 0.2 - 0.5$ and $N_{eff} = 0.8 - 1.7$ [1].

2.2.3.3 Stress Anisotropy

As previously defined, stress anisotropy is also not an intrinsic property of a magnetic material. The effect of change in the dimensions of a material from the exposure to a magnetic field is called magnetostriction. So, an altering external magnetic field can induce the rotation of magnetic moments, which changes the dimensions of crystal lattice and as a result material dimensions [34]. This change in the dimension (magnetostriction strain, $\lambda_{ms} = \Delta l/l_0$) causes the stress (σ) in the material, which can create an easy axis of magnetization, called stress anisotropy [1]. If stress is present in a uniaxial crystalline system, then the stress anisotropy must also be accounted for the total anisotropy field. Stress anisotropy energy (E_{sa}) can be expressed similar to magnetocrystalline anisotropy in Eq. (2.20) and shape anisotropy from Eq. (2.25) as:

$$E_{sa} = K_\sigma \sin^2 \theta \quad \text{Eq. 2.27}$$

The stress anisotropy constant can be written as: $K_\sigma = 3/2 (\lambda S \sigma)$, where σ is the stress in the material, S is the spin quantum number and λ is the magnetostriction strain. If the value of K_σ is positive, then the stress anisotropy is along the easy axis, whereby if it is negative then the stress axis is normal to the magnetization plane [1].

2.2.3.4 Induced Anisotropy

The mechanical and physiochemical processes can induce the magnetic anisotropy in a material, but these effects are not considered as the intrinsic magnetic properties. Induced anisotropy can be via: (1) Magnetic Field Annealing, (2) Plastic Deformation – i.e. mechanical working and (3) Magnetic Irradiation – radiation bombardment may alter the atomic and magnetic ordering [1].

2.3 Extrinsic Properties of Magnetic Materials

The magnetic properties related to the microstructure are called the extrinsic magnetic properties and they are strongly dependent on the processing routes as well. The magnetic materials differ in the sense that they can be magnetized. The relationship between the magnetization and the external magnetic field is termed as the hysteresis behavior, which is characteristic of the microstructure of a magnet. For the small applied fields producing

saturation magnetization, the materials are termed magnetically soft. While the hard magnets require for very large fields to magnetically saturate them. The extrinsic magnetic properties of a material are derived from hysteresis loop behavior (B vs H in engineering) or (M vs H in physical sciences), as shown in Figure 15 (A). The characteristic hysteresis loop of permanent magnets shows different points of merit: (1) saturation magnetization, (2) remanence B_r (3) intrinsic coercivity H_{Ci} and purple shaded square area in second quadrant is BH_{max} . The change in microstructure and morphology have a significant influence on the extrinsic magnetic properties of the magnets. The extrinsic properties are also closely related with defect crystal structure, presence of secondary phases and their morphology and volume fraction of the magnetic phases; defining the hysteresis behavior. Therefore, the effect of fabrication routes readily impacts the microstructure, and as a result the derivative magnetic properties can vastly be different in a bulk magnet.

2.3.1 Hysteresis Loop

The M vs H magnetization curves are linear for dia-, para- and antiferromagnetic materials, but the ferri- and ferromagnetic materials exhibit a non-linear behavior as the M and χ vary with H as shown in Figure 6. The demagnetization behavior provides characteristic information about the type of magnetic material, i.e. ferro-, ferri-, para- or antiferromagnet in the sense how they magnetize or with the demagnetization response to identify the hard or soft magnetic materials as illustrated in Figure 15 (B). For a ferromagnet, if the external field is applied in the direction of easy axis, the magnetization will spontaneously align the domains almost immediately to reach M_s . However, the applied field in the hard axes may require a much larger field to rotate the magnetic domains in the desired direction [34].

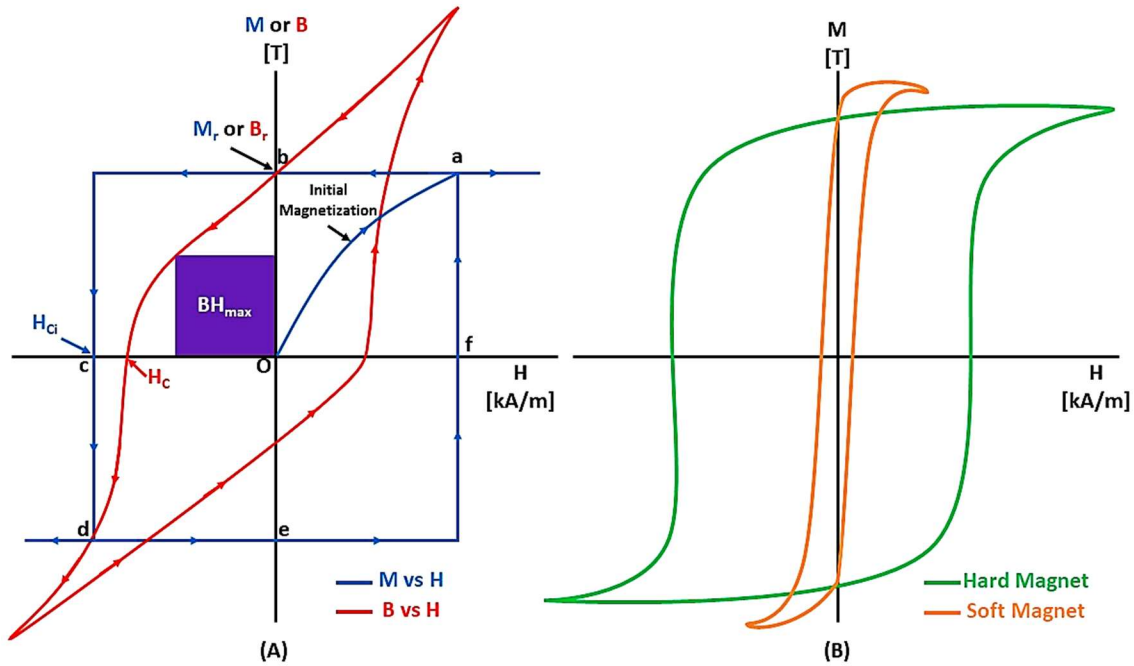


Figure 15: (A) characteristic (M vs H) and (B vs H) ferromagnetic hysteresis loops, and (B) the thickness of the hysteresis loop indicates the hard and soft magnetic materials.

In the M vs H (blue lines) hysteresis loop from Figure 15 (A), the origin point is given by “O” where the material is in a demagnetized state and the domains are randomly oriented, exhibiting net zero magnetization. With an applied external field, starting from “O” towards the saturation magnetization point “a”; the magnetic moments begin to align in the parallel direction and the magnetization equals M_s . For a material with uniaxial magnetocrystalline anisotropy, the relatively low H values are required to reach M_s and the magnetic domains align by rotating towards the magnetization easy axis. At this point M and H are both at the maximum value. Following the loop towards point “b” in the second quadrant, the external field H goes to zero. But even without the applied field, the domains in the permanent magnet are uniformly aligned towards easy axis. This definite magnetization without H is called remanence M_r (T). The M_r strongly depends on the degree of alignment of the domains in the hard phase grains and the close packing/densification of the grains. The remanent magnetization M_r is related to remanent magnetic induction B_r by relation in Eq. (2.1) as: $B = \mu_0 (H + M)$. Likewise, according to Eq. (2.2) the remanent induction B_r is related to remanent polarization J_r as: $B = (\mu_0 H) + J$ [1, 13].

The ferromagnetic grains can either have multi domain structure or they may be present as can the single domain grain(s), e.g. in Nd-Fe-B the single domain size is approx. 300 nm [36]. The random orientations of the domains will lower M_r , as they will create more domains walls to reduce the magnetostatic energy. Therefore, the parallel aligned (anisotropic) grains oriented towards the easy axis will give highest B_r and consequently also BH_{max} [1]. The energy product is given in a relationship as:

$$BH_{max} = \frac{J_r^2}{4\mu_0}$$

Eq. 2.28

Towards the point “c”, the demagnetization becomes larger and now the external field has started to increase in the reverse direction. So the M goes to zero at certain value of H , called the **coercivity**. The **intrinsic coercivity** H_{ci} (A/m) is defined as ability the of a magnet to withstand the demagnetizing field (H_d) as the magnetization (M) goes to zero [3]. During demagnetization, the H_{ci} is the measure of domain walls nucleating and moving within a magnetic material. If the domain walls experience hindrances in nucleating or their movement, then larger demagnetizing fields are required to switch the magnetization vector to zero. Therefore, a higher H_{ci} is achieved and the material is magnetically hard [13].

The (B vs H) hysteresis loop, shown with red lines in Figure 15 (A), measures the change in magnetic flux B with the applied field H . The H_c is the coercivity, dependent on the microstructure, which is lower than the intrinsic coercivity (which is strongly related to the anisotropy field and the chemical/lattice structure) [1]. The (B vs H) loops are used to determine the B_r and the maximum energy product (BH_{max}) of a magnet (purple square). So BH_{max} (kJ/m³) can be defined as the ability of a magnet to store the magnetostatic

energy. The $BH_{\max}$ increases with the H_C and B_r values, but it is limited by an approximation to: $BH_{\max} \sim M_r^2/4 \leq M_s^2/4$ [13].

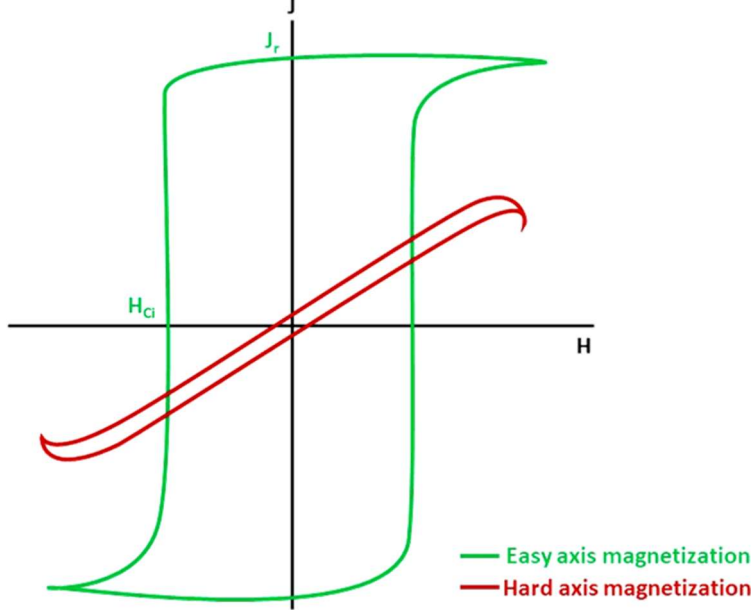


Figure 16: Hysteresis loops of magnetizing a uniaxial material with field towards the easy and hard axis, adapted from [1].

A square shaped loop for easy axis of magnetization is desirable as it indicates the magnet will produce uniform magnetization in an applied field, as shown in Figure 16. The domains are aligned parallel and the domain walls are 180° (antiparallel) with the easy axis of magnetization (energy minimization). The J_r of such uniaxial material is almost equal to the saturation magnetization. In such case the demagnetization will be hard in the homogenously magnetized domains, until the reverse domains uniformly nucleate to rotate the magnetization vector to zero. The magnetization reversal will follow the massive Barkhausen jumps (entirely due to motion of reverse domain walls) when the external field is equal to H_C . Whereby for the magnetization vector perpendicular to the easy axis, the change in J with the applied field is almost linear. The permeability, remanence and coercivity are significantly lower in this case, as the domains are difficult to align with the hard axis [1, 13].

2.3.2 Theoretical Coercivity

The term intrinsic coercivity (H_{Ci}) represents the point “c” in M vs H hysteresis loop used in theoretical physics, where the magnetization is reduced to zero by high enough demagnetizing field and it strongly depends on the lattice structure and the magnetocrystalline anisotropy of the hard-magnetic phase. In real sense, the H_{Ci} of Nd-Fe-B PMs is only a fraction ($\sim 15\%$) of the H_a value at 5350 kA/m at room temperature [36]. This discrepancy in the theoretical and experimental values was deduced as the Brown’s paradox and coercivity is limited due to the effective demagnetizing factor (N_{eff}) and Kronmuller’s factor (materials’ defect constant) “ α ” in Eq. (2.20) and (2.26) [13, 37]. So the non-magnetic impurities and crystal imperfections reduce the H_{Ci} value effectively to αH_a [38]. For bulk alloys the value of $\alpha \ll 1$ equates to the presence of nucleation centers (secondary soft magnetic phases), leading to a decline in the H_{Ci} . This detrimental effect

can be measured with R/δ_B ratio, where R is the approx. radius of harmful soft phase and δ_B is the Bloch wall width of the hard phase, given by Eq. (2.14). For a higher R/δ_B factor, the α value declines sharply, indicating even for ~ 10 nm sized soft phase is enough to significantly reduce the H_{Ci} [37].

The relationship for *maximum* intrinsic coercivity according to the Browns' theory can be written:

$$H_{Ci,max} = \frac{2K_1}{\mu_0 M_S} = H_a \quad \text{Eq. 2.29}$$

The dipolar interactions are substantial in grains larger than d_{crit} size and as the grains grow bigger, the coercivity will tend to decrease. According to Eq. (2.15) the coercivity of grains sized above the d_{crit} will be very high as the reverse domains in a magnetically decoupled system will not spread easily and their movement at low H_d can be reduced by the pinning sites. Also, the probability of defects is lower in the smaller grains. Reducing the grain size to less than the single domain size (300 nm approx.) will switch to superparamagnetic limits and the effective demagnetization strength will drop down substantially, due to a lack in the magnetic order (non-interacting moments in the single domains) [3, 13].

As an elaborative example, the presence of non-magnetic Nd-rich phase is favorable for achieving higher coercivity because it acts to reduce the defects on the surface of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, smoothens the triple pockets and the grain boundary interface. A non-ferromagnetic or paramagnetic composition of the Nd-rich phase is favorable to circumvent magnetic exchange interactions along the neighboring grains to prevent localized exchange coupling interactions. This layer also acts as pinning centers for domain wall movement, so the reverse domains are restricted [17, 39-48].

2.4 Coercivity Mechanisms

Depending on the composition, chemical structure and the microstructure of the magnet, the mechanism for coercivity can be vastly different. Three different types of coercivity mechanisms explain the conditions for demagnetization and quite possibly the controlling mechanisms in a system can work in combination as well. In some cases, the coercivity mechanism can be identified from the initial magnetization curves due to the differential response of domains under the applied fields.

2.4.1 The Stoner-Wohlfarth Model

The Stoner-Wohlfarth Model provides the simplest explanation of magnetization reversal by coherent rotation. It suggests that the magnetization in a ferromagnet does not vary, but its vector rotates with the applied field. For a uniformly magnetized ellipsoidal particle with uniaxial magnetocrystalline or shape anisotropy, a field applied at an angle φ to the easy axis, the total energy (E_t) can be written as:

$$E_t = K_t \sin^2 \theta - \mu_0 M H \cos(\varphi - \theta) \quad \text{Eq. 2.30}$$

Here K_t is the sum of magnetocrystalline and shape anisotropy constants. The first term in Eq. (2.30) refers to the MCA and the second term signifies the minimization of total energy due to spin moments parallel to the applied field, defined by Eq. (2.12). The hysteresis loop is perfectly square in the condition when $\varphi = 0$ i.e. nucleation field (H_N) component is antiparallel to the easy axis, so the coercive will be equal to the anisotropy field according to Eq. (2.35). According to Stoner-Wohlfarth model, the micromagnetic definition of coercivity is given for a single domain particle as:

$$H_{Ci} = \frac{2K_1}{\mu_0 M_S} - \frac{1}{2}(1 - 3\mathcal{N})M_S = -H_N \quad \text{Eq. 2.31}$$

Here $\mathcal{N}$ is the demagnetization constant defined from: $N_{eff} = \frac{1}{2}(1 - 3\mathcal{N})$ [1]. It predicts that the hysteresis loop develops a square shape when the field is applied along the easy axis and it flattens along the hard axes, as shown in Figure 16.

2.4.2 Coherent Rotation

In single domain grains, the division of domains by interacting domain walls becomes energetically unfavorable as the grains size is below the d_{crit} limit. So, each grain acts as a single domain uniformly aligned with the magnetization vector or in the uniaxial easy direction. During the demagnetization, each domain has to be flipped by coherent rotation under very high H_d , in a way similar to demagnetizing a uniaxial aligned anisotropic crystal away from the easy axis. The initial magnetization is very slow, as the applied field needs to be high enough to coherently initiate the single domain rotation away from the easy axis [13].

When the radius of the grain is smaller than the coherent rotation grain size (r_{coh}), the applied field is certain to reduce the magnetization vector by uniformly flipping the magnetic domains requiring very high nucleation fields as shown in Figure 17. For slightly larger, yet smaller than single domain grains (r_{SD}), the demagnetizing field would force the domains to curl on its axis towards H_d , which still requires high reverse nucleation fields. In multidomain grains, the required nucleation field is lower to demagnetize as the mobility of domain walls becomes easier. The application of this model to the hysteresis loop suggests $H_C/2K_t \sim 0.48$ and $M_r/M_S = 0.5$ [13].

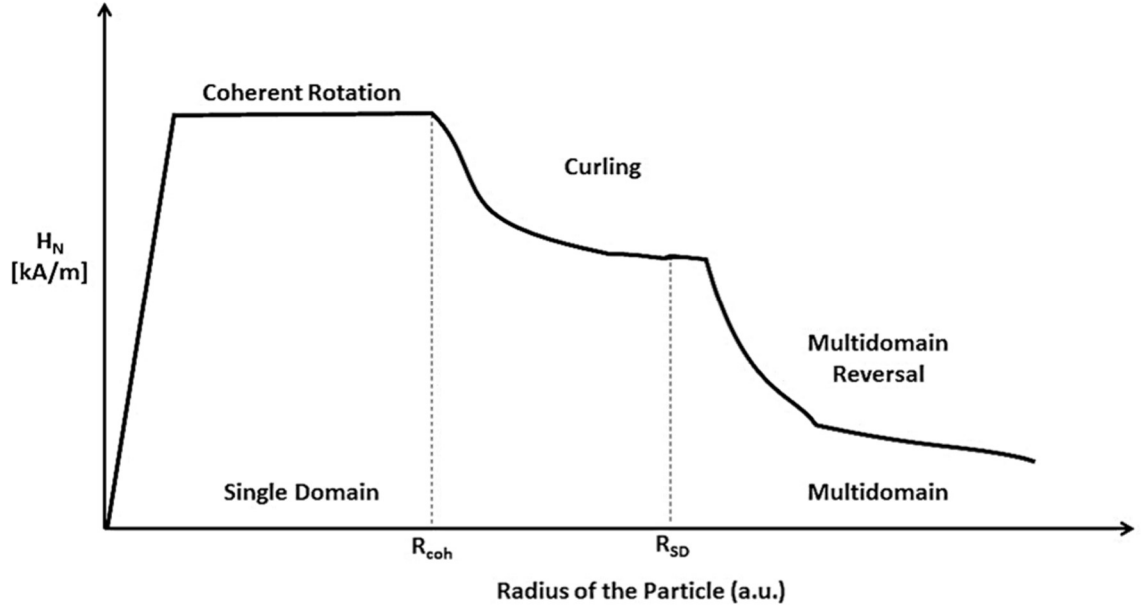


Figure 17: Nucleation field as a function of particle size with a change in the demagnetization mechanism, courtesy of J. M. D Coey [13].

2.4.3 Nucleation

The grain size refinement of the hard phase is considered as a principle mechanism for the coercivity improvement [3]. When the magnetization reversal follows domain wall motion, net M vector from the moments of individual domains is relatively small in every direction. The presence of crystalline imperfections, secondary or soft magnetic phases, grain boundaries and surface defects serve as the reversed magnetic domains' nucleation sites under the demagnetizing external field. These reverse nucleation sites create their own reverse domains, antiparallel to magnetization vector and grow with the demagnetizing H_d to change the net magnetization to zero. Higher nucleation sites at low demagnetizing fields, indicates lower coercivity [13]. For the Nd-Fe-B system, $H_C = \alpha H_a$, with “ α ” the dimensionless material constant depends on the defect structure (the atomic arrangement/crystal imperfections and the microstructural texturing). The value of constant ‘ α ’ has been approximated to $\sim 0.1 - 0.6$ [1]. M. Campos et al. [49] suggested the reverse domain nucleation in Nd-Fe-B occurs at surface region up to thickness ~ 30 nm and for this reason HREE elements are surface diffused to form shells with a relatively higher H_a on the $Nd_2Fe_{14}B$ core grains.

According to Eq. (2.20), if the critical domain size (d_{crit}) is greater than single domain particle size (d_{SD}), i.e. $d_{crit} > d_{SD} \geq 300$ nm, the material will be composed of a multidomain magnetic structure (such that the inhomogeneities can be neglected). In this case the magnetic susceptibility is large due to the free movement of Bloch walls throughout the multiple domains in a single grain [50, 51]. The initial magnetization curves of nucleation-controlled magnets indicate a rapid magnetization at low field values, due to the unhindered domain growth with the saturating field (H_S) as shown in Figure 18 (a).

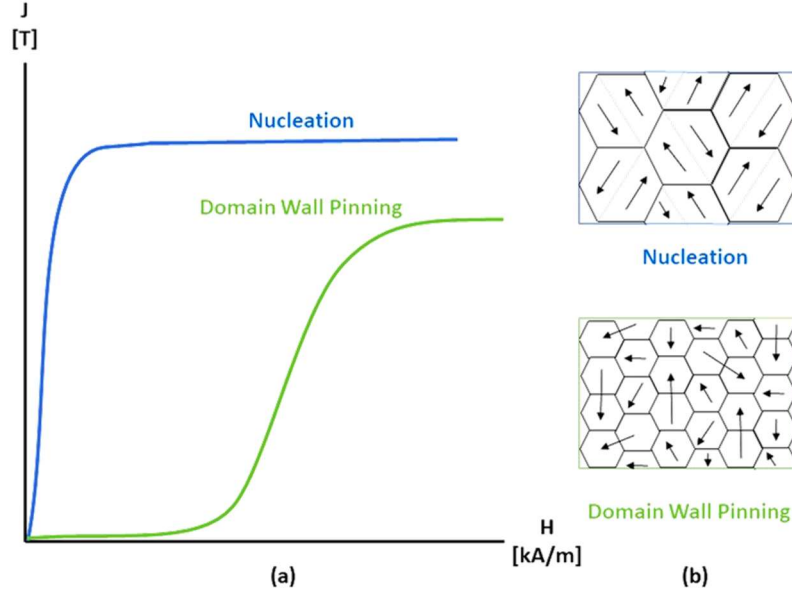


Figure 18: (a) initial magnetization curves with materials having different coercivity mechanisms and (b) domain structure in nucleation and pinning controlled magnets, sourced from [50].

The defects on the surface of hard phase grains can have an imperfect atomic arrangement, which will lower the magnetocrystalline anisotropy and act as the reverse domain nucleation sites, which will grow and spread throughout the grain under the influence of the applied demagnetizing field [1, 50].

2.4.4 Domain Wall Pinning

This approach exploits the significance of localized defects (dislocations) to restrict the generation and movement of reverse domain walls due to the demagnetizing field. This retains the original magnetization vector in the domains as the initial magnetization is slow as shown in Figure 18 (b), and requires a high saturation field to overcome the pinning effect of domain walls induced by point defects. If the hard phase grains contain inhomogeneities, the movement of the Bloch walls can be pinned at these sites if the energy of these walls attached to the inhomogeneity is lower than the surrounding matrix. Therefore, the Bloch walls can only be displaced if the external field exceeds the pinning field ($\mu_0 H_P$) [50].

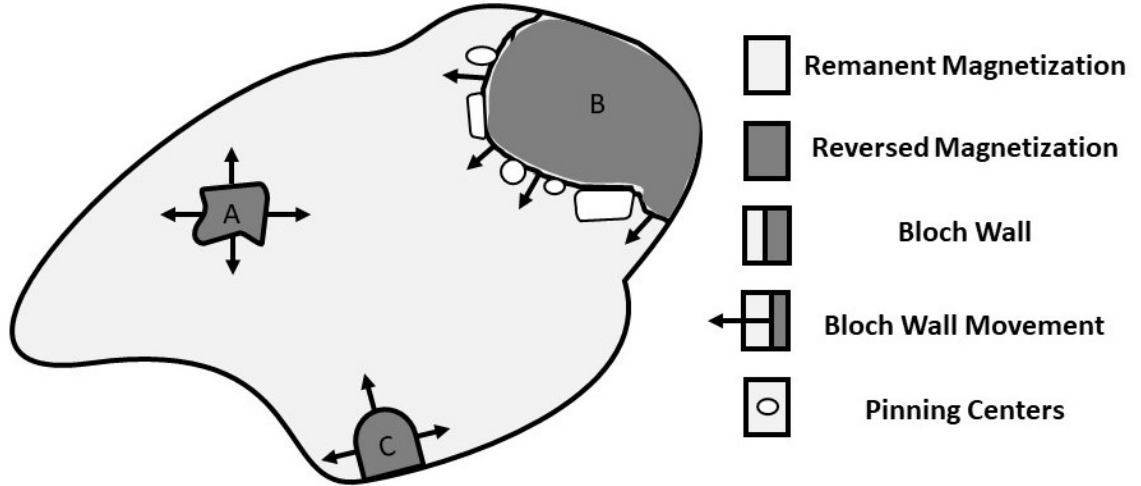


Figure 19: The processes in magnetization reversal, adapted from [13].

Figure 19 illustrates the magnetization reversal from the second quadrant of the hysteresis loop. Here “A” is the reverse domain nucleating instantaneously due to defect or spontaneous thermal fluctuation under low H_d . The reverse domain “B” has grown in size but small pinning centers have trapped it and further motion has been delayed until H_d increases more than the H_p . The “C”-type reverse domain has nucleated from a surface inhomogeneity and will further grow with the applied demagnetizing field [13].

2.5 The Sintering Process

Sintering is a thermodynamic process in which the diffusional mass transport leads to formation of a dense body, usually performed at $T > 0.5 T_m$ for the system [52]. The driving force for sintering is the reduction in surface free energy, which is due to three separate mechanisms: (a) curvature of particle surfaces, (b) applied pressure increasing the packing density and (c) chemical kinetics [53]. The specific surface energy (γ_{sv} i.e. surface energy per unit area) associated with particles in a system can be defined as:

$$E_s = \frac{3\gamma_{sv}V_m}{r} \quad \text{Eq. 2.32}$$

Here E_s represents the decrease in the surface energy, r is the average radius of the particles and V_m is the molar volume. In the absence of chemical reaction at the particle interfaces, pressure is the key mechanism to drive the consolidation, so the work done by applied pressure (P_a) on the system of particles can be defined as: $W = P_a V_m$. When the chemical activity is prominent in sintering, densification can be denoted due to the change in Gibbs free energy:

$$\Delta G^0 = -RT \ln K_{eq} \quad \text{Eq. 2.33}$$

Here $\mathbf{R}$ is the gas constant (8.3 J/mol.K), $\mathbf{T}$ is the absolute temperature (K) and $\mathbf{K}_{eq}$ is the equilibrium rate constant of the chemical reaction. When the concentration of diffusing particles is independent of time, the flux of diffusing species ($\mathbf{J}_x$) is proportional to the concentration gradient ($d\mathbf{C}/d\mathbf{x}$). This is termed as the Fick's First Law of Diffusion [54] and can be denoted in equation form as:

$$J_x = -D \frac{dC}{dx} \quad \text{Eq. 2.34}$$

From Eq. (2.34) the constant of proportionality $\mathbf{D}$ (m^2/s in SI Units) is the diffusion coefficient which effectively quantifies diffusivity of species [55]. The diffusivity is strongly dependent on composition and temperature. For measuring the change in concentration as a function of time, Fick's second law is the appropriate method:

$$\frac{dC}{dt} = D \frac{d^2C}{dx^2} \quad \text{Eq. 2.35}$$

Sintering is defined when densification and grain growth occurs by thermodynamic activity (and/or by chemical reaction) such that the reduction in surface free energy is also accompanied by a change in volume [53]. Mathematically it can be written as:

$$dG = \gamma_{ss}\Delta A_{ss} + \gamma_{sv}\Delta A_{sv} < 0 \quad \text{Eq. 2.36}$$

Here γ_{ss} and γ_{sv} are the specific surface energies and ΔA_{ss} and ΔA_{sv} indicates the reduction in surface area at the solid-solid and solid-vapor interfaces respectively. The densification is the underlying sintering mechanism when the specific surface free energy is lowered but the area remains the same. When the dG is greater than zero but the surface area changes, we can expect only the coarsening of particles. So a combined change in specific surface energy accompanied by the shrinking of bulk volume allows consolidation till $dG = 0$ (i.e. sintering stops, because no active surface area is available for the species to diffuse from vapor-solid interface to the solid-solid interface in the bulk), as shown in Figure 20 [52, 53].

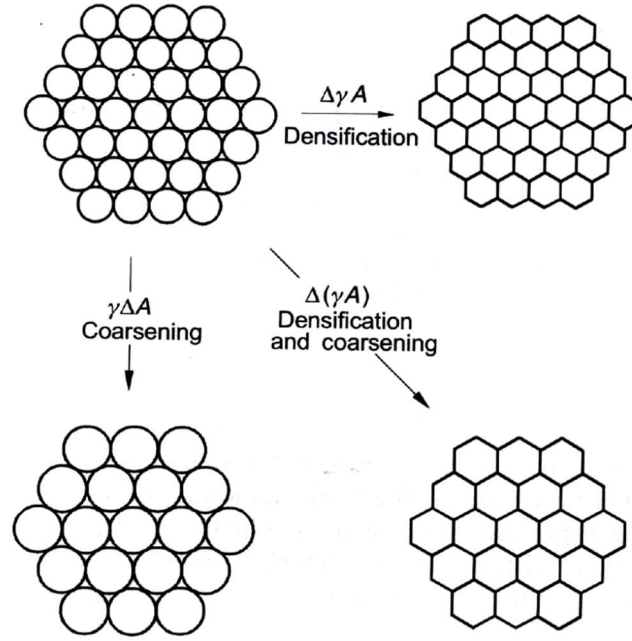


Figure 20: The mechanisms of sintering and coarsening due to reduction in specific surface area, courtesy of N. M. Rahaman [52].

2.5.1 Diffusion Mechanisms

Different types of defects in the lattice determine the diffusion path for mass transport and can be of three different types [53, 54]:

2.5.1.1 Lattice Diffusion

The lattice diffusion is also termed as the bulk or volume diffusion. It happens because of the movement of point defects through the crystal lattice. This type of diffusion is possible via either exchange of atoms/defects at the vacancies in the lattice or by their movement at the small interstitial sites. The lattice distortions due to microstress or impurity atoms also allow movement of interstitial atoms to different sites [53].

2.5.1.2 Grain Boundary Diffusion

Regions of mismatch separating the grains on a polycrystalline material are called grain boundaries and are also considered as defect sites as the dislocations can rapidly transverse through the grain boundaries. So, the grain boundary diffusion in principle should allow rapid diffusivity rather than through the lattice [53].

2.5.1.3 Surface Diffusion

The free surfaces are not perfect as they may contain vacancies, kinks, adatoms, edges, terraces etc. and are regions of high activity (chemical or physical, depending on the composition). The adsorption (physical bonding) or absorption (chemical bonding) of foreign adatoms or the movement of vacancies from the surface to the bulk is known as surface diffusion [53].

2.5.2 Mechanisms of Sintering

The sintering of polycrystalline materials is possible due to diffusional transport of species along definite paths, which define the mechanisms of sintering as explained in the 3-particle model from Figure 21.

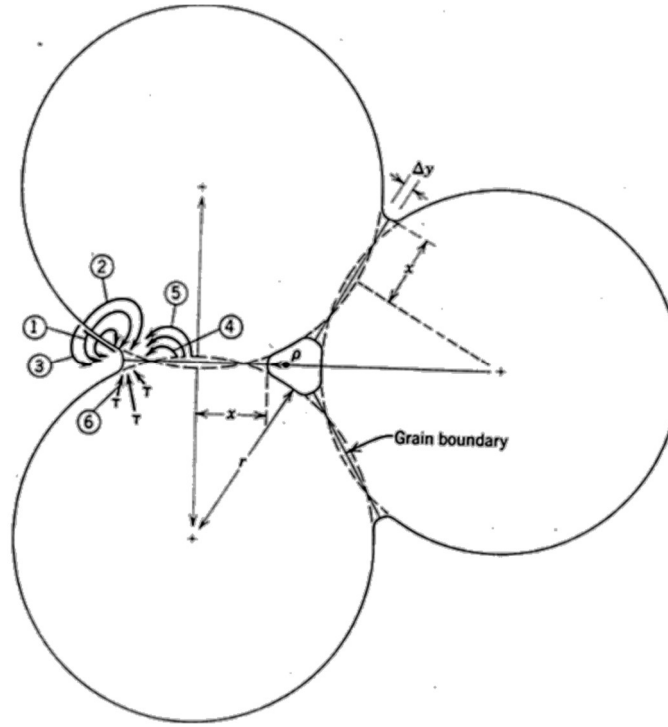


Figure 21: The 3 particle model explaining the sintering mechanisms via (1) surface diffusion, (2) surface + lattice diffusion, (3) vapor transport, (4) GB diffusion, (5) lattice + GB diffusion and (6) plastic flow, courtesy of M. N. Rahaman et al. [52].

The mass transport originating from vapor phase to the surface are the non-densifying processes as they simply denote the diffusion according to the Fick's diffusivity laws. The mechanism 1 – 3 in Figure 21 represent the surface to lattice diffusion. The diffusion is thermally activated and the vapors condense from gaseous phase to the solid surface. In terms of reducing the Gibbs surface free energy, the lattice transport takes the species to the necking regions (i.e. points of contact). The first 3 mechanisms only contribute to neck growth without densification. The non-densifying mechanisms are responsible for the reduction in curvature of neck surface (i.e. the driving force for initiating the sintering).

Table 1: Sintering Mechanisms from 3 Particle Model.				
Reaction	Mechanisms	Initiation Source	End Point	Densification Impact

1	Surface Diffusion	Surface	Neck	No
2	Surface Lattice Diffusion	Surface	Neck	No
3	Vapor transport	Surface	Neck	No
4	Grain Boundary Diffusion	Grain Boundary	Neck	Yes
5	Lattice + Grain Boundary Diffusion	Volume + GB	Pore + Neck	Yes
6	Plastic Flow	Dislocations	Pore + Neck	Yes

Now once the neck has grown and the point of contact has been made, the excessive surface free energy allows grain boundary diffusion of the species. The diffusion of species from the grain boundary to the pore (p) allows the consolidation as the free spaces are filled and specific surface energy gets lower. Finally, the plastic flow accommodates the motion of dislocations by filling up the pore and neck growth to a consolidated body. The flow of the slowest diffusing species along the fastest path controls the densification rate [52-54]. Therefore, the mechanisms 4 and 5 are the most important in terms of sintering. The amorphous materials do not contain the grain boundaries; therefore, the sintering involves deformation of particles by viscous flow. The presence of grain boundaries in the polycrystalline material controls the morphology of the grains and pores. During sintering, the decrease in Gibbs free energy is also partially due to the elimination of free surfaces as the new grain boundaries are formed [54].

2.5.3 Stages of Sintering

There are three sequential stages of sintering which can be defined in terms of changes introduced on the particle surface and the grain boundary area, as illustrated in Figure 22, by means of increasing the temperature and/or time.

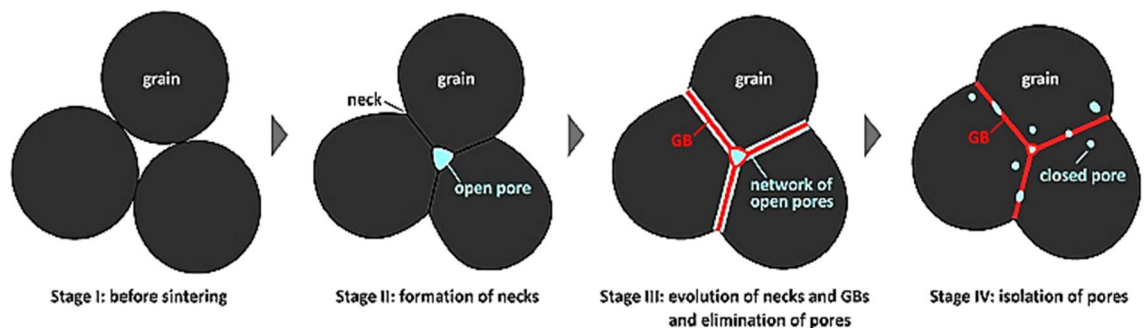


Figure 22: The stages of sintering: rearrangement, necking, evolution of necks and GBs and pore isolation, courtesy of N. Rahaman et al. [54].

2.5.3.1 Stage I: Particle Rearrangement

Often the necking begins with a prerequisite stage (rearrangement) in which the particles are in tangential contact brought together by the elastic deformation in response to reducing the Gibbs surface free energy at $T > 0.5 T_m$. Below this temperature range, the particle rearrangement is achieved by mechanical forces (pressure) and above this temperature the thermally activated surface and lattice diffusion allows the contact points to be developed [52].

2.5.3.2 Initial – Stage II: Neck Formation

In this stage, as the particles begin to coalesce the rapid necking occurs due to the vapor transport, plastic flow (viscous flow for amorphous materials) and surface – lattice diffusion at the interparticle junctions. It incorporates the mechanism 3 and 4 of sintering. The surface curvature is largely reduced and the pores are rounded by close particle contacts, accompanied by shrinkage of volume by up to 65% of the theoretical density value [52, 53].

2.5.3.3 Intermediate – Stage III: Evolution of Necking and Grain Boundaries

The particles adapt the shape of tetrakaidecahedron and the network of open pores is formed along the grain edges in the shape of continuous grain boundary channels. As the pores have reached their equilibrium shape and according to the mechanism 5 of sintering (GB + lattice diffusion), the reduction in their cross section is caused by the surface and interfacial tensions. So as the grain boundaries start forming up, the pore surface area is reduced and eventually get isolated. The intermediate stage is accompanied by 90% densification of the green body [53].

2.5.3.4 Final – Stage IV: Pore Isolation and Densification

The pores are isolated as the grain boundaries form up and take the shape of tetragonal inclusions at the corners where 4 tetrakaidecahedrons meet. To compensate for the reduction in grain boundary energy, the pores may completely be eliminated from the system which accounts to a further increase in densification effectively by 7 – 10%. The graphical explanation of tetrakaidecahedron formation shown in Figure 23 can be deduced from Stage III and IV explained in Figure 22, which is according to the grain boundary channel formation and pore closure [53, 56].

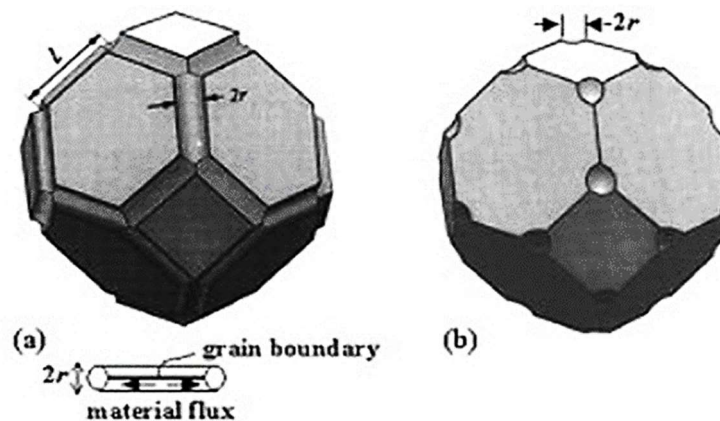


Figure 23: Particle and pore morphology during the sintering: (a) intermediate stage and (b) final stage, courtesy of M. N. Rahaman et al. [56].

2.5.4 Grain Growth and Shape of Pores

The grain growth can be explained in terms that the reduction in the surface free energy of the excessive species diffusing from the vapor phase is accommodated by coarsening of the particles ($\gamma\Delta A$) as shown in Figure 20. Following the law of conservation of mass and energy, an increase in average grain size is supplemented by the disappearance of the smaller grains [54, 57, 58]. The ‘coarsening’ process elaborates the grain growth combined with the growth of pores. The driving force for the grain coarsening is described in the form of the decrease in Gibbs free energy that is accompanied by reduction in total GB area. As the GBs are regions of disorder and the atoms have a high chemical potential, so the grain growth is possible if atoms diffuse to a distance less than interatomic separation from one side of grain boundary to the other. This will shrink one grain while the other grows at its expense. With a higher thermal energy this process will continue to consume the smaller grain as the interatomic diffusion increases [53, 57]. Thermodynamically, the atoms diffuse from the convex surfaces (of GBs) towards the concave surfaces, as shown in Figure 24 (a), because of the higher chemical potential associated with atoms diffusing from the convex surfaces. The tendency of grain boundary movement (as shown by arrows in Figure 24 (b)) is to reduce the curvature of the pore [53].

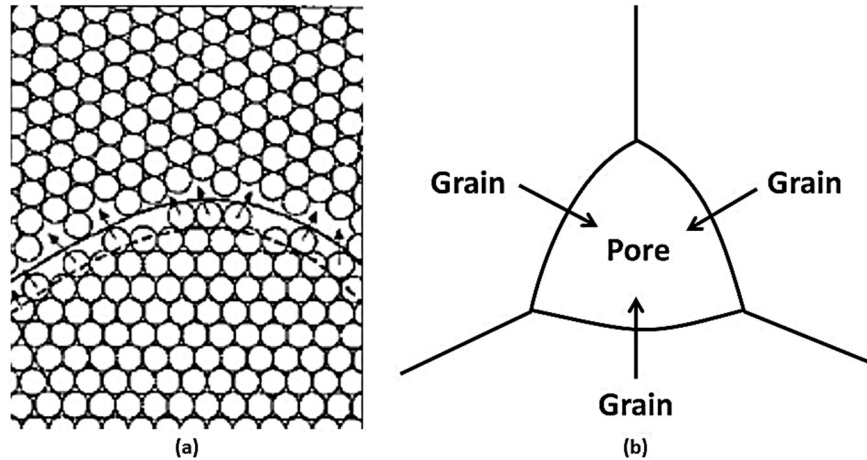


Figure 24 shows: (a) the migration of atoms towards the concave surfaces with the width less than the interatomic spacing is considered as a grain growth mechanism and (b) movement of grain boundary to truncate the pore curvature, courtesy of M. N. Rahaman [53].

2.5.4.1 Normal Grain Growth

In normal grain growth, the average grain size will increase but the shape and size of the grains remain in a narrow size distribution before and after the sintering. This is a key mechanism when the thermal energy for diffusion does not exceeds the boundary mobility by several orders of magnitude as explained by ‘mean field theories’:

$$G^2 - G_0^2 = Kt$$

Eq. 2.37

Here G_0 is the initial grain size, G is the nominal grain growth after time t and K is the temperature-dependent growth factor [54, 57]. The average rate of grain boundary migration v_b (instantaneous grain growth rate) can be written as: $v_b = dG/dt$, which can also be expressed as the product of force (F_b) responsible for the GB migration and the grain boundary mobility (M_b) i.e. ($v_b = F_b \cdot M_b$) [53]. Therefore, the value of K can be written as:

$$K = 2\alpha\gamma_{GB}M_b$$

Eq. 2.38

From the Arrhenius equation, K has the dependence on T given by: $K = K_0 \exp (-Q/RT)$, with K_0 and R constants and Q is the thermal activation energy for grain growth. Therefore, the boundary mobility is strongly related to diffusion in the form of atomistic jumps, which vary significantly with the temperature [54].

2.5.4.2 Abnormal Grain Growth

In the abnormal grain growth, also referred to as exaggerated or discontinuous grain growth, a few large grains develop and rapidly evolve in size as compared to the matrix consisting of smaller grains in the surrounding, such that the grain size distribution in the microstructure is bimodal. The control in grain growth during the sintering operation is vital since the derivative mechanical or functional properties strongly depend on the microstructure. The grain growth also increases the diffusion distance for mass transport, which in turn reduces the final densification. For rapid densification it is necessary to keep smaller diffusion distance from the source to the surface/bulk. In abnormal grain growth, the isolated pores get trapped between the grains since the diffusional transport path is either along the grain boundaries or through the lattice to necking regions[53, 56-58]. Figure 25 (a & b) illustrates the grains with different topological structures such that the GBs migrate towards the center of curvature, so the grains with more than six facets (type III) tends to grow while those with less than six sides will shrink (type I). Depending on the surface free energy and boundary mobility, the curvature of (type II) structure with 6 facets will either grow, shrink or remain metastable. Figure 25 (a) shows the GBs of 10 sides grains rapidly migrate and keep on growing. The effective isolation of pores in the grain boundaries (high pore mobility and grain boundary energy) will cause pore annihilation and the number of pores is reduced due to complete densification [53].

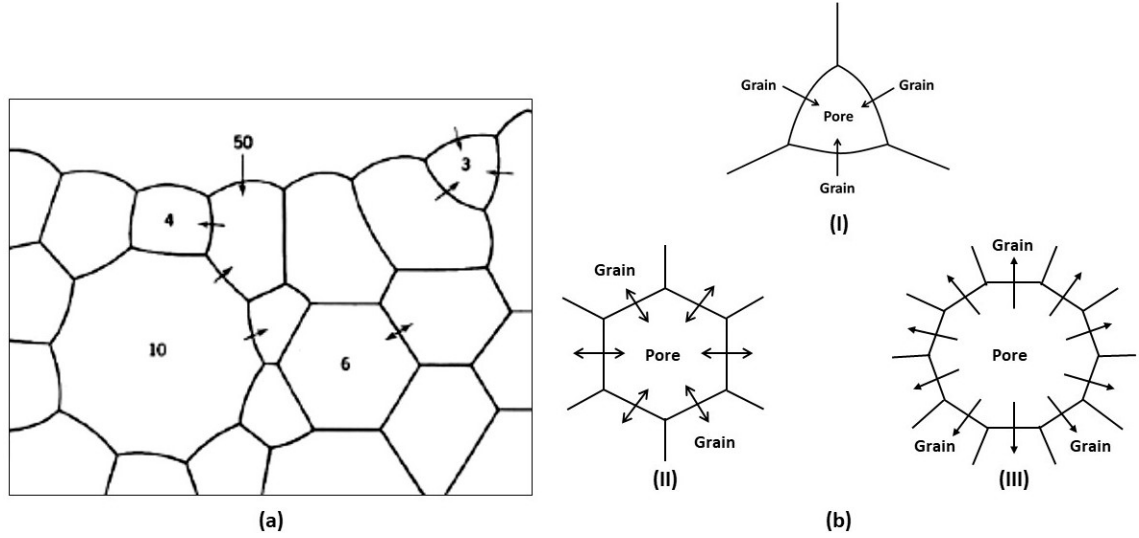


Figure 25: (a) for a dense polycrystalline solid the curvature of grain boundary changes with the number of facets and arrows indicate movement of GBs, (b) different pores in 2D and their mobility direction w.r.t stability, courtesy of M. N. Rahaman et al. [53].

When the grain growth rate is greater than the pore mobility, then the pores are isolated according to Figure 26, as the Gibbs free energy of the system and the grain boundary energies are minimized. Pores will shrink when the grain growth rate is controlled so the mobility of pores is high through the lattice, thus a reduction in system's free energy can be attributed to developing more necking contacts and new grain boundaries [53, 54, 56].

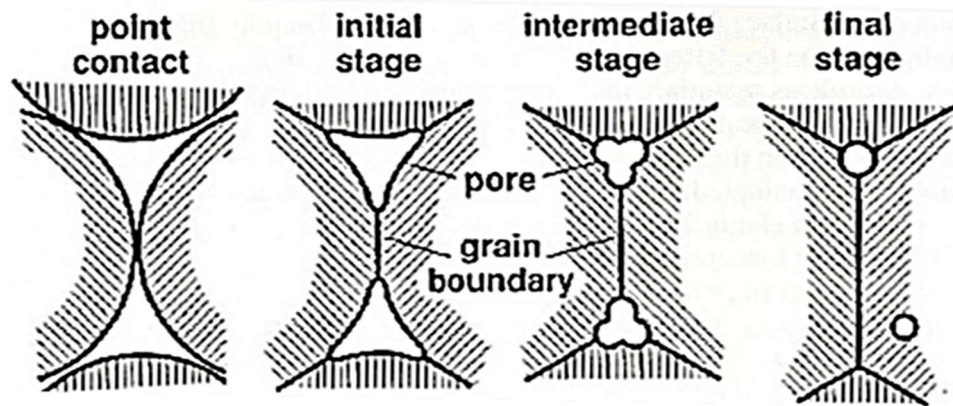


Figure 26: Stages of pore formation and isolation, courtesy of M. N. Rahaman et al. [54].

2.5.4.2.1 Ostwald Ripening

This theory explains the abnormal grain coarsening (secondary crystallization) in solid and liquid medium during the thermodynamic processing. The grains exposed to the surface are energetically less stable and energy can be reduced by moving the small curvature of GBs away from the larger stable grains (towards regions of larger curvature). These small grains are therefore rapidly consumed by a few larger evolving grains [54]. According to this theory, the growth rate of particle is equal to diffusional flux of atoms at the interface (surface, necks, GBs). So, with a change in relative GB mobility or energy, the grains as well as pores with > 6 sides will try to grow in size for accommodating the free energy of the system. The shrinkage of smaller grains and growth of highly faceted grains will lead

to a wide particle size distribution. The physical and chemical inhomogeneities (e.g. dopants, secondary phase, dislocations, stacking faults etc.) are a major cause of abnormal grain growth as these local variations in microstructure alter the GB mobility/energy [53].

Therefore, a tight control of the sintering parameters is requisite to prevent the stages of abnormal grain growth and Ostwald ripening, and for the formation of desirable microstructure and obtaining the necessary functional properties [52, 54, 57]. The parameters influencing the sintering process can be summarized as: diffusion kinetics of sintering, temperature, time, heating rate, pressure, green density, powder morphology (size, aspect ratio, shape, physical state), sintering atmosphere, additives, dopants, impurities and reinforcements/reactive agents (different chemical potential) [52-54, 57].

2.5.5 Sintering Types

The consolidation of powder or green compacts below the melting point can be of three different types: (1) solid state, (2) liquid phase and (3) reactive sintering.

2.5.5.1 Solid State Sintering

The sintering of green bodies, either monolithic metals or multi-phase alloys is performed below the melting point of constituent phase(s), such that densification is possible due to elastic rearrangement of particles followed by necking due to thermal diffusion kinetics and eventually grain growth as shown in Figure 27 [52, 53].

2.5.5.2 Liquid Phase Sintering

Sintering performed in the presence of a small amount of a phase which undergoes melting transition is called liquid phase sintering. The liquid phase must dissolve a small amount of solid phase and wet the surface via solution reprecipitation diffusion kinetics. The reduction in liquid vapor interface is the driving force in liquid phase sintering and the pores will form in liquid phase instead of the grains, which are truncated when the solution reprecipitation is complete [52]. The capillary forces from the liquid phase are responsible for wetting the atoms of the primary solid phase and with complete dissolution, the interparticle contact increases significantly. Solution reprecipitation is responsible for controlling the grain shape and densification. Upon completion of sintering, these solute atoms precipitate out of the liquid phase and grain boundaries rich with liquid phase begin to form in the vicinity. The diffusion-controlled coarsening is possible in liquid phase sintering when solid-liquid interface is replaced by the solid-solid interface and the pores do not fill out if the radius of liquid at the interface is lower than the curvature of large pores. Henceforth, the grain coarsening follows the solid-state sintering approach. Figure 27 presents the schematics of solid state and liquid phase sintering with 3 dominant mechanisms for each route [53, 54].

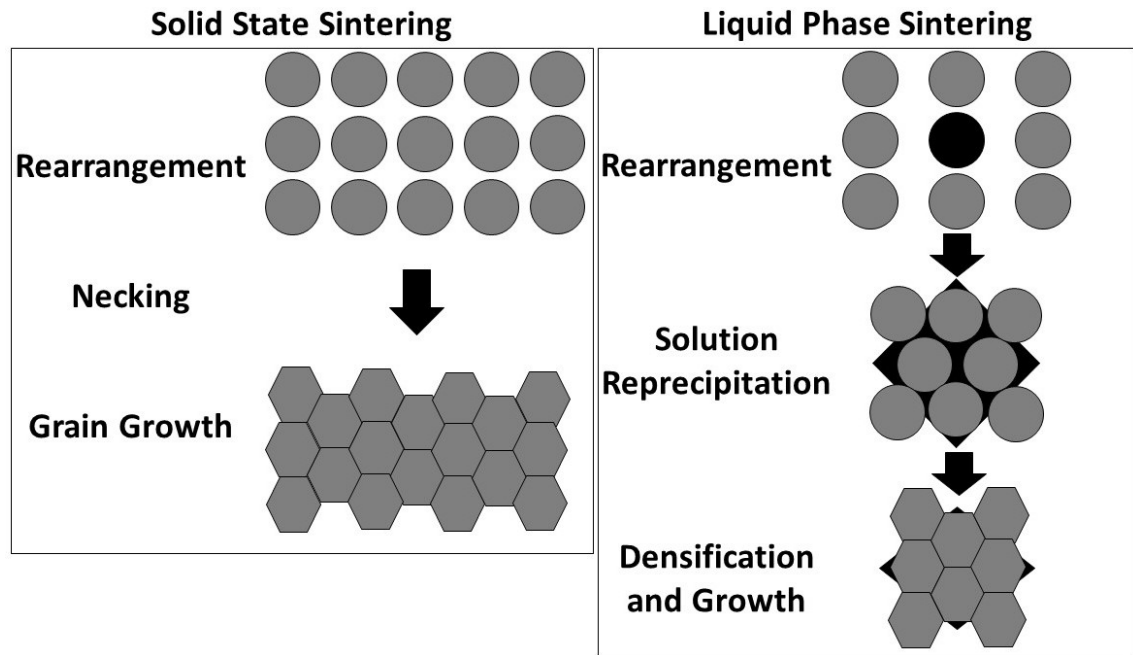


Figure 27: Schematic illustration of underlying mechanisms of solid state and liquid phase sintering.

2.5.5.3 Reactive Sintering

In reactive sintering, the different phases present react at elevated temperatures or the phase(s) are thermodynamically treated in a reactive atmosphere to induce a chemical change before consolidation is complete. This approach is very suitable for developing intermetallic compounds [52].

2.5.6 Spark Plasma Sintering

The Spark Plasma Sintering (SPS) also known as Field Assisted Sintering (FAST) and/or Pulsed Electric Current Sintering (PECS), is a contemporary metallurgical method for achieving enhanced consolidation of powders by simultaneous application of axial pressure and Joule's heating principle (rapid electric spark discharges create massive localized high temperature profiles). Due to the rapid pulsed current, the heat flows uniformly across the specimen and sintering is possible at effectively lower temperatures as compared to the conventional vacuum sintering [59-64]. The main characteristics of SPS sintering are:

- 1) Local plasma discharge generation and its effects on heat transport and mass diffusion.
- 2) Combined effect of high uniaxial pressures and electric field on the uniform densification of particles.
- 3) The electric current effect in surface and near-surface regions of conductors and semiconductors, called skin effect.
- 4) Rapid, non-equilibrium heating and cooling throughout the sample volume [60, 61].

The schematic illustration of SPS system is shown in Figure 28. The main unit has two electrodes (connected to super capacitor) and regulated with hydraulic/pneumatic pressure system. The pulsed DC generator controls the current input and the Joule's effect. The SPS unit can be evacuated with vacuum or the sintering can be performed in an atmosphere of reactive or inert gases. The powders are placed inside the upper and lower punches connected to the electrodes within conductive graphite or high-pressure steel/cermet dies. The thermocouples or infrared pyrometers are used to calibrate, control and measure the heating rate [61, 65].

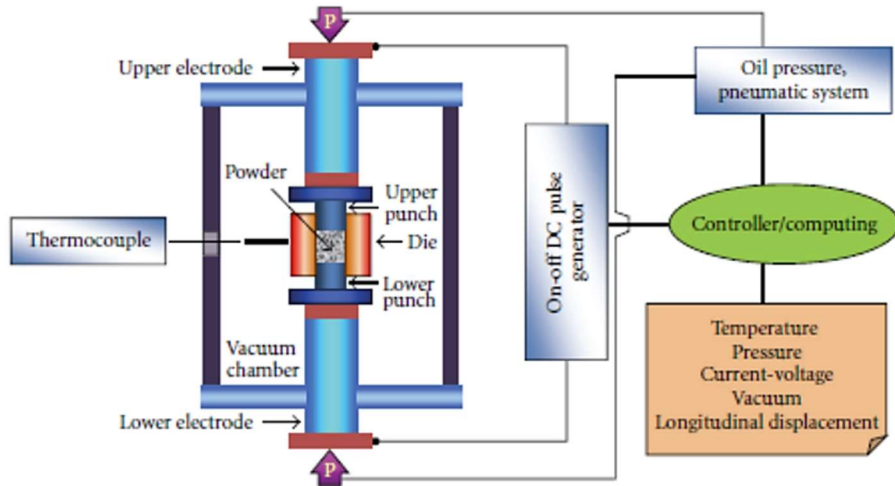


Figure 28: Graphical illustration of the SPS system, courtesy of N. Sahib et al. [65].

Primarily, a high energy and low voltage pulsed current generates very high localized temperature profiles (plasma discharge) between the powder particles, causing optimum thermal diffusion, and the sintering mechanisms of the SPS are illustrated in Figure 29 (a). This results in a completely uniform densification without any significant grain growth (Ostwald ripening) under the optimal conditions (current-pressure-temperature). The heat generated by the Joules Heating effect is given by the proportionality relationship H (Joule) $\propto I^2 R$, with pulsed electric current I (A) and R (Ohms) as the resistance in the specimen [64]. Plasma discharge is responsible for activating the surface whereby Joule's heating initiates the localized surface melting on the surfaces. The mass transfer by diffusion is initiated by vaporization at the contact points of the particles, leading to volumetric diffusion such that the grain boundary contacts are made by surface-activated neighboring particles. Then with the surface diffusion, these particles bond together and the necking starts. In the next step, the grain boundaries begin to form along the surface diffusion regions. Finally, the particles coalesce together to release Gibbs free energy and form up a dense body. Figure 29 (b) shows the mechanism of diffusion-activated material transfer, which begins with surface vaporization and spreads to the whole volume of particles. The activated surface starts to form bonds with neighboring particles. The

necking is initiated at the surface contact points. At the completion of sintering, during the solidification these interfaces will become the GBs [59, 61, 63, 65].

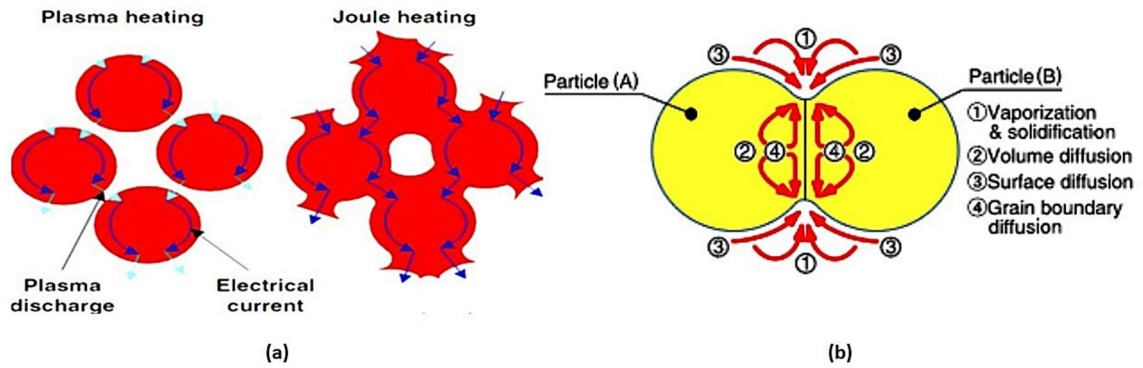


Figure 29: (a) SPS mechanisms and (b) interparticle interactions in activated sintering (thermally or plasma), courtesy of M. Suarez et al. [61].

The nominal heating rates with the SPS can go beyond 1000 °C /minute. With the application of the continuous uniaxial pressure (10 - 500 MPa), the particle contacts are increased and the diffusion is enhanced, so the pores are effectively eliminated by the rearrangement and capillary wetting during the liquid phase sintering. In REPMS, the Nd and Sm-rich phases are in a liquid state during the sintering. So, the liquid phase fills the voids and the hard-magnetic grains ($\text{Nd}_2\text{Fe}_{14}\text{B}$ and SmCo_5) are coalesced closely together due to excessive grain boundary diffusion. Importantly, the SPS processing of these permanent magnets can be done very fast (within a few seconds to minutes) and at relatively low temperature range of (600 – 800 °C), compared to conventional vacuum sintering at temperatures > 1000 °C for several hours [39, 66-73].

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Chapter 3

Rare Earth Permanent Magnet Systems

3.1 The Nd-Fe-B System

The Fe based ferromagnetic alloys, like $\text{Fe}_{65}\text{Co}_{35}$ exhibits the highest magnetic moment (Bohr's magnetron per atom, i.e. $m = -2.5 \mu_B/\text{atom}$) and $T_C \sim 900^\circ\text{C}$. From the aspect of alloy design, Fe should be the main constituent in the permanent magnets. However, the highly symmetric cubic crystal structure of Fe is responsible for intrinsically low magnetocrystalline anisotropy ($H_a \sim 32 \text{ kA/m}$). Therefore, Fe is alloyed with Nd (having $4f$ orbital electrons with unpaired spins) to develop intermetallics with $3d - 4f$ conduction electron band which results in exceptionally high spin-orbital coupling and magnetocrystalline anisotropy. The intrinsic magnetic properties of $\text{Nd}_2\text{Fe}_{14}\text{B}$ type permanent magnets were presented in 1984 after the joint discovery by M. Sagawa at Sumitomo Special Metal Japan [7] and J. Croat et al. [8] working at General Motors USA. The former used conventional powder metallurgical route to develop sintered magnet while the later utilized the melt-spinning process. The $\text{RE}_2\text{Fe}_{14}\text{B}$ structure is also possible in several different lanthanides but in a discretely narrow compositional range. The Nd-Fe-B intermetallic compound has a complex tetragonal crystal structure as illustrated in Figure 30, with the unit cell of $\text{P4}_2/\text{mmn}$ space group which comprises of a total of 68 atoms and 6 crystallographic Fe sites per unit cell [74]. The Nd-Fe-B lattice is identical to two cubical blocks, stacked on top of each other. On each top, middle and bottom plane Nd, B and 4 Fe atoms are placed. The hexagonal network of Fe atoms exists in the lattice above and below the middle plane. The Nd and B atoms have the same configuration in the top and bottom plane, whereby they swap places in the middle plane. The magnetic dipole moments of the Nd atoms prefer the alignment in the (001) direction to minimize the energy due to the spin interactions with the different arrangement of Fe atoms. The Fe dominates by factor of 5 in volume to the Nd atoms, so the overall contribution to magnetism comes from Fe atoms. The spin of Nd atoms organizes the orbital magnetic moments of Fe atoms in the unit cell (due to the participation of $3d$ outer shell electrons in metallic bonding and spin-orbital coupling). The Nd atoms first arrange themselves in a low energy configuration in the unit cell, which is followed by the Fe atoms reducing the overall magnetostatic energy and maximizing the magnetocrystalline anisotropy towards the c-axis. The Nd atoms in sublattice are responsible for $\frac{3}{4}$ of magnetocrystalline anisotropy component while Fe atoms contribute $\frac{1}{4}$ [74].

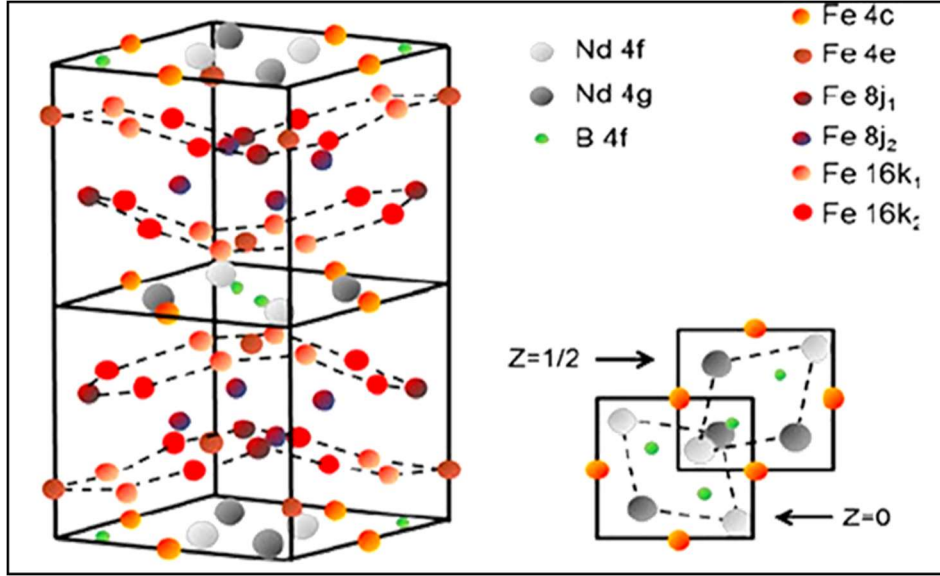


Figure 30: The tetragonal crystal structure of a single unit cell of Nd-Fe-B and the inset indicates the top and down view for a half unit cell showing inverse symmetry of Nd and B atoms, courtesy of F. J. Villacorta [74].

The 4f sub-shells in the lanthanide elements (Nd, Sm, Dy, Tb) provide the necessary spin-orbital coupling to achieve high MCA and magnetic hysteresis, while the 3d sub-shells in the transition metals (Fe, Co, Ni) are responsible for high M_s and T_C [36]. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase having body-centered tetragonal crystal structure exhibits a very high magnetocrystalline anisotropy (easy axis along (001) direction), a high intrinsic coercivity and the best in the class remanent magnetization and BH_{max} . The theoretically predicted remanence (B_r) and BH_{max} have reached 90 % of the theoretically predicted values, but the threshold coercivity (H_{Ci}) of Nd-Fe-B magnets has only reached 15 % of the anisotropy field values ($\mu_0 H_a$), which leaves exceptional room for improvement. The two known methods as shown in Figure 31 to enhance the H_{Ci} of Nd-Fe-B magnets are: by forming the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains of single domain size (reducing in multi-domain grain structure). In this way the demagnetization mechanism will be changed from nucleation of reverse domains to coherent rotation of single domain grains by a very large demagnetizing field as the multi-domain structure allows reverse domain nucleation sites from the surface defects with lower demagnetizing fields [1, 3]. The second scheme is to achieve interfacial control of microstructure between the $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase and Nd-rich intergranular phase, such that the surface of grains is reinforced against nucleation of reverse domains and localized exchange effects are circumvented.

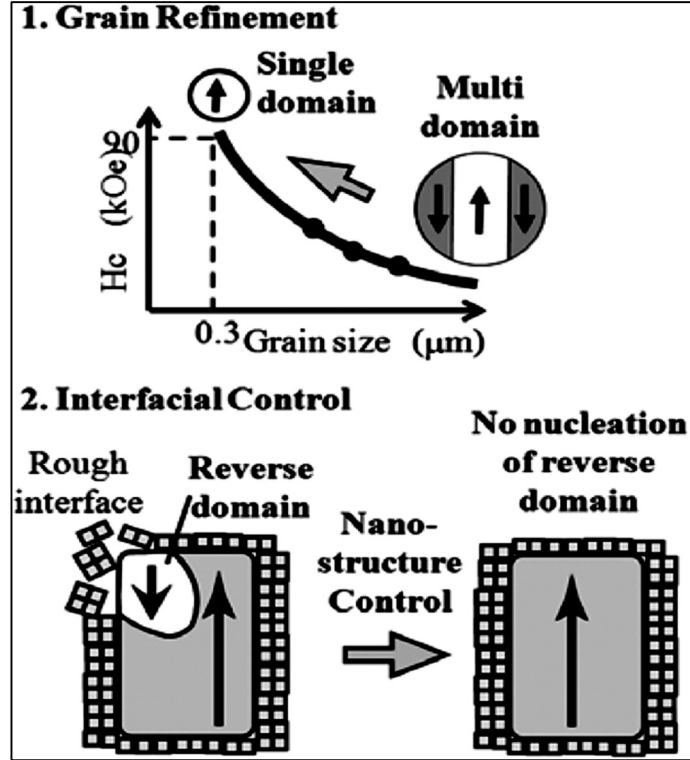


Figure 31: The mechanisms for coercivity enhancement in Nd-Fe-B magnets by grain size refinement and the grain boundary interfacial control, [3].

Different types of Nd-Fe-B magnets which are prepared by different processing methods are commercially used for a wide variety of applications. The usual processing route for Nd-Fe-B permanent magnets follow the powder metallurgy – sintering scheme as show in Figure 32 (a). The pseudo-binary phase diagram of ternary Nd-Fe-B system indicates different processing regimes w.r.t temperature and phase transformation. The commercial sintered Nd-Fe-B magnets typically consist of three distinct phases: A = tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase, B = the tetragonal B-rich (NdFe_4B_4) phase and the cubic Nd-rich phase (low melting point, L phase above 665 °C). From the phase diagram in Figure 32 (a), the Nd-rich phase undergoes liquid phase transformation above 665 °C and vacuum sintering is performed at 1050 – 1080 °C from 1 – 4 hours. This liquid phase is responsible for controlling the densification kinetics during the vacuum sintering. Later these sintered magnets are subjected to heat treatments (700 – 900 °C) and stress relief tempering (low temperature annealing) at 500 – 600 °C. Lastly magnets of optimal quality are coated with Ni or Al passive layers to prevent environmental degradation and survive high temperature service conditions [1, 3]. This processing scheme is also valid for sintered SmCo_5 -based REPMs with high coercivities prepared with micron size precursor powders.

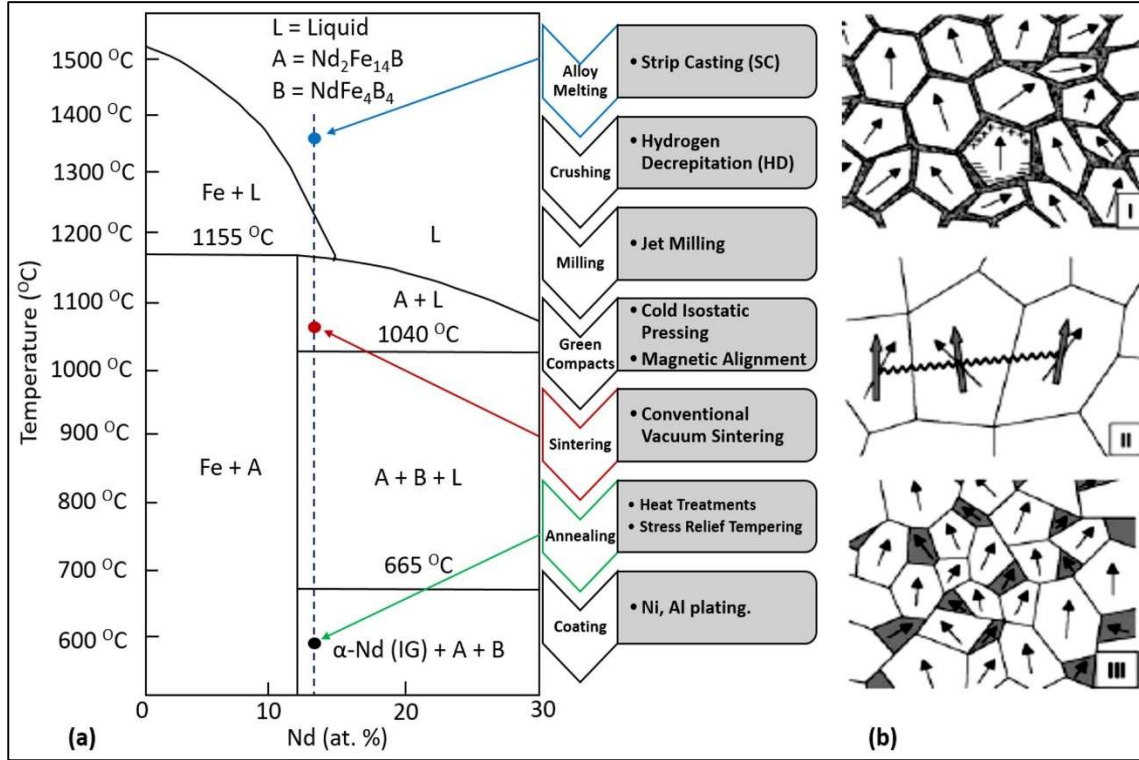


Figure 32: (a) the commercial processing scheme of sintered magnets from the pseudo – binary phase diagram of ternary Nd-Fe-B system, [3]; (b) the microstructure of REPMs with (I) RE-rich composition with individual crystallites separated by a uniform paramagnetic RE-rich layer – higher coercivity, (II) exchange coupled grains without spacer phase – remanence enhancement and (III) a hard and soft phase nanocomposite magnet – high remanence, [12].

Three different characteristic microstructures of the REPMs are represented in Figure 32 (b). In type I magnets, the single crystal grains are separated by a uniform paramagnetic Nd-rich spacer phase such that crystallites behave like tiny permanent magnets with high coercivity. If this microstructure can be realized on a single domain size range, the coercivities will be exceptionally high (close to the anisotropy field), since coherent rotation-based demagnetization will require very high external magnetic fields to reverse the domains. The sintered Nd-Fe-B magnets can be considered as type I REPMs. The type II magnets have a textured microstructure (aligned magnetic moments) and due to the lack of secondary phase exchange coupling is dominant here, leading to higher remanence but low coercivity. Type III nanocomposite magnets with less than stoichiometric Nd-content will have multi-phase exchange coupled phases (soft + hard) in the microstructure, leading to remanence enhancement [12].

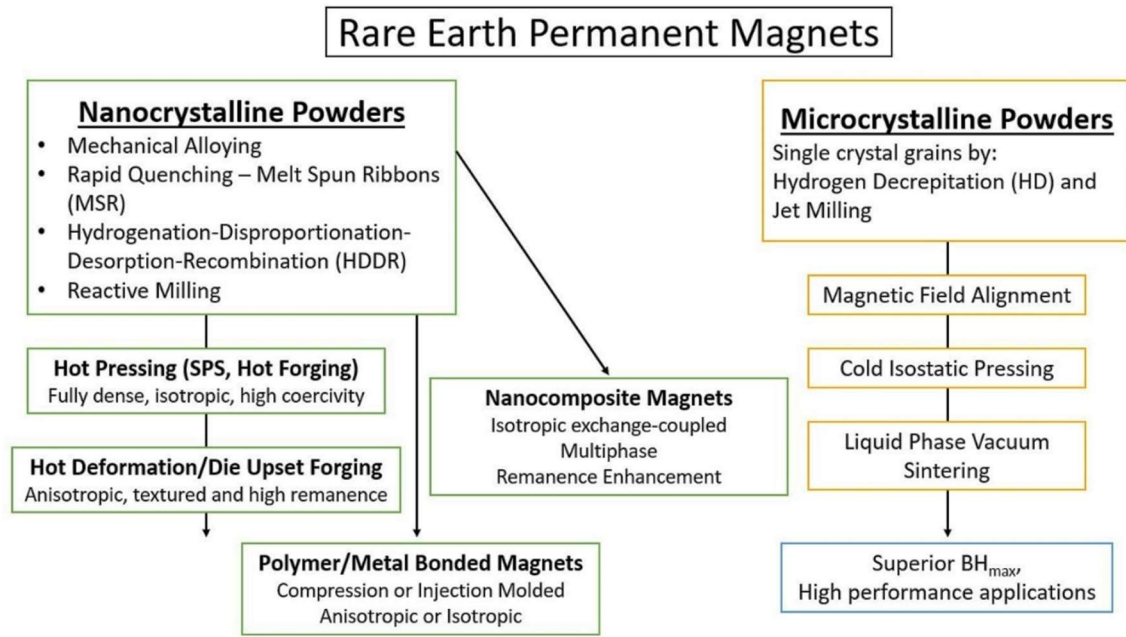


Figure 33: Classification of rare earth permanent magnets based on their crystallite sizes and the possible processing schemes, adapted from [12, 15].

The rare earth permanent magnets in terms of their production can be broadly classified into two categories: microcrystalline and nanocrystalline types, as shown in Figure 33. The most widely used type I – high performance magnets are derived from sintering the aligned microcrystalline precursor powders prepared by hydrogen decrepitation (HD) and jet-milling (JM). The type II and III magnets from Figure 32 (b) are based on nanocrystalline powders. The obvious advantages of nanocrystalline magnets are based on the grain size refinement as a coercivity enhancement mechanism given in Figure 31, with nanocrystalline grains of near single domain size corresponding to the theoretical values of the coercivity as high as the anisotropy field. At the General Motors USA in 1984, J. Croat et al. [8] prepared amorphous ribbons of Nd-Fe-B and Pr-Fe-B with the melt spinning process. The molten alloy is rapidly solidified with a possible quenching rate of 10^6 °C/s and the ribbons are free from α -Fe segregation due to the low devitrification kinetics of the $M_2Fe_{14}B$ phase ($M = Nd, Pr$) and nanocrystallites of 20 – 50 nm nucleate during annealing [12, 15]. The commercial melt-spun ribbons can have the intrinsic coercivity up to 1580 kA/m and in order to introduce texture and anisotropy for remanence enhancement, the hot deformation and/or die upsetting processes are carried out [3, 12, 75, 76]. The nanocrystalline magnets cannot be sintered by conventional methods, as the exponential grain coarsening at temperatures above 1000 °C will deteriorate the microstructure-dependent magnetic properties [44]. So rapid processing (shock compaction, hot forging) and low temperature consolidation techniques (spark plasma sintering – SPS) are the only practical alternatives for the nanocrystalline PMs [66]. Figure 34 shows the comparison of the magnetic properties of HREE-free Nd-Fe-B vacuum sintered magnets from the jet-milled powder with the hot-pressed and hot-deformed nanostructured melt-spun ribbons. After the hot pressing, the coercivity is high and fully dense isotropic magnets are formed. The remanence increases with hot deformation as the grains are textured along the pressing

direction, improving the B_r and BH_{max} , but the coercivity is significantly lower after the hot deformation, due to the rotation of the grain boundary phase in the direction perpendicular to the pressing direction [76]. But due to the nanocrystalline grains, the coercivity of the hot-deformed magnets is significantly higher than the HREE-free conventionally sintered magnets (composed of microcrystalline grains).

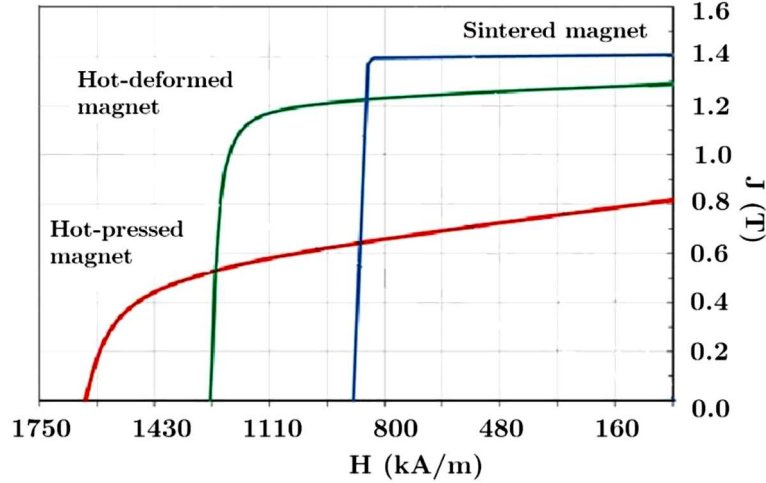


Figure 34: A comparison of magnetic properties of HRRE sintered magnet from the jet-milled powder and melt-spun ribbons which are hot-pressed and hot-deformed for inducing texture, [76].

The Hydrogenation Disproportionation Desorption Recombination (HDDR) technology is an alternate method of developing high coercivity nanostructured crystallites close to the single domain grain size of ~ 400 nm, based on hydrogen induced phase transformation. The HDDR is a reversible two-stage (HD – DR) process for grain size refinement due to hydrogen induced disproportionation of micron sized $Nd_2Fe_{14}B$ grains in to a nanoscale mixture of $NdH_2 + \alpha\text{-Fe} + Fe_2B$ at 800°C , which is allowed to recombine back to ~ 400 nm sized $Nd_2Fe_{14}B$ grains in the second stage. In the hydrogen decrepitation (HD) process, H_2 is absorbed by rare-earth rich grain boundary phases, which causes an intergranular collapse of the alloy. While in the HDDR process, hydrogen first diffuses into the grain boundary phase causing cracks due to the larger lattice parameters of neodymium hydride and then diffuses in to the $Nd_2Fe_{14}B$ grains as well which are later disproportionated at elevated temperatures in 1 bar H_2 pressure [12]. Bonded magnets are the primary application of HDDR Nd-Fe-B powder with $H_{Ci} = 900 - 1200$ kA/m and maximum service temperature of 150°C [3]. The nanostructured magnetic powders in large volumes are used in polymer-bonded magnets, which can be fabricated easily in a single (or two) stop processes: extrusion, injection molding, compression molding and relevant composites fabrication methods. Since the polymer bonded magnets do not require further secondary machining and finishing processes, these are readily made to tight tolerances. The advantages of polymer bonded magnets include: cost effective processing, complex shapes and scale up, a variety of polymer binders (nylon, epoxy, poly acetates/sulfide/chlorides, etc.) for a variety of applications, batch reproducibility, the flexibility of producing isotropic/anisotropic magnets and the ease of recycling [3, 15]. But the lack of high

temperature and environmental stability, and low energy products restrict their applications to less than 100 °C.

In the electric vehicle's traction or power steering motors, the sintered magnets operate at elevated temperatures (> 100 °C) and therefore experience very high demagnetizing fields and thermal stresses, which necessitates tailoring the composition with the HREEs, usually through the grain boundary diffusion process (GBD) for achieving the room temperature coercivities above 2000 kA/m [3, 16, 74].

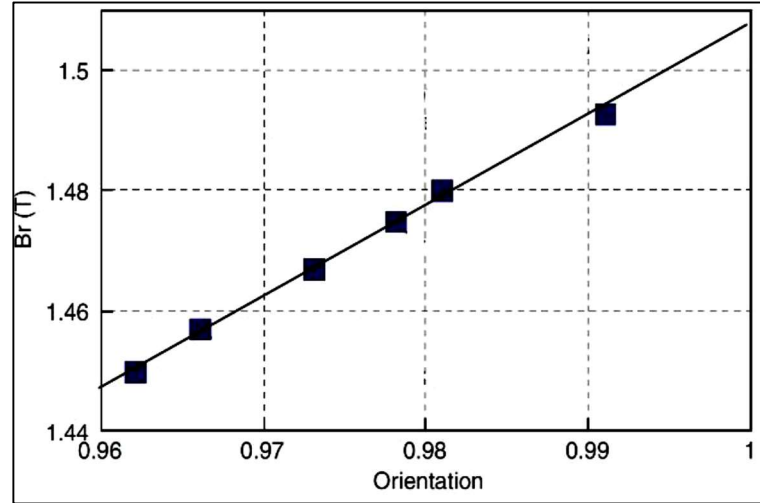


Figure 35: The relationship between the degree of grain orientation with the B_r values in the anisotropic sintered magnet of composition $\text{Nd}_{13.8}\text{Fe}_{80.5}\text{B}_{5.7}$, courtesy of Y. Matsuura [77].

In the appliances like VCMs or MRI, the high magnetization (M_s and M_r) is a requirement, therefore high performance anisotropic sintered magnets are suited. In case of isotropic Nd-Fe-B magnets, the B_r value is approx. 0.8 T, i.e. $\frac{1}{2}$ the $\mu_0 M_s$ value (1.6 T). For the anisotropic sintered magnets, the B_r is smaller than the $\mu_0 M_s$ value due to non-uniform grain alignment, the presence of secondary non-ferromagnetic phases, and compositional characteristics. The dependence of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain orientation as a relation to the remanent magnetization is shown in Figure 35 [77].

The back-scattered electron (BSE) microstructural illustration of complex multi-phases in a typical sintered Nd-Fe-B PM of nominal composition $\text{Nd}_{13.4}\text{Dy}_{0.6}\text{Fe}_{78.6}\text{B}_{6.1}\text{Nb}_{0.4}\text{Al}_{0.7}$ is given in Figure 36. This sintered magnet was produced by vacuum sintering at 1070 °C for 2 hours and the magnetic properties were: $H_{ci} = 1170$ kA/m and $B_r = 1.19$ T. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ tetragonal hard magnetic phase appears as the matrix with greyish contrast. The cubic Nd-rich phase, Nd-oxides (cubic NdO_x and cubic/hcp Nd_2O_3) appear as the bright contrast phases in Figure 36. The Nd-rich phase is in liquid state above the eutectic transition at 665 – 690 °C, while the Nd-oxides transform from NdO_x to Nd_2O_3 phase (cubic to hcp) as the temperature is raised above 700 °C. The hcp- Nd_2O_3 is a metastable phase transformation which can be retarded to cubic Nd_2O_3 by the addition of elements like Cu, Ga and Al [78-80]. The paramagnetic nature of Nd-rich phase was reported by F. Vial et al. [81] and K. Hono & co. [17, 42, 48]. The tetragonal B-rich $\text{Nd}_{1+\epsilon}\text{Fe}_4\text{B}_4$ phase is also part of the Nd-Fe-B sintered magnets and appears darker than the matrix due to B-rich composition [82].

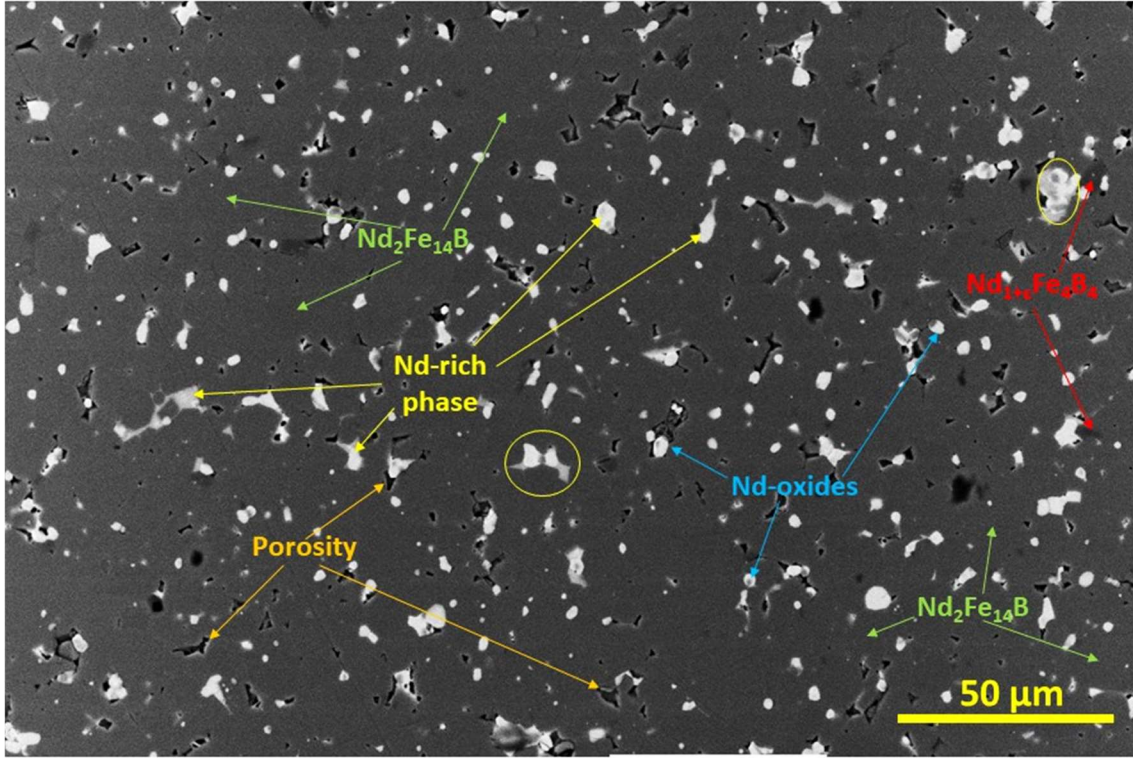


Figure 36: Typical microstructure of Nd-Fe-B permanent magnet, with different phases marked in colors, sourced from the graphical abstract [83].

In the sintered magnets, the Nd-rich phase is crucial as it smoothens the grain boundaries by eliminating the defects on the surfaces of the 2:14:1 grains for preventing the reverse domain nucleation at inhomogeneities and acts as a continuous non-ferromagnetic layer to decouple the neighboring grains which in turn increases the H_{Ci} . Four different types of Nd-rich phases have been classified in terms of their chemistry and structure in different Nd-Fe-B systems as shown in Table 2, [7, 81, 83-88].

Table 2: Different types of Nd-rich phases in sintered magnets.			
Phase Type	Structure Type	Space Group	Lattice Parameters (Å)
dhcp-Nd ₂ O ₃	Not known	dhcp	$a = 0.365 - 0.37, c = 1.18$
fcc-NdO _x	NaCl	Fm $\bar{3}$ m	$a = 0.507 - 0.524$
Complex Nd ₂ O ₃	Complex, not known	fcc + bcc	$a_{fcc} = 0.52, a_{bcc} = 1.04$
hcp-Nd ₂ O ₃	La ₂ O ₃	P $\bar{3}$ ml	$a = 0.383, c = 0.6$

The likelihood of attaining metallic Nd-rich phase in the sintered REPMs is significantly low due to the very high affinity of REEs forming compounds with oxygen, which is

inevitability introduced during the metallurgical processing. As a result, the grain boundaries in the sintered Nd-Fe-B magnets contain up to 0.65 wt. % oxygen as compared to the cast ingots containing less than 0.20 wt. %. The fcc Nd-rich phase forms due to the higher weight content of oxygen as compared to dhcp-Nd₂O₃, but after the thermal activation due to the processing operations, the latter phase becomes dominant above 0.6 wt.% oxygen content [89]. In near stoichiometric Nd-Fe-B systems, a higher oxygen content causes an increase in B-rich phase (Nd_{1+ε}Fe₄B₄) at the expense of the 2:14:1 phase, thereby the net oxygen content has a significant influence on the sinterability of the magnetic powders [81, 89, 90]. Corfield et al. [79] also reported a higher oxygen content than 0.4 wt. % contributes to abnormal grain growth during sintering at elevated temperatures, which is necessary for HREE-rich compositions, hence the control of inhomogeneities and oxygen content is a must in the powder metallurgical processing of the Nd-Fe-B magnets.

3.1.1 Production of Nd-Fe-B Permanent Magnets

The two different types of production schemes apply for the Nd-Fe-B-based permanent magnets, as shown in Figure 33, i.e. from the microcrystalline precursors or the nanocrystalline powders. The traditional powder metallurgical route has commercially been the most viable option for the microcrystalline powder to develop high BH_{max} (~ 400 kJ/m³) and H_{Ci} (≥ 1600 kA/m) sintered magnets; and in the latter case, the polymer processing has been the common industrial practice. Figure 37 shows a 3-way possible processing of Nd-Fe-B permanent magnets utilizing the concepts of conventional alloying, casting and powder metallurgy, and nanostructurization treatments in the form of melt-spinning or HDDR [3, 11].

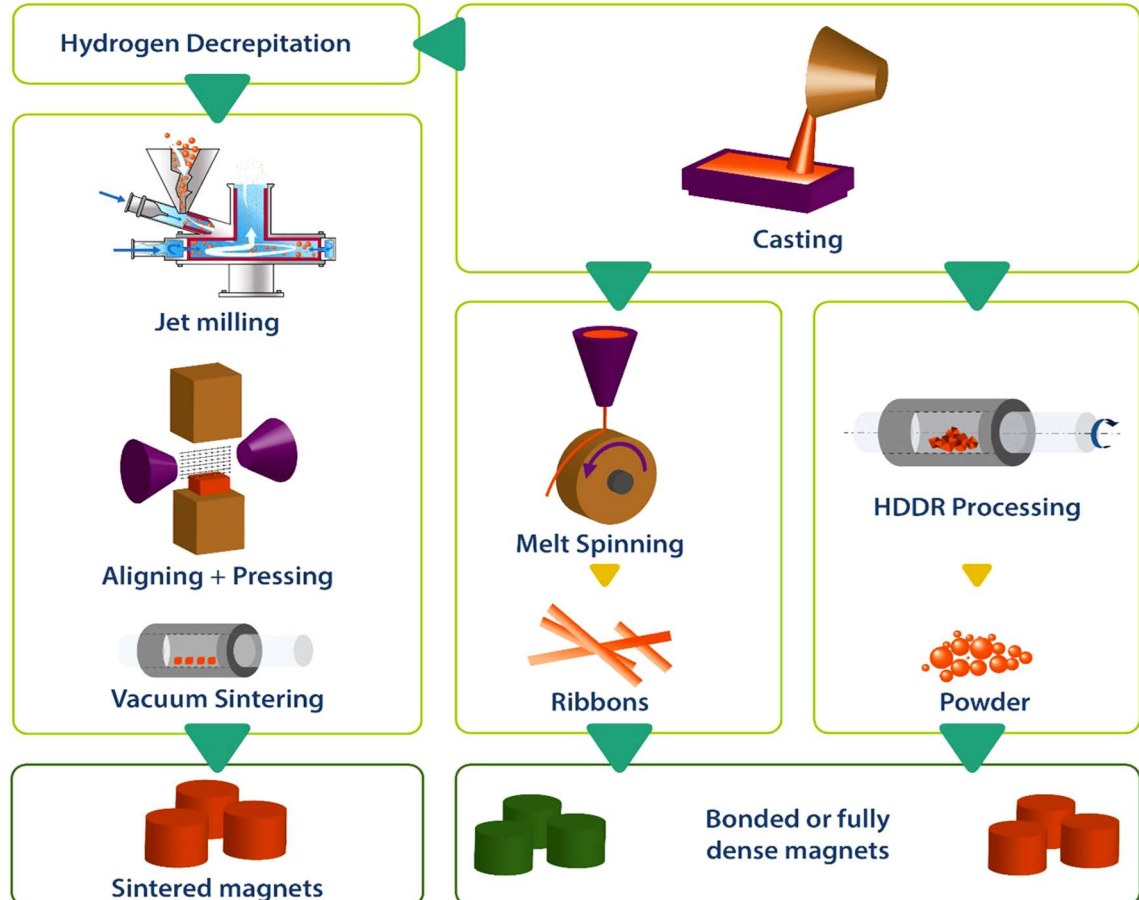


Figure 37: The manufacturing routes of Nd-Fe-B permanent magnets, courtesy of P. McGuinness and K. Binnemans et al. [11].

3.1.1.1 Conventional Alloying and Sintered Magnets

The first step in the production of sintered magnets is forming stoichiometric or RE-rich compositions by conventional casting techniques. The constituent elements in a certain stoichiometry are blended and then melted in the induction furnaces. The casting is done under the protective environment in the form of book molds or strips from the molten alloy. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is derived from the peritectic reaction (solid A + liquid phase L forms another solid phase B) upon cooling below 1200 °C. In case of book mold casting, if the cooling rate is slow enough, then α -Fe precipitates out in the form of dendrites upon cooling, which affects the crushability of the ingot because of iron's ductility. The homogenization treatments are carried out above 1000 °C for several hours or in periodic cycles to re-dissolve this free iron in the system containing excess of RE-rich phase or alloying elements like Nb, V, Ti [91, 92]. In case of a homogenized microstructure in the book-mold casting, most of the α -Fe recombines to B-rich phase or Laves phases of MFe_2 structure ($\text{M} = \text{Nb, Zr, V, Mo, Ti}$) [83, 93]. The book mold casting produces relatively coarse grains of $\sim 300 \mu\text{m}$ size, which are too big to sinter and achieve high coercivity.

As an alternative, the strip casting technique in Figure 37 allows better cooling rates ($\sim 10^4 \text{ K/s}$) which can suppress the formation of free iron in the flakes consisting of fine columnar $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains ($\sim 3 - 7 \mu\text{m}$) separated by the Nd-rich phase. This process is also more suitable for alloys with reduced rare-earth content, but if the cooling rate is not effectively controlled, then the fine precipitates of α -Fe can originate in such alloys. On the wheel side shown in Figure 38 cross-section of strips (a – c), the surface will have a higher cooling rate and the fine dendritic structure is more prominent (a). As we move towards the center of the strip, slightly lower cooling rate causes microstructure to change from coarse dendrite (b) at $55 \mu\text{m}$ to fine columnar type (c) at $82 \mu\text{m}$. The strip cast microstructure is therefore finer than the book-mold cast material. The free surface in Figure 38 (d) has the highest cooling rate and fine acicular microstructure is apparent [94].

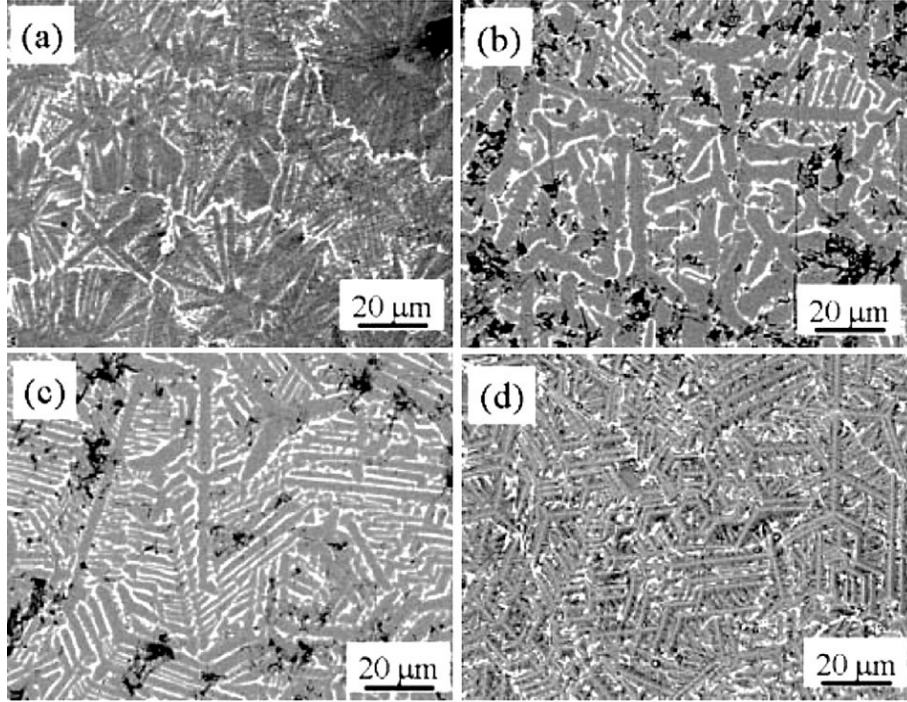


Figure 38: BSE SEM microstructure of strip cast $\text{Nd}_2\text{Fe}_{14}\text{B}$ samples with wheel side (a) fine dendritic structure at 0 μm which changes to (b) a coarse dendrite columnar structure at 55 μm , (c) fine columnar structure is apparent from region 82 μm away from the surface and (d) free surface with the highest cooling rate, courtesy of [94].

The book mold casting is then treated by hydrogen decrepitation (HD) to obtain friable loose coarse powder which can be further milled to 3 – 5 μm size. The HD process was invented by Harris et al. [95-97] in 1979 for Sm-Co alloys but was applied to newly developed Nd-Fe-B alloy in 1985. In this process, the Nd-Fe-B alloy ingot is exposed to 1 bar (0.1 MPa) pressure H_2 gas at room temperature. The hydrogen decrepitation reaction with the Nd-rich phase is given as:



The H_2 gas penetrates the Nd-rich phase to form NdH_x and as the system absorbs more hydrogen, the coarse grain structure is decrepitated due to the intergranular cracking induced by the volumetric expansion of $\text{Nd}_2\text{Fe}_{14}\text{BH}_{2.7}$ (~5 vol. %) and $\text{NdH}_2/\text{NdH}_3$ (16.4 vol. %):



Subsequently, due to exothermic nature of this HD reaction, the brittle alloy heats up, such that the matrix phase readily absorbs hydrogen and forms the $\text{Nd}_2\text{Fe}_{14}\text{BH}_x$ phase, which effectively renders the decrepitated powder non-magnetic (poor coercivity) and easier to jet mill down to desirable size range [98, 99]. The hydrogenation-induced embrittlement and volume expansion is throughout the whole magnet. P. McGuinness et al. [100] indicated that the HD treated anisotropic magnets preferentially absorb hydrogen gas along the

textured axis, such that the hydrogenation and decrepitation works from the surface towards the center of the magnet. The alloy ingots are isotropic, so they absorb hydrogen from all the surfaces with exposed RE-rich phase. The hydrogenated alloys contain a closely stoichiometric neodymium trihydride ($\text{NdH}_{2.7}$), which is unstable and forms hydroxide upon contact with oxygen. Further desorption of this trihydride to neodymium dihydride is possible at 220 – 380 °C and finally decomposition to cubic-Nd at 720 – 800 °C. The decrepitation rate is increased above 150 °C as the hydrogen is absorbed simultaneously by the Nd-rich phase as well as the 2:14:1 phase. The H_{Ci} and BH_{max} of hydrogenated powder are reduced due to the presence of hydrogen in the alloy, although the c-axis magnetization is possible, so thermal desorption is necessary to recover the magnetic properties [97, 100-102].

As shown in Figure 37, these hydrogenated powders are then sized down to 1 – 5 μm range via jet-milling. The HD process saves a lot of effort otherwise from mechanical pulverization of the cast ingots. The strip cast precursors can be directly jet milled to obtain single crystal grains in this narrow size distribution. The jet-milling has clear advantages over attrition or ball-milling because of: the large-scale continuous processing, contamination and oxygen control, rapid milling, inert gas recycling and no additional requirement for solvent drying (dry milling). In the milling chamber the high-pressure and high-speed jet streams of inert gas rapidly interact with the powder particles carrying streams, and this collision results in fine single crystalline particles. Due to fine size, the jet-milled powder must be handled with care in an oxygen-free environment [3].

Figure 37 shows that the jet milled powders are then subjected to sintering, which is a thermodynamic powder metallurgical process in which microstructural changes are brought in by elimination of porosity and diffusion assisted consolidation of the powder particles. During sintering, normally there is no chemical change. Only the microstructure changes with the removal of porosity causing shrinkage and the particles bond together forming bulk material [53]. The microstructure of sintered Nd-Fe-B magnet is presented by BSE-SEM image in Figure 36. The final magnetic properties of the consolidated magnet depend on the sintering parameters as well: temperature, time, heating rate, atmosphere, particle geometry/size, particle aspect ratio, pre-alignment, pressure and chemical composition. P. McGuinness et al. [97, 101] investigated the effect of jet milling and sintering temperatures on the final properties of the sintered magnets and concluded poor density $< 7 \text{ g/cm}^3$ is obtained for sintering at 970 °C (theoretical density $> 7.45 \text{ g/cm}^3$ for $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$). The Nd-rich phase is very important in achieving the complete densification during sintering and as a result optimal microstructure and the magnetic properties. Ormerod et al. [96, 97, 103] reported Nd-Fe-B alloys with $< 33 \text{ wt. \%}$ Nd resulted in incomplete densification and as a result magnetic properties were significantly lower. The presence of porosity is also a culprit behind the loss in coercivity (inadequate distribution of GB phase) and remanence (poor densification), which is more significant at lower sintering temperatures. With an increase in RE-content $> 34 \text{ wt. \%}$, intrinsic coercivity increased but the remanence declined because of excessive non-ferromagnetic secondary phase at the grain boundaries. Abnormal grain growth during high temperature sintering has also been reported for excessive RE-

content containing alloys [79, 97, 103]. Sugimoto [3] and Hono [17] reiterated an inversely proportional relationship between the H_{Ci} and the grain size, since the surface defects degrade the resistance to field demagnetization as reverse domain wall motion becomes easier on these sites. In larger grains, the probability of surface inhomogeneities is higher and as a result nucleation of reverse domains is favorable under low external demagnetizing fields. So the impurities, vacancies, oxides, inclusions, lattice distortions, microstructural strains, interfacial dislocations, soft magnetic phases, etc. are regions along the surface of hard grains that can cause reverse domain nucleation [13]. The researchers have also used the Pressless Sintering Process (PLP) to develop high coercivity magnets from ultrafine jet milled powders (1 – 2 μm size), which does not require pre-alignment of green compacts [104-106].

3.1.1.2 Melt spinning Nd-Fe-B

Croat et al. [8] introduced the melt-spinning as an alternative to the powder metallurgical processing of Nd-Fe-B, forming hard phase grains of size close to the single domain size. In the melt-spinning process, as shown in Figure 37, a molten jet of Nd-Fe-B alloy is coerced through an orifice on the water-cooled Cu wheel rotating at high speeds, such that the achieved cooling rates are 10^6 K/s. In principle, such rapid cooling should induce glassy transitions in the system and suppress any α -Fe formation, so the nanocrystallites of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase (~ 50 nm) form up with the amorphous Nd-rich phase due to the undercooling effect. The flake-like powder consists of high coercivity, brittle, chemically stable and magnetically isotropic ribbons of thickness $\sim 30 - 50$ μm [76, 82, 107]. Croat suggested that the coercivity values are strongly dependent on the quenching rate i.e. the speed of the wheel which influence the grain size of nanocrystallites. Under-quenching will produce larger sized grains while over-quenching will reduce the grain size to an amorphous regime, and both these cases are detrimental for the coercivity [8]. The amorphization of the crystallites can be transformed to the crystalline nanostructure by the annealing treatments above 500°C . These melt-spun ribbons (MSRs) can be used in the isotropic polymer bonded magnets or can be hot-deformed to induce excellent texture along the c-axis, reaching BH_{max} values ~ 286 kJ/m³. The measure of coercivity values of hot-deformed MSRs in comparison to the sintered Nd-Fe-B magnets is given in Figure 34 [76]. The diffusion processing with low melting eutectic alloys and HREE-rich species have been investigated for improving the coercivity of the hot-deformed MSRs [75, 108-117].

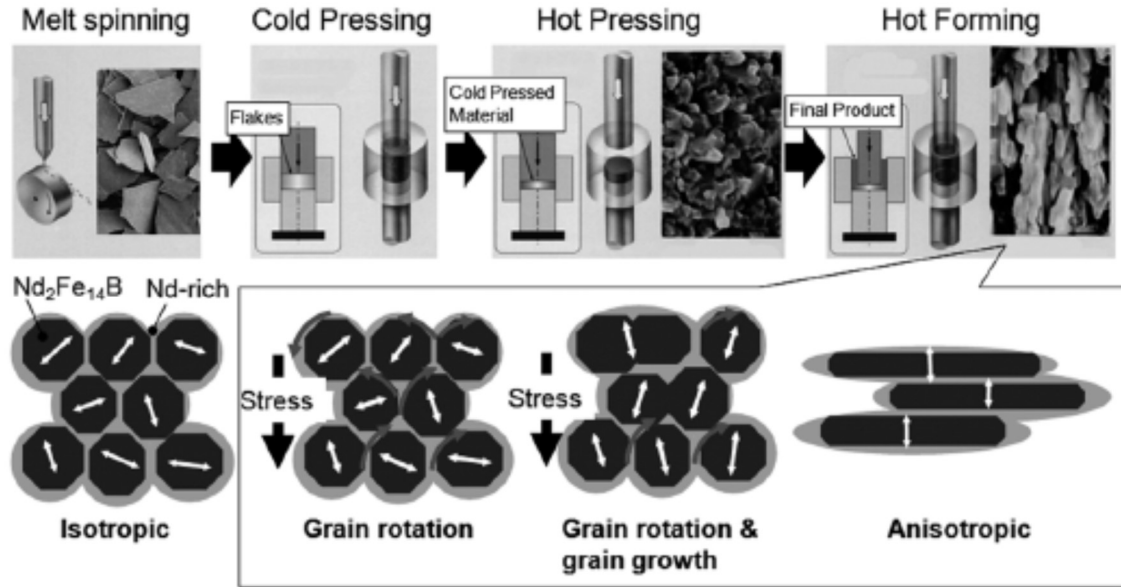


Figure 39: Illustration of the hot-deformation process of the Nd-Fe-B melt-spun ribbons, courtesy of S. Sugimoto [3].

Figure 39 illustrates the hot deformation process of Nd-Fe-B MSRMs to develop anisotropic nanocrystalline grains, which enhances the B_r and $BH_{\max}$ of isotropic precursors due to the c-axis plastic flow. The lack of coercivity after hot deformation can be associated with the rotation of the grain boundary phase in the region perpendicular to the c-axis as the grains elongate in size. Die-upsetting is a similar process applicable to MSRMs for developing anisotropic ring shaped magnets [3]. Figure 40 (a) shows the bright-field TEM images of the hot-deformed MSRMs, which are surface diffusion processed with the $\text{Nd}_{60}\text{Dy}_{20}\text{Cu}_{20}$ eutectic alloy in (b). The improvement in the H_{ci} is attributed because of the additional RE-rich, which modified the grain boundary chemistry for reducing the ferromagnetic effects arising from the grain boundaries (rich with transition metals) and suppressing the localized exchange coupling interactions of the nanocrystalline grains [108].

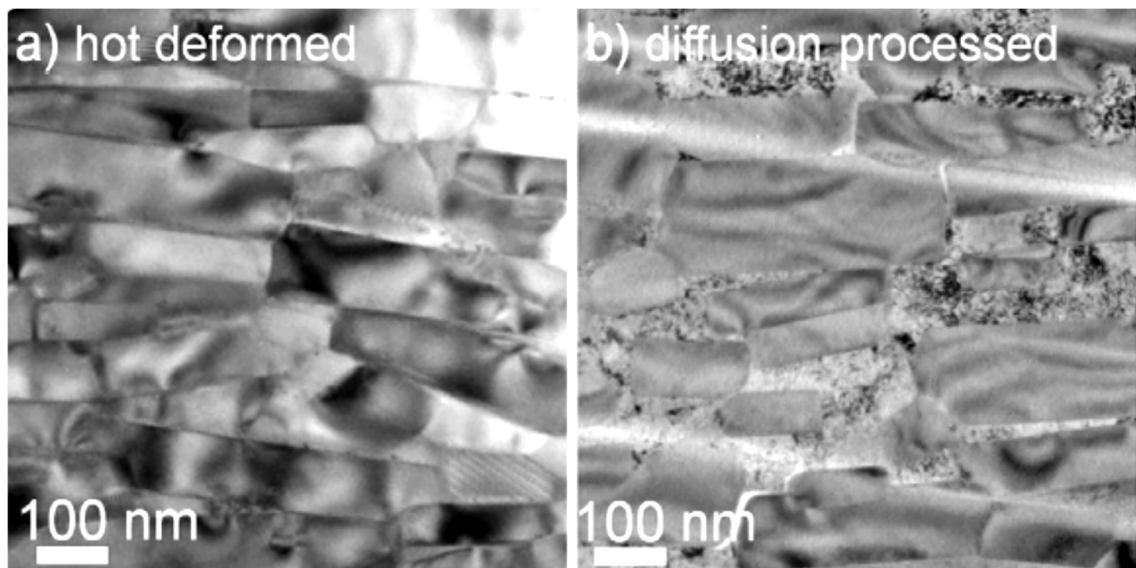
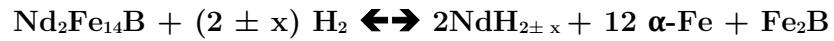


Figure 40: BF-TEM of (a) hot deformed Nd-Fe-B melt-spun ribbons, and (b) the surface-diffusion treated hot-deformed magnet with Nd-Dy-Cu alloy, courtesy of H. Sepehri-Amin et al. [108].

3.1.1.3 Hydrogenation Disproportionation Desorption Recombination (HDDR) treated Nd-Fe-B

The Hydrogenation Disproportionation Desorption Recombination (HDDR) is a reversible two stage hydrogenation and disproportionation process for refining the grain size of Nd-Fe-B alloys to ≤ 400 nm. In the hydrogen decrepitation (HD) process, the H_2 gas is absorbed at room temperature by the RE-rich grain boundary phase, which causes an intergranular collapse of the alloy. While in the HDDR process illustrated in Figure 41, hydrogen will first diffuse in to the grain boundary phase which causes cracking due to larger lattice parameters of hydride phase ($NdH_{2.7}$) and then it diffuses in to the matrix grains at a higher temperature. The HDDR process initiates with vacuum in Stage I (hydrogenation) and 1 bar pressure of H_2 . The H_2 gas is absorbed by rare earth grain boundary regions at room temperature. In Stage II (disproportionation): hydrogenated system is heated to 800 °C, such that the matrix $Nd_2Fe_{14}B$ grains decomposes to bcc α -Fe, tetragonal Fe_2B and fcc NdH_2 . The hydrogen gas is then evacuated at 800 °C in stage III (desorption) and replaced by vacuum. In Stage IV (recombination), the disproportionated species undergo reversible transformation to $Nd_2Fe_{14}B$ uniform ferromagnetic grains in the submicron size range (~ 300 nm) separated by continuous thin Nd-rich phase (of 2 – 3 nm) [118-125]. The hydrogen-induced reversible phase transformations during the HDDR process can be written as:



After the completion of the recombination step, the ultrafine $Nd_2Fe_{14}B$ grains nucleate at the interface of $NdH_2 - Fe_2B$ grains, while preferentially growing along the c-axis through the α -Fe – NdH_2 interface [3].

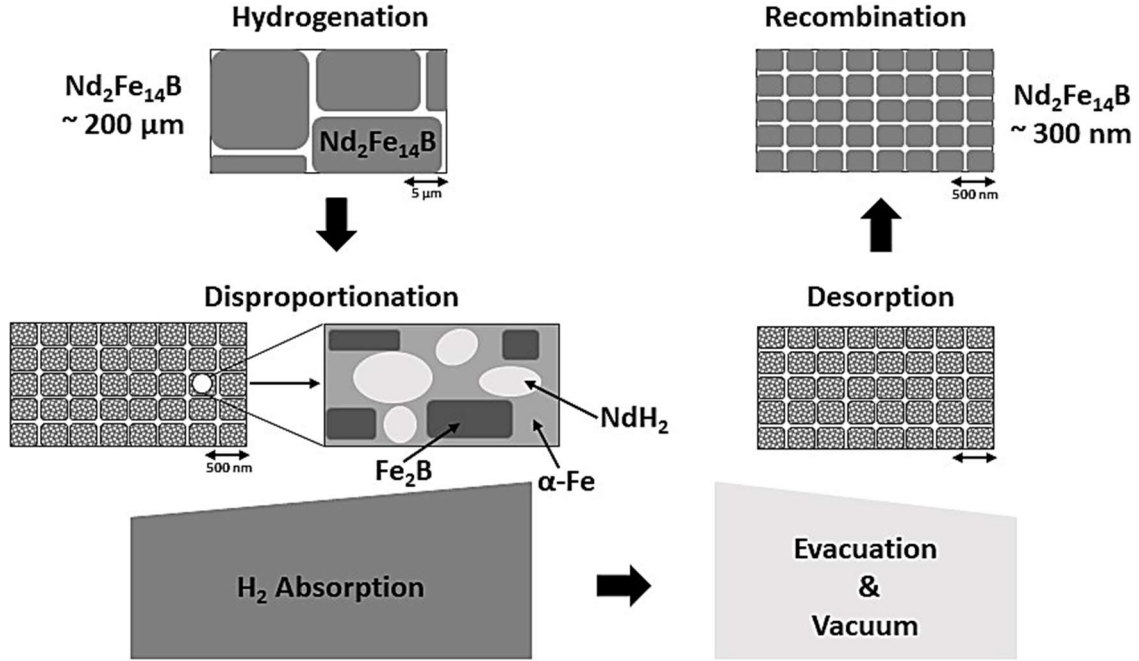


Figure 41: Schematic illustration of the two-stage hydrogenation and disproportionation induced transformation in the HDDR process, adapted from [3].

As a comparison to the melt-spinning process, the HDDR process can be tuned to develop anisotropic powders with ultrafine grains aligned towards the easy axis in each micron size particle. This modification in methodology is called texture memory effect and the process is termed as the dynamic-HDDR (*d-HDDR*). The anisotropy development in the HDDR powders is strongly dependent on hydrogen pressure (30 kPa) and temperature (800 – 820 °C) during the disproportionation stage, as shown in Figure 42, which shows that the hydrogen pressure of 100 kPa during HD stage leads to misaligned grains of Fe_2B boride phase at an early DR stage [126]. The studies indicate that the formation of the nanoscopic tetragonal Fe_2B boride phase in the disproportionated mixture at $P_{\text{HD}} = 30$ kPa holds the c-axis alignment of parent micron size $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. This c-axis alignment is unaffected throughout the disproportionation at 800 °C and also during hydrogen desorption. This has been labelled as the texture memory effect (TME). Therefore, during the recombination, this tetragonal boride phase remembers its texture and becomes the site for c-axis-oriented submicron-sized $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, separated by a thin paramagnetic Nd-rich grain boundary phase [119, 120, 125, 127-130].

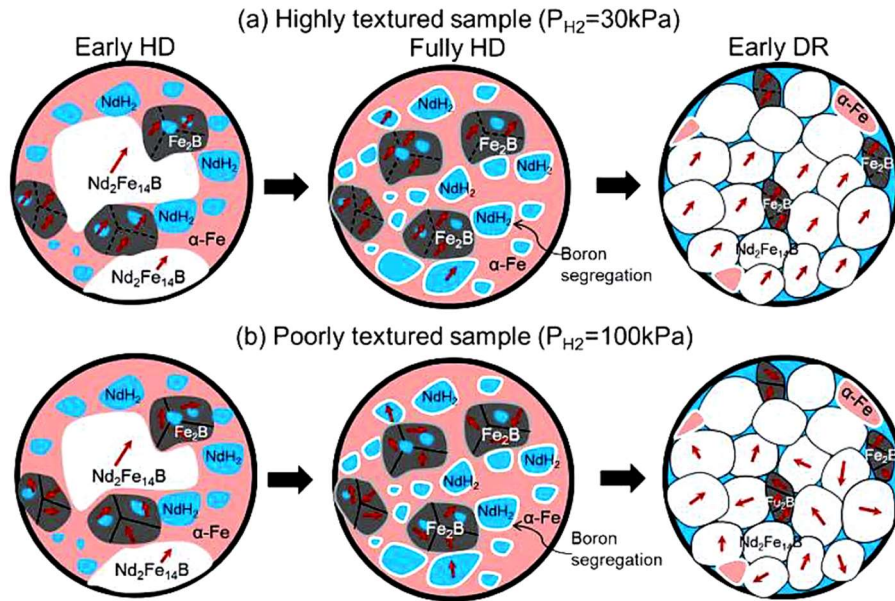


Figure 42: Microstructural evolution in d-HDDR process at (a) $P_{HD} = 30 \text{ kPa}$ and (b) $P_{HD} = 100 \text{ kPa}$, courtesy of H. Sepehri-Amin [126].

It is important to consider that the powder particles each hold the TME along the c-axis, but these particles unless consolidated as bonded or hot-pressed magnets are randomly oriented without field magnetization. By controlling the hydrogen pressure before vacuum desorption, the biaxial texture is introduced by the d-HDDR process (Figure 43), such that the TME effect recovers the c-axis alignment of the $\sim 300 \text{ nm}$ grains after the recombination is complete, whereby the initial grains of the isotropic sintered magnet or the crushed alloy ingots will have the orientation with a-axis and they may be randomly oriented. The randomness of a-axis should be less of a problem in the anisotropic sintered magnets, which can be d-HDDR-treated. After the field magnetization, the c-axis texture of all the HDDR grains will be the same [131].

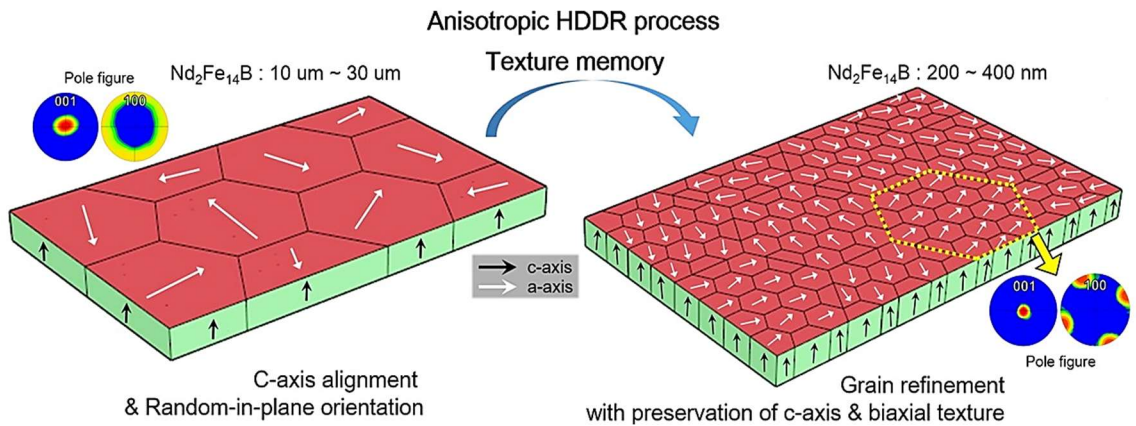


Figure 43: Schematics of the texture memory effect in HDDR Nd-Fe-B powder quantified with EBSD pole figures, graphical abstract courtesy of T. Kim et al. [131].

The microstructure of the HDDR powder particles in the range of $100 - 300 \mu\text{m}$ is shown in Figure 44 (a) with $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase grains approx. $300 - 400 \text{ nm}$ in size

from as shown in the SE image of Figure 44 (b) [132]. The characteristic microstructure of the HDDR powder is shown in Figure 44 (c) with bright Nd-rich phase distributed along the grayish matrix of ultrafine $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. Depending on the composition, the GB phase distribution is inhomogeneous throughout the microstructure. Figure 44 (d) shows the high resolution – TEM image of the HDDR Nd-Fe-B powder with less than stoichiometric value 12.9 at. % Nd and no aluminum in the composition. K. Morimoto et al. suggested that in such a case, the thickness of the Nd-rich intergranular phase is not more than 1.5 nm, which increased to more than 3 nm with the addition of 1.5 at. % Al. The improvement in the coercivity with 13.5 at. % Nd and 1.5 at. % Al is substantial, corresponding to the value 1550 kA/m [133].

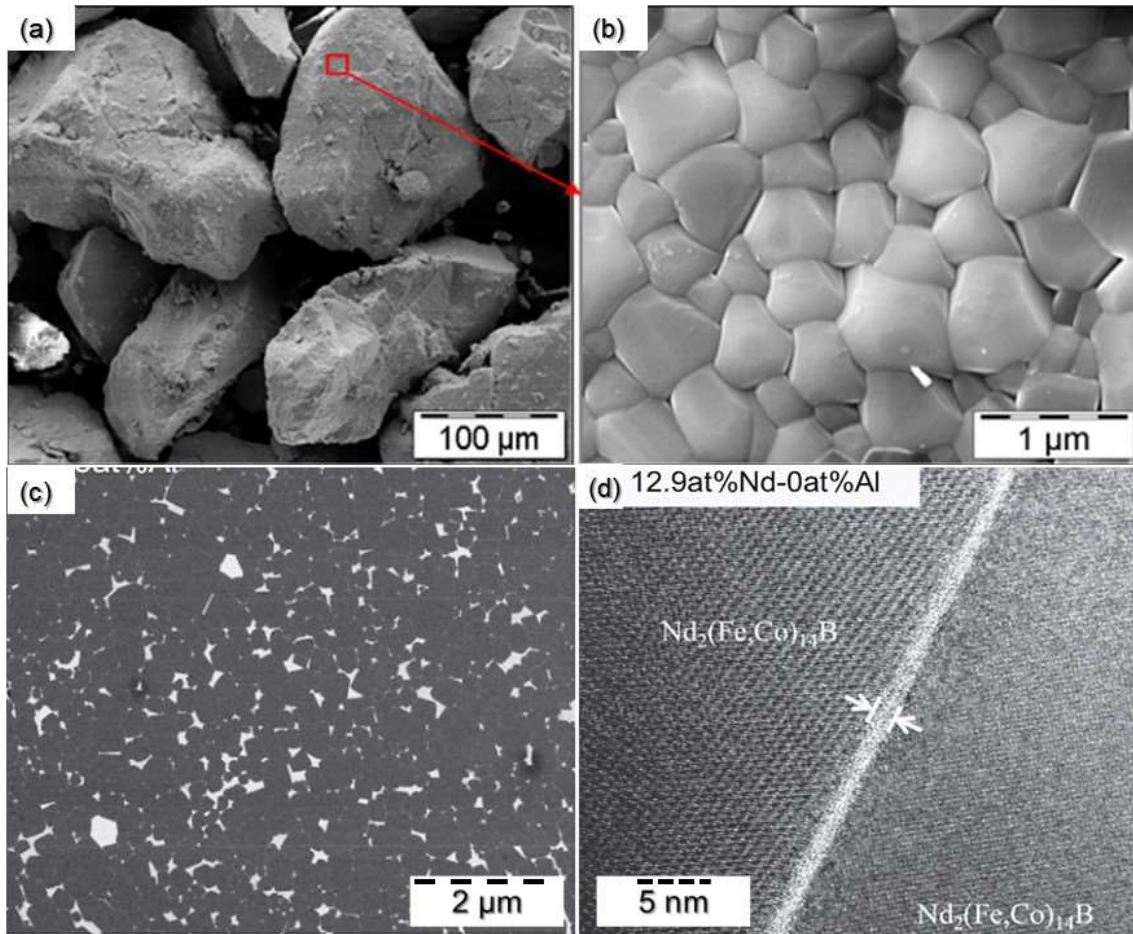


Figure 44: Microscopical characterization of HDDR Nd-Fe-B: (a) secondary electron (SE) of micron-sized powder particles, (b) high magnification SE image of ~ 400 nm-sized $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains courtesy of S. K. Pal et al. [132] for a & b; (c) the characteristic backscattered electron (BSE) image with bright regions as Nd-rich and grey matrix phase is $\text{Nd}_2\text{Fe}_{14}\text{B}$, and (d) high-resolution TEM image of HDDR powder with 12.9 at. % Nd and 0 at.% Al, courtesy of K. Morimoto et al. [133] for c & d.

Unlike the MSR, the Nd-rich phase in the HDDR Nd-Fe-B powder exposed on the surface is prone to room temperature oxidation. The Nd-rich phase is present in the form of NdO_x (NdO and NdO_2) in the HDDR powder along with the cubic Nd_2O_3 phase. With

a decrease in particle size $< 100 \text{ }\mu\text{m}$, the surface area of the HDDR powder increases significantly, thereby making it more susceptible to oxidation as more Nd-rich phase is exposed [134]. In such a case, the Nd-rich phase and cubic Nd_2O_3 phases undergo hcp-transformations [83, 135].

T. Horikawa et al. [120] reported that with a temperature-pressure and compositional controlled *d-HDDR* process, exceptionally high $B_r = 1.42 \text{ T}$ and $BH_{\text{max}} = 372 \text{ kJ/m}^3$ from the textured nanocrystalline powder is possible, and the $H_{\text{Ci}} = 1120 \text{ kA/m}$ without the HREEs. W. F. Lie et al. [46, 47] proposed that a thick and continuous non-ferromagnetic grain boundary phase is important for improvement in the coercivity of the HDDR Nd-Fe-B powder. Suresh and Goplan [39, 66] showed Spark Plasma Sintering (SPS) is suitable to fully consolidate or perform the hot-deformation on the HDDR powder. Suresh et al. [39, 66] reported anisotropic sintered magnets from the HDDR powder with $BH_{\text{max}} = 210 \text{ kJ/m}^3$ developed by SPS hot deformation. K. Takagi [134] utilized SPS on commercial HDDR power MF-15P and achieved $H_{\text{Ci}} \sim 1180 \text{ kA/m}$. The magnetically isolated nanocrystalline grains will theoretically have higher coercivities ($> 2000 \text{ kA/m}$) according to Eq. (2.15) but the absence of grain boundary phase causes localized exchange effects [47]. The exchange effects are also pronounced if the grain boundaries are ferromagnetic, containing excessive Fe and Co [46]. K. Morimoto [133] added up to 2 at. % Al in the HDDR system and reached $H_{\text{Ci}} > 1550 \text{ kA/m}$, due to reduction in the ferromagnetic constituents of the grain boundaries by Al. Therefore, H. Sepehri-Amin [41] introduced the Nd-Cu eutectic alloy during diffusion processing of the HDDR powder and the H_{Ci} increased to 1152 kA/m . The obvious effect of Nd-Cu diffusion treatment was widening of the grain boundary phase as shown in the bright field TEM images in Figure 45. The distribution of the Nd-rich phase in the microstructure increased for the diffusion treated sample. Similarly, T. Song reached $H_{\text{Ci}} \sim 1280 \text{ kA/m}$ and $B_r = 1.13 \text{ T}$ in the HDDR hot-pressed magnets by the eutectic Pr-Cu alloy diffusion [136]. Sugimoto et al. [137] investigated the combined effect of He-jet milling on the HDDR powder and reached superior $H_{\text{Ci}} \sim 1580 \text{ kA/m}$ after the diffusion treatment with the $\text{Nd}_{80}\text{Cu}_{10}\text{Al}_{10}$ alloy. Therefore, the room for improvement in the H_{Ci} of near single-domain-sized HDDR Nd-Fe-B powder is still large as the exact mechanism governing the coercivity and interplay of grain boundary phase is not thoroughly understood.

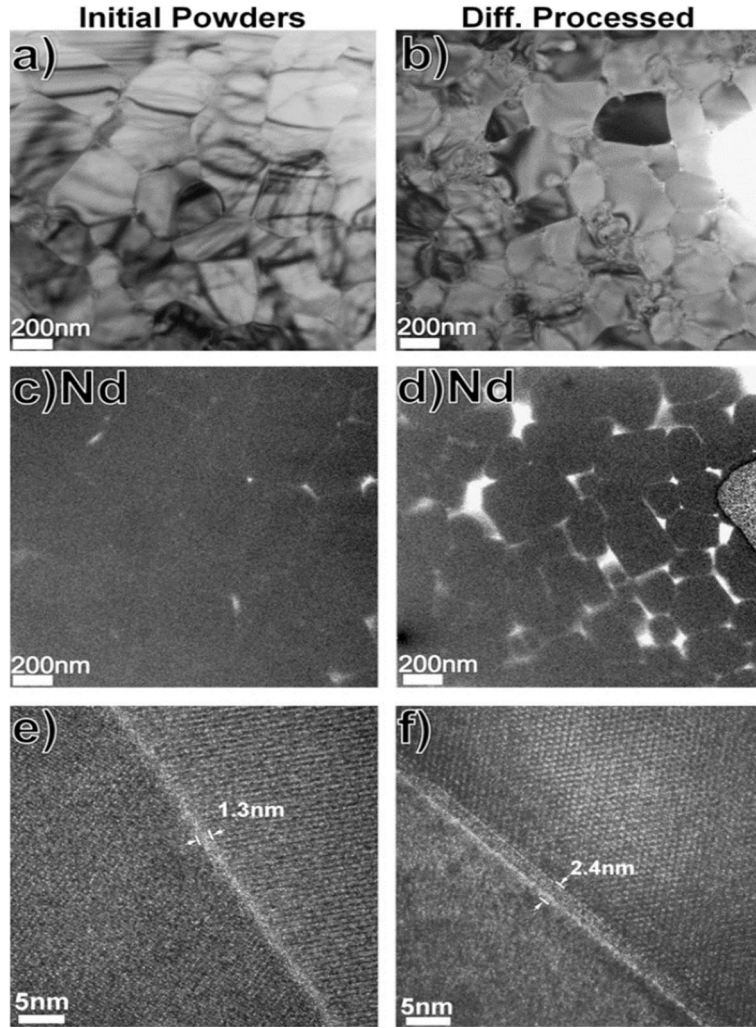


Figure 45: Bright field TEM images of (a) the initial HDDR powder, (b) the diffusion processed HDDR powder with Nd-Cu eutectic alloy; the energy filtered Nd map (c) of the initial HDDR powder and (d) diffusion-processed powder; and the HR-TEM micrographs of (e) precursor and (f) the diffusion-processed powder, courtesy of H. Sepehri-Amin [41].

The HD and HDDR processes can be considered as effective tools in recycling the end-of-life (EOL) magnets from industrial scrap or various discarded electronics, as explained in Figure 4. Since the hydrogen gas can be recycled, these methods exploit the resource conservation and green technology potentials. The HD treatment makes alloys prone to cracking, and therefore can be used to separate the friable loose Nd-Fe-B powder from the coarse protective coatings. The decrepitated powder can be effectively HDDR-treated and previous findings make them a promising candidate for the bonded magnet applications [19, 121, 130, 138-141]. This becomes important as the scrap magnets are recycled with the HDDR route and the complete understanding of HDDR system, the process control and derived microstructure will allow tailorable magnetic properties from these nanocrystalline powders.

3.1.1.4 Nd-Fe-B Bonded Magnets

For the polymer-bonded magnets, the main consumer requirements are: low costs (material and manufacturing), shape flexibility and mass production. Fine hydrogen decrepitation (HD) powders of Nd-Fe-B or Sm-Co and nanocrystalline powders (MSRs and HDDR) are usually mixed with a variety of resins like nylon, epoxy, rubbers, polyvinyl alcohol (PVA), polypropylene acetate (PPA), polypropylene sulfide (PPS), etc. The bulk of polymer bonded magnets are made through Injection Molding, Compression Molding, Extrusion and Hot Pressing shown in Figure 46. These bonded magnets have a maximum service temperature of 150 °C. They experience deterioration in the physical and magnetic properties with the rise in temperature due to the thermal degradation, creep, UV radiation, humidity/environmental severity, wear and large fluctuating stresses [32, 142-144]. The magnetic powder used for these bonded applications can be produced by melt spinning, atomization, cast alloy ingot crushing, jet/abrasive milling, HD, HDDR etc., which are then mixed with polymeric resins and pressed to various shapes depending on the type of application. The hybrid bonded magnets with Zn metal [145] or Nd-Fe-B/Mn-Bi dual hard phase composite magnets [146] also present an alternate opinion in making the bonded magnets suitable for high temperature applications.

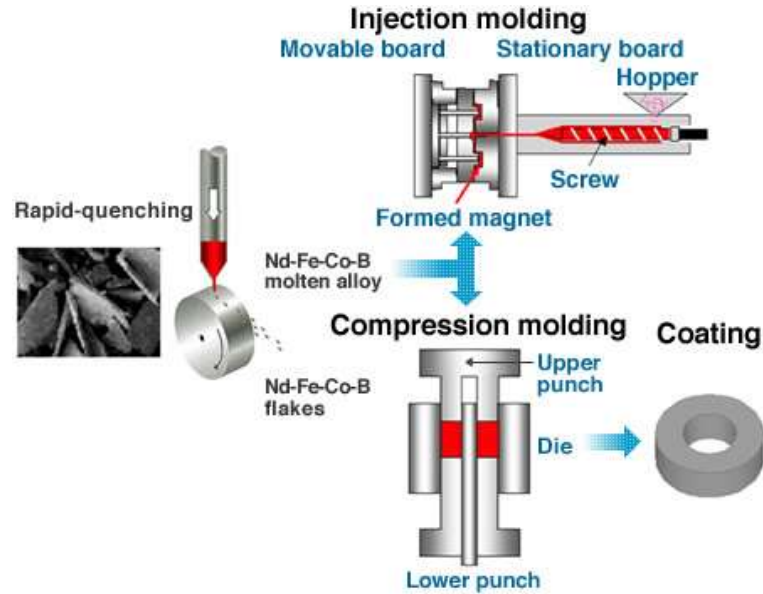


Figure 46: The popular manufacturing routes for bonded magnets, courtesy of Daido Electronics Japan, source:

http://www.daido-electronics.co.jp/english/product/neoquench_p/.

Due to magnetic phase dilution with the addition of polymer resins, the B_r and BH_{max} of the bonded magnets are significantly lower than sintered magnets, but the mass manufacturing at low cost and shape flexibility retains strong market demand for the bonded magnets [139, 142]. The BH_{max} of anisotropic Nd-Fe-B – epoxy bonded magnets made by compression molding are in the range of 120 – 145 kJ/m³. The BH_{max} values are only 40 – 48 kJ/m³ in case of bonded isotropic Nd-Fe-B injection molded magnets. The experimentally verified values of H_{Ci} are 900 – 1200 kA/m and $B_r = 0.7$ T. The reversible

temperature coefficient (RTC) of B_r (α) for anisotropic Nd-Fe-B magnets is approx. 10% smaller as compared to the isotropic bonded magnets and as previously explained this RTC theory is also valid for the sintered Nd-Fe-B magnets [139, 142, 147].

3.1.2 High Temperature Performance and its Modification in the Nd-Fe-B Permanent Magnets

The magnetic properties of Nd-Fe-B type sintered permanent magnets deteriorate severely above 100 °C due to a relatively low T_C and negative absolute temperature coefficients of intrinsic coercivity ($\beta = -0.55 - 0.65 \text{ }^\circ\text{C}^{-1}$) and remanence ($\alpha = -0.12\%/^\circ\text{C}$). This means that an increase in 10 °C of temperature will cause $\sim 6.5\%$ H_{CI} reduction in the Nd-Fe-B permanent magnets. At 200 °C, usually there is negligible magnetization left in HREE-free Nd-Fe-B permanent magnets. These values are substantially higher than the SmCo_5 -based magnets, having $T_C \geq 720 \text{ }^\circ\text{C}$, $\alpha \sim -0.03\%/^\circ\text{C}$ and $\beta \sim -0.15 \text{ }^\circ\text{C}^{-1}$ [3]. Figure 47 (a) shows the demagnetization plots for HREE-free Nd-Fe-B magnets tested at 25, 50, 70, 90 and 120 °C, indicating a representative decline in intrinsic coercivity and magnetization with operating temperature up to 120 °C and calculated the average value of $\beta = 1.773 \text{ }^\circ\text{C}^{-1}$ in this temperature range [148].

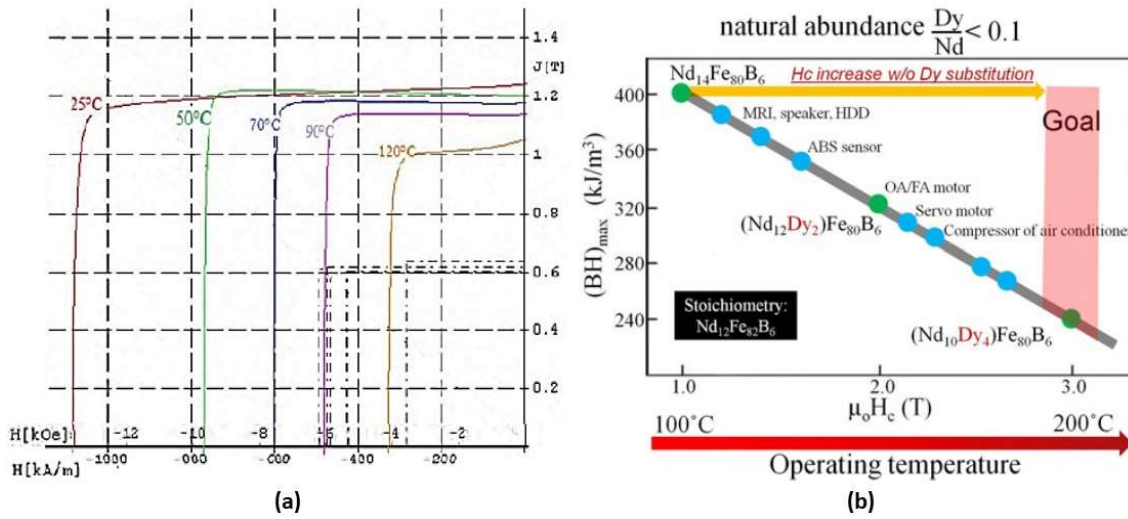


Figure 47: (a) the magnetization polarization curves at different temperatures of HREE free Nd-Fe-B sintered magnet, courtesy of M. Calin and E. Helerea [148] and (b) the projected temperature dependence of energy product and coercivity in the HREE free Nd-rich compositions, sourced from K. Hono et al. [17].

The T_C of Nd-Fe-B can be improved by substituting Nd with Dy or Tb and Co for a fraction of Fe in the system, which obviously has a negative impact on costs (raw material and manufacturing) as well as causes imbalance of rare earth criticality due to supply chain risk associated with the 2011 RE crisis [10, 11]. In case of pure $\text{Nd}_2\text{Co}_{14}\text{B}$ system, the T_C value is 722 °C and anisotropy field $\sim 3600 \text{ kA/m}$ approx. A small addition of Co to the Nd-Fe-B system invariably increases the T_C and α , but the H_{CI} decreases slightly due to the presence of the soft magnetic phases $\text{Nd}(\text{Fe},\text{Co})_2$, favoring the nucleation of reverse domains at lower demagnetizing fields. Alloying with Al, Cu and Nb can help prevent soft

magnetic phase formation [17, 40, 48, 91, 149, 150]. The superimposed goal in Figure 47 (b) for reaching room temperature $H_{Ci} \sim 2400$ kA/m ($\mu_0 H_C = 3$ T) has not yet been fully realized without HREEs additions. Although with the HREEs addition, the increase in T_C is only slight, but these elements contribute to the exceptional increment in the resistance to field demagnetization. The anisotropy fields for $\text{Dy}_2\text{Fe}_{14}\text{B}$ ($H_a = 11900$ kA/m) and $\text{Tb}_2\text{Fe}_{14}\text{B}$ ($H_a = 17500$ kA/m) are orders of magnitude higher than $\text{Nd}_2\text{Fe}_{14}\text{B}$ ($H_a = 5350$ kA/m). An alternate technique which allows HREE conservation in magnet production is the grain boundary diffusion process (GBDP) for achieving higher H_{Ci} in rare earth lean magnets [3, 16]. In the first case, the surface of the Nd-based hard phase grains can be reinforced with forming a shell structure of $\text{H}_2\text{Fe}_{14}\text{B}$ ($\text{H} = \text{Dy}, \text{Tb}$) which have subsequently higher anisotropy fields and coercivities than the underlying cores of $\text{Nd}_2\text{Fe}_{14}\text{B}$, so a higher demagnetizing field is required for the nucleation of reverse domains at the surface [3, 12, 16]. Nakamura et al. [151] presented the ‘Grain Boundary Diffusion Process (GBDP)’ in 2005, which suggested enriching the grain boundaries of Nd-Fe-B magnet with Dy from the surface, such that the anisotropy field at the surface of 2:14:1 grain is higher than the inside. The GBDP leads to the widening and uniform distribution of grain boundary spacer phase between the two adjacent $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains such that the localized exchange effects are reduced due to this magnetic decoupling [3, 17, 45]. The chemistry of this continuous Nd-rich intergranular phase is modified to make it paramagnetic, which in turn magnetically isolates the $\text{Nd}_2\text{Fe}_{14}\text{B}$ adjoining grains at the nanoscale. Usually low melting alloys with RE-rich composition are used, which can effectively diffuse from the surface to the bulk along the grain boundary channels, smoothening the grains’ surface and making the interface more uniform. These processes are favorable over the conventional two-alloy method because of the minimization of the HREE content used in the diffusion treatment (an approach towards HREE free REPMs), and secondly with a control of the microstructure, the reduction in remanence and saturation magnetization can be significantly lower [3, 12].

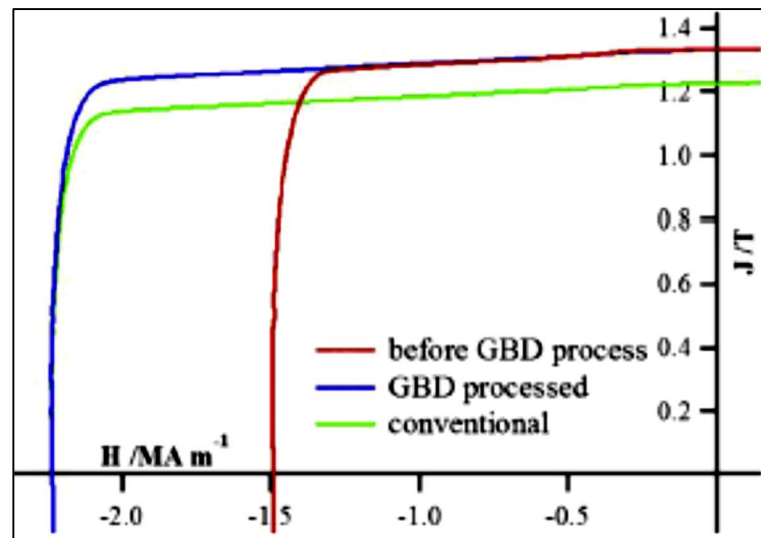


Figure 48: The demagnetization behavior of sintered magnets before and after the GBD process, courtesy of H. Nakamura [16].

Conventionally sintered magnets can be treated with small amounts of HREE based alloying species diffusing from the surface to the grain boundaries during heat treatment and finally solidifying at the local grains. This method improved the intrinsic coercivity by forming several nanometers thick HREE-rich $R_2Fe_{14}B$ shell on the surface of $Nd_2Fe_{14}B$ core grain, without a considerable reduction in the magnetization (M_r and M_s) [3]. The GBDP technique is also promising from the HREE criticality point-of-view as HRE content is usually ≤ 2 wt. %. Figure 48 shows the improvement in the H_{Ci} of $Nd_{12.4}Dy_{1.7}Fe_{bal}Co_{2.5}Al_{0.5}Cu_{0.2}B_{6.1}Zr_{0.1}$ sintered magnet by adding Tb-oxide as a diffusion source to > 2200 kA/m [16]. M. Tang [152] used Pr-Cu, Dy-Cu and Pr-Dy-Cu eutectic alloy ribbons to increase the H_{Ci} of the sintered magnets up to 1700 kA/m. Liu et al. [153] tested various binary eutectic alloys for surface GBD and found $Nd_{90}Al_{10}$ improved H_{Ci} to 1900 kA/m and Nd-Cu reached ~ 1840 kA/m. Similarly H. Sepehri-Amin et al. [110] reported achieving $H_{Ci} \sim 1990$ kA/m and $B_r = 1.3$ T in Pr-Cu diffusion processed hot-deformed magnets. M. Soderznik [154], S. E. Park [155, 156], S. Sawatzki [157, 158] and K. Zagar et al. [69] used DyF_3 as the doping agent to augment the coercivity of sintered magnets and hot-deformed melt-spun ribbons. Similarly, the Tb-based dopants have been equally effective for the sintered magnets in achieving the coercivities greater than 2000 kA/m [116, 159-161]. A variety of diffusion species ranging from Dy/Tb vapors, metal sputtering, HREE-oxides, fluorides, sulfides, hydrides, low melting eutectic ribbons and two-alloy precursor powders has been extensively reported [43, 111, 113, 137, 153, 154, 159, 161-171]. The drawback with the most GBD processes is that they only offer limited penetration and diffusion depths from the surface and therefore may only be applicable to thinner magnets (< 5 mm thick).

3.2 The Sm-Co System

Sm- Co_5 permanent magnets were discovered by Strnat et al. [5, 6] in 1967, having a hexagonal $CaCu_5$ type crystal structure with the $P6_3/mmm$ space group as shown in Figure 49. The lattice parameters of 1:5-unit cell are: $a = 4.99$ Å and $c = 3.98$ Å. The easy axis of magnetization is also along the hexagonal c-axis (0001) and the hard axis is towards the (10 $\bar{1}$ 0) direction. The $SmCo_5$ REPMs have the highest uniaxial magnetocrystalline anisotropy $H_a \sim 31800$ kA/m, the $H_{Ci} > 2000$ kA/m, $M_s \sim 1.12$ T and a superior $T_C = 720$ °C. The BH_{max} of $SmCo_5$ permanent magnet has reached experimental value of 160 kJ/m³. As compared to the Nd-Fe-B magnets, they have lower RTC of remanence, $\alpha = -0.05$ %/°C and for coercivity $\beta = -0.5$ %/°C [73].

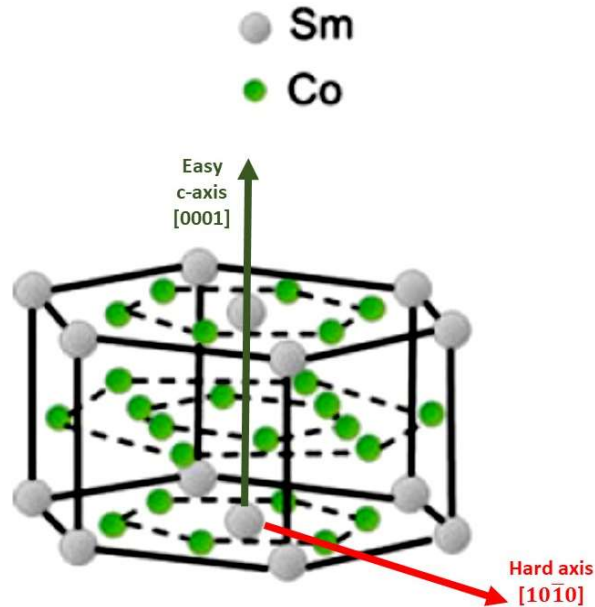


Figure 49: The crystal structure of the SmCo_5 type hexagonal compound with magnetization easy axis along the c-axis, courtesy of F. Villacorta [74].

Industrially, the SmCo_5 REPMs are produced as fully dense sintered magnets, but the bonded magnets are also made with thermoset resins having higher thermal stability. The Sm-Co powders are HD-treated and jet-milled to size range of 5 – 10 μm for field pressing and sintering. Figure 50 (a & b) shows the microstructure of HD-processed stoichiometric SmCo_5 powders. The microstructure of SmCo_5 sintered magnets is composed of 1:5 matrix phase and the Sm-rich phases: $\text{Sm}_2\text{Co}_{17}$ and $\text{Sm}_5\text{Co}_{19}$ and the oxides (SmO , Sm_2O_3) as shown in Figure 50 (c & d). The SmCoC carbide phase has also been reported recently [73].

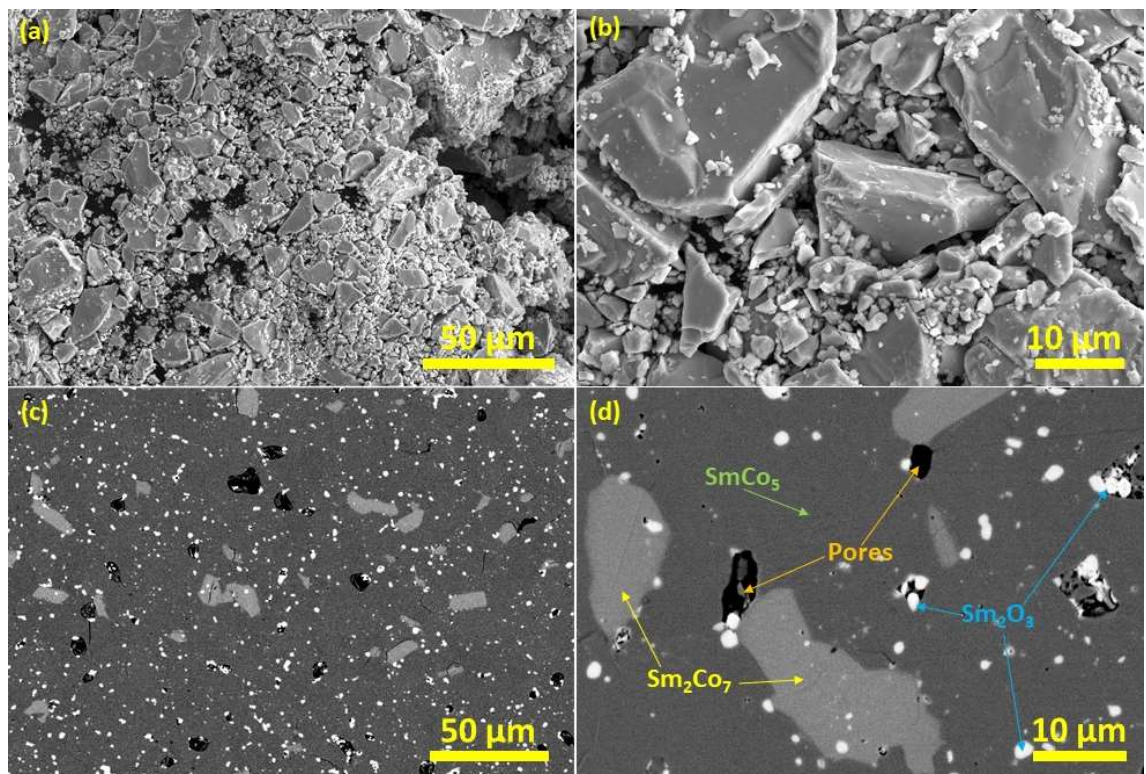


Figure 50: HR-SEM BSE micrographs of (a) HD treated SmCo_5 powder at low magnification, (b) high magnification of powder and (c) vacuum-sintered magnet from HD-treated SmCo_5 powder, (d) high magnification and possible phases identified with EDXS, adapted from the supplementary material of A. Eldosouky et al. [172].

The coercivity mechanism of the SmCo_5 type permanent magnets is based on pinning the movement of inverse domain walls by secondary phases, grain boundaries ($\text{Sm}_2\text{Co}_{17}$) and/or precipitates [173-175]. Therefore, the control in the amount of secondary Sm_2Co_7 -based Sm-rich liquid phase and reduced formation of Sm_2Co_3 is important during the sintering with the SPS. Excessive transformation of SmCo_5 i.e. the hard-magnetic phase to Sm_2Co_7 phase, leads to the decline in the magnetic properties, therefore the optimal SPS temperature and holding times were established for the HD-treated fresh and recycled SmCo_5 powder. The elevated temperature (180 °C) magnetic properties were determined and compared with the conventionally vacuum sintered SmCo_5 magnets.

3.2.1 Production of SmCo_5 Permanent Magnets

The bulk of industrially produced 1:5 magnets are made via conventional powder metallurgical methods, as shown in Figure 51. The Sm-Co (hcp 1:5) stoichiometric mixtures are commercially vacuum or induction cast in the form of blocks. These cast alloys are then grounded or HD treated before jet-milling to make fine-sized powders for the sintered magnets. Green compacts are made with axial (isotropic) or isostatic pressing (pre-aligned anisotropic) and then sintering is carried out at the temperature range $\sim 1100 - 1250$ °C. Normally 1:5 sintered magnets do not require additional thermal treatments, but possibly tempering treatments to reduce the brittleness, since they are more prone to chipping and cracking at the edges than the Nd-Fe-B magnets. Therefore, the overlay Ni/Ni-Cu or Al-based protective coatings are mandatory for the Sm-Co-based PMs [176].

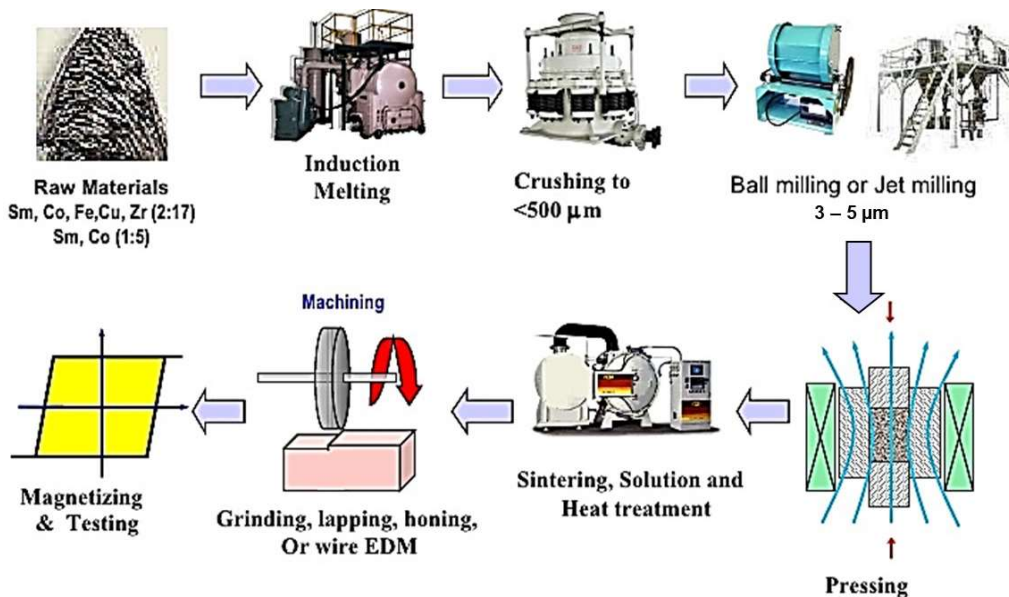


Figure 51: Schematics of the conventional powder metallurgical route for the Sm-Co-based permanent magnets, courtesy of J. Liu et al. [176].

3.2.1.1 Hydrogen Decrepitation (HD) of SmCo₅

Like for the Nd-Fe-B powder, the well-established HD treatment is also applicable to SmCo₅ alloys and magnets to develop fine-sized powder for sintering. At the room temperature conditions, about 2.5 mol of H₂ gas at a pressure of 20.3 bar (~2 MPa) is absorbed by the system in an exothermic reaction which converts the hexagonal structure to orthorhombic SmCo₅H₃ phase which expands the unit cell by 10 vol. %. The Sm-rich phase undergoes intergranular absorption of H₂ gas at the surface, which proceeds to the transgranular fracture of 1:5 matrix phase. The Sm-Co alloys with less than a stoichiometric amount of Sm will decrepitate at lower pressures of hydrogen while the Sm-rich compositions have higher absorption affinity than the stoichiometric hard magnetic phase. The decrepitation of 1:5 Sm-Co alloys strongly depends on the chemical compositions, temperature (for activation), hydrogen pressure and external support in the process, e.g. vibration, rotation, magnetic field etc. A. Eldosouky et al. [73, 172] showed that the HD-treated and milled powders when sintered resulted in higher densities than milled powders from cast ingots.

3.2.1.2 Hydrogenation–Disproportionation–Desorption–Recombination (HDDR) of SmCo₅.

The HDDR treatment of the SmCo₅ alloy can be described in terms of the disproportionation reaction as:



The desorption of hydrogen from the disproportionated mixtures leaves behind samarium dihydride ($\text{SmH}_{(2 \pm x)} \rightarrow \text{SmH}_2 + \frac{1}{2} x\text{H}_2$), which is reduced to Sm upon the completion of vacuum desorption of hydrogen. So during the recombination, Sm recombines with α -Co to form 1:5 phase [73, 177]. The disproportionation effect in SmCo₅ compounds is possible with a combination of high temperature-pressure processing (≥ 800 °C and ≥ 0.9 MPa), over prolonged periods with the aid of reactive or ball milling. After the recombination, a mixture of nanocrystalline Sm-Co species was identified: SmCo₅, Sm₂Co₇, Sm₂Co₁₇, SmCo₃, Sm₅Co₁₉ depending on the initial composition and disproportionation-recombination temperature/pressures [178–180].

3.2.1.3 Magnetic Properties of Sintered SmCo₅ Permanent Magnets.

The effective service temperature for SmCo₅ based permanent magnet is 300 °C, due to high T_C and less drastic changes to their RTC values at higher temperatures. The room temperature H_{Ci} of the sintered SmCo₅ magnets is greater than 2000 kA/m and $B_r \sim 0.9$ T. The coercivity mechanism of the precipitation-hardened 1:5 magnets is pinning controlled, therefore, the presence of uniformly distributed Sm-rich phase is very important in retaining high coercivities [73]. Figure 52 shows the variation in the magnetic properties of SmCo₅ permanent magnets with the temperature in the range of –100 to +300 °C. Clearly up to 150 °C, the $H_{Ci} > 2000$ kA/m and the decline in B_r is insignificant as compared to the room temperature magnetic properties [181]. The thermal stability at 300 °C beats the Nd-Fe-B magnets by all means as in this range, hardly any magnetization is left in the Nd-Fe-B REPMs with $T_C \sim 310$ °C [176, 182].

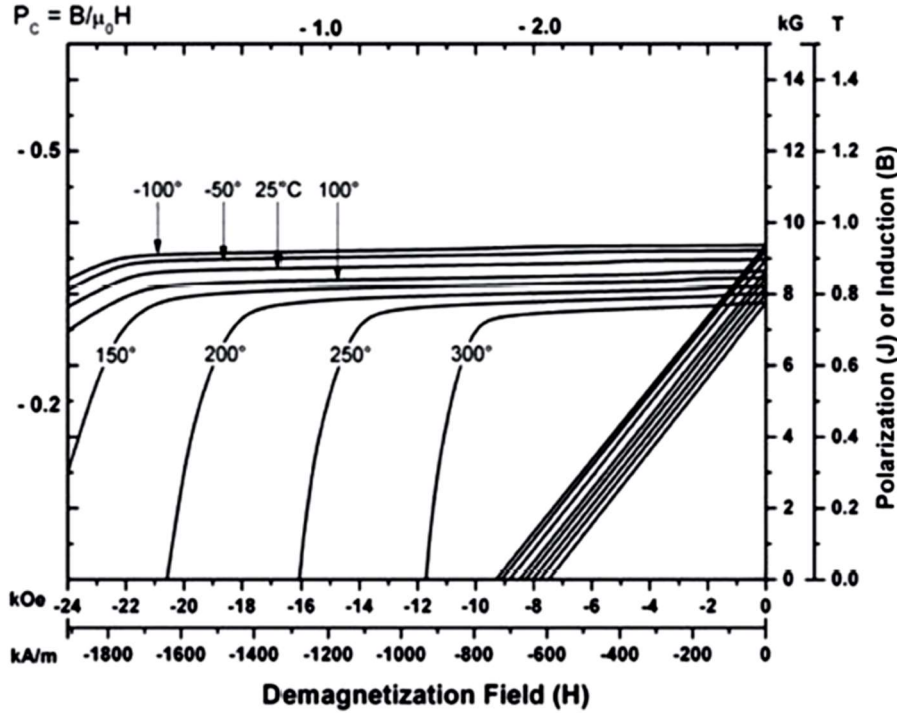


Figure 52: The demagnetization plots of SmCo_5 permanent magnet in a range of -100 to 300 °C, courtesy of S. Liu et al. [181].

3.3 The Essential Magnetic Properties of the RE-Based Permanent Magnets

The comparison of the magnetic properties of different rare-earth permanent magnets w.r.t the soft magnetic α -Fe is given in Table 3, which can serve as a guide for material selection for certain applications. Nd-Fe-B/Pr-Fe-B are preferred for high magnetization and < 100 °C temperature applications. The environmental stability of Nd-Fe-B magnets is also low, so protective coatings are applicable to prevent oxidation or corrosion. The Sm-Co-based magnets can operate at significantly elevated temperatures and therefore are preferred in high demagnetizing (alternating) fields and harsh environments. The SmCo_5 magnets have higher coercivities than the $\text{Sm}_2\text{Co}_{17}$ PMs, but the latter can withstand even higher temperatures and have better magnetization (M_r , M_s , BH_{max}). The stability and complex manufacturing of $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ permanent magnets hampers their widespread commercial usage. In terms of cost effectiveness and resource criticality, the Nd-Fe-B magnets are global leaders of REPMs [3, 13, 16, 36].

Table 3: Magnetic Properties of Permanent Magnets

REPM	Cry stal	M_s (T)	H_a (kA/m)	Bloch Wall Width (nm)	K (MJ/m ³)	H_{Ci} (kA/m)	BH_{max} (kJ/m ³)	T_c (°C)
SmCo₅	HCP	1.12	31840	2.6	17.2	>2000	160	747
Sm₂Co₁₇	RH	1.28	5200	5.7	2.9	1800	360	922
Nd₂Fe₁₄B	BCT	1.6	5680	4.2	4.3	1180	420	307
Pr₂Fe₁₄B	BCT	1.6	5680	3.7	5.6	1200	420	315
Sm₂Fe₁₇N₃	RH	1.5	11200	3.0	12.0	2240	380	470
α-Fe	BCC	1.62	5100	73.2	0.046	504	180	395

3.4 Adopting Conventional and Contemporary Processing Techniques in Recycling and Reprocessing of Nd-Fe-B and Sm-Co Permanent Magnets

Since there has been an increasing demand of these permanent magnets and the trade barriers restrict supply of rare-earth elements, the researchers as well as the industry have been looking for practical solutions. The magnetic scrap is diverse and it includes: bonded magnets for low temperature applications as well as sintered magnets from the motors in the hybrid/electric cars, electronics, computer equipment or wind turbines etc. So, the reprocessing can either follow the re-melting and casting route for modified alloys or follow the powder metallurgy methods (P/M) for sintered or bonded magnets. Using the P/M route, the important processes applied to magnetic scrap are: HD and HDDR treatment for making fine magnetic powders, which can be vacuum sintered or polymer bonded [11, 183].

M. Zakotnik et al. proposed the use of hydrogen decrepitation (HD) for the recycling of sintered Nd-Fe-B permanent magnets [99, 184, 185]. The magnet recycling has been gaining momentum since 2015, where A. Walton et al. [19] developed a flow scheme of hydrogen-based recycling and the HD treatment applicable on PMs in obsolete electronics and hard disk drives. This route produces the demagnetized and hydrogenated powder which can be re-sintered to recover up to 90% magnetic properties as shown in Figure 4 (red arrows for recycling). The hydrogen-based processing facilitates the recycling of EOL PMs due to recovery of H₂ gas used during material reprocessing and it has a positive environmental conservation effect. He reported a recovery of > 90% of magnetic properties in HD-treated Nd-Fe-B recycled permanent magnets with conventional vacuum sintering of recycled powders at 1050 °C for 1 hour. The recycled magnets are not yet commercially available. Hence by introducing techniques like SPS, even better recycled magnets can be

fabricated, therefore the potential for developing high performance Nd-Fe-B magnet by recycling the EOL PMs is remarkable [20, 21, 83, 99, 121, 125, 138-141, 184-194]. R. Sheridan et al. [121, 130] investigated the feasibility of the HDDR process after the HD treatment on the end-of-life (EOL) magnets, and reported $H_{Ci} \sim 1050$ kA/m and $B_r = 1.1$ T is possible (approx. 90 % recovery). Several reports suggest the improvised recycling philosophy and by modifying the chemical composition, the sintered magnets better than the starting EOLs can be adequately produced [138, 186, 189, 190, 195-197]. Similarly, A. Eldosouky et al. [73, 172] utilized the HD process for developing sintered magnets with lossless magnetic properties ($H_{Ci} > 2000$ kA/m) from the recycled decrepitated $SmCo_5$ powders. The magnetic properties in recycled magnets better than the commercial magnet were reasoned due to the fine structuration induced by HD treatment. A similar trend was also confirmed by rapidly sintering the HD-recycled $SmCo_5$ powders with the SPS, achieving RT $H_{Ci} \sim 2200$ kA/m and $B_r = 0.47$ T [198].

Recycling the polymer-bonded magnets is difficult because of the thermoplastic polymer degradation, whereby the thermoset polymers do not decompose and instead burn out, making the recovery of nanostructured Nd-Fe-B nearly impossible [193]. Bulk EOL magnets therefore show better promise of recyclability in comparison to the bonded magnets. The Nd-Fe-B magnets from hard disk drives are also recycled with the HDDR technique and the comparison of magnetic properties was drawn with the starting EOL magnet and commercial HDDR powder. Rather confining the application of anisotropic HDDR-recycled powder to bonded magnets only, the rapid consolidation via SPS was trialed to preserve the submicron-sized grains and ultimately the magnetic properties [83]. Alternately, these EOL sintered Nd-Fe-B magnets can be reprocessed with melt spinning [199] as well in the recycling route. These can then be consolidated by the SPS [83, 134] or hot-deformation/forging [111, 113, 200, 201] to develop isotropic and anisotropic nanocrystalline-sintered magnets.

The effects of oxygen and particle size are very important in establishing the strategy of tailoring the magnetic properties of the recycled powder. The oxidation of Nd-rich phase to Nd_2O_3 oxide is arguably the biggest challenge faced during recycling via HDDR process and the particle size range identification was necessary for industrial upscaling of the route. Formation of Nd_2O_3 scavenges the Nd from grain boundary phase which reduces the sinterability during the SPS reprocessing and the lack of grain boundary phase substantially degrades the coercivity due to the localized exchange effects. Moreover, in the sintered Nd-Fe-B magnets, a high oxygen content has been associated with abnormal microstructure formation due to the rapid grain coarsening without the liquid phase [81, 202].

The properties of the sintered nanocrystalline Nd-Fe-B permanent magnets are related to the microstructure and the coercivity mechanism is controlled by domain wall pinning. Addition of HREE elements contribute to an increase in anisotropy field of Nd-Fe-B, and the diffusion processing aids in the formation of core-shell structures which reinforces the surfaces of the grains by improving their demagnetization resistance from reverse domain

nucleation along the defects. Whereby, the diffusion of Pr and Nd-based eutectic alloys in the system accounts for adequate grain boundary phase which tends to reduce the localized exchange coupling of the grains as well as increases the number of pinning sites for reverse domains movements, thereby increasing the coercivity. The control of defects and pinning sites with the aid of RE-F₃ or RE-Cu eutectic alloys for the HDDR Nd-Fe-B system was also investigated.

The hydrogen-based reprocessing also provides an efficient and greener alternative for recycling the scrap/EOL or industrial waste SmCo₅ magnets as well. They can be hydrogen decrepitated (HD) and then rapid consolidation with the conventional vacuum sintering or rapid Spark Plasma Sintering (SPS) for achieving the magnetic properties at par with fresh commercial grade magnets [198].

At present the recycled Sm-Co magnets are missing in research horizon due to the ease of availability of Nd-Fe-B in EOLs and industrial scrap. However, the HD-reprocessed Sm-Co magnets can be utilized again, which has been comprehensively reported in this research study. To date, no state of the art report is available for reprocessed Sm-Co magnets even with conventional sintering or plastic-bonded methods [172, 198]. The spark plasma sintering (SPS) has also not been fully exploited for the HDDR Nd-Fe-B alloys, therefore the optimization of SPS system is necessary before determining its prospects in recycling and industrial upscaling.

Chapter 4

Aims and Hypothesis

4.1 Problem Description

Even by today the rare-earth (RE) elements' supply chain is constricted geopolitically and economically, whereby an up-surfing requirement of permanent magnets in hybrid/full electric vehicles and microelectronics necessitate sustainable control of the REE circular economy. The total recycling potential for end-of-life (EOL) Nd-Fe-B magnets only in the period 2016–2040 is estimated to be about 233 kt, corresponding to 66.6 kt of Nd and 7.9 kt Dy [203], while the total industrial waste or rare-earth alloys during magnet production accounts up to 25%. The energy intensive and wasteful conventional pyrometallurgical and complex chemical leaching processes used for rare-earth elements'/magnets' recycling are not environment friendly. The utilization of magnetic scrap, industrial wastes and EOL magnets holds great scientific and economic potential to meet the overgrowing demand of RE permanent magnets. Scrap magnets if properly collected and systematically separated from the waste stream can be suitably recycled with hydrogen-based routes.

4.2 Dissertation Goals

Discretely the objectives of this dissertation can be defined as following:

1. Sintered magnets using the recycled HD SmCo_5 and HDDR Nd-Fe-B powders for achieving 70% of the coercivity that would be achieved in case of using fresh, non-recycled powder via novel pressure-assisted pulsed electric field sintering, i.e. spark plasma sintering techniques (SPS).
2. Study the effect of particle size, oxygen sensitivity, pressure and SPS parameters for optimizing the sinterability and the magnetic properties of HDDR Nd-Fe-B recycled powder.
3. Microstructural understanding of complex non-equilibrium sintering mechanisms in SPS-reprocessed HDDR Nd-Fe-B and HD Sm-Co systems.
4. To develop anisotropic HDDR Nd-Fe-B magnets by hot deformation in SPS with magnetic properties comparable to the fresh sintered magnets ($H_{\text{Ci}} \sim 1000 \text{ kA/m}$ and $B_r \sim 1.1 \text{ T}$).

5. Investigate the effect of RE-F₃ (RE = Dy, Tb) dopants for the coercivity enhancement via grain boundary engineering of the recycled HDDR Nd-Fe-B powder.

4.3 Hypothesis

4.3.1 Hypothesis 1

The hydrogen decrepitation (HD) helps recover and break down the EOL RE-based magnets into non-magnetized friable powder, which can be separated from the coarse flakes of protective coatings and other waste residues. The grain size after the HD treatment is in order of several microns. The HD-treated Nd-Fe-B powder can further be recycled with the dynamic hydrogenation disproportionation, desorption, recombination (d-HDDR) route to form anisotropic submicron-sized grains (< 500 nm) in the individual powder particles. Additional hydrogenation in the HDDR route is suitable for achieving higher coercivities than the HD-treated powder due to nanostructurization of Nd₂Fe₁₄B grains and the Nd-rich grain boundary phase. The HDDR powder had only been used as bonded magnets since conventional sintering destroys the nano-size grains-based microstructure and the magnetic properties. Spark Plasma Sintering has proven as a very effective contemporary sintering technique to retain the microstructural control and achieving good densification even in hard to sinter materials. SPS offers the control of current density, pressures, heating rates, holding times and multi-step operation for a rapid sintering effect. The foremost parameter of interest will be the relative density of the final magnet owing to which other SPS conditions were optimized to gain the highest possible magnetic properties, since the hydrogen-based processing (HD and HDDR) of the magnetic scrap and EOL magnets is very promising in producing the powder to desired specifications. **Upon that the Hypothesis 1 was established: The SPS reprocessed sintered bulk magnets from the HDDR-ed Nd-Fe-B recycled feedstock can have the magnetic properties comparable to the non-recycled, i.e. “fresh” magnets.** The realization will only be possible with tight control of SPS processing parameters (temperature - time - pressure) and microstructure of sintered magnets to ensure the property-performance matrix conforms against the commercial grade sintered magnets.

Awais Ikram, et al. The sintering mechanism of fully dense and highly coercive Nd-Fe-B magnets from the recycled HDDR powders reprocessed by spark plasma sintering. Journal of Alloys Compounds 2019; 774: 1195-1206 [83].

4.3.2 Hypothesis 2

The effect of oxygen content and the recycled HDDR Nd-Fe-B powder particle size are very important in establishing the strategy of tailoring the magnetic properties of the recycled powder. Since the magnetic scrap or EOL magnets contains higher weight fraction of adsorbed oxygen or Nd₂O₃ converts, reprocessing to retain the magnetic properties can become difficult without the addition of RE-rich compositions. The oxidation of Nd-rich phase to Nd₂O₃ oxide is arguably the biggest challenge faced during recycling via HDDR process and the critical particle size range has to be identified for industrial upscaling of the route. The formation of hcp-Nd₂O₃ scavenges the Nd from grain boundary phase which reduces the sinterability during the SPS reprocessing and the lack of grain boundary phase substantially degrades the coercivity due to localized exchange effects. The Nd₂O₃ phase is stable and implies a strain along the adjoining matrix Nd₂Fe₁₄B grains, reducing the

coercivity. Hence the volume fraction of Nd_2O_3 phase has to be limited in the recycled powder, or an alternate strategy should be adopted to limit their detrimental effects on the magnetic properties.

Hypothesis 2 states that the particle size plays an important role in consolidation and ultimately the magnetic properties. The relationship of particle size with sinterability, oxygen content and the magnetic properties has to be established. With a decrease in particle size, the oxygen content is perceived to increase and in turn the sinterability should drop, but the useable particle size limit is to be identified. Sinterability and magnetic properties variation will be investigated for different particle size fractions of the recycled HDDR powder with different SPS treatment conditions. The effect of thermal treatments and the mechanism outlining the recovery of magnetic properties will also be elucidated.

Awais Ikram, et al. Particle size dependent sinterability and magnetic properties of the recycled HDDR Nd-Fe-B powders consolidated with Spark Plasma Sintering. Journal of Rare Earths 2019; (JRE_2018_668, accepted for publication – in production).

4.3.3 Hypothesis 3

The coercivity mechanism of the sintered Nd-Fe-B magnets is controlled by the nucleation of reverse domains [3, 16, 45]. Although it is still unclear if the nucleation of reverse domains on the surface of nanocrystalline $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains is of significant effect in the HDDR system [36]. W.F. Li et al. [46, 47] has suggested that the RE-rich grain boundaries in the HDDR Nd-Fe-B system play a significant role in pinning the domain wall movement. With an increase in grain boundary area, more sites will be present to deflect the domain wall movement, which in turn, improves the coercivity, since, the addition of HREE elements contributes to an increase in anisotropy field of the Nd-Fe-B magnets. Therefore, the grain boundary diffusion (GBDP) treatment in the formation of the core-shell structures which reinforces the surfaces of the 2:14:1 grains by improving their demagnetization resistance from reverse domain nucleation. Previous research has indicated that the addition of HRE- F_3 to the sintered Nd-Fe-B magnets have increased the coercivity by 5 – 35 % [69, 154-158, 169, 204]. With the additional of < 3 wt. % DyF_3 , the coercivity of sintered magnet (2400 kA/m) increased to 2790 kA/m due to the formation of higher anisotropy field and coercivity (Dy,Nd)-Fe-B “shells” on top of Nd-Fe-B matrix grains. The Nd-rich phase is replaced by the Nd-O-F-type phase, which is stable and does not oxidize to hcp- Nd_2O_3 . Such small additions of RE- F_3 do not degrade the remanence either. This theory has not been investigated on submicron sized HDDR powder so far.

The impact of DyF_3 doping on the recycled and fresh HDDR powder has to be evaluated and the hypothesis states that the core-shell structures may form through the bulk if by powder blending and thermal treatment, the uniform Dy diffusion through the liquid phase can be tweaked. Thereby characterizing the core-shell structure in the HDDR powder can be one way of achieving higher coercivities in the Nd-lean system.

Awais Ikram et al. Coercivity increase of the recycled HDDR Nd-Fe-B powders doped with DyF_3 and processed via Spark Plasma Sintering & the effect of thermal treatments. MDPI Journal of Materials, 2019; 12: 1498 [205].

4.3.4 Hypothesis 4

SPS can also be effectively used as a hot-deformation system to induce the texture in the sintered Nd-Fe-B samples. Application of high pressures (~ 500 MPa) can in turn severely deform the sintered magnets parallel to the pressing direction, by which the 2:14:1 grains elongate along the axis perpendicular to the pressing direction. As the texture is introduced along the easy magnetization axis, the B_r and BH_{max} increases. But due to the rotation of the grain boundary phase in the direction perpendicular to the pressing direction and the grain growth (elongation), the H_{Ci} drops as the degree of deformation increases. **In comparison to the $B_r = 0.92$ T of the recycled HDDR powder, the induced texture in SPS reprocessed magnets is expected to improve the remanence after the hot-deformation.** Therefore, a range of temperature and pressure conditions need to be identified for achieving the highest BH_{max} and $B_r \sim 1.1$ T in the recycled HDDR Nd-Fe-B, without significantly degrading the H_{Ci} . Control of the SPS pressures and strain rate will determine the final texture development in the recycled powders.

Chapter 9 details the verification of Hypothesis 4 on the hot deformation of the recycled HDDR Nd-Fe-B powder.

4.3.5 Hypothesis 5

The microstructure of HD-treated $SmCo_5$ powder consists of the main matrix phase 1:5, Sm-rich phase (Sm_2Co_7 , Sm_5Co_{19}) and Sm-oxides. The reciprocation of this microstructure is important for achieving superior magnetic properties and offers challenge to develop with the SPS. By HD treatment the powder becomes friable and is easier to mill down to < 20 μm in size which is necessary for achieving $H_{Ci} > 2000$ kA/m. **The SPS parameters if controlled can prevent any vaporization of metallic-Sm during the pulsed current induced sintering at the peak operational temperatures. Therefore, the control in the amount of secondary phases, i.e. Sm_2Co_7 -based Sm-rich liquid phase and reduced formation of Sm_2Co_3/Sm_2Co_{17} is important during the sintering, which in-turn will result in SPS-ed magnetic properties at par with conventionally vacuum sintered $SmCo_5$ magnets.** Excessive transformation of $SmCo_5$ main phase to Sm_2Co_7 phase leads to the decline in magnetic properties, therefore the optimal SPS temperature and holding times were defined for HD-treated fresh and recycled $SmCo_5$ powder. Elevated temperature (180 °C) magnetic properties will also be determined and compared with conventionally vacuum-sintered $SmCo_5$ magnets. The SPS reprocessing temperatures are 30% lower than vacuum sintering and optimal microstructure formation is possible if the heating rate and pressure are controlled to achieve full densification.

A. Eldosouky, A. Ikram et. al, Hydrogen decrepitation and spark plasma sintering to produce recycled $SmCo_5$ magnets with high coercivity. IEEE Magnetics Letters 2018;9: 1 – 4 [198].

Chapter 5

Materials and Methods

The HD-treated SmCo_5 and HDDR-reprocessed Nd-Fe-B recycled powders were made from the industrial scrap and EOL magnets respectively. The recycled powders were consolidated to full density with the contemporary Spark Plasma Sintering technique. The characterization techniques for measuring the magnetic properties, crystal phase identification and microstructural investigation are detailed in this chapter.

5.1 Materials

5.1.1 The Recycled HDDR Nd-Fe-B Powder

The recycled HDDR powder was prepared from EOL-sintered magnets with a nominal composition $\text{Nd}_{13.4}\text{Dy}_{0.67}\text{Fe}_{78.6}\text{B}_{6.19}\text{Nb}_{0.43}\text{Al}_{0.72}$ using the dynamic Hydrogenation-Disproportionation-Desorption-Recombination (d-HDDR) method as reported by R. S. Sheridan et al. [121, 130]. The theoretical density for this composition was calculated by multiplying the weight fraction and density of constituent elements, and approximated to $7.57 \pm 0.01 \text{ g/cm}^3$. The EOL magnets had measured oxygen content of 2660 ppm (0.266 wt. %). The intrinsic magnetic properties of the EOL magnets were: $H_{\text{Ci}} = 1170 \text{ kA/m}$ and $B_r = 1.19 \text{ T}$. The oxygen content increased to 4780 ppm after the HDDR treatment. The recycled HDDR powder has a wide particle size distribution ranging from $< 30 - 700 \text{ }\mu\text{m}$. The average particle size was approximated to $220 \text{ }\mu\text{m}$. The magnetic properties of the recycled HDDR powder were: $H_{\text{Ci}} = 830 \text{ kA/m}$ and $B_r = 0.92 \text{ T}$.

5.1.2 HD Treated Recycled and Fresh SmCo_5

The HD treatment was performed on the freshly sintered and the industrially rejected due to noncompliance with shape specifications (recycled) SmCo_5 magnets. The sintered magnets had a nominal chemical composition: Sm = 36 wt. %, Co = 63.8 wt. % and O = 0.2 wt. %. The hydrogen decrepitation process is explained by A. Eldosouky et al. [172]. The particle size after milling the HD-treated powder is $4 - 20 \text{ }\mu\text{m}$.

5.2 Powder Characterization

5.2.1 Crystal Phase Analysis

The phase and crystallographic identification were performed with PANalytical X'Pert pro multi-purpose X-ray diffractometer using the Bragg's principle of diffraction: $2d_{hkl}\sin\theta$

$= n\lambda$. Here λ is the wavelength of the incident X-ray, n is an integer, d_{jkl} is the interplanar spacing and θ is the scattering angle. The X-rays are electromagnetic waves having wavelength in the range of 0.01 – 10 nm and energies 120 eV – 120 keV. Usually a beam of electrons from tungsten filament is directed towards a target anode of Cu or Mo (under high potential difference), and release X-rays from characteristic shells (K, L subshells). These generated X-rays are directed toward the sample mounted on the goniometer and the incident radiation is diffracted to an angle 2θ from the crystal lattice. The XRD can be used effectively for characterizing the crystallinity and phase identification. It can also be used to determine the structural properties like crystallite (grain) size, microstructural strain, epitaxy, phase composition, quantitative volume fraction of phases, crystalline orientation relationship, thermal expansion, order-disorder transformation, film thickness and to analyze the atomic arrangement in a system. The detection limits suggest at least 3% wt. fraction of a phase in a multi-component system. The diffraction pattern for every phase is unique and therefore XRD is termed as a fingerprint identification technique.

5.2.2 Thermal Analysis

The thermogravimetric analysis was performed with Netzsch Jupiter 449 Simultaneous Thermal Analysis (STA) instrument with TG-DSC-cp sample holder and Pt-crucibles with Al_2O_3 liners. Thermogravimetry (TG) is related to the change in mass with temperature and the differential scanning calorimetry (DSC) evaluates the phase changes induced by heat flow versus the temperature (or time). DSC is applicable for determining the crystallization, phase transformations, glass transition, critical or Curie temperature measurements, oxidation or other heat significant chemical reactions.

5.2.3 Oxygen Content Analysis

The oxygen content of the powder samples and EOL magnets were measured by Eltra ON 900, oxygen/nitrogen analyzer.

5.2.4 Sieving

The sieving operation was performed in the glovebox under the protective Ar environment and the sieve sizes used ranged from 1000 – < 50 μm . The sieving, storage, powder handling and sample preparation operations were performed in the glove box as shown in Figure 53 with the oxygen and moisture content kept below 1 ppm.



Figure 53: The laboratory scale glove box for handling and storing the powder samples.

5.2.5 Magnetic Measurements

The magnetic measurements of the recycled powders were obtained with the Lakeshore Vibrating Sample Magnetometer calibrated at room temperature without considering the self-demagnetization factor, as pictured in Figure 54. The powder samples were weighed and placed inside the cylindrical sample holder. The magnetic pre-alignment of the powders was performed in the magnetic pulsar device with 2 T applied field. The VSM unit magnetizes the samples with capacitor discharge pulse magnetometer generating a 4 T aligning field and measuring the hysteresis loop behavior along the easy and hard directions. The sample is sinusoidally vibrated perpendicular to the applied field which allows coordination of the individual magnetic moments in the form of voltage induced in the pickup (detection) coils. From the nature of the hysteresis loop the type of material and characteristic magnetic properties can be determined.



Figure 54: Lakeshore MicroSense vibrating sample magnetometer (VSM) used for determining the magnetic properties of the powder samples.

5.3 Sintered Magnet Characterization & Treatment

5.3.1 Spark Plasma Sintering

The Spark Plasma Sintering unit used for the research work was Syntex 3000 (DR. SINTER) furnace which was calibrated for temperature ranges with K-type thermocouple and IR-pyrometer as shown in Figure 55. The 10 – 20 mm cylindrical graphite dies containing 3 – 10 g of the recycled and fresh magnetic powder were placed inside the chamber with graphite punches squeezing from the top and bottom. The samples were packed inside the glovebox with vacuum sheets to prevent further oxidation. The magnetic pre-alignment was performed in the magnetic pulsar with 2 T aligning field. The uniaxial pressing up to 50 MPa was also performed as necessary before the sintering operation. The sintering of Nd-Fe-B was performed in a vacuum of 2×10^{-3} MPa and constant uniaxial pressure of 50 MPa was applied. The final stage pressure was varied from 100 – 150 MPa. The heating rate was 50 – 100 °C /min during SPS runs. The HDDR Nd-Fe-B was sintered in the temperature range of 500 – 850 °C. The hot deformation experiments were conducted using high pressure suitable WC + Co cermet dies, which could withstand the pressure up to 300 MPa up to 700 °C. For the SmCo₅ powders, the sintering operation was performed under 0.2 MPa partial pressure of Ar gas. Furnace cooling initiated as soon as the pulsed current was switched off. The low voltage (2 – 3 V), high pulsed DC current (300 – 1400 A) was used in the sintering operations. The HD SmCo₅ powders were sintered in the temperature range of 800 – 1000 °C with the heating rate varying from 25 – 100 °C /min. The most optimum conditions for HDDR Nd-Fe-B were SPS-ing at 750 – 800 °C for 1 minute at 100 °C /minute and 100 MPa pressure, whereas for SmCo₅ the optimal temperature was 900 °C – 1 minute, reached at 50 °C/minute from the room temperature. The sintered magnets made under these conditions were 99% dense.



Figure 55: the multipurpose SPS sintering and hot deformation unit.

5.3.2 Sample Grinding and Polishing

The carbon layer from the samples was removed by mechanical methods on the Struers Rotopol-15 rotary disk units with 220 – 4000 grit size SiC grinding papers as shown in Figure 56 (a). Further polishing for preparing the microscope ready samples was performed using velvet cloth and 3 – ¼ micron diamond paste. The Nd-Fe-B samples were chemically etched with 3 M Cyphos based ionic-liquid and the HCl solution at the ambient conditions, with time varied from 10 – 60 seconds.

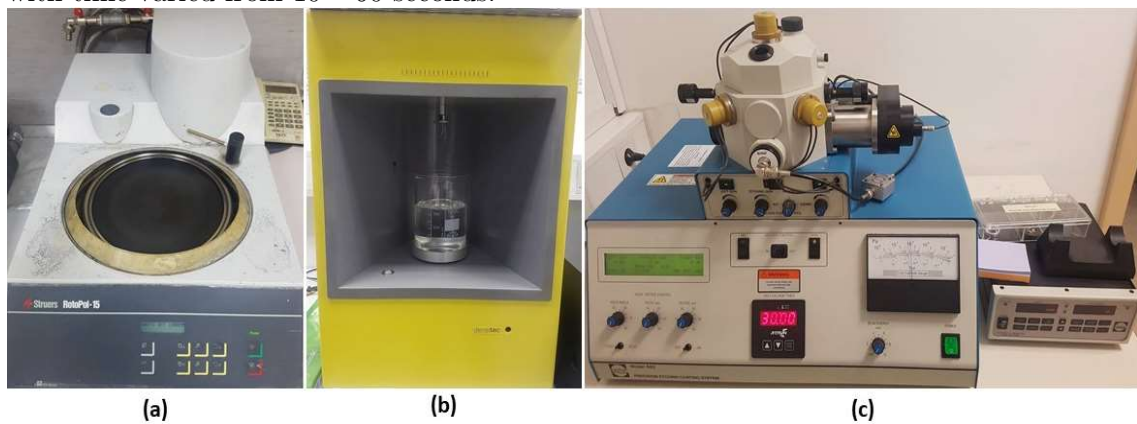


Figure 56 (a) grinding and polishing unit, (b) density measurement unit and (c) precision sputtering system.

5.3.3 Density Measurements

The density measurements of the sintered specimen were taken on the DENSITEC unit, as in Figure 56 (b), which utilizes the Archimedes principle of relative density in another medium. Silicone oil was used as the immersion medium during the density measurements.

5.3.4 Sputtering & Evaporation System

The polished samples were coated by a thin carbon layer on the surface to minimize the effects from non-conductive parts in the microstructure (oxides). The precision etching and coating system is shown in Figure 56 (c). The thermal evaporation and sputtering are physical vapor deposition processes. In evaporation by means of heating (resistive or induction) vapors are formed in vacuum or inert atmosphere which are then condensed on the target species towards the anode. In the sputtering process, a very high momentum is exchanged by the high-speed electrons from cathode (very high potential) accelerated to knock out inert gas electrons and forming up plasma. These positively charged ions are then bombarded on the negatively charged target, ejecting the species and depositing on the surface. By using reactive gases instead of Ar, chemical reactions can take place in the plasma state and compounds can be deposited with reactive sputtering. In order to shield the substrate and control the incident species, magnetron sputtering is used. Multiple sources can be used in the co-sputtering process to form layered films on the substrate.

5.3.5 Permeameter

The permeameter measures the magnetization of a parallel face specimen within the magnetizing coils, as shown in Figure 57. The unit consists of two electromagnetic coils connected to an external power supply. One coil measures the change in magnetic polarization with the external field and the second coil is used to measure the applied field produced by the electromagnets. Software performs the calculations from the first and second quadrant on the basis of equation: $B = \mu_0(H + M)$. Basically, the magnetized sample is placed between the coils and the applied field gradually increases to 2 T and then goes to zero (measuring the remanence). The direction of applied field is then reversed to reach demagnetization state up to approx. 1.9 T. This demagnetizing field value is not enough for SmCo_5 and HREE composition-based Nd-Fe-B magnets, since their coercivities are greater than 2000 kA/m. Therefore, higher temperature measurements up to 180 °C are taken with the permeameter to compensate for the demagnetization at the room temperatures.



Figure 57: Two electromagnetic coil-based permeameter on the left and 2 T magnetic pulsar on the right.

5.3.6 Scanning Electron Microscopy

The microstructural investigation was performed with the field emission high resolution scanning electron microscopes: JEOL 7600F (Figure 58) and the Helios NanoLab DualBeam 650 Focused Ion Beam Milling Microscope connected to 50 mm² Oxford Aztec electron energy dispersive X-ray spectroscopy (EDXS) Detector unit. The EDXS quantification analyses were performed at 15 – 20 keV accelerating voltages. The powder particles were embedded in a polymer matrix, which was followed by thorough polishing and sputter coating with carbon. The sintered magnets were either cut along their cross sections or directly mounted on the metallic stub after polishing with the carbon paste and sputter coated by several nm thick conductive layer. The back-scattered electron imaging (BSE) mode was used to expose the microstructural details in terms of identifying and quantifying the different phases present in the sample. The local compositional details were studied with the EDXS analysis. The analytical resolution of EDXS depends on the accelerating voltage, since X-ray peaks of the heavy elements (HREE and TMs) cannot be distinguished at lower voltages. The EDXS has a lateral resolution of approx. 1 μm at 20 keV accelerating voltage, so features smaller than 1 μm may involve standard deviation and the X-ray peaks are cumulative of the different phases in the vicinity.



Figure 58: JEOL 7600F FEG-SEM with Oxford Inca 20 mm² EDXS detector.

5.3.7 Thermal Treatments

The thermal treatments on the SPS-sintered samples were performed in a programmable Carbolite horizontal tube furnace connected with turbomolecular vacuum pump which can maintain up to 10^{-5} MPa high vacuum conditions, as shown in Figure 59. Alternately the inert gases (Ar, N₂) and H₂ can also be purged at a controlled rate in the furnace to induce rapid cooling or hydrogenation reactions in REPMs. The annealing, grain boundary modification and thermal treatments on HDDR Nd-Fe-B system were done at varying conditions in the temperature range of 600, 750 and 900 °C from 1 – 6 hours under high vacuum. Whereas the demagnetization was done for 10 minutes at 450 °C for Nd-Fe-B and 800 °C for SmCo, above their respective T_C . The cooling was done out of the furnace but under the dynamic vacuum conditions.

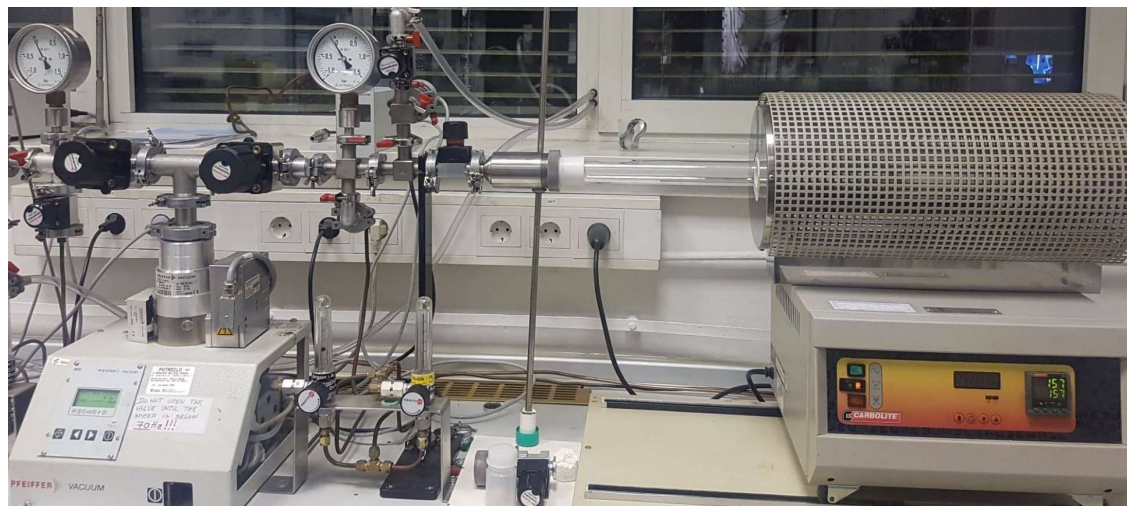


Figure 59: the heat treatment horizontal furnace (right) connected to high vacuum turbomolecular pump (left).

Chapter 6

The Sintering Mechanism of Fully Dense and Highly Coercive Nd-Fe-B Magnets from the Recycled HDDR Powders Reprocessed by Spark Plasma Sintering

In this chapter, the results from the article published in the Journal of Alloys and Compounds (2019) entitled: “The sintering mechanism of fully dense and highly coercive Nd-Fe-B magnets from the recycled HDDR powders reprocessed by spark plasma sintering”, by **Awais Ikram**, M. Farhan Mehmood, Matejka Podlogar, Anas Eldosouky, Richard Stuart Sheridan, Muhammad Awais, Allan Walton, Marjeta Maček Kržmanc, Tomaž Tomše, Spomenka Kobe, Sašo Šturm, Kristina Žužek Rožman [83] is presented. The authors report the suitability of contemporary spark plasma sintering technique for developing fully dense and high coercivity sintered Nd-Fe-B permanent magnets from the recycled HDDR powder.

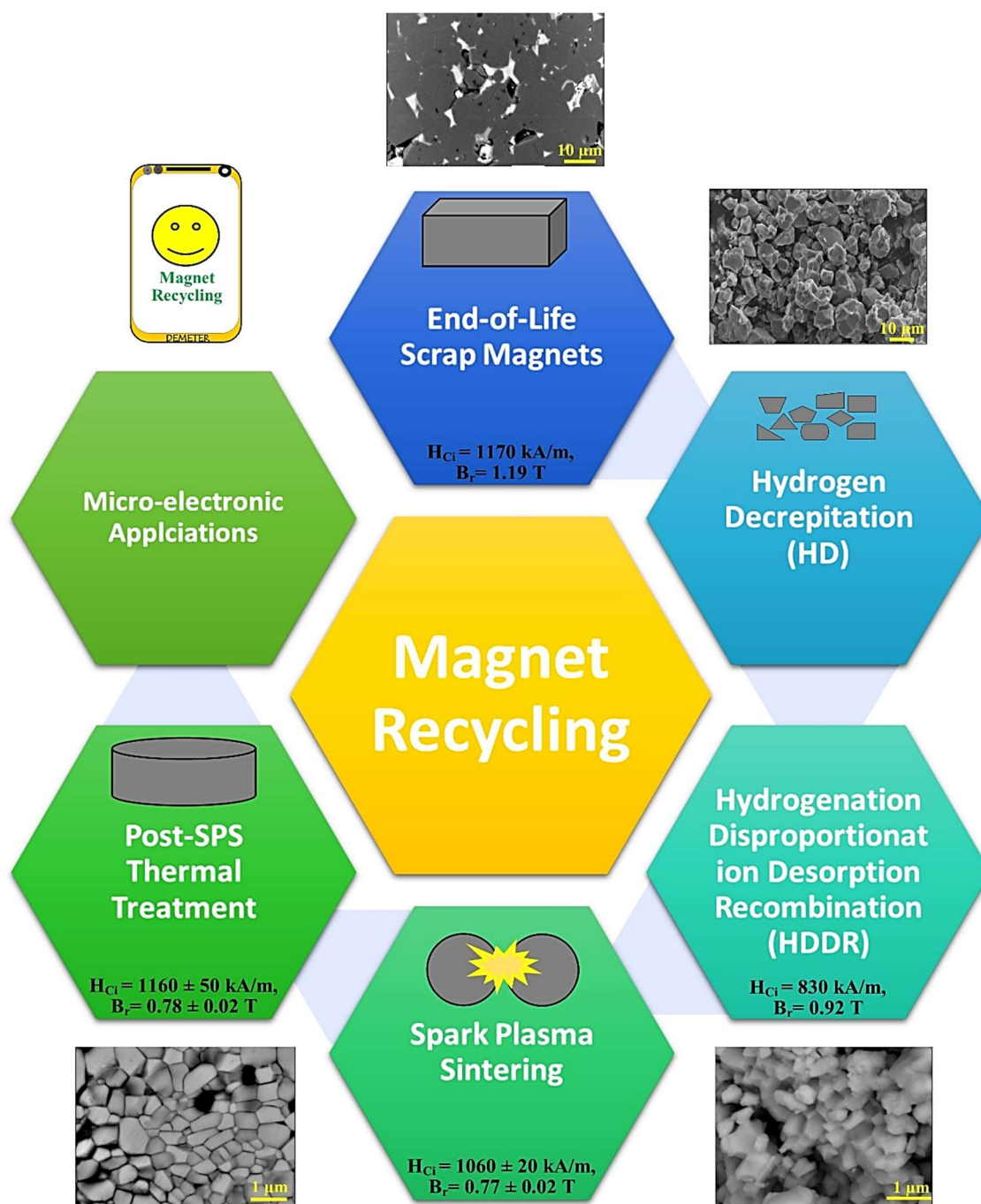
The nanostructured rare-earth-based magnets (Nd-Fe-B) have only been used as the bonded magnets with lower performance and limited energy products $BH_{\max}$ in comparison to the sintered magnets. Their nanocrystalline structure prevent them to be conventionally sintered, by which they will lose their microstructure dependent properties due to rapid grain coarsening at such high temperatures. In turn, the rapid consolidation techniques, i.e. hot-deformation or Spark Plasma Sintering (SPS) are the only left options to preserve the nanocrystalline microstructure and its dependent magnetic properties. The challenge here was to make dense sintered magnets retaining the initial nanocrystalline microstructure from the starting recycled HDDR powder and compare the properties to the fresh HDDR powders sintered by SPS. In this research study, we advocate the use of SPS for reprocessing the recycled HDDR powder which has nearly ten folds higher oxygen content (~ 4800 ppm) than the fresh commercial HDDR powder. This recycled HDDR powder was initially hypothesized to have poorer sinterability. The SPS temperature range and optimal conditions were identified with minimum possible holding time to avoid grain coarsening for achieving fully dense and high coercivity magnets. The optimal SPS temperatures are approx. 30% lower and the whole sintering process is significantly faster than the conventional vacuum sintering for achieving optimum magnetic properties from the fully dense magnets. The mechanism of sintering at different temperatures is discussed within the paper which directly impacts the coercivity of the SPS reprocessed powders.

These results were verified with the aid of high-resolution SEM imaging and the EDXS quantification. The effect of post-SPS thermal treatments have also been investigated and the mechanism for improvement in magnetic properties is incorporated in this study. The reported coercivity values are ~30% higher than the starting recycled HDDR powder and the isotropic SPS-ed magnets compete 1:1 in terms of their magnetic properties with SPS treated Aichi Steel's fresh HDDR powder [134]. These are the state-of-the-art values and highest achieved from the scrap material rapidly reprocessed to sintered magnets (without any REE alloy additive) [83]. These findings are projected as an alternative to the direct recycling/reprocessing technique of the magnetic scrap to the scale comparable with the commercial HREE free magnets as shown in Figure 60.

Authors' Contributions:

My contributions as the first and corresponding author in this paper can be summarized as following:

1. Corresponding Author: Awais Ikram;
2. Conceptualization: Awais Ikram;
3. Methodology: Awais Ikram and Tomaž Tomse;
4. Software: Awais Ikram;
5. Validation: Awais Ikram and Kristina Žužek Rožman;
6. Formal analysis: Awais Ikram;
7. Investigation: Awais Ikram, Muhammad Farhan Mehmood, Marjeta Maček Kržmanc and Matejka Podlogar;
8. Resources: Muhammad Awais, Richard Stuart Sheridan and Allan Walton;
9. Data curation: Awais Ikram and Anas Eldosouky;
10. Writing—original draft preparation: Awais Ikram;
11. Writing—review and editing: Awais Ikram, Muhammad Awais, Anas Eldosouky and Kristina Žužek Rožman;
12. Visualization: Awais Ikram;
13. Supervision: Allan Walton, Sašo Šturm, Spomenka Kobe and Kristina Žužek Rožman;
14. Project administration: Allan Walton, Sašo Šturm, Spomenka Kobe and Kristina Žužek Rožman;
15. Funding acquisition: Allan Walton, Sašo Šturm, Spomenka Kobe and Kristina Žužek Rožman.



The EOL scrap magnet reprocessing scheme—100% recovery of magnetic properties is possible. The direct recycling route can contribute in controlling the rare earth elements circular economy and scrap magnetic waste management.

Figure 60 presents the graphical abstract of HDDR reprocessing of the recycled powder from the EOL magnets, consolidated with the SPS and the variation of magnetic properties during each reprocessing stage.



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The sintering mechanism of fully dense and highly coercive Nd-Fe-B magnets from the recycled HDDR powders reprocessed by spark plasma sintering

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ABSTRACT

The goal of this study was to justify the reprocessing of recycled HDDR Nd-Fe-B powders with spark plasma sintering (SPS) and to investigate the dependence of the final magnetic properties on SPS and thermal treatment. The initial recycled HDDR powder of the composition Nd_{13.4}Dy_{0.6}Fe_{78.6}B_{6.1}Nb_{0.4}Al_{0.7} with 4760 ppm O₂ content, coercivity (H_{ci}) = 830 kA/m, and large particle size distribution <50–600 μm, was treated using the SPS parameters as follows: T = 650–850 °C for 1–5 min and 50 MPa pressure. The post SPS thermal treatment was performed at 750 °C for 15 min in vacuum. The optimal SPS conditions at 750 °C for 1 min, yielded fully dense magnets with the coercivity H_{ci} = 1060 kA/m, which was boosted to 1160 kA/m after the post-SPS thermal treatment. The grain growth was obvious in samples SPS-ed above 800 °C and subsequently, the H_{ci} was reduced. The SPS reprocessing beyond 850 °C was found to be detrimental to the overall magnetic properties due to the formation of bimodal grain size distribution origination from the abnormal grain growth (700–2600 nm). The redistribution of Nd-rich grain boundary phase between the Nd₂Fe₁₄B matrix grains in thermally treated magnets and the relaxation of the internal stresses induced via SPS are the possible reasons for the H_{ci} surpassing the H_{ci} of the starting recycled HDDR powder. It was shown that the SPS consolidation technique is suitable for producing fully dense nanograin bulk Nd-Fe-B magnets, with coercivities even exceeding the initial HDDR-powder and is one of the most suitable routes for revitalizing the Nd-Fe-B scrap magnets.

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1. Introduction

Since the discovery of the rare-earth-based Nd-Fe-B type permanent magnets in 1984 [1,2], they became essential in energy, telecommunication, microelectronics and aerospace applications, as well in medical equipment, computers, sensors, electric motors and fusion devices [3–5]. However, in 2011, the rare earth elements (REE) importers met a supply chain crisis and as a result, the prices

soared [6]. Since the REE are a backbone for the green technologies, the EU now considers them as the most critical raw materials in terms of supply risk [6]. In comparison with the light rare earth elements (LREE), the heavy rare earth elements (HREE) like Dy, Tb, Ho etc. are more scarce and hence, more expensive. Dy is consistently used as a dopant to increase coercivity in high-performance permanent magnets, suitable for applications above 100 °C [4,6]. This, however, decreases the remanence (B_r) and the BH_{max} , due to the antiferromagnetic coupling of Dy with Fe atoms. Increasing the coercivity (H_{ci}) of Nd-Fe-B magnets without the HREE addition can be done via grain boundary modification treatments, which increases the grain boundary phase thickness in a way that neighboring grains become magnetically decoupled [4]. The other option

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is to develop near single domain nanostructured $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (≤ 400 nm). This can be achieved via melt spinning or by utilizing the

Hydrogenation-Disproportionation-Desorption-Recombination (HDDR) process [5]. The grain size refinement is considered a very viable option as it enhances the H_{CI} [4] without HREE addition. However, such nanograin powder cannot be manufactured via the conventional sintering route, as the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains will grow exponentially with temperature exceeding 1000°C and the H_{CI} will be lost [4,5], therefore alternative processing routes have to be proposed.

In view of the REE crisis and knowing that the industrial processing wastes in permanent magnet production accounts to $\geq 25\%$ for REE [7,8] it became feasible to recycle and reprocess them. The end-of-life (EOL) permanent magnets can be recycled using the hydrogen deprecipitation process [8] to form non-magnetic powders, which can further be reprocessed and reused as suggested by Li Xiantao et al. [7]. Several researchers [7–19] have reported with varying degree of success on recycling the scrap Nd-Fe-B and reprocessing by conventional sintering of hydrogen deprecipitated (HD) and jet-milled recycled powder [8,9]. However, to date, no trials have been made on the sintered magnets from recycled HDDR powders and only low H_{CI} bonded magnets have been reported [7]. The HDDR reprocessing has been utilized in recycling by Walton et al. [9] and Sheridan et al. [13] to make nanocrystalline powders, but for bonded magnet applications only. However, the reports from McGuinness [20] and Mueller [21] on Zr-doped hot pressed HDDR powders indicate that fully dense magnets can be processed without a significant loss in the H_{CI} compared to the starting powder. It is evident that the rapid compaction techniques e.g. shock compaction can be used in the alternate strategy to develop nanocrystalline bulk sintered Nd-Fe-B magnets without degrading their H_{CI} [5]. The Spark Plasma Sintering (SPS) compaction method would represent a suitable alternative to produce dense magnets. The SPS-ed fresh and commercial grade HDDR Nd-Fe-B powder was already processed by Suresh et al. [22] and Takagi et al. [23], which have indicated the possibility to fully densify the HDDR powders within a few minutes at $600\text{--}750^\circ\text{C}$. These corresponding SPS temperatures are $30\text{--}40\%$ lower than the ones used in conventional vacuum sintering ($>1050^\circ\text{C}$). However, after SPS-ing the H_{CI} was lost and only regained subsequently by post-sinter annealing treatments, attributed to the redistribution of the Nd-rich grain boundary phase and the intergrain stress relaxation [22–26]. The reason for this overall low H_{CI} in compacted samples having near single domain structure has been attributed to inadequate grain isolation, by only a thin paramagnetic Nd-rich grain boundary phase, identified previously by Gopalan et al. [24] and Li et al. [25]. To achieve adequate localized grain decoupling, enough paramagnetic Nd-rich phase must be uniformly distributed between the matrix grains and for this reason, the excess Nd is added to the composition to compensate for the Nd-loss due to oxidation during the recycling process [4,10,15]. With the focus of increasing the BH_{max} , tackling the remnant magnetization is also one of the major factors, however, compacted HDDR powders express usually low remanence (B_r) which is reasoned to a poor degree of easy axis alignment (texture) after compaction [24]. The mechanism for microstructure development in the HDDR powder consolidated with the SPS is still to be determined, and only then the SPS parameters and resultant microstructure can be controlled for maximizing the H_{CI} of near single domain grained HDDR powder.

Our study proposes the reprocessing of HDDR powders from EOL magnetic scrap using the SPS process for the first time, to contribute to the already existing state-of-the-art of the nanocrystalline HDDR Nd-Fe-B powders. The EOL scrap magnet HDDR powder in comparison to the “fresh/commercial” HDDR powder has a higher overall oxygen content, therefore obtaining high H_{CI}

presents a challenge with such Nd-Fe-B system. As K. Takagi et al. [23] reported that the particle size distribution is crucial in determining the H_{CI} of SPS-ed HDDR powder, as different HDDR particle fractions were associated with the different degree of surface oxidation, leading to lower H_{CI} for smaller particles. However, to date, the H_{CI} decrease due to oxidation has not been yet fully understood in terms of the microstructure [23,27,28]. Unlike commercial or fresh SPS-ed HDDR powder in which the H_{CI} drops after SPS and the properties have to be recovered with proper annealing treatment [23], we have demonstrated that a direct SPS reprocessing of the recycled HDDR powders with near stoichiometric composition, does result in even higher H_{CI} than the starting HDDR powder. The combination of rapid high-temperature SPS and thermal treatment above the eutectic temperature allowed us to preserve the grains from growing, achieving full densification and redistributing the Nd-rich grain boundary phase, diminishing the intergranular stresses and increasing the H_{CI} . This research work approves the application of SPS for developing nanostructured sintered magnets, even from the recycled HDDR Nd-Fe-B powders.

2. Experimental

The original end-of-life (EOL) sintered Nd-Fe-B magnets had $H_{\text{CI}} = 1170$ kA/m and $B_r = 1.19$ T. These EOL magnets were HD treated and pulverized to reduce particle size. Further, these particles were HDDR reprocessed; complete details of this process has been previously reported by Sheridan et al. [13,29] for producing the anisotropic recycled powder. The EOL scrap magnet has an overall oxygen content of 2660 ppm (0.266 wt %). After the HDDR process, the oxygen content increased to 4760 ppm (0.476 wt %). The intrinsic magnetic properties of recycled HDDR powder were measured as a bonded magnet with the Lakeshore VSM (not adjusting for self-demagnetization). The measured J_s value accounts to 1.4 T. The EOL sintered magnets having a nominal composition of $\text{Nd}_{13.4}\text{Dy}_{0.6}\text{Fe}_{78.6}\text{B}_{6.1}\text{Nb}_{0.4}\text{Al}_{0.7}$ measured with Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) were HD treated and then the dynamic hydrogenation-disproportionation-desorption-recombination (d-HDDR) process was utilized to develop recycled powder with nanostructured anisotropic grains. Detailed description of HDDR processing is provided by Sheridan et al. [13]. The theoretical density was calculated by measuring the weight fraction of the individual elements with the respective density of each element in the HDDR powder composition and it was approximated to 7.57 ± 0.01 g/cm³. This recycled HDDR powder had a wide particle size distribution as measured from HR-SEM. The phase analysis for the recycled HDDR powder was performed using the XRD (PANalytical Empyrean Diffractometer).

The Curie temperature (T_c), endothermic eutectic melting and exothermic crystallization processes were determined by Thermogravimetric Differential Scanning Calorimetry (TG-DSC) in the temperature range of $30\text{--}900^\circ\text{C}$ with the heating and cooling rates of $20^\circ\text{C}/\text{min}$, under argon environment (99.99% purity, flow rate 50 ml/min) using Jupiter 449 Simultaneous Thermal Analysis (STA) instrument with TG-DSC-cp sample holder and Pt-crucibles with Al_2O_3 liners. The temperature and sensitivity calibration of the instrument was performed with In, Bi, Zn, Al and Au standards. Before the DSC analysis, the samples were exposed to air atmosphere only for a few minutes during weighing before repeated vacuuming (5×10^{-4} mbar) and purging with Argon. The oxygen content of the HDDR powder and particle fractions was measured by Eltra ON 900, oxygen and nitrogen analyzer. In order to estimate the average particle size, the sieving of HDDR powder was performed from 1 mm sieve down to <50 μm sieve size in a glove box to prevent any oxidation of the recycled powder before the XRD, the microstructural characterization and the SPS reprocessing.

For the preparation of the SPS sintered magnets out of the recycled HDDR powder, the cylindrical graphite dies of 16 mm internal diameter were used and 5 g of the recycled HDDR powder was added in between the graphite foils and spacers. Punches were placed in to squeeze the powder compactly. Further pre-pressing or magnetic pre-alignment of the HDDR powders in the graphite molds was not performed before sintering for making isotropic magnets. These prepared molds were then placed in Syntex 3000 (DR SINTER) SPS furnace with controlled pressure unit and a thermocouple. All the SPS experiments were performed under a vacuum of 2×10^{-2} mbar and a constant uniaxial pressure of 50 MPa was maintained. The sintering temperature was varied from 650 to 850 °C, with a heating ramp of 50 °C/minute. The holding time at the sintering temperature was kept from 1 to 5 min (s). The SPS temperature was controlled with a calibrated thermocouple. All the SPS-ed samples were grinded using 500 grit size SiC papers to peel off the graphite spacers. Fine grinding up to 4000 grit was done further and the samples were polished on rotary disks using 1/4 μ m diamond paste on the velvet cloth. Samples were then analyzed for the magnetic properties on a permeameter (Magnet-Physik Dr. Steingroever) by taking successive magnetization and demagnetization measurements. The density measurements were taken on density-meter (DENSITEC) utilizing the Archimedeian principle and immersed in silicone oil.

Post-sinter thermal treatments (PST) were performed under a vacuum of $>10^{-5}$ mbar at a heating rate of 50 °C/minute in a horizontal tube furnace. The isothermal annealing temperature was kept at 750 °C and the samples were held for 15 min at this temperature. The density and magnetic measurements were repeated after the annealing step. For the microstructural investigations SPS-ed and post thermally treated samples etched with 3M Cyphos. The microstructural investigation was performed on the recycled etched and non-etched HDDR powder, the SPS-ed and the PST specimens using Field Emission Scanning Electron Microscope (JEOL 7600F and FEI Helios NanoLab DualBeam 650 FIB with Oxford Aztec 50 mm²). Electron energy dispersive X-ray spectroscopy (EDS) was performed at 20 keV.

3. Results and discussion

3.1. Chemical, thermal, magnetic and crystal structure characterization of the recycled HDDR powder

In order to investigate the thermal behaviour of the starting HDDR powder to determine the SPS regime, thermal analysis was performed. Fig. 1 (a) illustrates the typical TG and DSC curves obtained for recycled HDDR powder during heating at a heating rate of 20 °C/min to 900 °C peak temperature. The increase of mass due to oxidation during thermal analysis experiment was not significant (0.23%) and as it is very small and continuous (500–900 °C), its contribution to thermal effects could be neglected. DSC heating curve in Fig. 1 (a) is characterized by several endothermic effects. The low-temperature DSC peak, which was noticed at 307 °C, belongs to the Curie temperature (T_C) of the Nd-Fe-B. The onset of T_C begins close to 260 °C. The enthalpy associated with this phase transition was 4.9 J/g, which is significant for this transition after several repeated experiments. Further on, the most intense DSC peak is observed at 743 °C with its transformation on-set at 665 °C. This DSC peak is very close to the already reported ternary eutectic temperature T_{E1M} (690 °C), where $Nd_2Fe_{14}B$ matrix phase is present with liquefied α -Nd [39], however slightly lower on-set temperature (665 °C) observed for HDDR powder in this study could be related to the presence of other elements such as Dy, Nb and Al in very low quantity, which might lower this eutectic temperature. Similarly, Vial et al. [42] also determined the eutectic temperature

lower than 690 °C (646 °C) for the composition $Nd_{12.4}Pr_{1.4}B_{5.8}Al_{0.3}Cu_{0.1}Fe_{7.9}$, which was very similar to the material used in this work. In the DSC curve of this alloy with a minor content of Al, Cu and Co an additional endothermic peak was also noticed at 527 °C by the authors [42]. This peak could originate from Co and Cu containing compounds with a low melting temperature. Although Co and Cu are not constituents of the HDDR powder in the present study, a weak endothermic peak was observed in the lower temperature range at 477 °C. The measured enthalpy (0.6 J/g) associated with this low-temperature melting was considerably smaller than the characteristic (6.7 J/g) determined for the melting at higher temperature eutectic transformation between 665 °C and 770 °C. The formation of a low-temperature endothermic reaction in both systems containing Al implies that this melting is perhaps related to Al and its interactions in the system with Dy and Nd at the grain boundary interface. The enhanced melting effect of the grain boundary phase due to the presence of Al and Ni was already reported by N. Oono et al. [32].

In the cooling DSC curves of the HDDR powder, the exothermic peak belonging to the paramagnetic to ferromagnetic phase transition is well defined (Fig. 1b). The onset begins close to 310 °C and the peak corresponds to $T_C = 293$ °C for HDDR powder, so the results match during heating and cooling runs. The cooling DSC curve of HDDR powder was additionally characterized by weak and broad exothermic peak extending from 760 °C to 700 °C, which could be ascribed to the crystallization of the Nd-rich grain boundary phase. Since this process was associated with a rather small change of enthalpy (0.7 J/g) we can assume that during cooling with the rate of 20 °C/min the majority of grain boundary phase may possibly end up amorphous instead of well-defined crystalline grain boundaries due to the absence of well-defined peak(s). DSC measurements of the recycled HDDR powder samples were performed several times and very reproducible results were obtained. The initial Dy and Al additions to bulk magnets are reasoned to reduce this grain boundary phase melting temperature [32,33,39]. Therefore, the SPS reprocessing temperatures were kept in the 650–850 °C range to correlate the effect of the temperature to the microstructural evolution and its result on the magnetic properties, which will be discussed later. These measured values of T_C and T_{E1M} are synonymous with the work done by Hono et al. [39] on Nd-Fe-B.

The XRD analysis of the HDDR recycled powder is shown in Fig. 2. The reflections correspond to the tetragonal $Nd_2Fe_{14}B$ hard magnetic phase with JCPDA reference numbers 00-036-1296 and 04-006-2691 as the major phase. The lattice parameters of matrix phase are: $a = 8.79$ (Å), $b = 8.79$ (Å) and $c = 12.2$ (Å), with $P4_2/mnm$ space group and space group number of 136. As the scrap magnet contained 0.6 at. % Dy, the $DyNdFe_{14}B$ phase (JCPDA # 01-089-3548) with multiple overlapping peaks can be adjusted with the similar lattice parameters: $a = 8.79$ (Å), $b = 8.79$ (Å), $c = 12.1$ (Å) and $P4_2/mnm$ space group. The Nd-oxide phases were also detected by XRD, attributing to the pickup of oxygen before and/or during the HDDR reprocessing. The cubic NdO_2 (JCPDA # 04-007-0500) and Nd_2O_3 (JCPDA # 00-040-1283) phases were detected. In addition, the $NdFe_4B_4$ (JCPDA # 01-081-3530) phase was also present in the recycled HDDR powder which was to be expected.

3.2. Characterization of the recycled HDDR powders

Fig. 3 shows the BSE SEM micrographs of polished recycled HDDR Nd-Fe-B powder prepared in epoxy resin. The particles have irregular shapes and a large particle size distribution, from 30 to 700 μ m, with an average particle size of 220 μ m. Fig. 3 (a) shows a typical microstructure of the HDDR powder whereby the grey matrix corresponds to $Nd_2Fe_{14}B$ (highlighted as 1) and the bright phases are Nd-rich intergranular phases, NdO_x (highlighted as 2)

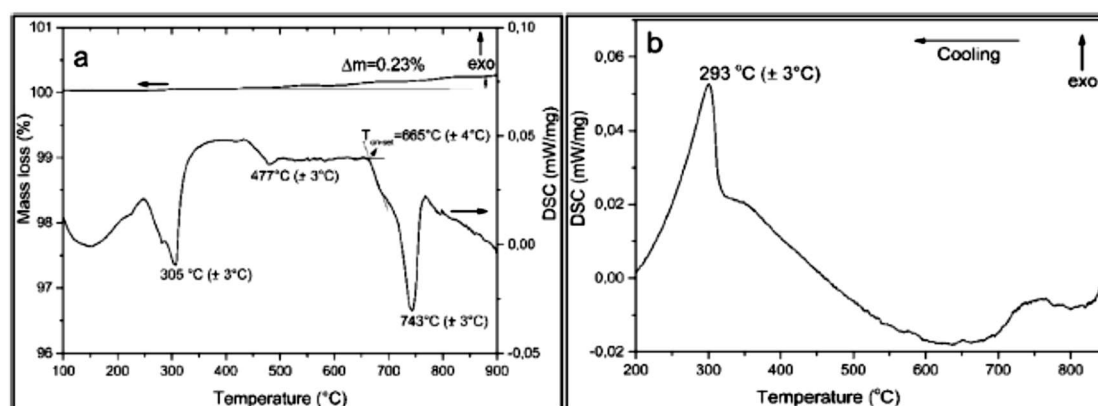


Fig. 1. TG and DSC curves of (a) the recycled HDDR Nd-Fe-B powder during (a) heating and (b) cooling.

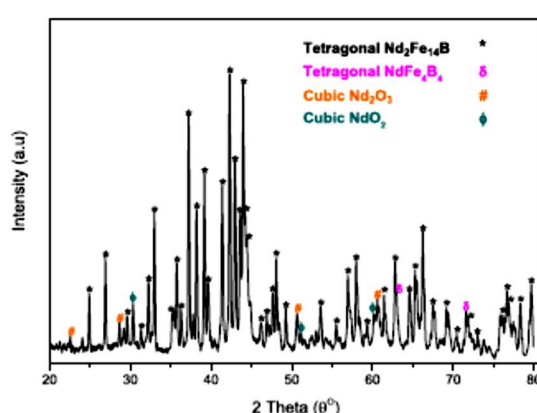


Fig. 2. Illustrates the XRD analysis of recycled HDDR powder.

and Nd₂O₃ (highlighted as 3) phases randomly scattered in the matrix. The EDS quantification of these phases is shown in Table 1. The darker contrast phases marked with "B" and "L" corresponding to NdFe₄B₄ type borides and NbFe₂ type Laves phases respectively. The Nb-rich phases are traced back from the EOL sintered scrap magnet forming NbFe₂ type Laves phases scattered in the Nd-Fe-B matrix which are nonetheless not significant in volume to be traced with the XRD analysis of the recycled HDDR powder. The Nb addition in sintered magnets also improves H_{ci} such that the grains of a hard phase become more regular and the interfaces with grain boundaries get wider and smoother [30]. Nb reportedly forms NbFe₂ Laves phase during the recombination reaction, such that precipitation of α-Fe is suppressed, as α-Fe is known to substantially reduce the H_{ci} [30,31]. The Laves phase reappears in the recycled HDDR powder as quantified in EDS results in Table 1 and therefore no free bcc iron (α-Fe) was detected with either EDS or XRD. The other dark grey phase corresponds to the conversion of the boride phase from Fe₂B phase to NdFe₄B₄ type phase after the HDDR reaction [52]. SEM-EDS cannot accurately quantify boron, but Nd:Fe ratio of 1:4 was detected from this phase as shown in Table 1.

Upon etching the matrix grains became more apparent and are

shown in Fig. 3 (b), as the Nd-rich phases were selectively removed, except the Nd₂O₃ oxides (as the bright phase marked as 3 in the inset of Fig. 3b). Most of the bright phases along the grain boundaries have an approximate atomic ratio Nd:O of 1:2 (Table 1) which indicates the chemical composition to NdO_x (NdO₂) type Nd-rich phases. The protruding light greyish Nd-rich features with Nd:O elemental ratio of 2:3 (Table 1), pointing to the presence of Nd₂O₃ type oxide as identified with the XRD. These oxides are randomly scattered in the recycled HDDR powder along the particle boundaries as obvious after etching in Fig. 3 (b), appearing in different morphologies and composition as discussed. The traces of Al were also observed at the interfaces of the Nd-rich grain boundaries and the Nd₂Fe₁₄B matrix grains. The Al signal was also detected within the Nd₂Fe₁₄B grains, and measured EDS values correspond to an overall ≤1.2 at. % Al in the Nd-Fe-B matrix phase. The Al addition has been reported to decrease the melting point of rare earth rich (Nd, Dy) grain boundary phase [32]. K. Morimoto et al. (2012) [33] reported that the addition of up to 2.5 at. % of Al causes the thickening of the Nd-rich grain boundary phase. Al is known to uniformly distribute the Nd-enriched phase from the triple junctions along the grain boundaries. This pins the domain walls at the grain boundaries and improves the isolation of the adjacent Nd₂Fe₁₄B grains, increasing the overall powder H_{ci} [33–35]. Higher magnification image of the nanocrystalline matrix grains in the recycled HDDR powder after etching is shown in Fig. 3 (c) and (d), with an average grain size in the range from 240 to 420 nm and a monomodal grain size distribution. In addition, there are also larger "residual" (marked as "R") micron-sized grains (2–10 μm) observed within the initial recycled powder which can be attributed to the incomplete HDDR reaction [29,52].

3.3. Magnetic properties and characterization of SPS reprocessed HDDR powder

After the HDDR reprocessing, the coercivity of the recycled powder as measured with the VSM (without self-demagnetization adjustment) was 830 kA/m. The first objective of our study was to find a range of SPS processing temperature where the recycled HDDR powder could be densified completely. The magnetic properties and density measurements for SPS-ed magnets in range of 650–850 °C and holding time of 1 min as shown in Fig. 4 indicate a very good possibility of obtaining fully dense Nd-Fe-B permanent magnets from recycled HDDR powders with SPS. At 650 °C, the

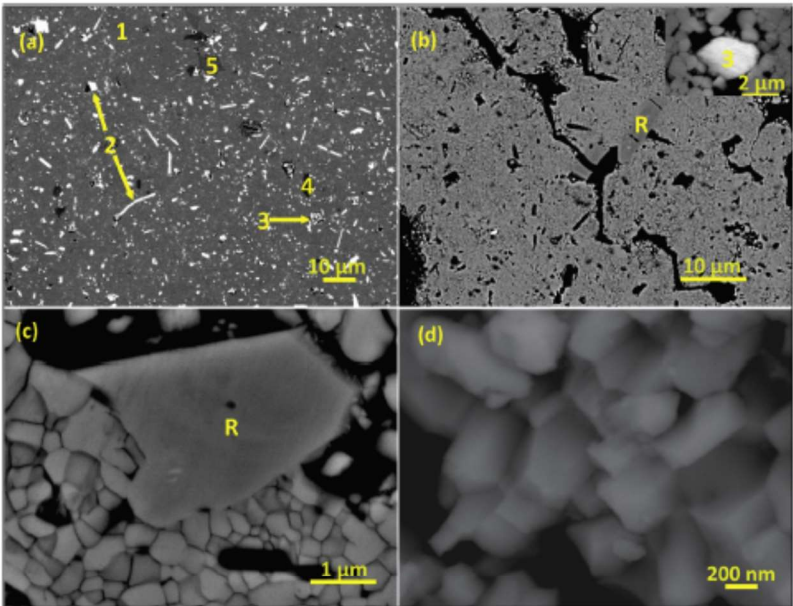


Fig. 3. HR-SEM BSE images of the initial recycled HDDR powder: (a) “1” $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase, “2” the bright Nd-rich grain boundary phase, “3” the Nd-oxide phase, “4” is Nb-Fe Laves phase and “5” are the NdFe_4B_4 type boride phase; (b) microstructure after etching; Nd-rich phases are etched away and nanocrystalline $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix grains are microscopically exposed; an inset shows Nd_2O_3 oxide phase marked with “3”; (c) higher magnification image of matrix phase consisting of mostly nanosized grains and approx. < 5 vol % fraction of large $\text{Nd}_2\text{Fe}_{14}\text{B}$ “R”- residual grains (not reacted during the HDDR process); (d) 50,000 $\times$ magnification of a powder particle fracture surface showing 240–420 nm single crystal $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains.

Table 1
EDS quantification of different phases in the recycled HDDR powder.

Phase Number	Phases	Nd (at. %)	Fe (at. %)	B (at. %)	O (at. %)	Nb (at. %)	Al (at. %)
1	$\text{Nd}_2\text{Fe}_{14}\text{B}$ Matrix	12.7	87.1	—	—	—	1.2
2	Nd-rich $\text{NdO}_x/\text{NdO}_2$	24.6	29.5	—	46.3	—	—
3	Nd_2O_3	35.2	12.2	—	47.3	—	—
4	NbFe ₃ Laves	0.7	47.6	—	—	51.7	—
5	NdFe_4B_4 Boride	10.9	39.6	—	2.5	—	—

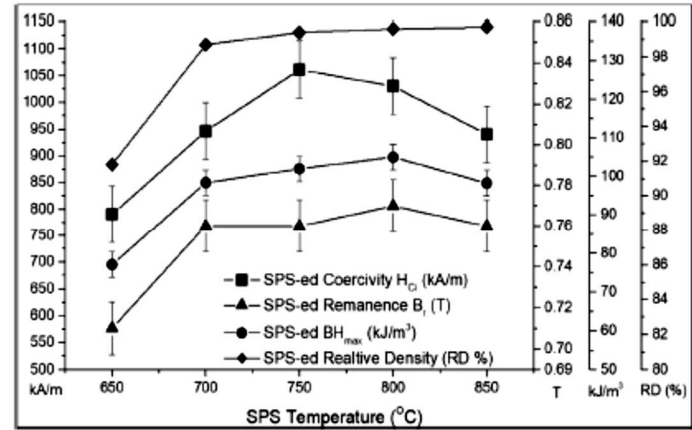


Fig. 4. The effect of SPS temperature on H_c , B_c , BH_{max} and density of the recycled HDDR Nd-Fe-B powders.

magnet density was only 91% of the theoretical value, however, the density was found to increase monotonically with the temperature and at $T \geq 700^\circ\text{C}$ where it starts to approach the theoretical value of 7.58 g/cm^3 . Here we have to emphasize that it is possible to sinter the scrap Nd-Fe-B with the oxygen content greater than 4500 ppm even though it is known that Nd-oxide phases don't sinter well [44–47].

Fig. 4 shows that nearly full densification is possible due to grain consolidation and effective pore elimination with the SPS. The $B_{H_{\text{max}}}$ increases simultaneously with the B_r , which was found to increase with the reprocessing temperatures above 700°C and reached the value of 0.77 T (105 kJ/m^3) in the sample SPS-ed at 800°C . Since the powder particles are not aligned before the SPS, the measured remanence in this range ($0.71\text{--}0.77\text{ T}$) implies the isotropic nature of the Nd-Fe-B reprocessed magnets.

The recycled powder $H_{\text{CI}} = 830\text{ kA/m}$ increased further with SPS reprocessing temperature of 700°C and reached a maximum value of $1061 \pm 50\text{ kA/m}$ at the optimal SPS temperature of 750°C as shown in Fig. 4. With the further increase in temperature, the H_{CI} drops down slightly which can be associated with moderate grain growth. With increased oxygen content in the scrap magnet from 2660 ppm to 4760 ppm after HDDR reprocessing, one would expect slower sintering kinetics of the recycled HDDR powder, as some of the metallic Nd is scavenged by oxygen. So with a reduction of the overall Nd content i.e. the Nd-rich liquid phase, proper wetting of the grain boundary phase will be limited. The Nd oxides (Nd_2O_3 and NdO_2) remain in the solid state during sintering and appear along the triple pockets and the grain junctions. In the HDDR system, the matrix grains and grain boundary phases are nanosized, with a significantly higher surface area, so the regions for Nd scavenging and oxide precipitation are considerably higher. In order to increase the H_{CI} of sintered [32] and the HDDR powder [33,34], the rare earth rich low-temperature eutectic alloys are blended into the compositions with leaner rare-earth content, which provides enough intergranular paramagnetic Nd-rich phase for the inter-grain decoupling [24–26]. In the conventional vacuum sintering route, the oxygen content is always kept below the 4000 ppm limit for sinterability and usually, the excess amount of NdH_2 is added to counter the Nd-enrichment loss due to oxidation [10,15]. On the contrary, SPS enables concurrent localized coalescence/melting [48–50] of the Nd-rich grain boundary phase in the bulk powder, which promotes the wetting of the particles even with O_2 ~5000 ppm, therefore to an experimentally identified limit of $\text{O}_2 < 8000\text{ ppm}$, sintering of the HDDR reprocessed scrap is possible with the SPS.

The SPS experiments performed at 650°C were below the eutectic temperature of the ternary phase transition ($\alpha\text{-Nd} + \text{Nd}_2\text{Fe}_{14}\text{B}$ and NdFe_2B_4). In this case, we can only expect solid-state mass transport and Nd-rich phase will not experience redistribution, although rearrangement of the particles is made under 50 MPa uniaxial pressure. So the SPS coalescence together these particles with high heat transfer at particle necking regions by pulsed current resistance heating [48] and in effect the short range mass transport only fills out few pores which are apparent from the density of 6.9 g/cm^3 (91% densification). Fig. 5 (a) shows the unetched surface of sample SPS-ed at 650°C , which can be correlated similarly to the recycled HDDR powder in terms of phase distribution and with several pores present, density is apparently lower (~90% densification). After etching in Fig. 5 (b), the average grain size range of SPS-ed samples at 650°C is between 280 and 440 nm, with an exception of few larger sized grains approx. $1\text{ }\mu\text{m}$. The SPS process changes from solid state sintering to liquid phase sintering when the SPS holding temperature is raised to 700°C , which is above the ternary eutectic temperature. Under pressure, the recycled powder particles rearrange and the liquid phase

diffuses towards the center of the powder particles into the grain boundaries at $T \geq 700^\circ\text{C}$. A slightly higher temperature of 750°C is optimal for the grain boundary diffusion during SPS, such that mass transport is efficient enough for near complete densification (99%) and pore annihilation as observed in the unetched specimen in Fig. 5 (c), but retaining a control with minimal grain growth as observed after etching in Fig. 5 (d). Near the Nd-rich pools the grain boundary phase acts as the spacers phase between the matrix grains, but the overall distribution of the grain boundary phase along the matrix grains and the particles are not uniform. The grain size distribution of recycled HDDR powder SPS-ed at 750°C corresponds to $330 \pm 120\text{ nm}$. Apart from normally grown nanocrystalline grains of $330 \pm 120\text{ nm}$ size at 750°C , the slightly larger residual grains ($\geq 5\text{ }\mu\text{m}$) were also observed. When the SPS holding temperature was 850°C , the coarsening of these “nanocrystalline” grains becomes apparent with an increase in average grain size to $750 \pm 260\text{ nm}$ and some grains larger than several microns were also observed. At $T_{\text{SPS}} > 850^\circ\text{C}$, the grain growth rate is faster than the pore mobility which leads to the isolation of the pores within larger grains as neighboring grains coalesce together rapidly and begin to merge with a higher degree of faceting [51]. This results in the abnormal grain growth labelled with “A” in Fig. 5 (d and f), that causes the bimodal grain size distribution. This abnormal grain growth in samples SPS-ed at $T > 800^\circ\text{C}$ is also one of the reasons for the H_{CI} reduction.

The redistribution of the Nd-rich phase between the matrix grains is considered to improve the localized decoupling effect which increases the H_{CI} [24,33–35]. Immediately after the removal of heat, the reprecipitation [51] of 2:14:1 matrix grains from solidifying Nd-rich phase causes pore eradication as the diffusion in the liquid phase augments the surfaces of the nanocrystalline grains and the grain boundary interfaces such that full densification is possible. This quick non-equilibrium sintering prevents any excessive mass transport of the liquid phase, and as the current stops, the cooling begins immediately which prevents grain coarsening [38]. Due to the lack of Nd-rich phase at the grain boundaries in the commercial grade, HDDR powders after SPS-ing is accounted for a drastic H_{CI} drop since the Nd-rich phase is absent between matrix grains and a significant localized exchange coupling effect may be predicted [24]. In the recycled HDDR powders, the Nd-rich phase was available at the particle boundaries of EOL magnets after the completion of d-HDDR reaction which then experienced the redistribution via liquidus state transformation during the SPS reprocessing at $T \geq 700^\circ\text{C}$. Therefore, the H_{CI} of SPS-ed magnets is higher than the starting recycled HDDR powder. It is evident that SPS allows controlled high heating rates which are suitable for rapid sintering of dense materials. The pulsed current and resistance heating at interparticle interfaces create very high localized temperature profiles, such that extensive mass transport is enhanced by grain boundary diffusion and pore annihilation [48,50]. Subsequently, faster cooling rates prevent the long-range diffusional transformation and grain growth can be controlled.

3.4. Magnetic properties and characterization of SPS-ed and thermally treated recycled HDDR powder

The effect of thermal treatment annealing was further studied on the recycled HDDR powder treated with SPS. The 750°C temperature for 15 min holding time was chosen to compare the findings with the previous findings of K. Takagi et al. [23]. Thermal treatment temperature ternary eutectic point of 665°C is set such that equilibrium diffusional mass transport can take place [51], and the Nd-rich phase can penetrate more intergranular channels so that the grain boundary phase distribution becomes more uniform. This temperature has experimentally proven to prevent the grain

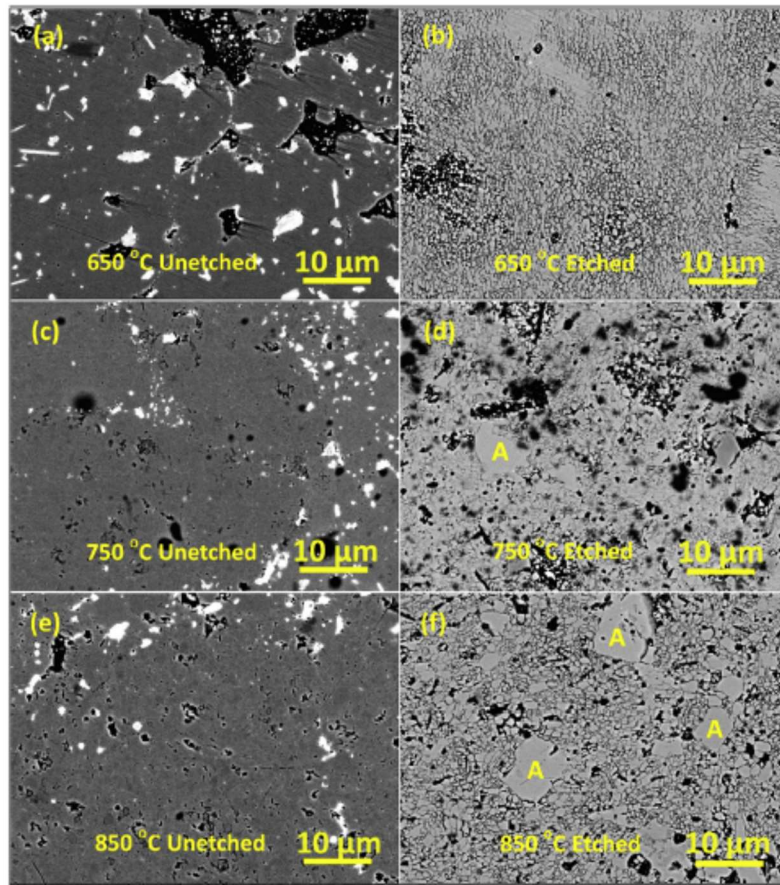


Fig. 5. BSE SEM micrographs of SPS-ed specimen: unetched surface at (a) 650 °C (c) 750 °C and (e) 850 °C; and etched surfaces showing grain structure at (b) 650 °C (d) 750 °C and (f) 850 °C. The increment of SPS temperatures from 650 to 850 °C indicates the evident grain coarsening at higher reprocessing temperatures; "A" features abnormal grain coarsening in samples SPS-ed at elevated temperatures.

coarsening, which will certainly reduce the H_{CI} . This post SPS annealing temperature cannot be reciprocated within the SPS furnace due to a different localized heating mechanism [48–50]. In SPS, the excessive localized heating at interparticle contacts will contribute to the coarsening of the Nd-rich pools as well as the nanocrystalline grains. Since the Nd-rich phase will not be uniformly distributed as required for improving the H_{CI} , further prolonging the holding time at 750 °C in the SPS has degraded the magnetic properties as shown in Table 2 (see below). Under conventional annealing treatments, the equilibrium diffusional heating [51] is applicable and the Nd-rich phase is allowed to redistribute via concentration gradients along the matrix grain surfaces [45–47].

The trend in Fig. 6 shows a comparative increase in H_{CI} of thermally treated samples over that of the as SPS-ed samples (Fig. 4), but the H_{CI} increase is milder in samples SPS-ed at temperatures higher than 750 °C. The sample SPS-ed at 650 °C experienced a substantial improvement in the H_{CI} = 1160 kA/m from 790 kA/m. This is approximately 30% higher than the starting HDDR powder. The H_{CI} increased only slightly for thermally treated

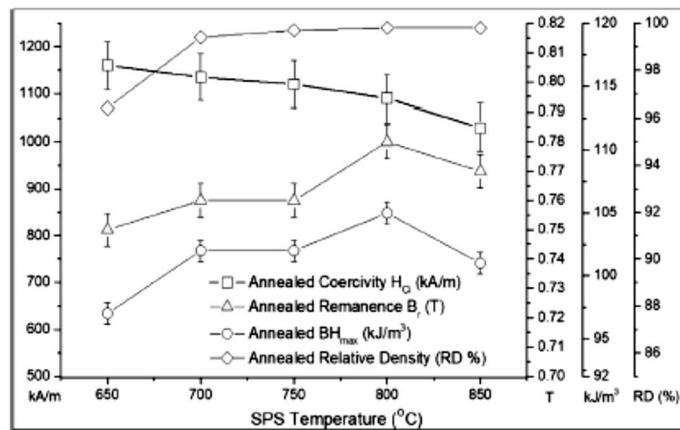
samples SPS-ed at 850 °C due to the breach of grain growth temperature above 820 °C [23]. The B_r , BH_{max} and density of the thermally treated samples also experienced a mild improvement in absolute values in all cases as shown in Fig. 6. After the thermal treatment B_r = 0.78 T and BH_{max} = 105 kJ/m³ was measured for the sample SPS-ed at 800 °C; however, the J_r/J_s ratio of 0.54 reaffirmed the 'isotropic nature' of reprocessed magnets. In the sample SPS-ed 850 °C a notable reduction in H_{CI} negates the application of higher SPS temperatures for the recycled HDDR powder since this temperature is above the grain growth temperature [23].

The post-SPS equilibrium diffusion controlled thermal treatment is done to uniformly redistribute this liquid Nd-rich phase, smoothen the matrix and grain boundary interface, by reducing the interfacial strains associated with hcp Nd_2O_3 formation [23,25,35,40]. Therefore these treatments have also been reported to increase the H_{CI} by the redistribution of Nd-rich grain boundary phase surrounding $Nd_2Fe_{14}B$ grains in sintered magnets [40–42] due to the localized decoupling of $Nd_2Fe_{14}B$ grains. Similarly, in the HDDR Nd-Fe-B magnets, the effect of localized decoupling can be combined with the domain wall pinning effect of the grain

Table 2

The variation of magnetic properties by altering SPS conditions and the improvement with annealing.

SPS Conditions ↓	100 °C/min Ramp and 1 minute holding time.			50 °C/min Ramp and 1 minute holding time.			100 °C/min Ramp and 5 minute holding time.		
SPS Temperature (°C)	H _{ci} (kA/m)	B _r (T)	Density (g/cm ³)	H _{ci} (kA/m)	B _r (T)	Density (g/cm ³)	H _{ci} (kA/m)	B _r (T)	Density (g/cm ³)
650	790	0.71	6.96	741	0.69	7.01	781	0.68	7.13
	↓	↓	↓	↓	↓	↓	↓	↓	↓
700	1160	0.75	7.31	1130	0.72	7.08	1140	0.70	7.42
	↓	↓	↓	↓	↓	↓	↓	↓	↓
750	946	0.76	7.49	893	0.74	7.36	888	0.74	7.51
	↓	↓	↓	↓	↓	↓	↓	↓	↓
800	1135	0.76	7.54	1108	0.75	7.39	1107	0.75	7.56
	↓	↓	↓	↓	↓	↓	↓	↓	↓
850	1061	0.76	7.54	1019	0.76	7.53	1040	0.75	7.56
	↓	↓	↓	↓	↓	↓	↓	↓	↓
850	1120	0.77	7.56	1100	0.77	7.55	1102	0.75	7.57
	↓	↓	↓	↓	↓	↓	↓	↓	↓
850	1030	0.77	7.55	980	0.76	7.55	992	0.75	7.57
	↓	↓	↓	↓	↓	↓	↓	↓	↓
850	1090	0.78	7.57	1074	0.77	7.56	1064	0.75	7.58
	↓	↓	↓	↓	↓	↓	↓	↓	↓
850	940	0.76	7.56	700	0.68	7.53	855	0.72	7.57
	↓	↓	↓	↓	↓	↓	↓	↓	↓
850	1030	0.77	7.57	790	0.69	7.56	953	0.74	7.58
	↓	↓	↓	↓	↓	↓	↓	↓	↓

**Fig. 6.** The effect of post-SPS thermal treatment at 750°C for 15 min on the H_{ci}, B_r, BH_{max} and densification of the reprocessed HDDR Nd-Fe-B powders.

boundaries [23,35]. For the HDDR powders, the post-sinter annealing mechanism for the H_{ci} improvement to date is not fully understood. According to K. Takagi et al. [23] the relaxation of

interfacial strains is believed to improve the H_{ci} in SPS-ed HDDR type magnets and suggested annealing did not change the thickness of the grain boundary phase. Whereby Li et al. [40], proposed

the increase in H_{CI} after annealing is due to the widening of the amorphous Nd-rich grain boundary phase. According to W. Mo et al. [46], the grain boundary phase transforms from crystalline to amorphous as its thickness decreases, and in the case of HDDRNd-Fe-B the grain boundary thickness varies from 1.6 to 3.0 nm only [23,33–35]. The thermal treatment temperature of 750 °C is adequately higher than the ternary eutectic (T_{ELM}) = 665 °C, so according to the pseudobinary phase diagram [39], the $Nd_2Fe_{14}B$ matrix and $NdFe_4B_4$ phases are in solid state but only the Nd-rich phase melts and undergoes diffusion controlled redistribution and therefore the thermal treatment should not contribute to grain growth significantly. The Nd oxide phases (hcp Nd_2O_3 and fcc NdO_x) also remain in the solid state during SPS-ing and thermal treatment but can experience the relaxation of the localized strain fields. Since T_{ELM} gets reduced due to the presence of Dy and Al from 685 °C to 665 °C [39], the Nd-rich phase must have high mobility at 750 °C for grain boundary diffusion, developing a controlled Nd-rich/ $Nd_2Fe_{14}B$ interfacial microstructure for higher H_{CI} . Therefore, one may speculate the redistribution of Nd-rich phase and relaxation of interfacial strains (at $Nd_2Fe_{14}B$ matrix grains, Nd-rich grain boundary phase and Nd oxide interjunctions) as a combined mechanism behind the H_{CI} improvement in the SPS-ed and post-annealed HDDR system. When the SPS temperature is higher than T_{ELM} , then the short-range redistribution of the grain boundary phase can be attributed to the increased H_{CI} . The complex microstructural effects associated with the Nd-rich phase and the interfacial grain chemistry as the governing mechanism behind the H_{CI} enhancement in the HDDR powder is not properly understood. The H_{CI} increase in the HDDR powder is associated with increased grain boundary width for effective grain decoupling from the ferromagnetic intergranular phase [33–35] as well as strain relaxation effects after the thermal treatment [23].

The most prominent feature from the microstructural comparison of SPS-ed unetched samples in Fig. 5 (a, c and e) with the post SPS thermally treated samples in Fig. 7 (a, c and e) attributed to the redistribution of the Nd-rich phase such that the areal fraction of thermally treated samples is higher than SPS reprocessed samples. On the contrary, when thermally treated specimens were etched, the difference in average grain size was minimal after the thermal treatment as evident in Fig. 7 (b, d and f) for 650, 750 and 850 °C respectively for the SPS reprocessed samples. Apart from normally grown nanocrystalline grains, the residual grains “R” from the EOL scrap magnets were also observed in the etched samples as shown in Fig. 7 (b and d). When the SPS reprocessing temperature was 650 °C, these residual grains were present without any expected increase in size because of the unavailability of the liquid phase to allow diffusion and grain growth [51]. The residual grains start faceting at $T > 750$ °C such that these large sized residual grains with more than 6 facets allow size augmentation due to excess thermal energy available at elevated SPS temperatures and so the normal grain growth is commenced [33]. At SPS temperature set at 850 °C, the residual, as well as larger nanocrystalline matrix grains, start consuming smaller grains and now the mechanism of grain growth proceeds to abnormal grain coarsening as shown in Fig. 7 (f). The abnormally coarsened grains contain isolated porosity, which makes them easier to distinguish from the residual grains. When the grain growth rate is higher than the pore mobility and the pores have surface energy higher than the grain boundary energy, then these pores get isolated within the abnormally coarsened grains and do not annihilate [51]. This, in turn, degrades the H_{CI} at complete densification, as shown for thermally treated samples in Fig. 6.

From Fig. 8 (a) it can be observed that the 2:14:1 matrix grains are surrounded by the Nd-rich phase in the region approximately 1–2 μm away from the spot where Nd-rich phase has solidified

after the SPS. The $Nd_2Fe_{14}B$ grains, further away approx. 10–20 μm from this region with the solidified Nd-rich phase, are observed to be in intimate contact with each other, as the grain boundary Nd-rich phase is absent or inadequately redistributed due to most probably short sintering times (10 min in total) and low temperatures (<750 °C) used in SPS.

After the thermal treatment performed in vacuum at 750 °C for 15 min, where the diffusion of the liquid phase is favorable (as the temperature exceeds the melting point of the Nd-rich phase), therefore the Nd-rich phase better surrounds the $Nd_2Fe_{14}B$ grains than in the SPS-ed samples from the condensed liquid phase. In the post thermally treated sample presented in Fig. 8 (b) it can be observed that instead of the Nd-pool a cavity appears in its place indicating to the Nd-rich phase has redistributed along the grain boundary channels to higher extent and longer lengths than in the SPS-ed only sample, as in Fig. 8 (a). This, in turn, results in an improvement in H_{CI} , which was only slight for temperatures above 750 °C. This indicates that the SPS reprocessing parameters, especially the current density and temperature, have a more significant effect in developing the final microstructure and the magnetic properties. The thermal treatments are considered as a complementary process to further augment the magnetic properties by relieving the microstructure of the stresses and redistribution of RE-rich grain boundary phase [23,25,35,40].

The study also examined how the magnetic properties of the reprocessed HDDR powder are influenced by the alteration of two SPS processing conditions: the holding time (1 and/or 5 min) and the SPS heating rate (50 and/or 100 °C/min), as shown in Table 2. The arrows (↑) in Table 2 indicate the improvement in the magnetic properties of SPS-ed magnets after the thermal treatment at 750 °C for 15 min. This helped in determining the optimal reprocessing conditions at 50 MPa applied uniaxial pressure. The observed trend of best achieved magnetic properties (green table), as shown in Figs. 4 and 6, was by keeping the heating rate of 100 °C/minute and short holding time of 1 min only. Slowing the thermal ramp to 50 °C/minute did not add any improvement to the former case, so a rapid reprocessing approach is not detrimental as long as current density in the SPS is kept optimal [48,50]. Slower ramps slacken the short-range diffusivity and the redistribution of the Nd-rich liquid phase diminishes due to a lower SPS current density. At SPS temperature of 750 °C, the drop in H_{CI} is insignificant even by prolonging the holding time due to better diffusion kinetics of the Nd-rich liquid phase. The magnetic properties degraded severely when the SPS temperature was higher than 820 °C, which is associated with the abnormal grain growth [23,37] and the results (from Figs. 5 and 7 of samples SPS-ed at 850 °C) are in agreement with these findings. Therefore, reducing the ramp at higher temperatures permits excess thermal energy to the system for grain coarsening. In the last case, when the holding temperature was increased to 5 min and the ramp was optimized to 100 °C/minute, the only persistent improvement observed was in the densification of the SPS-ed and thermally treated samples. The H_{CI} was consistently higher than slower ramped samples (50 °C/min), but nonetheless, H_{CI} was slightly lower than for the shorter holding time of 1 min. Although it can be expected that with higher overall densification, B_r , in turn, should increase, but the maximum value 0.75 T achieved disapproves the prolonged SPS holding times. Moreover, the abnormal grain growth kinetics can be activated with longer holding time and higher temperatures [48]. So by purpose, the SPS process has been verified as a significantly advantageous tool if the appropriate parameters are set for rapid sintering operations.

It is imperative to mention that SPS reprocessing is one of the few suitable techniques to obtain fully dense and high coercivity sintered magnets from the recycled HDDR powder since

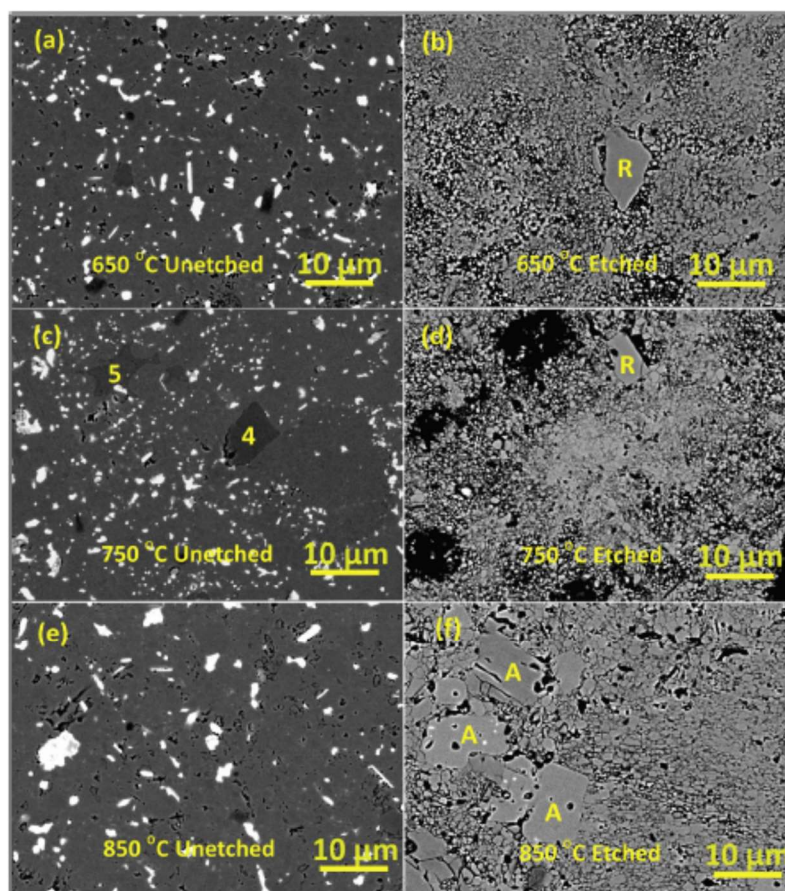


Fig. 7. BSE SEM micrographs of post SPS thermally treated: non-etched samples with better redistribution of Nd-rich grain boundary phase at (a) 650 °C (c) 750 °C and (e) 850 °C; and grain morphology of etched SPS-ed specimen at (b) 650 °C (d) 750 °C and (f) 850 °C; the grain marked with "R" indicate untransformed residual grains from EOL scrap magnet, "A" abnormally grown grains, "L" is NbFe₂ Type-Laves phase and "B" indicates tetragonal NdFe₄B₄ phase.

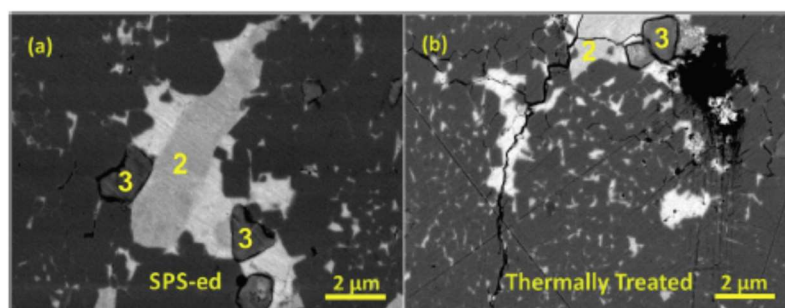


Fig. 8. High magnification micrographs showing the effect of grain boundary phase redistribution in (a) as SPS-ed sample synthesized at 750 °C and (b) thermally treated after SPS. Phase 2 and 3 corresponds to Nd-rich phase and Nd₂O₃ respectively.

conventional vacuum sintering was not applicable to the recycled scrap and to our experience have produced poor results. This lack of

sinterability in conventional vacuum sintering of the recycled HDDR powder is associated with the poor grain boundary phase

mobility and redistribution even at 1050 °C, therefore the powder particles do not coalesce together even in a well prepared green compact up to 100 MPa pressure. The simultaneous application of pressure and localized heating of powder particles in SPS allows the sintering to develop bulk magnet from scrap magnetic powders.

To summarize, the recycled HDDR Nd-Fe-B powder was subjected to a thorough SPS treatment. In all conditions, the coercivities of sintered magnets were higher than the starting recycled HDDR powder of average size 240 ± 100 nm due to the grain size preservation after the SPS reprocessing. The optimal temperature range of 750–800 °C for developing SPS-ed magnets was identified for reaching nearly full density and H_{CI} higher than the starting recycled HDDR powder. Post SPS thermal treatment at 750 °C for 15 min increased the H_{CI} due to the redistribution of thin Nd-rich grain boundary phase between the matrix grains, as confirmed by HR-SEM. The effect of redistribution is pronounced after thermal treatment above eutectic temperature on the samples SPS-ed at 650 °C due to limited diffusion in the solid state SPS. Whereby above the eutectic point, the sample SPS-ed at 700 °C experienced a higher degree of wetting of the matrix grains and subsequently the H_{CI} was high after SPS. The SPS-ed samples reached peak H_{CI} of 1060 kA/m value after SPS at 750 °C, whereby the full densification was achieved by SPS at 800 °C which can be associated with effective pore elimination. The post-SPS thermal treatment resulted in the H_{CI} improvement up to 30% higher than the starting recycled HDDR powder. The samples SPS-ed at lower temperatures like 650–750 °C experienced improvement in the H_{CI} due to better redistribution of Nd-enrichments from the particle to the grain boundaries. No evidence of abnormal grain growth was observed after the subsequent reprocessing with SPS and thermal treatment under the optimum conditions. The average grain size of samples SPS-ed at 650 °C and 750 °C were 280 ± 120 nm, and 330 ± 120 nm respectively. Post thermal treatments did not exaggerate the grain size and the average grain size only experienced a modest increment of approx. 100–200 nm. The magnetic properties begin to deteriorate when SPS temperature was greater than 800 °C due to a breach of grain growth temperature and defect generation due to localized overheating during the SPS. While the samples SPS-ed at $T \geq 850$ °C, a modest gain in the H_{CI} was reported after the thermal treatment, which may be associated only with the relaxation of the interfacial strains introduced by defects generation along the coarser grains. For the samples SPS-ed at 850 °C the normal grains ranged from 400 ± 250 nm whereby coarser grains extended from 750 to 2600 nm making a bimodal size distribution. Slowing down the SPS heating rate to 50 °C/minute did not add to the improvement of the H_{CI} . Also, increasing the holding time to 5 min only improved the densification, but not the H_{CI} . Disclosing the mechanism behind H_{CI} enhancement in terms of the microstructure after SPS reprocessing and the post-sinter thermal treatment signifies the magnetic performance relationship to develop suitable reuse and recyclability of the EOL/scrap magnets as well as the applicability of SPS reprocessed permanent magnets.

4. Conclusions

The two accomplished goals of this study include: reprocessing of the recycled HDDR Nd-Fe-B powders with SPS and thermal treatment in combination delivered fully dense bulk magnets with H_{CI} values synonymous to the SPS-ed commercial grade Aichi Steel's HDDR powder. Secondly, even with a high oxygen content in the recycled powders (4760 ppm), sinterability was not lost and the SPS-ed H_{CI} was higher than the starting HDDR. This route also verified 100% preservation of H_{CI} of the EOL scrap magnets by HDDR nano structurization and subsequent SPS treatment. The SPS performed below the eutectic do not provide enough grain boundary

phase in the liquid state, so after the thermal treatment at 750 °C, which is above the eutectic temperature, the melt formation wets the grain boundaries and H_{CI} is increased due to a better redistribution of the liquid phase from particle junctions it diffuses more along the nanocrystalline grains. Whereas the SPS reprocessing at 750 °C already has the intergranular Nd-rich phase in a liquid state and it begins to further wet as the liquid phase is redistributed under continuous uniaxial pressure from SPS. This short-order redistribution of the Nd-rich grain boundary phase at optimal SPS conditions is the proposed reason for the H_{CI} higher than the starting recycled HDDR powder. Only a slight grain growth of <100 nm on average from the recycled HDDR powder was identified after SPS-ing in the optimal conditions. The Nd-rich phase redistribution is effective for samples SPS-ed below the abnormal grain growth temperature of 820 °C as the liquid phase has already wetted the nanocrystalline grain boundary channels and the particle boundaries. At 850 °C the nanocrystalline grains grew to the size range of 750–2600 nm and in parallel, the residual grains also experience grain coarsening and grow to size larger than $\geq 10 \mu\text{m}$, with both processes the normal and the abnormal grain growth occurring simultaneously. Due to the abnormal grain growth kinetics at elevated temperature, the pores were observed to be isolated within the coarsened grains. These pores in larger grains create internal tension and as the grains expand in size, the microstructure might experience a localized strain from the grain boundaries and secondary phases. At this point (>820 °C), the localized SPS overheating (high current density and Joule's heating effect) causes the larger grains to grow at the expense of smaller nanocrystalline grains and Nd-enrichments which might generate a number of defects along the coarser grains, so the post-SPS thermal treatment may also contribute in the relaxation of the interfacial strains which increases the H_{CI} (approx. 5–10%) and not just to the Nd-rich phase redistribution especially for the samples SPS-ed above 820 °C. Thereby the strain in the microstructure at elevated SPS conditions can be associated with the high current density due to Joules heating, pore segregation, Ostwald ripening and secondary phases compressing the matrix grains. After the thermal treatment, the microstructure is relaxed of the strain arising from the SPS reprocessing. The observed grain growth after the thermal treatment is less than 100–150 nm in optimally SPS reprocessed sample at 750 °C. Upon that the SPS and thermal treatment in combination are the ideal tools to preserve the coercivity of the initial HDDR powder and therefore ideal to reprocess the recycled magnet scrap to sintered magnets. The SPS temperatures >820 °C should be avoided as it activates the Ostwald ripening and degrades the magnetic properties.

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Further reading

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Chapter 7

Particle Size Dependent Sinterability and Magnetic Properties of the Recycled HDDR Nd-Fe-B Powders Consolidated with Spark Plasma Sintering

In this chapter, the accepted article in the Journal of Rare Earths (2019) with title: “Particle size dependent sinterability and magnetic properties of the recycled HDDR Nd-Fe-B powders consolidated with Spark Plasma Sintering”, by **Awais Ikram**, M. Farhan Mehmood, Richard Stuart Sheridan, Muhammad Awais, Allan Walton, Anas Eldosouky, Sašo Šturm, Spomenka Kobe and Kristina Žužek Rožman is reported. This study evaluated the sinterability and magnetic properties of the reprocessed HDDR Nd-Fe-B powder after primary (direct HD & HDDR) and secondary recycling (coating removal and milling before the HDDR treatment). The relationship of powder particle size was developed with respect to the oxygen content, SPS densification and the magnetic properties.

The Nd-Fe-B-based magnetic scrap recovered from the EOL, the hard disk drives and electrical motors was reprocessed by utilizing the cost-effective Hydrogenation-Disproportionation-Desorption-Recombination (HDDR) process in UoB, which is a cheaper and greener alternative for making anisotropic and high coercivity magnets with nanostructured $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (~ 400 nm). However, nanostructured rare-earth-based magnets (Nd-Fe-B) had previously offered commercial applications in low performance bonded magnets with limited energy products BH_{max} in comparison to the sintered magnets.

In this article we have identified the relationship of the recycled HDDR Nd-Fe-B powder particles size, chemical composition and oxygen pickup with the magnetic properties. The sintered Nd-Fe-B magnets are usually coated to prevent corrosion or environmental degradation. During the recycling, HD process can initiate only if the coating has been ruptured, therefore the powder fragmentation necessitates the removal of these coatings. The coarser coating flakes are usually sieved out of the fine decrepitated powder, which in turn reduces the average particle size to below $100\text{ }\mu\text{m}$. The HDDR powder is susceptible to excessive oxidation if the particle size is reduced below $100\text{ }\mu\text{m}$. In the primary recycling methods as elucidated in Figure 61, the oxygen content is controlled to ~ 4800 ppm when the magnets have coatings removed and can be directly recycled systematically by HD and HDDR treatment. In case of secondary recycling route, the coating removal becomes

mandatory and as the particles are trimmed in size, the oxygen content starts to affect the magnetic properties.

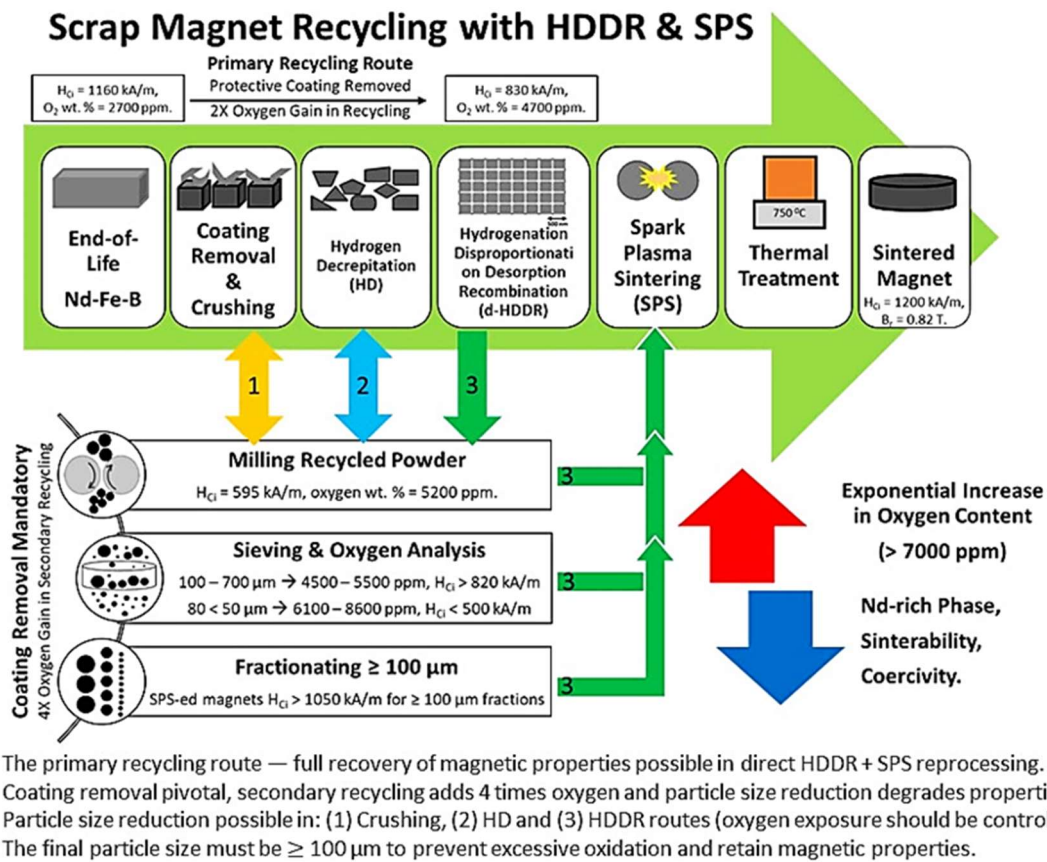


Figure 61: Graphical abstract of the primary and secondary recycling of the EOL magnets with HD and HDDR treatment. The relationship of the oxygen content and the powder particle size w.r.t the magnetic properties is indicated.

Since the HDDR powder is prone to oxidation, and in turn will lose its magnetic performance, it may limit the recyclability, so we experimentally identified the real cause behind the radical drop in coercivity and the loss of sinterability. The powder fraction was identified in which the oxygen content is two folds higher and phase formation was characterized with the HR-SEM and EDXS. The recycled powder particle and oxygen uptake relationship has been established in concurrent study in terms of the magnetic properties, such that the recycling with HDDR method is controlled and industrial upscaling has been advised.

The work presented in this publication suggests an alternate strategy for the magnetic scrap utilization, recyclability and production of sintered nanocrystalline magnets (without REE addition). The influence of recyclability on the final magnetic properties and sinterability of the recycled HDDR Nd-Fe-B powder has been elucidated. This to date has never been fully realized even for the commercial grade HDDR powders.

Authors' Contributions:

My contributions as the first and corresponding author in this paper can be summarized as following:

1. Corresponding Author: Awais Ikram;
2. Conceptualization: Awais Ikram;
3. Methodology: Awais Ikram;
4. Software: Awais Ikram;
5. Validation: Awais Ikram and Kristina Žužek Rožman;
6. Formal analysis: Awais Ikram;
7. Investigation: Awais Ikram, Muhammad Farhan Mehmood, and Anas Eldosouky;
8. Resources: Muhammad Awais, Richard Stuart Sheridan and Allan Walton;
9. Data curation: Awais Ikram and Anas Eldosouky;
10. Writing—original draft preparation: Awais Ikram;
11. Writing—review and editing: Awais Ikram, Muhammad Awais and Kristina Žužek Rožman;
12. Visualization: Awais Ikram;
13. Supervision: Allan Walton, Sašo Šturm, Spomenka Kobe and Kristina Žužek Rožman;
14. Project administration: Allan Walton, Sašo Šturm, Spomenka Kobe and Kristina Žužek Rožman;
15. Funding acquisition: Allan Walton, Sašo Šturm, Spomenka Kobe and Kristina Žužek Rožman.

Accept certificate of *Journal of Rare Earths*

Dear Awais Ikram,

Jožef Stefan Institute

The paper (Manu.No. JRE-2018-668) entitled “**Particle size dependent sinterability and magnetic properties of the recycled HDDR Nd-Fe-B powders consolidated with Spark Plasma Sintering**”, by Awais Ikram *, Farhan Mehmood, R. S. Sheridan, Muhammad Awais, Allan Walton, Anas Eldosouky, Saso Sturm, Spomenka Kobe, Kristina Zuzek Rozman, was accepted in 2018 and will be published in the *Journal of Rare Earths* in 2019.

Editorial office of *Journal of Rare Earths*



Particle size dependent sinterability and magnetic properties of the recycled HDDR Nd-Fe-B powders consolidated with Spark Plasma Sintering.

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Abstract

The dependence of the magnetic properties on the particle size of recycled HDDR Nd-Fe-B powders were investigated, with the aim to assess the reprocessing potential of the end-of-life scrap magnets via spark plasma sintering (SPS). The as received recycled HDDR powder had coercivity (H_C) = 830 kA/m and particles in the range from 30 – 700 μm (average 220 μm). After burr milling, the average particle size was reduced to 120 μm and subsequently the H_C of fine (milled) powder was 595 kA/m. Spark plasma sintering was exploited to consolidate the nanograined HDDR powders and limit the abnormal grain coarsening. The optimal SPS-ing of coarse HDDR powder at 750 °C for 1 min produced fully dense magnets with H_C = 950 $\pm$ 100 kA/m which further increased to 1200 kA/m via thermal treatment at 750 °C for 15 mins. The burr milled fine HDDR powder under similar SPS conditions and after thermal treatment resulted in H_C = 940 kA/m. The fine powder was further sieved down from 630 to less than 50 μm mesh size, to evaluate the possible reduction in H_C in relation to the particle size. The gain in oxygen content doubled for < 50 μm sized particles as compared to coarser fractions (> 200 μm). The XRD analysis for fractionated powder indicated an increase in Nd_2O_3 phase peaks in the finer (< 100 μm) fractions. Similarly, the H_C reduced from 820 kA/m in the coarse particles (> 200 μm) to 460 kA/m in the fine sized particles (< 100 μm). SPS was done on each HDDR powder fraction under the optimal conditions to measure the variation in H_C and density. The H_C of SPS-ed coarse fraction (> 200 μm) was higher than 930 kA/m and it fell abruptly to just 70 kA/m for the fine sized particles (< 100 μm). The thermal treatment further improved the H_C to > 1000 kA/m only up to 100 μm sized fractions with > 90% sintered density. The full densification (> 99%) was observed only in the coarse fractions. The loss of coercivity and lack of sinterability in the fine sized particles (< 100 μm) is attributed to a very high oxygen content. This implies that during recycling, if good magnetic properties are to be maintained or even increased the HDDR powder particles can be sized down only up to $\geq$ 100 μm .

Keywords: Reprocessing End-of Life Scrap, Rare Earth Permanent Magnets, HDDR, $\text{Nd}_2\text{Fe}_{14}\text{B}$, Recycling, Spark Plasma Sintering, Coercivity.

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1. Introduction

The Nd-Fe-B type rare earth permanent magnets since 1984^{1,2} has found applications in electric motors, microelectronics, MRI machines and wind turbine generators.³ The 2011 rare earth crisis has jeopardized the supply chain of rare earth permanent magnets,⁴ without any significant success in developing the rare earth free permanent magnets.^{3,5,6} Therefore, the researchers are keen to recycle the end-of-life permanent magnets and reutilize them directly. Alternatively, the treatments like re-sintering, melt-spinning and hydrogen related processing: hydrogen decrepitation (HD) and the hydrogenation-disproportionation-desorption-recombination (HDDR)⁷⁻²⁰ are possible in direct recycling of the magnetic scrap. The melt spinning and hydrogen routes are more promising from the economical perspective as the powder is directly suited for bonded magnet applications. The nanocrystalline powders cannot be conventionally sintered since the microstructure dependent magnetic properties i.e. the coercivity will be lost by such processing. The HDDR powder finds most of its commercial applications in isotropic and anisotropic bonded magnets,^{14,19} which have relatively lower magnetic properties than the sintered counterparts.

Refining the grain size is a well-established way to enhance the coercivity of Nd-Fe-B type permanent magnets.²¹ However, the nanocrystalline Nd-Fe-B powder are highly prone to oxidation due to formation of stable di-hexagonal close packed (dhcp) Nd_2O_3 oxides²²⁻³¹ especially with the increase in temperature, thereby restricting the top down operations as well as the recycling process.^{9-12,15-20} It was shown that the lower oxygen content and pore free microstructure inhibits the grain coarsening in the sintered magnets,³² because higher oxygen content means more fcc-Nd to be scavenged out of the grain boundaries, forming dhcp and eventually hcp Nd_2O_3 . The formation of these oxides causes defects at the intergranular junctions that locally reduce the magnetocrystalline anisotropy of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains.²⁷⁻³⁰ These intergranular defects also introduce strains along the Nd-Fe-B 2:14:1 matrix grain interfaces and act as primary nucleation sites during magnetization reversal.²⁸

To preserve the microstructure, the HDDR powder can be sintered by rapid compaction techniques e.g. hot deformation^{33,34} or Spark Plasma Sintering (SPS)³⁵⁻³⁷ without a significant loss in the magnetic properties. The challenge remains as the HDDR powder is prone to oxidation as H. Kwon³¹ and K. Takagi³⁵ reported on the loss of coercivity and remanence due to poorer sinterability in the finer sized HDDR powder, attributing it to the surface oxidation. Preparing the HDDR powder from the as cast ingots allows the freedom to maintain the close particle size range. But the recycling operation becomes tedious on EOL/scrap magnets as they are coated with protective films and the HD treatment cannot be performed without removing the coating. The protective coatings prevent the oxidation of

Nd-rich phase in sintered magnets, but the impurities from these coating will degrade the magnetic properties of the recycled material.¹⁶ Therefore, before the HDDR treatment, the decrepitated powder particles are milled down to $< 200 \mu\text{m}$ to sieve out the coating fragments. As the powder particles get smaller (the surface area increases), the Nd-rich phase at the particle boundaries exposed to the surface is prone to oxidation. This limits the applicability as the coercivity drops substantially.³¹

The fundamental aim of this study is to determine the relation between the EOL HDDR-ed Nd-Fe-B particle size to the oxygen content and the SPS sinterability of these recycled HDDR powders. As the hydrogen-based recycling method used to reprocess EOL Nd-Fe-B, demands a magnet coating removal and the average particle size of Nd-Fe-B for further reprocessing is reduced below $\leq 200 \mu\text{m}$. To establish the particle size limit for the recycled HDDR-processed powder to be viably reprocessed via SPS we have mimicked the real-world conditions of particle size reduction during milling and sieving the fraction to identify the changes in sinterability and the magnetic properties. This research work justifies to what extent, the recyclability via SPS as a case example of EOL/scrap magnets and HDDR powder reprocessing is possible. The emphasis of this study is to derive the correlations between the SPS conditions and the particle sizes for obtaining the best magnetic properties out of the recycled HDDR Nd-Fe-B powders.

2. Experimental

Sheridan et al.¹³ has provided full details of the HDDR route of the producing the recycled powder used in this study. The chemical composition measured with ICP-MS of the recycled powder was: $\text{Nd}_{13.4}\text{Dy}_{0.67}\text{Fe}_{78.6}\text{B}_{6.19}\text{Nb}_{0.43}\text{Al}_{0.72}$. For this composition, the theoretical density calculated by multiplying the weight fraction and density of individual elements was approximated to $7.57 \pm 0.01 \text{ g/cm}^3$. The end-of-life scrap magnets has measured oxygen content of 2660 ppm (0.266 wt. %). The oxygen content increased to 4760 ppm (0.476 wt.%) in the recycled powder after the HDDR reprocessing. The coarse recycled HDDR powder was burr milled for 6 hours in argon to reduce the average particle size. Sieving was done in glove box from $1000 \mu\text{m}$ to $< 50 \mu\text{m}$ mesh size. The magnetic properties of recycled HDDR powder and sieved fractions were measured as a bonded magnet with the Lakeshore VSM (self-demagnetization is not adjusted). Eltra ON 900 oxygen and nitrogen analyzer was used to measure the variation in oxygen content of the HDDR powder (coarse and fine) and in the powder fractions. The crystal phase identification was performed using the XRD (PANalytical Empyrean Diffractometer) using $\text{CuK}\alpha$ radiation analysis on the different particle size fractions of the recycled HDDR powder. The Curie temperature (T_c) = $305 \pm 3 \text{ }^\circ\text{C}$ and endothermic ternary eutectic temperature = $665 \pm 4 \text{ }^\circ\text{C}$ were

determined by Jupiter 449 Simultaneous Thermal Analysis (STA) instrument in the range of 30 – 900 °C using 20 °C/min heating and cooling rates, under argon environment (99.99% purity and flow rate 50 ml/min.).

For SPS sintering, about 3 g of the recycled HDDR powder (coarse and fine) and fractionated powder were added to 10 mm graphite dies. Graphite spacers and punches were placed and the dies are packed in vacuum sheets within the glove box to prevent oxidation during handling. Further 5 kN of uniaxial pressing was applied to squeeze the powder compactly without magnetic alignment. Just before the SPS, the chamber was purged with over pressure of Ar gas and vacuum sheets are removed. The dies were then positioned in the Syntex 3000 (DR. SINTER) SPS furnace with a controlled pressure unit. All the SPS experiments were done under 2×10^{-2} mbar dynamic vacuum and 100 MPa uniaxial pressure was continuously applied. Sintering temperature was varied from 650 – 850 °C, with a heating ramp of 100 °C/minute. The holding time at the sintering temperature was kept to 1 minute. The SPS temperature was controlled with a calibrated infrared pyrometer. After sintering, the samples were grinded with 220 grit size SiC papers to remove the graphite foil. The magnetization and demagnetization behavior were measured on a permeameter (Magnet-Physik Dr. Steingroever). The Archimedeian principle density measurements were taken on (DENSITEC) density-meter by immersing the samples in silicone oil medium.

The post SPS thermal treatments (PST) were accomplished under a dynamic vacuum of $> 10^{-5}$ mbar with a heating rate of 50 °C/minute within a horizontal tube furnace. The heat treatment was performed at 750 °C for 1 hour. Subsequent density and magnetic measurements were made after the thermal treatment. For the scanning electron microscopy (SEM), the samples are fine grinded up to 4000 grit and then polished with 1/4 µm diamond paste on the velvet cloth. The microstructural examination was performed with Field Emission Scanning Electron Microscope (JEOL 7600F). Electron energy dispersive X-ray spectroscopy (EDS) analysis was performed at 20 keV with 20 mm² Oxford X-Max detector.

3. Results and Discussion

3.1 Characterization of coarse recycled HDDR Nd-Fe-B powder.

As obtained recycled HDDR Nd-Fe-B powder particles are sized in the size range of 30 – 700 µm. Figure 1 (a) shows the low magnification image of the as received coarse HDDR powder particles with random morphology and an average particle size of 220 µm. Figure 1 (b) shows the typical microstructure of the HDDR powder with the grey matrix phase composed of nanocrystalline Nd₂Fe₁₄B hard magnetic

grains (240 – 400 nm) and the bright Nd-rich phase that is randomly distributed along the grain boundaries. NdO_2 type phase were identified via EDXS (Table 1) as the main Nd-rich phase, except for Nd_2O_3 which appeared slightly greyish and more regular in shape.

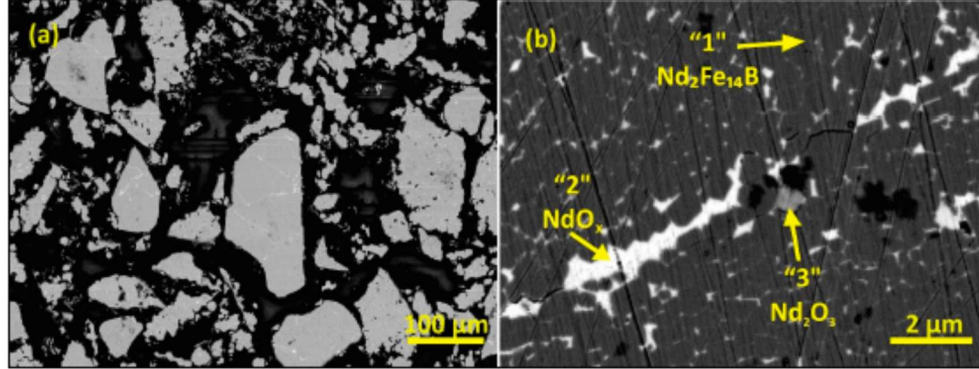


Figure 1: backscattered HR-SEM micrographs of the recycled coarse HDDR powder (a) particles of average 220 μm size, (b) intraparticle features showing "1" grey $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, "2" bright Nd-rich phase in the vicinity of grains and "3" Nd-oxide phase; the pores are black.

Table 1: EDS Analysis of Recycled HDDR Nd-Fe-B Powder.						
Phase Number	Microstructure Feature	Nd [L α] (at. %)	Fe [K α] (at. %)	O [K α] (at. %)	Dy [L α] (at. %)	Al [K α] (at. %)
1	$\text{Nd}_2\text{Fe}_{14}\text{B}$	10.6	81.6	4.2	-	1.2
2	NdO_x	24.5	29.5	46.4	-	-
3	Nd_2O_3	27.4	22.1	43.1	0.2	0.3

3.2 Magnetic properties and characterization of coarse SPS reprocessed HDDR powder.

The recycled HDDR powder coercivity $H_{\text{ci}} = 830 \text{ kA/m}$ was measured with the VSM (without self-demagnetization adjustment). The coercivity (H_{ci}) is directly related to the microstructure and composition. The peak H_{ci} was achieved by optimizing the SPS reprocessing at 750 – 800 $^{\circ}\text{C}$ as shown in Figure 2 (a). Subsequently the thermal treatment at 750 $^{\circ}\text{C}$ for 1 hour improved all the magnetic characteristics and the H_{ci} increased from 950 kA/m to 1195 kA/m for the sample SPS-ed at 750 $^{\circ}\text{C}$, without a notable increase in the grain size distribution ($\leq 100 \text{ nm}$). The H_{ci} of as SPS-ed samples at 800 – 850 $^{\circ}\text{C}$ was higher ($> 1000 \text{ kA/m}$), which is associated with an appreciably higher diffusivity of liquefied Nd-rich phase and better distribution in to the grain boundaries.³⁸ In this case, the thermal treatment only slightly improved the H_{ci} of as SPS-ed samples $\geq 800 \text{ }^{\circ}\text{C}$, since the adequate redistribution of Nd-rich phase was already achieved during sintering, which means that most

probably the strain relaxation must have caused this minor increment in H_C after the thermal treatment. The nominal grain size corresponds to: 330 ± 120 nm range for the recycled HDDR powder SPS-ed at 750°C . The H_C started to decline (1150 kA/m) at SPS temperature of 800°C and further deteriorated to 1112 kA/m for the sample SPS-ed at 850°C . This reduction in coercivity is facilitated by the rapid grain coarsening above 820°C .^{35,38}

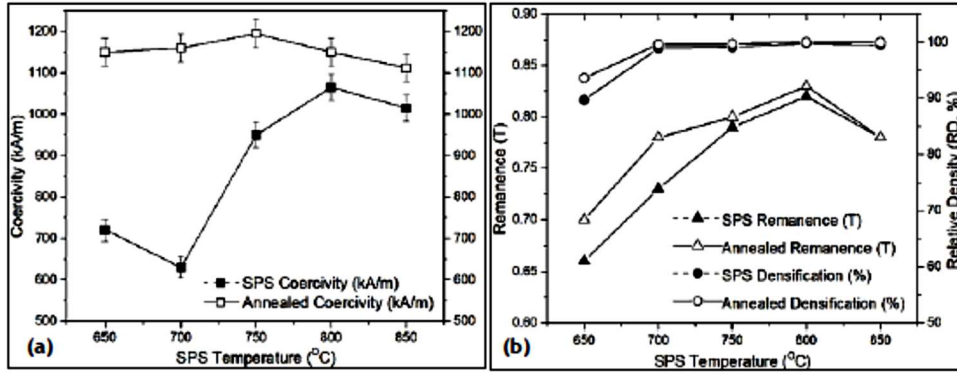


Figure 2: the effect of SPS temperature and thermal treatment on (a) coercivity H_C , and (b) remanence B_r and density of the recycled coarse HDDR powder.

In contrast, the $650 - 700^\circ\text{C}$ samples recovered up to 50 % H_C only after the thermal treatments. This is due to inadequate redistribution of liquid phase at this temperature range, which is apparent because of lower sintered density. The thermal treatment above this temperature facilitated substantial diffusional transport of the liquid phase from the particle boundaries towards the intergranular channels, which enhances the H_C .^{39,40} Moreover, the thermal treatments are associated with smoothening grain surfaces and strain relaxation from the secondary phases (Nd-oxides).^{41,42}

The B_r and density increased monotonically with the SPS temperature as shown in Figure 2 (b). The B_r reached 0.82 T for fully dense sample at SPS temperature of 800°C which increased slightly to 0.83 T ($BH_{\text{max}} = 118$ kJ/m³) with the thermal treatment at 750°C . As the magnetic alignment of recycled HDDR powder was not made prior to SPS, the B_r in range of 0.8 – 0.83 T indicates isotropic nature of reprocessed magnets ($J_r/J_s = 0.59$). Nonetheless, with SPS reprocessing above 700°C , the density begins to approach the theoretical value of 7.57 ± 0.01 g/cm³.

Previous work^{38,43} confirmed the thermal treatment facilitated in the redistribution of the Nd-rich phase along the hard phase grain boundaries, smoothening the surface of the grains as well as releasing the interfacial strains from hcp-Nd₂O₃ at intergranular junctions.^{35,40–42}

3.3 Characterization, properties and SPS reprocessing fine HDDR Nd-Fe-B powder.

In order to understand the limit of sizing down the recycled HDDR particles when they are separated from the protective Ni/composite coatings, the particle size reduction was performed with ball milling. The average particle size was reduced from 220 μm to 120 μm as shown in Figure 3 (a) which is in fact in the suitable range for sieving out particles without the flakes of the protective coatings. With this reduction in average particle size, the H_c of the fine recycled HDDR powder was also reduced to 595 kA/m (28.3 % reduction). The microstructural features of the fine HDDR powder as in Figure 3 (b) are similar to the coarse HDDR powder as presented in Figure 1 (b), with the exception of increased porosity and microcracks. It seemed obvious that additional pores may have formed due to the loss of Nd-rich phase exposed on the surface during ball milling as the powder particles were trimmed.

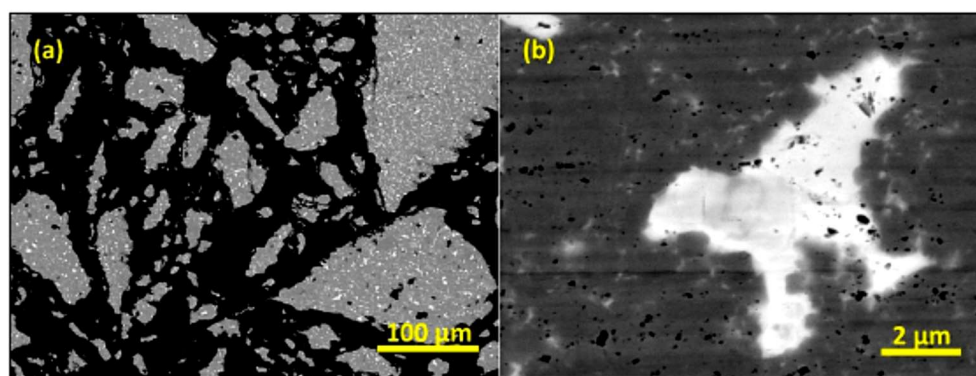


Figure 3: HR-SEM micrographs of fine HDDR powder (a) low magnification for particle size distribution and (b) higher magnification image of fine powder grain morphology which is similar to the coarse HDDR powder.

Utilizing the aforementioned SPS conditions from 650 – 850 $^{\circ}\text{C}$ for 1 minute and 100 MPa uniaxial pressure, the measured H_c was reduced by 64 % (350 kA/m) at 750 $^{\circ}\text{C}$ from the fine HDDR powder, whereby the coarse HDDR powder yielded 950 kA/m after SPS-ing. Even at higher temperatures, the H_c of as SPS treated fine HDDR powder did not increase over 500 kA/m as shown in Figure 4(a). With post SPS thermal treatment the H_c recovered and was greater than the starting coarse as well as the fine HDDR powder. Nonetheless, the H_c dropped after ball milling and after thermal treatment, the fine HDDR powder has ~25% lower H_c than the coarse HDDR powder reprocessed under similar conditions. Figure 4 (b) shows complete densification was only possible for the samples SPS-ed above 750 $^{\circ}\text{C}$ and successively heat treated. The remanence on the contrary increased with the SPS temperature and the sample SPS-ed ≥ 750 $^{\circ}\text{C}$ resulted in $B_r = 0.8$ T (RD. ~98 %). The B_r value of 0.83 T ($BH_{\text{max}} = 116$ kJ/m 3) was observed for the 850 $^{\circ}\text{C}$ SPS-ed fine HDDR powder sample after the heat treatment, but the H_c reduced to 880 kA/m. This B_r value was possible at 800 $^{\circ}\text{C}$ in case of the coarse

HDDR powder, indicating fine powders require higher temperature to fully sinter and densify. Since the volume fraction of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is the same after burr milling, and the relative density scales similarly, therefore the deviation in the remanence of the isotropic magnets from coarse and fine powders is negligible as long as experimental relative density reaches 100% of the theoretical value of $7.57 \pm 0.01 \text{ g/cm}^3$.

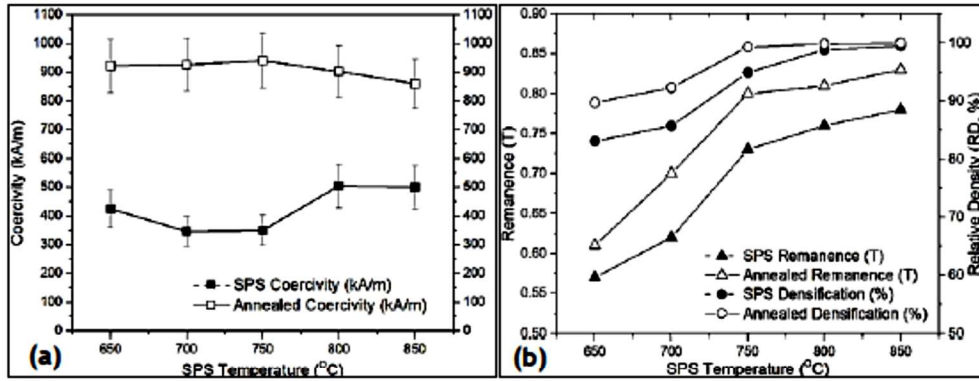


Figure 4: the magnetic properties of fine HDDR powder after SPS reprocessing and thermal treatment (a) coercivity and (b) density vs remanence.

To identify the particle size range suitable for sintering in relation to the oxygen content, the fine HDDR powder was fractionated from 630 μm and down to < 50 μm mesh size in the glove box. The effect on magnetic properties by varying the powder particle size after fractionation was studied. The recycled HDDR powders (coarse and fine) as well as the sieved fractions were analyzed for their nominal oxygen uptake. The oxygen content analysis shown in Figure 5 revealed that the fine HDDR powder has slightly higher oxygen wt. % (5100 ppm) as compared to coarse HDDR powder (4760 ppm), although the average particle size is approximately reduced by 50%. The oxygen content increased rapidly in < 100 μm fine sized particles, but the gain is insignificant for particles sized above 200 μm . The oxygen content increased by two folds approx. in < 50 μm fraction, even though the milling operation, sieving and oxygen analysis was performed under inert atmosphere. Up to 100 μm , the oxygen content was less than (5500 ppm).

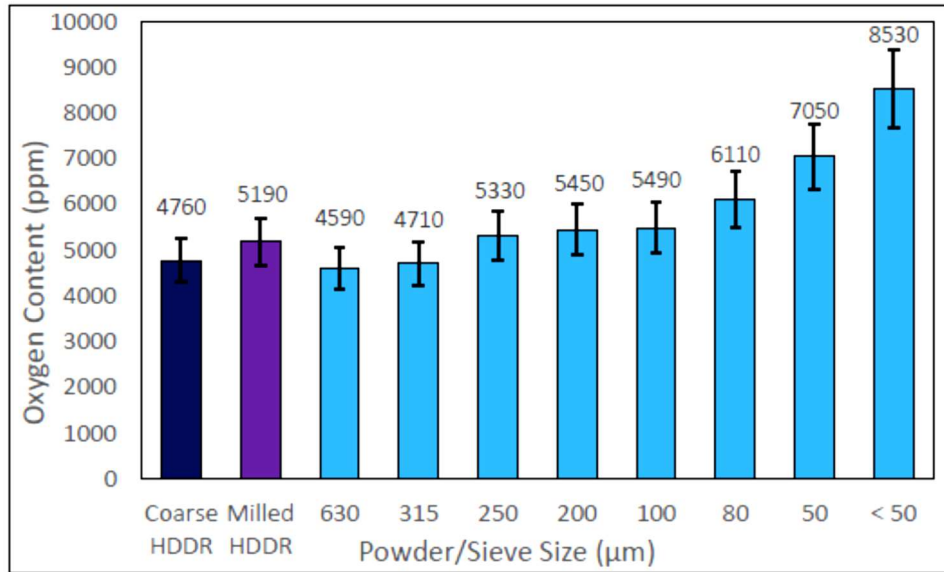


Figure 5: O_2 content analysis of the coarse, fine and post milling fractionated HDDR powder.

After burr milling, the H_C was reduced by 28% (595 kA/m) in the fine HDDR powder which is obvious due to the gain in oxygen content, as represented in Figure 6. The H_C measurements were also taken for each sieved fraction. For the coarser fractions (630 – 200 μm), the measured H_C (830 ± 15 kA/m) was equivalent to the coarse recycled HDDR powder. The 100 μm fraction did not lose much of the coercivity, but the finer sized fractions (< 100 μm) experienced a radical coercivity reduction (500 ± 50 kA/m) with higher oxygen uptake. Oxygen scavenges the Nd-rich phase and leads to the formation of Nd_2O_3 phase which considerably reduces the sinterability since the amount of liquid phase for wetting the grains is inadequate and sintered density is much lower.^{22–24}

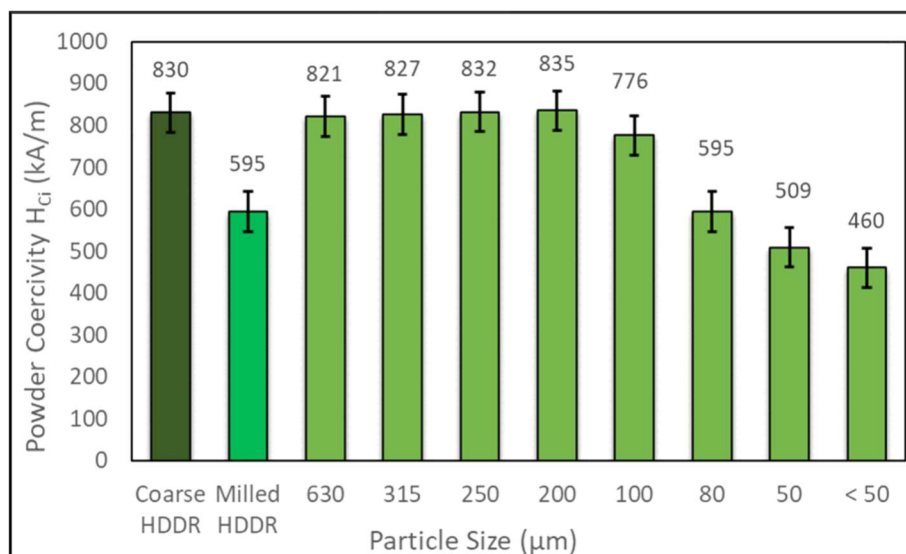


Figure 6: coercivity variation with the powder particle size after burr milling.

Comparative XRD analysis of coarse, fine and fractionated powders (315, 100, 50 and < 50 μm) is given in Figure 7. The XRD analysis of coarse HDDR powder reveals majority of peaks correspond to hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase with JCPDA serials: 00-036-1296 and 04-006-2691. The lattice parameters of tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ belong to $P4_2/mnm$ space group with $a = 8.79$ (Å), $b = 8.79$ (Å) and $c = 12.2$ (Å). The matrix phase remained the same even after the burr milling and no dissociation to $\alpha\text{-Fe}$ was detected. The tetragonal NdFe_4B_4 (JCPDA # 01-081-3530) boride phase was also present. Several types of Nd-rich phases were identified with the XRD. The volume fraction of metallic Nd was below the detection limit, hence most of the Nd-rich ensembles comprised of NdO (JCPDA # 04-007-3961) and NdO_2 phases (JCPDA # 04-007-0500). This NdO_x type Nd-rich phases are present in all the samples, irrespective of particle size. The NdO phase peak is observed in all the samples, while NdO_2 peak are more distinguished in 315 and 100 μm fractions as well as the coarse HDDR powder. The NdO_2 peak intensity diminishes in the fine fractions (50 and < 50 μm) as well as the milled HDDR powder. With an increasing oxygen content in the smaller particles, the NdO_x phase partially transforms to cubic $c\text{-Nd}_2\text{O}_3$ oxide (JCPDA # 00-040-1283). The peaks and relative intensities of $c\text{-Nd}_2\text{O}_3$ increased in the fine HDDR powder as well as < 100 μm sized fractions. Additionally, the fine HDDR powder and < 100 μm sized fractions also featured hexagonal $hcp\text{-Nd}_2\text{O}_3$ type oxide phase (JCPDA # 00-040-1282 and 04-006-0997). This hcp oxide phase is known to introduce larger interfacial strains along the grain boundaries which reduces the H_{ci} .^{29,30} With an increasing volume fraction of $hcp/cubic$ Nd_2O_3 , the overall grain boundary area is reduced and so the grains experience localized exchange effects without a continuous intergranular phase.^{35,37,40} With the increase in oxygen content in finer fractions, the

peak intensities of Nd_2O_3 oxides was found to increase, which must be the reason behind the inferior sintered density for the samples SPS-ed up to 750 °C, as in Figure 4 (b). The thermal treatment slightly improved the sintered density, and conversely higher SPS temperatures (≥ 800 °C) were required to fully densify the fine HDDR powder.

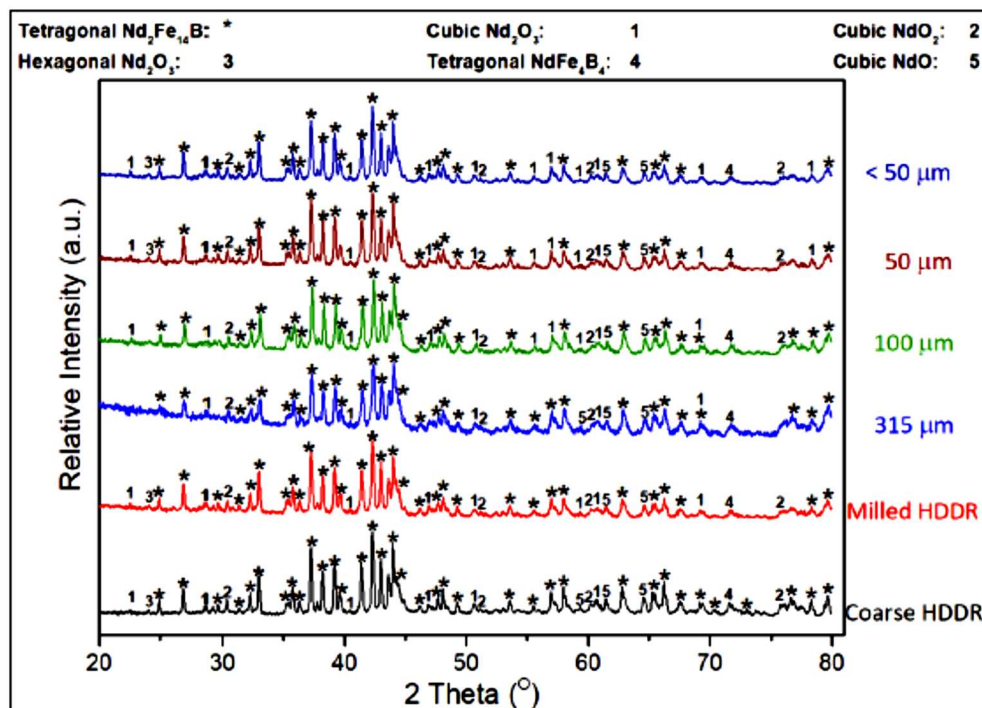


Figure 7: XRD analysis of coarse, fine and fractions (315, 100, 50 and $< 50 \mu\text{m}$) of recycled HDDR powder.

3.4 SPS reprocessing of fractionated fine HDDR powder.

These powder fractions were SPS reprocessed at 750 and 800 °C to identify how the magnetic properties change for each fraction and knowing the state of oxygen uptake. As shown in Figure 8 (a) and (c), the coarse fractions reproduced $H_C = 900 \pm 50$ kA/m, which is equivalent to the non-milled HDDR powder. The SPS-ed H_C declined below 450 kA/m for $\leq 200 \mu\text{m}$ sized fraction in the 750 °C and 800 °C SPS-ed samples are shown in figure 8 (a) and (c) respectively. In the $\leq 100 \mu\text{m}$ powder fractions, the H_C got reduced drastically to less than 100 kA/m. The thermal treatment improved the overall H_C in $\geq 100 \mu\text{m}$ sized fractions by a mere 50 – 100 kA/m, but nonetheless the H_C was significantly lower than 200 kA/m in the finer sized HDDR powder fractions. The H_C of $\leq 50 \mu\text{m}$ fractions after SPS was less than 100 kA/m and only increased to ~ 245 kA/m, which is substantially lower than both the fine HDDR powder (595 kA/m) and $< 50 \mu\text{m}$ powder fraction's coercivity (460 kA/m). This is possibly due

to a phase transformation during the SPS further deteriorated the H_c of $< 100 \mu\text{m}$ sized fractions. The possible phase transformation during the SPS should be of Nd-rich phase, i.e. of NdO_x and $\text{c-Nd}_2\text{O}_3$ to $\text{hcp-Nd}_2\text{O}_3$ ²⁶⁻³⁰ for oxygen content greater than 6000 ppm. This also degraded the sinterability as the SPS-ed density of fine fractions was 6.3 g/cm^3 and 6.5 g/cm^3 at 750°C and 800°C respectively.

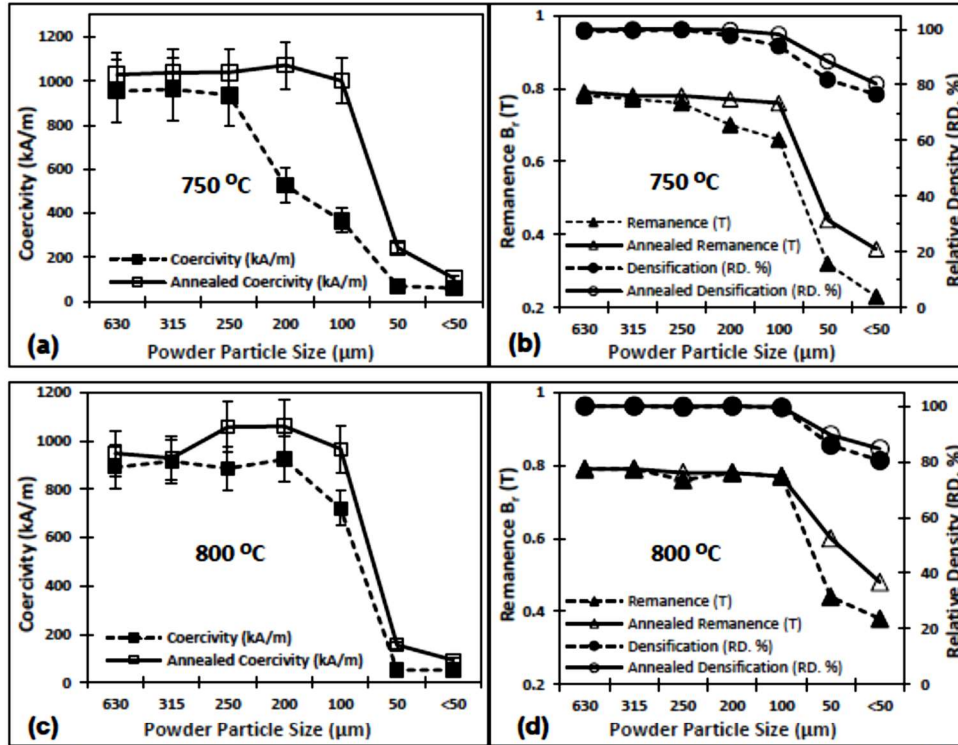


Figure 8: magnetic properties of fractionated powder SPS reprocessed (a & b) at 750°C in and (c & d) at 800°C .

Dashed lines show magnetic properties after SPS sintering, whereby the properties after the thermally treatment are represented by solid lines.

At SPS reprocessing temperature of 800°C (figure 8d) the densification was marginally higher than with the SPS temperature of 750°C (figure 8b). The densification dropped as the particle size was reduced below $100 \mu\text{m}$. The densification was lower than $\sim 80\%$ after the SPS for these fine fractions and after the thermal treatment only improved to $\sim 84\%$ approx. Predictably the B_r was approx. 50% lower for the finer fractions ($< 100 \mu\text{m}$) as shown in Figure 8 (b) for 750°C and (d) for 800°C SPS-ed fractions. The B_r of the coarse fractions 630 and $315 \mu\text{m}$ was 0.79 T in 800°C SPS-ed sample. The coarse fractions sintered at 750°C had slightly lower remanence (2%) and reached $B_r = 0.79 \text{ T}$ ($BH_{\text{max}} \sim 108 \text{ kJ/m}^3$) after the thermal treatment. The B_r and density was slightly higher when the powder fractions were SPS-ed at 800°C , except for the finer fractions ($\leq 100 \mu\text{m}$), which did not recover their

magnetic properties after the thermal treatment (and not even comparable to the fine HDDR powder). Since the remanence ratio ($J_r/J_s \sim 0.58$) for the fully dense samples (i.e. coarser fractions ($\geq 100 \mu\text{m}$)) does not change substantially with the SPS reprocessing temperatures, the absolute B_r values indicate the miniscule changes in sintered density of the isotropic magnets. The J_r/J_s ratio of 0.34 is significantly lower for the $< 50 \mu\text{m}$ fraction, implying poor densification of isotropic magnets from the fine HDDR powder.

On the contrary, milling has introduced more oxygen in to the system as the particle size was reduced. The excess of non-oxidized intergranular Nd-rich phase is attributed to improve the H_{ci} of the original HDDR powder^{13,40,44} as well as SPS processed magnets.^{35–37} So, the presence of pristine NdO_x type enrichments contributed to retaining the H_{ci} after milling and subsequent SPS reprocessing in coarser fractions ($\geq 200 \mu\text{m}$). The reduction of $100 - 200 \text{ kA/m}$ H_{ci} in coarse fractions as compared to the non-milled HDDR powder ($\sim 1200 \text{ kA/m}$) is due to the mechanical degradation of the powder surfaces which activates the surface for oxygen uptake,^{38,43–47} and thermal processing (SPS) permits phase transformation of Nd-oxides, as more of the surface oxygen reacts with intergranular Nd-rich phase to form cubic and hcp- Nd_2O_3 .^{25–31}

The most obvious reason identified for the degradation of sinterability and the magnetic properties is clearly the exponential gain in the oxygen content, which leads to the formation of hcp- Nd_2O_3 oxide phase. This phase remains stable during the SPS process, and in finer fractions with higher surface area, its occurrence of hcp- Nd_2O_3 phase is more apparent. Therefore, the amount of the liquid phase during SPS is not enough to fully densify the recycled HDDR powder. The lack of formation of optimal microstructure after SPS in finer fractions therefore is the reason why H_{ci} , B_r and the density are low, which do not recover even after the thermal treatment due to substantial oxidation (Nd-rich phase transformation to cubic and hcp Nd_2O_3).

The original EOL sintered magnet had $H_{ci} \sim 1160 \text{ kA/m}$, and recycled HDDR powder's coercivity is 830 kA/m . During the HDDR based recycling it is essential that all disproportionated phases especially $\alpha\text{-Fe}$ must recombine back to $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase and the Nd-rich intergranular phase is uniformly distributed along the grains. During desorption, the hydrogen dissociates from NdH_2 and promotes the diffusion of Nd during recombination stage by forming continuous grain boundary phase surrounding the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix, which in turn reduces grain's surface defects and increases the H_{ci} ⁴⁸. Such recycled HDDR powder will have magnetic properties close to EOL magnet because of nanostructurization of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains i.e. near the single domain grain size^{3, 5, 13}. During the

recycling with HDDR process, if Nd content is low or gets reduced as the oxygen scavenges it to form Nd_2O_3 , then its uniform distribution will be affected which can cause grain boundary regions running dry. Therefore, the adjacent grains across such dry grain boundary channels are in contact with each other, leading to localized exchange coupling which reduces the coercivity.^{3,40} The presence of micron sized residual grains after d-HDDR process can also reduce the HDDR powder coercivity, so control of the HDDR technology and improvements are necessary.⁴³⁻⁴⁷ Excessive addition of Nd and up to 2 at. % Al in the composition has been reported to increase the coercivity of HDDR powder to 1560 kA/m due to continuous grain boundary layer of Nd-rich phase⁴⁸, but such methodology may not be applicable to modify the composition of magnetic scrap during the HDDR recycling route. The diffusion treatment of the HDDR powder with up to 20 wt. % $\text{Nd}_{90}\text{Cu}_{10}$ resulted in H_{ci} of 1552 kA/m⁴⁹, may seem a more feasible approach after HDDR recycling to augment the coercivity. However, the target of this study was also to determine the highest possible magnetic properties from the SPS processed recycled HDDR powder, without any addition of RE-rich diffusing alloys.

Comparing the findings of this study with state-of-the-art on recycling and HDDR Nd-Fe-B, it is clear that the obtained $H_{ci} = 1200$ kA/m of coarse non-milled powder is highest for this composition of the recycled HDDR powder^{13-19, 36-38, 50-52}, even compared to our previous results³⁸ due to application of higher pressure and preservation of the original HDDR microstructure after SPS and optimal thermal treatments. The recovery of H_{ci} values of original EOL magnet asserts that the HDDR recycling route is a very feasible option in terms of retaining the ultrafine microstructure and the correlated magnetic properties. The SPS has proven as an indispensable tool to sinter bulk magnets out of the recycled HDDR powder without compromising on the magnetic properties. The H_{ci} values in this study are slightly higher than the commercial HDDR powder as well³⁵, where the authors also described finer particles losing the magnetic properties but not classifying with an explanation of how oxidation disrupts the microstructure and the effects of annealing in recovery of the magnetic properties.

The initial magnetic properties in the recycled Nd-Fe-B system can be recovered only if the Nd-rich phase remain unattached and/or in NdO_x form which has not been further oxidized to stable hcp- Nd_2O_3 phase, which put a limit on sizing down the particle size to ≥ 100 μm .^{38,50} At sintering temperatures used in the present study, it is expected for the oxygen adsorbed on the surface of Nd-rich phase to undergo further oxidation to metastable hcp- Nd_2O_3 phase which consumes more Nd, henceforth the smaller HDDR particles are more prone to this phase transformation³¹ during the SPS and thermal treatment. This effectively limits both; the sinterability and the coercivity. When the metallic Nd from the intergranular regions excessively transforms to oxides because of the adsorbed

surface oxygen, the diffusion kinetics of Nd-rich liquid phase during the thermal treatment will be limited to redistribute it uniformly across the intergranular region leading to lower coercivities, which would otherwise recover the magnetic properties of the recycled feedstock. The thermal treatment was found to be beneficial as it relieves the microstructure of SPS processing stresses, refines the surface morphology of the matrix grains³ and the grain boundary channels are widened^{40, 41, 48, 49} with the Nd-rich phase being redistributed, which in turn increases the coercivity.

3.5 SEM examination of the SPS reprocessed fractions.

The SEM analysis in Figure 9 revealed the coarser fractions (630 and 315 μm) after SPS-ing at 750 °C and subsequently thermally treated, formed up nearly dense microstructure. The Nd-rich phase is adequately distributed along the particle boundaries in the microstructure as shown in figure 9 (a) and (c) as well as the grain boundary region along of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase (b) and (d). The average grain size does not change and it says in the range 300 – 500 nm after the burr milling as in Figure 9 (b) of 630 μm and (d) of 315 μm .

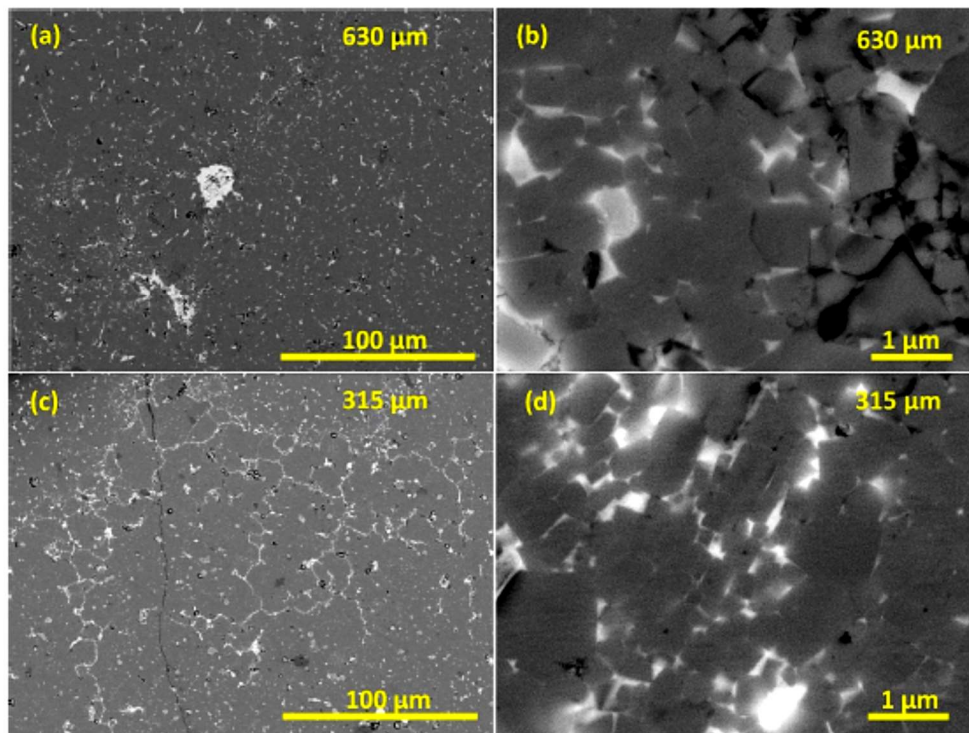


Figure 9: HR-SEM images of 750 °C SPS treated coarse powder fractions, (a & b) 630 μm and (c & d) 315 μm .

Comparatively, the microstructure of the finer sized fractions SPS-ed at 750 °C and thermally treated samples is noticeably different as shown in Figure 10 (a) and (c) of 50 and < 50 µm respectively. Clearly with the reduction in the particle size, overall very high porosity in the microstructure is evident which is attributed to poor sintered densities. The Nd-rich phase is distributed like an extensive network in the coarser fractions (630 and 315 µm) in Figure 9 (a & c), which is contrary to the fine fractions (50 and < 50 µm) as the intergranular phase is truncated to the rounded shape. At higher magnification Figure 10 (b) and (d), it was confirmed that these rounded features are Nd₂O₃ type oxides. So in the fine fractions, most of the Nd-rich phase existed with a different (greyish) contrast and morphology which was due to the oxidation of the secondary phase (Nd₂O₃ phase transformation). The intergranular Nd-rich phase was mostly squeezed out to the surface during the SPS and it oxidized on the surface with adsorbed oxygen, subsequently forming Nd₂O₃ as confirmed with EDS, therefore the porosity was left over in these finer fractions. Lower density samples from fine sized HDDR powder had reportedly poorer magnetic properties, which were unrecoverable even after thermal treatments.³⁵

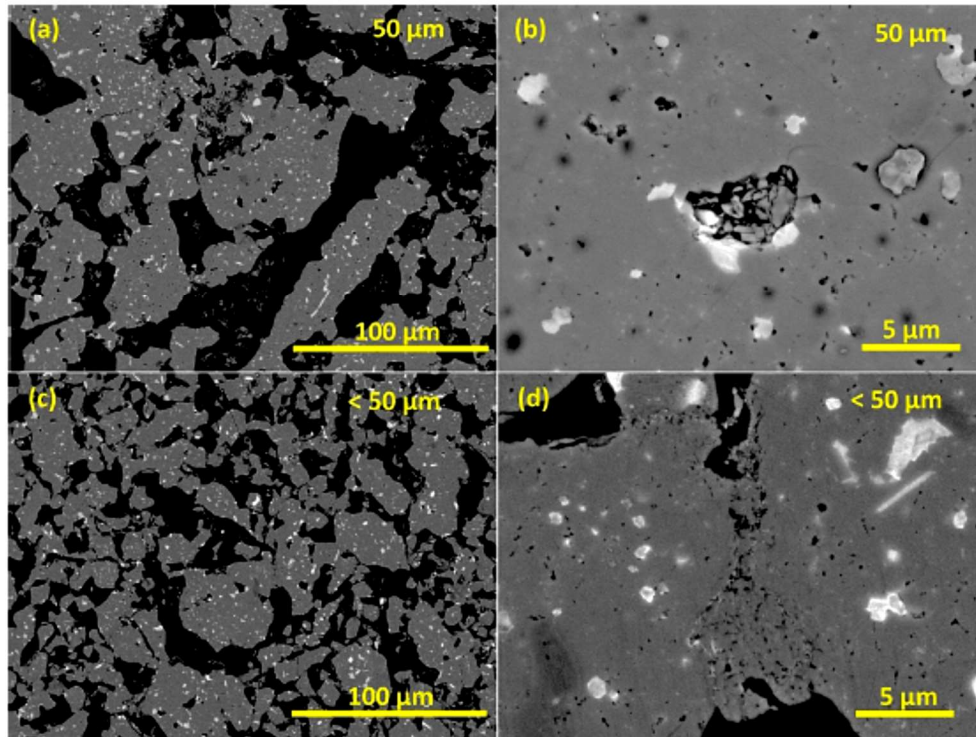


Figure 10: BSE SEM micrographs of SPS reprocessed finer fractions 50 µm (a & b) and (c & d) < 50 µm at 750 °C.

This verifies the fact that the overall reduction in the total volume fraction of the hard-magnetic phase after burr milling is virtually insignificant. But the secondary Nd-rich phase experience phase change due to excessive formation of Nd_2O_3 oxides, which radically drops the recycled powder and sintered magnets' coercivity, moreover reduces the sinterability for finer fractions as well.^{22,23,31,40} In effect, it reduces the diffusivity of liquid phase due to excessive Nd_2O_3 oxides formation, therefore loss of Nd-rich liquid phase due to the formation of stable hcp- Nd_2O_3 as the most probable reason for lower sintered density and remanence.^{26,28} Even though the interfacial strains associated with Nd_2O_3 formation along intergranular junctions are reduced by thermal treatments which improves overall the magnetic properties as well as the sintered density, it is a fair indicator that a much higher volume fraction of Nd-oxides will ultimately deteriorate the magnetic properties (beyond repair and may require excessive addition of Nd).^{25,35,40} Henceforth the presence of secondary phase is very important for the development of optimal magnetic properties and it degrades severely as Nd-rich phases gets exponentially oxidized with the particle size reduction. Thereby it is suggested to maintain the powder particle size $> 100 \mu\text{m}$ during the HDDR reprocessing of end-of-life scrap magnets to achieve higher H_c and sintered densities. Alternative recycling strategy should be adopted for coated magnets to remove the protective coatings prior to pulverization of EOL scrap magnet's particles, which must not be below $100 \mu\text{m}$ if HDDR reprocessing is opted. Moreover, the $< 100 \mu\text{m}$ sized recycled HDDR powder may require supplementary RE-rich alloy to recover the degradation of the magnetic properties and sinterability.

4. Conclusions

The magnetic properties and the sinterability of the recycled HDDR Nd-Fe-B powder from end-of-life scrap magnets were evaluated in relation to the oxygen content. Spark Plasma Sintering was used to fully densify non-milled HDDR powder with H_c values corresponding to fresh commercial grade Aichi Steel's HDDR powder. The fine HDDR powder ($< 100 \mu\text{m}$) underperformed with SPS reprocessing and could not gain similar properties as the coarse HDDR powder ($\geq 100 \mu\text{m}$). After the optimal SPS reprocessing at 750°C for 1 minute, the $H_c = 945 \text{ kA/m}$ of the isotropic sintered magnets made from burr milled recycled powder and the coarser fractions was $\sim 50\%$ higher than this fine HDDR powder. The optimally SPS treated coarser fractions ($\geq 200 \mu\text{m}$) had virtually unchanged coercivity ($> 1000 \text{ kA/m}$) and full densification, similar to the coarse recycled HDDR powder. The finer sieved fractions ($\leq 50 \mu\text{m}$) were found as the culprit behind the radical coercivity drop due to the substantial gain in the oxygen content ($> 8000 \text{ ppm}$). SEM/EDS analysis confirmed the loss of in intergranular Nd-rich phase and sweeping formation of Nd_2O_3 phases on the surface of the fine fractionated HDDR powder. Thereby the fine powder size fractions ($\leq 50 \mu\text{m}$) loose the sinterability in the SPS and resultant the

magnetic properties are poor. Based on our study results the 100 μm particle size is proposed as the minimum limit for reprocessing of the HDDR powder without sacrificing the magnetic properties.

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Chapter 8 Results

Coercivity Increase of the Recycled HDDR Nd-Fe-B Powders Doped with DyF₃ and Processed via Spark Plasma Sintering & the Effect of Thermal Treatments

In this chapter, the article published in the MDPI Journal of Materials titled: “Coercivity increase of the recycled HDDR Nd-Fe-B powders doped with DyF₃ and processed via Spark Plasma Sintering & the effect of thermal treatments” by **Awais Ikram**, M. Farhan Mehmood, Zoran Samardžija, Richard Stuart Sheridan, Muhammad Awais, Allan Walton, Sašo Šturm, Spomenka Kobe and Kristina Žužek Rožman is included [\[205\]](#).

The Nd-Fe-B-based magnetic scraps recovered from the hard disk drives and the electrical motors are reprocessed by utilizing the cost-effective Hydrogenation-Disproportionation-Desorption-Recombination (HDDR) process that is able to produce the anisotropic and high coercivity powders with nanostructured Nd₂Fe₁₄B grains (≤ 400 nm), suitable for making bonded magnets. However, the polymer-bonded HDDR Nd-Fe-B magnets cannot be used in high temperature applications above 150 °C. Sintered magnets from the HDDR Nd-Fe-B powder can be potentially substituted by rapidly consolidating with the SPS, as it preserves the nanocrystalline microstructure and related magnetic properties. In order to increase the coercivity of the recycled HDDR Nd-Fe-B, which can already compete with the fresh commercial HDDR MF-15P powder [\[83\]](#), doping with DyF₃ nanoparticles has been evaluated. So far, the characteristic core-shell microstructure typical for GBD treated sintered/hot deformed magnets [\[69, 154-158, 169, 204\]](#) was not reported for the HDDR Nd-Fe-B system.

In the HDDR system, the diffusion of the HREEs (Dy) is not trivial to approach because of the complex HDDR microstructure which can be oxidized, especially in the case when dealing with EOL magnets and losing the effective Nd-rich phase and eventually the sinterability. Therefore, the diffusion lengths are limited from the surface toward the interior. In order to achieve uniform local diffusion profiles of the Dy, we blended the recycled powder with dopant nanoparticles based on DyF₃. This study complimented the rapid SPS consolidation of the recycled HDDR Nd-Fe-B powder and DyF₃ (nano)particles blend. The effects of vacuum thermal treatment conditions were studied over a wide range to temperatures from 600 – 900 °C from 1 – 6 hours by varying the DyF₃ dopant content from 1 – 5 wt. %, in order to optimize the diffusion conditions for uniform core-shell structure formation [(Dy,Nd)₂Fe₁₄B] shell on the Nd₂Fe₁₄B cores] and achieving desirable magnetic properties. These rare earth fluorides (Dy and Tb) have been used previously on the sintered magnets as well as the melt spun ribbons, where the researchers have reported

an increase in the coercivity from 10 – 30 % due to the characteristic core-shell structure [69, 151, 154-156, 158, 169, 204]. Utilizing the same concept, we achieved ~70% higher coercivities than the starting HDDR powder and ~18% higher than the commercial HDDR powder MF-15P. The added benefit of such HREEs doping is that very small weight fractions are effective to induce high coercivities. The control of heat treatment conditions and weight fractions of the dopants has been proposed for the commercial scale up in the HDDR Nd-Fe-B system. Moreover, the influence of complex intermetallic compounds on the microstructure, diffusion and the magnetic properties has also been elucidated. A new diffusion mechanism model applicable to the HDDR Nd-Fe-B systems is given in this manuscript as shown in Figure 62.

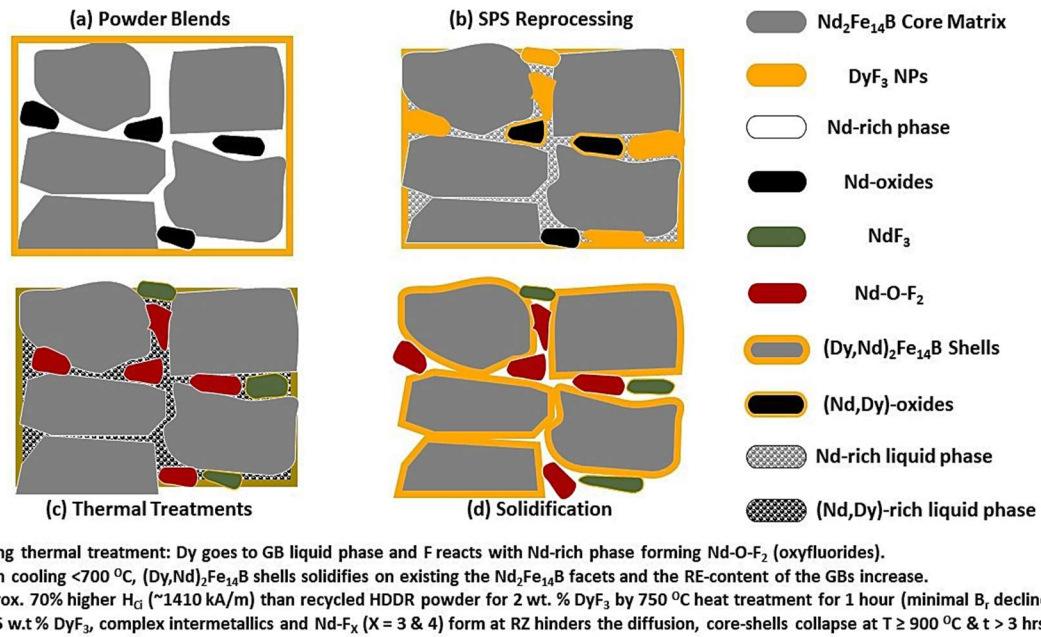


Figure 62: Graphical illustration of the diffusion mechanism of Dy in the HDDR Nd-Fe-B system.

Authors' Contributions:

My contributions as the first and corresponding author in this paper can be summarized as following:

1. Corresponding Author: Awais Ikram;
2. Conceptualization: Awais Ikram;
3. Methodology: Awais Ikram;
4. Software: Awais Ikram;
5. Validation: Awais Ikram and Kristina Žužek Rožman;
6. Formal analysis: Awais Ikram;
7. Investigation: Awais Ikram, Muhammad Farhan Mehmood and Zoran Samardžija;
8. Resources: Muhammad Awais, Richard Stuart Sheridan and Allan Walton;
9. Data curation: Awais Ikram;
10. Writing—original draft preparation: Awais Ikram;
11. Writing—review and editing: Awais Ikram and Kristina Žužek Rožman;
12. Visualization: Awais Ikram;
13. Supervision: Allan Walton, Sašo Šturm, Spomenka Kobe and Kristina Žužek Rožman;

14. Project administration: Allan Walton, Sašo Šturm, Spomenka Kobe and Kristina Žužek Rožman;
15. Funding acquisition: Allan Walton, Sašo Šturm, Spomenka Kobe and Kristina Žužek Rožman.



Article

Coercivity Increase of the Recycled HDDR Nd-Fe-B Powders Doped with DyF₃ and Processed via Spark Plasma Sintering & the Effect of Thermal Treatments

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Abstract: The magnetic properties of the recycled hydrogenation disproportionation desorption recombination (HDDR) Nd-Fe-B powder, doped with a low weight fraction of DyF₃ nanoparticles, were investigated. Spark plasma sintering (SPS) was used to consolidate the recycled Nd-Fe-B powder blends containing 1, 2, and 5 wt.% of DyF₃ grounded powder. Different post-SPS sintering thermal treatment conditions (600, 750, and 900 °C), for a varying amount of time, were studied in view of optimizing the magnetic properties and developing characteristic core-shell microstructure in the HDDR powder. As received, recycled HDDR powder has coercivity (H_{CI}) of 830 kA/m, and as optimally as SPS magnets reach 1160 kA/m, after the thermal treatment. With only 1–2 wt.% blended DyF₃, the H_{CI} peaked to 1407 kA/m with the thermal treatment at 750 °C for 1 h. The obtained H_{CI} values of the blend magnet is –69.5% higher than the starting recycled HDDR powder and 17.5% higher than the SPS processed magnet annealed at 750 °C for 1 h. Prolonging the thermal treatment time to 6 h and temperature conditions above 900 °C was detrimental to the magnetic properties. About –2 wt.% DyF₃ dopant was suitable to develop a uniform core-shell microstructure in the HDDR Nd-Fe-B powder. The Nd-rich phase in the HDDR powder has a slightly different and fluorine rich composition i.e., Nd-O-F₂ than in the one reported in sintered magnets (Nd-O-F). The composition of reaction zone-phases after the thermal treatment and Dy diffusion was DyF₄, which is more abundant in 5 wt.% doped samples. Further doping above 2 wt.% DyF₃ is ineffective in augmenting the coercivity of the recycled HDDR powder, due to the decomposition of the shell structure and formation of non-ferromagnetic rare earth-based complex intermetallic compounds. The DyF₃ doping is a very effective single step route in a controlled coercivity improvement of the recycled HDDR Nd-Fe-B powder from the end of life magnetic products.

Keywords: rare earth permanent magnets; HDDR Nd₂Fe₁₄B; recycling; spark plasma sintering; coercivity; doping DyF₃

1. Introduction

The Nd-Fe-B type permanent magnets are vital from a technological point of view, spanning in applications like: Electric motors, medical imaging, telecommunication, and consumer electronics because of their high energy product [1–3]. Since the supply chain of rare earth elements (REE) was

plagued with the crisis in 2011 [4], they are effectively considered as the most critical raw materials especially for incessantly growing automotive applications [1,5]. Therefore, to meet this demand, the recycling of the rare earth (RE) based permanent magnet is a feasible option [6–18], which has proven successful in developing sintered magnets from the end-of-life (EOL) scrap. The hydrogenation disproportionation desorption recombination (HDDR) Nd-Fe-B powder, from the recycled scrap, has been effectively consolidated to fully dense magnets via pulsed electric current sintering technique, retaining the coercivity (H_{CI}) of the EOL magnet [19]. The HDDR powder has less than 30 wt.% of rare earth elements (i.e., RE lean), so modification of the grain boundary structure is necessary for increasing the coercivity [12,20]. The coercivity enhancement helps prevent higher temperature demagnetization in high torque permanent magnet motors [5].

Several researchers have utilized rare earth fluorides (RE-F₃) as dopant or surface diffusion agents, to increase the coercivity in sintered magnets; with the coercivities reaching up to 2790 kA/m (35 kOe) [21–32] and in rapidly consolidated melt-spun ribbons, where coercivities reached up to 1990 kA/m [33,34]. On the contrary, no such research has been made on the HDDR Nd-Fe-B powders, which is a relatively cheap hydrogen reprocessing alternative for the EOL magnetic products [6]. In this study, we compared the magnetic properties and microstructural characteristics after doping the recycled HDDR powder with DyF₃. These blends are rapidly consolidated with Spark Plasma Sintering (SPS), which has been proven to preserve the microstructure, as well as the magnetic properties of HDDR Nd-Fe-B powder. The magnetic properties of DyF₃ blended recycled HDDR powder are compared with un-doped powder, consolidated with the SPS. The discussion is focused on the mechanism of diffusion at different thermal treatment conditions and the formation of core-shell structure in the HDDR Nd-Fe-B system.

2. Experimental

The recycled HDDR powder, as used in the previous study [19], has a nominal composition: Nd_{13.4}Dy_{0.67}Fe_{78.6}B_{6.19}Nb_{0.43}Al_{0.72}. The oxygen content of 4760 ppm was measured with Eltra ON 900 oxygen and nitrogen analyzer (Haan, Germany). The DyF₃ powder was grounded by a mortar and mixed in weight fractions of 1, 2 and 5% with the recycled HDDR powder.

A total 3 g of the powder blend was added to 10 mm graphite dies, with spacers on the top and bottom. The dies were sealed in a vacuum bag within the glove box to avoid oxidation during the sample handling. A uniaxial pressure of 5 kN was applied to squeeze the powder blend. No prior magnetic alignment was made on the blended powder. Under protective Ar gas, the graphite dies, containing blends, were placed inside the Syntex 3000 (Fuji DR. SINTER, Saitama, Japan) SPS furnace with a uniaxial pressure controller. The SPS operation was performed under 2×10^{-2} mbar vacuum. The sintering temperature was kept at 750 °C, which was optimized from the previous study and 100 MPa uniaxial pressure was constantly applied. The heating rate of 100 °C/min was maintained until 700 °C and reduced to 50 °C/min for reaching the maximum temperature; 1 min of holding time was given at 750 °C to reach nearly full densification. The sintering temperature was measured with a calibrated infrared pyrometer. After the SPS operation, the samples were grinded with SiC papers to remove the graphite spacers. The demagnetization measurements were taken on a permeameter (Magnet-Physik Dr. Steingroever, Cologne, Germany). The relative density was measured with bulk density-measurement system (Exelia AG DENSITEC, Zurich, Switzerland) based on Archimedes principle by submerging the samples in silicone oil.

The thermal treatments were performed at 600, 750, and 900 °C within a horizontal tube furnace under a vacuum of $> 10^{-5}$ mbar with a heating rate of 50 °C/minute. The magnetic measurements were retaken on thermally treated samples. The samples were thermally demagnetized at 400 °C for 15 min in the vacuum furnace. For the microstructural analysis, the demagnetized samples were finely grinded by 2400 grit SiC papers and polished with 1/4 µm diamond paste on a velvet cloth. The microstructural studies were carried out with a Field Emission Scanning Electron Microscope (JEOL 7600F, Tokyo, Japan). The phase identification and elemental distribution were carried out

at 20 keV with an electron energy dispersive X-ray spectroscopy (EDXS, Oxford Instruments, High Wycombe, UK) analysis fitted with a 20 mm² Oxford X-Max detector (High Wycombe, UK).

3. Results and Discussion

Characterization of Coarse Recycled HDDR Nd-Fe-B Powder.

Figure 1a shows the initial recycled HDDR Nd-Fe-B powder, with an average particle size of 220 μm . The agglomerates of DyF_3 powder, shown in Figure 1b. These can be grounded to a fine powder of size <500 nm on average as in Figure 1c before blending with Nd-Fe-B powder. The weight fractions of 1, 2, and 5% DyF_3 dopant were grounded and then mixed with the recycled HDDR powder. Figure 1d shows fine individual nanoparticles of DyF_3 uniformly dispersed on the recycled HDDR powder grains of 400 nm average size.

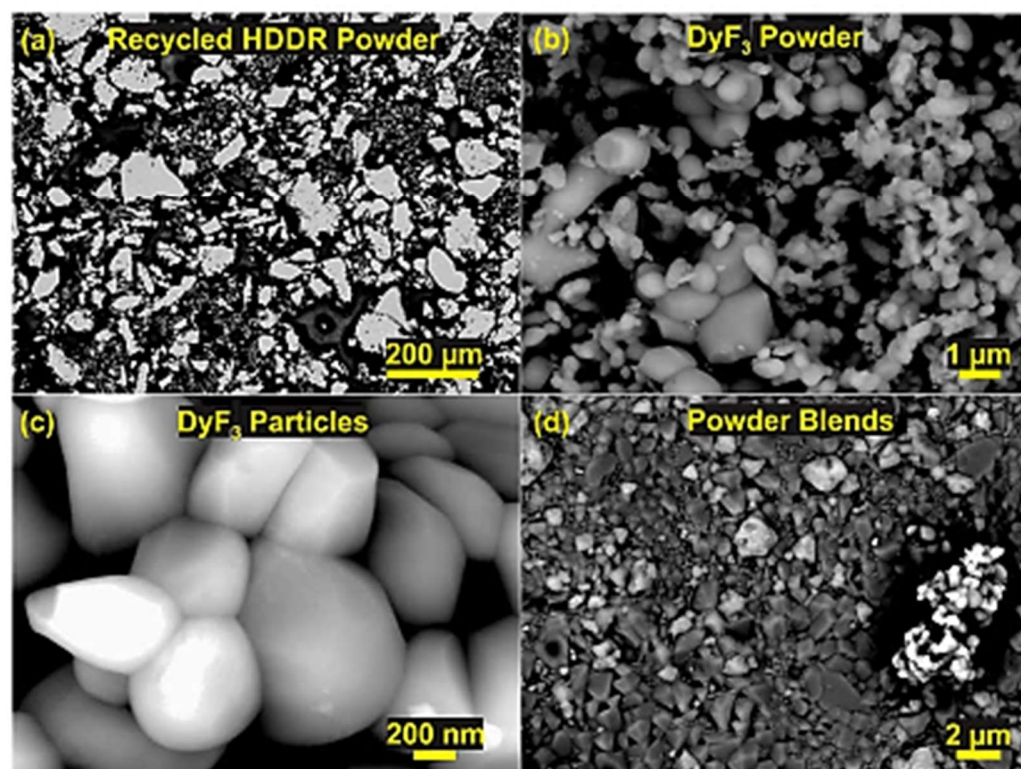


Figure 1. SEM backscattered mode images of (a) Hydrogenation disproportionation desorption recombination (HDDR) powder particles, (b) DyF_3 nanoparticles, (c) DyF_3 grains and (d) recycled HDDR powder blended with DyF_3 nanoparticles.

Figure 2 shows the dopant distribution in the back-scattered electron (BSE) microstructure of as SPS samples, with DyF_3 in different weight fractions. It is quite clear that for 1 wt.% DyF_3 , the microstructure appears quite similar to the representative microstructure of the sintered HDDR powder [19] and the distribution is uniform. With higher content of DyF_3 , the dopant nanoparticles are concentrated along the edges of the HDDR powder particles and also the bright contrast increased towards the center of the particle. In the case of 1 and 2 wt.% DyF_3 , the dopant clustering (<5 μm) was not very prominent and its distribution along the HDDR particles can be considered as uniform. The dopant agglomerates in size range, from 10–100 μm , were observed for 5 wt.% DyF_3 SPS sample, as shown in Figure 2c. The presence of non-ferromagnetic phase was projected to reduce the sintered density, as well as remanence [34].

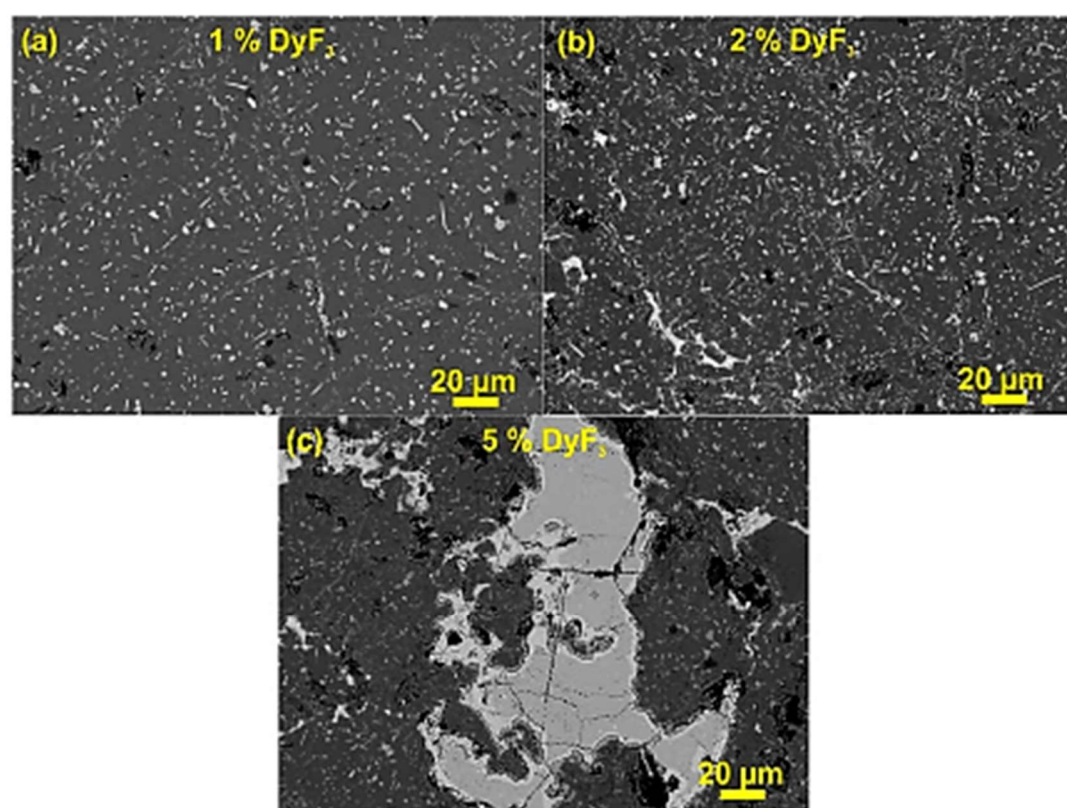


Figure 2. SEM backscattered electron (BSE) images of as-SPS samples with DyF_3 in (a) 1 wt.% (b) 2 wt.% and (c) 5 wt.%.

Figure 3 shows the magnetic properties of DyF_3 doped recycled HDDR powder, consolidated with SPS at 750°C for 1 min and then vacuum heat-treated at 600°C for 6 h to compare the annealing parameters from the literature [33,34]. The blended magnets with 1, 2 and 5 wt.% DyF_3 after annealing at 600°C , resulted in coercivity values of 1274, 1252, and 201 kA/m, respectively. Since no prior magnetic alignment of the blend powder was performed before the sintering, the presented results of remanence conclude that the samples were isotropic. The B_r was 0.78 T for 1 wt.% dopant and reduced to 0.75 T for 2 wt.%, and then dropped down substantially to 0.53 T for 5 wt.% DyF_3 . The un-doped recycled HDDR powder has $H_{CI} = 830$ kA/m and $B_r = 0.92$ T. Using similar SPS reprocessing conditions, the sintered magnets from the un-doped recycled HDDR powder resulted in $H_{CI} = 1060$ kA/m and $B_r = 0.76$ T, which improved to $H_{CI} = 1160$ kA/m and $B_r = 0.77$ T after vacuum heat treatment at 750°C [19].

The melting temperature (T_m) for DyF_3 is 1350°C and previous reports on doped sintered Nd-Fe-B magnets suggested a high thermal treatment temperature range (800 – 950°C) [26,28,34]. The eutectic liquid phase transformation in the HDDR system begins at 665°C and transformation is complete at 743°C [19]. Thereby, in order to determine the magnetic property variation, temperatures of 750°C (above the eutectic transformation temperature) and 900°C (above the HDDR Nd-Fe-B grain growth temperature [35,36]) were selected. As the annealing temperature was increased to 750 and 900°C , the holding time was varied from 1 to 6 h to identify the changes in magnetic properties. In the thermal treatment at 900°C , the coercivity, as shown in Figure 4a, reached a maximum value of 1279 kA/m for 2 wt.% doped magnets thermally treated for a relatively shorter timeframe (1 h). By increasing the dopant weight fraction as well as holding time, the coercivity declined substantially to 452 kA/m (5 wt.% DyF_3 for 6 h). The B_r dropped from 0.77 T to 0.72 T for 1 wt.% dopant after annealing for 1 and

6 h respectively. For higher weight fraction of dopant, the reduction in B_r was more significant after thermal treatments at 900 °C as compared to 750 °C sample as shown in Figure 4b.

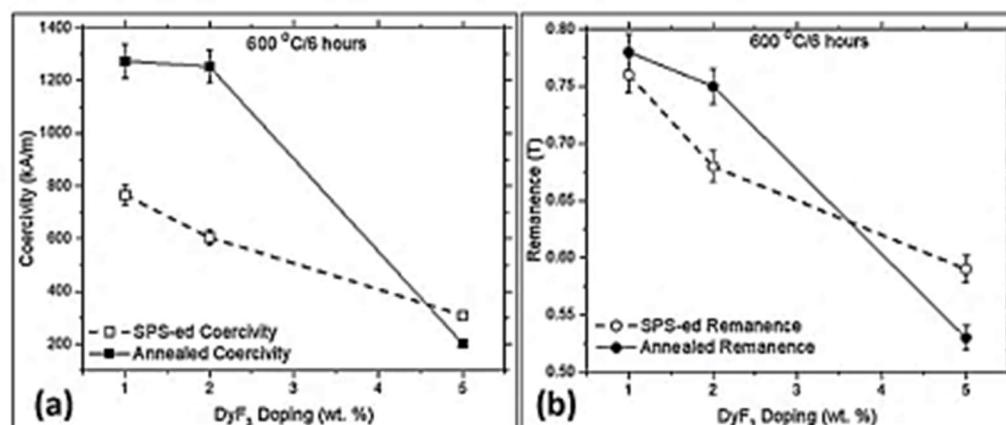


Figure 3. Shows the magnetic properties in DyF₃ doped magnets before and after annealing at 600 °C for 6 h, (a) coercivity and (b) remanence.

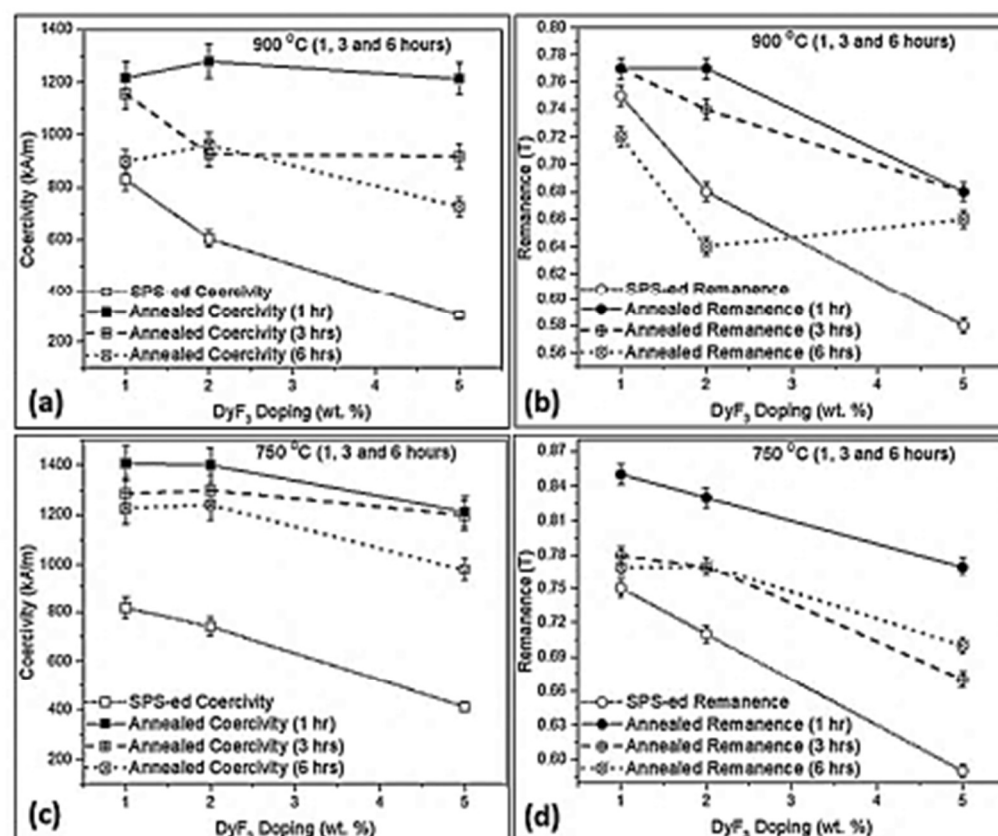


Figure 4. Variation in the magnetic properties of SPS reprocessed blend of DyF₃ doped recycled HDDR powder with thermal treatment temperatures of 900 °C (a) coercivity, (b) remanence; and 750 °C (c) coercivity, (d) remanence.

Figure 4c shows the coercivity increased to 1407, 1399, and 1212 kA/m for 1, 2, and 5 wt.% DyF₃ respectively after the heat treatment at 750 °C for 1 h. The coercivity began to decline by increasing the holding time from 1 to 3, and 6 h. The coercivity for 1 and 2 wt.% DyF₃ remained over ~1200 kA/m even after 6 h of thermal treatment, whereby it declined sharply to 977 kA/m for 5 wt.% sample held for 6 h. The H_{CI} of 2 wt.% DyF₃ was slightly higher when heat treatment was increased to 3 h or more as compared to 1 wt.% doped samples. The B_r increased from 0.75 T to 0.85 T for 1 wt.% DyF₃ blend sample after 1-h thermal treatment. The B_r was in the range of 0.77–0.78 T after the heat treatment up to 6 h for 1 and 2 wt.% DyF₃, as shown in Figure 4d. The B_r values were gradually reduced from 0.77 T to 0.70 T as the holding time was increased from 1 to 6 h in the 5 wt.% doped samples.

Figure 5 shows the SEM microstructure in backscattered mode after the thermal treatment at 750 °C for 6 h of 1–5 wt.% SPS-ed HDDR powder. As compared with Figure 2, with the thermal treatment, there has been an evident formation of core-shell structure. At low dopant weight fraction (1%), the microstructure consists of two zones as shown in Figure 5a,b: Zone A consists of a core-shell structure and zone B is characteristic of HDDR powder i.e., a thin grain boundary film between the matrix grains. The core shell microstructure is more homogenous with an increase in dopant content up to 2 wt.% as shown in Figure 5c,d. As the DyF₃ weight concentration is increased to 5%, the microstructural homogeneity was reduced. Figure 5e shows a core-shell zone with the unreacted and non-diffused dopant (bright phase). This microstructure was not homogenous for the 5 wt.% doped samples as Figure 5f shows an abnormal growth zone with excessive formation of DyNdFe₁₄B shells over the Nd₂Fe₁₄B matrix grains. This abnormal grain coarsening in 5 wt.% doped samples also reflected in significantly poor magnetic properties (H_{CI} = 977 kA/m and B_r = 0.7 T).

After thermal treatment, the region of dopant nanoparticles becomes the reaction zones (RZ), from where the Dy diffuses with the liquid phase towards the center of the particle and precipitate on the surface of the matrix grains, as shown in Figure 6. The morphology and phase formation of bright phases change with an increase in dopant concentration. The reaction zones are smaller in 1 wt.% samples, as in Figure 6a, where the Dy diffusion is limited to matrix phase in the vicinity of the reaction zone. The 2 wt.% DyF₃ sample has the most optimal microstructure and magnetic properties after the thermal treatment at 750 °C, the reaction zone widens and the formation of complex interphases was identified with EDXS in Figure 6b. The phase No. 1 corresponds to the Nd₂Fe₁₄B matrix phase and after the Dy diffusion, the shell structure of DyNdFe₁₄B reinforces the matrix phase. The shell structure has ~6 at.% Dy as compared to the cores with ≤ 1.2 at.% of Dy. The nominal phase composition of the core-shell structure measured with EDS is presented in Table 1. Before thermal treatment, the DyF₃ nanoparticles do not react or decompose and the Nd-rich phase composition corresponds to NdO_x (No. 2). The Nd₂O₃ oxide phase (No. 3), NbFe₂ Laves (No. 4), and the tetragonal NdFe₄B₄ boride (No. 9) phases, were initially present in the recycled HDDR powder. From Figure 6b, the primary Nd-rich phase identified (No. 12) in the HDDR Nd-Fe-B system has fluorine-rich composition Nd-O-F₂. Similar to the conventionally sintered magnets and melt-spun ribbons, the oxyfluoride phases Nd-O-F (No. 5) and Dy-O-F (No. 6) were also detected along the RZ. The complex interphase compounds were easy to analyze in the relatively larger RZ of the 5 wt.% doped sample, as shown in Figure 6c–f. The Nd-rich oxyfluoride regions Nd-O-F and Nd-O-F₂ had similar greyish contrast and could only be identified with the EDXS. After the thermal treatment the constituent dopant particle has a composition of DyF₄ (No. 10) as shown in Figure 6c. As the core-shell structure forms up and Dy begins to diffuse further from the RZ towards the HDDR particles, this phase is reduced to NdF₄ (No. 7). The interphase complexes are shown in Figure 6e,f surrounding the RE-F₄ phase (dopant particle) are listed in Table 1 as Nd-Fe-O-F (No. 8), DyFe₂ (No. 11), Nd-Fe-F (No. 13 and 15) and Dy-Nd-O-F₂ (No. 14). During the prolonged thermal treatment (750 °C–6 h), the core-shell structure in 5 wt.% sample is obvious in regions closer to the RZ (Figure 6e), whereby the matrix structure collapses, due to the exaggerated growth of shells, as shown in Figure 5f. The presence of porosity in the RZ of Figure 6f indicates the diffusion of Dy until the core-shells grow throughout the microstructure, which gets circumvented as the diffusion stops and the complex RE-Fe-F intermetallic phases begin to form (No. 11, 13 and 15).

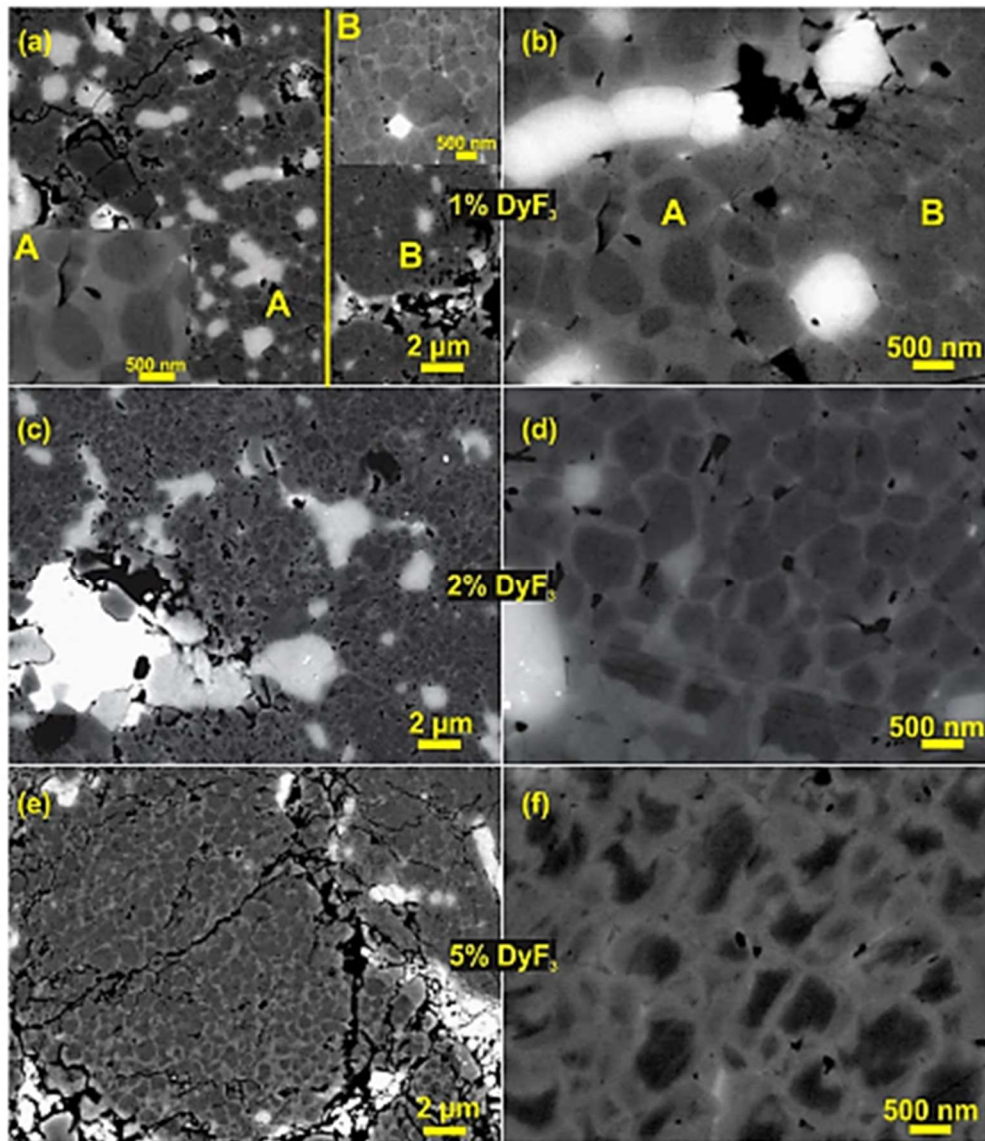


Figure 5. Shows the microstructure of DyF_3 doped samples after thermal treatment for 6 h at 750°C , (a) 1 wt.% doped samples with two zone microstructure (inset A shows core-shell zone and inset B shows normal HDDR microstructure), (b) at higher magnification 1% doped samples; (c) 2% DyF_3 blend samples and (d) uniform core-shell structure formation throughout the microstructure; (e) 5 wt.% DyF_3 samples, with excessive growth zone of $\text{DyNdFe}_{14}\text{B}$ shells at the expense of matrix phase clearly shown in (f).

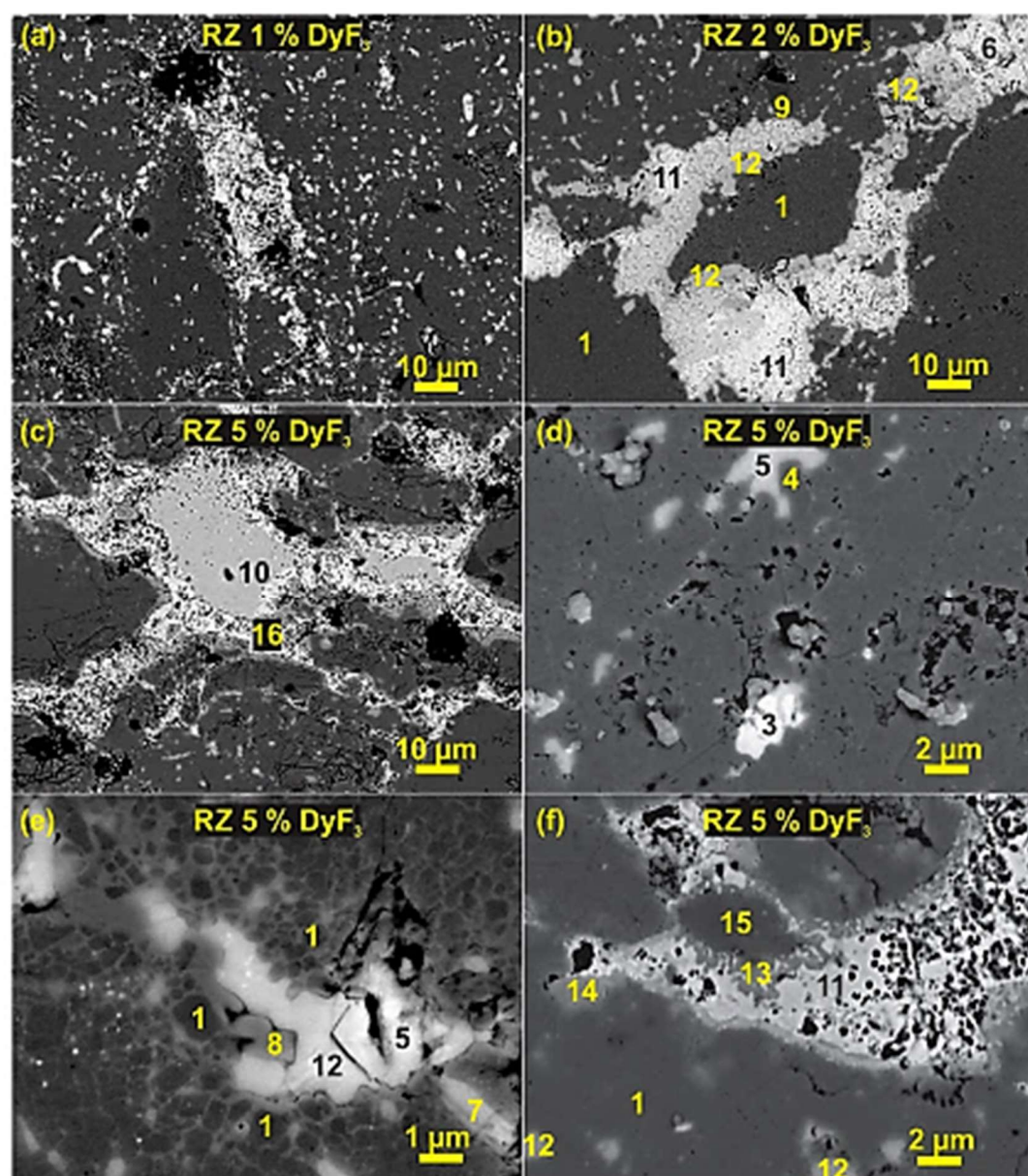


Figure 6. Signifies the reaction zones (RZ) in the microstructure of doped samples after the thermal treatment at 750 °C for 6 h, (a) relatively small RZ in 1 wt.% DyF_3 samples, (b) 2 wt.% doped samples have the optimal magnetic properties but RZ contains RE-F_4 (rare earth fluoride) and Nd-O-F_2 (oxyfluoride) phases, (c–f) the relatively wider RZs of 5 wt.% doped samples containing additional interphase compounds along with rare earth fluorides and oxyfluoride based Nd-rich phase.

Table 1. EDXS quantification of different phases in the DyF₃ doped and SPS-ed recycled HDDR Nd-Fe-B.

Phase No.	Phases	Nd (at.%)	Fe (at.%)	F (at.%)	O (at.%)	Nb (at.%)	Al (at.%)	Dy (at.%)
1	Nd ₂ Fe ₁₄ B Cones	12	85	-	-	0.9	0.9	1.2
	DyNdFe ₁₄ B Shells	8.1	85.5	-	-	-	-	5.8
2	Nd-rich Nd ₂ O ₃ /NdO ₂	24.6	29.5	-	46.3	-	-	-
3	Nd ₂ O ₃	34.7	1.8	-	63.5	-	-	-
4	NbFe ₂ Laves	0.7	47.6	-	-	51.7	-	-
5	Nd-O-F	28.2	1.8	38.5	31.5	-	-	-
6	Dy-O-F	4.5	18.8	20.9	28.9	-	-	26.9
7	Nd-F ₄	18	-	81.1	-	-	-	0.9
8	Nd-Fe-O-F (interphase)	10.8	45.4	28.7	9	-	-	6.1
9	NdFe ₄ B ₄	18.8	68.5	9.6	-	-	-	-
10	Dy-F ₄	-	-	80.8	-	-	-	19.2
11	Dy-Fe ₂ (interphase)	2.4	54.6	4.6	10.4	-	-	28
12	Nd-O-F ₂	20.7	2.4	61.3	13.7	-	-	1.9
13	Nd-Fe-F (interphase)	11.9	47.2	33.3	3.6	-	2.3	1.7
14	Dy-Nd-O-F ₂ (interphase)	8.9	6.8	48.8	21.7	-	-	13.8
15	Nd-Fe-F (interphase)	13.3	39.2	39.3	3.9	-	1.3	3

4. Discussion

The concept of recycling the permanent magnets includes the techniques like: hydrometallurgical, pyro-metallurgical, direct reusage and indirect recycling approaches [37–46]. The advantage of direct recycling and re-usage methods, based on hydrogen-based technologies and sintering, which we have proposed in our previous study [19] and the present work, is that they have a smaller environmental footprint, as compared to conventional hydro- and pyro-metallurgical methods, which are energy intensive and require plentiful of highly corrosive chemical mediums. Therefore, the hydrogen-based methods offer more economical and energy efficient route to obtain pulverized and demagnetized powder from the end-of-life (EOL) magnets. The added benefit of hydrogenation disproportionation desorption recombination route is that the powder with anisotropic nano-crystalline grains can be used as plastic bonded as well as sintered magnets.

The rapidly sintered magnets from the recycled HDDR powder were prepared by blending low weight fraction of fine DyF₃ powder, by rapidly consolidating it with spark plasma sintering and thermally treating at different conditions. The recycled HDDR powder has a nominal grain size of 240–420 nm, which is slightly above the critical single domain size. Developing this characteristic microstructure from the EOL magnet is vital during the HDDR reprocessing for achieving the desired level of magnetic properties is important. The suitable reuse of reprocessed powder can be difficult if the scrap magnet has already been excessively oxidized or corroded in the harsh environments. The recovery of magnetic properties is strongly dependent on the initial chemical composition of the EOL magnets and recycling different magnets in a single batch, which were used in different service conditions, is challenging. Nonetheless the rejected industrial waste or the EOL material from similar appliances can be effectively recycled by the hydrogen processing routes. Practically, it is difficult to increase the coercivity of the as prepared recycled HDDR powder, if the EOL magnets do not contain an excessive amount of heavy rare earth elements (HREE: Dy, Tb). It is also not technologically feasible to add the HREEs in multiple stages of the HDDR process. Contemporary solution for increasing the H_{C1} of the recycled HDDR powder is by blending small amounts (1–5 wt.%) of DyF₃ powder and

SPS to bulk magnets, followed by the experimentally-determined optimal heat treatment at 750 °C, increasing the H_{CI} > 1400 kA/m, which is 69.5% higher than the starting recycled HDDR powder as shown in Figures 3 and 4. The H_{CI} increment is more prominent at 1–2 wt.% dopant addition and subsequent thermal treatment above eutectic liquidus transition temperature i.e., 750 °C for shorter periods, due to the formation of uniform core-shell microstructure. It is relatively easy for Dy to diffuse at temperatures above the eutectic transition at 665 °C. The activation energy for decomposition of heavy rare earth based fluorides like DyF_3 is lower than NdF_3 , which stimulates the high diffusivity of Dy via Nd-rich grain boundary channels, from the edges of the HDDR particles to the center during the thermal treatments [22].

According to U. M. R. Seelam et al. [36], in vapor sorption treated conventionally sintered magnets, the Dy vapors become part of the liquid phase at 900 °C (above the ternary transformation temperature) and the Dy-rich $(DyNd)_2Fe_{14}B$ shells precipitate out of the liquid phase upon cooling and condense on the surface of 2:14:1 grains. At 900 °C, the surface of $Nd_2Fe_{14}B$ grains experience partial melting and more Nd atoms become part of this Nd/Dy rich liquid phase. Since the sintered magnets have single, crystal $Nd_2Fe_{14}B$ grains, in the size range of 5–10 μm , and the continuous grain boundary phase surrounding all the matrix grains, a high Dy concentration at the GBs during sorption treatment effectively develops the $(DyNd)_2Fe_{14}B$ core-shell structure. The core-shell formation mechanism, as proposed by U. Seelam [36], is based on the solidification of Dy-enriched liquid $Nd_2Fe_{14}B$ that partially melted upon annealing and the Nd-rich phase, which connects all the grains in the sintered magnet. The $(DyNd)_2Fe_{14}B$ shell begins to develop coherently below 900 °C on the $Nd_2Fe_{14}B$ facets as the Nd-rich phase is still in a liquid state above 665 °C. Below this ternary transition temperature –400 nm thick $DyNdFe_{14}B$ shells already have deposited on the surface of $Nd_2Fe_{14}B$ grains and the solidifying liquid phase now contains a lesser amount of Dy, but a higher concentration of Nd. Since the formation energies of $Dy_2Fe_{14}B$ structure is more negative (favorable) than $Nd_2Fe_{14}B$, a preferential solidification proposes $DyNdFe_{14}B$ phase to solidify on the facets of partially melted $Nd_2Fe_{14}B$ grains. Dy remains part of the liquid phase until solidification below 700 °C. With negative enthalpy of formation, $DyNdFe_{14}B$ shell will form the first along the partially molten surface of the $Nd_2Fe_{14}B$ grains.

In the case of the recycled HDDR blended with the DyF_3 nanoparticles, the explanation of complex diffusion process may not adhere entirely to this theory. The recycled HDDR powder particle are sized on average 220 μm , whereas each particle is composed of networked –400 nm sized nanocrystalline grains. The Nd-content of the recycled HDDR powder is lean, as from the previous studies, due to higher oxygen content and the multiple grains are sometimes even in direct contact with each other, due to the low amount and lack of the grain boundary phase in some places [19]. Since the grain boundary thickness is not more than 3 nm in the HDDR system, the capillary forces are responsible for the liquid phase transport and uniform dispersal along the 2:14:1 grains [10,47,48].

The mechanism for subtle H_{CI} increment with the low weight fraction of dopant in the recycled HDDR based magnets and subsequent degradation of magnetic properties for ≥ 5 wt.% DyF_3 , containing samples, is characterized with the aid of EDS composition analysis for various thermal treatment conditions. After SPS reprocessing, diffusion of Dy was limited, as shown in Figure 2 and up to 2 wt.%, the dopant nanoparticles remain finely distributed along the HDDR particles whereby for 5 wt.% dopant, the larger DyF_3 nanoparticles were segregated along the HDDR particles. Since the optimal SPS reprocessing temperature was 750 °C, short range diffusion of Dy can be expected [33,34] during the liquid phase sintering, allowing the transformation of Nd-rich phase to Nd oxyfluorides, but the typical $(DyNd)_2Fe_{14}B$ core-shell structure was not observed prior to the thermal treatment. Pressure during SPS consolidation aids in the uniform dispersal of dopant nanoparticles [19] and increases their surface distribution with the HDDR powder particles. The short SPS holding time is 1 min, however this restricts any diffusion process and rapid cooling retains the short range order of the dopant nanoparticles, settled along the HDDR powder particles. During the SPS, the only expected transformation is the partial formation of Nd-oxyfluorides along the particle boundaries.

However, when Nd-rich liquid phase comes in contact with DyF_3 nanoparticles above 665°C , it should decompose and form Nd-oxyfluorides and Dy will become part of the liquid phase. The enthalpy of formation NdF_X ($X = 3 \text{ \& } 4$) is higher than DyF_3 [33,34]. On the other hand, as the heating and cooling are rapid, the diffusive transport of Dy/Nd-rich liquid phase is restricted during the SPS [19].

During the post-SPS thermal treatment at 600°C , a partial decomposition of DyF_3 restricts the formation of the core-shell structure, even at prolonged time periods and H_{CI} increment is $\sim 6\%$ approx. This indicates the thermal decomposition is favored for substitution between Nd and Dy even at 600°C [33]. Therefore, the thermal treatment at 600°C results in only ~ 70 kA/m improvement of coercivity. With the availability of liquefied Nd-rich phase above the ternary eutectic temperature 665°C , the Dy gets transported from the edges of the particles towards the center and $(\text{DyNd})_2\text{Fe}_{14}\text{B}$ shells form upon cooling below 700°C . Therefore, during the thermal treatment at 750°C (which is above the ternary eutectic temperature), the DyF_3 particle decomposes at this temperature and the surface of Nd-Fe-B grain experience melting. Now the HDDR particles ~ 220 microns in size have the dopant particles sitting at their edges only. The Nd-rich phase is in a liquid state above the ternary eutectic point and connects the GBs to the edges of the particles. In order to form uniform core-shell facets, which are attached to the GBs, liquid phase diffusion is necessary. The decomposed Dy becomes part of the liquid phase and is transported via capillary forces towards the GB interface of nanocrystalline grains. During this thermal treatment, the overall RE-content of GBs is higher than the starting HDDR powder and the liquid phase contains both, Dy atoms from the dopant, as well as the Nd atoms from the partially decomposed grain surfaces. The formation enthalpy of $(\text{DyNd})_2\text{Fe}_{14}\text{B}$ grains is higher than $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, so when the cooling begins, the shells are more thermodynamically favorable to precipitate out, as compared to the original $\text{Nd}_2\text{Fe}_{14}\text{B}$ composition on the activated surfaces [36]. At the onset of cooling, and when the 2:14:1 phase begins to condense, the Dy atoms from the liquid phase partially substitute the Nd atoms on the surface of matrix grains (favorable thermodynamic kinetics) and precipitate out as the $(\text{DyNd})_2\text{Fe}_{14}\text{B}$ shell structure [33] of thickness ≤ 100 nm, forming thoroughly in 2 wt.% doped samples. The diffusion of Dy atoms is not localized at the particle edges as in case of 600°C heat treated samples and rapidly diffuses via GB channels to all the intergranular regions of the individual HDDR particle. Above the eutectic transition temperature (665°C), the three processes in chronological sequence explain the core-shell formation mechanism are: liquid phase diffusion increase in GB RE-content, upon cooling the Dy-Nd substitution and the $(\text{DyNd})_2\text{Fe}_{14}\text{B}$ shells precipitation from the solution are definitive in the HDDR Nd-Fe-B system. The B_r trend indicates the optimal presence of hard magnetic phase $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{DyNd}_2\text{Fe}_{14}\text{B}$ for up to 2 wt.% of the dopant. The B_r decline can be attributed to the formation of non-ferromagnetic intermetallic compounds in 5 wt.% samples.

Nd is found in the intergranular regions to combine with fluorine and oxygen to form oxyfluorides of composition Nd-O-F₂. For shorter thermal treatment time at 750°C in 1 wt.% DyF_3 sample, the coercivity reaches 1400 kA/m, due to the diffusion of Dy which was found to degrade over prolonged treatments. A partial decomposition of the shell structure is observed, thereby developing two distinct zones in the microstructure, as shown in Figure 5 (A: core-shell near the reaction zone and B: normal HDDR microstructure). The excessive Dy is not available in 1 wt.% samples in forming complex interphase compounds near the reaction zone. With the increase in dopant concentration at 5 wt.%, the reaction zone widens and the intermetallic species (DyFe_2 and RE-Fe-F), as analyzed in EDS Table 1 originate due to concentration gradient of Dy from the grain boundaries towards the activated facets of $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix grains.

The lower activation energy for the thermal decomposition of DyF_3 , above the eutectic transformation temperature, promotes the liquid phase Dy diffusion and the partial substitution of Nd atoms from the activated surfaces of the matrix phase; whereby the highly reactive residual fluorine atoms preferentially react with the Nd-rich phase, forming a higher stability cubic Nd-O-F phase [22]. The intergranular phase of the starting HDDR powder is composed of Nd-rich metallic phase and the NdO_2 phase with Nd_2O_3 (cubic + hcp) oxide phase [19]. The diffused, yet unreacted, F

atoms promote the formation of cubic Nd-O-F phase from NdO₂ phase and the oxyfluorides phase has a smaller lattice mismatch of 2.62% with Nd₂Fe₁₄B matrix, as compared to cubic Nd₂O₃ with 3.11%, therefore the smaller the lattice mismatch, the more positive the influence on the H_{CI} [22]. The hcp-Nd₂O₃ having a lattice mismatch of 12.1% with the matrix phase develops micro-strains at the interface and reduce the H_{CI} [49], remains stable and does not react anymore as it was traced in the doped samples. For greater than 1 wt.% DyF₃, the main intergranular phase was composed of Nd-O-F₂ due to excessive fluoride ions available to react with the Nd-rich phase as Dy is consumed in shell formation. The stoichiometric 1:1:1 type oxyfluorides RE-O-F (RE = Dy, Nd) replaced the NdO₂ phase, whereby the oxyfluorides composition changes to 1:1:2 and Dy-Nd-O-F₂ (interphase) species accommodating more F in the sample with ≥ 2 wt.% dopant. The DyF₃ readily decomposes during the thermal treatment even for a shorter holding time of 1 h at 750 °C, allowing complete liquid phase diffusion of Dy via grain boundaries throughout the bulk microstructure and developing a core-shell structure. The liquefied GB, due to the diffusion process are enriched with Dy atoms, which will precipitate in shells on the grains' surface upon cooling and, in turn, the substituted Nd atoms will become part of the intergranular phase. Therefore, in Figure 5b,d the core-shells structures are separated by continuous thin grain boundary layers. So the overall system should not be lean of Nd-content anymore. Therefore, the core-shell formation and supplication of Nd-rich grain boundary phase in turn increases the coercivity by 69.5%.

At 5 wt.% dopant, the formation of DyF₄, NdF₄ and Nd-Fe-F phases at the triple point regions and particle boundaries increases. The neodymium trifluoride (NdF₃) having higher formation enthalpy of -1713 kJ/mol, compared to DyF₃ (-1678 kJ/mol), and has been reported to reduce the magnetic properties as the intermetallic compounds have higher chemical and thermal stability than dysprosium trifluoride (DyF₃), and form barriers against the Dy diffusion with the liquid phase [33], as shown in Figure 6. The report suggests lanthanide (Nd and Dy) tetrafluorides formed during annealing treatment are more thermally stable than DyF₃ compound [50], which is a plausible reason for their presence in higher dopant concentration as more Dy diffuses from the DyF₃ particle towards the matrix, DyF₄ becomes the composition of residual dopant particle. After the thermal decomposition of DyF₃ dopant, the shell structure is formed by partial substitution of the Nd atoms by the Dy atoms from the RE-rich liquid phase, which precipitates on the activated surface of Nd₂Fe₁₄B grains and the mechanism is illustrated in Figure 7. During the SPS reprocessing minimal DyF₃ decomposition or Dy diffusion is expected due to rapid consolidation phenomenon as can be seen in Figure 2. When the thermal treatment begins, the dopant decomposes and Dy atoms become part of the liquid phase. Above the ternary transition temperature, the surface of Nd₂Fe₁₄B grains partially experience melting and Nd atoms infiltrate the Dy-enriched grain boundaries. Upon cooling below 700 °C, the (DyNd)₂Fe₁₄B shells precipitate on the activated Nd₂Fe₁₄B grains' surfaces as more energetically favorable phase transformation. Finally, below the eutectic point, the excessive Nd atoms become part of the Nd-rich grain boundary phase and, therefore, the GBs are continuous and more uniformly distributed, as compared to the starting recycled HDDR powder. The formation of high anisotropy field (DyNd)₂Fe₁₄B shells and the continuous Nd-rich GB layer surrounding these grain act as a spacer phase to effectively reduce the localized exchange effects, and therefore these two reasons can be associated with the H_{CI} increment by -69.5% over the recycled HDDR powder.

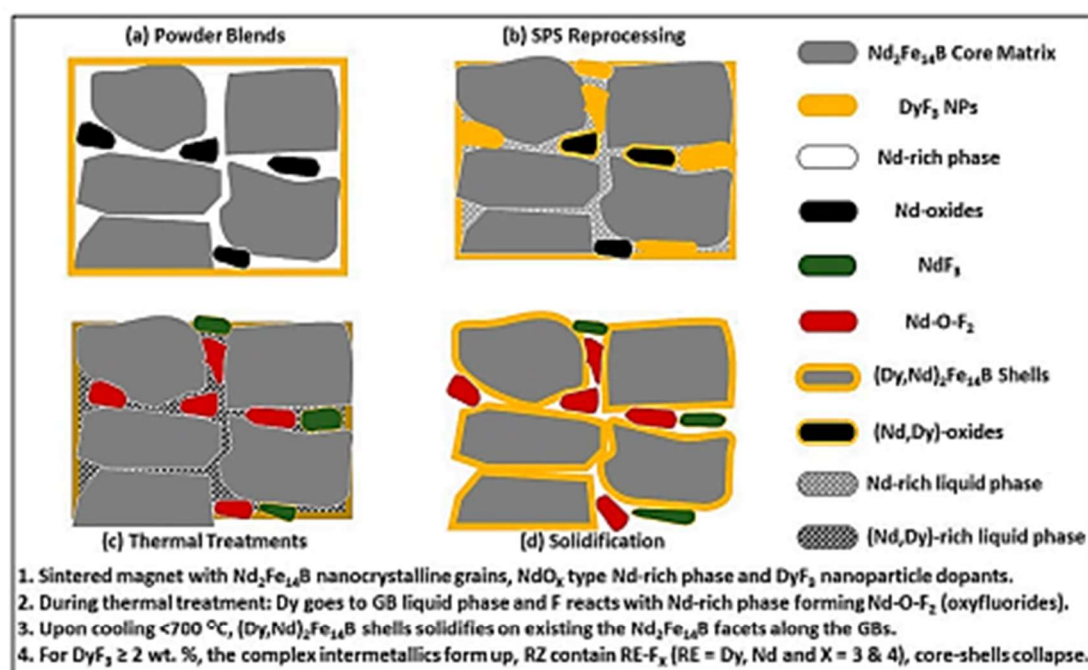


Figure 7. The mechanism of core-shell structure formation in the HDDR Nd-Fe-B system: (a) blend of HDDR Nd-Fe-B powder and DyF_3 particles, (b) liquid phase sintering, lack of long range Dy diffusion, (c) Dy diffuses with the liquid phase and F reacts with Nd-rich phases; and (d) the $(\text{Dy,Nd})_2\text{Fe}_{14}\text{B}$ core-shell structures form up upon solidification.

A larger concentration of fluoride anions reacts with this metallic Nd (reduced) and NdO_2 , leading to the formation of NdF_4 , and Nd-O-F_2 , respectively, as shown in Figure 6. The EDS results in Table 1 indicated that, with the increase in dopant weight fraction, the concentration of unreacted DyF_4 , intergranular NdF_4 , and RE-Fe-F interphase compounds increase exponentially, which contribute to a significant reduction in the magnetic properties, as shown in Figure 4. The prolongation of thermal treatment at 750 or 900 °C to 6 h also deteriorate the magnetic properties because of the thermally induced disintegration of the core-shell structure as in Figure 5f. As Dy forms more 2:14:1 structure, the substituted Nd is forced to react with highly reactive and mobile F ions in the vicinity, and subsequently, the total amount of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is reduced in the system.

The results of the present study classify the addition of DyF_3 in the recycled HDDR Nd-Fe-B system shows to be very effective for forming the $(\text{Dy,Nd})_2\text{Fe}_{14}\text{B}$ core-shell structure. But there is an effective limit of DyF_3 doping to ≤ 2 wt.%, which not only gives the best magnetic properties, but it is also pivotal to REE criticality and conservation [1,2]. The controlled post-SPS thermal treatment in recycled HDDR system is very efficient for shorter durations and lower temperatures in developing higher coercivity and the core-shell structure, as compared to conventionally sintered magnets treated at elevated temperatures [21–23] or prolonged periods [33], due to ultrafine microstructure. For shorter periods, the formation of smaller RZ is important as only Dy forms core-shell structure by Nd substitution to Nd-O-F phase. With excess of F anions, the cubic intergranular phase transforms to Nd-O-F₂ structure. The DyF_3 concentration of >5 wt.% contributes to the formation of complex intermetallic compounds with REE (Dy, Nd) as well as stable non-decomposing trifluorides and tetrafluorides (NdF_3 and NdF_4) at the expense of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase as the Dy diffusion is circumvented at large RZs, which plagues the microstructure with excessive non-ferromagnetic species.

5. Conclusions

The DyF₃ powder was blended with the recycled HDDR powder prior to SPS reprocessing, in order to determine the variation in magnetic properties and to investigate the microstructural evolution. As SPS blend samples had the magnetic properties lower than the starting HDDR powder, which increased significantly with annealing. The thermal treatment conditions were varied from 600 to 900 °C and from 1 to 6 h. The best annealing conditions were determined for the recycled HDDR powder, i.e., 750 °C for 1 h. By annealing at 750 °C for 1 h, even with 1 wt.% DyF₃, the coercivity (H_{CI}) of sintered magnets can be increased to 17.5%, as compared with the undoped magnets. Up to 2 wt.% DyF₃, these coercivity value ~1400 kA/m are ~69.5% higher than the starting recycled HDDR powder. Additionally, the reduction in remanence (B_r) was insignificant up to 2 wt.% DyF₃ for thermal treatment at 750 °C for 3 h. Prolonging the thermal treatment time to 6 h causes a reduction in the magnetic properties. The thermal treatment at 900 °C for shorter intervals (1 h) resulted in H_{CI} = 1280 kA/m in 2 wt.% DyF₃ samples and above 1200 kA/m for all doping conditions. With a further increase in holding time to 6 h at 900 °C, the magnetic properties decline rapidly to: H_{CI} = 726 and B_r = 0.66 T, which is associated with the formation of NdF₃ and non-ferromagnetic interphase compounds. By optimal thermal treatments, the microstructure of DyF₃ doped recycled HDDR based magnets exhibit core-shell structure (DyNdFe₁₄B shell and Nd₂Fe₁₄B core). Optimal core-shell formation occurs at 1–2 wt.% DyF₃ and above this concentration, the Dy diffusion in the microstructure from the liquid phase is heterogeneous leading to the formation of complex intermetallic phases at the reaction zones. The secondary phase composition was identified as: Nd-O-F₂. Moreover, the Nd₂O₃ and RE-O-F phases were also observed, due to the transformation of NdO_x type Nd-rich phase in the recycled HDDR powder. For the higher weight fraction of dopant, the DyF₃ is the main composition of the undiffused aggregates, even after prolonged thermal treatments. Therefore, for very small weight fractions, keeping the rare earth's criticality and recyclability in perspective, the DyF₃ doping of the recycled HDDR powder is very effective in forming a uniform core shell microstructure in the sintered magnets, which is indicated by a marked improvement in the magnetic properties.

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Chapter 9 Auxiliary Nd-Fe-B Results

SPS Hot Deformation of the Recycled HDDR Nd-Fe-B Powder

In this chapter, the hot-deformation experiments on the recycled HDDR Nd-Fe-B powder are elucidated. The development of textured materials for remanence enhancement is carried out in two steps: first, aligning the recycled powder in applied magnetic field and then hot-pressing to full density; secondly, hot-forging or deforming under higher pressures to induce texture in the microstructure along the pressing direction. The hot-pressing process is similar to the results previously shown in Chapter 5 [83]. So, the SPS conditions were kept similar to achieve high coercivity and the optimal microstructure, i.e. at 750 °C for 1 minute, 100 MPa uniaxial pressure and the post-SPS thermal treatment was done for 1 hour at 750 °C. These hot-pressed magnets had $H_{CI} \sim 1150$ kA/m and $B_r = 0.8$ T.

The hot deformation experiments on the optimally SPS reprocessed Nd-Fe-B permanent magnets were performed by varying the terminal pressures from 100 – 150 MPa at the holding temperature of 750 °C – 1 minute as shown in the schematics in Figure 63.

Since the recycled powder was prepared by the d-HDDR process, the resultant powder was expected to be anisotropic and bonded magnet from this material resulted in $B_r = 0.9$ T. The hot-deformation experiments were performed by placing the hot-pressed magnets in a 16 mm WC + Co cermet die to withstand high pressures. The pressure of 40 MPa and heating rate 50 °C/minute was maintained up to 700 °C in order to avoid high current density in the sample, which otherwise may induce undesirable microstructural changes (grain growth, Nd-rich GB and oxide phase transitions). The heating rate was kept the same till the holding temperature of 750 °C was reached but the pressure in final 50 °C was subsequently increased to 100 – 150 MPa in one minute. A total of 3 minutes at the maximum pressure were given, i.e. one minute to 750 °C, another one-minute holding at hot-deformation temperature and the final one minute when SPS current is switched off and cooling starts instantly.

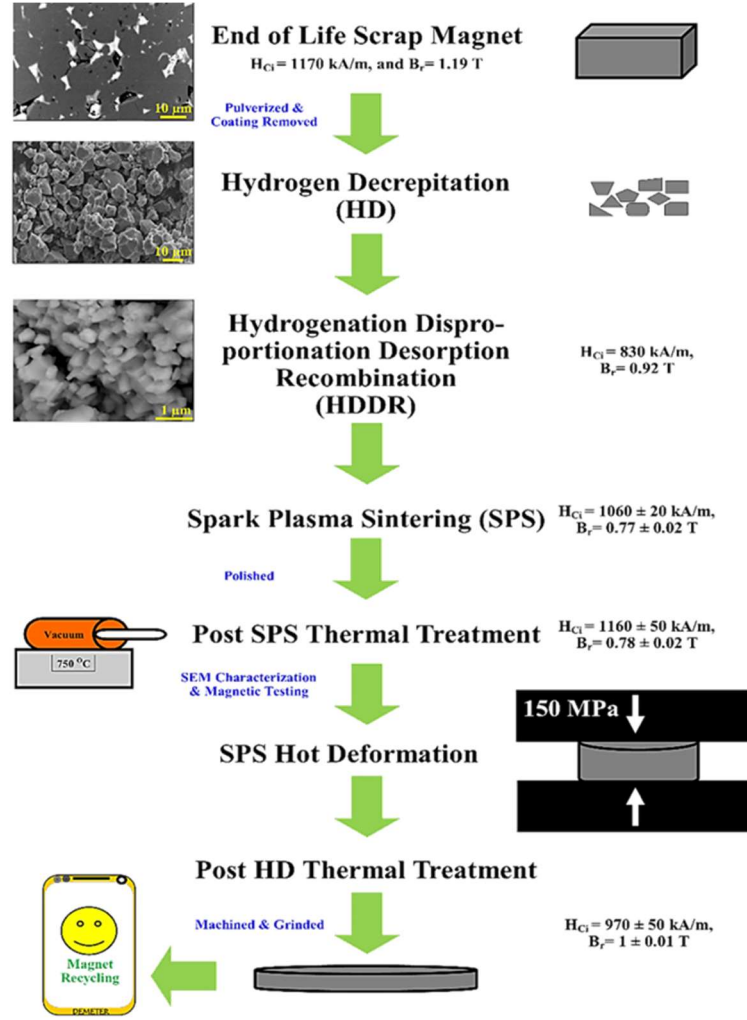


Figure 63: The process flow of the hot-pressing and hot-deformation of the recycled HDDR Nd-Fe-B powder at 150 MPa pressure for B_r improvement.

For the hot-deformation at 100 MPa pressure, the starting fully dense hot-pressed magnet after the thermal treatment had $H_{Ci} \sim 1150 \text{ kA/m}$ and $B_r = 0.8 \text{ T}$. The hot-deformation process yielded 40% height reduction in the sample and the magnetic properties were: $H_{Ci} = 690 \text{ kA/m}$, $B_r = 0.87 \text{ T}$ and $BH_{\max} = 99 \text{ kJ/m}^3$. The hot deformation is a high strain process and therefore the stresses induced during the deformation can be considered to reduce the coercivity apart from the grain elongation [67, 107, 206, 207]. The thermal treatment at 750°C for 1 hour was repeated to release the microstructure of processing stress and achieve the improvement in the magnetic properties due to the redistribution of the Nd-rich phase. Thus, after the heat treatment, the magnetic properties improved to: $H_{Ci} \sim 1060 \text{ kA/m}$, $B_r = 0.91 \text{ T}$ and $BH_{\max} = 144 \text{ kJ/m}^3$, as shown in Figure 64.

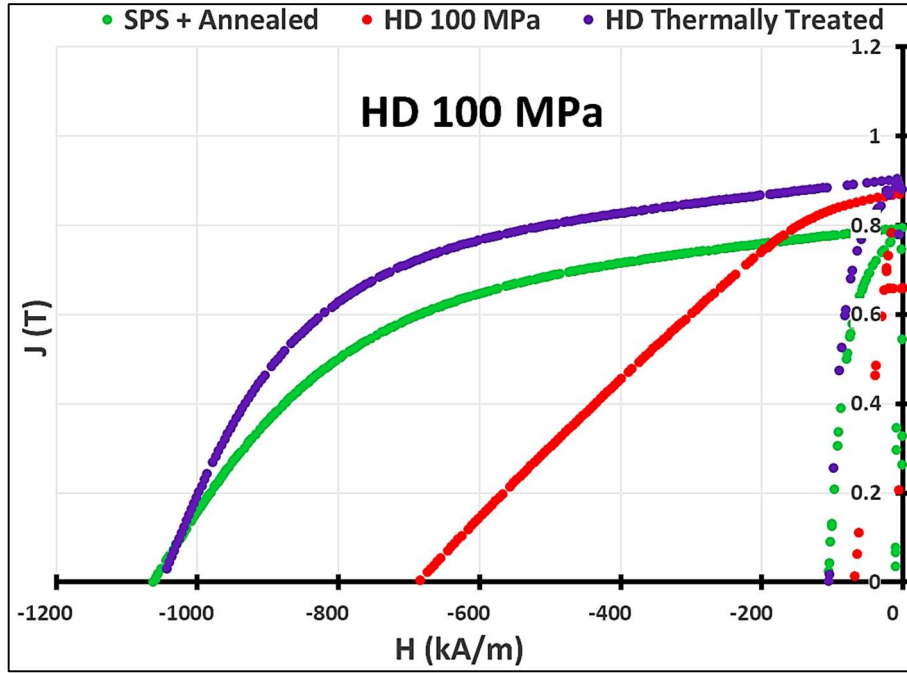


Figure 64: Comparison of the magnetic properties of recycled HDDR Nd-Fe-B based magnets after the hot-pressing (green), hot-deformation at 100 MPa (red) and post hot-deformation thermal treatment (purple).

Similarly, the hot-deformation experiments repeated at higher pressures resulted in slightly better remanence than 100 MPa samples or hot-pressed magnets. The heating rate was kept constant at 50 °C/minute and during the final 3 minutes of pressure was maintained at 150 MPa in the second instance. The magnetic properties of the starting hot-pressed magnet were: $H_{Ci} \sim 1150$ kA/m, $B_r = 0.8$ T and $BH_{max} = 105$ kJ/m³. The hot-deformation at 150 MPa resulted in remanence enhancement and up to 55% height reduction. Therefore, the magnetic properties were measured to be: $H_{Ci} \sim 770$ kA/m, $B_r = 0.96$ T and $BH_{max} = 165$ kJ/m³. Subsequently the thermal treatment improved the overall magnetic properties of the hot-deformed magnet at 150 MPa and were: $H_{Ci} \sim 960$ kA/m, $B_r = 1.01$ T and $BH_{max} = 180$ kJ/m³. The measured magnetic properties for 150 MPa hot-deformed sample are illustrated in Figure 65.

The applicable pressure of 150 MPa was in a sense limit for the operation mode and further increase was not possible on the system. Therefore, from the comparison of 100 and 150 MPa range, an improvement is evident of 0.1 T approx. for 50 MPa increase. Thereby, if the system allowed hot deformation up to 500 MPa, the recycled HDDR powder is capable of reaching the remanence values much higher than these obtained.

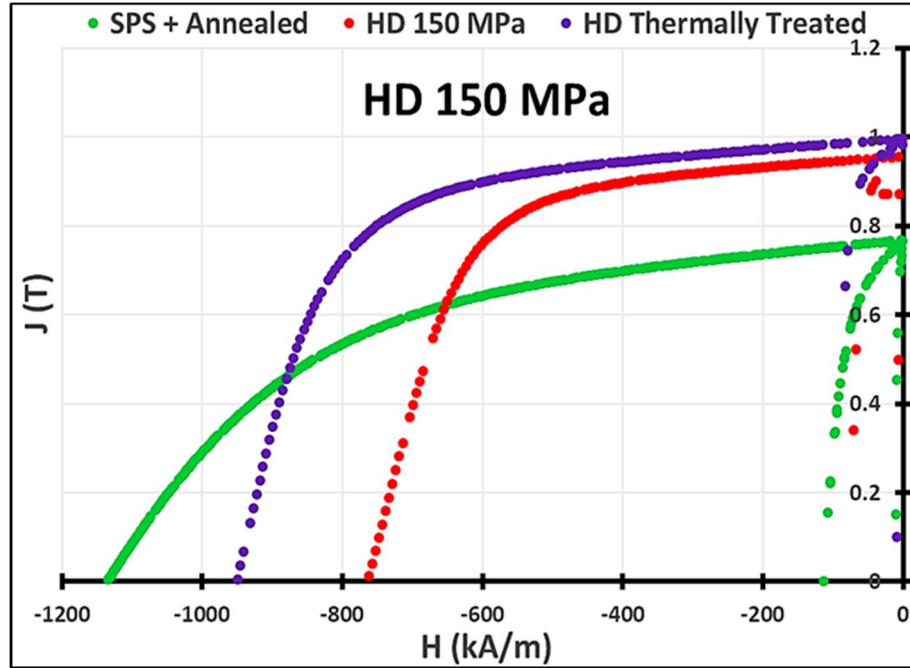


Figure 65: The magnetic properties comparison of recycled HDDR Nd-Fe-B based magnets after the hot pressing (green), hot deformation at 150 MPa (red) and post hot deformation thermal treatment (purple).

The cross sections of hot deformed magnets were characterized for their microstructure by HR-SEM in backscattered electron imaging mode as shown in Figure 66. The pressing direction in each case is indicated by the arrows. As clearly seen from Figure 66 (a), when the hot deformation pressure is low at 100 MPa only, the microstructure is similar to the initial recycled HDDR Nd-Fe-B powder in Figure 36 or the hot-pressed (optimally SPS-ed) samples in Chapter 5 and 6. Apart from only a few grains, the majority of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are not aligned with the pressing direction. This suggests incomplete hot-deformation or the lack of uniform texture in the sample. The matrix grains are also not excessively deformed, which is the reason for higher coercivity than the starting material. After the thermal treatment, we can expect relaxation of deformation stresses, which improved the overall magnetic properties.

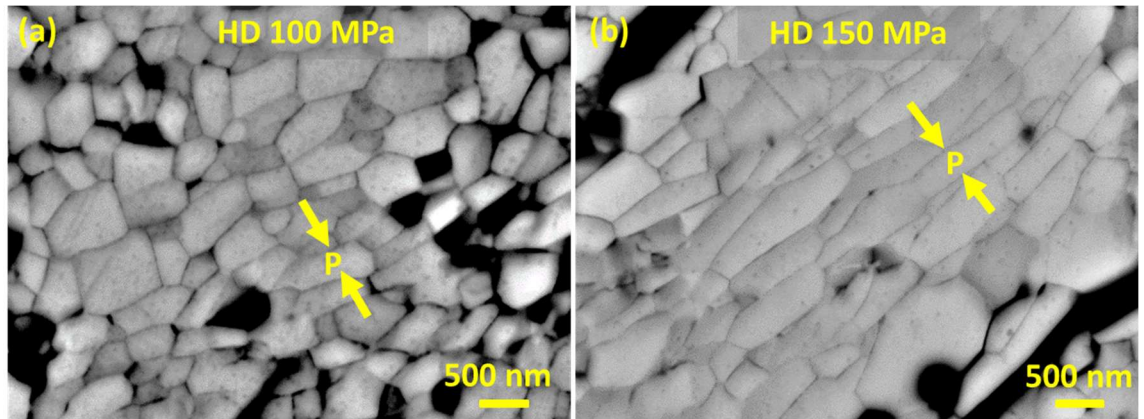


Figure 66: BSE micrographs of (non-annealed) hot deformed samples at (a) 100 MPa and (b) 150 MPa; the arrows indicate the direction of pressing during SPS hot deformation.

In case of hot-deformation at 150 MPa pressure, the microstructure in Figure 66 (b) is more textured and several grains are deformed in the pressing direction which resulted in higher B_r . The elongation of matrix grains is considered as grain growth, so the coercivity starts to decrease as grains begin to grow, but more importantly with higher percentage reduction in height, the deformation stresses on the microstructure are higher, which degrade the H_{Ci} [67, 107, 206, 207]. During the hot-deformation, it has been advocated that the liquid grain boundary phase is squeezed out above the ternary transition temperature of 665 °C as it rotates and get redistributed along the smaller aspect ratio grain facets [208]. Therefore, the Nd-rich phase perpendicular to the pressing direction is forced out of the intergranular regions where textured parallel facing grains get into intermittent contact with each other. So, the localized exchange coupling effects at these regions without the Nd-rich phase contribute to lowering of the coercivity [66]. In comparison X. Q. Li et al. [67] attained up to 69% height reduction with $B_r = 1.22$ T and $H_{Ci} = 181$ kA/m only.

The enhancement of coercivity along with B_r in hot-deformed magnets is becoming a subject of interest due to successful application of grain boundary modification of hot deformed melt-spun ribbons yielded high $B_r \sim 1.4$ T and $H_{Ci} > 2000$ kA/m [44, 71, 72, 75, 108-110, 112, 114-116, 166, 209]. In case of Nd-Fe-B HDDR system, Song et al. [136] utilized Pr-Cu low melting alloys to improve the coercivity of hot deformed HDDR Nd-Fe-B-type magnets to 1230 kA/m. Similarly, up to 2. wt. % Nd-Cu alloys were reported to improve the coercivity of hot-deformed magnets to 1042 kA/m [113]. A subtle improvement of 640 kA/m was also indicated after the grain boundary modification treatment of the HDDR-based Nd-Fe-B magnets with milled powder blend of $NdH_x + Cu$ [111]. Henceforth, with the application of higher deformation pressures and the subsequent addition of low melting eutectic alloys or RE-rich nanoparticles blends, not only the remanence enhancement and BH_{max} are possible but coercivity can also be improved. The potential is very high for the HDDR based commercial as well as recycled materials.

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Chapter 10 Results

Hydrogen Decrepitation and Spark Plasma Sintering to Produce Recycled SmCo_5 Magnets with High Coercivity

In this final chapter, the article: “Hydrogen Decrepitation and Spark Plasma Sintering to Produce Recycled SmCo_5 Magnets with High Coercivity” by **Anas Eldosouky, Awais Ikram**, Muhammad Farhan Mehmood, Xuan Xu, Sašo Šturm, Kristina Žužek Rožman and Irena Škulj is presented.

The industrially rejected SmCo_5 magnets, which do not meet the specifications are either sold as waste or recycled by the re-melting process with losses surmounting over 20%, moreover, it is an energy intensive and time-consuming method. These scrap SmCo_5 magnets were recycled by hydrogen decrepitation (HD) treatment. The SPS technique was effectively used to rapidly compact the HD recycled SmCo_5 powder to fully dense sintered magnets with the magnetic properties as good as the freshly prepared sintered magnets. The sintering temperature was varied from 800 – 1000 °C with a holding time of 1 minute and 80 MPa uniaxial pressure. The best condition for achieving $H_{\text{Ci}} > 2000 \text{ kA/m}$ at the room temperature was 900 °C. The $B_r = 0.47 \text{ T}$ of the optimally SPS-ed sample indicated isotropic nature of the sintered magnets. The microstructural examination with SEM indicated the formation of an optimal mixture of Sm_2Co_7 -type Sm-rich phase in the SmCo_5 matrix at 900 °C, which resulted in high coercivity values. At the SPS temperature below 900 °C, the densification was lower than 90%, Sm-oxides (Sm_2O_3) and $\text{Sm}_2\text{Co}_{17}$ were more than the desired percentage in the matrix which resulted in poor magnetic properties. During sintering at the elevated temperatures, complete densification was possible but the Sm-rich phase decomposed to less favorable $\text{Sm}_2\text{Co}_{17}$ and $\text{Sm}_5\text{Co}_{19}$ phases in the matrix. So, the magnetic properties were yet again lower than that at 900 °C. These phases were appropriately verified with the XRD phase analysis as well. The magnetic properties were also measured at 180 °C to compare the effectiveness of SPS-developed magnets with the conventionally sintered magnets. The results indicate that the HD treatment is very effective in producing the friable magnetic powder with finer particles in the range of 4 – 20 μm which can be densely compacted with the SPS under a controlled atmosphere (preventing the oxidation).

Authors' Contributions:

My contributions as the joint first author in this paper is summarized as following:

1. Corresponding Author: Anas Eldosouky;
2. Conceptualization: Awais Ikram;

3. Methodology: Awais Ikram and Anas Eldosouky;
4. Software: Awais Ikram and Anas Eldosouky;
5. Validation: Awais Ikram and Anas Eldosouky;
6. Formal analysis: Awais Ikram and Anas Eldosouky;
7. Investigation: Awais Ikram, Anas Eldosouky and Muhammad Farhan Mehmood;
8. Resources: Irena Škulj;
9. Data curation: Awais Ikram and Anas Eldosouky;
10. Writing—original draft preparation: Anas Eldosouky;
11. Writing—review and editing: Awais Ikram and Anas Eldosouky;
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15. Funding acquisition: Irena Škulj, Sašo Šturm and Kristina Žužek Rožman.

Hard Magnetic Materials

Hydrogen Decrepitation and Spark Plasma Sintering to Produce Recycled SmCo_5 Magnets With High Coercivity

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Abstract—The spark plasma sintering (SPS) technique is applied in combination with the hydrogen decrepitation process for the recycling of SmCo_5 magnets. The SmCo_5 magnets for recycling were first decrepitated by hydrogen gas at a pressure of 4 bar for 3 h to produce decrepitated powder. This powder was then used to prepare isotropic sintered magnets using the SPS technique by sintering at 800 °C–1000 °C for 1 min. Full densification of the SPS magnets was possible at a temperature of 1000 °C. The sample that was sintered at 900 °C showed the best internal coercivity (iH_c) of higher than 1500 kA/m with a high remanence (B_r) value of 0.47 T and energy product (BH_{max}) of 43.4 kJ/m³. The properties of the SPS sample sintered at 900 °C are compared to the conventionally sintered (CVS) sample prepared by using fresh SmCo_5 powder. The results show an improvement in the magnetic properties of the SPS sample in comparison to the CVS sample at room temperature, and the possibility to use the SPS sample at a high temperature of 180 °C, where the sample showed good magnetic properties of iH_c of 1502 kA/m, B_r of 0.44 T, and BH_{max} of 36.4 kJ/m³. Microstructure and X-ray diffraction patterns of the SPS and the CVS samples show that they consist of a SmCo_5 matrix with Sm_2Co_7 and Sm oxides.

Index Terms—Hard magnetic materials, hydrogen decrepitation, recycling, SmCo_5 , spark plasma sintering.

I. INTRODUCTION

Permanent magnets are known to have much technical importance as they are used in a range of important applications as in motors, generators, sensors, and hard disc drives. NdFeB and SmCo magnets dominate the market of permanent magnets production [Gutfleisch 2011]. SmCo magnets can be produced having compositions close to $\text{Sm}_2\text{Co}_{17}$ or SmCo_5 . SmCo_5 offers a very high anisotropy field of 31 840 kA/m, with excellent coercivity of a value of 2388 kA/m. Also, SmCo_5 magnets have very good temperature resistance: Curie temperature of 750 °C, reversible temperature coefficient of coercivity of $-0.2\%/^\circ\text{C}$, and reversible temperature coefficient of remanence of $-0.05\%/^\circ\text{C}$ [Pan 2014]. But, as SmCo_5 is composed of Sm and Co, and both elements are recently identified as elements of supply risk and technical importance, innovative recycling routes have to be defined for the magnet [European Commission 2017].

Hydrogen decrepitation (HD) is a process where the material absorbs hydrogen gas in its interstitial sites. This absorption causes volumetric expansion and the reduction of the material's particle size [Harris 1987]. The conditions needed for the decrepitation and the particle size produced depend on the material's chemical composition and microstructure. Recently, Walton [2015] and Eldosouky [2018] showed the possibility to use HD for the recycling of NdFeB and SmCo_5 magnets, by using a conventional sintering (CVS) route for

the densification of the decrepitated powder after milling. After the CVS of the decrepitated SmCo_5 powder, the microstructure of the original magnet, which consists of a SmCo_5 matrix, and Sm_2Co_7 and Sm-oxides as randomly distributed phases, has been reformed.

Spark plasma sintering (SPS) is a process where a pulsed dc current passes through a die, which contains the powder of interest. The process is usually combined by an applied pressure. The mechanism of densification in SPS is different than CVS, where CVS consists of slow diffusion mechanisms such as grain boundary and volume diffusions. On the other hand, SPS is a rapid densification technique, where only the surface of the particle experiences localized heating, with no observed contribution from the bulk of the particles [Diouf 2012]. Zhao [2008] described the densification mechanism in SPS to consist of the following four steps.

- 1) Powder activation and refining.
- 2) Formation of sintering neck; the first two steps involve removing the surface oxide and heating the powder due to the voltage breakdown effect and formation of the neck by evaporation and condensation and diffusion.
- 3) Growth of the sintering neck.
- 4) Plastic deformation densification, usually enhanced by the applied pressure.

Due to the local heat generation, the sintering temperature required for the full densification of the powder is usually lower than the one required for the CVS, with much lower sintering time as low as minutes in comparison to days, sometimes for CVS. There are many parameters which can be optimized in the SPS experiments, such as the pressure applied, the heating rate, the sintering temperature, the holding time, and the partial pressure.

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The SPS technique is now a well-established technique for the production of NdFeB magnets of high coercivity and excellent magnetic properties [Mo 2007, Liu 2010]. Moreover, the use of the SPS for the sintering of SmCo_5 magnets was shown to be an effective technique for the preparation of bulk nanocrystalline SmCo_5 or SmCo/Fe(Co) of good magnetic properties. Zhang [2010] and Yue [2011] used the SPS for the preparation of bulk nanocrystalline SmCo_5 magnets. They showed that the internal coercivity (iH_c) value of 2273 kA/m and a remanence (B_r) value of 0.5 T can be achieved by using ball milled SmCo_5 , where the sintering temperature was 700 °C at an applied pressure as high as 500 MPa. Fang [2018] showed that the use of wet-milling for the preparation of the SmCo_5 results in the oxidation of the powder during the processing, and the formation of $\text{Sm}_2\text{Co}_{17}$, with a decrease of iH_c of the magnets to a value as low as 280 kA/m. Saravanan [2013] studied the magnetic properties and microstructure of SmCo_5/Fe nanocomposite bulk magnets at different temperatures between 700 °C–850 °C, 75 MPa, where the highest coercivity of 654 kA/m was achieved at 800 °C, where the produced magnet had composition of mainly Sm(Co,Fe)_5 with other secondary phases such as $\text{Sm}_2(\text{Co,Fe})_{17}$ and $\alpha\text{-Fe(Co)}$. Saito [2018] showed that decreasing the sintering temperature to 600 °C results in an enhancement in the coercivity to 980 kA/m, whereas Lu [2015] showed that the BH_{max} value for the SPS SmCo_5 can be improved by the addition of NdFeB. BH_{max} of 115 kJ/m³ was obtained for SmCo/NdFeB (4:1), which is 50% higher than the single-phase SmCo_5 magnets.

The aim of this study was to use a combination of HD and SPS routes for the recycling of sintered SmCo_5 magnets and the production of isotropic SmCo_5 magnets at different sintering temperatures. The magnetic properties, microstructure, X-ray diffraction (XRD) patterns, and density and oxygen content of the recycled magnets made by the SPS route are compared with those for industrially produced sintered magnet prepared by the CVS route.

II. EXPERIMENTAL PROCEDURES

Two SmCo_5 powders were used for this study. Freshly prepared powder of particle size 4–20 μm was used, prepared by milling the as-cast alloy in a nitrogen atmosphere jet mill. The chemical composition of the powder was as follows: 36 wt% Sm, 63.8 wt% Co, and 0.2 wt% O. The second type was the recycled powder prepared by HD of SmCo_5 sintered magnets. The magnets for recycling were collected out of industrial lines, as they do not meet the shape specifications. The measured chemical composition of the magnet was 36.30 wt% Sm, 63.22 wt% Co, and 0.37 wt% O. The decrepitation experiment was done in a rotating equipment as described by Eldosouky [2018]. The conditions for the decrepitation reaction were 4 bar of hydrogen, and 250 rpm at room temperature for 3 h. The produced powder after decrepitation was milled in a jet mill with nitrogen atmosphere to a particle size lower than 20 μm . A total of 1 wt% of Sm metal was added for the milled powder to compensate for the oxygen in the starting material before recycling and for the oxidation during the decrepitation and further processing steps.

The milled decrepitated powder was sintered using the SPS route. Inside a glove box, 3 gm of the milled powder with the Sm addition was put in a 10 mm inner diameter graphite die. The die was then

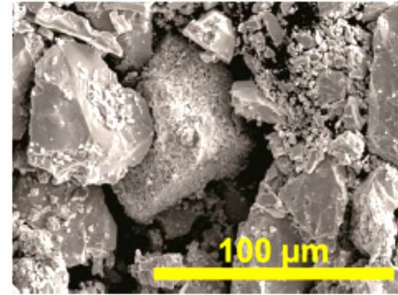


Fig. 1. SE image of the powder produced by the decrepitation of SmCo_5 magnets.

handled in air for less than 5 min to be put in the SPS machine, where, in between, the powder inside the die was pressed by a hydraulic press to 5 bar. The SPS sintering parameters were 800 °C–1000 °C sintering temperature (50 °C step), and heating rate of 50 °C/min. The sample was kept at the sintering temperature for 1 min, where the applied pressure was 80 MPa. After evacuating the SPS chamber to 0.05 mbar, partial pressure of 200 mbar Ar was kept during sintering to reduce the Sm evaporation. The sintering experiments were done by using SPS 25 series, model 615, Fuji Electronic Industrial Co., Ltd., Osaka, Japan. A CVS route was used to produce SmCo_5 magnets made out of the fresh powder, without alignment, similar to the SPS experiments. A silicon mold of volume of 8 cm³ was filled by the fresh powder to reach to a density of about 3 g/cm³. The mold was then isostatically pressed at a pressure of 2500 bar. The pressed sample was then sintered at 1180 °C for 2 h and heat treated for 3 h at 880 °C.

The microstructure analysis for the powder after decrepitation was carried by a Helios NanoLab 650 scanning electron microscope, whereas an Jeol JSM-7600F scanning electron microscope was used for the sintered samples. A PANalytical X'Pert pro multipurpose diffractometer was used for the crystallography measurement. The demagnetization curves for the sintered samples were measured by a Magnet-Physik's permagraph with maximum applied pressure of 1500 kA/m, after magnetization by 6 T field. The oxygen content was measured by an Eltra ON 900, oxygen/nitrogen analyzer. The density was measured by Archimedes' principle.

III. RESULTS AND DISCUSSION

Fig. 1 shows the secondary electron (SE) image for the produced powder after the decrepitation of SmCo_5 magnets. The decrepitated powder is of irregular shape with some sharp features and wide particle size distribution (~300 nm to ~200 μm). The powder is characterized with the presence of transgranular fractures in the SmCo_5 matrix phase, in addition to the intergranular fractures due to the hydrogen absorption by the $\text{Sm}_2\text{Co}_{17}$ phase, as described by Harris [1987].

Fig. 2 shows the demagnetization curves for the SPS samples produced by sintering at 800 °C, 850 °C, 900 °C, 950 °C, and 1000 °C. Table 1 shows the magnetic properties, density, and the oxygen content for the magnets. The density has shown to increase with the sinter-

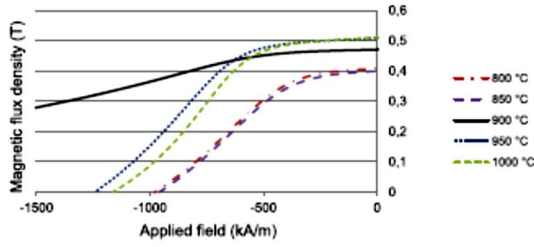


Fig. 2. Demagnetization curves for the SPS samples sintered at 800 °C–1000 °C. The sample sintered at 900 °C showed the best coercivity.

Table 1. Density, oxygen content, and magnetic properties of the SPS samples sintered at 800 °C–1000 °C.

Temperature	ρ [g/cm ³]	Oxygen cont. [wt%]	(BH) _{max} [kJ/m ³]	JH_c [kA/m]	B_r [T]
800 °C	6.86	1.20	31.9	978.6	0.41
850 °C	7.14	0.76	30.5	960.0	0.40
900 °C	8.11	0.66	43.4	>1500	0.47
950 °C	8.38	0.49	49.8	1243	0.51
1000 °C	8.40	0.47	50.1	1164	0.51

ing temperature from 6.86 g/cm³ at 800 °C to 8.4 g/cm³ at 1000 °C, which is about 100% of the theoretical density of the magnets. On the other hand, the oxygen content showed to decrease with increasing the sintering temperature, as the densification in SPS involves removing the surface oxide because of the voltage breakdown effect, which means increasing the sintering temperature, would lead to more efficient removing of the surface oxygen toward the full densification [Diouf 2012].

As expected from the relative relationship between the density and the sintering temperature, the B_r and BH_{max} of the samples also showed to increase with the sintering temperature to reach to a value of 0.51 T and 50.1 kJ/m³, respectively, for the sample sintered at 1000 °C. The sample sintered at 900 °C showed a B_r of 0.47 T, which is about 50% of the value for the anisotropic SmCo₅ magnets produced industrially, which have a B_r of 0.80–0.96 T [Pan 2014]. For the samples sintered at lower than 900 °C, due to the incomplete phases formation for those samples and the presence of high oxygen content and large pores percentage, the coercivity value was lower than the one for the industrial CVS SmCo₅ magnets, with JH_c of less than 1000 kA/m. Sintering at 900 °C at the same conditions has the effect of properly densifying the magnet to reach to a density of 96% of the theoretical density. The measured JH_c value for this sample was higher than 1500 kA/m. Increasing the sintering temperature further showed to negatively affect the shape of the demagnetization curve, where the JH_c value was dropped to 1243 kA/m and 1164 kA/m for 950 °C and 1000 °C samples, respectively. The decrease of the JH_c upon increasing the sintering temperature is believed to be due to the excessive formation of the Sm₂Co₇, as it will be shown from the

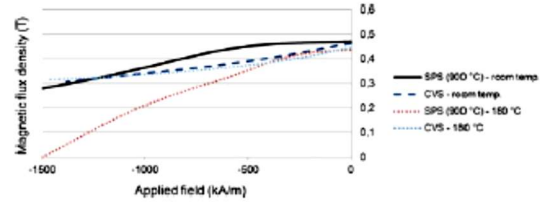


Fig. 3. Comparison between the demagnetization curves of the SPS sample sintered at 900 °C and the CVS sample; at room temperature and 180 °C.

Table 2. Density, oxygen content, and magnetic properties of the SPS sample sintered at 900 °C and CVS sample; at room temperature and 180 °C.

	(BH) _{max} [kJ/m ³]	JH_c [kA/m]	JH_c [kA/m]	B_r [T]	ρ [g/cm ³]	Oxygen cont. [wt%]
SPS (900 °C) - room temp.	43.4	>1500	366.8	0.47	8.11	0.66
CVS - room temp.	38.0	>1500	328.4	0.46	8.25	0.4
SPS (900 °C) - 180 °C	36.4	1502	322.4	0.44	-	-
CVS - 180 °C	34.8	>1500	314.2	0.44	-	-

microstructure and XRD studies later, and smoothing out of the grain surface, as described by Menushenkov [2006] for the decrease in the coercivity of the SmCo₅ magnets after heat treatment above 900 °C for CVS magnets with Sm content of 36.4 wt%. Note that the level of the carbon uptake from the graphite die during the SPS sintering is not enough to drastically change the magnetic properties of the produced magnets, as shown by Mackie [2016] for Sm(Co, Fe, Cu, Zr)₂.

In order to compare between the SPS and CVS techniques for the production of sintered SmCo₅ magnets, Fig. 3 shows the demagnetization curves at room temperature and 180 °C for the SPS sample produced at 900 °C, as it showed to have the best coercivity among other SPS samples, and a fresh SmCo₅ sample produced by the CVS route. Table 2 shows a comparison between their density, oxygen content, B_r , BH_{max} , JH_c , and external coercivity (H_c). At room temperature, the SPS sample showed to have better B_r , coercivity, and BH_{max} in comparison to the CVS samples, even though, the latter has better density and lower oxygen content than the former. This is likely to be due to the microstructure refinement after HD due to the large particle size distribution of the decrepitated powder [Eldosouky 2018]. Heating to 180 °C has resulted in a more deterioration effect for the magnetic properties of the SPS sample because of its lower density and the higher affinity for the interstitial oxidation. Nevertheless, even at 180 °C, the latter is still showing good properties: B_r of 0.44 T, JH_c of 1502 kA/m, and BH_{max} of 36.4 kJ/m³, which confirms the applicability of the magnet for high temperature applications as in electric vehicles and space applications.

Fig. 4 shows the back scattered electrons (BSE) images of the CVS sample and the SPS samples sintered at 800 °C, 900 °C, and 1000 °C; Fig. 5 shows their XRD patterns. The detected phases in the samples by the EDX were as follows: the matrix SmCo₅, randomly distributed light gray Sm₂Co₇ phase with random size, and white small spots which were analyzed to be a mixture of Sm-oxides and Sm-rich

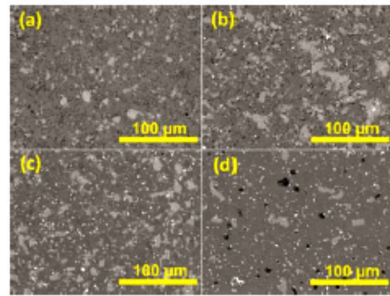


Fig. 4. BSE images of the SPS samples sintered at (a) 800 °C, (b) 900 °C, (c) 1000 °C, and (d) the CVS sample.

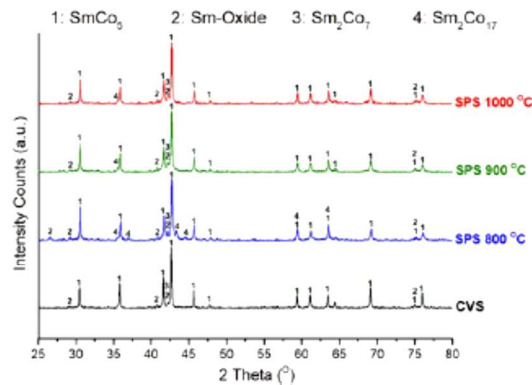


Fig. 5. XRD patterns of the CVS sample and SPS samples sintered at 800 °C, 900 °C, and 1000 °C.

phases. From the XRD patterns, both the SPS samples at 800 °C and 900 °C showed the presence of small fractions of the $\text{Sm}_2\text{Co}_{17}$ phase, with higher concentration in the 800 °C samples. The appearance of $\text{Sm}_2\text{Co}_{17}$ is due to the increase of the oxygen concentration and the consumption of Sm in these samples and results in the decrease in the iH_c values for the samples sintered at temperature lower than 900 °C, as mentioned above. The $\text{Sm}_2\text{Co}_{17}$ phase has disappeared by increasing the sintering temperature with increasing the percentage of the Sm_2Co_7 phase, where the SPS samples at 1000 °C showed to have Sm_2Co_7 with higher percentage than other samples, without the appearance of any traces of the $\text{Sm}_2\text{Co}_{17}$ phase.

IV. CONCLUSION

The SPS technique was successfully used for the densification of SmCo_5 powder produced by the HD of SmCo_5 sintered magnets at 4 bar. The properties of the SPS samples showed to drastically depend on the sintering temperature. The SPS sample produced by sintering at 900 °C showed the most promising results among other SPS samples, with iH_c higher than 1500 kA/m. The samples prepared by the

SPS route showed to have comparable results in comparison to fresh SmCo_5 samples made by the CVS route. The SPS samples also showed relatively good magnetic properties at 180 °C. This indicates the possibility to use SPS technique for the production of recycled SmCo_5 magnets of high coercivity, which enable them to be used in various applications.

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Conclusions

The two different rare earth permanent magnet powders Nd-Fe-B and Sm-Co recycled by hydrogen-based routes were rapidly sintered with the spark plasma sintering (SPS) technique. The research targets concluded with this dissertation include that with the optimized reprocessing of the recycled rare earth permanent magnet powders we were able to achieve above 70% of the magnetic properties as compared to the “fresh” commercial magnetic powders.

The hydrogenation-disproportionation-desorption-recombination (HDDR) reprocessed Nd-Fe-B powders from the end-of-life magnets in the electronic appliances were rapidly sintered with the SPS to determine the suitable reuse except as the plastic bonded magnets. The differential scanning calorimetry study resolved the ternary eutectic transition temperature for the HDDR Nd-Fe-B powder at 665 °C. The produced recycled HDDR Nd-Fe-B powder with an $H_{Ci} = 830$ kA/m were SPS-ed in the temperature range of 650 – 850 °C to verify the optimal sintering conditions for reaching full densification and retain the pristine HDDR submicron-sized $Nd_2Fe_{14}B$ grain microstructure. The optimally SPS-ed samples at 750 – 800 °C under 100 MPa uniaxial pressure had $H_{Ci} \sim 1000$ kA/m which increased further to 1200 kA/m by vacuum thermal treatment at 750 °C for 1 hour. The improvement in the magnetic properties after the thermal treatment is associated with uniform redistribution of the Nd-rich grain boundary phase and possibly also due to the relaxation of interfacial/processing strains. Sintering above 820 °C was found to be detrimental for the magnetic properties because of the exaggerated grain coarsening, featuring bimodal grain distribution of normally grown grains 700 – 2600 nm and the abnormally coarsened grains up to 10 μm . The thermal treatment did not significantly improve the magnetic properties of samples SPS-ed at 850 °C because the grain coarsening occurs at the expense of small matrix grains and Nd-rich phase that gets consumed upon that. Therefore, in such a case, the thermal treatments were expected to only relieve the reprocessing strain as Nd-rich phase distribution has already been achieved during the sintering at elevated temperatures. Nonetheless the SPS treated recycled HDDR Nd-Fe-B powder has coercivity values slightly higher than the commercial HDDR MF-15P powder because of the initial HDDR grain-size, microstructure preservation and the SPS processing control. The application of higher pressures during SPS can develop texture in these originally isotropic magnets. The hot deformation pressure of 150 MPa resulted in 55% height reduction and improvement in B_r to 0.96 T which subsequently improved to 1.01 T (~10% improvement over the recycled material) after the thermal treatment at 750 °C for 1 hour.

The HDDR-based recycling is more viable for magnets if the protective coating is removed prior to hydrogenation. In secondary processing, as the coating flakes are to be removed prior to the HD treatment, the crushed magnets are pulverized to size below 100 μm , which makes them susceptible to oxygen gain. The sinterability, oxygen uptake and the magnetic properties of the recycled HDDR Nd-Fe-B powder fractions from 700 to < 50 μm were tested individually. The results indicate that the powder fractions up to 100 μm were able to retain their magnetic properties during optimal SPS reprocessing as the oxygen content was lower than 5500 ppm. For the powder fractions 50 and < 50 μm , the oxygen content increased rapidly (> 7000 ppm) as compared to the coarse HDDR Nd-Fe-B powder mix. Subsequently these fractions lose their sinterability due to the excessive formation of the Nd_2O_3 phase at the expense of the Nd-rich phase. Thereby it is concluded/suggested to try to retain the HDDR powder particle size above the 100 μm size range during the industrial processing, so that the magnetic properties are not lost in case of the bonded magnets and additionally the sinterability for the bulk magnets.

The improvement in coercivity of the recycled HDDR Nd-Fe-B based permanent magnets was realized by doping with DyF_3 particles which led to the pioneering development of the $(\text{Dy,Nd})_2\text{Fe}_{14}\text{B}$ -type core-shell structure in this type of material. The DyF_3 dopant content was varied from 1 – 5 wt. % in the HDDR Nd-Fe-B powder and the blend was optimally SPS-ed at 750 °C for 1 minute. The thermal treatment conditions were ranged from 600 – 900 °C, for 1 – 6 hours in vacuum to obtain the highest possible coercivities. The peak coercivity value was obtained at 750 °C for 1 hour in case of 1 and 2 wt. % DyF_3 , reaching ~1410 kA/m which is approx. 70% higher than the starting recycled HDDR Nd-Fe-B powder. These values are also ~18% higher than the commercial MF-15P Nd-Fe-B HDDR powder. Apparently, the core-shell microstructure formed uniformly from Dy diffusion in 1 and 2 wt. % sample even for 1 hour of thermal treatment at 750 and 900 °C. In case of 5 wt. % DyF_3 doped samples, prolonging the thermal treatment to 3 and 6 hours resulted in decomposition of the core-shell structure. The Dy diffusion is circumvented by complex intermetallic compounds (based on Nd-Fe-F) and the excessive formation of non-ferromagnetic NdF_X ($X = 3 \text{ \& } 4$) phases in such samples contributes to deterioration of the magnetic properties. In view of rare earth sustainability, the optimal magnetic properties from the recycled material can be obtained from 2 wt. % HREE-based dopants by controlling the thermal treatments. Therefore, substituting higher weight fractions will only contribute to poor magnetic properties and inarguably high costs (of raw material consumption and production). Besides this method is more effective for a uniform localized HREE diffusion than the surface grain boundary diffusion (GBDP), where the diffusion depth is only limited to a thickness of ~3 mm.

The HD-recycled SmCo_5 powder with particle size in the range of 4 – 20 μm were SPS-ed to nearly full densification at 900 °C, which had room temperature magnetic properties: $H_{\text{Ci}} > 2000 \text{ kA/m}$ and $B_r = 0.47 \text{ T}$ typical for isotropic magnets. The magnetic properties of optimally sintered SmCo_5 magnets from the recycled powder were slightly better than the conventionally sintered magnets because of the better grain size control in pressure-assisted sintering. The magnetic properties up to 180 °C from the recycled powder were also higher because of optimal microstructure. The latter consisted of a uniform distribution of a primary Sm-rich phase: Sm_2Co_7 (and controlled formation of secondary $\text{Sm}_2\text{Co}_{17}$ & $\text{Sm}_5\text{Co}_{19}$ phases) in the SmCo_5 matrix when sintered at 900 °C. Increasing the temperature above 900 °C improved the densification to 8.4 g/cm^3 ($\sim 100\%$ of theoretical density), but the room temperature H_{Ci} was reduced to $\leq 1200 \text{ kA/m}$ because of the dissociation of the Sm-rich phase to the less favorable $\text{Sm}_2\text{Co}_{17}$ phase. It is therefore advocated that the HD-recycled powder is effectively as good as the fresh powder or the commercially available sintered magnets of the matching composition. These findings suggest that as long as the microstructure is preserved during the rapid consolidation, the recycling with the HD route is very effective to treat the industrial scrap and revitalize it for commercial usage.

Overall the recycling of rare-earth-based permanent magnets holds great potential for future rare-earth sustainability, supply chain and magnet production. The technological control of recycled material processing can develop magnets as good as the commercially available grades or fresh magnetic powders. In combination the hydrogen-based greener recycling routes and the contemporary SPS method holds great industrial potential especially for permanent magnets in microelectronics, electrical appliances and automotive traction motors.

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Biography

The author of this dissertation is a Pakistan national, born on 7th June 1989 in Islamabad. He completed his BSc. in Materials Science & Engineering in 2011 with the senior design project in developing smart body armour utilizing shear thickening fluids composed of the nanoceramics in Kevlar hybrid matrix. Afterwards he worked for 2 years (marketing, management and quality enhancement cell) before embarking on the MS Engineering in Nanotechnology from the same alma mater Ghulam Ishaq Khan Institute, Pakistan in 2013. His MS Thesis was related to solution chemical and electrochemical synthesis of 1D nanostructures of rutile titanium dioxide. As a fellow he also worked as lab instructor and lectured on courses in composites, powder metallurgy, alloy design, surface engineering and metallographic characterization. At present, he is a 3rd year student in Jozef Stefan International Postgraduate School. He recently finished his employment at K-7 Department for Nanostructured Materials as a Doctoral Researcher. His research was framed in the European Training Network for the Design and Recycling of Rare-Earth Permanent Magnet Motors and Generators in Hybrid and Full Electric Vehicles (DEMETER)² (ETN-DEMETER) project towards developing fully dense and high coercivity magnets by rapidly reprocessing of the end-of-life magnetic scrap (Nd-Fe-B and Sm-Co (SmCo₅)) with the Spark Plasma Sintering. He has also worked towards the grain boundary modification of the recycled Nd-Fe-B based magnets to increase the coercivity utilizing low temperature eutectic alloys and RE-F₃ (TbF₃ and DyF₃) based nanoparticle dopants. The task was to achieve 70% of the magnetic properties by making 50-50% blends with the fresh commercial powder. Not only he was able to obtain the coercivity values at par with the fresh grade powder and sintered magnets, he improved the coercivity of the recycled HDDR powder by 77% approx. He has acquired training in the operation of scanning electron and ion-beam milling microscope during his fellowship. He is well versed with powder metallurgy, magnetometry and the characterization techniques for engineering materials, ceramics and functional nanomaterials. He has published four papers in international peer-reviewed journals and another joint publication is a conference paper.