

NOVEL MULTICOMPONENT Nd-Fe-B PERMANENT MAGNETS

Tomaž Tomše

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NOVI VEČKOMPONENTNI Nd-Fe-B TRAJNI MAGNETI

Doktorska disertacija

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To my beloved sister, whose absence still leaves me speechless.

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Abstract

Nd-Fe-B permanent magnets have become indispensable components of many different devices in the past few decades. Their excellent overall magnetic performance originates in the intrinsic properties of the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Bulk magnets are polycrystalline and their magnetic properties are governed by the material's microstructure. To compensate for the unfavorable microstructural characteristics such as the large grain size and imperfect magnetic isolation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, heavy rare earth (HRE = Dy or Tb) elements are often added to the Nd-Fe-B alloy to increase the magnetocrystalline anisotropy of the hard magnetic phase. This improves the material's resistance to demagnetization, measured by the intrinsic coercivity value. A major drawback of this approach, in addition to the high prices and low natural abundance of the HRE elements, is the reduced saturation magnetization due to the antiferromagnetic coupling of the magnetic moments of the HRE atoms with the moments of iron, which results in lower magnetic flux density.

Magnetic properties deteriorate with increasing temperature. Some applications like traction motors for electric vehicles and wind turbines require magnets with high concentrations of the HRE elements, since the operating temperatures are high and certain parts of the magnets are exposed to large demagnetizing fields. The local reversal of magnetization, if not prevented, can lead to an overall reduction of the magnetic flux density, which has a pronounced negative impact on the magnet's performance. A novel approach to achieve the resource efficiency and to minimize the loss of the flux density without degrading the magnet's resistance to demagnetization is presented in this thesis. As an alternative to the homogeneously distributed Dy or Tb throughout the magnet, multicomponent magnets containing regions with different magnetic properties were manufactured from Dy-containing and HRE-free Nd-Fe-B magnetic powders.

Manufacture of magnets starts with the production of magnetic powders. Preparing a dense magnet from the powder is a crucial step that determines the material's final properties. Consolidation of the polycrystalline nanostructured powders is especially challenging due to the undesired grain growth that can significantly degrade their magnetic properties when the consolidation temperatures are too high. By using a special kind of hot-pressing technique called Pulsed Electric Current Sintering (PECS), the material can be densified at lower temperatures and with shorter processing times compared to the conventional high-temperature sintering and hot pressing techniques. This is achieved by simultaneously applying pressure and heat, generated internally by means of a pulsed DC current that passes through the conductive powder compact. Consequently, the grain growth is suppressed and the magnetic properties of the initial powder are retained. Three different types of Nd-Fe-B magnetic powders (melt-spun, gas-atomized and hydrogenation-disproportionation-desorption-recombination-processed) were considered as possible candidates for the preparation of the multicomponent magnets. Processing parameters have been optimized for each of the materials investigated with the aim of finding a combination of powders that can be consolidated together without deteriorating the materials' respective magnetic properties. Among the materials chosen for the study, only the neodymium-rich

melt-spun powders are commonly used for hot pressing, while the hydrogenation-disproportionation-desorption-recombination-processed materials are intended for bonded magnets. The gas-atomized powders are seldom used for magnetic applications and a novel type of Nd-Fe-B magnet was prepared from a neodymium-rich gas-atomized powder with the PECS technique. On the other hand, the Nd-lean gas-atomized powder proved to be unsuitable for the PECS processing: the material did not condense at temperatures low enough to preserve the powder's magnetic properties. This was correlated to the absence of the Nd-rich liquid phase, which hinders the densification kinetics.

The hydrogenation-disproportionation-desorption-recombination-processed powder needed the highest temperature to reach the maximal density (≈ 800 °C) and the dense sample required an additional post-consolidation heat treatment to retain the powder's initial magnetic properties. A strong dependence of the samples' intrinsic coercivity values on the PECS processing parameters was observed. Based on the microscopic investigation, the trend was attributed to the redistribution of the Nd-rich phase during the consolidation and subsequent heat treatment. In general, the Nd-rich phase has an important role in the development of coercivity in the Nd-Fe-B-type materials.

As a rapid solidification technique, the gas atomization process can be adopted for the manufacture of the Nd-Fe-B powders, but the cooling rates are not sufficiently high to prevent the formation of α -iron and large $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains in alloys with commonly used compositions. Another reason that this technique is rarely used is that the Nd-rich powders experience a significant loss of hard magnetic properties at temperatures close to or higher than 150 °C. In the PECS experiments, the maximal density was reached at 700 °C with the Nd-rich gas-atomized powder and the sample's intrinsic coercivity was much higher than the value of the initial powder, even after the latter was heat-treated in order to improve its magnetic properties. Another advantage of the bulk magnet prepared with the PECS technique, compared to the raw powder, is improved high-temperature stability of magnetic properties. This was achieved with the reduction of the surface area, which hinders the surface nucleation reversal mechanism, believed to be responsible for the deterioration of the magnetic properties of the raw Nd-rich gas-atomized powders.

The melt-spun powders performed exceptionally well in the PECS experiments and dense single component magnets were prepared from the Dy-free and Dy-containing powders at similar consolidation temperatures (650 and 670 °C, respectively) without deteriorating their magnetic properties, which were significantly better than the properties of other types of powders chosen for the study. For these reasons, the melt-spun powders were selected for the preparation of multicomponent magnets.

Two different approaches were considered for the manufacture of magnets with locally different magnetic properties. The first sample was prepared from the raw powders by placing one powder on top of the other, after which the powder compact was densified in a single PECS consolidation step. The second sample was manufactured from the dense single component Dy-free and Dy-containing magnets, previously prepared from the respective powders. The two parts were then condensed into a single magnet body in a second PECS consolidation step. SEM and EDX analysis of the as-prepared multicomponent magnets revealed that the compositions of the respective materials remained unchanged. This corresponded with the results of the magnetic characterization, which showed that the magnetic properties of the respective materials were preserved in the multicomponent magnet.

Povzetek

Nd-Fe-B trajni magneti so v zadnjih nekaj desetletjih postali nepogrešljiv sestavni del številnih naprav. Njihove odlične magnetne lastnosti izvirajo v intrinzičnih lastnostih trdo magnetne $\text{Nd}_2\text{Fe}_{14}\text{B}$ faze. Pravi magneti so polikristalinični, njihove magnetne lastnosti pa so odvisne od mikrostrukture materiala. Nezaželene mikrostrukturne lastnosti, kot na primer velika zrna $\text{Nd}_2\text{Fe}_{14}\text{B}$ faze in nepopolna magnetna izolacija zrn, se pogosto kompenzirajo z dodatkom elementov težkih redkih zemelj (Dy, Tb) v osnovno Nd-Fe-B zlitino z namenom povečanja magnetokristalne anizotropije trdo magnetne faze. Tako se izboljša odpornost materiala proti demagnetizaciji, katerega merilo je vrednost intrinzične koercitivnosti. Slabost tega pristopa, poleg visokih cen in nizkih naravnih zalog težkih redkih zemelj, je predvsem zmanjšana nasičena magnetizacija, ki je posledica antiferomagnetne sklopitve magnetnih momentov težkih redkih zemelj z momenti železa, kar ima za posledico nižjo gostoto magnetnega polja.

Magnetne lastnosti s temperaturo pešajo. Nekatere aplikacije, kot na primer vlečni motorji za električna vozila in vetrnice za vetrne elektrarne, potrebujejo magnete z visoko koncentracijo težkih redkih zemelj, ker so delovne temperature visoke, določeni deli magnetov pa so izpostavljeni močnim demagnetizacijskim poljem. Lokalna sprememba smeri magnetizacije, če se le-te ne prepreči, lahko vodi v zmanjšanje gostote magnetnega polja, kar izrazito negativno vpliva na kvaliteto magnetov. V tej doktorski disertaciji je predstavljen nov pristop za optimizacijo izrabe naravnih virov ter preprečitev zmanjšanja gostote magnetnega polja, brez da bi bila ogrožena odpornost materiala proti demagnetizaciji. Kot alternativo homogeni koncentraciji Dy ali Tb v magnetu sem pripravil večkomponentne magnete, ki vsebujejo območja z različnimi magnetnimi lastnostmi, za kar sem uporabil prah z dispropzijem in prah brez težkih redkih zemelj.

Izdelava magnetov se začne s proizvodnjo magnetnih prahov. Priprava magnetov iz prahu je kritičen korak, ki vpliva na njegove končne lastnosti. Konsolidacija polikristaliničnih, nanostrukturnih prahov predstavlja dodaten izziv, saj lahko nezaželena rast zrn, ki spremlja konsolidacijo pri visokih temperaturah, znatno poslabša njihove magnetne lastnosti. Z uporabo posebne metode vročega stiskanja, t. i. PECS (Pulsed Electric Current Sintering) tehnike, se material zgosti pri nižji temperaturi in v krajšem času, kot je to značilno za konvencionalno visokotemperaturno sintranje in ostale vrste tehnik vročega stiskanja. To je možno zaradi sočasno apliciranega tlaka in temperature, ki se generira v materialu, ko skozi njega steče električni tok. Rast zrn je posledično zatrta, magnetne lastnosti izhodnega prahu pa se ohranijo. Kot potencialne kandidate za pripravo večkomponentnih magnetov sem izbral tri različne tipe magnetnih prahov (hitro ohlajeni, plinsko atomizirani in tipa HDDR). Da bi našel primerno kombinacijo prahov, ki se lahko procesirajo hkrati brez poslabšanja magnetnih lastnosti, sem parametre procesiranja optimiziral za vsak preiskovan prah posebej. Izmed izbranih materialov so le z neodimijem bogati hitro ohlajeni prahovi namenjeni za uporabo v vročem stiskanju, medtem ko je HDDR prah namenjen za izdelavo plastomagnetov. Plinsko atomizirani prahovi se zelo redko uporabljajo za magnetne aplikacije. Z neodimijem bogat atomiziran prah sem uporabil za pripravo novega tipa Nd-Fe-B magnetov s pomočjo PECS tehnike. Z

neodimijem reven atomiziran prah pa se je izkazal kot neprimeren za pripravo magnetov s PECS tehniko, saj se material ni zgostil pri dovolj nizkih temperaturah, da bi se ohranile njegove magnetne lastnosti. Izkazalo se je, da je razlog za to pomanjkanje tekoče z neodimijem bogate faze, kar zavira kinetiko zgoščevanja.

Izmed vseh uporabljenih prahov je HDDR prah potreboval najvišjo temperaturo ($\approx 800\text{ }^{\circ}\text{C}$), da je bila dosežena maksimalna gostota. Poleg tega pa je moral biti tako izdelan magnet še dodatno toplotno obdelan, da so se povrnila izhodne magnetne lastnosti prahu. Intrinzična koercitivnost magnetov je bila močno odvisna od parametrov konsolidacije. S pomočjo mikroskopske študije je bila vzpostavljena korelacija med intrinzično koercitivnostjo in redistribucijo z neodimijem bogate faze med konsolidacijo in kasnejšo termično obdelavo. Z neodimijem bogata faza ima v splošnem pomembno vlogo pri razvoju koercitivnosti v materialih tipa Nd-Fe-B.

Kot metoda hitrega strjevanja ima plinska atomizacija potencial, da se jo uporabi za proizvodnjo Nd-Fe-B magnetnih prahov, vendar pa hitrost ohlajanja ni zadosti velika, da bi se preprečil nastanek α -železa in velikih zrn $\text{Nd}_2\text{Fe}_{14}\text{B}$ faze v materialih s klasično sestavo. Drugi razlog, da se ta tehnika redko uporablja, pa je termična nestabilnost z neodimijem bogatih atomiziranih prahov, ki delno izgubijo magnetne lastnosti pri temperaturah blizu $150\text{ }^{\circ}\text{C}$. S PECS metodo sem iz takšnega prahu pripravil trden magnet pri $700\text{ }^{\circ}\text{C}$. Njegova intrinzična koercitivnost je bila znatno višja od vrednosti izhodnega prahu, tudi zatem, ko je bil slednji toplotno obdelan z namenom izboljšanja njegovih lastnosti. Trden PECS magnet je tudi izkazal izboljšano visokotemperaturno stabilnost magnetnih lastnosti. To sem dosegel z zmanjšanjem površine materiala, s čimer se je zmanjšala verjetnost površinske nukleacije povratnih domen, za katero se predvideva, da je odgovorna za izgubo magnetnih lastnosti prahov.

Hitro ohlajeni prahovi so se odrezali izredno dobro v PECS eksperimentih. Trdni enokomponentni magneti so bili pripravljene iz prahu z dodatkom disprozija in prahu brez disprozija pri podobnih temperaturah konsolidacije (650 in $670\text{ }^{\circ}\text{C}$) in brez izgube magnetnih lastnosti. Te so bile znatno boljše od lastnosti ostalih prahov, uporabljenih v tej študiji. Zato sem hitro ohlajene prahove izbral za izdelavo večkomponentnih magnetov.

Za pripravo magnetov z lokalno različnimi magnetnimi lastnostmi sem uporabil dva pristopa. Prvi magnet je bil pripravljen direktno iz prahov. Pri tem sem en prah nasul na drugega in tako pripravljen vzorec zgostil s pomočjo PECS tehnike. Drugi magnet je bil pripravljen iz enokomponentnih magnetov, predhodno izdelanih iz posameznih prahov. Magneta sta se nato združila v en sam sestavljen magnet v dodatnem PECS koraku. SEM in EDX analiza tako pripravljenih večkomponentnih magnetov je pokazala, da je kemijska sestava izhodnih materialov ostala nespremenjena, kar je sovpadalo z rezultati magnetnih meritev, ki so potrdili, da so se prvotne magnetne lastnosti izhodnih materialov ohranile v večkomponentnem magnetu.

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Abbreviations

BSE	... backscattered electron
EDS	... energy-dispersive X-ray spectroscopy
EPD	... electrophoretic deposition
EPS	... electric power steering
GBD	... grain boundary diffusion process
HD	... hydrogen decrepitation
HDDR	... hydrogenation disproportionation desorption recombination
HRE	... heavy rare earth
ICP-AES	... inductively coupled plasma atomic emission spectroscopy
LRE	... light rare earth
MRI	... magnetic resonance imaging
PECS	... Pulsed Electric Current Sintering
PFM	... pulsed field magnetometer
RE	... rare earth
SEM	... scanning electron microscope
TRE	... total rare earth
VCM	... voice coil motors
VSM	... vibrating-sample magnetometer
XRD	... X-ray diffraction

Symbols

$(BH)_{max}$	... maximum energy product
H_{ci}	... intrinsic coercivity
B_r	... remanent induction (remanence)
M	... magnetization
v	... velocity
r	... radius
e	... electronic charge
h	... Planck's constant
m	... mass of the electron
μ_B	... Bohr magneton
H	... magnetic field
B	... magnetic induction
μ_0	... permeability of the free space
J	... magnetic polarization
Φ	... magnetic flux
χ	... magnetic susceptibility
μ	... magnetic permeability
T_c	... Curie temperature
M_s	... saturation magnetization
M_r	... remanent magnetization
J_r	... remanent polarization
H_c	... coercivity
E_a	... crystal anisotropy energy
K_i	... anisotropy constant
H_d	... demagnetizing field
N_d	... demagnetizing factor
E_F	... Fermi level
H_A	... anisotropy field
N_{eff}	... effective demagnetization factor
β	... absolute temperature coefficient of intrinsic coercivity
α	... absolute temperature coefficient of remanence
Q	... heat
I	... electrical current
R	... electrical resistance
t	... time

Chapter 1

Introduction

A permanent magnet is a material that produces its own magnetic field. If properly handled, it remains magnetized indefinitely. The earliest known use for a permanent magnet was the needle of a compass. Today, permanent magnets are indispensable in numerous applications where a constant field is needed [1].

In the 1960s, new magnetic materials based on the rare earth (RE) elements emerged and the progress following the invention of the first RE-based high-performance magnet (SmCo_5) has been very rapid [2]. The Nd-Fe-B permanent magnets were developed in the early 1980s [3], [4] and are nowadays often the material of choice. Their magnetic properties originate in the intrinsic properties of the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase [4], but the overall performance of the bulk Nd-Fe-B magnets heavily depends on the material's microstructure, which is determined by the manufacturing route and chemical composition of the alloy [4], [5].

Anisotropic sintered magnets manufactured from the single crystalline micron-sized jet-milled powders are used in electric motors, voice coil motors (VCM) for hard disc drives, magnetic resonance imaging (MRI) and many other devices [6]. Their maximum energy product ($(BH)_{\max}$), a value often used as a figure of merit for magnets, is much higher than the $(BH)_{\max}$ values of other magnetic materials developed in the past (cobalt magnet steel) and permanent magnets currently on the market (hard ferrites, alnicos and Sm-Co), as shown in Fig. 1. For the same performance, less magnetic material is needed, which effectively leads to miniaturization of devices [2].

The disadvantage of sintered Nd-Fe-B magnets is the fact that their intrinsic coercivity (H_{ci}), which is a measure of the magnet's capability to withstand the external demagnetizing fields, heavily depends on the use of heavy rare earth (HRE) elements dysprosium and terbium. These elements substitute the Nd atoms in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and additions up to 10 wt. % are common in the high-coercivity magnets [7]. As a result, the magnetocrystalline anisotropy, a property of hard magnetic materials, is increased. But at the same time, the saturation magnetization of the system is lowered due to the antiferromagnetic coupling of the magnetic moments of Dy and Tb atoms with the moments of iron, which weakens the field produced by the magnet. The values of remanent magnetization (B_r) and maximum energy product are thus reduced [8]. In addition, the HRE elements are less abundant than Nd and much more expensive [7], [9].

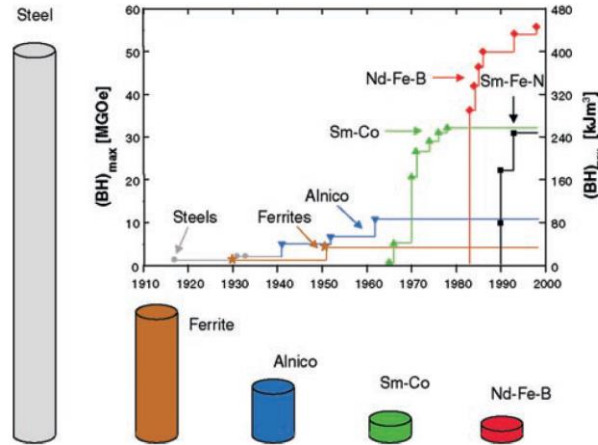


Figure 1: Development in the maximum energy product of hard magnetic materials and comparison of the respective volumes of different types of materials with identical $(BH)_{max}$ value [5].

Besides the jet-milled powders, other types of Nd-Fe-B powders with different microstructure and magnetic properties are also used for the production of magnets. Hot-pressed magnets prepared from the nanostructured melt-spun Nd-Fe-B powders have higher H_{ci} values than sintered magnets even without the addition of Dy or Tb, but their B_r values are much lower due to the isotropic nature of the powder [3]. Hot deformation of a hot-pressed nanostructured magnet increases the remanent magnetization and such a magnet can be used for a variety of applications in electronics and automotive industry. Alternatively, a nanostructured powder can be mixed with a binder to make a small-sized or near-net-shaped magnet, but such a specimen has lower magnetization due to the reduced volume ratio of the hard magnetic material [7]. Demagnetization curves of three classes (sintered, hot-pressed and hot-deformed) of commercially available Dy-free Nd-Fe-B magnets are compared in Fig. 2. Ideally, a Nd-Fe-B magnet would have the high remanent magnetization of a HRE-free sintered magnet (≈ 1.4 T) and the excellent intrinsic coercivity of a nanostructured material (≈ 1600 kA/m). In practice, often a choice between one or the other has to be made and different grades of magnets are available on the market today [2].

In some applications like traction motors of (hybrid) electric vehicles and electric power steering (EPS) motors, magnets suffer from demagnetization due to the large reverse magnetic fields that are strong enough to change the direction of the specimen's magnetization. Although the standard approach is to use HREs throughout the magnet body to increase its H_{ci} value, certain parts of the magnet are more exposed than others [6], [10]. A new approach to prevent the loss of the magnetic flux density associated with the use of Dy or Tb and at the same time improve the magnet's resistance to external demagnetizing factors is presented in this dissertation. Magnets with locally different magnetic properties (multicomponent magnets) were manufactured from the Dy-containing and Dy-free melt-spun powders with a special kind of hot pressing technique called Pulsed Electric Current Sintering (PECS).

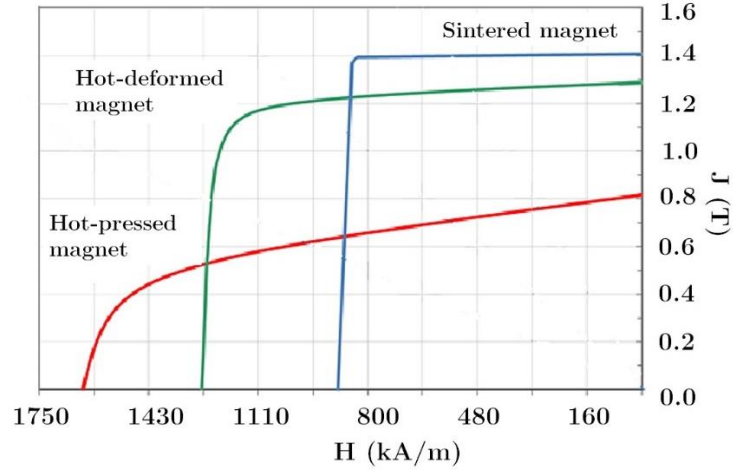


Figure 2: Demagnetization curves of hot-pressed, hot-deformed and sintered HRE-free Nd-Fe-B magnets (adapted after [7]).

To prevent deterioration of the powders' respective magnetic properties during consolidation, the optimal PECS processing parameters, most notably the temperature, must be similar for both materials used in a multicomponent magnet. In addition to the melt-spun powders, other types of powders (gas-atomized and hydrogenation-disproportionation-desorption-recombination-processed) were also investigated with the aim of finding a suitable combination of materials that can be processed together in a single PECS consolidation step. Hydrogenation-disproportionation-desorption-recombination (HDDR) powders are commercially used for the production of bonded magnets. The densification behavior of the material used in this study was markedly different from the performance of the rapidly solidified powders (melt-spun and gas-atomized) with neodymium-rich compositions, which are required in order to successfully densify the material. The gas-atomized powders are seldom used for magnetic applications for at least two reasons. The cooling rates that can be achieved with the gas atomization technique are too low to prevent the formation of α -iron and large $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains in alloys with commonly used compositions. Another reason is the high-temperature instability of the Nd-rich atomized powders. A new type of Nd-Fe-B magnet was prepared from the atomized material with the PECS technique. Compared to the raw powder, the specimen's intrinsic coercivity was improved and its room-temperature magnetic properties were not degraded after the magnet was exposed to high temperatures. However, the sample's overall magnetic properties were not comparable to the excellent properties of the magnets prepared from the melt-spun powders.

Two different approaches were taken to prepare a multicomponent magnet. The first sample was manufactured directly from the raw powders in a single PECS consolidation step. The second sample was manufactured with a two-step procedure from the single component magnets, previously prepared from the Dy-free and Dy-containing powders. The samples were then combined into a single magnet body in a second PECS step. In this way, magnets containing regions with high intrinsic coercivity and regions with high remanent magnetization were prepared. By using a low consolidation temperature ($\approx 650^\circ\text{C}$) and limiting the holding time at this temperature to one minute, the respective compositions and microstructural characteristics of the melt-spun materials were preserved in the multicomponent magnets. The samples were isotropic, but the PECS approach can also be used to consolidate highly anisotropic jet-milled powders. Alternatively, an

anisotropic nanostructured multicomponent magnet could be prepared from the hot-deformed dense precursors with the two-step PECS procedure.

This dissertation starts with an introduction of basic concepts of magnetism and Nd-Fe-B materials (Chapter 2). Aims and hypotheses are presented in Chapter 3. Novel types of Nd-Fe-B magnets, materials used and methods employed for the preparation and characterization of samples are listed in Chapter 4. Results obtained in the scope of this study are presented and discussed in Chapters 5 and 6, respectively, and the most important conclusions are gathered in Chapter 7.

Chapter 2

Basics of Magnetism and Nd-Fe-B Magnetic Materials

Basic concepts of magnetism, most often encountered terms and magnetic properties, used to characterize a magnetic material, are explained in the first part of this chapter. The second part is dedicated to the Nd-Fe-B permanent magnets and contains a comprehensive list of the established powder production methods, as well as the bulk magnet manufacturing routes. In the last part, the concept of the local demagnetizing fields and their effect on the magnet, which is the basis for the multicomponent magnet approach, is introduced.

2.1 Magnetism Basics

The magnetization (M) is a property of a material that originates in the spin and orbital magnetic moments of the electrons in the atoms. By comparison, the nuclear magnetism is negligible. M represents the sum of all magnetic moments per unit volume that is large on the atomic scale [11].

The orbital motion of an electron around the nucleus is equivalent to the circulation of a charge and can be compared to the electrical current in a loop of a wire having no resistance. Correspondingly, the orbital contribution to the magnetic moment of an electron can be written as:

$$\mu = (\text{area of loop})(\text{current}) \quad (2.1)$$

The area of the loop is πr^2 where r is the atomic radius. In the Bohr theory of the atom, the electron moves with velocity v in a circular orbit of radius r . Considering that the charge of the electron is measured in coulombs, the current is $ev/2\pi r$. Therefore:

$$\mu(\text{orbit}) = \frac{evr}{2} \quad (2.2)$$

An additional postulate of the theory was that the angular momentum of the electron is an integral multiple of $h/2\pi$, where h is the Planck's constant. Therefore:

$$mvr = n \frac{h}{2\pi} \quad (2.3)$$

where m is the mass of the electron. Combining Eq. (2.2) and (2.3), we get:

$$\mu(\text{orbit}) = \frac{eh}{4\pi m} \quad (2.4)$$

for the magnetic moment located in the first ($n = 1$) Bohr orbit.

The electron behaves as if it were spinning about its own axis. Using Eq. (2.4) ($e = 1.60 \times 10^{-19}$ C, $h = 6.62 \times 10^{-34}$ Js and $m = 9.11 \times 10^{-31}$ kg), the magnetic moment due to electron spin is equal to

$$\mu(\text{spin}) = 9.27 \times 10^{-24} \text{ Am}^2 = \mu_B \quad (2.5)$$

The magnetic moments due to the motion in the first Bohr orbit and due to spin are equal. This amount of magnetic moment was given a special symbol μ_B and a special name, the Bohr magneton. Just as the electronic charge e is a natural unit of electric charge, the Bohr magneton is the natural unit for the magnetic moment.

There are many electrons in an atom (except for the hydrogen atom), each with its own moment. The magnetic moment of the atom is the vector sum of the individual electronic moments. If the magnetic moments cancel one another out, the atom as a whole has no net magnetic moment and the material is diamagnetic. If the atom is left with a net magnetic moment, such an atom is often referred to as a magnetic atom. Materials composed of atoms of this kind are para-, ferro-, antiferro- or ferrimagnetic [1].

When a magnetic material is placed in a magnetic field (H), the individual atomic moments contribute to its total response, which is called magnetic induction (B):

$$B = \mu_0(H + M) \quad (2.6)$$

where μ_0 is the permeability of the free space. The SI unit of magnetization and field is A/m and the unit of magnetic induction is T (tesla). It is also possible to express the magnetization in units of tesla by multiplying its value in A/m with μ_0 , in which case the term magnetic polarization (J) is used instead. Magnetic induction is the density of flux (Φ) inside the medium. Within a homogeneous material, $B = \Phi/A$, by analogy with $H = \Phi/A$, where A is a finite area.

All materials respond to the applied magnetic field in some way. A useful value that provides basic information about the material's magnetism is magnetic susceptibility (χ), which is the ratio between M and H :

$$\chi = M/H \quad (2.7)$$

Similarly, the ratio between B and H is called magnetic permeability (μ).

Diamagnetic materials have a negative susceptibility and the diamagnetic response toward an external magnetic field is usually very small. In contrast, susceptibilities of paramagnetic materials are positive. Their magnetic moments are randomly orientated by thermal agitation, as shown in Fig. 3a. When exposed to a magnetic field, the moments temporarily align in accordance with the direction of the field, which results in a net magnetization. In some paramagnetic materials, magnetic phase transitions occur at low temperatures and the exchange and dipolar interactions between magnetic moments prevail over the thermal energy. This results in cooperative ordering of the moments. Below the phase transition temperature (called Curie temperature - T_c), ferromagnetic and antiferromagnetic materials have parallel and antiparallel vector arrangements of moments, respectively (Fig. 3b, c). A special case is ferrimagnetism, where a net moment exists in spite of a partial antiparallel arrangement.

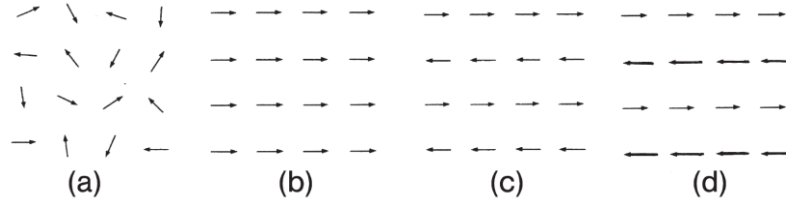


Figure 3: Disordered state of magnetic moments in a paramagnetic material (a) and ordered states in ferromagnetic (b), antiferromagnetic (c) and ferrimagnetic (d) materials [12].

The flux density inside a material is different from that outside: when the Φ inside is less than the Φ outside, the material is diamagnetic. For paramagnetic or antiferromagnetic materials, the Φ inside is slightly higher than the Φ outside. For ferro- and ferrimagnetic materials, the Φ inside is much greater than outside [12].

2.1.1 Hysteresis loop

The curves M vs H are called magnetization curves and are linear under normal circumstances for dia-, para- or antiferromagnetic materials. For ferro- and ferrimagnetic materials, they are nonlinear and the magnetic susceptibility depends on H . At sufficiently large values of H , the magnetization becomes constant at its saturation value (M_s) (Fig. 4a). When the field is decreased to zero after the saturation was reached, the magnetization is not reduced to zero but retains a certain value that is called remanent magnetization (M_r). If the applied field is then increased in the opposite direction, the magnetization will reach zero when H equals the intrinsic coercivity (H_{ci}). A large field is needed to demagnetize a hard magnetic material (large H_{ci} value) and the opposite is true for soft magnetic materials. When the reversed field is further increased, saturation will be reached again at $-M_s$. Reducing the field to zero and then increasing it in the original direction will bring the magnetization back to its saturation value M_s . In this way, the whole M vs H hysteresis loop is obtained [1].

Another type of hysteresis loop is the B vs H loop where magnetic induction is plotted as a function of H . Due to the relation $B = \mu_0(H + M)$, the slope of the B vs H curve reflects the constant magnetic susceptibility after the saturation point is reached and does not saturate. The value of remanent induction (B_r) is the same as the value of remanent magnetization expressed in tesla (remanent polarization $-J_r$) and often the term remanence is used. The point in the B vs H loop where B is zero is called coercivity (H_c). For soft magnetic materials, this value can be very similar to the intrinsic coercivity (H_{ci}) obtained by measuring the M vs H loop. For hard magnets, the difference can be substantial (Fig. 4b), but often the term coercivity is used to describe the H_{ci} value. The point where the product of B and H reaches its maximum value is called the maximum energy product $((BH)_{max})$. It is a convenient measure of the magnet's overall quality. Its unit is kJ/m^3 and it is the largest rectangular area under the B vs H curve in the second quadrant [1], [13].

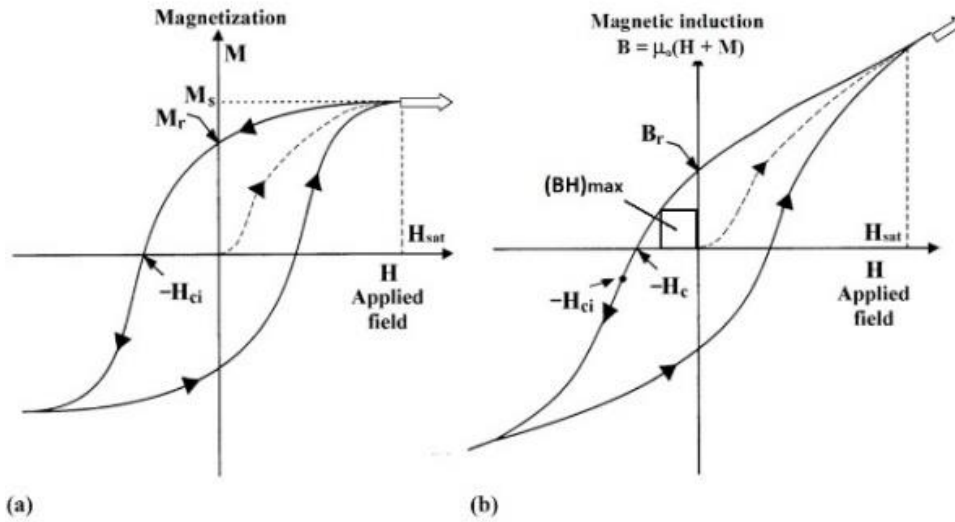


Figure 4: M vs H (a) and B vs H (b) hysteresis loops (adapted after [13]).

2.1.2 Anisotropy

Magnetic anisotropy is the most important factor affecting the shape of the hysteresis loop. Several kinds of anisotropy exist:

- Magnetocrystalline anisotropy (often called crystal anisotropy)
- Shape anisotropy
- Stress anisotropy
- Exchange anisotropy
- Anisotropy induced by
 - Magnetic annealing,
 - Plastic deformation,
 - Irradiation.

Magnetocrystalline anisotropy and shape anisotropy will be discussed in this section. Of the two, only the former is intrinsic to the material [1].

2.1.2.1 Magnetocrystalline anisotropy

Magnetocrystalline anisotropy is the inclination of the magnetization to align itself in a preferred crystallographic direction, called the easy direction.

The exchange interaction between two neighboring spins, called spin-spin coupling, can be very strong and acts to keep the spins parallel or antiparallel to one another. Because the associated exchange energy is isotropic and depends only on the angle between adjacent spins but not on the direction of the spin axis relative to the crystal lattice, the spin-spin coupling does not contribute to the crystal anisotropy. However, the spin is also coupled to the orbital motion of each electron. Therefore, when an external magnetic field acts on the spin of an electron trying to reorient it, the orbit of that electron also tends to be reoriented. But the orbit is strongly coupled to the crystal lattice and therefore resists the external field [1]. These relationships between spin-orbit and lattice are illustrated in Fig. 5.

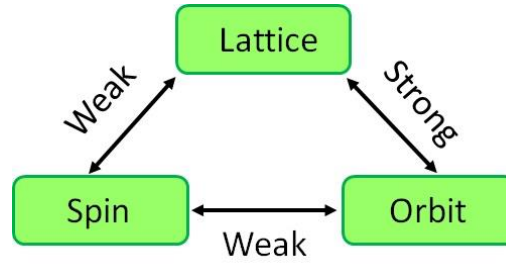


Figure 5: Spin-lattice-orbit interactions.

In case of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase, the easy axis of magnetization is aligned along the tetragonal c -axis at room temperature (at temperatures below 135 K, it is tilted with respect to the c -axis). The magnetization can point either up or down and both options are equivalent, as demonstrated in Fig. 6.

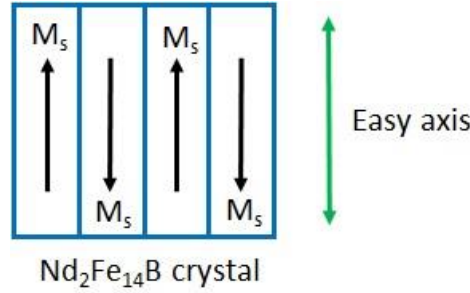


Figure 6: Domain structure of a uniaxial crystal.

In order to turn the magnetization vector away from the easy direction, the applied external field must work against the anisotropy force. The energy required for this task is called the crystal anisotropy energy (E_a). It is calculated using the temperature-dependent anisotropy constants K_0 , K_1 , K_2 ..., specific for a particular material. Constants of order higher than the first and second order are generally not needed and even K_2 is sometimes so small that the term containing it can be neglected. K_0 is angle-independent and is usually ignored. Units of E_a and K_i are J/m^3 [1], [11].

For a $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystal, the anisotropy energy depends on the angle between the magnetization and the c -axis (θ) and the anisotropy is termed uniaxial. The expression for E_a in uniaxial crystals is usually written in powers of $\sin\theta$. It follows from Eq. 2.8 that the energy E_a is minimal when the magnetization points in the direction of the easy axis ($\theta = 0$):

$$E_a = K_0 + K_1 \sin^2\theta + K_2 \sin^4\theta \quad (2.8)$$

2.1.2.2 Shape anisotropy

A polycrystalline magnet with no preferred orientation of its grains is magnetically isotropic in contrast to an anisotropic magnet with the grains aligned along the c -axis. External magnetic field applied on an isotropic magnet will magnetize it to the same extent in any direction, if the sample is spherical in shape. In contrast, a nonspherical sample like a bar

magnet will be easier to magnetize along the long axis than along the shorter one. The reason for this is the demagnetizing field H_d that acts in the opposite direction to the magnetization M which creates it and is weaker for the long and stronger for the short axis of the sample. It can be expressed as:

$$H_d = -N_d M \quad (2.9)$$

where N_d is the demagnetization factor that depends mainly on the shape of the specimen.

The H lines, originating in the north pole and ending in the south pole, constitute a field not only outside but also inside the magnet where its direction is from north to south and therefore tends to demagnetize the sample. For a bar-shaped permanent magnet magnetized along its length, this is illustrated in Fig. 7. After the magnet is removed from the external magnetic field, H_d is the only field acting and the magnetic induction B is lowered according to the relation [1]:

$$B = -\mu_0 H_d + \mu_0 M \quad (2.10)$$

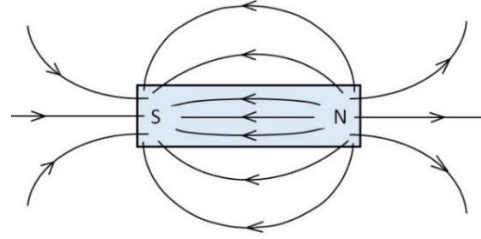


Figure 7: H field of a bar magnet in zero applied field.

2.1.3 Magnetic domains

Below its Curie temperature (T_c), a ferromagnet in the demagnetized state is divided into many small regions called magnetic domains. The size of each domain depends on the material and is typically ≈ 200 nm for Nd-Fe-B magnets. Due to the exchange interactions between the magnetic moments, each domain is spontaneously magnetized to the saturation value M_s . The interface between two adjacent domains with different directions of spontaneous magnetization is called a domain wall. Because the exchange energy between two magnetic moments is minimal when the moments are aligned parallel, the change of direction is gradual (over a few hundred atoms) and the wall thickness depends on the magnetocrystalline energy. Alternatively, coherent rotation is possible in very small particles in a sense that, during reversal, the magnetization stays homogeneous with the same direction and magnitude everywhere in the particle.

The specimen as a whole has no net magnetization, because the directions of magnetization of the numerous domains are different. When a sufficiently strong external field is applied, the specimen converts from a multi-domain state into a state of a single domain magnetized in the direction of the applied field, as illustrated in Fig. 8, and the material is magnetically saturated [1], [11].

In magnets with multi-domain grains, domain walls are readily swept across each grain when an external field is applied. Development of coercivity therefore depends on preventing the nucleation and growth of the reverse domains from the fully magnetized

state. The reverse domains can be prevented from growing if the domain walls are pinned at planar defects or inclusions that are comparable in size to the domain wall [11].

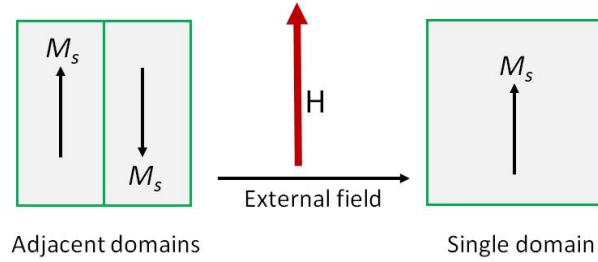


Figure 8: The magnetization process in a ferromagnet with a 180° domain wall.

2.2 Nd-Fe-B Magnets

Nd-Fe-B-type permanent magnets were simultaneously developed in 1983 at General Motors [3], [14], Sumitomo Special Metals Co., Ltd. [4], [15] and at the US Naval Research Laboratory [16]. The search for new materials was driven by the need to replace the SmCo_5 -type and $\text{Sm}_2\text{Co}_{17}$ -type permanent magnets that were extensively used in high-temperature applications [17]. The cobalt crisis between 1978 and 1981, initiated by the rebellion in Zaire (now Democratic Republic of Congo), resulted in a six-fold increase in the cobalt price, thus necessitating the need for cheaper materials [18].

The origin of the excellent magnetic properties, characteristic for the Nd-Fe-B magnets, is the $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase with a body-centered tetragonal crystal structure belonging to the space group $P4_2/\text{mmn}$. Its superior uniaxial magnetocrystalline anisotropy favoring the c -axis gives the Nd-Fe-B magnets the potential to have a high coercivity [4]. A unit cell of this phase consists of four formula units with 68 atoms in total, arranged in two crystallographically inequivalent Nd sites, six inequivalent Fe sites and one B site as shown in Fig. 9. All Nd and Fe magnetic moments are aligned parallel to the c -axis due to the ferromagnetic coupling. Isomorphous compounds with other rare earth elements also exist (including the non-magnetic Y, La, Yb and Lu) and often a fraction of Nd atoms is substituted with heavy rare earths (Tb or Dy) in order to tailor the material's magnetic properties. Similarly, isomorphous compounds with cobalt substituting for iron exist for most of the light rare earth (LRE) elements, as well as for Gd and Tb [11], [14], [19]. Iron can also be substituted by other elements (Al, Si, Ti, Cr, Mn etc.) with mostly negative impact on the material's magnetic properties [11].

Thanks to their superior magnetic properties and lower price of raw elements, the Nd-Fe-B magnets rapidly replaced Sm-Co magnets [1], [2]. Different grades of the Nd-Fe-B magnetic powders are produced today by established manufacturing techniques, namely powder metallurgy for high-performance anisotropic sintered magnets and melt spinning for isotropic nanostructured powders intended for bonded magnets or for hot pressing and hot deformation [11]. While some applications like magnetic resonance imaging (MRI) and voice coil motors (VCM) require high magnetic flux density, others like traction motors for (hybrid) electric vehicles and electric power steering motors also require a high coercive force (> 2000 and > 1500 kA/m, respectively), since the magnets operate at high temperatures and experience large demagnetizing fields [6].

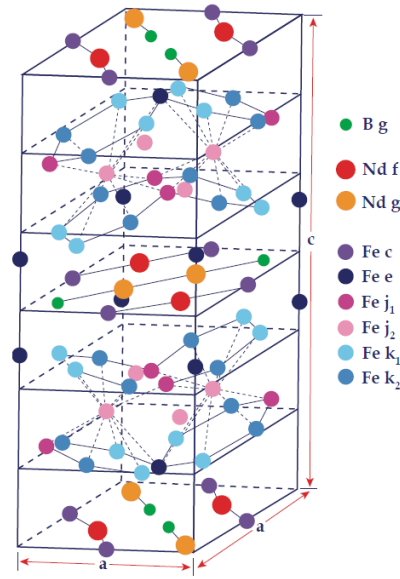


Figure 9: Tetragonal unit cell of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase [19].

2.2.1 Intrinsic properties of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard magnetic phase

For a compound to be exploited as a permanent magnet material, some requirements need to be fulfilled. The magnetocrystalline anisotropy needs to be sufficiently high to provide an easy axis of magnetization. Curie temperature must be well above room temperature and the saturation magnetization must be high enough to provide a strong magnetic field. The intrinsic magnetic properties of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase are governed by the exchange interactions involving the unpaired spins in the $3d-4f$ system [1], [11].

The conduction-electron band in the $3d-4f$ intermetallics is formed by the $4d/6s$ rare-earth and $3d/4s$ transition-metal electrons. The f level of rare earths lies 2 - 8 eV below the Fermi level (E_F). In the rare earth elements, the electrons with unpaired spins are located in the $4f$ orbitals and not in the outermost electronic shell of the atom. Because they are localized, the orbital contribution is significant. The spin-orbit coupling results in the strong anisotropy, often referred to as single-ion anisotropy, which is to a large extent intrinsic to the atom and does not depend on its surroundings. Magnetic moments of the ferromagnetic $3d$ transition metals are different in a sense that the magnetic electrons are located in the outer shell and participate in metallic bonding, therefore they are delocalized. Alloying rare earth elements with the transition metals such as Fe and Co results in a unique combination of intrinsic magnetic properties not observed in the systems based on the rare earths or transition metals alone. At room temperature, approximately three-quarters of the magnetocrystalline anisotropy of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is provided by the neodymium sublattice and one-quarter by the iron sublattice [11].

2.2.1.1 Curie temperature

The magnitude of the anisotropy generally decreases with increasing temperature faster than the magnetization and disappears at a certain temperature called Curie temperature (T_c), which is intrinsic to the material and to a large extent controls the temperature dependence of magnetic properties near room temperature. Since the coercivity depends on the anisotropy, both properties come to zero at T_c . When this temperature is reached, the spontaneous magnetization in a ferromagnetic material is vanquished and the material

becomes paramagnetic. Probably the biggest disadvantage of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is its relatively low T_c (312 °C), which is why the Sm-Co magnets with T_c values as high as 800 °C are still being used in high-temperature applications [1], [11], [20].

2.2.1.2 Anisotropy field

For small deviations of the magnetization from the easy direction, the magnetocrystalline anisotropy acts like a magnetic field resisting the change. This field is called the anisotropy field (H_A) and is approximately 5350 kA/m at room temperature. For a uniaxial crystal, it is the magnitude of the field that can completely overcome the anisotropy forces by rotating the magnetization through 90 degrees when applied perpendicular to the easy axis. In practice, it can be quantified by measuring the field that is required to reach magnetic saturation in the hard direction [1], [5], [11].

2.2.1.3 Saturation magnetization

At large enough values of an external field H applied along the c -axis of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, the magnetization of the material reaches a maximum value, called saturation magnetization (M_s). After this point, the magnetization becomes constant and it cannot be increased further by increasing the field H . The high room-temperature $\mu_0 M_s$ value (1.61 T) of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase leads to high remanence and $(BH)_{max}$ values, surpassing those of other permanent magnetic materials [1].

2.2.2 Microstructure and extrinsic properties

Intrinsic magnetic properties describe infinite crystals. In contrast, extrinsic magnetic properties are derived from the hysteresis loop and reflect the material's real structure [21]. The latter strongly depends on the processing route and chemical composition of the alloy [4], [5].

The primary phase comprising the microstructure of a Nd-Fe-B magnet is the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, with a portion of Nd and Fe atoms often replaced with other elements. The grains of this matrix phase can range between a few tens of nanometers and several microns in size. The secondary phase, the so-called Nd-rich phase, is present in materials with an excess of Nd (in respect to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ stoichiometric composition). Ideally, this phase is non-ferromagnetic. The general name Nd-rich phase is appropriate, because it is not a single phase with a well-defined structure, common to all types of Nd-Fe-B magnets. In fact, a number of different phases, including amorphous and crystalline metallic phases and various types of oxides have been found and their influence on the coercivity was investigated. Their chemical compositions and crystal structures depend on several factors like the alloy composition, processing route and heat treatment history. According to the phase diagram of the Nd-Fe-B ternary system, it is in a liquid state at temperatures above ≈ 680 °C, which enables the liquid-phase sintering during consolidation of magnetic powders into bulk magnets. Because it is present in the triple grain junctions and at the grain boundaries, it is often referred to as the grain-boundary phase. It is easy to oxidize and precautions need to be taken to prevent the degradation of magnetic properties during processing (inert atmosphere or vacuum) and during the magnet's operation (protective coatings). The third phase, often observed in the microstructure of sintered magnets, is a B-rich phase (NdFe_4B_4). Besides these three phases, other minor phases like $\text{Nd}_2\text{Fe}_{17}$, $\alpha\text{-Fe}$ and Fe_2B can also be present in a material [2], [11], [22].

Microstructure of a Nd-Fe-B sintered magnet with distinguishable matrix grains (dark contrast) and Nd-rich phases (brighter regions) is shown in Fig. 10.

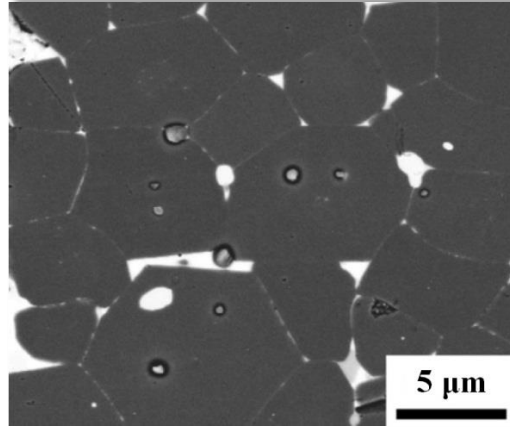


Figure 10: Typical microstructure of a Nd-Fe-B sintered magnet with distinguishable matrix grains (dark contrast) and Nd-rich regions (bright contrast) [23].

2.2.2.1 Remanence and maximum energy product

The remanence of the Nd-Fe-B magnets is related to the saturation magnetization of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Accordingly, it depends on the volume fraction of the latter, crystallographic alignment (grain orientation) of the matrix grains and magnet's density. In isotropic magnets, exchange interaction across the interfaces between nanocrystalline grains where the Nd-rich phase is absent can also increase the remanence. The coupling of the electron spins turns the direction of magnetization at the boundaries of crystallites away from their respective easy axes. The driving force is the reduction in the total magnetic energy when the magnetic moments are aligned parallel [5].

For isotropic magnets, B_r is approximately half of the $\mu_0 M_s$ value ($\approx 0.5 \times 1.61 \text{ T}$). In general, for textured magnets, B_r is smaller than 1.61 T due to imperfect alignment of grains, compositional characteristics and presence of other phases [5], [6], [11]. Fig. 11 shows the relation between the B_r values of anisotropic sintered magnets and grain orientation, which is defined by $B_r/\mu_0 M_s$.

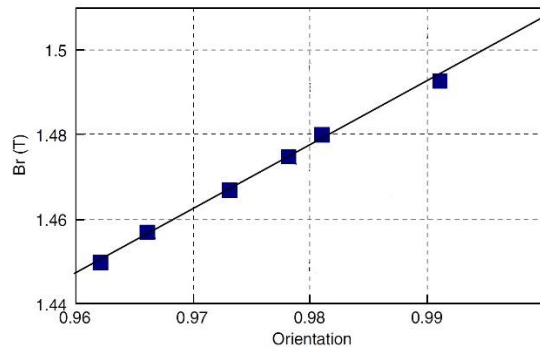


Figure 11: Relation between the B_r values of sintered magnets with composition $\text{Nd}_{13.8}\text{Fe}_{\text{bal}}\text{B}_{5.7}$ and the degree of grain orientation (adapted after [6]).

The maximum energy product is often used as a figure of merit for the magnet's quality. It is limited by the remanence according to equation:

$$(BH)_{max} = \frac{J_r^2}{4\mu_0} \quad (2.11)$$

where J_r is remanent polarization and μ_0 is the permeability of the free space. The highest energy products are characteristic for highly anisotropic magnets with a square-like demagnetization curve. The improvement in coercivity also leads to higher $(BH)_{max}$ values [5].

2.2.2.2 Intrinsic coercivity

The H_{ci} value primarily depends on the magnetocrystalline anisotropy of the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Unfortunately, due to the microstructural characteristics, only a fraction of the H_A (20 - 30 % of approximately 5350 kA/m at room temperature) is reached in the Nd-Fe-B magnets [5], [23]. Considering the equation [23]:

$$H_{ci} = -N_{eff}M_s + \alpha H_A \quad (2.12)$$

where N_{eff} is the effective demagnetization factor and M_s the spontaneous magnetization, the first factor reducing H_{ci} is the influence of dipolar interactions, which are the source of a demagnetizing field of the order of material's magnetization [24]. The second factor arises from the defects present on the surface of the matrix grains (the second term in Eq. 2.12). These regions with altered atomic arrangement have lower magnetocrystalline anisotropy and can act as nucleation sites for reverse magnetic domains, which then grow and spread throughout the grain, reversing the magnetization [2], [11].

The presence of a layer of the non-magnetic Nd-rich phase is beneficial for high H_{ci} values for the following reasons:

- The layers act to reduce or remove defects at the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain surfaces, although some distortions of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ unit cell are intrinsic to the microstructure itself and the extent of distortions depends on the nature of the secondary phase [25];
- Because their crystal anisotropy is lower than the anisotropy of the matrix grains, the layers can act as pinning centers for domain walls, preventing the spreading of the reverse domains. They also tend to magnetically decouple the grains with respect to magnetic exchange interactions [11], [23], [26].

Considering the above, the grain size of the matrix phase can have a remarkable influence on the coercivity. The probability of surface defects is lower in smaller grains and if the latter are magnetically decoupled, reverse domains do not spread through the whole magnet. In addition, the dipolar interactions are larger in bigger grains. Coercivity dependence on the grain size of sintered magnets is shown in Fig. 12. If the grain size is reduced further and below the single-domain size (≈ 300 nm), increase in H_{ci} is even more pronounced [5], [27].

Overview of magnetic properties (B_r and H_{ci}) of different grades (relating to their magnetic performance) of sintered magnets reveals that the high coercivity comes at the expense of remanence: the trend can be seen in Fig. 13 left. The remanence is inevitably decreased when the heavy rare earth elements are used in order to boost the room-temperature coercivity. Experiments have also shown that very high grain alignment leads to a reduction of intrinsic coercivity. For a perfect alignment of the grains (value 1 on the x -axis, Fig. 13 right), H_{ci} is expected to decrease by 30 % from the value of the isotropic magnet with the same composition (value 0.5 on the x -axis). The sharpest decrease happens when the grain orientation exceeds 0.9 [6].

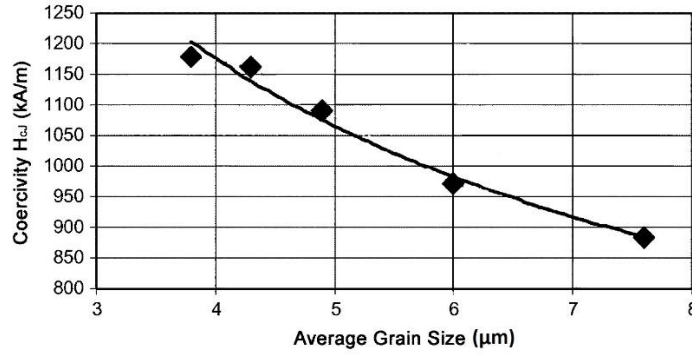


Figure 12: Trend of the room-temperature intrinsic coercivity dependence on the grain size of sintered Nd-Fe-B magnets (adapted after [28]).

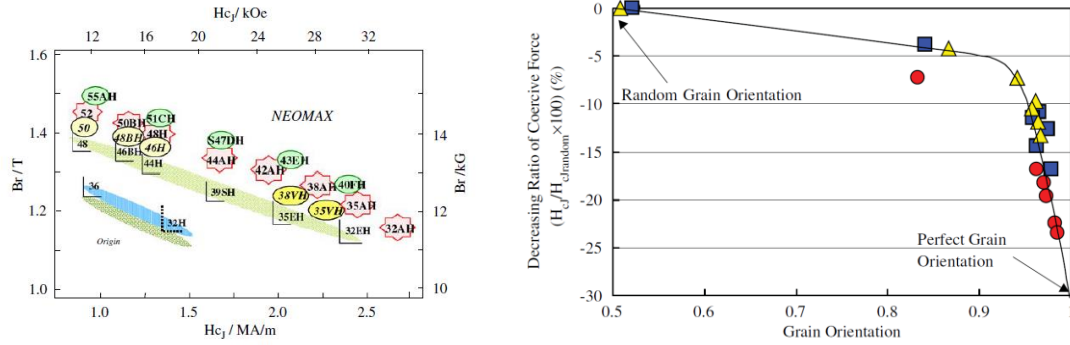


Figure 13: Different grades of Nd-Fe-B sintered magnets (left) and the relation between the ratio of H_{ci} values of oriented and isotropic magnets and grain orientation (right) [6].

2.2.3 High-temperature performance

The magnetic properties of a Nd-Fe-B magnet, regardless of their room-temperature values, deteriorate when the operating temperature is increased, which affects the performance of the magnet. This effect arises from the temperature dependence of the intrinsic magnetic properties [1]. Demagnetization curves of a commercial isotropic powder, obtained at different temperatures, are shown in Fig. 14.

Higher coercivities at elevated temperatures can be achieved by raising the room-temperature H_{ci} value. This is especially important, for example, in traction motors, where magnets operate at 100 °C or more [7]. Reducing the grain size of the matrix phase is one way to achieve this. Another positive outcome of this approach is that the absolute temperature coefficient of intrinsic coercivity (usually written as β and expressed in %/°C), which is used to describe the rate of the H_{ci} decrease with temperature, is reduced, but only to a certain degree. Nanostructured melt-spun ribbons can reach -0.48 %/°C [30], while microcrystalline sintered magnets have β values around -0.6 %/°C, depending on the grade [11], [31]. The temperature coefficient of remanence (α) is smaller (typically between -0.10 and -0.15 %/°C) and can be improved with the addition of cobalt. For comparison, other types of permanent magnets like alnico, SmCo_5 and $\text{Sm}_2\text{Co}_{17}$ have much smaller β values (-0.03, -0.02 and -0.20 %/°C, respectively) [11].

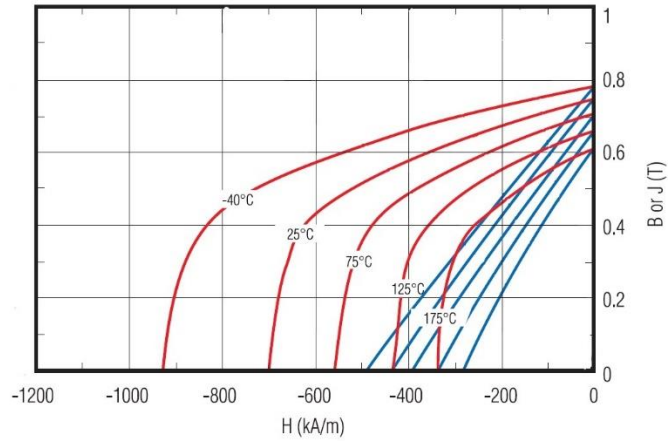


Figure 14: J vs H (red) and B vs H (blue) demagnetization curves of a commercial isotropic Nd-Fe-B powder (gas-atomized MQP-S from Magnequench), obtained at different temperatures (adapted after [29]).

For sintered Nd-Fe-B magnets which have the highest $(BH)_{max}$ values, the grain size refinement leading to higher room-temperature H_{ci} values and smaller temperature dependence of intrinsic coercivity is only possible to a limited extent, due to the manufacturing process that involves milling of the polycrystalline material and high-temperature sintering. An altogether different approach to improve the magnet's high-temperature performance has to be considered in this case. Tailoring the intrinsic properties of the matrix phase by changing the chemical composition of the alloy is an elegant solution to enhance the magnetic properties of the Nd-Fe-B magnets.

2.2.3.1 Cobalt additions

The Curie temperature is primarily governed by the exchange interaction between the $3d$ spins and to a smaller extent by the interaction between the $3d$ and $4f$ spins. Relatively low T_c of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound is due to the dependence of the $3d$ – $3d$ interaction on the interatomic distance: antiferromagnetic coupling is possible for Fe–Fe bonds shorter than approximately 0.25 nm. Some of the Fe sites have enough short bonds to significantly weaken the coupling. The T_c value can be increased by substituting a fraction of iron atoms with cobalt. Due to the difference in atomic size and electronegativity, Co preferentially occupies the smaller sites, leaving Fe in the larger sites with fewer rare earth neighbors, thus improving the ferromagnetic coupling and raising the T_c of the system. For pure $\text{Nd}_2\text{Co}_{14}\text{B}$ phase, this value is 720 °C. Even small Co additions increase the Curie temperature and reduce the temperature coefficient of remanence (α).

Although the anisotropy field of the $\text{Nd}_2\text{Co}_{14}\text{B}$ phase is lower compared to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase (≈ 3600 and 5350 kA/m, respectively), the anisotropy does not change much with small Co additions. The intrinsic coercivity of Co-substituted Nd-Fe-B magnets is nevertheless reduced. This is attributed to the formation of soft magnetic phases such as $\text{Nd}(\text{Fe},\text{Co})_2$, which serve as nucleation sites for reverse domains. Additional alloying with aluminum can prevent the formation of this phase [8], [11].

2.2.3.2 Heavy rare earth additions

Substituting neodymium with heavy rare earth elements (terbium and dysprosium) only slightly increases the Curie temperature. The real advantage of using Dy or Tb is the

remarkable increase in the anisotropy field H_A (≈ 11900 and 17500 kA/m for $\text{Dy}_2\text{Fe}_{14}\text{B}$ and $\text{Tb}_2\text{Fe}_{14}\text{B}$, respectively), which substantially increases the intrinsic coercivity of a magnet. Dy is preferred over Tb because it is less expensive. The tendency of Dy atoms to occupy the f sites (Fig. 9), which has been associated with the preferential occupation of larger g sites with the bigger Nd atoms, results in a nonlinear concentration dependence of the anisotropy field.

Although using up to 10 wt. % of Dy or Tb is standard for the commercial sintered Nd-Fe-B magnets, this approach has a major drawback (in addition to the high prices of these elements). While the elements of the first half of the 4f series (light rare earths) exchange-couple ferromagnetically with the 3d elements, magnetic moments of the heavy rare earths couple antiferromagnetically to the iron moment. As a result, the saturation magnetization of a $(\text{Nd,Dy})_2\text{Fe}_{14}\text{B}$ -based system is reduced [8], [11].

2.2.3.2.1 Heavy rare earth criticality

Currently, the market for rare earth elements is dominated by the demand for neodymium for Nd-Fe-B magnets. Before the purified REs became attractive, older applications used mixtures of REs like mischmetal, an alloy of LREs with the same atomic ratios as found in the ore minerals. In the past century, the need for europium used in color television screens emerged, followed by samarium for Sm-Co magnets and finally neodymium and dysprosium. Because the natural abundance of Nd and Dy is relatively low compared to other elements, cerium, praseodymium and samarium are produced in excess and need to be stored. The balance problem is therefore a major issue for the RE market and will have to be addressed in order to avoid a drastic increase in prices. This can be achieved by diversifying the resources and reducing the use of REs, substituting the critical REs with other materials and by finding new applications for currently less desired elements [9]. Finding efficient and economically attractive ways to recycle the scrap, end of life Nd-Fe-B magnets is also important. Recently, the hydrogenation disproportionation desorption and recombination (HDDR) process has been adapted to this purpose with attractive results [32].

Compared to the LREs, the HRE elements are less abundant and are produced in a smaller quantity [9]. Dy and Tb are much more expensive than Nd. The market for rare earths is highly volatile and the price of dysprosium reached \$3410 per kg in 2011 [7]. In a response, the European Commission classified Dy and Tb as critical raw materials and several projects were financed with the aim of finding new magnetic materials, improving the properties of already known magnets, minimizing the use of HREs or avoiding them completely and to develop efficient recycling routes [32], [33], [34], [35]. Even so, HREs are at the moment inevitably used in high-performance Nd-Fe-B magnets.

2.2.3.2.2 Grain boundary diffusion process

To minimize the use of HREs with the aim of reducing the cost of raw materials and avoiding the decrease in remanence, a special method called grain boundary diffusion (GBD) process was developed. Prior to the GBD, a HRE-free magnet is coated with a HRE-containing material (either pure metal, oxide, fluoride or eutectic alloy) [36], [37], [38], [39]. This is followed by an appropriate heat treatment above the eutectic temperature of the Nd-Fe-B system (≈ 680 °C, [22]). During the heat treatment, the HRE diffuses along the grain boundaries into the sample. The surfaces of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix grains are melted in the HRE-enriched grain-boundary phase [38], [40]. In case of dysprosium, the $(\text{Nd,Dy})_2\text{Fe}_{14}\text{B}$ mixed phase afterwards solidifies in the grain regions adjacent to the grain-boundary phase and the excess of Nd is most likely dissolved in the latter. The explanation for this preferential deposition of the Dy-rich matrix phase can be

found in different crystallization temperatures of $\text{Dy}_2\text{Fe}_{14}\text{B}$ (670 °C) and $\text{Nd}_2\text{Fe}_{14}\text{B}$ (560 °C) phases [38], [41]. As a result, the so-called core-shell structures are formed. The schematic of this mechanism is shown in Fig. 15. The core of the matrix grain retains its original HRE-free composition, while the outer part of the grain (shell) is enriched with Dy (or Tb). In this way, the intrinsic coercivity of the magnet is increased by increasing the magnetocrystalline anisotropy of the grain's surface, thus protecting it against demagnetization [42]. At the same time, the high saturation magnetization of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is preserved, since a large volume fraction of the grain is HRE-free, which significantly improves the remanence and overall magnetic properties compared to the homogeneously distributed HRE element. A comparison between the demagnetization curves of an untreated sample and the ones treated with Dy and Tb is shown in Fig. 16.

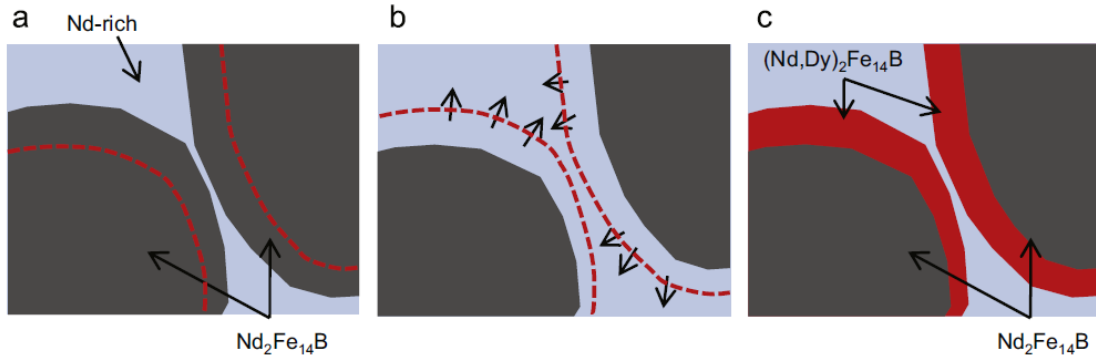


Figure 15: Possible mechanism for substitution of Nd with Dy: Before GBD process (a), during heat treatment (b) and after heat treatment (c) [38].

A proper coating technique has to be used in order to evenly coat the magnet with the optimum amount of Dy- or Tb-containing powder and rationalize the material use. Electrophoretic deposition (EPD) of TbF_3 powder proved to be a good alternative to sputtering the surface with metal or dipping the magnet into a HRE-containing slurry. Large intrinsic coercivity ($\approx 2000 \text{ kA/m}$) was achieved in a low HRE-content (1.37 wt. %) sintered magnet after the subsequent grain boundary diffusion process [43]. The core-shell-type microstructure of a sample prepared in this way is shown in Fig. 17.

A major drawback of the GBD approach is that it can be applied on thin magnets only due to the limited penetration depth of the HRE material. Oono et al. showed that sintered magnets as thick as 5 mm can be GBD processed with the $\text{Dy}_{73}\text{Ni}_{9.5}\text{Al}_{17.5}$ eutectic alloy thanks to the good diffusivity of this material in its liquid state [38].

GBD process is usually applied on sintered magnets. Several Dy- and Tb-based eutectic alloys with melting points lower than the metallic Dy or Tb have also been used to increase the intrinsic coercivity of nanocrystalline magnets either by mixing the material with the magnetic powder prior to consolidation or by applying a low-temperature GBD process. The eutectic alloys, together with their respective melting points, are gathered in Table 1.

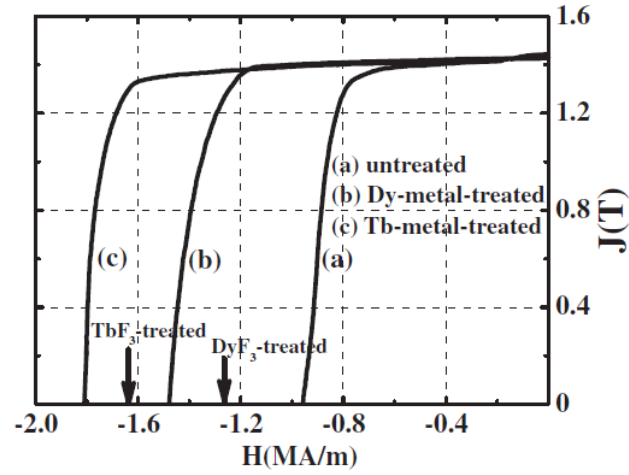


Figure 16: Demagnetization curves of untreated magnet (a), Dy-metal-treated (b) and Tb-metal-treated (c) [39].

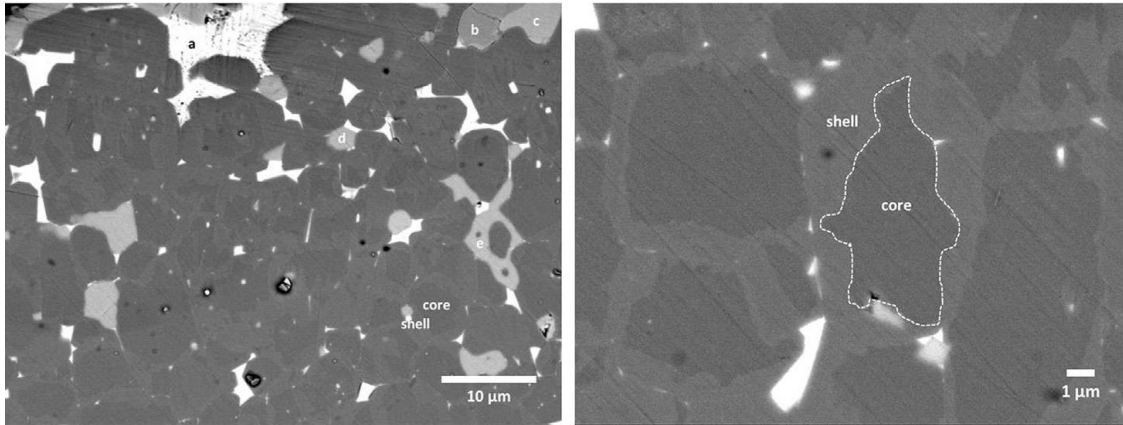


Figure 17: SEM images of the core-shell-type microstructure [43].

Table 1: Eutectic alloys used for the GBD process and their respective melting points [44], [45], [46].

Alloy	Melting point
$\text{Nd}_{60}\text{Dy}_{20}\text{Cu}_{20}$	618 °C
$\text{Nd}_{50}\text{Dy}_{20}\text{Cu}_{30}$	555 °C
$\text{Tb}_{50}\text{Dy}_{20}\text{Cu}_{30}$	527 °C
$\text{Dy}_{70}\text{Cu}_{30}$	790 °C
$\text{Tb}_{70}\text{Cu}_{30}$	730 °C
$\text{Dy}_{73}\text{Ni}_{9.5}\text{Al}_{17.5}$	810 °C

2.2.4 Nd-Fe-B magnetic powders

This section contains an overview of established techniques for the production of different grades of Nd-Fe-B magnetic powders. Besides the ones mentioned here, alternative approaches like mechanical alloying for the preparation of powders and direct casting of anisotropic magnets have also been taken for the preparation of Nd-Fe-B magnets in the laboratory [11].

2.2.4.1 Conventional powder metallurgy

The manufacture of sintered Nd-Fe-B magnets starts with the production of powders. The Nd-Fe-B alloy is prepared by the induction melting of the constituent elements. For the best magnetic properties like high intrinsic coercivity and improved high-temperature performance, complex chemical compositions such as $(\text{Nd}_{11.1}\text{Fe}_{77.5}\text{Tb}_{2.7}\text{Dy}_{0.6}\text{Co}_{1.1}\text{Zr}_{0.2}\text{Al}_{0.5}\text{Cu}_{0.2}\text{B}_{6.1})$ are used [47]. To avoid the formation of α -iron dendrites which, in addition to providing nucleation sites for reverse domains, toughen the material and make it harder to crush, fast cooling of the melt is desirable [11]. Book-molded and strip-casted alloys are typically used, with the latter having a more homogeneous microstructure and better chemical stability. Microstructure of the alloy obtained by the strip casting technique is shown in Fig. 18. The columnar grains of the matrix phase are separated by the RE-rich phase and the α -iron is absent. Hydrogen decrepitation (HD) process can be employed on such a material in order to obtain a coarse powder appropriate for further milling [47], [48]. The process is based on the absorption of H_2 , primarily on the Nd-rich phase, forming NdH_3 . Due to large volume expansion of the grain boundary phase, the material breaks along the grain boundaries, after which the hydrogen is desorbed from the alloy [49]. Alternatively, relatively fine powder ($\approx 20 \mu\text{m}$ average diameter) can be prepared by a co-reduction of metal oxides [11].

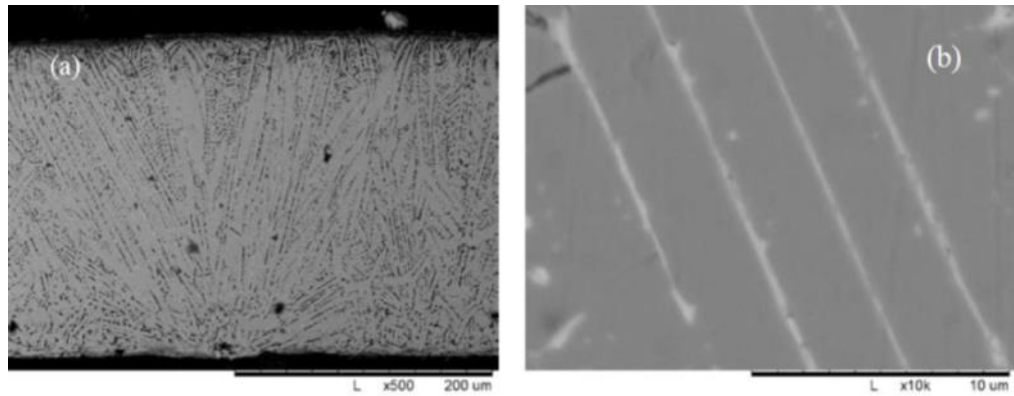


Figure 18: Overall microstructure of the strip-casted alloy (a) and higher magnification showing columnar grains of the matrix phase, separated by the RE-rich phase (b) [47].

The crushed or hydrogen-decrepitated alloy is then milled to a fine powder with an average size of $3 \mu\text{m}$. Jet milling has several advantages compared to the ball milling, such as continuous process, faster milling, less contamination, less oxygen pick-up and solvent-free milling which eliminates the additional drying step. In the milling chamber, one or more streams of high-pressure (5 – 10 bars) and high-velocity inert gas carrying powder particles interacts with another high-velocity stream. The collision breaks the particles up into finer single crystalline particles and the high-purity inert gas is recycled

after use [6], [11], [50]. The jet-milled powder, due to its small particle size, is highly sensitive to oxidation and has to be handled with care [51].

The magnetically anisotropic powder is aligned along the crystallographic c -axis in a magnetic field and pressed in the direction either parallel or perpendicular to the alignment field. The density of such a compact is approximately 60 % of the theoretical density, which allows the sample to be easily handled, while high orientation of the crystallites is achieved [11]. Today, the combination of strip casting, hydrogen decrepitation, jet milling and conventional high-temperature sintering is widely used for the production of fully-dense, high-performance Nd-Fe-B permanent magnets [2].

2.2.4.2 Melt spinning

Melt spinning as a production route for permanent magnets has not been used before the invention of Nd-Fe-B permanent magnets. The development of melt-spun Nd-Fe-B powders by Croat and Herbst at General Motors ran parallel with that of sintered magnets by Sagawa at Sumitomo. In this process, a jet of molten alloy is ejected onto the water-cooled surface of a wheel rotating at high speed, as demonstrated in Fig. 19, and is rapidly solidified in the form of thin ($\approx 30 \mu\text{m}$) ribbons with fine grain size, typically around 50 nm and below the single-domain size ($\approx 200 \text{ nm}$) [11]. The high-coercive nanostructured ribbons are magnetically isotropic. The cooling rates can be as high as 10^6 K/s [52], which prevents the formation of $\alpha\text{-Fe}$ that is predicted to form upon cooling by the phase diagram [22]. The alloys used in the process are usually rich in Nd, which improves the glass forming ability through enhancement of the undercooling effect [53].

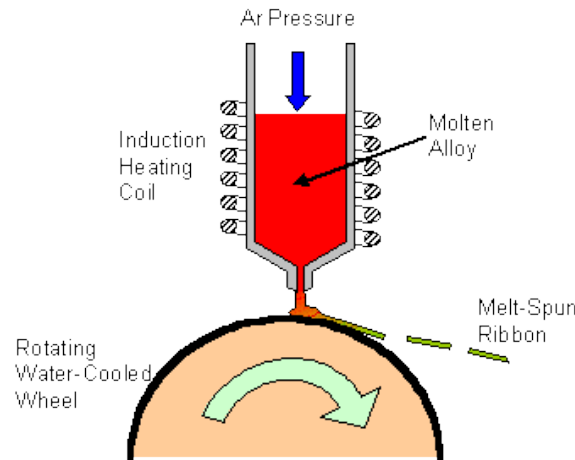


Figure 19: Melt spinning process [54].

Croat et al. showed that the coercivity values depend on the quench rate, determined by the melt spinning wheel velocity, which influences the grain size [3], [14]. Over-quenched (finer grains or amorphous) or under-quenched ribbons (larger grains) displayed a lower coercivity (Fig. 20). The parameters of the melt spinner can either be optimized for a specific composition, or the ribbons are produced in an amorphous state and subsequently annealed for higher H_{ci} values. They are used for the preparation of bonded magnets or hot-pressed into bulk magnets in order to preserve their fine microstructure [7], [11].

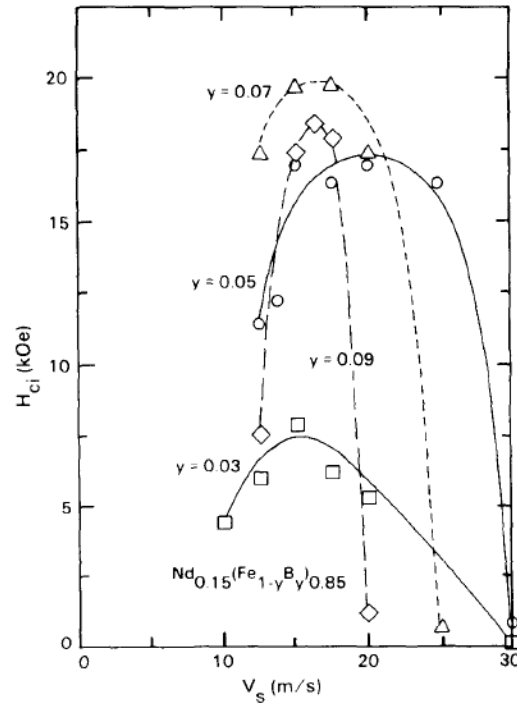


Figure 20: Intrinsic coercivity of melt-spun Nd-Fe-B ribbons vs wheel speed [3].

2.2.4.3 Gas atomization

An alternative to the melt spinning process is inert gas atomization, another rapid solidification technique that can be used for production of Nd-Fe-B powders directly from the melt. The technique offers the possibility to produce a large amount of powder in a single step [55]. The powder particles have a spherical morphology. The schematic representation of the atomization process is shown in Fig. 21.

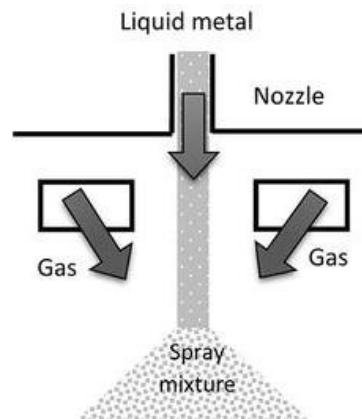


Figure 21: Schematic of gas atomization process [56].

Molten alloy is poured through a nozzle and the melt stream is broken into fine droplets by a high-velocity gas [11]. The inert gas is usually argon or helium with the latter providing much finer particles [57]. Compared to the melt spinning, the characteristic

cooling rates are slower, ranging from 10^4 to 10^5 K/s [58]. The quenching effect depends on the size of the individual droplet, which results in a non-uniform microstructure of the powder with larger particles containing α -iron which lowers the remanence and coarser $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains due to insufficient cooling rate [55], [59]. Consequently, the intrinsic coercivity depends on the particle size with smaller nanocrystalline spheres having the highest H_{ci} values [59], [60], [61]. Magnetic properties of the as-produced powders can be improved with post-atomization heat treatment [55], [62]. An example of the particle-size dependence of H_{ci} and B_r is shown in Fig. 22.

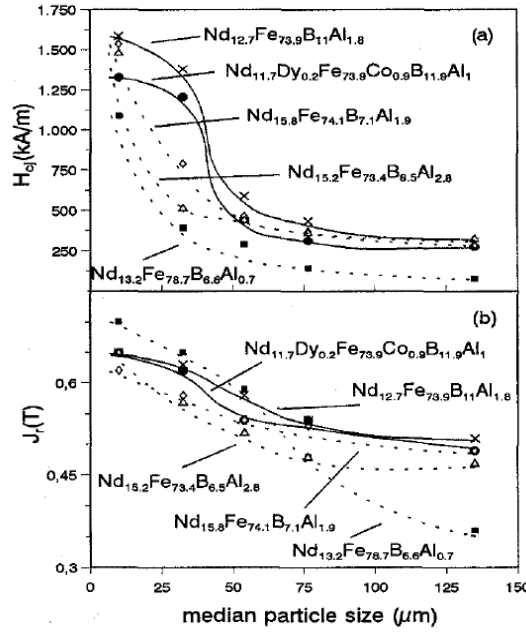


Figure 22: Intrinsic coercivity and remanence of gas-atomized powders as a function of the particle size [61].

Kramer et al. showed that the microstructure of the gas-atomized powders can be improved by adding TiC into the melt which alters solidification [63]. As a result, the nucleation of peritectic iron is inhibited and the cooling rate required to obtain fine microstructure is reduced. TiC precipitates at the grain boundaries and does not change the composition and intrinsic properties of the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. The carbide-stabilized microstructure also hinders the grain growth during heat treatment at temperatures as high as 900 °C [64].

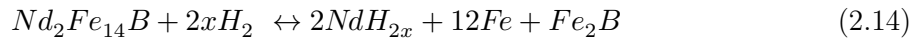
Good corrosion resistance of gas-atomized Nd-Fe-B powders has been reported and attributed to the partially nanocrystalline or amorphous structure [65] and to the Nd_2O_3 native surface oxide layer which prevents further oxidation [62], [66]. In practical terms, this is a highly desired feature since the powders produced by the conventional metallurgy process are sensitive to the environmental degradation.

Sellers et al. reported reversible loss of hard magnetic properties (degradation of the loop shape and reduction of H_{ci}) at 150 °C in air for gas-atomized powders with high (35 wt. %) total rare earth (TRE) content [62]. The properties were then recovered using a heat treatment at 650 °C. The authors argued that the observed instability at high temperatures renders these types of powders inappropriate for the preparation of bonded magnets, since the manufacturing process exposes the powder to increased temperatures. The addition of a polymer does not allow the necessary heat treatment to be performed

after the magnet is made. In another article, they improved the high-temperature stability by reducing the TRE content of a nanocrystalline powder [66]. The authors proposed that the nucleation of reversed domains from defects located at the surface area is the degradation mechanism in the TRE-rich powders and that it is triggered by oxygen reaction.

2.2.4.4 Hydrogenation disproportionation desorption recombination

The hydrogenation disproportionation desorption and recombination (HDDR) process, an attractive alternative to milling, can be used to obtain a fine-grained Nd-Fe-B powder from ingots. The ingot is usually exposed to hydrogen decrepitation process, resulting in a coarse powder susceptible to corrosion and consequently to degradation of the magnetic properties, before being subjected to the HDDR treatment [67]. The latter was developed by Takeshita and Nakayama [68] and later characterized by McGuiness et al. [69], [70]. Exposing the Nd-Fe-B-type material to hydrogen atmosphere under high temperature (700 – 900 °C) results in the formation of the neodymium hydride from the Nd-rich phase of the starting material, followed by disproportionation of the matrix grains into neodymium hydride, iron and iron boride:



Upon reducing the hydrogen pressure, the disproportionated mixture of fine reaction products is recombined into hard magnetic Nd₂Fe₁₄B phase. Reaction is finished when the hydrogen is desorbed from the Nd-rich phase. From the starting coarse-grained and potentially non-homogeneous cast alloy containing Fe dendrites, fine-grained homogeneous material can be obtained [70]. The grain size was found to be dependent on the HDDR process temperature [69] and can be as small as 300 nm, which is one order of magnitude smaller than sintered magnets and close to the single-domain limit for Nd₂Fe₁₄B-based materials [71]. Since each HDDR powder particle consists of many fine grains, this type of powder is more resistant to corrosion than jet-milled powders.

An important advantage of the HDDR process, compared to rapid solidification of the melt, is the possibility of producing an anisotropic powder with high grain alignment, for which a careful control of the HDDR process parameters is required. Kinetics of the process can be altered by the addition of elements such as Co, Ga, Zr or Nb [72]. Alternatively, the so-called dynamic HDDR (*d*-HDDR) is a good approach to produce a highly textured material through a careful control of the hydrogen pressure [73]. After heating the material to the processing temperature, hydrogen is introduced and disproportionation takes place at a slower rate compared to isotropic HDDR processing. When the disproportionation reaction is complete, slow reduction of the hydrogen pressure at high temperature results in hydrogen desorption and recombination of reaction products into fine Nd₂Fe₁₄B grains, aligned along the crystallographic *c*-axis. The mechanism behind anisotropy evolution is termed “texture memory effect” [74]. In the optimally disproportionated mixture, the tetragonal Fe₂B phase is aligned parallel to the *c*-axis of the original micron-sized Nd₂Fe₁₄B grain and is the source of texturing observed in the optimally processed anisotropic product. The visualization of the structural changes corresponding to the anisotropic process is shown in Fig. 23. The orientation of the small matrix grains that nucleate upon hydrogen desorption follows the orientation of the iron boride grains.

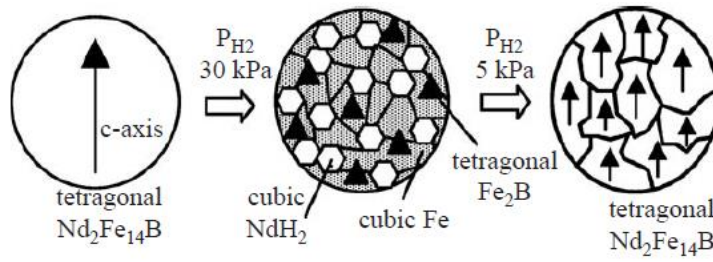


Figure 23: The evolution of texturing during the anisotropic HDDR process: before *d*-HDDR (left), disproportionated mixture under the hydrogen pressure at high temperature (middle) and fine-grained, textured material after hydrogen desorption (right) [74].

A lot of research has been focused on explaining the characteristic values of intrinsic coercivity ($\approx 1000 - 1200$ kA/m) of the HDDR-processed Nd-Fe-B powders. For the magnetically isolated submicron-sized grains, much larger H_{ci} (≈ 2000 kA/m) would be expected following the extrapolation of the H_{ci} dependence on the grain size of sintered magnets [75]. This corresponds with the initial investigation of the powders' microstructure which shows that the Nd-rich grain-boundary phase is mostly absent [71] and that the highest H_{ci} values are obtained with compositions rich in Nd [70]. The low H_{ci} values have also been attributed to the high concentration of ferromagnetic elements Fe and Co in the grain-boundary phase (composition $\text{Nd}_{19.8}\text{Fe}_{63.2}\text{Co}_{13.7}\text{B}_{3.3}$ was estimated from an atom probe analysis), which increases the magnetic exchange interaction between neighboring grains compared to the phase richer in Nd that is present in conventionally sintered magnets. In addition, it is found that the grain boundary layer is thin and crystalline, unlike in sintered magnets where it is amorphous, and therefore has higher magnetocrystalline anisotropy which further limits the coercivity [76]. In another paper, it is argued that the coercivity mechanism is of pinning type and that domain walls are pinned in the grain boundary layer [77]. When this layer is uniform and 2 nm thick, the coercivity is higher compared to samples where the grain-boundary phase is absent, which inhibits the pinning. The same research group also showed that the intrinsic coercivity of the as-produced HDDR powders can be increased by increasing the amount of the grain-boundary phase, which improves the pinning [78]. This was achieved by mixing the magnetic powder with the $\text{Nd}_{70}\text{Cu}_{30}$ eutectic alloy that diffused into the powder particles when the mixture was annealed at $700 - 800$ °C. The composition of the as-modified grain-boundary phase was similar to the untreated sample and was therefore not a key factor in the coercivity increase.

The HDDR process was shown to have a high potential to be used as an efficient route for reprocessing of scrap Nd-Fe-B magnets with the aim of addressing the need for improved resource efficiency. Hydrogen decrepitation can be used to separate the Nd-Fe-B magnets from their protective coating and from other scrap materials, such as iron-based components in personal computers [79]. Decrepitated powder can then be HDDR treated. Magnetic properties of a recycled HDDR powder ($B_r = 1.1$ T and $H_{ci} = 840$ kA/m) are good enough to consider such a material as a promising candidate for the production of bonded magnets [32].

2.2.5 Bulk Nd-Fe-B magnets

2.2.5.1 High-temperature sintering

Preparation of sintered Nd-Fe-B magnets based on the powder metallurgy techniques was first announced by Sagawa et al. at Sumitomo Special Metals [4], [15]. The green compacts with composition $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ were sintered for 1 hour at 1080 °C in an argon atmosphere. Slightly higher sintering temperatures are needed for compositions containing Dy [11]. Liquid-phase sintering and densification follows the melting of the Nd-rich phase at the grain boundaries, which occurs at approximately 680 °C [2], [4], [11].

The chemical composition and consequently the amount of different phases present in sintered magnets has to be carefully controlled in order to achieve good magnetic properties [80]. Although remanence is improved by increasing the volume ratio of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix phase through reduction of the Nd content in the alloy, the presence of the Nd-rich phase is important to achieve liquid-phase sintering and to magnetically isolate respective grains. During sintering, it may react with soft magnetic impurity phases ($\text{Nd}_2\text{Fe}_{17}$, $\alpha\text{-Fe}$ and Fe_2B), changing them to the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase [81].

After sintering, appropriate heat treatment is necessary to achieve high H_{ci} values. It is believed to cause reversible phase changes, most probably within intergranular Nd-rich regions. It also helps to remove the defects from the grain-boundary area, therefore decreasing the number of nucleation sites for the reversed domains [4], [82].

Sintered Nd-Fe-B magnets with $(BH)_{max}$ over 450 kJ/m³ are produced commercially, for which the alloy composition, ingot and powder preparation, magnetic pressing and also surface coating to protect the magnet against environmental deterioration need to be optimized [2]. The H_{ci} value, on the other hand, is limited by the grain size of sintered magnets, which is typically around 5 μm [11].

In order to minimize the amount of HRE elements, routinely used in sintered magnets to increase their room-temperature H_{ci} values, the reduction of the grain size has to be considered. The uniform size distribution of the powder particulates leads to a uniform microstructure and smaller grain size, which consequently results in an increase in intrinsic coercivity [80]. By using helium jet milling and the so-called pressless sintering process that is based on the preparation of magnetically aligned green compacts without applying pressure, sintered magnets with a grain size of about 1 μm were prepared [83]. The result was improved room-temperature H_{ci} (1517 kA/m) for a HRE-free composition. This value is reasonably close to the value obtained by extrapolating the plot of H_{ci} dependence on the grain size of sintered magnets to 1 μm , which is ≈ 1900 kA/m according to Lee et al. [84].

2.2.5.2 Hot pressing

Hot pressing offers some advantages compared to conventional sintering routes. The magnetic powder densifies by means of heat and pressure applied simultaneously (Fig. 24). This shortens the total manufacturing time and allows for lower temperatures to be used, which minimizes the grain growth during consolidation and preserves the initial magnetic properties of the fine-grained powder. Nanostructured melt-spun ribbons with TRE-rich compositions are best suited for hot pressing, since they cannot be sintered at high temperatures. When isotropic powders are used, the bulk magnet is also magnetically isotropic, although plastic deformation can induce a small degree of texturing in the material. Alternatively, anisotropic polycrystalline HDDR powder can be magnetically aligned prior to consolidation in order to preserve its anisotropic nature in the hot-pressed magnet [11], [85].

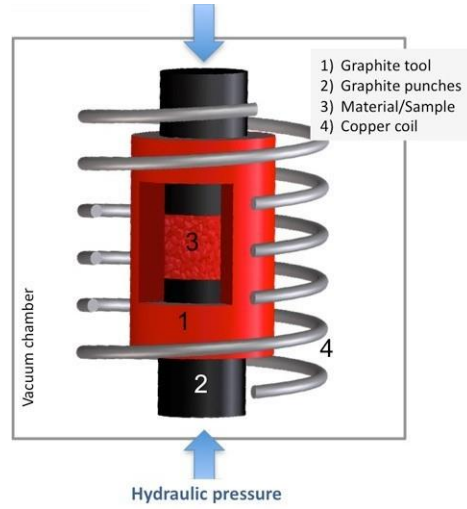


Figure 24: Schematic of inductive hot pressing [86].

Anisotropy can be induced in a previously hot-pressed magnet in a process called hot deformation. Hot-pressed magnet is placed in a bigger die and hot pressed again, which reduces the sample's height to about 25 % of its initial thickness and increases its dimensions at right angles to the pressing direction. This results in a textured magnet with a c -axis grain alignment parallel to the pressing direction and consequently increased remanence. In addition to the reorientation of the crystals, the grains start to grow in the direction perpendicular to the c -axis during the treatment. Deformation and alignment are consequences of plastic deformation, grain-boundary migration and grain-boundary sliding [11], [87], [88].

2.2.5.2.1 Melt-spun powders

The flake-like morphology of the melt-spun materials makes them especially suitable for hot pressing applications. In contrast to bonded magnets, high density can be reached, which makes the hot-pressed magnets highly resistant to corrosion and oxidation [11].

The challenge to produce fully dense, anisotropic magnets from the melt-spun isotropic ribbons has been addressed by R. W. Lee [89]. Considering the expected grain growth during the initial hot pressing process, he used over-quenched ribbons (amorphous). Maximum density was achieved at 700 - 750 °C temperature and 70 - 210 MPa pressure. The temperature was significantly lower than in conventional sintering. The optimum magnetic properties were achieved with processing times of the order of a minute, which is much less than it takes to sinter jet-milled powders (several hours). Lee prepared a hot-deformed magnet and achieved a maximum energy product of 320 kJ/m³ with the corresponding remanent magnetization of 1.35 T and intrinsic coercivity of 875 kA/m. The latter was reduced by more than 40 % compared to the hot-pressed precursor. Even higher $(BH)_{max}$ value (380 kJ/m³) was achieved by Mishra et al., who underlined the importance of optimizing processing and alloying conditions in order to increase the fraction of aligned grains in hot-deformed magnets [90]. Akiya et al. showed that the magnetic isolation of the Nd₂Fe₁₄B grains in the hot-deformed magnets can be improved with the grain boundary diffusion process of Nd-Cu eutectic alloy, which substantially increased the intrinsic coercivity of their sample from 1315 to 2040 kA/m [91].

Today, the $(BH)_{max}$ values of commercially available nanostructured hot-pressed magnets can be as high as 120 kJ/m³, while hot-deformed magnets can reach 400 kJ/m³ [92].

2.2.5.2.2 Gas-atomized powders

Horton et al. used hot pressing to consolidate two types of gas-atomized Nd-Fe-B powders into bulk magnets and evaluate the approach of TiC addition to Nd-leaner material [93]. Powder with higher Nd content (35 wt. %) was densified under pressing conditions similar to those required for melt-spun powders (800 °C). Much higher temperature (975 °C) was needed to prepare dense magnets from the powder with lower Nd content (30 wt. %). The addition of TiC in the latter effectively suppressed the grain growth during hot pressing and the grains observed in the bulk sample were found to be 30 – 50 nm in size. The authors showed that the maximum energy product of bulk samples depends on the powder particle size and pressing condition. The $(BH)_{max}$ value was the highest for the porous TiC-containing sample prepared from fine particle fraction (10 – 20 µm) at 800 °C and was higher than the peak value obtained with the Nd-richer composition with similar particle size (76.4 and 73.2 kJ/m³, respectively). The H_{ci} values of the initial powders and bulk magnets were not reported in the article.

2.2.5.2.3 HDDR powders

Early work in fabricating hot-pressed HDDR magnets, carried out by McGuinness et al., showed that dense bulk magnets can be prepared without decrease in H_{ci} (≈ 1200 kA/m was achieved) [94]. The authors reported that the Nd-rich phase is scarcely found at the grain boundaries and that it is unevenly distributed in the magnet. Ragg et al. investigated the effect of processing parameters (temperature, time and pressure) on the magnetic properties of hot-pressed HDDR magnets [95]. They showed that the remanence depends on the bulk density as expected, as well as the intrinsic coercivity which was higher for denser samples. Later, Nozawa et al. confirmed that H_{ci} depends on the sample's density: the intrinsic coercivity reached a minimum just prior to the full densification, while the H_{ci} value of the fully dense sample was 25 % higher than that of the starting powder [75]. Similar to the previous findings [76], [77], the highest H_{ci} values measured for a dense sample corresponded with the homogeneously distributed grain-boundary phase, rich in Fe and Co. No significant grain growth was observed in the hot-pressed sample, indicating that the development of coercivity is indeed correlated to the distribution of the secondary phase.

2.2.5.3 Pulsed Electric Current Sintering (PECS)

A special kind of hot pressing technique, called Pulsed Electric Current Sintering (often Spark Plasma Sintering – SPS or Field Assisted Sintering Technique - FAST), is similar to other hot pressing techniques: the powder is placed inside a graphite or metal die where it is densified by means of heat and uniaxially applied pressure. In contrast to the conventional hot pressing that uses external heating elements, the heat is generated internally by means of a pulsed DC current that passes through the die and the powder compact (in the case of conductive powders) in the direction parallel to the pressing (Fig. 25). The amount of the heat produced (Q) is proportional to the square of the electric current (I):

$$Q \propto I^2 R t \quad (2.15)$$

where R is the electrical resistance and t is time.

This enables very high heating and cooling rates (up to 1000 K/min) and consequently a fast sintering process and reduced energy costs [96]. It has been shown that this kind of heating, which is called Joule heating, allows for the theoretical density to be achieved at lower temperatures compared to conventional sintering and hot pressing and with shorter sintering times [97], [98].

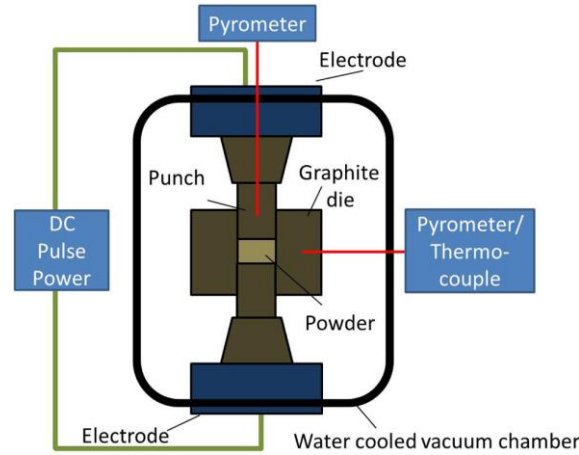


Figure 25: Schematic of PECS design [96].

Although the first patent describing the use of current for sintering was issued in 1933, the number of papers on PECS rapidly increased since 1994. It has been utilized for a wide spectrum of materials, notably ceramics, alloys and composites [96], [99]. Kondoh et al. used the technique to sinter zirconia/alumina composites [97]. They reported high strength, hardness and fracture toughness and good density at a sintering temperature lower than in the classic hot pressing process. Similar findings were reported by Tamari et al. for silicon carbide composites [98] and Nishimura et al. who PECS-sintered silicon nitride nano-ceramics at lower temperatures and achieved smaller grain size [100].

The first magnetic material that was consolidated with the help of the PECS technique was a Nd-Fe-B alloy. The paper was published in 1999 [101]. Since then, PECS was utilized for the densification of different magnetic powders, including Sm-Co materials, ferrites and different composites. When it comes to net shape Nd-Fe-B permanent magnets, no reports on using the PECS for producing magnets with shapes other than cubes or discs can be found in the literature. Nevertheless, it has recently been demonstrated that PECS can be used to manufacture ceramic samples with complex shapes, for which alumina powder was used [102], [103].

2.2.5.3.1 Jet-milled anisotropic powders

Several researchers showed that the PECS approach could be used as an alternative to conventional sintering for preparation of high-performance magnets from highly anisotropic Nd-Fe-B powders. Yue et al. studied the magnetic properties, microstructure, bending strength and corrosion resistance of anisotropic Nd-Fe-B PECS magnets [104], [105], [106]. They prepared green compacts from aligned anisotropic jet-milled powders which were PECS processed at 780 °C. The samples were then heat-treated for 2 hours at 1000 °C. Their magnetic properties were comparable to those of sintered Nd-Fe-B magnets, prepared from the same powders at 1120 °C of sintering temperature. The authors reported better corrosion resistance of the PECS magnets compared to the sintered magnets. They attributed this fact to the finer and uniform grains and to the segregation of the Nd-rich phase in the triple junctions between the grains, which restricted the pathways for

inter-granular corrosion propagation in the material. A higher mechanical strength of PECS-consolidated magnets was also observed. Similar findings were reported by other authors [107], [108]. Mo et al. showed that post-consolidation heat treatment improves wetting of the Nd-rich phase and that a continuous thin film of the Nd-rich phase is formed at the grain boundaries, magnetically isolating the matrix grains, which increased H_{ci} from 750 to 1200 kA/m [109].

2.2.5.3.2 Melt-spun powders

The potential of the PECS technique for the preparation of bulk magnets from the melt-spun Nd-Fe-B material was initially demonstrated by Liu et al. [101]. They showed that lower consolidation temperature, characteristic for the PECS approach, preserves the magnetic properties of the initial powder. The authors evaluated the importance of the basic process parameters in terms of optimal properties of the end product and established that the temperature is more important than the pressure and the holding time at desired temperature. Ma et al. observed homogenous microstructure and fine grains (50 – 100 nm) in a sample consolidated at 700 °C and found that the coercivity was controlled by the pinning mechanism [110]. At higher PECS temperatures, abnormally large grains appeared and the sample's microstructure was less homogeneous. The authors also reported that materials with Nd-rich compositions are easier to consolidate to full density at PECS temperatures low enough to minimize the grain growth and retain the initial intrinsic coercivity of the starting powder. High Nd content leads to higher volume fraction of the liquid Nd-rich phase and the grain coalescence (as well as the grain growth) is faster when the grain-boundary migration is due to liquid diffusion compared with solid diffusion [111]. Microstructures of the Nd-rich (13,6 at. %) melt-spun ribbons (MQU-F powder from Magnequench Corporation) and a hot-pressed magnet prepared from this material at 650 °C are shown in Fig. 26. Fine microstructure without coarse grains can be observed in the PECS sample (right) with a H_{ci} value comparable to that of the initial powder (≈ 1600 kA/m) [112].

Saito et al. used amorphous ribbons to study the effect of the PECS parameters on the grain size and grain orientation of the as-consolidated magnets [113]. After the onset of crystallization above 500 °C, the coercivity of the material increased, but the H_{ci} values rapidly declined when the temperature reached 800 °C due to the accelerated grain growth and the occurrence of α -iron. PECS consolidation of amorphous ribbons at 700 °C under higher pressure (100 instead of 50 MPa) induced texturing in the material, resulting in 1.2 T of remanent magnetization. According to the authors of this research, high pressure destroyed the carbon die in the process. Although not discussed in the paper, there is a high probability that some plastic deformation of the sample, originating in the freedom to expand in the direction perpendicular to the applied pressure after the die broke, contributed to the improved c -axis alignment of the already nucleated crystallites.

Yue et al. used the PECS technique to prepare hot-deformed magnets [114]. The H_{ci} value of the anisotropic sample was significantly lower than the value of the corresponding isotropic precursor (510 and 1140 kA/m, respectively) and the maximum energy product was 280 kJ/m³. A correlation between the reduction of H_{ci} and changes in the distribution of the secondary Nd-rich phase observed in the hot-deformed magnets was established: during hot deformation, the Nd-rich phase redistributes from the grain boundaries to the triple grain junctions, which enhances the intergranular exchange coupling.

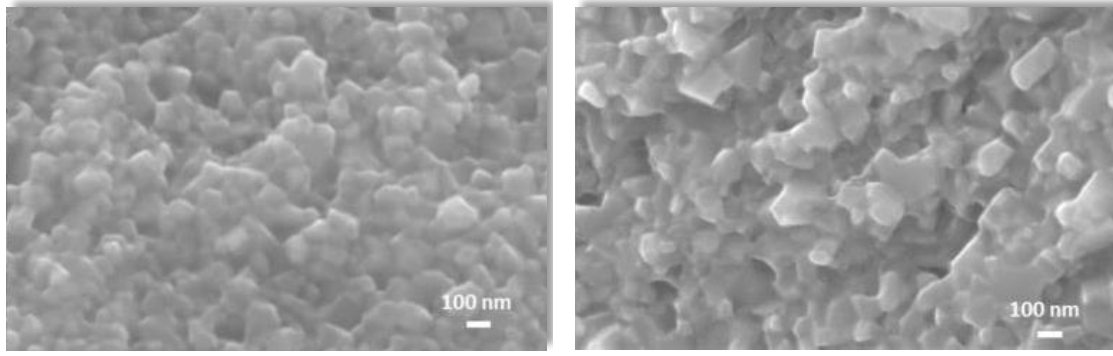


Figure 26: SEM images of commercial MQU-F powder (left) and a hot-pressed PECS sample, prepared from this material (right) [112].

Liu et al. reached a $(BH)_{max}$ of 400 kJ/m³, a value that is comparable to the commercially available sintered magnets [115]. Elongated Nd₂Fe₁₄B grains with excellent texturing observed in an anisotropic PECS magnet, hot-deformed under optimal conditions, are shown Fig. 27.

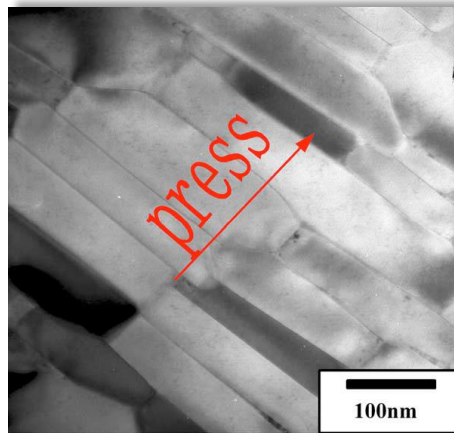


Figure 27: TEM image of a textured hot-deformed magnet prepared with the PECS technique. The arrow shows the pressing direction [115].

2.2.5.3.3 HDDR powders

Gopalan et al. prepared hot-pressed and hot-deformed HDDR magnets with the PECS technique [85]. The remanence of the starting powder was 1.07 T, indicating an imperfect texturing. The B_r value of the hot-pressed sample prepared at 700 °C from aligned green compact was similar (1.15 T) and the X-ray diffraction (XRD) studies revealed that the degree of the c -axis texture was $\approx 30^\circ$. Hot deformation of a specimen cut from the PECS sample increased B_r of the final magnet to 1.35 T on account of the improved crystallographic alignment ($\approx 15^\circ$). Compared to the intrinsic coercivity of the starting material (1170 kA/m), H_{ci} values of the PECS-consolidated and hot-deformed samples were slightly reduced (1090 and 1000 kA/m, respectively). The grain size of the PECS sample was comparable to the starting powder and the Nd-rich phase was observed along the grain boundaries, corresponding with reasonably high H_{ci} value (Fig. 28).

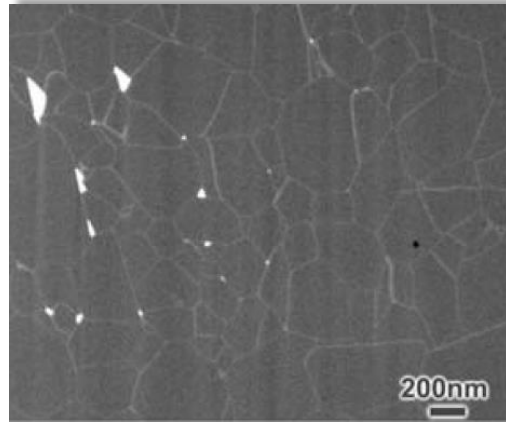


Figure 28: SEM image of a high-coercivity PECS magnet prepared from the HDDR powder. Matrix grains (dark contrast) and the intergranular phase (bright contrast) can be distinguished [85].

In another article, it was reported that the intrinsic coercivity of the low-density hot-pressed samples prepared at 550 – 600 °C was lower compared to the initial powder [116], a trend that was later confirmed by Lee et al. [117]. This corresponded with the findings of Nozawa et al. who showed that high-density hot-pressed samples have the highest H_{ci} values [75]. Lee et al. also showed that increasing the PECS temperature above the value necessary for densification leads to a pronounced grain growth and deterioration of intrinsic coercivity (Fig. 29).

Takagi et al. proved that the intrinsic coercivity of the electric-current-sintered samples prepared from the HDDR powder, regardless of their density, can be recovered (in terms of the initial powder) with a short post-consolidation heat treatment at 750 °C in vacuum [118]. They used commercial Aichi's MF-18P HDDR powder for this purpose. The authors did not establish any correlation between the coercivity reduction during consolidation or coercivity recovery by heat treatment and changes in the grain boundary layer. The grain boundary layer present in the initial powder, as well as in the PECS and heat-treated samples, was found to be amorphous. Amorphous grain-boundary phase of the PECS samples was also reported by other authors [116].

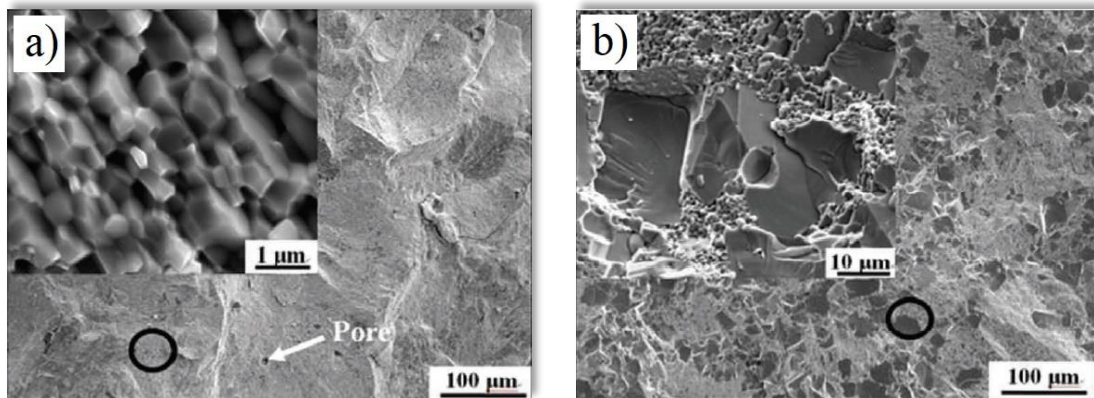


Figure 29: SEM images of fractured surfaces of PECS samples prepared from the HDDR powder at 800 °C (a) and 900 °C (b) with high-magnification images of regions marked with the dark circles shown in the insets [117].

2.2.5.4 Bonded magnets

Bonded Nd-Fe-B magnets are manufactured from polycrystalline powders. The temperatures used in the production process are low, which preserves the fine microstructure of the rapidly solidified and HDDR-processed materials. Bonded magnets are useful in applications where small-sized or near-net-shaped magnets are desired, such as electric motors, automobiles and sensors [2]. Examples of bonded Nd-Fe-B magnets of different sizes and shapes are shown in Fig. 30.



Figure 30: Bonded Nd-Fe-B permanent magnets [119].

Compression molding is used to shape the mixture of powder and resin into a bulk magnet. This type of magnets contains approximately 80 vol. % of the magnetic powder. Alternatively, the Nd-Fe-B material can be blended with a polymer and injection-molded, which gives a bonded magnet with lower powder-to-binder ratio (typically 65 vol. %). Bonded magnets are used extensively in applications where temperatures do not exceed 100 °C. In some cases, this temperature can be increased to 180 °C by using an appropriate binder [11], [120]. The permeability of the binder matrix to oxygen and water necessitates the need to coat the magnet with a protective metal in order to prevent corrosion [11]. With appropriate tooling, both types of bonded magnets can be produced in a near net shape [120].

The main disadvantage of bonded magnets prepared from rapidly solidified powders, in addition to the maximum operational temperature that is determined by the thermal stability of the binder, is their low remanent magnetization (most commonly around 0.60 T), originating in the low volume ratio of the hard magnetic phase. Higher loading factors can be reached when gas-atomized spherical powders are used instead of melt-spun ribbons. The spherical powders have better flow characteristics, which is much desired in injection molding. In addition, the mechanical strength of magnets prepared from spherical powders is better compared to magnets prepared from ribbons [120]. Using anisotropic HDDR powder instead of rapidly solidified powders is an attractive approach to increase the remanent magnetization of a bonded magnet up to 0.98 T [121].

To avoid the temperature limitation stemming from the addition of the polymer, Kelhar et al. took a different approach and used zinc as a binder to consolidate the MQP-B powder from the Magnequench Corporation into a metal-bonded magnet [122]. This type of bonded magnets can be used in applications exceeding 180 °C. The authors used the PECS technique and consolidation temperatures below 500 °C in order to preserve the

powder's magnetic properties. Compared to a commercial polymer-bonded magnet prepared from the same powder, the intrinsic coercivity of the PECS sample was higher (800 vs 700 kA/m), while B_r value was slightly reduced.

2.2.5.5 Additive manufacturing

For some applications, basic magnet design, like rods and discs, do not satisfy the requirements for best performance. Toyota, for example, has demonstrated that a 50 % increase in the motor output power can be expected if magnets are arranged in the so-called “V” shape configuration compared to the traditionally used flat-shape arrangements. Additional improvement would be possible if these “V” magnets could be replaced by a single magnetic body [123].

Additive manufacturing is a new approach to prepare a magnet with complex shapes, which has so far only been partially possible to achieve with injection molding. Initial investigation has shown that two different approaches can be employed to prepare 3D-printed net shape binder-containing magnets [124]. Material extrusion with the Big Area Additive Manufacturing (BAAM) system proved to be the most promising [125]. The mixture of a commercial isotropic crushed melt-spun ribbons (MQP-B+ from Magnequench Corporation) and polymer (Nylon-12) with 65 vol. % loading factor was used and the printed sample's magnetic properties were found comparable to the injection-molded magnet prepared from the same material. Another approach is binder jetting which is based on the preparation of a printed sample with a subsequent heat treatment at 100 – 150 °C to cure the thermoset powder [124]. The drawbacks of this approach are low volume fraction of magnetic powder and high porosity, resulting in a low B_r value [126]. Although the authors showed that anisotropic HDDR powder can be used in the process, the in-situ alignment remains a major challenge for binder jetting.

Especially intriguing are the results of Jaćimović et al., who proved that Selective Laser Melting (SLM) technique can be adapted for manufacturing binder-free, highly dense Nd-Fe-B magnets with large design freedom in the magnet's geometry [127]. SLM is a metal printing technique that uses a high-temperature laser (pulsed Nd:YAG-Laser in this case) to melt the powder and print the object layer by layer. The major advantages of such a magnet are higher operation temperature compared to bonded magnets based on standard polymers and the prospect of reaching high B_r values. The authors used gas-atomized MQP-S powder from Magnequench Corporation with under-stoichiometric composition in respect to the $\text{RE}_2\text{Fe}_{14}\text{B}$ hard magnetic phase to prepare a bulk magnet with 92 % of theoretical density and magnetic properties ($B_r = 0.59$ T and $H_{ci} = 695$ kA/m) much similar to the original powder. Examples of printed magnets are shown in Fig. 31.

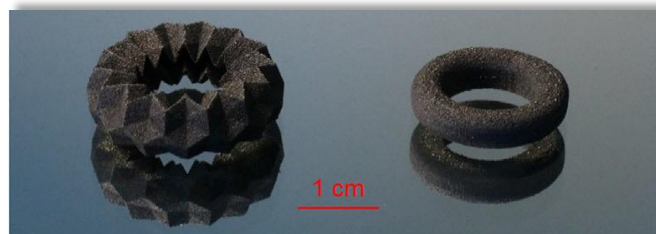


Figure 31: Photograph of binder-free Nd-Fe-B magnets, printed from the gas-atomized MQP-S powder with the SLM technique [127].

2.3 Local Demagnetizing Fields

In applications such as traction motors of (hybrid) electric vehicles and electric power steering motors, magnets are exposed to large reverse magnetic fields originated from the stator coils. Such fields can either demagnetize a part of the magnet or the whole magnet body [6], [10]. Additionally, a large change in the magnetic flux that may occur during start-up or fault conditions can induce eddy currents in the magnet. These currents produce a countervailing magnetic flux that provides some protection against demagnetization. The countervailing flux at the edges of the magnet tends to be smaller than in the center. The periphery of the specimen suffers more demagnetization and also experiences significant increase in temperature [10]. Therefore, regions of the magnet that are more at risk of being demagnetized need to contain a high-coercivity material in order to prevent the loss of the magnetic flux density.

2.4 Conclusions

Magnetic properties of bulk Nd-Fe-B permanent magnets strongly depend on the material's microstructure, which is determined by the chemical composition and the magnet manufacturing route. The latter starts with the production of the magnetic powder and several types of Nd-Fe-B powders are commercially available. Consolidation of the powder into a bulk magnet is a crucial step, since the material's magnetic properties can be significantly degraded if the consolidation technique chosen for a certain powder is inappropriate or if the processing parameters are not optimized. Polycrystalline powders are especially sensitive to high temperatures due to their fine grain size and are often used for the preparation of bonded or hot-pressed magnets.

For a majority of applications, magnets with high intrinsic coercivity or high remanent magnetization are needed. Some applications, on the other hand, require both, but often a compromise between the two has to be made, since the high intrinsic coercivity, achieved with the addition of the HRE elements, comes at the expense of remanence in the commercially available sintered magnets with the best overall magnetic properties. To prevent the decrease in B_r when Dy or Tb are used, the grain boundary diffusion process was developed, but this approach can only be used on thin magnets. In most cases, large concentrations of Dy or Tb are used to protect the magnet against demagnetization, even when only certain regions of the specimen experience strong demagnetizing fields and high temperatures. A much more efficient approach would therefore be to design a magnet with locally different magnetic properties.

Chapter 3

Aims and Hypotheses

Incorporating the heavy rare earth elements (HRE = Dy, Tb) into the Nd-Fe-B-type material is a commonly employed strategy to produce high-coercivity magnets. The excellent magnetocrystalline anisotropy of the $(\text{HRE})_2\text{Fe}_{14}\text{B}$ hard magnetic phase comes at the expense of a reduced saturation magnetization. The grain boundary diffusion (GBD) process of Dy or Tb was developed in the past in order to minimize the use of these elements and prevent the loss of the magnetic flux density, but the process can only be applied on thin samples. The aim of this dissertation was to develop a new type of Nd-Fe-B permanent magnet with a reduced amount of HRE elements without diminishing the magnet's ability to withstand the demagnetizing fields.

As an alternative to the homogeneous distribution of the HRE elements throughout the material, a magnet with locally different magnetic properties can be used in applications where only certain parts of the specimen experience strong demagnetizing fields and significant increase in temperature. Accordingly, a multicomponent magnet containing high-coercivity regions can be designed. The advantage of this approach is that the bulk of the specimen can be HRE-free with high remanent magnetization, which would improve its overall performance. Such a magnet can be prepared from a HRE-containing material and a HRE-free material.

The main challenge that this novel approach presents is the strong dependence of a material's magnetic properties on its chemical composition. Conventional sintering is performed at temperatures well above the eutectic temperature of the Nd-Fe-B system and the consolidation process can last for several hours. Under these conditions, the diffusion of the HRE elements can be very pronounced and it is highly unlikely that the original compositions of the respective parts can be preserved in a sample composed of different materials. In an extreme case, the result would be a sample with a HRE gradient or even homogeneously distributed dysprosium or terbium.

Pulsed Electric Current Sintering (PECS) technique is a fast hot pressing technique that can be used to consolidate different types of Nd-Fe-B powders into dense magnets at much lower temperatures than conventional sintering. Therefore, it is theoretically possible to simultaneously process two materials with their respective chemical compositions without providing enough energy to diffuse Dy or Tb from the HRE-containing into the HRE-free part of the specimen. However, some materials exhibit a narrow range of the optimal processing parameters in terms of the density and magnetic properties. For that reason, several types of Nd-Fe-B powders will be investigated with the aim of finding a suitable combination of powders that can be consolidated under the same conditions in order to successfully prepare a dense multicomponent magnet.

Two approaches for the manufacture of magnets with locally different magnetic properties will be considered. The first approach is to start from the raw powders and

prepare the sample in a single consolidation step. The second approach is a two-step procedure. In the first step, single component magnets with different magnetic properties are prepared from the respective powders. The magnets are then combined into a new composed magnet with an additional PECS consolidation step. To prove the concept, the multicomponent magnets will be isotropic, although an additional powder alignment step can be applied when anisotropic materials like jet-milled or hydrogenation-disproportionation-desorption-recombination-processed powders are condensed into anisotropic bulk magnets with the PECS technique. Alternatively, if the results prove that the two-step process can be performed without degrading the properties of the pre-consolidated magnets, the same approach could be adapted for the hot-deformed magnets prepared from the nanostructured melt-spun powders in order to prepare an anisotropic nanostructured multicomponent magnet.

Chapter 4

Novel Types of Nd-Fe-B Permanent Magnets, Materials and Methods

Novel types of Nd-Fe-B permanent magnets, prepared with the Pulsed Electric Current Sintering technique, are presented here. Magnetic powders selected for this study, bulk magnet manufacturing procedures and the methods used to characterize the materials are also listed in this chapter.

4.1 Novel Types of Nd-Fe-B Magnets

4.1.1 Bulk magnets, prepared from the gas-atomized powder

Gas-atomized Nd-Fe-B powders are rarely used for magnetic applications. One reason for this are the cooling rates that can be reached in the process of atomization. Those rates are usually several orders of magnitude lower than the rates achieved with the melt spinning. Another reason is the reversible loss of hard magnetic properties at 150 °C in air, observed for powders rich in neodymium, as discussed in Section 2.2.4.3. Unlike the melt-spun materials, the gas-atomized powders have not been consolidated into bulk magnets with the PECS technique until now. However, since their magnetic properties, most notably the intrinsic coercivity, highly depend on the grain size, it was expected that the performance of the bulk PECS magnets, prepared from the gas-atomized powders, will depend on the ability of such a powder to be consolidated at relatively low temperatures. Two different gas-atomized powders were investigated. The first was a TRE-lean material (MQP-S) with an under stoichiometric composition (in respect to the $\text{RE}_2\text{Fe}_{14}\text{B}$ hard magnetic phase). This material is a representative of commercially available spherical Nd-Fe-B powders and it is intended for the preparation of bonded magnets. The second powder (GA-34) was custom-made for the purpose of this research. Its neodymium-rich composition was chosen with the aim to prepare a dense magnet at PECS temperatures similar to the ones needed to consolidate the melt-spun materials.

4.1.2 Magnets with locally different magnetic properties

To address the issues associated with the use of heavy rare earth elements, a novel type of Nd-Fe-B permanent magnet was prepared [128]. Multicomponent magnets consisting of regions with different magnetic properties were manufactured with the PECS technique. Such a magnet combines the excellent intrinsic coercivity of a HRE-containing material and high saturation magnetization of a HRE-free material.

In order to simultaneously process two different Nd-Fe-B powders together in a single PECS consolidation step, the materials' densification behaviors must be similar so that high density can be achieved without deteriorating the magnetic properties of the respective powders. Three different types of Nd-Fe-B powders were investigated as possible candidates for the preparation of magnets with locally different magnetic properties: melt-spun, gas-atomized and hydrogenation-disproportionation-desorption-recombination-processed. Among them, only the melt-spun materials are commonly used in hot pressing.

MQU-F and MQU-G nanostructured melt-spun ribbons were chosen for the preparation of the multicomponent magnets based on their similar optimal PECS processing parameters and good magnetic properties. Dense samples were prepared from the gas-atomized GA-34 material at PECS temperatures similar to the ones required to consolidate the melt-spun powders. However, since the samples' magnetic properties were inferior to the properties of the dense nanostructured magnets, the gas-atomized material could not contribute to the overall magnetic performance of a multicomponent magnet. The TRE-lean MQP-S gas-atomized powder was found to be an unfitting candidate for the preparation of bulk PECS magnets. This material and the hydrogenation-disproportionation-desorption-recombination-processed MF-18P powder were designed for bonded applications. Dense magnets were prepared from the HDDR powder at PECS temperatures exceeding the optimal values for the TRE-rich rapidly solidified powders by ≈ 100 °C, which makes it an unlikely candidate for the preparation of multicomponent magnets from powders, since it cannot be processed together with a rapidly solidified material.

Two different approaches to manufacture a multicomponent magnet were considered. The first approach is to start from the raw powders and prepare a multicomponent magnet in a single step. The second approach is a two-step procedure in which the individual dense magnets are first prepared from the respective magnetic powders. Afterwards, the magnets are processed together in a second PECS process step in order to prepare a single magnet body with locally different magnetic properties.

4.2 Materials

Three types of polycrystalline Nd-Fe-B magnetic powders, obtained via different processing routes, were chosen for the studies of the influence of the PECS processing parameters on the density, magnetic properties and microstructure of the bulk magnets: melt-spun MQU-F and MQU-G, gas-atomized MQP-S and GA-34 and the hydrogenation-disproportionation-desorption-recombination-processed MF-18P. Magnetic powders, their intended use, powder production route and bulk PECS samples produced from them are listed in Table 2.

4.2.1 Melt-spun powders

Two MQU-grade nanostructured melt-spun powders in the form of crushed ribbons were purchased from the Magnequench Corporation: HRE-free MQU-F and Dy-containing MQU-G with corresponding compositions $\text{Nd}_{13.6}\text{Fe}_{73.6}\text{Co}_{6.6}\text{Ga}_{0.6}\text{B}_{5.6}$ and $\text{Nd}_{12.3}\text{Dy}_{1.5}\text{Fe}_{77.8}\text{Co}_{2.2}\text{Ga}_{0.6}\text{B}_{5.6}$ (at. %), respectively. They were selected based on their high Nd-content, suitable for hot pressing. The powders have a flake-like morphology, beneficial for achieving high densities with the PECS technique.

4.2.2 Gas-atomized powders

The gas-atomized MQP-S material (Magnequench Corporation), a representative of commercially available spherical Nd-Fe-B powders, was used for the PECS study. Its composition is $\text{Nd}_{7.5}\text{Pr}_{0.7}\text{Fe}_{75.4}\text{Co}_{2.5}\text{B}_{8.8}\text{Zr}_{2.6}\text{Ti}_{2.5}$ (at. %).

Custom-made GA-34 powder with composition $\text{Nd}_{15.4}\text{Fe}_{69.8}\text{Co}_{7.2}\text{Ga}_{0.5}\text{B}_{6.2}\text{Al}_{0.2}\text{Zr}_{0.7}$ (at. %) was provided by TLS Technik GmbH & Co. Spezialpulver KG. The powder was prepared by inert gas atomization with argon. The Nd-rich composition (34 wt. %) was chosen with the aim of reaching high densities in the bulk samples consolidated with the PECS technique.

4.2.3 HDDR powder

In contrast to the rapidly solidified (melt-spun and gas-atomized) Nd-Fe-B powders, the MF-18P HRE-free HDDR powder used in this study is magnetically anisotropic. The material, purchased from the Aichi Steel Corporation, was developed for bonded magnets. Its composition is $\text{Nd}_{11.0}\text{Pr}_{0.9}\text{Fe}_{80.4}\text{B}_{6.4}\text{Al}_{0.7}\text{Cu}_{0.4}\text{Nb}_{0.2}$ (at. %). The powder production process involves blending the hydrogenation-disproportionation-desorption-recombination-processed Nd-Fe-B material with NdCuAl eutectic alloy. During a subsequent heat treatment above its eutectic temperature, the Nd-rich material diffuses into the powder particles. This increases the amount of the grain-boundary phase and, as a consequence, the intrinsic coercivity is enhanced [129].

Table 2: Magnetic powders employed in the PECS experiments, their intended use, powder production route and bulk PECS samples produced from them. *Dy-containing powder.

Powder and its chemical composition (at. %)	Intended use	Powder production route	PECS samples
MQU-F $\text{Nd}_{13.6}\text{Fe}_{73.6}\text{Co}_{6.6}\text{Ga}_{0.6}\text{B}_{5.6}$	MQU TM powders for fully dense anisotropic magnets	Melt spinning	Single component
MQU-G* $\text{Nd}_{12.3}\text{Dy}_{1.5}\text{Fe}_{77.8}\text{Co}_{2.2}\text{Ga}_{0.6}\text{B}_{5.6}$			Multicomponent
MQP-S $\text{Nd}_{7.5}\text{Pr}_{0.7}\text{Fe}_{75.4}\text{Co}_{2.5}\text{B}_{8.8}\text{Zr}_{2.6}\text{Ti}_{2.5}$	MQP TM powder for isotropic bonded magnets	Gas atomization	Single component
GA-34 $\text{Nd}_{15.4}\text{Fe}_{69.8}\text{Co}_{7.2}\text{Ga}_{0.5}\text{B}_{6.2}\text{Al}_{0.2}\text{Zr}_{0.7}$	Custom-made powder		
MF-18P $\text{Nd}_{11.0}\text{Pr}_{0.9}\text{Fe}_{80.4}\text{B}_{6.4}\text{Al}_{0.7}\text{Cu}_{0.4}\text{Nb}_{0.2}$	MAGFINE powder for anisotropic bonded magnets	Dynamic HDDR process	

4.3 Sieving

Gas-atomized powders contain spherical particles with a wide size distribution, ranging from a few to more than 100 μm in diameter. Their magnetic properties, especially the intrinsic coercivity, are highly size-dependent, as discussed in Section 2.2.4.3. The GA-34 material was sieved to smaller fractions (< 50 and < 20 μm , respectively) to obtain powders with higher H_{ci} values. The sieved fractions were then used for the preparation of bulk magnets.

4.4 PECS Processing of Bulk Magnets

Magnetic powders were consolidated into disc-shaped bulk magnets with the pulsed electric current sintering device (Dr. Sinter, Fuji Electronic Industrial Co. Ltd) under vacuum (≈ 20 Pa) and with 50 MPa of uniaxially applied pressure. The temperature was measured using a K-type thermocouple inserted into the graphite die close to the sample. The heating rate was approximately 100 $^{\circ}\text{C}/\text{min}$. A standard 12:2 on-off current pulse sequence was applied to heat the sample.

4.4.1 Single component magnets

For each experiment, 2.5 g of a respective powder (melt-spun MQU-F and MQU-G, gas-atomized MQP-S, gas-atomized GA-34 and its sieved fractions and the hydrogenation-disproportionation-desorption-recombination-processed MF-18P) was placed in a cylindrical graphite die with a 10 mm of inner diameter. Thin graphite foil was used to separate the sample from the die and punches for easier handling. The as-prepared powder was then transferred into the sintering chamber of the PECS device. The consolidation temperature was varied between 550 and 900 $^{\circ}\text{C}$ with 50 $^{\circ}\text{C}$ increment, depending on the powder used. The holding time at the processing temperature was either 1 or 10 minutes.

Additional 10 mm samples were prepared from the melt-spun powders at 670 $^{\circ}\text{C}$ with the same procedure. After the magnets were made, they were polished with a silicon carbide paper to remove the graphite foil. Each magnet was then placed back into the 10 mm die and PECS processed again at 650 $^{\circ}\text{C}$ in order to evaluate the effect that a two-step PECS consolidation has on the magnetic properties of the respective melt-spun materials.

Larger samples were also prepared from the melt-spun powders at temperatures ranging from 640 to 730 $^{\circ}\text{C}$. Each time, 10 g of a respective powder was placed in a die with a 16 mm of inner diameter and the material was consolidated at the selected temperature with 1 minute of holding time. One sample was made by preparing a homogeneous mixture of both powders in a 1:1 ratio. 10 g of the powder mixture was then PECS processed at 670 $^{\circ}\text{C}$.

4.4.2 Multicomponent magnets

4.4.2.1 One-step procedure (sample MC1)

A multicomponent magnet composed of the MQU-F and MQU-G materials was prepared from the powders. 5 grams of the first powder (MQU-F) was placed in a 16 mm die. The powder-containing die was lightly tapped to smooth the powder's surface. Afterwards, the same amount of the second powder (MQU-G) was placed on top of the first. The PECS consolidation was done with 1 minute of holding time at 670 $^{\circ}\text{C}$.

spectroscopy (ICP-AES) technique. The compositions of the melt-spun powders were provided by the manufacturer.

All samples (powders and bulk magnets) were magnetized in a pulsed field of 6 T to ensure full magnetic saturation prior to magnetic measurement.

Measurements of the powders were performed with a Lakeshore vibrating-sample magnetometer (VSM). For that, the powders were placed in a plastic holder and covered with a cold-curing resin to prevent particles from being moved by the magnetic field during measurement. The results were not corrected for the self-demagnetization effect; therefore, B_r values were not quantified.

10 mm and 16 mm PECS samples were analysed using a closed-loop permeameter (Magnet-Physik). MQP-S samples, GA-34 samples and HDDR samples were measured at room temperature. Due to the high intrinsic coercivity of the melt-spun ribbons used in this study, magnetic properties of the 10 mm samples prepared from the MQU-F and MQU-G powders were measured at 70 °C in order to fully demagnetize them in a permeameter. Larger samples (16 mm) were measured at 120 °C. The estimation of the uncertainty of the results obtained with the permeameter is not a straightforward task. The contribution of the measuring coil and the integrators has to be considered, and if there is no saturation effect of the pole-piece, the uncertainty is less than 2 %, which shall be assumed in the following.

High-temperature measurements of selected samples and room-temperature measurements of magnets prepared from the melt-spun ribbons were performed with a Pulsed Field Magnetometer (PFM, HyMPulse from Metis).

Samples' densities were determined via Archimedes' principle.

For the scanning electron microscopy (SEM) analysis, the gas-atomized powders were embedded in a conductive polymer matrix. The disc-shaped PECS samples were cut in half in the direction perpendicular to their circular surface to expose the cross-section. All samples were first ground with a silicon carbide abrasive paper, starting with the 120 and finishing with the 2400 grade. The polishing was done with a 3 μm diamond slurry in the first step and with a 0.25 μm slurry in the last step. The polished samples were then cleaned with isopropanol, dried with hot air and mounted on an aluminium SEM holder. Microstructural and compositional analyses were performed with a field emission gun scanning electron microscope FEG-SEM JEOL JSM-7600F. Backscattered electron (BSE) imaging was used to reveal the major phases present in the samples. Local chemical composition was determined using energy-dispersive X-ray spectroscopy (EDS) point analysis. The analytical spatial resolution depends on the accelerating voltage used, which was 20 keV in order to ensure the peaks from the high-energy X-ray spectrum and an interaction volume close to 1 μm^3 [130]. For nanostructured materials such as the melt-spun Nd-Fe-B powders, this means that the local chemical composition determined from the spectrum represents the average of different phases like the metallic Nd-rich grain-boundary phase, Nd-oxides and the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

Chapter 5

Results

This chapter contains the results of the density measurements, magnetic characterization and microstructural investigation of the polycrystalline Nd-Fe-B powders chosen for this study, and bulk magnets prepared from the powders with the PECS technique.

5.1 Single Component Magnets

The first step in the preparation of the multicomponent magnets with the PECS technique is optimization of the PECS consolidation parameters for each individual Nd-Fe-B powder. Three different types of Nd-Fe-B powders (melt-spun, gas-atomized and hydrogenation-disproportionation-desorption-recombination-processed) were investigated with the aim of finding a suitable combination of materials that can be consolidated into one dense magnet body without degrading their respective magnetic properties.

5.1.1 Rapidly solidified Nd-Fe-B powders

Fig. 34 shows the dependence of the absolute densities and magnetic properties (intrinsic coercivity – H_{ci} and remanence – B_r) on the PECS consolidation temperature for samples prepared from the melt-spun and gas-atomized powders. The holding time at the desired temperature (550 – 900 °C) was one minute. Longer holding times were found to be largely inefficient in improving the final densities and magnetic properties of the samples.

The room-temperature magnetic properties of the powders and bulk magnets, discussed in this section, are gathered in Table 3. The absolute values of the temperature coefficients of intrinsic coercivity (β) and remanence (α) were calculated from the H_{ci} and B_r values measured at room temperature and at 120 °C using the equations:

$$\beta = \frac{H_{ci} (120 \text{ } ^\circ\text{C}) - H_{ci} (25 \text{ } ^\circ\text{C})}{H_{ci} (25 \text{ } ^\circ\text{C}) \times \Delta T} \times 100 \quad (5.1)$$

$$\alpha = \frac{B_r (120 \text{ } ^\circ\text{C}) - B_r (25 \text{ } ^\circ\text{C})}{B_r (25 \text{ } ^\circ\text{C}) \times \Delta T} \times 100 \quad (5.2)$$

where ΔT is the temperature interval between the high (120 °C) and low (25 °C) measurement temperatures.

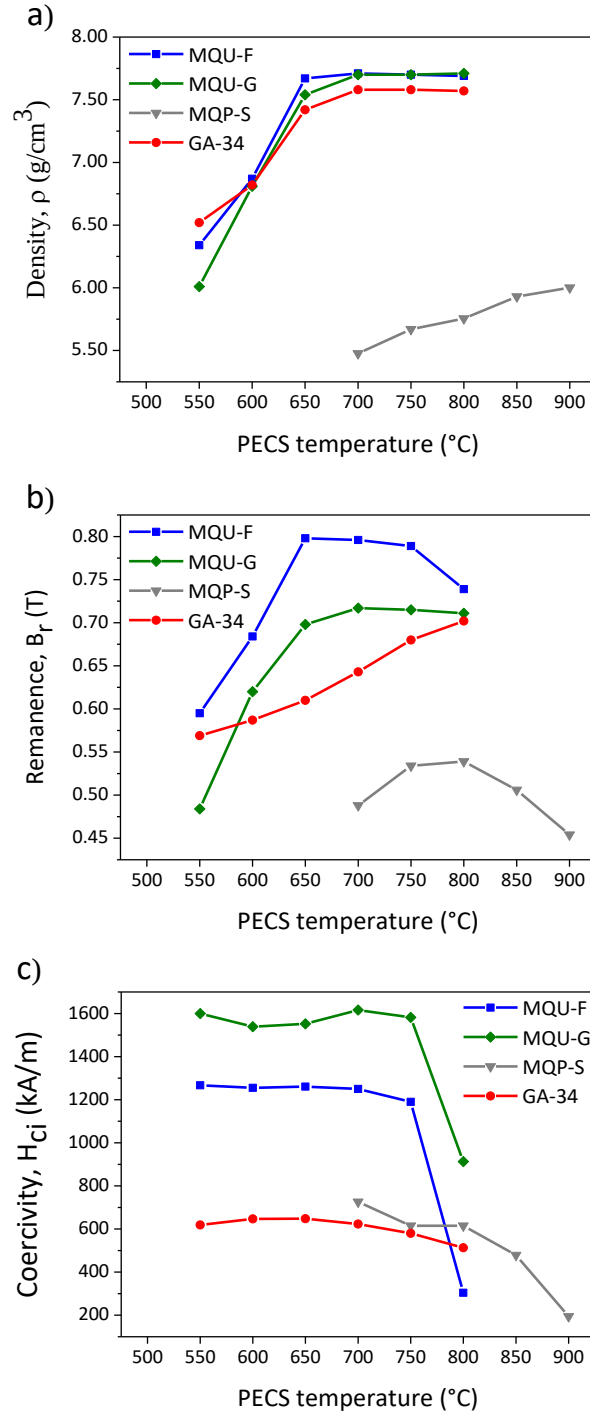


Figure 34: Dependence of the absolute density ρ (a), remanence B_r (b) and intrinsic coercivity H_{ci} (c) of the as-prepared samples on the PECS consolidation temperature (1 minute of holding time). B_r and H_{ci} values of the MQU-F and MQU-G samples were measured at 70 °C, while the corresponding values of the MQP-S and GA-34 samples were obtained at room temperature.

Table 3: Room-temperature magnetic properties, absolute densities and absolute values of the temperature coefficients of intrinsic coercivity and remanence of selected samples (powders and bulk magnets prepared with the PECS technique at the temperatures indicated in the left-side column). *Values provided by the manufacturer. **Values of heat-treated samples (10 minutes at 650 °C in vacuum) with the corresponding H_{ci} values of untreated samples between the brackets.

Sample	H_{ci} (kA/m)	B_r (T)	$(BH)_{max}$ (kJ/m ³)	ρ (g/cm ³)	β (%/°C)	α (%/°C)
MQU-F powder	1680	/	/	7.63 *	/	/
MQU-F – 650 °C	1665	0.82	123	7.67	-0.45	-0.09
MQU-F – 800 °C	523	0.81	96	7.69	-0.72	-0.21
MQU-G powder	2080	/	/	7.63 *	/	/
MQU-G – 700 °C	2075	0.75	105	7.67	-0.42	-0.10
MQU-G – 800 °C	1290	0.76	99	7.70	-0.56	-0.14
MQP-S powder	665	/	/	7.43 *	-0.40 *	-0.13 *
MQP-S – 800 °C	615	0.54	37	5.75	-0.39	-0.12
MQP-S – 900 °C	195	0.45	11	6.00	/	/
GA-34 powder	565 ** (165)	/	/	/	-0.61 **	/
GA-34 – 700 °C	670 ** (625)	0.65 **	53 **	7.58	-0.61 **	-0.20 **
GA-34-50 – 700 °C	820 ** (770)	0.72 **	76 **	7.54	-0.56 **	-0.16 **
GA-34-20 – 700 °C	1015 ** (980)	0.75 **	94 **	7.65	-0.53 **	-0.11 **

5.1.1.1 Melt-spun powders

As shown in Fig. 34a, maximal density was achieved within one minute of holding time at 650 and 700 °C for the melt-spun MQU-F (blue curve) and MQU-G (green curve) powders (7.67 g/cm³ in both cases), when 50 MPa of pressure was applied. The maximal B_r values (Fig. 34b) were reached when the powders were completely densified (0.82 T for the MQU-F and 0.75 T for the MQU-G). High intrinsic coercivities, comparable to the corresponding values of the powders, were also obtained at these temperatures (1665 and 2075 kA/m for the MQU-F and MQU-G samples, respectively, Fig. 34c and Table 3). Increase in the processing temperature led to a decrease in H_{ci} . Similarly, longer holding times (10 min) degraded the intrinsic coercivity while the improvement in the density was not significant. Major differences in magnetic properties of the bulk magnets prepared from the two melt-spun powders originate in their respective chemical compositions: Dy-free MQU-F samples have higher B_r and $(BH)_{max}$ values, whereas the addition of Dy in the MQU-G powder allows higher H_{ci} values to be reached.

An important advantage of the nanostructured Nd-Fe-B magnets, compared to their sintered counterparts, is their improved high-temperature performance. Both dense MQU-F and MQU-G samples have smaller absolute values of the temperature coefficients of intrinsic coercivity ($\beta = -0.45$ and -0.42 %/°C, respectively) and remanence ($\alpha = -0.09$ and -0.10 %/°C, respectively) than commercial anisotropic magnets. Similar values for the PECS-processed melt-spun ribbons have been measured by other authors [30].

Both melt-spun powders have a fine microstructure with nanosized grains as reported elsewhere [131], [132]. SEM analysis of the polished cross-sections of the optimally processed PECS samples with the best magnetic properties (MQU-F – 650 °C and MQU-G – 700 °C,

Table 3) and over-processed samples with degraded magnetic properties due to the processing temperature exceeding the optimal conditions (800 °C for both materials) was performed to confirm the correlation between the H_{ci} values and changes in the microstructure upon consolidation. As seen in Fig. 35, original powder particles (crushed ribbons) can be observed in all samples investigated (MQU-F – 650 °C (a), MQU-F – 800 °C (b), MQU-G – 700 °C (c) and MQU-G – 800 °C (d)). The high Nd content of the phase separating the individual flake-like particles is responsible for the bright contrast in the BSE observation mode. The ribbons of both samples processed at optimal temperatures have a fine microstructure with no discernible grain growth (Fig. 35a, c). The $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are too small to resolve with this technique. However, the slight contrast between the two surfaces of an individual ribbon hints at a difference in the grain size. This is characteristic for any type of melt spinning process, where the side of the ribbon that was in contact with the cooling wheel (wheel side) experiences a higher quenching rate than the side away from the cooling wheel (free side) [133]. On the other hand, both samples prepared from the individual powders at 800 °C (over-processed samples) have regions of micrometre-size grains, corresponding to the dark contrast in Fig. 35b and d. Large grains of the matrix phase can be observed in both samples, with the over-processed MQU-F sample (Fig. 35b) showing more pronounced grain growth. Regions with finer grains are observed as light grey contrast due to a significant volume ratio of the secondary Nd-rich phase.

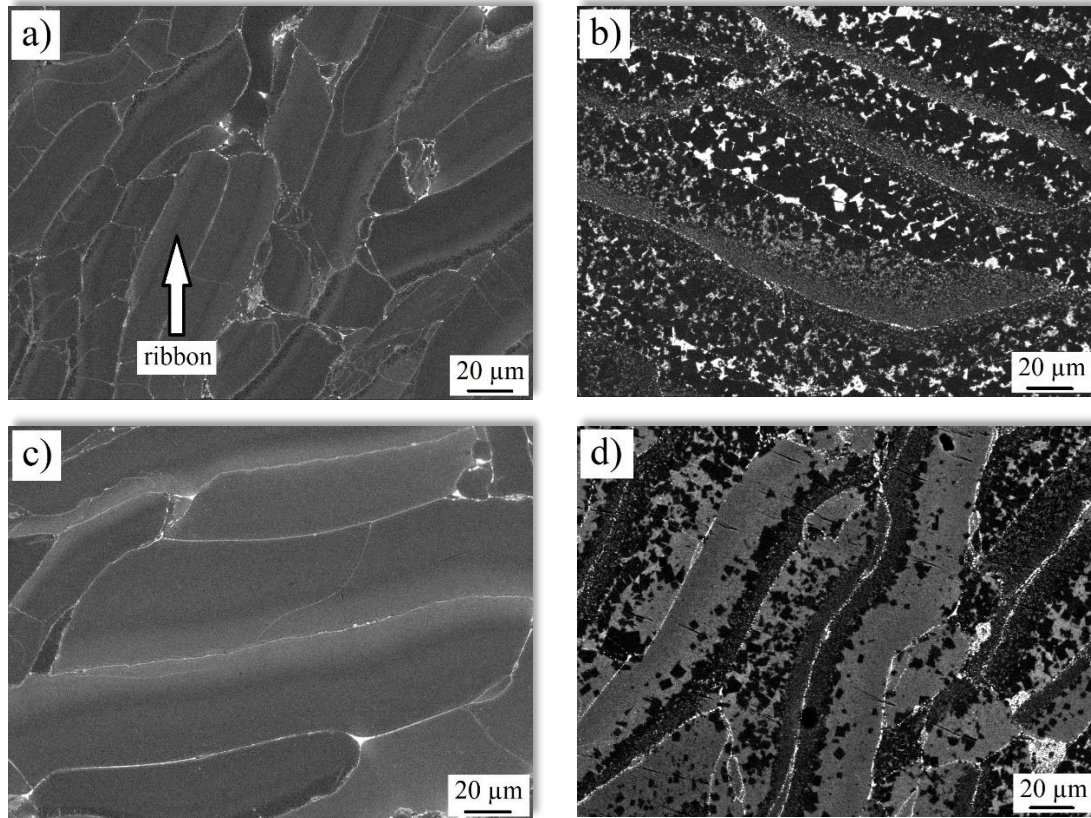


Figure 35: BSE images of optimally processed (left) and over-processed (right) dense samples prepared with the PECS technique from the melt-spun ribbons: MQU-F – 650 °C (a), MQU-F – 800 °C (b), MQU-G – 700 °C (c) and MQU-G – 800 °C (d).

During consolidation of the MQU-F and MQU-G powders at high temperatures (≥ 750 °C), a small amount of a metallic material was squeezed out of the powder bed and solidified on the graphite punches, as shown in Fig. 36. ICP-AES analysis revealed that it consisted mostly of Nd (≈ 90 wt. %). Since the microstructures of the optimally processed and over-processed magnets are markedly different, the decrease in the volume ratio of the Nd-rich phase is not apparent from the BSE images in Fig. 35.



Figure 36: Graphite punch after processing the MQU-F powder at 800 °C.

5.1.1.2 Gas-atomized powders

Two gas-atomized powders were used for the PECS experiments. The first one was the commercial MQP-S with under-stoichiometric composition. The second one was a custom-made GA-34 material with a high Nd-content, comparable to the melt-spun powders. For this reason, different densification behaviors were expected to be observed for the two spherical powders.

5.1.1.2.1 TRE-lean MQP-S

Fig. 34a shows the dependence of the absolute density of bulk PECS samples prepared from the TRE-lean MQP-S spherical powder on the PECS consolidation temperature (grey curve). Comparison with the densification behaviours of other rapidly solidified powders chosen for this study shows that this material, developed for bonded applications, could not be sufficiently densified at the temperatures usually required to process the Nd-Fe-B materials with the PECS technique. Only 77 % of the theoretical density (5.75 g/cm^3) was measured for the sample consolidated at 800 °C. At this temperature, the remanence reached a maximum value (0.54 T, Fig. 34b). H_{ci} of this sample (615 kA/m) was relatively close to the value of the starting powder (665 kA/m, Fig. 34b and Table 3). PECS consolidation at higher temperatures had a pronounced negative effect on the material's magnetic properties. While the samples were still porous and brittle, increase in the processing temperature to 900 °C degraded both remanence and intrinsic coercivity significantly.

The temperature coefficients β and α of the MQP-S sample prepared at 800 °C are almost identical to the values of the corresponding powder (Table 3). The β value is very

low ($-39\text{ }^{\circ}\text{C}$) even when compared to the melt-spun ribbons due to the very small grain size. However, the potential use of this material in high-temperature applications is limited by its low room-temperature coercivity.

BSE image of the commercial gas-atomized MQP-S powder embedded in a polymer matrix is shown in Fig. 37a. The results of the EDS analysis performed at different locations on several powder particles corresponded with the chemical composition of this material as determined with the ICP-AES analysis ($\text{Nd}_{7.5}\text{Pr}_{0.7}\text{Fe}_{75.4}\text{Co}_{2.5}\text{B}_{8.8}\text{Zr}_{2.6}\text{Ti}_{2.5}$ in at. %). A single-phase microstructure can be observed in the MQP-S material. A few spherical particles are damaged or broken. Some of the spheres are hollow, which is an undesired peculiarity leading to a decrease in the bulk density. SEM investigation of the PECS sample prepared from this material at $800\text{ }^{\circ}\text{C}$ revealed a porous structure with powder particles showing very much the same single-phase microstructure as the original powder. The observed porosity is reflected in the magnet's low density. Nanosized equiaxed grains of this sample are shown in Fig. 37b.

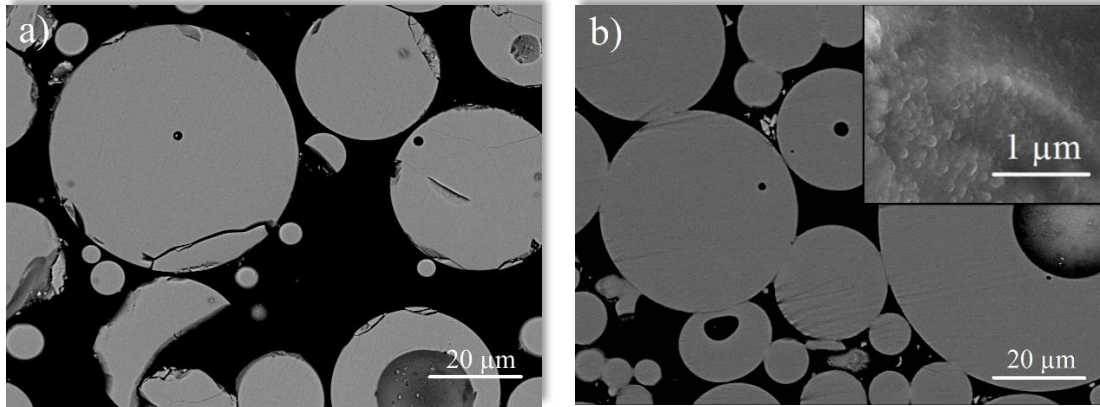


Figure 37: BSE image of the MQP-S powder, embedded in a polymer matrix (a) and cross-section of the PECS sample, prepared from the MQP-S powder at $800\text{ }^{\circ}\text{C}$; the inset shows the grain size of this sample (b).

5.1.1.2.2 TRE-rich GA-34

Red curve in Fig. 34a demonstrates the dependence of the absolute density of bulk PECS samples prepared from the TRE-rich GA-34 powder on the PECS consolidation temperature. Unlike the MQP-S material, good density (7.58 g/cm^3) was achieved when the GA-34 powder was consolidated at $700\text{ }^{\circ}\text{C}$. This value is similar to the densities of the magnets prepared from the MQU-F and MQU-G melt-spun ribbons (blue and green curves in Fig. 34a). On the other hand, the sample's magnetic properties ($B_r = 0.65\text{ T}$ and $H_{ci} = 625\text{ kA/m}$) were lower than the properties obtained with the melt-spun materials. Interestingly, H_{ci} of the dense magnet was significantly higher than the value of the corresponding GA-34 magnetic powder (165 kA/m). To improve the magnetic properties of the latter, several heat treatment conditions were tested. The best results were obtained when the powder was heat-treated in vacuum for 10 minutes at $650\text{ }^{\circ}\text{C}$. Although the increase in H_{ci} of the initial powder was significant (from 165 to 565 kA/m), the intrinsic coercivity of the heat-treated powder was still lower than the value of the PECS magnet. On the other hand, H_{ci} of the as-prepared PECS sample was only slightly improved with additional heating (from 625 to 670 kA/m). B_r and $(BH)_{max}$ values were unaffected by the heat treatment.

In contrast to what was observed for the flake-like powders, a significant amount of the liquid phase was squeezed out of the powder bed and solidified on the graphite punches during consolidation of the GA-34 material. This effect was already observed at relatively moderate processing conditions (700 °C) and became more pronounced at higher temperatures. The loss of the Nd-rich liquid phase corresponds with the increased remanence of dense samples. As seen in Fig. 34, B_r increased with the increase in the processing temperature even though the bulk density reached maximum value at 700 °C. Correspondingly, processing temperatures exceeding 700 °C had a pronounced negative effect on H_{ci} .

5.1.1.2.2.1 High-temperature stability

As discussed in Section 2.2.4.3, the TRE-rich gas-atomized Nd-Fe-B powders experience a reversible loss of hard magnetic properties at high temperatures in air, which is a highly undesired characteristic, since the properties can only be recovered with heat treatment at 650 °C.

The heat-treated GA-34 powder and a bulk PECS magnet prepared at 700 °C were exposed to 200 °C in air in order to compare their high-temperature stability. After 15 minutes, the samples were left to cool down to room temperature and their magnetic properties were measured again. As shown in Fig. 38, exposure to high temperature did not degrade the room-temperature magnetic properties of the PECS sample. In contrast, the raw powder suffered significant loss of the shape of the demagnetization curve, as well as a decrease in B_r and H_{ci} , with the latter being decreased by 45 %. Although not shown here, the saturation magnetization remained unchanged. The curves belonging to the powder (measured with the VSM) were not corrected for the self-demagnetization effect; therefore, B_r values were not quantified.

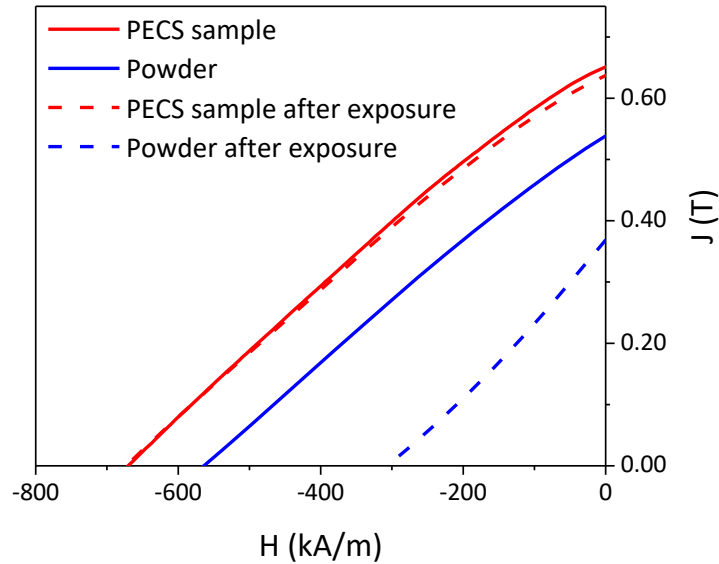


Figure 38: Room-temperature demagnetization curves of the optimally heat-treated GA-34 powder and PECS sample, before and after exposure to 200 °C in air for 15 minutes.

5.1.1.2.2.2 Magnetic properties of sieved fractions

To exploit the advantages of the PECS approach (short processing time, low consolidation temperature) for the production of the Nd-Fe-B magnets with improved intrinsic coercivity, fine-grained powders with high H_{ci} values are preferred. For gas-atomized Nd-Fe-B powders, the particle size dependence of H_{ci} was established by other researchers [59], [60] and was therefore not carried out in this work. To obtain powders with finer particle size, the GA-34 material was sieved to two fractions with particle sizes of < 50 and < 20 μm , respectively. The powders were then consolidated into bulk magnets with the PECS technique (GA-34-50 and GA-34-20 samples, Table 3) at 700 °C. Comparison of the demagnetization curves of the dense samples consolidated and heat-treated under the same conditions (Fig. 39) shows a significant improvement in the overall magnetic properties after sieving. H_{ci} of the sample prepared from the < 20 μm fraction increased from 670 to 1015 kA/m and B_r increased by 15 %.

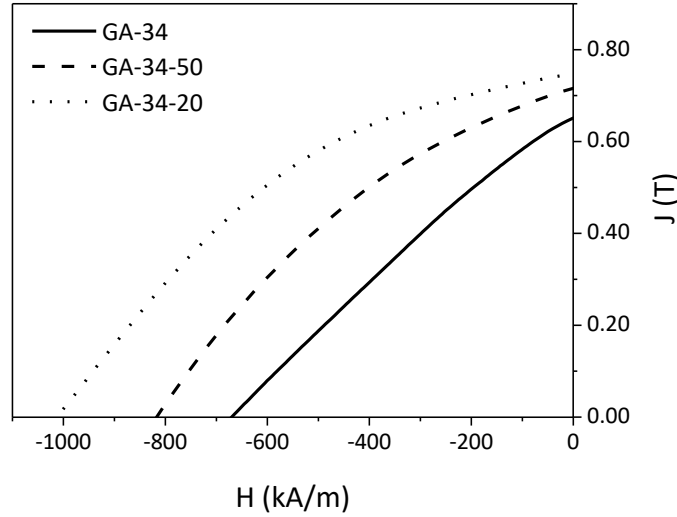


Figure 39: Room-temperature demagnetization curves of the PECS-processed and heat-treated samples, prepared from the as-received GA-34 powder (GA-34) and its sieved fractions (GA-34-50 and GA-34-20) at 700 °C.

5.1.1.2.2.3 Microstructure

Fig. 40 shows the microstructural characteristics of the gas-atomized GA-34 powder. It can be instantly noticed that the microstructure is markedly different from the single-phase microstructure of the TRE-poor MQP-S (see Fig. 37). Most of the particles have dendritic morphology, a consequence of a non-equilibrium solidification attributable to high cooling rate. Some of the particles have several crystallization centres due to heterogeneous nucleation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (Fig. 40b). A significant amount of dendritic precipitates with a black contrast can be observed in larger particles (Fig. 40a). As confirmed with the EDS, this phase is free Fe. The formation of α -Fe upon cooling of the melt is predicted by the phase diagram [22]. High amount of the Nd-rich phase (white phase observed in the BSE mode) can be seen in most of the particles examined. The smallest spheres appear to be nanostructured or amorphous; additional analysis would have to be performed in order to determine the exact size of the crystallites. Coarse-grained spheres with shells of finer microstructure were also formed (example shown in Fig. 40c).

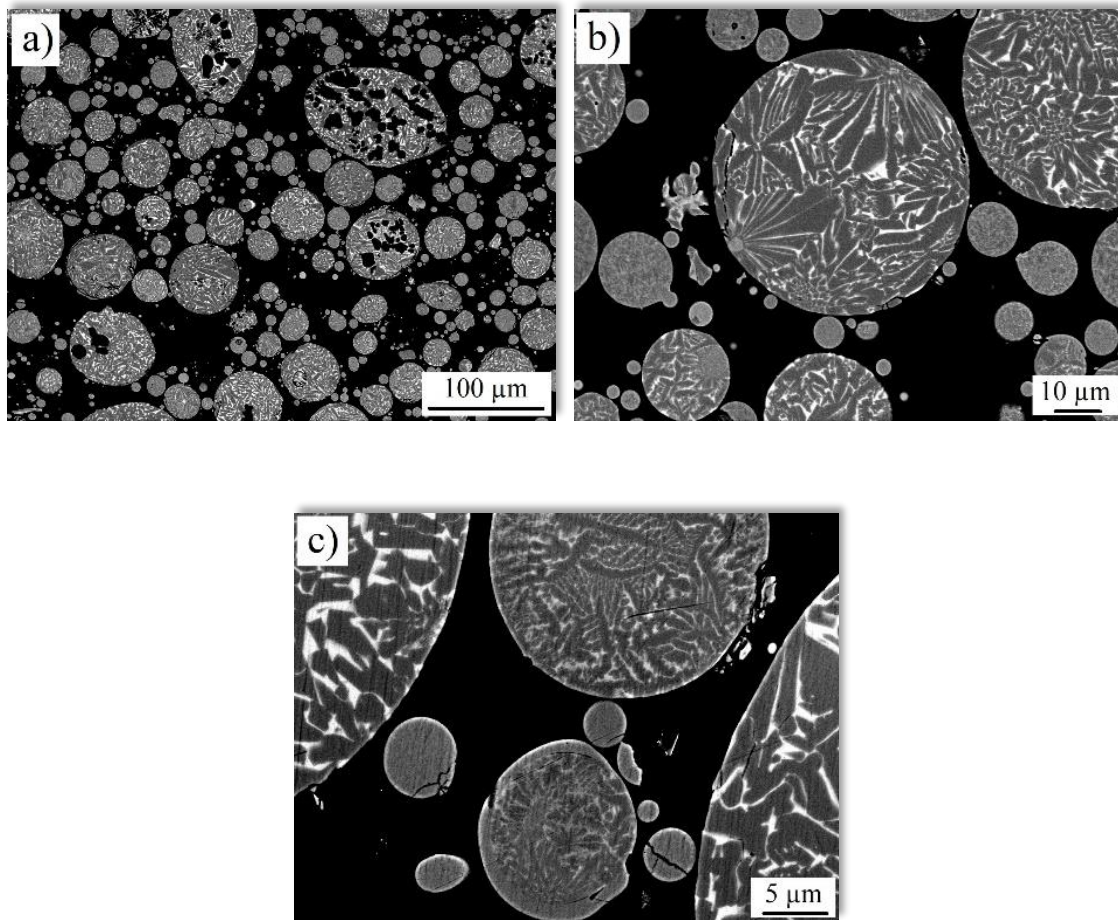


Figure 40: Microstructural characteristics of the GA-34 gas-atomized powder (BSE mode). (a) Overall microstructure with Fe precipitates (black phase) seen in the larger spheres, (b) spheres with several crystallization centres and (c) sphere with a fine-grained shell.

Fig. 41 shows backscattered SEM images of polished dense magnets, prepared with the PECS technique at 700 °C from the GA-34 powder (a, d) and from its sieved fractions (b, e for < 50 μm fraction and c, f for < 20 μm fraction). Original powder particles of roughly spherical shape, closely packed together, can be distinguished in all cases. Compared to the initial powder, the dendritic structure is no longer a dominating feature, as seen in Fig. 41d. Instead, elongated $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains up to several tens of micrometres in size can be observed in the larger spheres together with some iron precipitates (Fig. 41a), which originated from the initial powder. The smallest spheres have a significantly finer microstructure with submicron and nanosized $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains and contain no discernible Fe grains. Sieving gradually eliminated the bigger particles with a high amount of α -Fe precipitates, leaving the smaller spheres with finer grains and higher percentage of the hard magnetic phase. However, spheres with micron-sized grains are still present in the sieved fractions.

EDS analysis of the white phase seen in Fig. 41a revealed that it contained mostly Nd (≈ 62 at. %); other elements detected include Ga, Co and Fe. Similar results were obtained when the compositional analysis of phases with the same contrast was performed on several other locations. Large oxide grains, otherwise characteristic for sintered magnets, were not found in the investigated PECS samples. The small amount of oxygen measured throughout the sample (max. 6 at. %) was attributed to the surface oxidation during the

metallographic polishing of the magnet. The metallic nature of the Nd-rich phase enables PECS processing at low temperatures and conforms to the environmental stability of the Nd-Fe-B gas-atomized powders as reported by other researchers [62], [66].

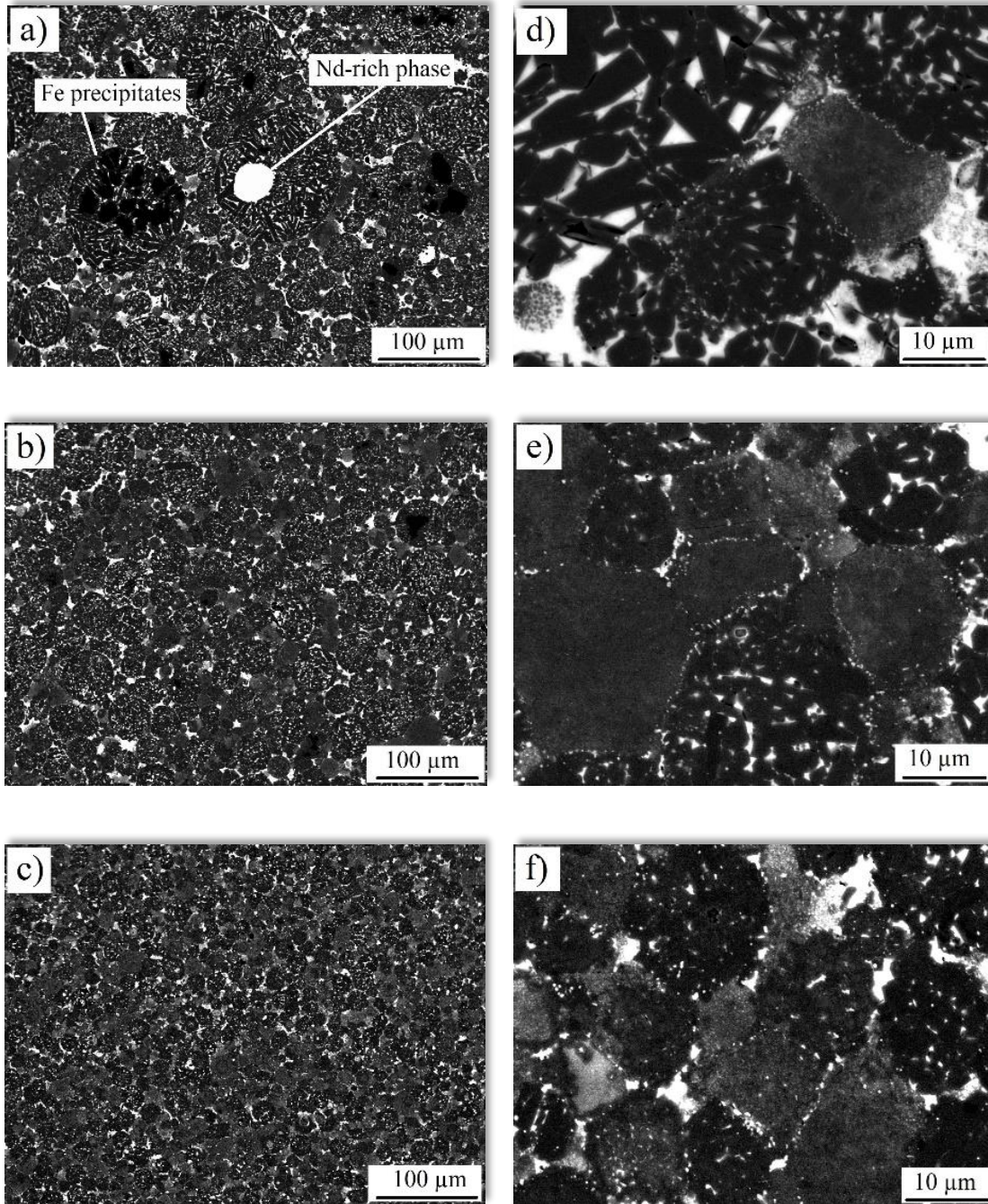


Figure 41: BSE images of samples, prepared with the PECS technique at 700 °C from the GA-34 powder (a and d), sieved < 50 μm fraction - GA-34-50 (b and e) and sieved < 20 μm fraction - GA-34-20 (c and f).

5.1.2 HDDR powder

Bulk samples were prepared from the MF-18P powder at PECS consolidation temperatures ranging from 700 to 900 °C. In contrast to the rapidly solidified powders, longer holding times (10 minutes) were found to be beneficial for improving the samples' densities. With one minute of holding time, maximal density was reached at temperatures close to 800 °C (7.52 g/cm³), whereas a similar value (7.56 g/cm³) was reached at approximately 750 °C when the holding time was prolonged.

5.1.2.1 Magnetic properties

The remanence reached maximal values in dense samples (0.81 and 0.82 T for 1 and 10 minutes of holding time, respectively). Substantial drop in B_r was measured for samples consolidated at 900 °C. The samples' absolute densities and room-temperature magnetic properties are shown in Fig. 42.

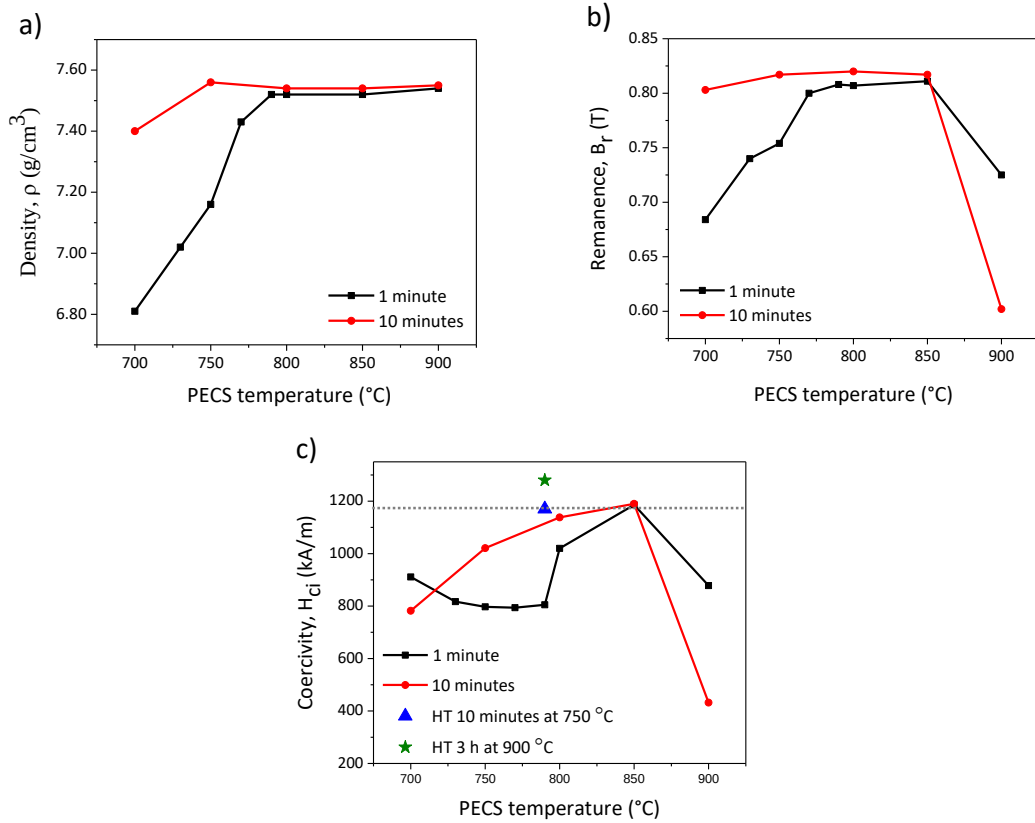


Figure 42: Temperature and holding time dependence of absolute densities (a), B_r values (b) and H_{ci} values (c) of the PECS-processed samples prepared from the MF-18P powder (the horizontal line represents H_{ci} of the initial powder). Star and triangle symbols represent H_{ci} obtained with PECS samples prepared at 790 °C and 1 minute of holding time and then heat-treated for 10 minutes at 750 °C and 3 hours at 900 °C, respectively.

The intrinsic coercivity peaked at 850 °C regardless of the holding time and its value (1190 kA/m) was similar to H_{ci} of the initial powder (horizontal line at 1170 kA/m in Fig. 42c). However, H_{ci} was reduced significantly when the consolidation temperature deviated from the optimal value. Although the trend indicates that longer holding time

contributes to the development of coercivity at lower temperatures, the consolidation temperature appears to be the most important factor in achieving high H_{ci} in the as-prepared bulk PECS magnets.

5.1.2.2 Heat treatment

Takagi et al. reported that a post-consolidation heat treatment for 10 minutes at 750 °C can effectively recover the intrinsic coercivity (in terms of the raw powder) of electric-current-sintered magnets prepared from this material, regardless of the sample's initial H_{ci} [118]. Therefore, a dense PECS sample prepared at 790 °C and 1 minute of holding time was used for the heat treatment study. Its intrinsic coercivity (800 kA/m) was relatively low. In accordance with the results of Takagi et al., H_{ci} of the PECS sample reached the value of the powder after it was exposed to a short heat treatment regime (10 minutes at 750 °C). Additional heat treatment experiments were performed in order to see if the intrinsic coercivity of the MF-18P material can be further improved. Three hours at 900 °C proved to be the most effective and the H_{ci} was increased from 800 to 1280 kA/m, surpassing the powder's coercivity (Fig. 42c). Heat treatment did not affect the remanence of the magnets. Their dimensions and densities also remained unchanged.

Two other as-consolidated dense samples were also subjected to heat treatment with the aim to investigate a potential correlation between the initial H_{ci} of the sample and the final value of the heat-treated magnet. The first one was the best PECS sample ($H_{ci} = 1190$ kA/m), prepared at 850 °C with one minute of holding time. The second one was a low-coercivity sample ($H_{ci} = 430$ kA/m), prepared at 900 °C with 10 minutes of holding time. The intrinsic coercivity of the former remained almost the same after the heat treatment ($H_{ci} = 1180$ kA/m). The low H_{ci} of the latter, on the other hand, was reduced even further and only 130 kA/m was measured (Fig. 43).

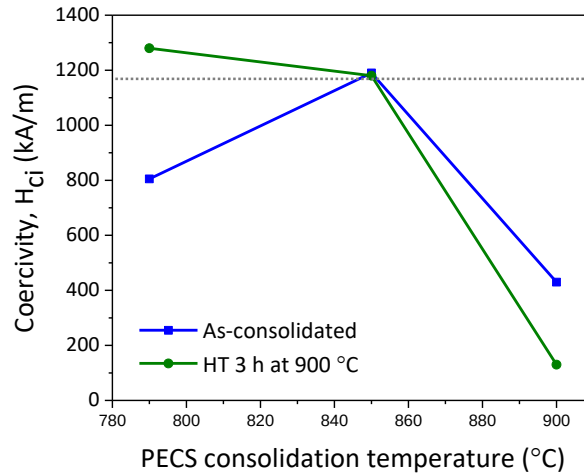


Figure 43: Intrinsic coercivities of the dense PECS samples, prepared at different consolidation temperatures, before and after the heat treatment for 3 hours at 900 °C (the horizontal line represents H_{ci} of the initial powder).

5.1.2.3 Microstructure

Polished cross-sections of the as-consolidated (1 min at 790 °C) and two heat-treated PECS samples were examined with an SEM. As seen in Fig. 44, original powder particles can be distinguished in all samples, as well as the Nd-rich phase (white contrast). On the other

hand, individual $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains cannot be observed in this image due to their small size. The main difference between the samples is the apparent area ratio of the Nd-rich phase. In the as-prepared sample, this phase primarily exists in the form of pools at the triple particle junctions, but is also present at the particle boundaries. It can also be observed in the particles, which indicates the existence of the intergranular Nd-rich regions (Fig. 44a). In the sample heat-treated for 10 minutes at 750 °C, individual pores can be observed at some of the larger particle junctions, but the overall microstructure looks very similar to the untreated sample (Fig. 44b). The sample heat-treated for 3 hours at 900 °C appears to be porous and the majority of the particle junctions does not contain Nd-rich phase (Fig. 44c). The latter is still present in the particles, at the particle boundaries and in some of the smaller particle junctions.

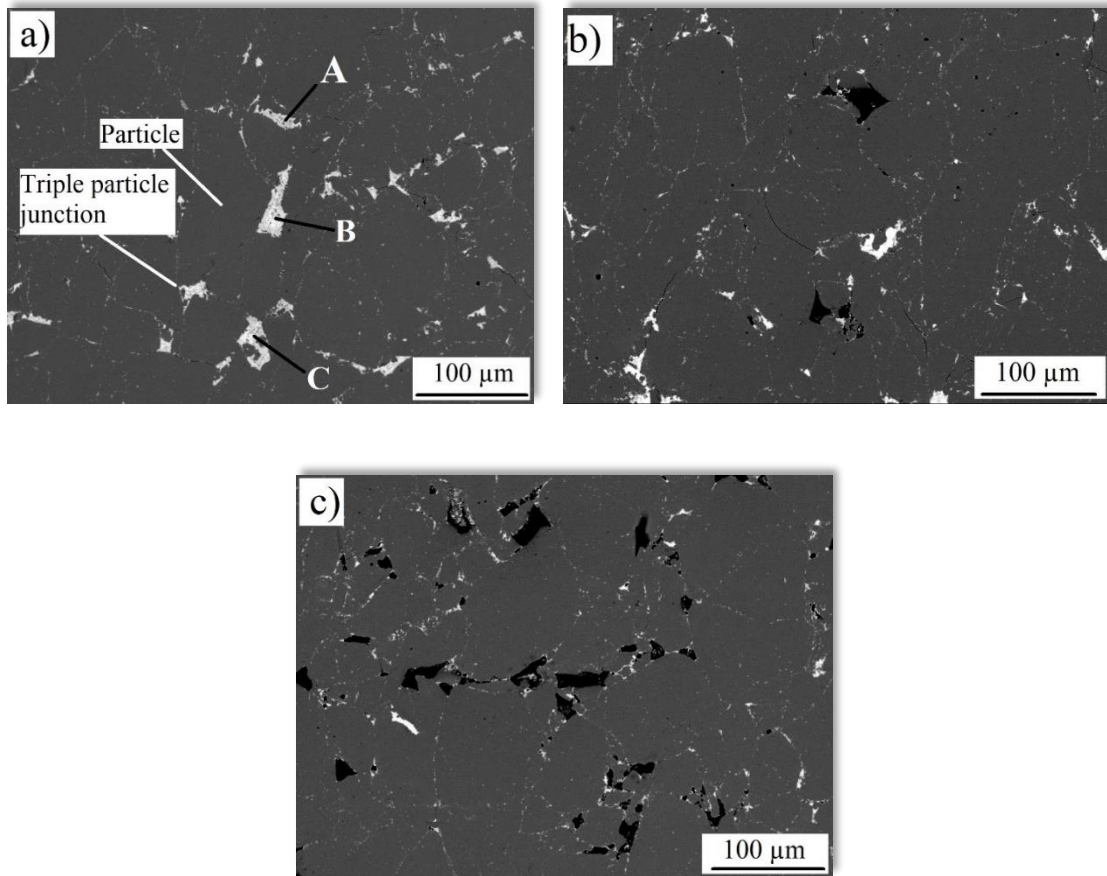


Figure 44: BSE images of samples prepared from the MF-18P powder at 790 °C and with 1 minute of holding time: as-processed sample (a), heat-treated for 10 minutes at 750 °C (b) and heat-treated for 3 hours at 900 °C (c).

EDS analysis of the Nd-rich pools observed in the triple particle junctions (locations A, B and C in Fig. 44a) was performed and the results are shown in Table 4. Neodymium is the major constituent ($\approx 70 - 75$ at. %). Copper and iron were also detected. The oxygen content varies from 9.9 to 18.0 at. %.

Table 4: Chemical composition of the Nd-rich pools observed in the triple particle junctions.

Composition (at. %)				
	O	Fe	Cu	Nd
A	15.8	7.4	1.0	75.7
B	9.9	7.1	11.7	70.8
C	18.0	1.6	5.2	75.2

5.2 Multicomponent Magnets

Investigation of the densities, magnetic properties and microstructures of the single component magnets prepared with the PECS technique was performed and the results are presented in the previous section. PECS processing parameters were optimized for each of the Nd-Fe-B magnetic powders selected for this study. The nanostructured melt-spun powders (Dy-free MQU-F and Dy-containing MQU-G) were chosen for the preparation of the multicomponent magnets based on their similar optimal PECS consolidation temperatures and the best overall magnetic properties.

5.2.1 One-step procedure (sample MC1)

The optimal consolidation temperature of the Dy-free MQU-F powder (650 °C), in terms of density and magnetic properties, was found to be lower than that of the MQU-G powder (700 °C, see Fig. 34a-c). Because the initial experiments were performed at 600, 650 and 700 °C, the actual difference in the optimal temperatures could be larger or smaller than 50 °C. To further optimize the temperature that would be used to process both materials together and reach high density without deteriorating their respective magnetic properties, additional samples were prepared at PECS temperatures ranging from 620 to 730 °C. The consolidation temperature dependence of the samples' absolute densities, as well as their H_{ci} and B_r values, is shown in Fig. 45.

According to these additional results, the lowest PECS consolidation temperature required to reach the maximal density with the MQU-G material (7.67 g/cm³) is 670 °C, which is 30 °C lower than what the previous study showed. B_r of the 670 °C sample is 0.70 T (measured at 120 °C). The trend of the H_{ci} dependence on the consolidation temperature, as seen in Fig. 45c, shows that the intrinsic coercivities of the MQU-G samples, prepared at PECS temperatures ranging from 640 to 700 °C, are very similar (≈ 1180 kA/m), considering the 2 % uncertainty of the results obtained with the permeameter.

The consolidation temperature needed to reach the maximal density with the MQU-F material (7.67 g/cm³) is 655 °C, which is in a good agreement with the initial results that placed this value at 650 °C. H_{ci} is the highest when the consolidation temperature is close to 650 °C (≈ 970 kA/m, measured at 120 °C) and degrades at higher temperatures, with a significant decrease occurring above 700 °C. At 670 °C, the intrinsic coercivity is only reduced by 5 % (from 970 to 920 kA/m). The remanence of the 670 °C sample is 0.78 T, which is the maximal value obtained with this powder.

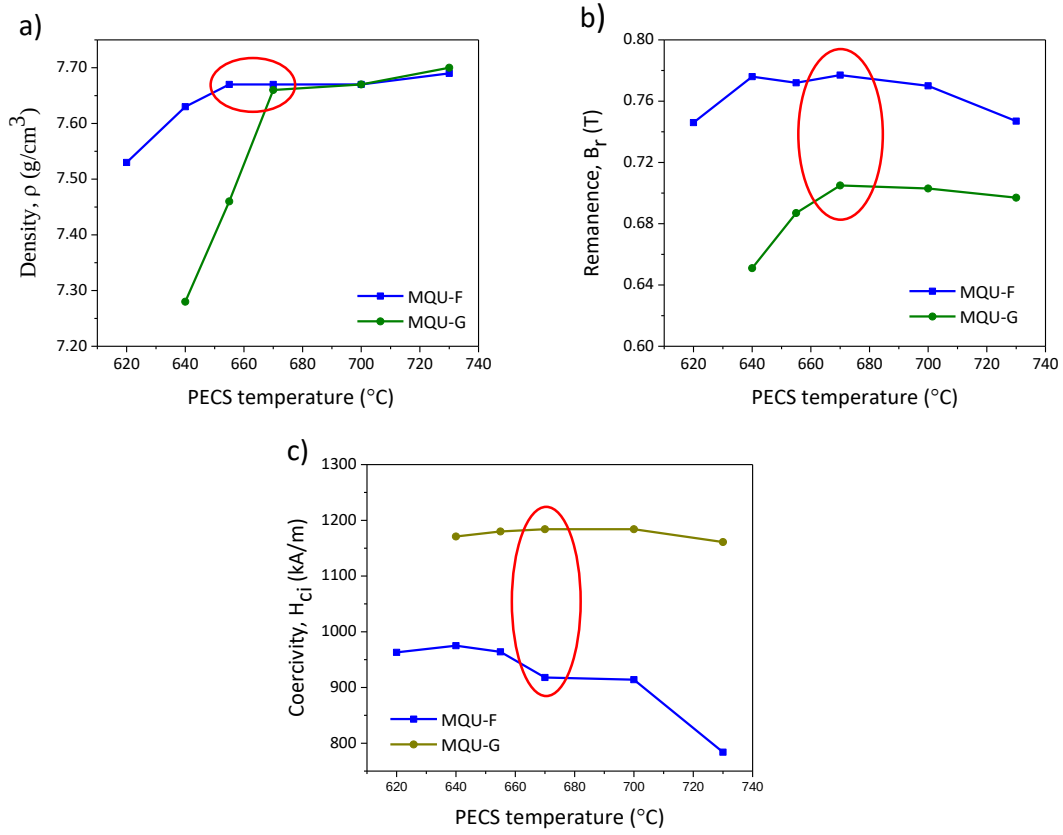


Figure 45: Dependence of absolute densities (a), B_r values (b) and H_{ci} values (c) of samples prepared from the melt-spun materials on the PECS consolidation temperature. The holding time was 1 minute. B_r and H_{ci} values were measured at 120 °C.

Based on these results, a multicomponent Nd-Fe-B permanent magnet was manufactured at 670 °C directly from the powders in a single PECS consolidation step, according to the procedure described in Section 4.4.2.1.

5.2.1.1 Microstructure and local chemical composition

The microstructure of the polished cross-section of the MC1 multicomponent magnet manufactured with the PECS technique at 670 °C is shown in Fig. 46a. In general, it looks much the same as the microstructures of the optimally processed single component MQU-F and MQU-G samples (Fig. 35). Individual ribbons and the Nd-rich phase at the particle boundaries can be observed, but the interface between both materials is not apparent from the image. This is not surprising, considering that both initial powders have similar morphology and microstructural characteristics.

The EDS point analysis was performed throughout the sample's cross-section in the direction parallel to pressing with the aim of locating the interface between both parts of the magnet. When the interface was found by measuring the dysprosium content, which is the most important feature distinguishing both materials, the chemical compositions of the adjacent ribbons (locations 1 – 8 in Fig. 46b) were analyzed and the results are presented in Table 5. The respective compositions of the powders are added for comparison. Based on these results, the part of the sample below the interface highlighted in Fig. 46b is dysprosium-free and the composition matches the MQU-F material. Particles on the other

side of the interface contain dysprosium and their compositions match that of the MQU-G powder.

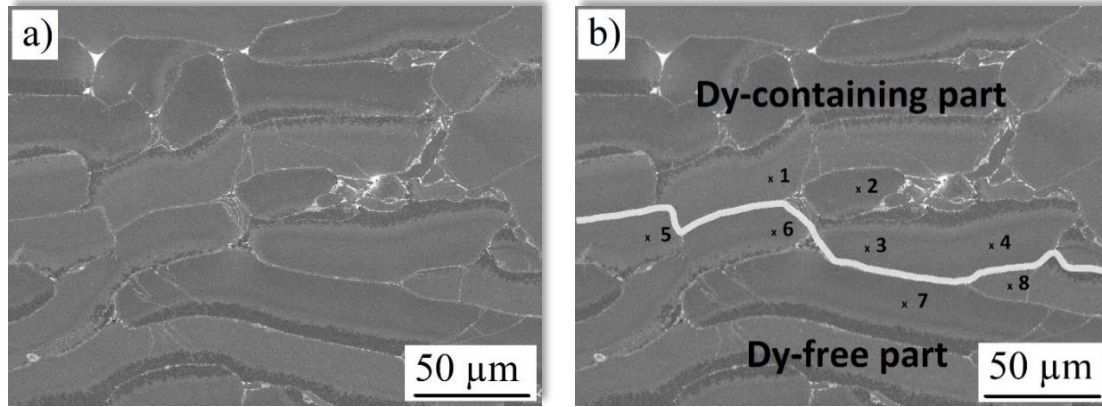


Figure 46: BSE image of the MC1 multicomponent magnet (a) and the same image with the highlighted interface between both materials and marked locations of the EDS point analysis (b).

Table 5: Chemical compositions of the interface ribbons (MC1 multicomponent magnet). Compositions of the respective powders are added for comparison.

		Composition (at. %)					
		Fe	Co	Ga	Nd	Dy	B
MQU-G	1	78.0	2.7	0.4	11.9	1.5	5.6*
	2	76.7	2.9	0.5	12.9	1.5	5.6*
	3	76.9	3.4	0.7	12.3	1.1	5.6*
	4	78.4	2.8	0.0	11.7	1.5	5.6*
		77.8	2.2	0.6	12.3	1.5	5.6*
	5	74.0	5.4	0.7	14.2	0.0	5.6*
	6	74.0	6.0	0.5	13.8	0.0	5.6*
	7	73.2	6.4	0.5	14.3	0.0	5.6*
MQU-F	8	73.0	6.4	0.9	14.2	0.0	5.6*
		73.6	6.6	0.6	13.6	0.0	5.6*

The results were corrected for the boron content, as measured using ICP analysis of the powder (5.6 at. %, noted with *). The concentration of light elements (from beryllium to fluorine) is generally difficult to quantify with the EDS technique due to the inherent physical effects (low fluorescence yield and peak overlaps with L, M and N lines of heavier elements) and technical issues relating to the design of the instrument [134]. For these reasons, the boron content was not quantified with the EDS analysis. The oxygen content varied between 3 and 4 at. % and was attributed to the surface oxidation.

5.2.1.2 Magnetic properties

The demagnetization curve of the MC1 multicomponent magnet, measured with the permeameter at 120 °C, is shown in Fig. 47. For an easier interpretation of the results, the curves belonging to the single component magnets prepared from the individual powders at the same PECS temperature (670 °C) are added. The sample prepared from the homogenous 1:1 mixture of both powders was also measured and added to the graph for comparison. All four samples have the same density (7.67 g/cm³).

As can be seen in Fig. 47, the high intrinsic coercivity of the MQU-G and the high remanent magnetization of the Dy-free MQU-F powder are not reflected in the demagnetization curve of the MC1 sample. Curiously, the shape of the curve is almost identical to the curve belonging to the 1:1 homogeneous mixture of powders. In both cases, the curve is smooth without any stepwise appearance and its shape is what is usually expected to observe for a magnet composed of a single magnetic phase. The overall magnetic properties as measured are a compromise between both magnetic materials. In fact, the H_{ci} , B_r and $(BH)_{max}$ of the multicomponent magnet are arithmetic means of the values measured for the single component magnets (Table 6).

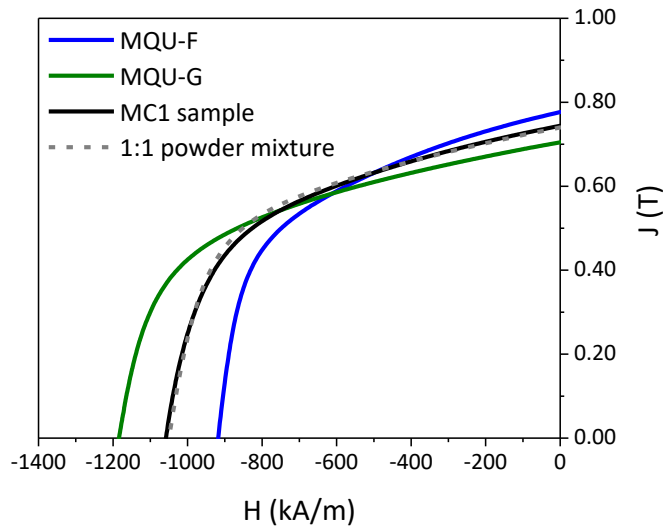


Figure 47: Demagnetization curves of the MC1 multicomponent magnet, single component magnets prepared from the MQU-F and MQU-G powders and magnet, prepared from the 1:1 homogeneous mixture of both powders. The measurements were performed at 120 °C.

Table 6: Magnetic properties of PECS samples, prepared at 670 °C. The measurements were performed at 120 °C.

Measured at 120 °C			
	B_r (T)	H_{ci} (kA/m)	$(BH)_{max}$ (kJ/m ³)
MQU-F	0.78	920	101
MQU-G	0.71	1190	87
MC1 sample	0.74	1060	95
Powder mixture	0.74	1050	94

This contradicts the findings provided by the microstructural investigation, since the results imply that a single magnetic phase is present in the sample, while the chemical analysis of the individual ribbons showed that the original compositions of the respective magnetic materials were preserved. This suggests that the measurement and the way it was conducted do not provide information on the local magnetic properties, assuming that the distinct parts with different properties exist in the sample. Therefore, the sample was cut into two parts, presumably composed of the original respective materials, as schematically presented in Fig. 48. The individual parts were measured with the permeameter and the results are shown in Fig. 49. The demagnetization curves belonging to the individual parts (dashed curves in Fig. 49) match the ones measured for the single component magnets, taking into account the 2 % uncertainty of the results obtained with the permeameter.

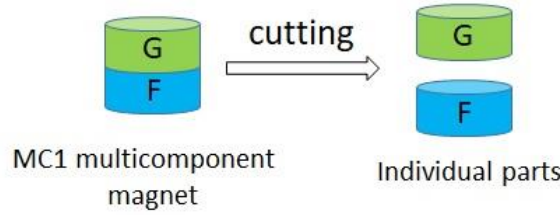


Figure 48: Cutting the MC1 multicomponent magnet into two parts.

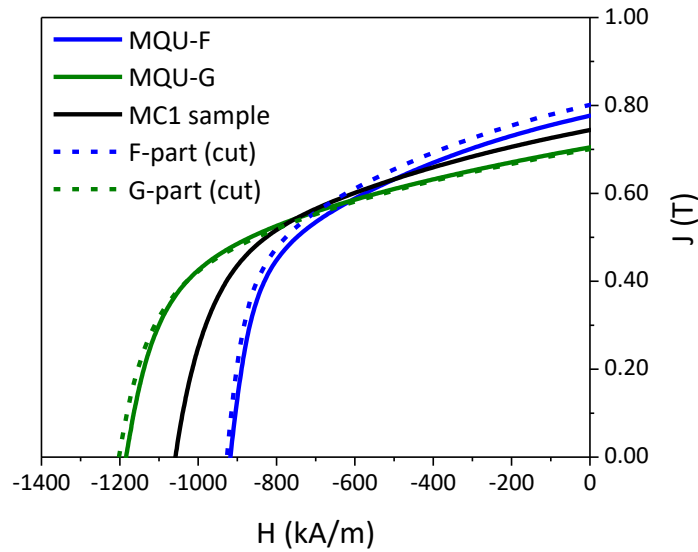


Figure 49: Demagnetization curves of the MC1 multicomponent magnet, single component magnets prepared from the MQU-F and MQU-G powders and individual parts obtained by cutting the multicomponent magnet in half. The measurements were performed at 120 °C.

To further prove that the demagnetization curve of the MC1 sample, as measured with the permeameter, is not due to the existence of a single magnetic phase formed during the manufacture of the multicomponent magnet, an additional experiment was performed. The single component MQU-F and MQU-G samples with their respective properties (see Fig. 47) were placed together in the configuration mimicking the MC1 sample and the net

magnetic properties of the as-assembled specimen were analyzed in order to demonstrate the averaging effect of the measuring device. The results shown in Fig. 50 confirm that when a sample is composed of two distinct Nd-Fe-B materials forming regions with different magnetic properties, the curve obtained with a permeameter does not provide straightforward information on the local properties. This is true regardless of the specimen being a single magnet or assembled from two individual magnets. The same overall properties were measured for the disc-shaped samples (MC1 multicomponent magnet and a sample assembled from the MQU-F and MQU-G magnets) with a defined geometry and a fixed volume ratio of a HRE-free and a Dy-containing material.

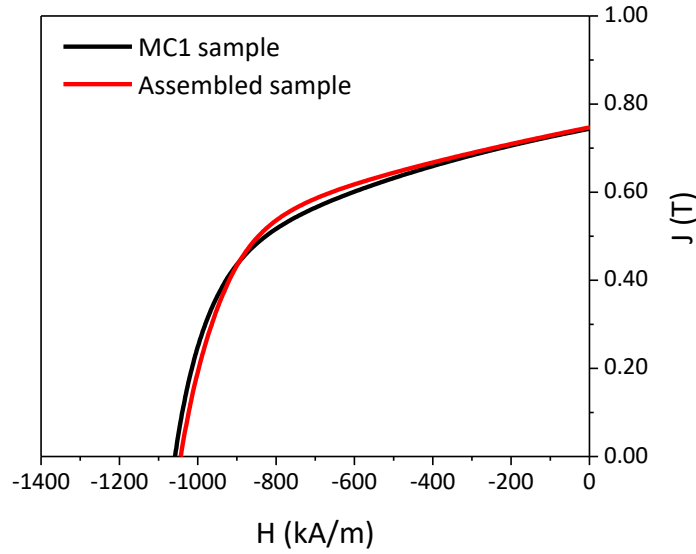


Figure 50: Comparison of the demagnetization curve of the MC1 multicomponent magnet and net magnetic properties of the single component MQU-F and MQU-G samples, measured together with a permeameter (assembled sample), demonstrating the averaging effect of the measuring device. The measurements were performed at 120 °C.

5.2.2 Two-step procedure (sample MC2)

The MC2 multicomponent magnet was manufactured from the dense MQU-F and MQU-G samples, prepared at their optimal PECS consolidation temperatures (650 and 670 °C, respectively) according to the procedure described in Section 4.4.2.2.

5.2.2.1 Microstructure and local chemical composition

SEM examination of the sample's polished cross-section was performed and the microstructure is shown in Fig. 51. As in the case of the MC1 sample, individual powder particles and the Nd-rich phase can be observed. The interface between both parts of the magnet was located by means of the EDS point analysis. In the BSE image, the interface can be distinguished by the Nd-rich phase forming a straight line that separates the two respective halves of the disc-shaped sample. EDS analysis was performed on the discrete areas of the ribbons adjacent to the interface (locations 1 – 8 in Fig. 51b) and the results are shown in Table 7. The values were corrected for the boron content (5.6 at %), which was not quantified. The oxygen content as measured with the EDS analysis (up to 4 at. %) was attributed to the surface oxidation. Similar to what was discerned for the

multicomponent magnet prepared from the raw powders, the local chemical compositions of the ribbons left of the interface match the composition of the MQU-F material, and no dysprosium was detected in this side of the sample. The compositions of the particles located on the right side correspond to the MQU-G material.

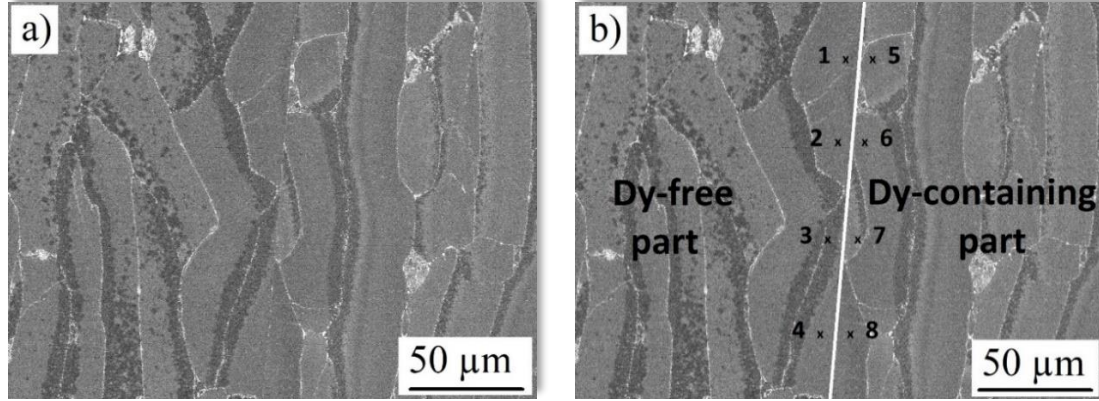


Figure 51: BSE image of the MC2 multicomponent magnet (a) and the same image with the highlighted interface between both materials and marked locations of the EDS point analysis (b).

Table 7: Chemical compositions of the interface ribbons (MC2 multicomponent magnet). Compositions of the respective powders are added for comparison.

Composition (at. %)						
	Fe	Co	Ga	Nd	Dy	B
1	75.4	5.4	0.0	13.6	0.0	5.6*
2	75.0	5.5	0.0	13.9	0.0	5.6*
3	75.5	6.1	0.0	12.8	0.0	5.6*
4	74.6	5.2	0.6	14.0	0.0	5.6*
MQU-F	73.6	6.6	0.6	13.6	0.0	5.6*
5	76.5	3.6	0.5	12.4	1.3	5.6*
6	75.9	3.6	0.8	12.7	1.5	5.6*
7	77.3	3.4	0.0	12.3	1.3	5.6*
8	75.9	3.5	0.8	12.7	1.5	5.6*
MQU-G	77.8	2.2	0.6	12.3	1.5	5.6*

5.2.2.2 Magnetic properties

Magnetic properties of the MC2 multicomponent magnet were measured with the permeameter. Fig. 52 shows the demagnetization curve of this sample and the curves belonging to the MC1 sample and single component MQU-F and MQU-G magnets.

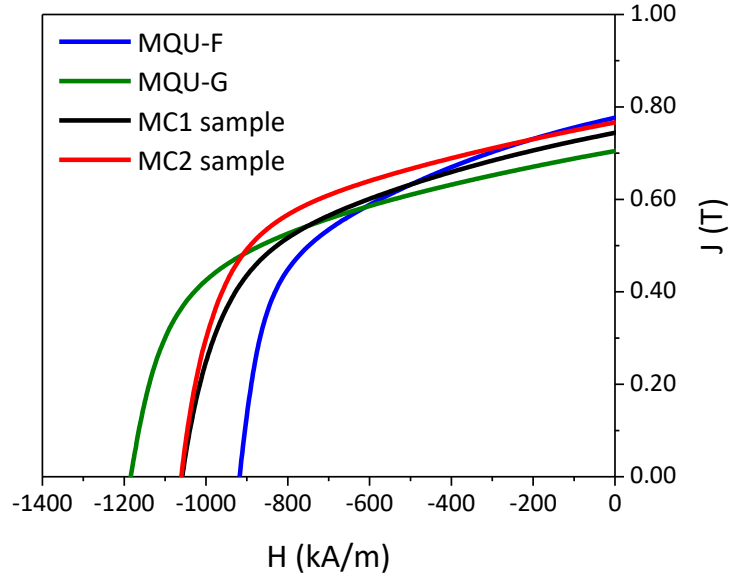


Figure 52: Demagnetization curves of the MC1 and MC2 multicomponent magnets and single component magnets, prepared from the MQU-F and MQU-G powders. The measurements were performed at 120 °C.

Comparison of the magnetic properties revealed that the intrinsic coercivity values of the multicomponent magnets, as measured with the permeameter, are the same (1060 kA/m). On the other hand, the measured remanence and maximum energy product of the MC2 sample are equivalent to the values of the single component Dy-free MQU-F sample, taking into account the uncertainty of the measurement (Table 8). This seemingly contradicts the previously established fact that the permeameter does not provide information on the sample's local magnetic properties. The results suggested that the second PECS process step, required to consolidate both magnets into a single magnet body, impacts the samples' original properties.

Table 8: Magnetic properties of PECS samples, measured at 120 °C.

	Measured at 120 °C		
	B_r (T)	H_{ci} (kA/m)	$(BH)_{max}$ (kJ/m ³)
MQU-F	0.78	920	101
MQU-G	0.71	1190	87
MC1 sample	0.74	1060	95
MC2 sample	0.77	1060	102

To evaluate the effect of the second PECS processing step on the magnetic properties of the individual materials, dense single component magnets were prepared from the MQU-F and MQU-G powders at their respective optimal consolidation temperatures. After

their properties were measured with the permeameter, the samples were PECS processed the second time, as described in Section 4.4.1. Demagnetization curves of the once- and twice-processed samples are shown in Fig. 53.

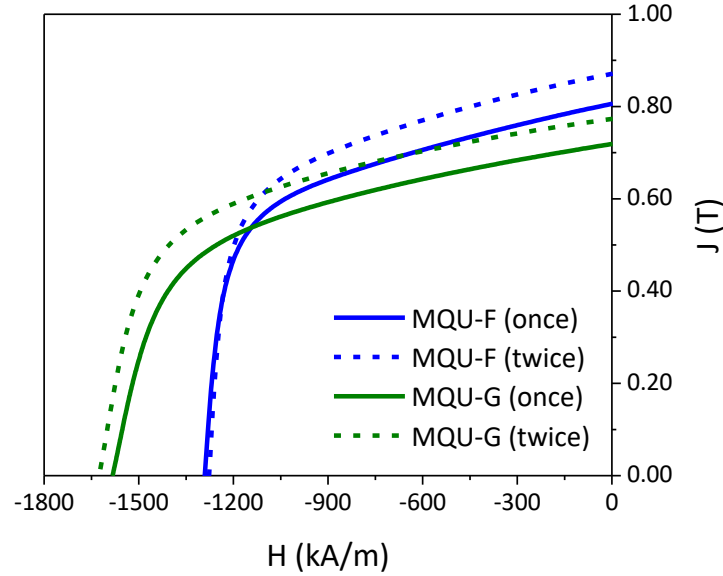


Figure 53: Demagnetization curves of the single component MQU-F and MQU-G samples, processed once (full curves) or twice (dashed curves) with the PECS technique. The measurements were performed at 70 °C.

The second PECS step increased the remanence of both samples by approximately 7 % (Table 9). Consequently, the maximum energy product was increased by 17 % in both cases. The intrinsic coercivity of the MQU-F sample was not affected. A slightly higher H_{ci} was measured for the MQU-G sample after the second PECS processing (1620 compared to 1580 kA/m), but the difference is smaller than the 2 % uncertainty of the measurement.

Table 9: Magnetic properties of once- and twice- processed single component magnets, measured at 70 °C.

	Measured at 70 °C		
	B_r (T)	H_{ci} (kA/m)	$(BH)_{max}$ (kJ/m ³)
MQU-F (once)	0.81	1290	115
MQU-F (twice)	0.87	1280	135
MQU-G (once)	0.72	1580	94
MQU-G (twice)	0.77	1620	110

Chapter 6

Discussion

6.1 Single Component Magnets

6.1.1 Melt-spun powders

Bulk magnets with good overall magnetic properties were prepared from the melt-spun powders with optimized PECS process parameters. In general, the Dy-containing compositions need slightly higher consolidation temperatures in order to reach high density [11]. The remanence peaked when the MQU-F and MQU-G powders were completely densified (at 650 and 700 °C, respectively), because B_r depends on the bulk density, volume fraction of the matrix $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains and on the grain alignment. Due to the isotropic nature of the melt-spun materials chosen for this study, the remanent magnetization is limited to approximately 0.8 T (one-half of the intrinsic saturation magnetization of the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase) in HRE-free hot-pressed Nd-Fe-B magnets. To preserve the excellent intrinsic coercivity (1680 kA/m) of the original HRE-free MQU-F material, a short (1 minute of holding time) PECS consolidation step at 650 °C was used. No discernible grain growth was observed in the dense sample with the SEM technique. In contrast, the significant reduction in H_{ci} (69 %) of the MQU-F sample prepared at higher temperature (800 °C) can be associated with the pronounced grain growth seen in Fig. 35b. Other authors have described a similar two-zone structure in the PECS-processed melt-spun ribbons. Ma et al. attributed the abnormal grain growth to the effect of the local high temperature generated at the particle boundaries during the PECS process [110]. Liu et al. argued that the fine grain zones correspond to the interior of the ribbons [30]. However, the results of the microstructural investigation of the over-processed MQU-F material contradict the previously published hypothesis. It appears that the coarse grain zones observed in this sample are mostly located on one side of the ribbons only, with a much finer microstructure on the other side. This strongly implies that the difference in the microstructure of the wheel side / free side of the as-spun ribbons results in a noticeable grain growth predominantly on one side of the ribbons during the high-temperature PECS consolidation. Similar results were obtained with the Dy-containing MQU-G powder, although the grain growth observed in the over-processed sample prepared from this material appeared to be less pronounced.

The coarsening of the microstructure at higher PECS temperatures also affects the otherwise excellent high-temperature performance of both materials. The more pronounced grain growth of the Dy-free MQU-F results in larger absolute values of β and α (-0.72 and -0.21 %/°C, respectively) compared to the MQU-G sample (-0.56 and -0.14 %/°C, respectively, Table 3).

Another factor that can contribute to the reduction of the intrinsic coercivity is the loss of the Nd-rich grain-boundary phase, which is squeezed out of the powder bed when the PECS processing temperature substantially exceeds the optimal value (≈ 800 °C). Decreased volume ratio of this phase inhibits the pinning of the domain walls at the grain boundaries in the regions with fine microstructure and increases the magnetic exchange interactions between two adjacent $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. Nd-rich grain-boundary phase in an ideal system also helps reduce defects (regions with altered atomic arrangement and lower magnetocrystalline anisotropy) close to the grain boundaries, which lowers the possibility for nucleation of reverse domains [11], [25].

6.1.2 Gas-atomized powders

6.1.2.1 MQP-S

Composition of the alloy is important for the development of appropriate microstructure during the solidification of the Nd-Fe-B melt. In the MQU-F and MQU-G materials with TRE-rich compositions, the non-equilibrium conditions achieved by rapid cooling of the liquid below the peritectic temperature (1181 °C, Fig. 54) suppress the Fe precipitation. Excess Nd improves the glass forming ability through enhancement of the undercooling effect [53]. In contrast, the schematic equilibrium phase diagram predicts the formation of Fe and $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase upon cooling of the Nd-lean Nd-Fe-B alloys [22]. In the MQP-S material, the glass forming ability is enhanced with the addition of Zr and Ti to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase [53], [135].

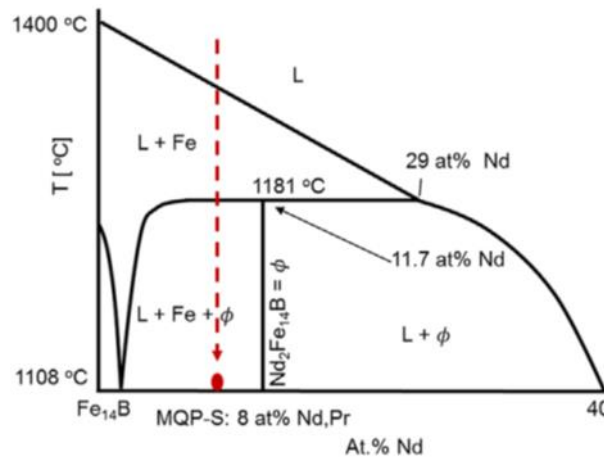


Figure 54: Schematic view of the pseudo binary Nd-(Fe_{14}B) phase diagram, where Φ is the desired hard magnetic phase ($\text{Nd}_2\text{Fe}_{14}\text{B}$) and L is the liquid phase. This is a schematic visualization focusing only on the phase formations around the peritectic point (1181 °C) of the phase diagram (adapted after [22]). The red line corresponds to the Nd content of the MQP-S material.

The densification behaviour of the commercial TRE-lean gas-atomized MQP-S powder reflects its under stoichiometric composition. In this material, Zr is substituting for some of the Nd atoms in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystal structure [135]. As a result, no Nd-rich liquid phase that would assist the sintering process is formed. The low Nd content of this alloy hinders the sintering kinetics and inhibits the grain growth during processing [111]. Zr is also known to help minimize the grain growth [136]. While the grain size of the porous

magnet prepared with the PECS technique at 800 °C is favourable, the lack of the Nd-rich grain-boundary phase has a detrimental effect on the development of coercivity.

The magnetic properties and microstructure of samples prepared from the MQP-S powder show that this material is not suited for the PECS processing due to its low TRE content. However, although initially intended for bonded magnets, it has recently been demonstrated that a net shape permanent magnet with good density and magnetic properties can be manufactured from this powder using the Selective Laser Melting technique [127].

6.1.2.2 GA-34

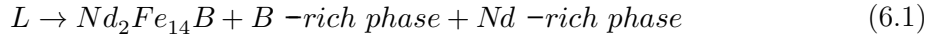
To reach high density at a relatively low temperature in order to avoid the grain coarsening during consolidation of the Nd-Fe-B powders with the PECS technique, materials with high TRE content are favourable [110]. The high Nd content (34 wt. %) of the HRE-free GA-34 gas-atomized powder resulted in high density of the sample when the material was consolidated at 700 °C.

The volume fraction of the liquid Nd-rich phase increases with the increase of the PECS temperature whereas its viscosity decreases. An almost linear increase in B_r values with the processing temperature was measured for the PECS samples even after the maximum density was reached at 700 °C (Fig. 34). This corresponds to the increase of the volume ratio of the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase after the loss of a fraction of the Nd-rich phase, which solidified on the graphite punches. Analogous to the melt-spun ribbons, loss of the Nd-rich phase coincides with a decrease in the H_{ci} values. Due to the presence of $\alpha\text{-Fe}$, the excess Nd that would otherwise precipitate in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystal lattice is consequently precipitated as a secondary non-magnetic Nd-rich phase. Compared to the flake-like powder, more Nd-rich material was squeezed out of the powder bed during consolidation of this spherical powder due to the higher percentage of Nd in the original alloy and presence of Fe precipitates.

The low intrinsic coercivity of the powder, as well as the dense sample prepared at 700 °C, can be attributed to the microstructural characteristics, as observed with the SEM technique. The presence of coarse hard magnetic grains and Fe precipitates, which is an undesired soft magnetic phase, is a consequence of the insufficient cooling rate experienced by the larger spheres during the atomization process. This is detrimental to the development of the coercivity, since the iron grains act as nucleation sites for the reverse domains, which inevitably leads to the reversal of magnetization of the large $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. In addition, the remanence of the isotropic $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based materials directly depends on the volume fraction of the hard magnetic phase. Formation of the Fe grains therefore affects the overall magnetic performance of a dense magnet prepared from such a powder. In addition to the low room-temperature H_{ci} , the values of the coefficient β for the powder and dense magnet prepared at 700 °C (-0.61 %/°C for both samples) are inferior to the values of the optimally processed melt-spun ribbons. This is not surprising, since the powder contains a significant proportion of the coarse-grained particles.

6.1.2.2.1 Heat treatment

Short heat treatment regime (10 minutes at 650 °C) improves H_{ci} of the powder and, to a lesser extent, of the dense samples (Table 3). The mechanism behind the coercivity increase with heat treatment is not clear at this point. According to the phase diagram of the Nd-Fe-B ternary system for Nd-rich compositions [40], the eutectic reaction



occurs during solidification of the alloy in the gas atomization process. Because the melt cools very fast, the reaction time is short and the equilibrium state is not reached. Heat treatment could facilitate elements diffusion between the Nd-rich phase and the epitaxial layer of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain, as proposed by Zhou et al. who studied the effect of annealing on the magnetic hardening of sintered Nd-Fe-B magnets [137]. Additional experiments would have to be performed to confirm this hypothesis.

The best as-consolidated PECS sample has a substantially higher intrinsic coercivity than the untreated powder (625 and 165 kA/m, respectively), which indicates that a similar mechanism may take place during the consolidation in the PECS furnace. In addition, the Nd-rich phase is liquid at 700 °C during the PECS processing and it can wet the grain boundaries through capillary action, thus reducing the exchange interactions between the grains of the matrix phase. The effect may be significant during consolidation, but is less likely to cause a substantial increase in H_{ci} during the heat treatment due to the low heat treatment temperature (below the eutectic temperature of the Nd-Fe-B system at ≈ 680 °C [22]) and the short time of exposure. This explains the higher H_{ci} of the as-consolidated (10 %) and heat-treated (18 %) PECS samples, compared to the heat-treated raw powder.

6.1.2.2.2 High-temperature stability

As discussed in Section 2.2.4.3, Sellers et al. showed that the Nd-rich gas-atomized Nd-Fe-B powders experience reversible loss of hard magnetic properties at 150 °C in air. The authors argued that they are inappropriate for the preparation of bonded magnets, since this temperature is reached during magnets' production and because their magnetic properties can only be recovered with heat treatment at 650 °C, which is not possible due to the addition of a polymer [62], [66]. Conforming with these findings, magnetic properties of the GA-34 powder were also substantially degraded after exposure to high temperature. An important advantage of the PECS-processed dense magnet prepared from the GA-34 material, compared to the raw powder, is its high-temperature stability. The sample proved to be stable at temperatures up to 200 °C in air for a period of 15 minutes with no effect on the magnet's room-temperature performance. The reduction of the surface area, achieved with compaction of the powder particles into a dense bulk magnet, hinders the surface nucleation reversal mechanism, supposedly responsible (according to Sellers et al.) for the reversible loss of hard magnetic properties of raw powders.

6.1.2.2.3 Grain size refinement

Separating the as-atomized powder into fractions smaller than 50 and 20 μm with sieving removed the larger particles containing coarse $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains and Fe precipitates. Consequently, the intrinsic coercivity of the PECS magnet prepared from the < 20 μm fraction was effectively increased by more than 50 % compared to the sample prepared from the unsieved powder. Improved uniformity of the microstructure is reflected in the smooth demagnetization curve with a higher degree of squareness (Fig. 39). The temperature coefficients β and α of magnets prepared from the sieved fractions were also improved, which corresponds to the observed differences in the microstructure: both bulk magnets prepared from the sieved fractions have a significant volume ratio of fine-grained spheres, thus proving that the PECS technique can effectively restrain the grain growth during powder consolidation. The absolute value of β was decreased from -0.61 to -0.53 %/°C for the smallest powder size. Following the observed correlation between the grain size and β value, additional improvement in the high-temperature performance can be expected with further refinement of the microstructure.

Although sieving of the gas-atomized powder is a simple way to obtain a fine powder fraction with a microstructure appropriate for PECS processing, only 20 wt. % of the powder used in this study contained spheres smaller than 20 μm . While some of those spheres were nanostructured, others contained coarser grains, which makes this approach impractical. A better way to achieve a fine microstructure would be to change the quenching characteristics of the liquid melt during the gas atomization. Kramer et al. proposed the addition of TiC in order to obtain a nanograined and amorphous powder [63]. While this is a good approach to improve the glass forming ability and reduce the Nd content at the same time, it can also be used in the Nd-rich compositions. TiC addition also slows the grain growth during hot pressing [93]. Optimizing the composition of the alloy will have to be considered in future research in order to adapt the gas atomization process for the production of the Nd-Fe-B powders with desired characteristics. Nevertheless, the results showed that the fast consolidation at relatively low temperatures hinders the grain growth and retains the magnetic properties of the initial powder.

6.1.3 HDDR powder

Bulk magnets were prepared from the HDDR MF-18P powder with the PECS technique. The main purpose of the investigation was to find the optimal PECS processing conditions for achieving the maximal density with this material. Therefore, although the material is anisotropic, the powder particles were not aligned prior to the consolidation and the samples were magnetically isotropic. As can be seen in Fig. 42, the remanence of the bulk HDDR magnets increased as their density was increased, either by raising the PECS temperature or by using longer holding times. When the temperature exceeded 850 $^{\circ}\text{C}$, B_r was reduced significantly. According to Li et al., this can be attributed to the abnormal grain growth: they observed grains several tens of micrometres in size in their HDDR samples consolidated at 900 $^{\circ}\text{C}$. The authors argued that, at high PECS temperatures, the grains preferentially grow in the direction perpendicular to pressing due to the large volume fraction of the liquid phase [117]. This effect is most probably even more pronounced when the holding time is prolonged. Accordingly, B_r of the MF-18P sample consolidated at 900 $^{\circ}\text{C}$ and with 10 minutes of holding time was reduced by about 25 % compared to its maximum value.

6.1.3.1 Coercivity evolution

The intrinsic coercivity of the as-prepared bulk HDDR magnets highly depends on the PECS consolidation parameters (Fig. 42c), even more so than in the case of the melt-spun ribbons (Fig. 34c): H_{ci} of the low-density nanostructured samples prepared from the rapidly solidified powders (MQU-F and MQU-G) is comparable to the values of the initial powders and special care has to be taken to make sure that the processing temperature is low enough to prevent the grain growth, but at the same time high enough to reach good density.

At the lowest consolidation temperature (700 $^{\circ}\text{C}$), the intrinsic coercivities of the PECS MF-18P samples prepared with 1 minute and 10 minutes of holding time (910 and 780 kA/m, respectively) were lower than the value of the raw powder (1170 kA/m, Fig. 42c). Increase in the PECS temperature further decreased H_{ci} of the samples prepared with shorter holding times, until the trend changed at 770 $^{\circ}\text{C}$ and the H_{ci} quickly increased to 1020 kA/m at 800 $^{\circ}\text{C}$. The intrinsic coercivity peaked at 850 $^{\circ}\text{C}$ (1190 kA/m). However, H_{ci} of the samples prepared with longer holding times steadily increased, until the intrinsic coercivity peaked at the same temperature and reached the same value as the 1-minute sample. After that point, H_{ci} rapidly decreased and the 10-minutes sample prepared at

900 °C retained less than 40 % of the maximum value. Corresponding with the trend observed for the remanence, this decrease is explained with the abnormal grain growth.

The mean grain size of the HDDR MF-18P powder is 350 nm [118]. While it is not possible to quantify the extent of the grain growth during the PECS consolidation without a detailed microscopic study, it can be concluded from the results that, at least below 850 °C, the contribution of the grain growth is not the major factor controlling the development of the coercivity, otherwise the trend would be reversed and a decrease in H_{ci} would be observed with an increase in temperature. In fact, Takagi et al. reported that the dense HDDR samples with high H_{ci} had larger grains than the samples with low H_{ci} , prepared at lower temperature [118]. The authors observed a reduction of coercivity during consolidation and coercivity recovery by heat treatment, but did not establish any correlation with the changes in the microstructure.

Intrinsic coercivity of the HDDR-type materials is strongly correlated to the presence and distribution of the Nd-rich phase. Powders, as well as hot-pressed and PECS-consolidated samples, were studied in the past and the highest H_{ci} values were often reported for samples with continuous, homogenously distributed layers of the grain-boundary phase [75], [77], [85].

The observed trend of the coercivity dependence on the temperature and holding time, as described above, can therefore be explained with the redistribution of the Nd-rich phase, which is liquid during the PECS consolidation. Copper and aluminium, added to the MF-18P material in a form of a NdCuAl eutectic alloy, reduce the melting point of the grain-boundary phase [45], [129] and the latter was found to be amorphous in the initial powder, as well as in the PECS-processed and heat-treated samples [118]. At the initial stage of the PECS consolidation or at low consolidation temperatures (700 °C), the applied pressure and the capillary action cause the liquid phase to redistribute from the grain boundaries to the triple grain and particle junctions, where the Nd-rich pools are formed. Similar Nd-rich regions were also observed in the low-coercivity PECS-sintered anisotropic magnets prepared from the jet-milled powders [104]. Lack of the Nd-rich phase at the grain boundaries decreases H_{ci} by increasing the exchange interactions between the matrix grains. When the temperature is increased and the consolidation time is kept short, the liquid phase becomes less viscous and a larger fraction is squeezed from the grain boundaries, thus the further reduction of H_{ci} of the 1-minute samples processed at 700 - 770 °C. At temperatures near 800 °C and higher or when the holding time is increased, the capillary action causes the liquid phase to (at least partially) redistribute along the grain boundaries from where it condensed at the initial stages of the densification process and the intrinsic coercivity is increased.

6.1.3.2 Heat treatment and coercivity recovery

EDS analysis of the Nd-rich pools observed in the dense PECS sample (Fig. 44a) with relatively low H_{ci} (≈ 800 kA/m) was performed. In addition to the Nd ($\approx 70 - 75$ at. %) and smaller amount of Cu and Fe, oxygen was detected, but the content did not exceed 18 at. % (Table 4). The deviation in the chemical composition between the three pools analysed corresponds with the fact that several minor phases can be present in the grain-boundary phase, including different types of oxides [2]. The oxygen content can be attributed to the surface oxidation and presence of smaller oxide grains. Due to its metallic nature, the Nd-rich phase liquefies during the heat treatment and redistributes along the grain boundaries, leaving an empty space in its place. This results in a porous structure in the vicinity of the particle junctions where a large quantity of the Nd-rich phase was concentrated in the as-consolidated sample. Such a structure can be seen in Fig. 55 left. It gives the appearance of an etched surface, unlike the surrounding area which is smooth. In

addition to the porosity caused by the liquid phase redistribution, the porous and brittle regions of the material can collapse under the applied force during metallographic polishing of the sample prior to the SEM analysis and even larger pores are left in their place, such as the one shown in Fig. 55 right. The heat treatment did not affect the samples' density or B_r values.

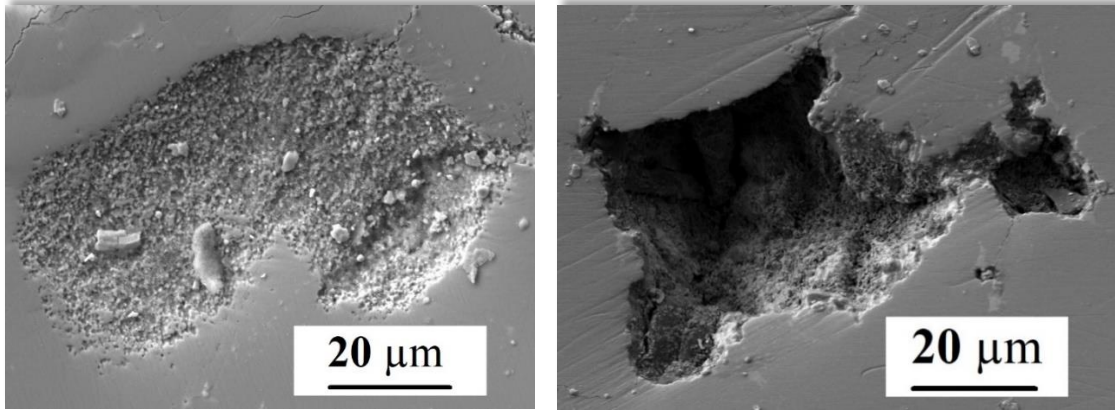


Figure 55: Secondary electron images (SEI) of pores, observed on the polished cross-sections of the PECS samples consolidated at 790 °C with 1 minute of holding time and heat-treated for 10 minutes at 750 °C (left) and 3 hours at 900 °C (right). The smooth surfaces belong to the original powder particles and the pores are located at the particle junctions.

The results of the heat treatment study indicate that the grain growth does contribute to the observed trend of the coercivity development during PECS consolidation. H_{ci} of the low-coercivity sample prepared at 900 °C (430 kA/m) was not recovered with the heat treatment (Fig. 43), probably because it is limited by the large grains that grew during the high-temperature consolidation. Similarly, H_{ci} of the best sample prepared at 850 °C (1190 kA/m) could not be improved any further with the heat treatment and its coercivity can be attributed to the good distribution of the grain-boundary phase. The highest H_{ci} of the heat-treated PECS sample consolidated at 790 °C (1280 kA/m) is most likely the result of the limited grain growth during the PECS processing and improved distribution of the grain-boundary phase achieved with the post-consolidation heat treatment.

When considering the PECS as a potential technique for the large-scale production of Nd-Fe-B magnets, an important requirement that has to be met is high density of the final product. Since the heat treatment is necessary to reach high H_{ci} in the HDDR bulk samples as this study and the previous one by Takagi et al. ([118]) revealed, it is not necessary to use high PECS temperatures or long consolidation times, as long as the bulk sample is dense.

6.2 Multicomponent Magnets

6.2.1 One-step procedure (sample MC1)

Single component magnets prepared from the MQU-F and MQU-G powders at the same PECS temperature that was used to manufacture the MC1 multicomponent magnet (670 °C) have good magnetic properties. The remanence of the MQU-F material, as well as the intrinsic coercivity of the MQU-G material, reach their maximal values (0.78 T and 1180 kA/m, respectively) when the powders are consolidated at this temperature (Fig. 45).

In terms of the local magnetic properties of a multicomponent magnet where the high B_r of the Dy-free material and the high H_{ci} of the Dy-containing material are combined, the results are promising, presuming that the properties can be retained when the powders are consolidated together in a single step. For that, one important condition needs to be fulfilled: the compositions of the respective materials must be preserved, since the composition is an important factor determining the magnetic properties. To achieve this, the diffusion of dysprosium from the Dy-containing part of the magnet into the Dy-free part must be prevented.

6.2.1.1 Dysprosium diffusion

The chemical compositions of the discrete areas of the individual powder particles, as determined with the EDS point analysis, match the compositions of the respective starting powders to a good extent (Table 5). The material is nanostructured, while the analytical spatial resolution is limited by the interaction volume, which is close to $1 \mu\text{m}^3$. Therefore, the compositional fluctuation between the individual locations on each side of the interface is attributed to the differences in the local distribution of the grain-boundary phase and variation in the average $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain size.

In the conventional sintering, for the heat treatment of the sintered magnets and for the grain boundary diffusion process discussed in Section 2.2, high temperatures and long processing times are used. During the treatment above the eutectic temperature of the Nd-Fe-B system ($\approx 680^\circ\text{C}$, [22]), the Nd-rich phase melts and the surfaces of the matrix grains are dissolved in the liquid phase, according to the phase diagram of the Nd-Fe-B system [40]. If the HRE elements are present in the liquid phase, they can diffuse along the grain boundaries and afterwards solidify as $(\text{Nd,Dy})_2\text{Fe}_{14}\text{B}$ mixed phase in the grain regions adjacent to the grain-boundary phase and form the so-called core-shell structures. When a HRE source, such as a HRE-coated surface of a sintered magnet is present (GBD process), a diffusion gradient can be observed in the sample after the heat treatment [39]. Similarly, in a system like a multicomponent magnet having HRE-rich regions, a diffusion profile might form. Alternatively, the direct lattice diffusion from the source results in an almost planar diffusion if the matrix grains are small and the processing time is sufficiently long or / and the temperature sufficiently high [138].

In the hot pressing techniques like PECS, the average sample temperatures are much lower than in the conventional sintering or in the high-temperature heat treatment steps. Diffusion is therefore restricted to much shorter distances and when the processing time is kept short, the lattice diffusion is suppressed and the diffusion proceeds only along the grain boundaries [138].

In the MC1 multicomponent magnet, no dysprosium concentration gradient was observed and no dysprosium was detected with the methods used in the part of the magnet corresponding to the original Dy-free MQU-F material, even in the vicinity of the interface between both materials. The grain boundary diffusion that might take place during consolidation is therefore prevented or limited to the extent that it was not detected with this investigation.

6.2.1.2 Local magnetic properties

Magnetic properties of the MC1 multicomponent magnet were characterized with the permeameter. The investigation did not provide information on the local magnetic properties when the whole magnet was measured. This is correlated with the basic working principles and the design of the measuring system.

To perform the measurement, the sample is placed between the poles of the electromagnet that generates the external field. Magnetization of the sample, which

represents the sum of magnetic moments per unit volume, is determined by means of a measuring coil encircling the sample. At zero applied field, the magnetization of a magnetically saturated sample (remanent magnetization) composed of two hard magnetic materials depends on the volume fraction of the individual parts and the materials' respective magnetization values. For that reason, B_r of the multicomponent magnet as provided by the permeameter is an arithmetic mean of both materials.

The same reasoning can be used to explain H_{ci} of the multicomponent magnet, as measured by the permeameter. The intrinsic coercivity is equivalent to the strength of the external field that is required to reduce the magnetization of the specimen to zero. When the reverse field is applied on the sample during the measurement, the magnetization of each individual part of the magnet is gradually reduced. At a certain value of the field, the magnetization of the low-coercivity part is reduced to zero, while the high-coercivity part is still partially magnetized. Because the net magnetization still exists in the sample, the reverse field continues to increase. This further decreases the magnetization of the high-coercivity part, but the applied field also acts on the low-coercivity part, trying to increase the magnetization in the opposite direction. When the bulk magnetization as determined with the measuring coil is zero, the high-coercivity part remains partially magnetized.

A different strategy had to be taken to characterize the magnetic properties of the respective parts of the magnet. The sample was cut in half in order to measure each part separately. The results showed that the properties of the individual parts are a close match to the properties of the corresponding single component magnets. This complemented the results of the microstructural study: two distinct regions with their respective chemical compositions and magnetic properties exist in the multicomponent magnet.

6.2.2 Two-step procedure (sample MC2)

Two dense isotropic single component magnets with different magnetic properties and chemical compositions were prepared from the Dy-free and Dy-containing melt-spun powders. The samples were polished before they were placed in the graphite die and PECS processed a second time. The second consolidation step successfully fused the two parts into a single magnet body. The fine microstructure of the melt-spun materials was preserved in the multicomponent magnet. No changes in the chemical composition of the respective parts were detected with the EDS point analysis. By all appearances, the MC2 multicomponent magnet did not look any different from the other dense samples prepared directly from the melt-spun powders. Its polished cross-section appeared smooth and homogenous, just like the cross-section of the multicomponent magnet prepared from the raw powders (Fig. 56).

The interface between both halves of the sample, as observed with the SEM, was straight (Fig. 51), which reflected the flat surfaces of the original pre-compacted parts. This proved that the shape of the interface can be controlled by the geometry of the individual parts, at least to a certain extent. When the uniaxial pressure is applied on the disc-shaped parts during heating, the force is evenly distributed over the surface and the plastic deformation due to the compression stress and increase in temperature does not significantly change the shape of the initial parts, providing that the material is constrained in the graphite die in all other directions. For parts with a complex geometry, the plastic deformation might be significant.



Figure 56: Polished cross-sections of the multicomponent magnets prepared from the raw powders (left) and pre-consolidated parts (right). The shining part on the right-hand side is an artifact due to the reflection of the illuminating spots.

Compared to the multicomponent magnet manufactured directly from the powders, higher B_r and consequently $(BH)_{max}$ were measured for the MC2 magnet, although the same amount of the MQU-G and MQU-F material was used in both cases. The increase in B_r corresponded with the 7 % increase in the remanence, measured for the individual dense MQU-F and MQU-G single component magnets after they were PECS processed the second time (Table 9). In general, the remanence depends on the exchange interactions between the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, volume fraction of the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and crystallographic alignment of the grains. Redistribution of the grain-boundary phase during the second processing could increase the remanence by increasing the exchange interactions between the grains, but this would have a negative impact on the intrinsic coercivity, which was not observed. Since the samples were dense and no liquid phase was squeezed out of the material during processing, the most probable explanation for the increased remanence is a partial c -axis alignment of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. Because the magnet is not completely constrained by the walls of the graphite die, the plastic deformation of the dense nanostructured sample can induce an anisotropy in the magnet, although the effect is more pronounced when the sample has additional freedom to expand in the direction perpendicular to pressing [87].

6.3 Questions that Remain Open

Using a fast consolidation technique like Pulsed Electric Current Sintering is currently the best practical approach to consolidate the polycrystalline Nd-Fe-B magnetic powders into dense bulk permanent magnets without deteriorating the material's original magnetic properties. Those properties reflect the microstructure of the material and therefore highly depend on the chemical composition of the alloy and on the powder manufacturing route.

When considering a specific type of Nd-Fe-B powders as a possible candidate for PECS processing, an important condition that has to be met is the ability of the powder manufacturing technique to be adapted for the production of the TRE-rich, fine-grained powders. Melt-spun Nd-Fe-B nanostructured powders are today widely used for the production of isotropic, as well as the anisotropic dense magnets. Gas-atomized powders, on the other hand, are seldom used for magnetic applications. One reason for this is the inherent inability of the gas atomization process to reach cooling rates comparable to those achieved with the melt-spinning. Another reason is the high-temperature instability of the

gas-atomized powders with TRE-rich compositions. The results presented in this work prove that the high-temperature instability is overcome when such a powder is consolidated into a bulk magnet with the PECS technique. In addition, PECS processing significantly increases the intrinsic coercivity of the material. Insufficient cooling rates achieved with the gas atomization process, on the other hand, are a major issue and result in an inhomogeneous microstructure with α -iron precipitates and large $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. Insufficient cooling can be compensated with the compositional modification of the alloy. This is achieved with the addition of Ti and Zr in the commercial MQP-S powder. The under stoichiometric composition of this material makes it unsuitable for the PECS processing, but using the same approach for the TRE-rich compositions might be possible and the glass forming ability could be even more pronounced with the addition of extra Nd.

The hydrogenation-disproportionation-desorption-recombination-processed (HDDR) Nd-Fe-B powders are commercially used for the production of bonded magnets. The HDDR process is an interesting approach to convert a microcrystalline material into an anisotropic polycrystalline powder with the grain size close to the single-domain limit for the $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based materials. In spite of that, the characteristic intrinsic coercivity values of the HDDR powders are much lower than what would be expected from their grain size, as discussed in Section 2.2.4.4. This limits the potential use of such a material in the high-performance applications and the question remains if the HDDR process can be perfected in order to reach its full potential. Nevertheless, the PECS approach offers the possibility to consolidate such a material into bulk anisotropic permanent magnets without degrading its magnetic properties.

6.4 Perspectives for the Multicomponent Magnet Approach

This work showed that the isotropic magnets with locally different magnetic properties (multicomponent magnets) can be manufactured from the melt-spun powders with the PECS technique. Although simple two-layer disc-shaped samples were prepared, different arrangements of the Dy-free and Dy-containing materials can be designed according to the intended application, with the aim of minimizing the use of the HRE elements.

For the energy conversion devices like traction motors for electric vehicles or wind turbines, highly anisotropic magnets are needed to provide a sufficiently strong magnetic field. Such magnets can be prepared from the jet-milled powders with the PECS technique at much lower temperatures than with the conventional sintering (Section 2.2.5.3.1). Starting from two powders with different compositions, a multicomponent anisotropic magnet could be manufactured. It is unclear at this point if the post-consolidation heat treatment, required to improve the low magnetic properties of the as-prepared PECS magnets, can be performed without affecting the chemical compositions of the respective parts. However, it is known from the GBD process that the penetration depth of the HRE elements is limited to a few millimetres from the surface, even when a HRE-based material with low melting point is used as a HRE source [38]. This makes it unreasonable to expect a significant redistribution of Dy (or Tb) into the HRE-free part of the magnet during the heat treatment, especially in a larger multicomponent magnet.

Alternatively, anisotropic multicomponent magnets could be manufactured in a two-step procedure from the hot-deformed magnets, prepared from the melt-spun powders. Such a multicomponent magnet would combine the excellent room-temperature intrinsic coercivity of a nanostructured Dy-containing material, high magnetic anisotropy of the hot-deformed magnets and improved overall performance due to the minimized use of the HRE elements. This study showed that a short, low-temperature PECS process is adequate

to consolidate two magnets into a single magnet body without deteriorating the initial properties of the respective materials.

Chapter 7

Conclusions

Three different types of polycrystalline Nd-Fe-B powders (melt-spun, gas-atomized and hydrogenation-disproportionation-desorption-recombination-processed) were considered as potential candidates for the manufacture of magnets with locally different magnetic properties (multicomponent magnets). Pulsed Electric Current Sintering (PECS) technique was chosen for the preparation of dense isotropic magnets. PECS process parameters were optimized for each powder in order to prevent the deterioration of the materials' respective magnetic properties during consolidation and find a suitable combination of powders that could be processed together in a single step.

The hydrogenation-disproportionation-desorption-recombination-processed MF-18P material displayed a strong dependence of the magnetic properties, most notably the intrinsic coercivity, on the PECS process parameters. The maximal density was reached at consolidation temperatures close to 800 °C when the holding time was one minute or at ≈ 750 °C when the holding time was prolonged. The intrinsic coercivity peaked at 850 °C and was significantly decreased when the temperature deviated from the optimal value. Post-consolidation heat treatment improved the low intrinsic coercivity of the dense sample prepared at 790 °C (from 800 to 1280 kA/m) and the value surpassed H_{ci} of the initial powder (1170 kA/m). Microscopic investigation of the as-consolidated and heat-treated samples revealed a correlation between the distribution of the Nd-rich phase and the coercivity reduction during consolidation and coercivity recovery with heat treatment. When the material is densified with the PECS technique, the Nd-rich phase liquefies and agglomerates in the triple particle junctions. Upon heat treatment, the liquid phase redistributes along the grain boundaries, which increases the intrinsic coercivity by reducing the magnetic exchange interactions between the Nd₂Fe₁₄B grains.

The two gas-atomized powders chosen for this study displayed markedly different densification behaviors. The MQP-S material could not be successfully densified at PECS temperatures up to 900 °C. This was attributed to the under-stoichiometric composition of this material with respect to the Nd₂Fe₁₄B hard magnetic phase. Consequently, no secondary Nd-rich phase that would assist in the sintering process was observed with the SEM investigation.

On the other hand, the Nd-rich gas-atomized powder performed much better and a novel type of Nd-Fe-B magnet was prepared from this material. The intrinsic coercivity of the dense sample manufactured at 700 °C (625 kA/m) was much higher than the value of the initial powder (165 kA/m), even after the latter was heat-treated in order to increase its H_{ci} (565 kA/m). In addition, the high-temperature instability of the powder that results in a significant degradation of the hard magnetic properties when the material is exposed to 150 °C in air was effectively overcome with compaction of the powder into a bulk magnet. Microstructural investigation of the powder and dense sample revealed an inhomogeneous microstructure with matrix grains ranging up to several micrometres in size and significant amount of iron precipitates, mostly observed in the larger spherical particles that experienced slower cooling rate during the gas atomization. The material was sieved to smaller fractions in order to obtain a powder with a finer microstructure. The intrinsic coercivity of the PECS sample prepared from the fraction with particles smaller

than 20 μm was increased by more than 50 % compared to the sample prepared from the unsieved powder. The results showed that bulk magnets can be prepared from the gas-atomized powders with the PECS technique, but their magnetic properties reflect the unfavourable microstructural features of the material. In order to adapt the gas atomization process for the production of the Nd-Fe-B powders with desired characteristics, the composition of the alloy must be modified in order to change the quenching characteristics of the materials.

The best results were achieved with the nanostructured Dy-free and Dy-containing melt-spun powders. Dense samples were prepared from these powders at 650 and 670 $^{\circ}\text{C}$, respectively, without degrading their original magnetic properties. Based on the excellent room-temperature intrinsic coercivity of the Dy-containing material (2080 kA/m) and high remanent magnetization of the Dy-free powder (0.82 T), as well as the materials' similar optimal consolidation parameters, the nanostructured powders were chosen for the manufacture of the multicomponent magnets.

Two different approaches were taken to prepare the magnets with locally different magnetic properties and the same amount of the Dy-free and Dy-containing material was used each time. The first sample was manufactured directly from the raw powders at 670 $^{\circ}\text{C}$ in a single consolidation step. The second sample was manufactured from the previously prepared single component magnets by placing one magnet on top of the other and applying an additional PECS processing step in order to consolidate both parts into a single magnet body. Microstructural investigation of the samples' polished cross-sections was performed. The results revealed that the fine microstructures of the melt-spun powders are preserved in the multicomponent magnets. In both cases, the interface between the initial materials could not be distinguished from the backscattered images and it was located with the help of the EDS point analysis. In case of the sample prepared from the respective pre-compacted magnets, the interface was a straight line, corresponding with the flat polished surfaces of the initial parts. Analysis of the local chemical compositions of the powder particles adjacent to the interface did not reveal any compositional changes, proving that the initial materials' compositions were preserved in the multicomponent magnets.

Overall magnetic properties of the two samples were comparable, with the sample manufactured in a two-step procedure having a slightly higher remanence. It was found that the additional PECS processing increases the remanence of the dense isotropic magnets by approximately 7 %, due to the plastic deformation of the sample that is not perfectly constrained by the graphite die. Information on the local magnetic properties was provided by cutting the multicomponent magnet in half and measuring each part individually. The magnetic properties of the respective parts matched the properties of the initial powders, thus proving that a multicomponent magnet can be prepared in a short, low-temperature PECS consolidation step without degrading the properties of the respective nanostructured materials.

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Publications Related to the Thesis

Journal Articles

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Other Publications

Journal Article

P. Djinović, T. Tomše, J. Grdadolnik, Š. Božič, B. Erjavec, M. Zabitsky, and A. Pintar, "Natural aluminosilicates for catalytic depolymerization of polyethylene to produce liquid fuel-grade hydrocarbons and low olefins," *Catalysis Today*, vol. 258, pp. 648-659, 2015.

Conference paper

P. Djinović, T. Tomše, J. Grdadolnik, Š. Božič, B. Erjavec, M. Zabitsky, and A. Pintar, "Natural aluminosilicates for catalytic depolymerization of polyethylene," European Meeting on Chemical Industry and Environment, 10-12 June 2015, Tarragona, Spain. *Conference Proceedings*. Tarragona, pp. 395-396, 2015.

Biography

The author of this thesis was born in Trbovlje on 8 March 1985. He graduated from the GESŠ Trbovlje in 2004. He obtained a Bachelor degree in chemistry in 2014 at the Faculty of Chemistry and Chemical Technology, University of Ljubljana. The research topic of his Bachelor Thesis was pyrolysis of polyethylene by using modified natural aluminosilicates as catalysts. He enrolled in the doctoral study program Nanosciences and Nanotechnologies at the Jožef Stefan International Postgraduate School in 2014. He is employed at the Department for Nanostructured Materials (K7), Jožef Stefan Institute. His field of research are the Nd-Fe-B permanent magnets. In the scope of a bilateral project between the K7 Department and the ABB Company, Switzerland, new approaches to improve the performance of the Nd-Fe-B-type magnets were invented. The methods to minimize the use of critical heavy rare earth elements, which are currently a vital component of the commercially available Nd-Fe-B magnets, have been developed.