Key techniques for ultrahigh performance sintered Nd-Fe-B magnets preparation

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1. Knowledge of rare earth permanent magnets Nd-Fe-B

1.1. Compositions of sintered Nd-Fe-B

Iron boron neodymium alloys are multiphase materials, typically processed slightly rich in Nd and B relative to the primary ferromagnetic phase in the system, Nd₂Fe₁₄B. Typically, most magnets contain 20-30 vol. % of nonmagnetic phases which are important for good magnetic properties. Powder metallurgy, melt pinning and mechanical alloying have been used to produce magnets although only the first two approaches have proven to be commercially successful¹,².

The matrix phase Nd₂Fe₁₄B which is often referred to as 2-14-1 has a tetragonal crystal structure with a space group of P4₂/mmm. The unit cell which contains 68 atoms is shown in figure 1.1. There are 6 different Fe sites, 2 Nd sites and 1 B site. The structure may be interpreted as distorted σ phase type hexagonal nets of Fe separated by basal planes containing Nd and B³,⁴. The layered stacking of the large positive Nd cores is responsible for the strong c-axis magnetocrystalline anisotropy. At room temperature, the anisotropy field

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Figure 1.1. Unite cell of the ferromagnetic Nd$_2$Fe$_{14}$B phase. The space group is P4$_2$/nm$\bar{m}$ and there are 68 atoms in the unit cell.

H$_a$ of Nd$_2$Fe$_{14}$B has been measured to be 55kOe. The saturation magnetization of the phase has been measured to be 167 emu/gm.

The Nd-Fe-B ternary phase diagram is shown in figure 1.2. The Nd$_2$Fe$_{14}$B phase is denoted by $\Phi$ while the Nd$_{1+\varepsilon}$Fe$_4$B$_4$ phase is denoted by $\eta$. Typically, for reasons which will be discussed subsequently, the magnets with the best properties are those with compositions slightly rich in Neodymium relative to the ferromagnetic $\Phi$ phase.

The coercivity of these magnets is affected by the Nd$_2$Fe$_{14}$B grain size as well as the type and distribution of the secondary phases which are controlled by processing. In order to maximize $M_r$, it is critical that the volume fraction of the hard magnetic 2-14-1 phase be as high as possible and that the c-axes of the 2-14-1 grains be well aligned$^5$. It is interesting to note that although melt spinning and sintering approaches produce different microstructures, the resultant magnetic properties are comparable. Investigations of the microstructure and magnetic behavior of these materials have concluded that
Figure 1.2. Ternary Nd-Fe-B phase diagrams. The ferromagnetic Nd$_2$Fe$_{14}$B phase is denoted $\Phi$ by $\eta$ while represents Nd$_{1+x}$Fe$_x$B$_4$.

The reversal mechanism is through nucleation and growth of (reverse magnetic) domain with the specifics of whether reversal is nucleation or growth controlled being determined by the microstructure.

In melt spun (and mechanically alloyed) material, the Nd$_3$Fe$_{14}$B grain size, typically 200-500 nm, is in the range of the calculated single domain size $D_c \sim 300$ nm$^6$, $^7$, $^8$. There is also a distribution of nonmagnetic Nd precipitates and secondary phases which may serve as domain wall pinning sites$^9$. In addition, although the subsequent die pressing steps required to produce a usable bulk magnet induces some c-axis texture$^{10}$, the alignment of the easy axis is poorer than in the sintered material. For an isolated, highly anisotropic single domain size particle, spin rotation or flipping is the method of magnetic reversal. The expected coercivity for such a particle should be equal to the anisotropy field which in the case of Nd$_3$Fe$_{14}$B is 55 kOe, far greater than the observed values of 10-20 kOe. Microstructural observation of both melt spun and mechanical alloyed materials indicate the isolation of the ferromagnetic grains by the magnetic phases is poor and there is evidence that the 2-14-1 gains are magnetically coupled. This suggests that a nucleation and growth type process rather than spin flipping is responsible for magnetization.
The grain boundaries and secondary phases may serve both as nucleation sites where reverse domain are formed and as pinning sites that hinder domain wall motion; hence the reversal mechanism in these materials is pinning controlled.

In sintered materials as seen in figure 1.3, the microstructure consists of 10-20 μm size, defect-free ferromagnetic grains of Nd$_2$Fe$_{14}$B with predominantly NdO, and to a lesser amount Nd$_2$O$_3$ and Nd$_{1+x}$Fe$_4$B$_4$ present as intergranular pockets$^{13-16}$; NdO plays a critical role in processing which will be discussed shortly. Good 2-14-1 c-axis texture is obtained by aligning the powders in a magnetic field before pressing and sintering at typically 1000°C. The observed defect free nature of the 2-14-1 phase indicates that domain wall motion is relatively unimpeded in the grain. Lorentz microscopy investigations show that the Nd$_2$Fe$_{14}$B grain boundaries do not effectively pin domain walls and that in the unsaturated condition, the grains are multi-domain. Other work has shown that coercivity decreases with increasing 2-14-1 grain or particle size indicating that grain boundaries and interphase interfaces are suspected sites for reverse domain nucleation$^{17}$. The nonferromagnetic, intergranular phases which physically isolate groups of 2-14-1 grains from one another also serve to magnetically isolate the 2-14-1 grains. Therefore, since each grain group acts independently and because domain wall motion is unimpeded within the group, it is the nucleation of reverse domains that ultimately controls the coercivity.

Nd-Fe-B powders for sintered magnets are obtained by milling cast ingots of the appropriate composition (i.e. excess Nd and B relative to Nd$_2$Fe$_{14}$B) followed
by sintering. NdO is important for successful processing because of the following:

1) Its melting point 680°C is lower than that of the sintering temperature ~1000°C which therefore facilitates liquid phase sintering as well as removal of any damaged material from the particle surfaces.
2) During sintering, the liquid NdO will dissolve any damaged material left on the 2-14-1 particle surface as a result of milling.

During milling, the Nd₂Fe₁₄B powder surface will be damaged and possibly oxidized which can lead to the formation of α-Fe on the surface. The damaged particle surfaces will lower the coercivity and is thought to be responsible for the poorer performance of resin or epoxy bonded magnets. It is imperative that any damaged layer be removed by the subsequent processing either by dissolution or reaction with the melt. Thus in powder processed Nd-Fe-B; the intergranular phases affect both the processing and magnetic properties.

1.2. Coercivity

To differentiate between a permanent, or hard, magnet (PM) and a soft magnet, a quantity known as coercivity is used to describe the amount of applied magnetic field required to demagnetize it. This extrinsic property is determined in part by the microstructure of the material as a result of the solidification process and by its thermal history. The intrinsic coercive field \( H_c \) needed to reverse magnetic alignment in a magnet is however a function of its limiting magnetic saturation based on the equation. Where \( K_1 \) is a constant relating a material’s preferred alignment of the magnetic dipole moments, known as magnetocrystalline anisotropy, and \( \mu_0 \) is the permeability of free space.

\[
\mu H_c = \frac{2K_1}{\mu_0 M_{sat}}
\]

The greater an applied field needed to reduce magnetization to zero, the greater the strength of the PM, whereas an ideal soft magnet would have coercivity near zero. As mentioned, another attribute of a magnet is its saturation magnetization \( M_{sat} \), meaning the extent to which it can be magnetized. Saturation is dependent only on the magnitude of the atomic magnetic moments and number of atoms per unit volume. Soft magnets tend to have a greater saturation over permanent magnets, an intrinsic compositional effect. Upon saturation and removal of an applied field, the magnetization of a magnet will revert to a
residual magnetic state, or its remanence $M_R$. These properties, of a magnet, can be directly inferred from a hysteresis loop as seen in Figure 1.4, with $H$ being the applied field and $B$ the induced magnetism (where remanent induction $B_R = \mu_0 M_R$).

1.3. Remanence

The remanence $B_r$ of NdFeB magnets is expressed as

$$B_r = J_s \frac{d}{d_0} (1 - V_{\text{nonmag}}) f_\phi$$

Where $J_s$ is the saturation magnetization of Nd$_2$Fe$_{14}$B phase, $d$ is the density of the magnet, $d_0$ is the theoretical value of the density and $V_{\text{nonmag}}$ is the volume of fraction of nonmagnetic phases. $f_\phi$ is the degree alignment of the main phase.

1.4. The maximum energy

The maximum energy product, $(BH)_{\text{max}}$, represents a magnet’s ability to store energy or deliver work outside of its volume, thereby indicating the performance or strength of the PM. As illustrated with the shaded region in Figure 1.4, a magnet’s energy product is directly proportional to the material’s $M_{\text{sat}}$ through the equation$^2$. Therefore, a magnet’s performance can be greatly enhanced if its intrinsic saturation is increased through using elements with higher initial $M_{\text{sat}}$.

$$(BH)_{\text{max}} = \mu_0 \left( \frac{M_{\text{sat}}}{2} \right)^2$$

Figure 1.4. Generalized magnetic hysteresis loops, $H$ being the applied field and $B$ the induced magnetism.
1.5. Magnetostatic moment alignment

Magnetostatic moment $M_T$ of powder under field can be expressed as \(^{20}\)

$$M_T = HM_s \sin \theta$$

(1)

Where $M_s$ is saturation moment, $H$ is magnetic intensity; $\theta$ is the angle between $H$ and c-axis. Figure 1.5 shows the force functioning on a spherical particle under the applied magnetic field. Assuming that the particles are ideally close packed, there are 12 closed-packed particles. The followed equation can be deduced \(^{21}\)

$$\frac{4}{3} \pi r^3 M_T = r 12 \left( \frac{d_1}{d_0} \right) f F + F_m + F_a$$

(2)

Where $F$ is the compression force, $F_m$ is the mechanical resistance, $F_a$ is the agglomerating force, $f$ is the friction coefficient of powder with the radius of $r$, $d_1$ is the packing density and $d_0$ is theory density. According to the formula (1) and (2), $\theta$ can be expressed as

$$\theta = \sin^{-1} \left\{ \frac{3}{\pi r^2 M_s H} \cdot \frac{3F \left( \frac{d_1}{d_0} \right)}{4} + \frac{F_m + F_a}{4} \right\}$$

(3)

![Figure 1.5. Force diagram model of a spherical particle powder under applied magnetic field.](image-url)
References

2. Development of Nd-Fe-B magnets

The search for a more feasible permanent magnet (PM) with equally impressive magnetic properties, compared to Sm-Co, resulted in a more notable RE-TM hard magnetic phase, based on the ternary compound RE₂Fe₁₄B (RE = Nd, primarily) with a tetragonal structure and magnetic axis along its c-axis. It was simultaneously discovered through two separate processing routes. A chill-casting/annealing/grinding and powder sintering method was developed by Sagawa et al. at Sumitomo Special Metals of Japan and a rapid quenching process, termed magnequench was developed by Croat et al. at General Motors of the U.S. in 1984. The advantage of this alloy was that its main constituents, Fe and Nd, are more abundant than those of Sm-Co type magnets, allowing for significantly reduced raw materials cost. Also, their (BH)ₘₐₓ was superior with a predicted Mₘₛₙ of 10.1 kGs surpassing that of Sm-Co (6.1kGs), which made them desirable for numerous applications. The principle drawback pertains to their temperature dependence, with a Curie temperature of only 312°C, compared to the most widely used magnetic materials and their associated Tₐ values and applicable energy products, (BH)ₘₐₓ, in Table 1.5. The Curie temperature is defined as the transition temperature at which magnetic alignment or ordering is destroyed and the material goes from ferromagnetic or ferrimagnetic to paramagnetic behavior.

Actually, the practical operating temperature for Nd₂Fe₁₄B magnets is in the range of 125°C to 150°C, well below its respective Tₐ. This sensitivity to temperature has been a limitation for Nd-Fe-B type magnets and has hindered its use in high temperature applications.

Table 2.1. Curie temperature and energy product of common magnetic materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Tₐ (°C)</th>
<th>(BH)ₘₐₓ theoretical (MGOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>770</td>
<td>0.2</td>
</tr>
<tr>
<td>Nickel</td>
<td>358</td>
<td>-</td>
</tr>
<tr>
<td>Cobalt</td>
<td>1130</td>
<td>-</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>Terfenol (Tb₀.₃Dy₀.₇Fe₂)</td>
<td>380-430</td>
<td>-</td>
</tr>
<tr>
<td>Nd₂Fe₁₄B</td>
<td>312</td>
<td>65.6</td>
</tr>
<tr>
<td>Alnico (Fe₃₂Co₃₅Ni₁₅Al₄Cu₄Ti₄)</td>
<td>850</td>
<td>9.4</td>
</tr>
<tr>
<td>SmCo₅</td>
<td>720</td>
<td>20</td>
</tr>
<tr>
<td>Sm₂Co₁₇</td>
<td>810</td>
<td>30</td>
</tr>
<tr>
<td>Hard ferrites (SrO·₆Fe₂O₃)</td>
<td>400-700</td>
<td>2.5</td>
</tr>
<tr>
<td>Barium ferrite (BaO·₆Fe₂O₃)</td>
<td>450</td>
<td>3.5</td>
</tr>
</tbody>
</table>
A further problem surrounding Nd-Fe-B magnets has been its rather low corrosion resistance. RE elements are highly susceptible to oxidation and corrosion in applications with increased temperature and high humidity\(^6\), leading to reduced magnetic properties over time. It is known that the light rare earth elements, such as Nd, are easily oxidized\(^7\). The formation of the oxide, \(\text{Nd}_2\text{O}_3\), reduces the amount of the Nd-rich phase which is responsible for pinning of the domain walls. As the Nd-rich grain boundaries break down, the effective \(H_c\) declines rapidly\(^8\). Without providing a protective surface coating, i.e. epoxy or metallic, or alloying addition to a RE element, exposure to moisture was found to cause the reactions listed as equations (1) and (2). The decomposition of water vapor reacting with Nd results in the local production of hydrogen\(^9\). Hydrogen, known to easily diffuse throughout the bulk of the material, reacts with the Nd-rich areas, equation (2). This leads to intergranular hydrogen embrittlement which escalates the corrosion process throughout the volume of the material and further degrades its useful properties, magnetically and structurally.

\[
\text{Nd} + 3\text{H}_2\text{O} \rightarrow \text{Nd(OH)}_3 + 3\text{H} \quad (1)
\]

\[
\text{Nd} + 3\text{H} \rightarrow \text{NdH} \quad (2)
\]

Today, permanent magnets based on Nd-Fe-B constitute as interesting area for continued commercial development through basic research focused on enhancing their attractive intrinsic properties and applied research targeted to customizing the extrinsic magnetic properties for specific use\(^10\). Typically, modifications have aimed at improving the lifetime and reducing the cost of anisotropic sintered PM due to their desirable energy products. However, in recent years polymer bonded isotropic permanent magnets (PBPM) have grown in interest\(^11, 12\) for their ability to form complex net shapes at low cost for use in electric motors and other automotive devices, a topic to be discussed in a following section.

As industry demands continually increase, required operating temperatures for bonded magnets are nearing 200°C and current commercial RE\(_2\)Fe\(_{14}\)B alloys are incapable of maintaining adequate magnetic performance. To combat the need for increased reliability and performance at 200°C, a MRE-Fe-B alloy modification (MRE = Nd, Y, Dy; currently) has been designed to maintain a sufficient \((BH)_{\text{max}}\) at elevated temperatures through judicious “mixed RE” alloying additions\(^13\). The development of a MRE\(_2\)Fe\(_{14}\)B solid solution was founded on previous magnetic studies of the individual intrinsic 2-14-1 properties\(^14, 15\). Figure 1.1 shows the temperature dependence of the magnetic moment (affecting remanence) and anisotropy energy (affecting coercivity) for each respective RE\(_2\)Fe\(_{14}\)B. It was noticed that
Nd₂Fe₁₄B possesses the highest saturation (Figure 1.1a), while Dy₂Fe₁₄B (Figure 1.2b) has the greatest anisotropy; however each is strongly dependent on temperature and declines rapidly at increased T. Conversely, Dy₂Fe₁₄B exhibits a diminished saturation dependency on temperature (Figure 1.1a) as does Y₂Fe₁₄B with anisotropy (Figure 1.1b); although their respective magnetic property levels are substantially lower at room T.

References

3. Key techniques for ultrahigh performance Nd-Fe-B

3.1. Improved response to thermal variations of NdFeBZr magnets

Since their discovery in 1983, demand for sintered NdFeB magnets has greatly increased, due to their superior magnetic properties. Total output of sintered NdFeB magnets in China reached 52400 tons in 2008 and is still growing. The sintering temperature plays an important role in the magnetic properties of the final material, especially during industrial scale production. An optimum sintering temperature has to be applied, accompanied by appropriate heat treatment, in order to densify the green NdFeB compacts and achieve the best magnetic properties. Generally more than 250 kg of the material is loaded into an industrial furnace during mass production. This material is then sintered by heat radiation. Typical problems with heat distribution during the sintering stage often result in sintered magnets being over or under-sintered in the outer or central regions of the bulk material respectively, due to this uncontrolled temperature variation. Therefore the magnetic properties of the NeFeB magnets produced in this way often display significant fluctuations. Quality control of these sintered magnets is thus a problematic and time consuming part of industrial magnet production. Theoretically, reducing the sensitivity of the magnetic material to sintering temperatures could solve this problem. It was decided to achieve this by fine tuning magnet composition to obtain more uniform properties of the resulting sintered magnets.

It was previously reported that a ZrB$_2$ phase emerged upon Zr addition to the PrFeB magnetic system, resulting in a material that displayed improved coercivity and a classical square shape during the demagnetising loop. It was also established that during preparation of nano-composite NdFeB, addition of Zr had an impact on the grain size and its distribution. Other researchers have investigated the effects of various elemental additions of Dy, Nb, Al, Cu, Co, and preparation techniques on the properties of NdFeB magnets. In this paper we now demonstrate how optimum additions of Zr can significantly reduce the influence of sintering temperature on the final magnetic properties of NdFeB sintered magnets produced at industrial scale.

3.1.1. Prepare method

The starting materials employed in sample preparation were of 99.9 wt. % purity for Nd, Fe, Al, Dy, Zr, Ga and an FeB alloy (20 wt. % B). The magnets, with approximate compositions of Nd$_{13.3}$Dy$_{0.48}$Fe$_{80.7}$B$_{5.9}$ and (NdDy)$_{12.99}$(Fe)$_{80.7}$B$_{5.9}$ (at. %) with additions of Al, Ga, Zr, were prepared by a
strip casting technique, with a line speed of 2 m/s produce by the Zhongbei Shenyang company. These alloys were subjected to a standard hydrogen decrepitated (HD) treatment, followed by jet-milling to produce fine powders with an average particle size of 3.4 µm. The powders were aligned by applying a 1.8 T magnetic field and then isostatically pressed at a pressure of 6 MPa, to produce green compacts. These compacts were heated under argon at a rate of 5 °C/min followed by sintering at 1065-1105 °C for 3 h in furnace made by the ULVAC vacuum furnace (Shenyang) Co. Ltd. Sintered magnets were quenched to room temperature, under Ar gas, to prevent oxygen pick up. This was followed by heat treatment, again under Ar, for 2 h at 900 °C and then for 3 h at 600 °C, followed by quenching to room temperature, seen in figure 3.0.

The magnetic properties reported in this work were obtained by averaging the results from a number of samples analysed using by B-H tracer (model AMT-4); three samples were obtained from outer region and two samples from central region of the bulk magnetic material obtained from an industrial furnace after sintering. The microstructure was investigated by using a JEM-2010 transmission electron microscope and by optical microscopy(OLYMPUS-MX50). Corrosion properties were measured by the PCT-30-2 high pressure acceleration life tester at 121 °C under 2 atm for 48h and 96h.

Figure 3.0. Schema of NdFeB magnets preparation technique.
3.1.2. Zr effects on sintering temperatures

The starting material for this study was Nd\(_{13.3}\)Dy\(_{0.48}\)Fe\(_{Bal}\)B\(_{5.75}\)A\(_{0.24}\)Ga\(_{0.1}\)Zr\(_{y}\); the addition of Al was to improve wettability of the grain boundary material whilst small additions of Ga and Dy were designed to improve the coercivity of the resulting magnets. It was then decided that small additions of Zr might be required to suppress grain growth at higher sintering temperatures. In order to optimise the procedure and densify the powders into sintered magnets, a range of sintering temperatures were selected; from 1065°C to 1105°C. The low temperature (1065°C) seems to be associated with reduced grain growth during the furnace sintering. However higher sintering temperatures (1100°C) are associated with the best magnetic properties and good densification to the sintered magnet. The results are presented in Table 3.1, which summarises of the magnetic properties for the sintered magnets. Nearly full densification (about 98 vol %) was achieved for material sintered at temperatures \(\geq 1100\)°C. The result for the best magnet composition is shown in figure 3.1. The variations in magnetic properties indicate the (NdDy)\(_{13.32}\)Fe\(_{Bal}\)B\(_{5.75}\)A\(_{0.24}\)Ga\(_{0.1}\)Zr\(_{0.07}\) composition sintered at 1100 °C was found to give optimum magnetic properties. Further this is accompanied by a slight fall in the coercivity, possibly indicating that a high temperature oxidation corrosion happened.

Table 3.1. Properties of sintered magnets.

<table>
<thead>
<tr>
<th>Magnet content</th>
<th>Sintered (B_r)</th>
<th>(\mu H_c)</th>
<th>((BH)_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NdDy)(<em>{12.99})Fe(</em>{Bal})B(_{5.75})</td>
<td>1065</td>
<td>1.37</td>
<td>626</td>
</tr>
<tr>
<td>(NdDy)(<em>{12.99})Fe(</em>{Bal})B(_{5.75})</td>
<td>1085</td>
<td>1.40</td>
<td>526</td>
</tr>
<tr>
<td>(NdDy)(<em>{12.99})Fe(</em>{Bal})B(<em>{5.75})A(</em>{0.24})Ga(_{0.1})</td>
<td>1065</td>
<td>1.36</td>
<td>741</td>
</tr>
<tr>
<td>(NdDy)(<em>{12.99})Fe(</em>{Bal})B(<em>{5.75})A(</em>{0.24})Ga(<em>{0.1})Zr(</em>{0.07})</td>
<td>1085</td>
<td>1.39</td>
<td>560</td>
</tr>
<tr>
<td>(NdDy)(<em>{12.99})Fe(</em>{Bal})B(<em>{5.75})A(</em>{0.24})Ga(<em>{0.1})Zr(</em>{0.07})</td>
<td>1085</td>
<td>1.36</td>
<td>846</td>
</tr>
<tr>
<td>(NdDy)(<em>{12.99})Fe(</em>{Bal})B(<em>{5.75})A(</em>{0.24})Ga(<em>{0.1})Zr(</em>{0.07})</td>
<td>1100</td>
<td>1.42</td>
<td>865</td>
</tr>
<tr>
<td>(NdDy)(<em>{12.99})Fe(</em>{Bal})B(<em>{5.75})A(</em>{0.24})Ga(<em>{0.1})Zr(</em>{0.07})</td>
<td>1105</td>
<td>1.43</td>
<td>857</td>
</tr>
</tbody>
</table>
In order to understand this variation in properties, magnets of the base composition, with and without addition of Zr, were sintered at the indicated temperatures and the resulting material sectioned and its microstructures studied by optical microscopy. It is worth noting that grain growth in excess of 100 μm occurred in the Zr-free containing magnets at the higher sintering temperature (1100 °C) shown in Figure 3.2b. It is clear from Figure 3.2 (NdDy)\textsubscript{13.32}Fe\textsubscript{bal}B\textsubscript{5.75}A\textsubscript{0.24}Ga\textsubscript{0.1}Zrx composition decreased the average grain size, from 10.6 μm to 8.7μm respectively. During the sintering process Zr is segregating on the grain boundary which is suppressing the grain growth and that is associated with the observed reduced temperature sensitivity of the sintering process.

3.1.3. Zr effects on microstructures

The TEM microstructures of the sintered magnets are shown in Figure 3.4. The microstructure shows evidence of a ZrB\textsubscript{2} precipitated phase in the Nd\textsubscript{2}Fe\textsubscript{14}B grains that has been ascribed \cite{9,10} to the presence of Zr additions. This Zr addition is suggested to inhibit of grain growth. This addition of the Zr made these magnets insensitive to sintering temperature and hence more suitable for production scale magnet preparation using equipment with weak temperature control. Adding the appropriate amounts of the Zr to the base composition is therefore a good method of producing magnets on a large scale with consistent properties.
Figure 3.2. An optical image showing the microstructure sintered at different temperatures and Zr additions respectively (a) 1065 °C, Zr=0, (b) 1100 °C, Zr=0, (c) 1100 °C, Zr=0.07%, (d) 1100 °C, Zr=0.43%.

Figure 3.3. The effects of Zr content on the magnetic properties for Nd$_{13.3}$Dy$_{0.48}$Fe$_{57.5}$Al$_{0.24}$Ga$_{0.1}$Zr$_y$ sintered magnets.

The effects of Zr additives on weight loss are presented in Table 3.2. It can be seen that the magnets without Zr additions, sintered at 1065 °C and 1100 °C, resulted in material that displays rapid weight loss up to 48 hours exposure. During more extended exposure, corrosion products become more
Figure 3.4. The TEM microstructures of sintered magnets (a) Zr=0, (b) Zr=0.43%.

Table 3.2. Corrosion analysis for the different Zr containing sintered magnets, with a Nd\textsubscript{13.3}Dy\textsubscript{0.48}Fe\textsubscript{bal}B\textsubscript{5.75}Al\textsubscript{0.24}Ga\textsubscript{0.1}Zr\textsubscript{y} composition.

<table>
<thead>
<tr>
<th>Zr content</th>
<th>0</th>
<th>0.07%</th>
<th>0.14%</th>
<th>0.29%</th>
<th>0.43%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight loss 48h (mg/cm\textsuperscript{2})</td>
<td>43.37</td>
<td>4.25</td>
<td>2.47</td>
<td>0.7</td>
<td>1.81</td>
</tr>
<tr>
<td>Weight loss 96h (mg/cm\textsuperscript{2})</td>
<td>136.34</td>
<td>21.21</td>
<td>15.19</td>
<td>2.3</td>
<td>12.13</td>
</tr>
</tbody>
</table>

apparent in the Zr-free material. These products detached from the rest of the magnetic phase may explain the increased weight loss observed for Zr-free magnets when compared to that of the Zr containing magnets. This would indicate that good corrosion resistance for Zr-containing magnets probably results from an increased density of sintered magnets produced from this alloy.

The Addition of Zr to the NdFeB system can decrease grain size and weaken the temperature sensitivity of this magnetic material to sintering. The addition of Zr therefore had beneficial effects during high volume production of the final magnets: improved sinterability and consistent magnetic properties. Furthermore, improved corrosion resistance was achieved by adding the Zr to the base composition.

3.2. Effect of B addition

3.2.1. Prepare method

Starting materials for the preparation of the alloy samples included Nd, Fe, Dy, Al, Nb, Zr, Ga all 99.9 wt% in purity, and a Fe-B alloy with 20 wt% B and 80 wt% Fe. Nd\textsubscript{13.3}Fe\textsubscript{bal} (AlGaNbZr) \textsubscript{0.48}B\textsubscript{x} (at %) alloys were prepared by a strip casting
technique, with a line speed of 2.6 m/s. The strip cast ingot was decrepitated for 10 h in an air-tight vessel under room temperature. After this, the coarse particles were dehydrogenated under 570 °C for 8 h, followed by jet-milling to fine powders with an average size of 3.3 μm. The fine powders were then pressed at 6 MPa, aligned with a perpendicular field of 1.8 T. The green compacts were heated slowly and sintered in vacuum at 1090 °C for 3 h to reach full densification, and quenched to room temperature under a stream of Ar gas. A post sintering cycle at 900 °C for 2 h followed by a quenching to room temperature and annealing at 560 °C for 3 h was employed finally.

3.2.2. B effects on magnetic properties

Effects of B on magnetic properties of Nd13.79FeB0.01AlGaNbZr 0.48Bx are shown in figure 3.5. It can be seen that at a content of 5.53 % B the magnetic properties had low values. When B content increase, the magnetic properties increased greatly, and optimum values obtained at 5.76 %, with Br of 1.40 T, \( H_c \) of 1078 kA/m and \( (BH)_m \) of 373 kJ/m³. As B content higher than 5.9 % properties of \( B_r \) and \( (BH)_m \) decreased dramatically, and \( H_c \) with a little increase.

![Figure 3.5](image.png)

**Figure 3.5.** Effect of B content on magnetic properties of magnets. The error bar represents the standard deviation.
3.2.3. B effects on corrosion resistance

Polarization curves of magnet with different amounts of B in NaOH solution are shown in Figure 3.6. It can be found that at a content of 6.16% B, corrosion current density had highest value of 1.57E-04A/cm². This can be attributed to formation of easily corrosive anode B rich phase, which resulted in lowest corrosion resistance. As B content decreased to 5.76%, near stoichiometric composition of Nd₂Fe₁₄B, the magnet exhibited highest corrosion resistance, and the current density decreased 2/3 with a value of 5.17E-05A/cm². As B content lowered to 5.53%, the current density increased to 1.06E-04A/cm².

Microstructures of magnets with different amounts of B are shown in Figure 3.7. Obtained Nd and Fe content by analysis with EDX of the grains and
grain boundary materials, and not any B content would be measured by this technique. Even though, the main phase \( \text{Nd}_2\text{Fe}_{14}\text{B} \), \( \text{Nd}_2\text{Fe}_{17} \) phase, B rich phase \( \text{NdFe}_4\text{B}_4 \) and Nd rich phase \( \text{Nd}_9\text{Fe} \) could be identified in the magnets by Nd and Fe relative content and marked in Figure 3.7. With the consumption of 0.1% Nd oxide, volume percent of phases in magnets with different amounts of boron were calculated by theory formula, details were studied by Zhou\(^\text{11}\). As B content increased from 5.53%, the volume of main phase increased and easy-plane type \( \text{Nd}_2\text{Fe}_{17} \) phase decreased in magnet, which resulted in \( B_r \), \( H_c \) increase (seen in Figure 3.5). As B content increased higher than 5.82%, more B rich phases formed which well isolated mainphase grains and resulted in \( H_c \) increase. But too much B rich phase would decrease main phase proportion and lead to \( B_r \) decrease.

Moreover, as B content increase from 5.53% to 6.16%, average matrix grain size was enlarged from 6.5\( \mu \)m to 8.2\( \mu \)m and the proportion of sharp shape grains (A regions marked in Figure 3.7) was relatively increase as well. According to Rodewald’s study\(^\text{12}\), abnormal grain growth was easily happened at higher B content, which was in agreement with these experimental results. In addition, the decreased squareness \( H_k/H_c \) of magnets at higher B content (shown in Figure 3.5) also suggested inconsistent distribution of grain size/shape\(^\text{13}\). Corrosion test of magnets showed that \( \text{Nd}_2\text{Fe}_{17} \) phase (formed at lower B content) or B rich phase (at higher B content) were not benefit for corrosion resistance improvement.

### 3.3. Effects of Dy and Nb compound addition

#### 3.3.1. Prepare method

The pure Nd, Fe, Al, Dy, Nb and the B–Fe alloy containing 20%B were used as the raw materials. Alloys with compositions \( \text{Nd}_{29.5}\text{Fe}_{69.15}-x_3\text{B}_1.1\text{Al}_{0.25}\text{Dy}_x\text{Nb}_y \) (\( x, y=0–3.0 \) wt %) were prepared in an induction furnace under an argon atmosphere. Through the mechanical milling and the jet milling, the alloys were refined to powders with an average size of 4.5 \( \mu \)m. Then the powders were pressed isostatically under a pressure of 1600 kg/cm\(^2\). The alignment magnetic field was 20 kOe. After that the compact was sintered at 1125°C for 2.5 h and annealed at 520°C for 2 h.

The magnetic properties were measured by a B–H tracer. The microstructure was observed through optical microscopy. Anodic polarization experiments of NdFeB samples were carried out with an EG&G model 273A potentiostat. All experiments were performed in a standard three electrode cell consisting of NdFeB working electrode, saturated calomel (SCE) reference and Pt counter electrode. Experiments were conducted at
room temperature in a solution containing NaCl27.3g/l and MgCl23.8g/l. The NdFeB electrode was placed into the cell and the open circuit potential was monitored for approximately 10 min until it stabilized. Then the potential was altered by 25mV for every 3 min, and the corrosion current was recorded.

3.3.2. Dy\Nb effects on magnetic properties

The effects of Dy and Nb on the magnetic properties of Nd$_{29.5}$Fe$_{69.15-x}$B$_{1.1}$Al$_{0.25}$Dy$_x$ and Nd$_{29.5}$Fe$_{68.15-y}$B$_{1.1}$Al$_{0.25}$Dy$_{1.0}$Nb$_y$ are shown in Figures 3.8 and 3.9, respectively. From Figure 3.8 it can be seen that when the content of Dy increases from 0% to 3.0%, remanence $B_r$ decreases from 13.5 to 11.95 kGs, while intrinsic coercivity $H_c$ increases from 10.1 to 17.34 kOe. At 1.0% Dy addition, the maximum energy product $(BH)_{max}$ can be obtained. As shown in Figure 3.9, $B_r$ increases when the Nb content increases from 0% to 0.8%, and reaches a maximum value of 13.39 kGs at 0.8% Nb. Over 0.8% Nb, $B_r$ decreases slowly. The dependence of $(BH)_{max}$ on the Nb content is the same as that of $B_r$. $H_c$ increases with the increase of Nb content, up to 3%.

Dy can partially replace Nd in the main phase Nd$_2$Fe$_{14}$B, forming Dy$_2$Fe$_{14}$B$_{14}$. The anisotropy field of Dy$_2$Fe$_{14}$B is 12.57 MA/m, which is 7MA/m higher than that of Nd$_2$Fe$_{14}$B. But the saturation magnetization of Dy$_2$Fe$_{14}$B is 0.7 T, which is lower than that of Nd$_2$Fe$_{14}$B, 1.6 T. So addition of Dy enhances $H_c$ but decreases $B_r$. However, from Figure 3.9 it can be found that simultaneous addition of Dy and Nb significantly enhances $H_c$, and only slightly decreases $B_r$. This finding is consistent with Tokunaga’s report$^{15}$.

![Figure 3.8.](image)

Figure 3.8. Effects of Dy content on the magnetic properties of Nd$_{29.5}$Fe$_{69.15-x}$B$_{1.1}$Al$_{0.25}$Dy$_x$. 

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The effect of Nb on the microstructure of NdFeBAIDy magnets is shown in Figure 3.10. It is evident from Figure 3.10 that with the increase of Nb the grain size of the main phase drops dramatically, and the grain boundaries of Nd$_2$Fe$_{14}$B become clear and smooth. This microstructural evolution is responsible for the observed increase in $H_c$. Moreover, Lin16 reported that the addition of Nb reduced the amount of precipitated $\alpha$-Fe, thus the small amount of decrease in $B_r$ could be related to the decrease of soft-magnetic $\alpha$-Fe phase.
3.3.3. Dy\Nb effects on corrosion resistance

Polarization curves of Nd$_{29.3}$Fe$_{69.15-x-y}$B$_{1.1}$Al$_{0.25}$Dy$_x$Nb$_y$ magnets in salt water are shown in Figure 3.11. With the increase of Dy content, the current densities of magnets decrease, indicating that the corrosion resistance of magnets increases with the increase of Dy content. It also can be seen that the corrosion resistance of magnets with 1.0% Dy and 0.8% Nb is superior to that with 1.5% Dy, but inferior to that with 3.0% Dy. This suggests that Nb exerts the similar effect on the corrosion resistance of magnets.

In the electrochemical reactions of NdFeB magnets, Nd-rich and B-rich intergranular phases act as the anode, and Nd$_2$Fe$_{14}$B phase acted as the cathode$^{17, 18}$. The anode was attacked firstly, desquamated the Nd$_2$Fe$_{14}$B phase. As Dy and Nb content increases, more stable intermetallic phases develop within the intergranular regions. This can promote the electrochemical potentials of intergranular phases, resulting in the improvement of corrosion resistance.

On the other hand, the speed of electrochemical reactions is also affected by the size of anode. As mentioned above, the addition of Nb refines Nd$_2$Fe$_{14}$B grains. As a result, the Nd-rich phase is distributed more uniformly within the intergranular regions. This is also considered to be of reasons for the observed improvement in the corrosion resistance of our materials.

![Figure 3.11. Polarization curves of Nd$_{29.3}$Fe$_{69.15-x-y}$B$_{1.1}$Al$_{0.25}$Dy$_x$Nb$_y$ in the salt water.](image)
3.4. Production for high thermal stability NdFeB magnets

3.4.1. Prepare method

Alloy ingots with a nominal composition of Nd29.5FebalB1.1Dy2.0Al0.25GdxCuy (x = 0–1.0, y = 0–0.5) (wt %) were prepared through vacuum induction melting. Ingots were first crushed and pulverized to less than 250 um under the Ar atmosphere, and then through jet milling the coarse powders were milled to fine powders with an average particle size of 4.0 um. The jet-milled powders were pressed at a pressure of 6 MPa, and magnetized with a perpendicular magnetic field of 1.65 T. The green compacts were sintered in vacuum at 1120°C for 2.5 h, quenched to room temperature with a stream of Ar gas, and finally subjected to annealing treatment at 510°C for 3 h. The microstructure of sintered samples was examined by an optical microscopy. The magnetic properties were measured using a magnetic measurement device AMT-4. The temperature dependence of the open flux was measured with a Helmholz coil and integrating digital flux meter. All samples were machined to a diameter of 10mm and a length of 8 mm.

3.4.2. Gd effects on magnetic properties

Figure 3.12 shows effects of Gd on temperature coefficient \( \alpha \) and the magnetic properties of Nd29.5FebalB1.1Dy2.0Al0.25 magnet. It was found that with Gd content increase from 0% to 1.0%, the \( B_r \) decreased dramatically from 1.332 to 1.265 T, with the same trend as \( (BH)_{max} \). The \( iH_c \) increased linearly from 1178 to 1267 kA/m. The composite of Gd2Fe14B had lower saturated magnetization and larger anisotropy field than that of Nd2Fe14B at 293K, which resulted in \( B_r \) decrease and coercivity increase. The absolute value of temperature coefficient \( \alpha \) was linearly increased from -0.15% to -0.05%/°C as Gd content reached 1.0%. It is because the magnetic moment of element Gd has ferromagnetic coupling with 3d metal, which exhibited a positive temperature coefficient and led to \( \alpha \) increase.

3.4.3. Cu effect on Gd-containing magnets

Although the temperature coefficient improved by Gd addition, the magnet had too low \( (BH)_{max} \) to be used. Combined addition of Cu in Nd29.5FebalB1.1Dy2.0Al0.25Gd0.8 magnet was investigated and their effects on magnetic properties are shown in figure 3.12. It was found that with Cu content increase, \( B_r \) and \( (BH)_{max} \) increased first and obtained the optimum value \( B_r=1.34 \) T, \( (BH)_{max}=340 \) kJ/m\(^3\) at 0.2% Cu content. \( iH_c \) increased almost
Figure 3.12. Effects of Cu content on properties of Nd$_{29.5}$Fe$_{bal}$B$_1$$_1$Dy$_{2.0}$Al$_{0.25}$Gd$_{0.8}$ magnets. The error bar represents the standard deviation obtained from 5 samples.

linearly from 1230 to 1415 kA/m. Effects of Cu content on microstructures of magnets are shown in figure 3.13. It can be seen that with Cu content increase the grain boundaries became clear and smooth, and main phase grains were well isolated, which was a benefit for coercivity improvement. In addition, it was found that Cu addition had little effect on temperature coefficient $\alpha$.

The temperature coefficient $\alpha$ improved with addition of Gd, but the remanence and maximum energy product linearly decreased. As Cu was added, the remanence, maximum energy product and coercivity increased due to the density improvement and main-phase grains were well isolated. By combined addition of Gd =0.8% and Cu=0.2%, optimum magnetic properties with temperature coefficient $\alpha$=-0.05%/°C, (BH)$_{max}$=339 kJ/m$^3$ were obtained.

3.5. Change of microstructure and properties by annealing

3.5.1. Prepare method

Alloy ingots with a nominal composition of Nd$_{12.0}$Dy$_{2.8}$Fe$_{74.7}$Co$_{3.4}$Cu$_{0.2}$B$_{6.9}$ (at %) were prepared through vacuum induction melting. Ingots were first crushed and pulverized to less than 250um under an Ar atmosphere; then through jet-milling the coarse powders were milled to fine powders with an
average particle size of 4 μm. The jet-milled powders were pressed at a pressure of 6 MPa, and magnetized with a perpendicular magnetic field of 1.65 T. The green compacts were sintered in vacuum at 1090°C for 2 h, quenched to room temperature with a stream of Ar gas, and finally subjected to annealing treatment. Different annealing temperatures, ranging from 300 to 650°C, and different annealing times, ranging from 0.5 to 8 h, were employed.

### 3.5.2. Annealing temperature effects

The magnetic properties of Nd₁₂₀Dy₂₈Fe₇₄₇Co₃₄Cu₀₂B₀₉ magnets annealed at different temperatures for 2 h are shown in Figure 3.14, in comparison with those of as-sintered magnets. It can be seen that the annealing temperature has little effect on the remanence, B_r. However, the intrinsic coercivity, H_c, is rapidly increased with the increase of annealing temperature. The maximum value of H_c, 1849 kA/m, is attained at 480°C. Annealing over 480°C, the H_c decreased rapidly, being 1099 kA/m when annealed at 600°C. For as-sintered magnets, the H_c has the lowest value, 800 kA/m. The dependence of (BH)_{max} has the same trend as that of H_c.
Figure 3.14. Effect of annealing temperature on the magnetic properties of Nd$_{12.0}$Dy$_{2.8}$Fe$_{74.7}$Co$_{3.4}$Cu$_{0.2}$B$_{6.9}$ magnets (annealing time 2 h).

Figure 3.15. SEM images of Nd$_{12.0}$Dy$_{2.8}$Fe$_{74.7}$Co$_{3.4}$Cu$_{0.2}$B$_{6.9}$: (a) as-sintered, (b) annealed at 400°C, (c) annealed at 480°C, and (d) annealed at 520°C (annealing time 2h).

Observed through SEM, the RE$_2$Fe$_{14}$B phase has an average size of 9um. The RE-rich phases are located in the boundaries and the triple point of grains. No REFe$_4$B$_4$ is detected. Figure 3.15 presents the SEM backscattered images of magnets without annealing treatment, annealed at 400°C for 2h, 480°C for 2h, and 520°C for 2h, respectively. In Figure 3.15a, it is
difficult to distinguish the interface between the RE-rich phases (white) and the main phase (gray). In Figure 3.15b, the grain boundaries are distinguishable, but relatively fuzzy and discontinuous. In Figure 3.15c, the RE-rich phases and RE$_2$Fe$_{14}$B grains interface is well defined. The grain boundaries of RE$_2$Fe$_{14}$B annealed at 480°C are smooth. The distribution of RE-rich phases between RE$_2$Fe$_{14}$B grains is continuous and very uniform. Annealed at 520°C, aggregation of RE-rich phases increased drastically, as shown in Figure 3.15d. Thus, the $iH_c$ of magnets decreases.

### 3.5.3. Annealing time effects

The $iH_c$ of magnets annealed at 480°C for different annealing times is shown in Figure 3.16, in comparison with that of as-sintered magnets. It is evident that the change of $iH_c$ with the increase of annealing time can be divided into three stages. First, $iH_c$ increases rapidly from 800kA/m for the as-sintered magnets to 1776kA/m for magnets with 1h annealing. Second, the increased velocity of $iH_c$ begins to slow down between 1 and 2h annealing time. The maximum value of $iH_c$, 1849kA/m, is attained in the magnets annealed for 2h. Third, the $iH_c$ remains almost constant with a further increase of annealing time.

![Figure 3.16. Effect of annealing time on $iH_c$ of Nd$_{12.0}$Dy$_{2.8}$Fe$_{74.7}$Co$_{3.4}$Cu$_{0.2}$B$_{6.9}$ magnets at 480°C.](image)
Figure 3.17. SEM images of Nd$_{12.0}$Dy$_{2.8}$Fe$_{74.7}$Co$_{3.4}$Cu$_{0.2}$B$_{6.9}$ magnets annealed at 480°C for (a) 1h and (b) 4h.

The SEM backscattered images of magnets annealed at 480°C for 1 and 4h are presented in Figure 3.17. When compared with Figure 3.17a and c, the images of the as-sintered and annealed at 480°C for 2h, it can be found that the microstructure of the grain boundaries annealed at 480°C for 1h (Figure 3.17a) is much better than that of the as-sintered (Figure 3.17a). But, at some part the RE-rich phases are still not continuous. As the annealing time increases to 2–8h, the RE-rich phases between RE$_2$Fe$_{14}$B grains get more continuous and uniform, resulting in the enhancement of $H_C$.

Our experimental results show that the annealing can obviously optimize microstructure and improve the coercivity of magnets. Great change of the microstructure for the annealed magnets can be understood by the change of the atomic diffusion coefficient $D$:

$$D = D_0 \exp \left( -\frac{Q}{RT} \right)$$

Where $D$ is atomic diffusion coefficient, $D_0$ a constant, $Q$ the activation energy of atomic diffusion, $R$ the atmosphere constant, and $T$ the temperature. As shown in the above equation, $D$ exponentially increases with $T$. However, the $H_C$ of the magnets, annealed at 350°C for 2h, is improved as compared with that of the as-sintered magnets. The optimum microstructure of grain boundaries has not been attained because of the lower atomic diffusion capability and the shorter annealing time. It can be expected that the microstructure could be improved with a further increase of annealing time. When the annealing temperature is increased to 480°C, atomic diffusion capability is enhanced. The RE$_2$Fe$_{14}$B grain boundaries get smooth, and the distribution of RE-rich boundary phases becomes more continuous and uniform. This
microstructure decouples the exchange effect between the RE$_2$Fe$_{14}$B grains more effectively. Thus, the maximum $H_c$ is attained. As the atomic diffusion has reached a balance, further increase of annealing time at 480°C has little effect on the distribution of RE-rich boundary phases, which results in an almost constant iHc value. When the annealing temperature is further increased, atomic diffusion capability is enhanced and the interface balance between the RE-rich phases and RE$_2$Fe$_{14}$B grains is broken. The aggregation of RE-rich boundary phases occurs, and the contact area between hard magnetic RE$_2$Fe$_{14}$B grains increases. As a result, $H_c$ of the annealed magnets decreases by exchange coupling.

### 3.6. Improved properties and fracture strength by dehydrogenation

#### 3.6.1. Prepare method

Starting materials for the preparation of the alloy samples included Nd, Fe, Al, Dy, Ga, all 99.9wt% in purity, and a Fe–B alloy with 20wt% B and 80 wt% Fe. (NdDy)$_{14}$(FeAlGa)$_{79.8}$B$_{6.2}$ (at %) alloys were prepared by a strip casting technique, with a line speed of 2m/s. The strip casting was decrepitated for 10h in an airtight vessel under room temperature, with a hydrogen pressure of 0.17MPa. After HD, the coarse particles were dehydrogenated in a vacuum furnace under 5 different conditions, as listed in Table 3.3, followed by jet-milling to fine powders with an average size of 3.4um. The fine powders were then pressed at 6MPa, aligned with a perpendicular field of 1.8T. The green compacts were heated slowly and sintered in vacuum at 1070°C for 3h to reach full densification, and quenched to room temperature under a stream of Ar gas. A post-sintering cycle at 900°C for 2h followed by quenching to room temperature and annealing at 560°C for 3h was employed finally. The hydrogen content was determined with a LECO Hydrogen Determinator. The

<table>
<thead>
<tr>
<th>Dehydrogenation condition</th>
<th>Hydrogen content (ppm)</th>
<th>Phase composition</th>
<th>Lattice parameter</th>
<th>$\alpha$ (nm)</th>
<th>$c$ (nm)</th>
<th>$c/\alpha$</th>
<th>$V$ (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>3600</td>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
<td>0.8910</td>
<td>1.2329</td>
<td>1.3837</td>
<td>0.9788</td>
<td></td>
</tr>
<tr>
<td>300°C, 5h</td>
<td>1540</td>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
<td>0.8841</td>
<td>1.2231</td>
<td>1.3835</td>
<td>0.9560</td>
<td></td>
</tr>
<tr>
<td>450°C, 5h</td>
<td>870</td>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
<td>0.8823</td>
<td>1.2218</td>
<td>1.3848</td>
<td>0.9511</td>
<td></td>
</tr>
<tr>
<td>550°C, 5h</td>
<td>769</td>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
<td>0.8813</td>
<td>1.2211</td>
<td>1.3855</td>
<td>0.9484</td>
<td></td>
</tr>
<tr>
<td>650°C, 10h</td>
<td>472</td>
<td>Nd$<em>2$Fe$</em>{14}$B</td>
<td>0.8810</td>
<td>1.2208</td>
<td>1.3857</td>
<td>0.9475</td>
<td></td>
</tr>
</tbody>
</table>
oxygen content was measured by an Infrared Oxygen Determinator IRO-I.

Specimens for bending tests with dimensions of 4mm×7mm×30mm were cut from the sintered blocks by spark erosion. The surface was mechanically polished using 500-grit SiC paper to eliminate the possible influence of the surface roughness. The 3-point bending strength was measured with a SHIMADZU universal testing machine. The crosshead was perpendicular to the alignment direction, with a speed of 0.05mm/min. The impact toughness was measured by a JB-5 shock test machine, using V-type notch specimens (10mm×10mm×55 mm in size), according to the national standard GB 229-63 (Chinese standard).

3.6.2. Dehydrogenated powders properties

Table 3.3 shows hydrogen content, phase composition and lattice parameters of the HD powders desorbed at different conditions prior to the jet-milling step. It can be seen that with increasing temperature and time the hydrogen content decreased significantly, from 3600ppm of the untreated HD powders to 472ppm after dehydrogenation at 650°C for 10h. The XRD patterns of HD powders treated under the above conditions are shown in Figure 3.18. As can be seen, the patterns were similar but showed a discernable shift toward higher diffraction angles with increasing dehydrogenation degree. This shift reveals that the tetragonal structure of the NdFeB phase was retained but the lattice parameters a and c decreased with decreasing hydrogen content. The phases and lattice constants derived from XRD patterns are also listed in Table 3.3. It can be seen that the expansion of the matrix lattice increased from a =0.8810nm in the Nd$_2$Fe$_{14}$B phase to a

![Figure 3.18. The XRD patterns of HD powders desorbed at different conditions.](image-url)
=0.8910nm in the Nd$_2$Fe$_{14}$BH$_{4.73}$ phase, which is in good agreement with Isnard et al.$^{19}$.

Also, it can be seen from Figure 3.18 that when the HD powders desorbed at 650°C for 10h, no significant amount of iron-rich phase can be observed. So it is believed that the disproportionation process has not happened.

### 3.6.3. Magnetic properties

Magnetic properties of the sintered NdFeB prepared using HD powders subjected to the various dehydrogenation conditions are given in Figure 3.19. The remanence $B_r$ of the sintered magnets increased linearly, from 12.72 to 13.14kGs, with decreasing hydrogen content of the HD powder. The $(BH)_{\text{max}}$ shows the same trend as that of $B_r$. The intrinsic coercivity $H_{ci}$ increased sharply from 7.86 to 17.48 kOe, about 220% improvement was achieved, as hydrogen content decreased from 3600 to 870 ppm, and remained almost constant at 17.5 kOe with further decreasing hydrogen content to 472 ppm. It is clear that lower hydrogen content benefits the magnetic properties of the sintered NdFeB.

### 3.6.4. Mechanical properties

Figure 3.20 illustrates both bending strength and impact toughness of the sintered magnets, as a function of the hydrogen content in HD powders. When the hydrogen content decreased from 3600 to 472 ppm, it nearly doubled the bending strength and the impact toughness increased greatly from 2.78 to 7.58kJ/m$^2$. It has been noted that, for all final sintered magnets, the contents of hydrogen and oxygen are almost the same for about 20 and 1200 ppm, respectively.

![Figure 3.19](image_url)  
*Figure 3.19. Effects of hydrogen content in HD powders on the magnetic properties of the sintered magnets.*
Figure 3.20. Effects of hydrogen content in HD powders on mechanical properties of the sintered magnets. The error bar represents the standard deviation obtained from 5 samples.

Figure 3.21. Macrostructure of magnets produced by HD powders untreated (a) and dehydrogenated at 300°C for 5h (b).

3.6.5. Structure of magnets

The macrostructure and microstructure of magnets produced by HD powders desorbed under different conditions is shown in Figures 3.21 and 3.22, respectively. In Figure 3.21(a), for the final magnet produced by untreated HD powders, the macrocracks were distributed even at the surface. In Figure 3.22, more pores were found in the magnet prepared by powders dehydrogenated at 300°C for 5h than that by powders dehydrogenated at 650°C for 10h. The magnet produced by HD powders with lower hydrogen content possessed more perfect grains and clearer, smoother grain boundaries.

The magnetic behavior of the sintered magnets using the various dehydrogenation conditions can be attributed partly to the effects of
hydrogen on magnetic properties of the powders. The lattice parameters ratio c/a increased with decreasing hydrogen content in HD powders, also, the magnetocrystalline anisotropy decreased from 8 to 2T when the x value of Nd₂Fe₁₄BHₓ increased from 0 to 4. This means that the powder alignment of Nd₂Fe₁₄B will be higher than that of Nd₂Fe₁₄BHₓ under the same applied perpendicular field of 1.8T in the present experiment. As a result, higher values of B_r and H_ci were obtained for the magnets produced by HD powders with lower hydrogen contents.

According to Williams et al., the dehydrogenation process can be divided into 2 stages. The first stage occurred between 200 and 400°C, due to the matrix-phase desorption, and the second stage occurred at around 650°C, due to the RE-rich boundary-phase desorption. In case of untreated HD powders, a large amount of hydrogen existed in both the matrix-phase Nd₂Fe₁₄BH₄.₇₃ and the RE-rich phase diffused out during sintering. The macrocracks shown in Figure 3.21(a) can be seen in the magnet, and it exhibited the lowest values of H_ci for 7.86 kOe and bending strength for 135.8MPa. For HD powders desorbed at 300°C for 5h, the hydrogen remained in the matrix-phase Nd₂Fe₁₄BH₁.₈₆ and RE-rich phase diffused out during sintering and induced plenty of microcracks and pores, but no macrocracks were found. For HD powders with even lower hydrogen content of 472 ppm, the hydrogen had almost desorbed totally from the matrix-phase Nd₂Fe₁₄B and only few remained at grain boundaries, which resulted in only small amounts of microcracks and pores. In addition, this magnet had a fine microstructure and clear grain boundaries which reduced the nucleation of reverse domain and hence possessed a value of H_ci for 17.48 kOe and higher mechanical properties. This can well explain the curve of H_ci shown in Figure 3.19.

The bend fracture of NdFeB magnets has been found to be mainly intergranular. It can thus be concluded that the fracture strength is affected greatly by the grain boundaries. During sintering, the hydrogen atoms diffused out through grain and grain boundaries of the green compact. The microcracks induced by the hydrogen atoms out-take channel aggravated inevitably the microstructure of grain and grain boundaries. Thus, a higher hydrogen content in HD powders prior to sintering resulted in a lower mechanical property for final magnets.

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