MAGNETIC PROPERTIES AND CORROSION RESISTANCE OF UNCOATED AND COATED RARE-EARTH BASED PERMANENT MAGNETS

By

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MAGNETIC PROPERTIES AND CORROSION RESISTANCE OF UNCOATED AND COATED RARE-EARTH BASED PERMANENT MAGNETS

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Dedicated to my mother, family and father-in-law for their prayers, persistent support, motivation and encouragement throughout the thick and thin towards the completion of present research work and the thesis.
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Amjad Ali
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<th>Symbol</th>
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<tr>
<td>$H_C$ or $H_{Ci}$</td>
<td>Intrinsic Coercivity</td>
</tr>
<tr>
<td>$B_H$</td>
<td>Coercivity</td>
</tr>
<tr>
<td>$B$</td>
<td>Magnetic Flux density or Induction</td>
</tr>
<tr>
<td>$B_r$</td>
<td>Remanent Induction or Remanence</td>
</tr>
<tr>
<td>$B_i$</td>
<td>Intrinsic Flux Density or Induction</td>
</tr>
<tr>
<td>$BH_{max}$</td>
<td>Maximum Energy Product</td>
</tr>
<tr>
<td>$R$</td>
<td>Rare earth component</td>
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<tr>
<td>$H_A$</td>
<td>Anisotropy field</td>
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<tr>
<td>$K$</td>
<td>Anisotropy constant</td>
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<tr>
<td>$\phi$ phase</td>
<td>$\text{Nd}<em>2\text{Fe}</em>{14}\text{B}$ phase</td>
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<tr>
<td>$\eta$ phase</td>
<td>$\text{Nd}_{1+\epsilon}\text{Fe}_2\text{B}_4$ phase</td>
</tr>
<tr>
<td>$\rho$ phase</td>
<td>$\text{Nd}_5\text{Fe}_2\text{B}_6$ phase</td>
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<tr>
<td>$T_C$</td>
<td>Curie Temperature</td>
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<tr>
<td>$M_S$</td>
<td>Saturation Magnetization</td>
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<tr>
<td>$\mu_B$</td>
<td>Bohr Magnetron</td>
</tr>
<tr>
<td>$h$</td>
<td>Plank’s constant</td>
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<tr>
<td>$m$</td>
<td>Mass of electron</td>
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<tr>
<td>$e$</td>
<td>Electronic charge</td>
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<tr>
<td>$\mu_0$</td>
<td>Magnetic constant</td>
</tr>
<tr>
<td>$J$</td>
<td>Magnetic moment per unit volume</td>
</tr>
<tr>
<td>$H_d$</td>
<td>Demagnetization field</td>
</tr>
<tr>
<td>$\chi_m$</td>
<td>Magnetic Susceptibility</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Magnetic Permeability</td>
</tr>
<tr>
<td>$i_{app}$</td>
<td>Applied current density</td>
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<tr>
<td>$i_{Corr}$</td>
<td>Corrosion current density</td>
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<tr>
<td>$E$</td>
<td>Applied potential</td>
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<tr>
<td>$E_{Corr}$</td>
<td>Open circuit potential or Free corroding potential</td>
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<td>$C$</td>
<td>Interfacial capacitance associated with electrochemical double layer</td>
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<td>Tafel co-efficient related to the slope of polarization curve in the cathodic region</td>
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\( \frac{dE}{dt} \)  Scan rate or rate of change of applied potential

\( \rho \)  density

\( k \)  \( 1.288 \times 10^5 \) when CR is in mills per year (mpy)

\( E_{\text{Pit}} \)  Pitting potential

\( E_{\text{Prot}} \)  Protection potential

\( 2\theta \)  Bragg’s angle of diffraction

\( R_p \)  Polarization Resistance

\( Z_{\text{re}} \)  Real Impedance

\( Z_{\text{im}} \)  Imaginary Impedance

\( R_{\text{ct}} \)  Charge transfer resistance

\( \alpha \)  The ratio of the lowest measured phase angle to the phase angle for ideal capacitor

\( f \)  Frequency of applied potential

\( F_n \)  Normal Force

\( d_L \)  Linear distance

\( \text{AE} \)  Acoustic Emission
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SYNOPSIS

The thesis presents the study of the magnetic properties, microstructure and corrosion resistance of sintered NdFeB permanent magnets with and without coatings. The sintered NdFeB permanent magnet is an exceptional technological material with the highest energy product of any permanent magnet material ever developed. At ambient temperature, NdFeB magnets are best known for their efficient utilization of electrical energy and thus occupied a leading position among the strong permanent magnetic materials for variety of engineering applications, namely computer peripherals, automation, automobile, aerodynamic, magnetic resonance, biomedical, acoustics and consumer electronics. However, the sintered NdFeB magnets are sensitive to temperature and corrosiveness of the working environment due to the electrochemically active phases in their microstructure, that deteriorate their efficiency as they corrode during exposure to humid or moist environments.

Surface engineering has been employed to synthesize non-magnetic ceramic and composite coatings on the sintered NdFeB magnets and the effect of these barriers on the magnetic properties and oxidation resistance of coating-substrate system have been investigated. The present work has employed the CAPVD titanium nitride coating in a novel way to provide corrosion protection to the sintered NdFeB magnets. A nickel strike layer was electrodeposited on sintered NdFeB magnets prior to the CAPVD process to produce a composite Ni/Ti$_2$N coating.

The purpose of this work is to provide improved corrosion protection to sintered NdFeB magnets without compromising the magnetic properties. To this end the coating morphology and the anti-corrosion characteristics of the composite coating in simulated marine and industrial environments have been evaluated by employing standard dc and ac electrochemical techniques.

The morphology of CAPVD Ti$_2$N ceramic coating is inherently incapable of completely encapsulating the substrate and therefore provides limited protection to the substrate. The limitation was catered by the novel composite coating that successfully protected the sintered NdFeB permanent magnets from corrosion. The Ni/Ti$_2$N composite coating for sintered NdFeB magnets significantly enhanced the corrosion resistance in both the chloride and the sulphate environment without affecting the magnetic properties.

The dc and ac electrochemical techniques proved that the composite coating provided improved and prolonged protection to the sintered NdFeB magnets compared to the ceramic and the nickel-copper-nickel coatings.
INTRODUCTION

Chapter 1

The chapter 1 gives the brief introduction of the permanent magnetic materials with their applications and functioning mechanism. It also gives the developmental history of permanent magnets and utilization of Lanthanides for producing anisotropic permanent magnets with high energy product. It also summarizes the effect of different elements on the properties of permanent magnets and the future challenges.
1.1 Scope of Thesis
The work presented in this thesis is intended to study the magnetic properties, microstructure and corrosion resistance of uncoated and coated sintered R-Fe-B permanent magnets.

The effect of multilayer ceramic and composite coatings on the magnetic properties and corrosion resistance of the coating-substrate system has been investigated with varying simulated environmental conditions employing different electrochemical techniques. The attempt for an incremental contribution to the existing scientific knowledge is marked by the surface engineering to synthesize better anti-corrosion barrier for the sintered NdFeB permanent magnets having improved corrosion resistance without any sacrifice of magnetic properties.

1.2 Introduction
A Permanent Magnetic Material is the material that maintains a permanent magnetic field without an energy input. Permanent magnets are indispensable in modern life and their role in today’s technology is still growing. Modern permanent magnets have major influence on the size, efficiency, response, stability and cost of magneto-electronic devices and systems. Today the permanent magnet is a vital component in a wide range of industrial, consumer and defense products.

Major applications involve the conversion of mechanical to electrical energy and vice versa. Permanent magnets are employed to exert a force on soft ferromagnetic objects that in turn perform mechanical work. General categories of permanent magnet functions are

- **Mechanical to Mechanical** such as attraction or repulsion
- **Mechanical to Electrical** such as generators and microphones
Electrical to Mechanical such as motors, loudspeakers, charged particle deflection
Mechanical to Heat such as eddy current and hysteresis torque devices
Special effects such as magneto-resistance, Hall Effect devices and magnetic resonance.

The usage of permanent magnet materials in information technology are continuously growing. Prominent examples are voice coil motors and hard disc drives. In early 1980’s, hard disk drives of under 10 MB with random access time of 65 milliseconds were the norm. Today, the standard drive is well over 100 GB having an access time of 10 milliseconds, is smaller in size and costs less than the old drives.

1.3 History of Permanent Magnet Materials
The oldest magnetic material known to mankind is the “Lodestone”, a form of magnetite (Fe₃O₄) that is magnetic in its natural state. This material was given the name “Magnes” because it was found in Magnesia, now Manisa in western Turkey. The first artificial magnet was made nearly three centuries ago, that was an iron needle which was “touched” or magnetized by a lodestone.

The development of magnetic devices and systems for a wide variety of applications are all products of the 20th century. Till the invention of Alnico in late 1930’s, steel compositions, with low energy product and coercivity, were the lone available permanent magnets. The Alnico magnets allowed product size reduction by replacing induction coils. Applications requiring thermal stability over wide temperature ranges still rely on alnico. Alnico magnets lead to the discovery of a new magnetic material approximately every 12 years thereafter as shown in Fig. 1.1. Ferrites were introduced in 1961 that remains the largest selling permanent magnet material on a weight basis primarily because of its relatively low price.

Fig. 1.1 Development of permanent magnetic materials

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1 S. Constantinides, MRS Conference and Exposition, San Francisco, May 1995
Next was Samarium-Cobalt and then Neodymium-Iron-Boron, the lanthanide based permanent magnets having a “square” second quadrant intrinsic curve.

### 1.3.1 Permanent Magnets Based On Lanthanides

In 1935, Urbaine, et al. reported that Gadolinium is ferromagnetic [1]. This work marked the beginning of using a lanthanide element in permanent magnets. It was found that large magnetic moments are present in some of the lanthanides but their Curie temperatures are at or far below room temperature.

The LnCo$_5$ compounds (Ln = Any Lanthanide) were recognized as excellent candidates for permanent magnetic materials in mid 1960’s, due to their high magnetocrystalline anisotropy and moderate saturation magnetization [2] [3] [4]. In the LnCo$_5$ structure, the heavy lanthanide moment coupled antiferromagnetically with the cobalt moment, reducing the saturation magnetization. So the primary interest focused on the light lanthanides, i.e. La, Ce, Pr, Nd, Sm and Y. In general, light lanthanides have smaller magnetic moments than the heavy lanthanides. In late 1960’s and early 1970’s, the first SmCo$_5$ magnets appeared due to the research and development efforts of several organizations, most notably, General Electric, Raytheon, Bell Telephone laboratories, Wright Patterson Air Force Base, N. V. Philips and Brown Boveri et Cie.

When SmCo$_5$ became a commercially viable magnet, research began in two directions. One direction was partial or total substitution for Samarium in the alloy, by one or more of the more abundant and less expensive lanthanides such as Ce, La, Nd, Pr and Mischmetal (MM). Second direction was partial or total substitution of Cobalt with Iron as iron has a slightly larger magnetic moment per atom and is less expensive than Cobalt. The goal was to reduce the cost of the magnet, by reducing the raw material cost, without adversely affecting the magnetic properties. Four distinct alloys evolved from that research.

The first was MMCo$_5$, which was far less expensive but had poor magnetic properties. So the tradeoff of magnetic properties versus alloy cost was unfavorable for MMCo$_5$. Similar behavior was also observed for CeCo$_5$, LaCo$_5$ and NdCo$_5$ [3]. The main fault was that the anisotropy was much lower for these compounds, making difficult to obtain acceptable i$H_C$ levels [5].

The second material was Sm$_{x}$Pr$_{1-x}$Co$_5$. Praseodymium is more abundant, less expensive and has a slightly larger magnetic moment than Samarium. A partial substitution of Pr for Sm actually improved $B_t$ and $BH_{max}$. But as the Pr/Sm ratio increases above 1, the stability of Sm$_x$Pr$_{1-x}$Co$_5$ alloy above room temperature was reduced and it was difficult to keep $iH_C$ as high as that of SmCo$_5$. Therefore, most commercial materials have a Pr/Sm under 0.5, for a good combination of magnetic properties and raw material cost. Attempts were also made for the PrCo$_5$ magnet [6, 7] but nothing is commercial as of this writing.

The third material was Sm$_2$(Co, Fe, Cu, Zr or Hf)$_{17}$ alloy system, referred as 2:17 magnets. This is a metallurgically complicated alloy system, with high $iH_C$ based on precipitation hardening. The Sm and Co levels are reduced while the magnetic properties are generally superior to SmCo$_5$. The major drawback to 2:17 magnets is their complicated processing, due in part to the fact that the alloy has at least 5 components, which must be held to tight tolerances. It is difficult to obtain the desired
microstructure for the best magnetic properties. The heat treatments are much longer and more complicated than heat treatments of SmCo$_5$. The limited availability of 2:17 magnets stem from these complications [8].

The fourth material was Nd$_2$Fe$_{14}$B that achieved the original goals of replacing Sm and Co in SmCo$_5$. The binary compounds of Ln-Fe, including Nd-Fe, were also examined in 1970’s but had at least one of the following problems, making them unsuitable as permanent magnets. The problems are:

- A Curie temperature near or below room temperature
- Unfavorable anisotropy
- Antiferromagnetic coupling between the lanthanide and the iron magnetic moments, resulting in low saturation magnetization

The critical addition of the metalloid element boron to the Nd-Fe alloy resulted in a slightly expanded crystal structure, overcoming the above mentioned drawbacks. In 1983, several groups reported independently, excellent permanent magnet properties based on the Nd-Fe-B alloy system [9, 10, 11, 12, and 13].

**1.3.2 The Lanthanides**

The lanthanides consist of elements number 57, Lanthanum, to 71, Lutetium, at the bottom of the periodic table. These elements have historically been called the rare earths, but this name is misleading, as they are neither rare like Gold nor earths like Magnesium or Calcium. At the time these elements were discovered, rare was an apt term. However, several large deposits are found all over the world. Cerium, the most abundant lanthanide, is more common in earth’s crust than Nickel. Lanthanide, the second most abundant lanthanide, is more common than Lead or Tin [14, 15].

Lanthanides are unusual in that they are all found together in the ore. Fig. 1.2 shows the breakdown of the most common lanthanide ores, *Bastnasite* and *Monazite*.

![Rare earth oxide breakdown](image-url)

_Fig. 1.2 The breakdown of the common lanthanide ores_
The periodic table shows that in the lanthanide series, the inner 4f electron shell is being filled from Lanthanum to Lutetium. This in part explains some of the facts known about the lanthanides.

- Chemically the lanthanides are all very similar since there is little difference in the outer electron configuration
- The lanthanide oxides are extremely stable since the outer electrons are easily removed from the metals
- The metallic form of any lanthanide is not found in nature. Lanthanides are always found as compounds, usually a complex oxide or fluoride
- Because the lanthanides are chemically similar and are found together in the ore, their separation is difficult

There are two methods of separating lanthanides, i.e. Solvent Extraction and Ion Exchange. Purities, as high as 99.999%, can be obtained with either technique.

Lanthanide metals are generally reduced by Calciothermic Reduction of a salt, usually fluoride or chloride. The exceptions are Samarium and Europium, which due to their low boiling point are distilled in the presence of mischmetal.

Electrolytic techniques may also be used but are cost effective and feasible for large production volumes.

1.4 Samarium Iron Nitride (Sm$_2$Fe$_{17}$N$_3$)
In 1990 Coey et. al. [16] showed Sm$_2$Fe$_{17}$N$_3$ exhibits good intrinsic magnetic properties and could be used for permanent magnets. The intermetallic compound is an interstitial modification of Sm$_2$Fe$_{17}$. The nitrogen atoms are diffused into the interstitial sites resulting in the lattice expansion and strong uniaxial anisotropy with high saturation magnetization and high Curie temperature [17]. The problem is with the compaction and densification of these magnetic powders. As the powders are heated to about 550°C they decompose to SmN, FeN$_x$ and α-Fe. Therefore, the high coercivity anisotropic Sm$_2$Fe$_{17}$N$_3$ powders are particularly suitable for bonded magnets [18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28]. The Sm$_2$Fe$_{17}$N$_3$ powders are bonded either in resin or low melting metals such as Zn, Sn, Al, Ga and related alloys. Among such bonded magnets prepared to date, Iriyama et. al. [25] have recorded the highest properties [BH$_{max}$= 134 kJ/m$^3$, iH$_C$= 0.81MA/m] on anisotropic Zn metal-bonded Sm$_2$Fe$_{17}$N$_3$. Machida et. al. [29] used In-Zn alloy as the metal binder and have reported the BH$_{max}$= ~151 kJ/m$^3$ and iH$_C$= 0.72MA/m.

1.5 The R$_2$Fe$_{14}$B Permanent Magnets
These magnet materials are characterized by strong magnetic anisotropy. The exchange interaction is supplemented by a further mechanism which removes the directional freedom of the magnetization. The rare earth component ‘R’ is responsible for the magnetic anisotropy while the 3d-component of transition element provides a sufficiently high magnetization and Curie temperature.

1.5.1 Magnetic Anisotropy
A magnetic material exhibits magnetic anisotropy if its internal energy depends on the direction of the spontaneous magnetization. Magnetic anisotropy is the preference of magnetic moments to lie along a specific direction. There are different
forms of anisotropy namely shape anisotropy, crystal anisotropy, strain anisotropy, surface anisotropy and exchange anisotropy.

For any source of anisotropy the intrinsic coercivity “$H_{ci}$” may be calculated by following the changes in the equilibrium positions of the magnetization. Mathematically,

$$H_{ci} = H_A = \frac{2K}{B_i}$$

Where ‘$K$’ is the anisotropy constant and its value depends on its physical origin. ‘$H_A$’ is the anisotropy field.

In most materials the spin-orbit coupling is fairly weak, and so the magnetocrystalline anisotropy is not particularly strong. In rare earth materials, however, the spin-orbit coupling is strong because rare earth elements are heavy. Once magnetized, a large field must be applied in the direction opposite to the magnetization in order to overcome the anisotropy and reverse the magnetization. A polycrystalline sample with no preferred orientation of its grains will have no overall crystalline anisotropy. If the sample is spherical, the same magnetic field will magnetize it to the same extent in every direction. However, if the sample is not spherical, then it will be easier to magnetize it along a long axis. This phenomenon is known as “Shape Anisotropy”. The anisotropy constant increases as the axial ratio increases.

Shape anisotropy arises from the dipole-dipole effects in various particle shapes. The crystal anisotropy or “Magnetocrystalline Anisotropy” is an intrinsic effect. It arises because the electrons orbit with their small contributions to the magnetic moment, are coupled to the crystal lattice, causing the moments to prefer to align themselves along certain crystallographic axes. The orbital motion then couples to the spin moments. The effect is quite sensitive to crystal symmetry and is often largest in crystals of lowest symmetry. The rare earth permanent magnet materials are actually the compounds with high crystal anisotropy.

Other forms of anisotropy are not of as much significance as shape and crystal anisotropy.

### 1.5.2 The Nd$_2$Fe$_{14}$B System

The Nd-Fe-B system contains three ternary stable phases i.e. Nd$_2$Fe$_{14}$B ($\phi$), Nd$_{1.5}$Fe$_4$B$_4$ ($\eta$) and Nd$_5$Fe$_2$B$_6$ ($\rho$) [30, 31]. The phase responsible for the exceptional hard magnetic properties was identified as being the 2:14:1 phase. The Nd$_2$Fe$_{14}$B is a tetragonal compound with its easy direction of magnetization along the c-axis [32].

The isothermal sections of this ternary system are strongly temperature dependent. When a molten alloy of the composition Nd$_2$Fe$_{14}$B would be allowed to cool infinitely slowly, the liquidus is traversed at about 1280°C. Further cooling leads to the crystallization of crystals of pure Fe from the melt. Their number and magnitude increases steadily until at about 1180°C the peritectic melting point of the Nd$_2$Fe$_{14}$B phase is reached. Below this temperature the Fe crystals and the remaining less Fe-rich liquid phase are no longer equilibrium phases and have to transform into Nd$_2$Fe$_{14}$B. After sufficient time only the phase Nd$_2$Fe$_{14}$B will be left, being also the phase stable at room temperature [33].
In a normal casting process, the peritectic formation of Nd$_2$Fe$_{14}$B will be incomplete, leaving residues of primary Fe crystals in the Nd$_2$Fe$_{14}$B grains, which in turn, are surrounded by a relatively Nd-rich liquid that has solidified at the eutectic temperature at about 630°C. The presence of the primary Fe crystals is harmful for the attainment of sufficiently high coercivity owing to wall nucleation. This is the reason that cast Nd$_2$Fe$_{14}$B magnets have low coercivity.

Another approach is to choose alloys with a concentration range where the crystallization of primary Fe is avoided. One of these commercially available alloys is known as “Neomax” having composition Nd$_{15}$Fe$_{77}$B$_8$.

### 1.5.3 The Effect of Individual Alloyning Elements

The usefulness of small additions of several alloying elements has been one of the interesting aspects of the development of Nd-Fe-B magnets. Most of the periodic table has been tried to improve the performance of the basic alloy, in some respect. Table-1.1 summarizes the effect of the most popular alloying elements and the mechanism on their influence.

<table>
<thead>
<tr>
<th>Element</th>
<th>Typical Addition (wt.%)</th>
<th>Cause</th>
<th>Effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dysprosium</td>
<td>0 – 5</td>
<td>Increase $K$</td>
<td>Decreases $B_r$</td>
<td>34</td>
</tr>
<tr>
<td>Praseodymium, Cerium, Lanthanum. Yttrium, Hafnium, Europium, Thulium, Lutetium,</td>
<td>25 (Nd)</td>
<td>Decreases $T_C$</td>
<td>Decreases $M_S$ &amp; $H_A$</td>
<td>35</td>
</tr>
<tr>
<td>Samarium, Terbium, Gadolinium</td>
<td>25 (Nd)</td>
<td>Increases $T_C$</td>
<td>Decreases $M_S$ Increases $H_A$</td>
<td>35</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0 – 10</td>
<td>Increases $T_C$</td>
<td>Increases operating temperature</td>
<td>34</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0 – 1</td>
<td>Grain boundary modification</td>
<td>Increases $H_C$</td>
<td>36</td>
</tr>
<tr>
<td>Gallium</td>
<td>0 – 1</td>
<td>Grain boundary modification</td>
<td>Lower losses</td>
<td>36</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0 – 1</td>
<td>Grain boundary modification</td>
<td>Decreases Corrosion</td>
<td>37</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Element</th>
<th>Range</th>
<th>Grain boundary modification?</th>
<th>Effect</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molybdenum</td>
<td>0 – 1</td>
<td></td>
<td>Corrosion, lower losses</td>
<td>38</td>
</tr>
<tr>
<td>Niobium</td>
<td>0 – 1</td>
<td></td>
<td>Lower losses</td>
<td>39</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0 – 1.2</td>
<td></td>
<td>Decreases Corrosion</td>
<td>40</td>
</tr>
<tr>
<td>Carbon</td>
<td>0 – 0.14</td>
<td></td>
<td>Decreases Corrosion</td>
<td>40</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0 – 0.1</td>
<td></td>
<td>Decreases Corrosion</td>
<td>40</td>
</tr>
</tbody>
</table>

Many elements are effective at very low addition levels, up to 1% by weight, indicating that these elements are influencing the grain boundary phases. Elements like Dy and Co require larger additions to be useful and seem to be substituting for Nd and Fe, respectively in the matrix phase.

1.6 The Future
The rare earth based permanent magnets have been a very popular area of research in recent past. Their development has been rapid and their commercialization has been extraordinarily rapid. Yet many challenges remain unanswered, e.g.

- What improvements are possible with the basic Nd-Fe-B system
- What are the alternating processing techniques
- Which technique is preferable for a given application
- How to improve the corrosion resistance of Nd-Fe-B magnets
- What surface treatments or coatings are possible and which one is suitable for a given environmental application
- How to raise the maximum operating temperature for the Nd-Fe-B system
- How to lower the cost
- How to recycle the scrap material

1.7 References

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MAGNETISM AND NdFeB MAGNETS

Chapter 2

The chapter reviews the literature so as to refresh the basic definitions and units pertaining to the magnetism and magnetic properties of the magnetic materials. The microstructural phases in the sintered NdFeB permanent magnets and their corrosion potentials have been reviewed. At the end, a comparison for the corrosion control solutions adopted so far has also been drawn.
Magnetism & NdFeB Magnets

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  2.6.2 Paramagnetism 17
  2.6.3 Ferrimagnetism 17
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2.1 Origin of Magnetism

In 1827, Ampere suggested that the magnetic force is due to the electrical currents continually circulating within the atom [41]. Over the years it was established that “Magnetism” is a property of certain materials by which they develop a field of force around them known as Magnetic Field. A magnetic field is produced whenever a charge is in motion and the magnetization of a piece of material has its origins in the spin and angular momentum of its electrons, see Fig. 2.1 (redrawn’).

The magnetic force or field associated with a single spinning and revolving electron is termed as magnetic moment of the electron. Each spinning electron behaves as a magnetic dipole and has a dipole moment called Bohr Magnetron – $\mu_B$.

Mathematically,

$$\mu_B = \frac{e\hbar}{4\pi m}$$

Where ‘e’ is the electronic charge, ‘h’ is Plank’s constant and ‘m’ is electronic mass. The SI units of Bohr Magnetron is ampere/sq. meter (A·m$^2$).

$$1\mu_B = 9.27 \times 10^{-24} \text{ A·m}^2$$

In an atom most electrons are paired in the orbitals and have opposite spin. Due to this opposite spin, the electrons exhibit positive and negative magnetic moments. The positive magnetic moments are counter-balanced with the negative magnetic moments. Only an un-paired electron can have a small positive magnetic moment. The un-paired electrons are present in the valence shells and in the partially filled, inner 3d orbitals of transition elements and 4f orbitals of rare-earth elements. The valence electrons are engaged in bonding with other electrons and thus counter-balance each other’s magnetic moment. The magnetic moments of electrons of partially filled, inner 3d/4f orbitals are not counter-balanced by other electrons and the effect is manifested in the form of a strong magnetic moment.

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Mostly, these moments are randomly aligned, resulting in no net magnetization in the bulk material. But in certain materials the magnetic moments of adjacent atoms are aligned in a parallel direction by a phenomenon known as **Spontaneous Magnetization**. This parallel alignment of atomic magnetic dipoles occurs only in microscopic volume regions called **Magnetic Domains**; see Fig. 2.2 (redrawn²).

### 2.2 Definitions and Units

The parallel alignment of magnetic domains in a bulk solid means that the material is magnetized. Thus **Magnetization** is the parallel alignment of magnetic domains or a measure of the increase in magnetic flux of a material in a magnetic field of strength “H”. The magnetization of a magnetic material is denoted by “M” and is proportional to the applied magnetic field denoted by “H”.

#### Table 2.1 Symbols, definitions and units

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Definitions</th>
<th>CGS</th>
<th>SI</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi )</td>
<td>Flux or lines of force</td>
<td>Maxwell</td>
<td>Weber (Wb)</td>
</tr>
<tr>
<td>( B )</td>
<td>Flux density or induction ( B = \phi/ A = \mu_0 H + B_i )</td>
<td>Maxwell/cm² = gauss (G)</td>
<td>Wb/m² = tesla (T)</td>
</tr>
<tr>
<td>( H )</td>
<td>Magnetic field strength</td>
<td>Oersted (Oe)</td>
<td>Ampere-turns/meter (A/m)</td>
</tr>
<tr>
<td>( \mu_0 )</td>
<td>Magnetic constant</td>
<td>Unity i.e. 1G=1Oe</td>
<td>( 4\pi \times 10^{-7} ) henry/m (( 4\pi \times 10^{-7} ) Wb/Am)</td>
</tr>
<tr>
<td>( \mu_0 H )</td>
<td>Field flux density in space</td>
<td>Gauss (G)</td>
<td>Tesla (T) or Wb/m²</td>
</tr>
<tr>
<td>( B_i )</td>
<td>Intrinsic flux density ( B_i = B - \mu_0 H )</td>
<td>Gauss (G)</td>
<td>Tesla (T)</td>
</tr>
<tr>
<td>( B_{is} )</td>
<td>Saturation flux density ( B_{is} = 4\pi J_s )</td>
<td>Gauss (G)</td>
<td>Tesla (T)</td>
</tr>
<tr>
<td>( J )</td>
<td>Intensity of magnetization or magnetic moment per unit volume ( (J=B/4\pi) )</td>
<td>Gauss (G)</td>
<td>Tesla (T)</td>
</tr>
<tr>
<td>( H_d )</td>
<td>Demagnetizing field (self)</td>
<td>Oe</td>
<td>A/m</td>
</tr>
<tr>
<td>( H_a )</td>
<td>Applied or external magnetic field strength</td>
<td>Oe</td>
<td>A/m</td>
</tr>
<tr>
<td>( H_c )</td>
<td>Coercivity, magnetic field strength to reduce ( B ) to zero after saturation</td>
<td>Oe</td>
<td>A/m</td>
</tr>
<tr>
<td>( H_{ci} )</td>
<td>Intrinsic coercive force, magnetic field strength to reduce ( B_i ) to zero after saturation</td>
<td>Oe</td>
<td>A/m</td>
</tr>
<tr>
<td>( (BH)_{max} )</td>
<td>Maximum Energy Product</td>
<td>Million Gauss-Oersted (MGOe)</td>
<td>Kilojoules/meter³ (kJ/m³)</td>
</tr>
</tbody>
</table>

Table 2.2 Conversion factors for some units

<table>
<thead>
<tr>
<th>Quantity</th>
<th>CGS to SI</th>
<th>SI to CGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>1 maxwell = $10^{-4}$ Wb</td>
<td>1 Wb = 1 V.s = $10^4$ maxwell</td>
</tr>
<tr>
<td>$B$</td>
<td>1 G = $10^{-4}$ T</td>
<td>1 T = 1 Wb/m$^2$ = $10^4$ G</td>
</tr>
<tr>
<td>$H$</td>
<td>1 Oe = 79.58 A/m</td>
<td>1 A/m = $12.57 \times 10^{-3}$ Oe</td>
</tr>
<tr>
<td>$\mu_0 H$</td>
<td>1 Oe = $10^{-4}$ T</td>
<td>1 T = $10^4$ Oe</td>
</tr>
<tr>
<td>$(BH)_{max}$</td>
<td>1 MGOe = 7.96 kJ/m$^3$</td>
<td>1 kJ/m$^3$ = $12.57 \times 10^{-2}$ MGOe</td>
</tr>
</tbody>
</table>

Mathematically,

$$M \propto H$$

or

$$M = \chi_m \cdot H$$

where ‘$\chi_m$’ is constant of proportionality and is known as Magnetic Susceptibility. It has no dimensions. The SI unit for magnetization and magnetic field is same i.e. ampere/meter (A/m).

Table-2.1 presents different units with their definitions and symbols while Table-2.2 gives their conversion factors.

The unit of magnetic field is derived from the equation

$$H = \frac{0.4 \pi ni}{l}$$

Where ‘n’ is the number of turns of the current carrying solenoid, ‘i’ is the current and ‘l’ is the length of the solenoid.

When a magnetic material is placed in an applied magnetic field the intensity of magnetic field is increased. This increase in magnetization is measured by a quantity called Magnetic Permeability - $\mu$. It is the ratio of the magnetic induction to the applied magnetic field.

Mathematically,

$$\mu = \frac{B}{H}$$

The Permeability of Vacuum is $\mu_0 = 4\pi \times 10^{-7}$ Tesla·m/A whereas the Relative Permeability is $\mu_r = \mu/\mu_0$ which is a unit less quantity.

Here ‘$B$’ is the Magnetic Induction, defined as the sum of the applied field and the external field that arises from the magnetization of a material inside the field.

Mathematically,

$$B = \mu H = \mu_r H + \mu_r M = \mu_r H + J$$
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The SI unit for B is Weber/meter\(^2\) (Wb/m\(^2\)) or Tesla (T).

Where ‘J’ is known as Magnetic Polarization, defined by the equation

\[ J = \mu_0 M \]

The unit for ‘J’ is same as that for ‘B’ i.e. Weber/meter\(^2\) (Wb/m\(^2\)) or Tesla (T).

### 2.3 Domain Theory

In 1852, Weber [42] suggested that the atomic magnetic moments with in the bulk solid could be randomly aligned to give a zero vector sum over the whole solid for the demagnetized condition and upon magnetization the moments become ordered or aligned under the influence of applied field. In 1893, Ewing also explained the magnetized and demagnetized conditions of iron bar as aligned and randomly oriented molecular magnets in the material [43]. These ideas were developed further by Weiss who in 1906-1907 [44, 45] explained the existence of magnetic domains in ferromagnets in his “Domain Theory”. According to the theory, the ferromagnets have volume regions, the “Domains” in which large number of atomic magnetic moments, typically, \(10^{12}\) to \(10^{15}\), are aligned parallel even without any external magnetic field. The magnetization in a domain is almost saturated. The direction of alignment varies from domain to domain in a random manner with narrow zones that separate the two domains – the domain walls or Bloch Walls. The directions of magnetic moments continuously change from one domain to the next domain. The Bloch Walls are about 1000 °A thick. The main points of the theory are;

- Atomic magnetic moments exist permanently
- A magnetic domain always consists of aligned atomic magnetic moments even in the demagnetized state of ferromagnet
- The magnetic domains are randomly aligned in a demagnetized ferromagnet
- The magnetization involves re-orientation of domains so that the volumes of domains aligned with the field are greater than those aligned opposite to the field

### 2.4 Magnetization Curve

When magnetic field is applied to a magnetic material, it tends to orientate the magnetic domains in the direction of the applied field. This re-orientation of the magnetic domains under the influence of applied field is termed as induced magnetization or magnetization of the material. The magnetization curve for a ferromagnetic material is shown in the Fig. 2.3 (redrawn\(^2\)).
At the onset, the domains with magnetic moments in opposite direction to the applied field referred as “unfavourably oriented domains” start shrinking in size where as the “favourably oriented domains” grow in size. At the final stage the grown domains rotate in the direction of the field in order to achieve saturation. The field strength required for the growth of favourably oriented domains at the expanse of unfavourably oriented domains is much less than that required for the rotation of domains to achieve the saturation. Any increase in the field strength after achieving saturation cannot induce further magnetization in the material, the material is said to be “Saturated”.

2.5 Magnetic Hysteresis

If the applied field is removed after achieving saturation, the reversion of domains back to the random orientation is resisted by the Bloch Walls and many of the domains remain oriented and a residual magnetization, known as the Remanence – $B_r$ persists in the material. The virgin magnetization curve is not re-traced rather it takes the path $\overline{AC}$ shown in the Fig. 2.4 (redrawn$^2$).

On applying the field in the reversed direction, the domains aligned in the opposite direction start growing and the magnetization start decreasing to zero. The negative field strength required to demagnetize the material or to bring the magnetization to zero is termed as the Coercivity or Coercive Force – $H_c$. Further increase in the negative field strength eventually aligns the domains to saturate in the opposite direction. Again removing the field does not bring the magnetization to zero and increasing the field to saturate the material does not re-trace the path on the virgin curve but the material saturates through a different path (EFGA) forming a closed
loop known as **Magnetic Hysteresis Loop**. The hysteresis loop of a ferromagnetic material gives the quantitative measure of the **Saturation Magnetization** – $M_s$, **Remanence** – $B_r$, **Coercivity** – $H_c$ and **Energy product** – $BH_{\text{max}}$.

### 2.6 Types of Magnetism

The different responses to an applied field leads to the division of materials into five categories, diamagnetic, paramagnetic, ferrimagnetic, ferromagnetic and anti-ferromagnetic.

#### 2.6.1 Diamagnetism

A weak, negative, repulsive reaction of a material to an applied magnetic field is known as **Diamagnetism**, see figure-2.5. The diamagnetic materials have $\mu < \mu_0$. The magnetic susceptibility is of the order of $-10^{-6}$ ($\chi_m = -10^{-6}$). Diamagnetism occurs in all materials, but its negative effect is cancelled by positive magnetic effects. Cd, Cu, Ag, Sn and Zn are diamagnetic materials. Diamagnetic behaviour has no significant engineering importance.

#### 2.6.2 Paramagnetism

A weak, positive, attractive reaction of a material to an applied magnetic field is known as **Paramagnetism**, see figure-2.5. The paramagnetic materials have $\mu > \mu_0$. The magnetic susceptibility is of the range of $10^{-6}$ to $10^{-2}$ ($\chi_m = 10^{-6}$ to $10^{-2}$). Al, Ca, Pt, Ti and O are paramagnetic materials. An increase in temperature decreases the paramagnetic effect. The diamagnetism and paramagnetism in materials disappear as the applied field is removed.

#### 2.6.3 Ferrimagnetism

The anti-parallel alignment of magnetic dipole moments of different ions of an ionic solid due to an applied magnetic field, resulting in a net positive magnetic moment is known as **Ferrimagnetism**, see figure-2.5. As a group, ferrimagnetic materials are called “Ferrites”. Ferrites are ceramic materials. One group is based on magnetite ($\text{Fe}_3\text{O}_4$). Ferrites are useful for many electronic applications owing to their low conductivities.

#### 2.6.4 Ferromagnetism

The creation of a very large magnetization in a material due to an applied magnetic field is known as **Ferromagnetism**; see Fig. 2.5 (redrawn$^3$).

A ferromagnetic material retains much of the magnetization even after the removal of magnetic field. Fe, Co and Ni are ferromagnetic materials. They have un-paired 3d electrons and positive exchange energies which result in spontaneous magnetization. Gadolinium (Gd), a rare earth element, is also ferromagnetic but below 16°C which limits its industrial applications. Large magnetic fields that can be retained or eliminated as desired can be produced in ferromagnetic materials.

---

2.6.5 Antiferromagnetism
In this type of magnetization, the magnetic dipoles of atoms are aligned in opposite direction to an applied magnetic field, so that there is no net magnetization. Mn and Cr are anti-ferromagnetic materials. They have un-paired 3d electrons but negative exchange energies that do not produce spontaneous magnetization.

2.7 Energies in Ferromagnetism
The total magnetic energy of a ferromagnetic material is the resultant of five types of energies that is, exchange energy, magneto-static energy, magneto-crystalline anisotropy energy, domain wall energy and magneto-strictive energy. The most stable domain structure is attained when the overall potential energy of the ferromagnetic material is a minimum.

2.7.1 Exchange Energy
It is the energy associated with the coupling of individual magnetic dipoles into a single magnetic domain. In other words, it is the energy required to align the atomic magnetic dipoles in one direction within a magnetic domain. The parallel alignment of magnetic dipoles within a magnetic domain occurs only when the exchange energy has positive value that is when “a/d” ratio is in the range of 1.4 – 2.7, see Fig. 2.6 [46].
2.7.2 Magnetostatic Energy
It is the magnetic potential energy associated with the external magnetic field surrounding a sample of ferromagnetic material. The formation of multiple domains reduces the magneto-static energy of a unit volume of material.

![Exchange Energy Graph](image)

Fig. 2.6 Exchange energy as a function of a/d ratio. Elements with positive exchange energy are Fe, Co & Ni – Bathe-Slatter Curve

2.7.3 Magnetocrystalline Anisotropy Energy
It is the energy required to rotate the magnetic domains during magnetization of a ferromagnetic material. Due to crystalline anisotropy, it depends upon the direction of magnetization. In a polycrystalline material, the grains with orientations in the easy direction of magnetization, reach saturation magnetization at low applied fields. Grains of poly-crystalline ferromagnetic materials, reach saturation magnetization at different field strengths.

2.7.4 Domain Wall Energy
The magnetic potential energy associated with the disorder of magnetic dipole moments in the wall volume between magnetic domains is known as the Domain Wall Energy. A domain changes orientation gradually with a domain boundary being about 300 atoms wide. The wider the wall, the greater will be the number of dipoles forced to lie in directions different from those of easy magnetization and the magneto-crystalline anisotropy energy will be increased. The equilibrium wall width will be reached at the width where the sum of exchange and magneto-crystalline anisotropy energy is a minimum, see Fig. 2.7 (redrawn^2).

2.7.5 Magneto-strictive Energy
During magnetization the material either expands or contracts in the direction of magnetization. This change in dimension is attributed to the change in bond length between the atoms of the material due to the rotation of magnetic dipoles as they
align in the direction of magnetization. This magnetically induced reversible elastic strain is known as “Magnetostriction” and is of the order of $10^{-6}$. The Magnetostrictive Energy is the magnetic potential energy associated with the mechanical stress caused by magnetostriction in a ferromagnetic material.

![Diagram of energy vs. wall width]

Fig. 2.7 The equilibrium wall width corresponding to the minimum of the sum of exchange and magneto-crystalline anisotropy energies

### 2.8 Suitability criteria and general coercivity mechanism

Besides high values of Curie temperature, saturation magnetization and anisotropy, the suitability of a permanent magnet depends upon;

- High magnetization which is sufficiently temperature independent in the operational range of the magnets
- Persistent magnetization on removal of magnetizing field
- Persistent magnetization under demagnetizing fields

The demagnetization behaviour of a magnetic material is characterized by the nucleation of reversed domains and the motion of domain walls through the lattice. This is not an intrinsic property but depends strongly on the processing of the magnetic material. A magnetic material is said to be ideal, when the magnetic polarization “J” is field independent over a sufficiently large range of demagnetization field giving a linear decrease of the flux density “B” with the field “H” as shown in the Fig. 2.8 (redrawn).

The coercivity $B_HC$ is defined as the field for which the magnetic induction is zero. It is a measure of the resistance of magnet against demagnetizing fields. Another property is $H_C$ the intrinsic coercivity which is important in many static applications. The performance of a magnet is usually specified by its energy product $BH_{max}$ which is the product of magnetic induction and the corresponding demagnetizing field. It is
also known as the “Figure of Merit”. The energy products corresponding to all points on the BH curve are plotted on the abscissa in the right side of the Fig. 2.8 where the largest value is indicated by $BH_{\text{max}}$.

Industrial applications require stable coercivities and magnetizations up to 200°C. However, these properties decrease with increasing temperature resulting in a loss of magnetic performance. The loss of magnetic performance is usually reversible and recovered at a return to room temperature. For certain materials the loss in performance is partially irreversible. Therefore, the temperature coefficients of coercivity and remanence hold importance in designing magnets for a particular application.

The mechanism responsible for the development of large coercivity differs from material to material. Generally, for obtaining high values of coercivity the domain wall motion must be impeded. This can be achieved by pinning the domain walls either by inclusions or by micro-strains.

**2.8.1 Pinning by Inclusions**

Magnetic inclusions are the isolated regions of second phase materials having different magnetic properties compared to the matrix phase. These magnetic inclusions impede the domain wall motion by reducing the energy of domain walls. The magnetic inclusions intersect and attract the domain walls and thus reduce their energy resulting in the pinning of domains.
2.8.2 Pinning by Micro-strains
There are certain regions of inhomogeneous strain in the materials e.g. dislocations. These regions of inhomogeneous strain impede the motion of domain walls by interacting with the magnetic moments through magnetostriction. The domain walls need additional energy to overcome these energy barriers so as to continue their motion.

2.9 Single Domain Magnetic Particles
Decreasing the size of the magnetic particles to an extent less than the size of the equilibrium domain wall width - $E_{\text{Wall}}$, see Fig. 2.7 destabilizes the domain wall and the resulting material is a single domain magnetic particle. In the absence of domain walls, the magneto-static energy associated with the external magnetic field completely surrounds the particle, see Fig. 2.9 (redrawn²). When a domain wall is placed in the particle, the external magnetic field is concentrated at the two ends of the particle and the magneto-static energy is reduced approximately by a factor of two. It therefore means that the driving force for domain wall formation decreases as the particle size decreases. In other words, the particles smaller than a critical size are too small to support a domain wall.

![Formation of multiple domains reduces the magneto-static energy of a unit volume of energy](image)

When such a particle is magnetized along its easy axis, the demagnetization by domain wall motion cannot occur. As a consequence, large magnetic fields are required to rotate the magnetization from one easy direction through the hard direction into a reverse easy direction. Clearly, the coercivity of fine particles is quite large.

2.10 Processing Routes
There are several manufacturing routes for RFeB permanent magnets namely;

- Casting
- Powder metallurgical processing
- Melt spinning
- Mechanical alloying
Among these routes, the powder metallurgical processing leads to high performance magnet bodies. The casting route gives isotropic magnet bodies with considerably lower energy products compared to magnets produced by powder metallurgical techniques. On the other hand, the powder metallurgically produced magnets have poor corrosion resistance. The performance of melt spun ribbons depends strongly on the phases that form during the rapid solidification process, which in turn depends on the solidification rate and the nature and quantity of additives. Only powder metallurgical route is discussed here.

The Master Alloy is prepared either by Vacuum Melting of Elements or by Calciothermal Reduction. Induction melts of the nominal compositions \( \text{Nd}_x\text{B}_y\text{Fe}_{100-x-y} \) with \( x=13-19 \) and \( y=4-17 \) are made in alumina crucible under an argon gas atmosphere [47]. The master alloy is then subjected to crushing and milling in argon or nitrogen environment for size reduction. The ingots are crushed in a jaw crusher to a particle size \( \sim 1 \text{ mm} \), in a disc mill to \( \sim 100 \mu\text{m} \) and then pulverized in a ball mill containing 1,1,2-trichloro-1,2,2-trifluoroethane with stainless steel balls and lining to about 3 \( \mu\text{m} \).

An alternate method of size reduction is the “Hydrogen Decrepitation – HD” where ternary hydrides of the type \( \text{R}_2\text{Fe}_{14}\text{BH}_x \) can be prepared relatively easily by exposing powdered material to a positive pressure of hydrogen gas atmosphere at room temperature. The \( \text{Nd} \)-rich intergranular material and the matrix phase absorb a total of about 0.4 wt% hydrogen. The volume increase accompanying the absorption of hydrogen gas leads to pulverization of even large lumps of the cast material which, when combined with jet milling or disc milling, is an effective means of producing fine particles of \( \text{NdFeB} \).

After milling, the powder is pre-compact and aligned with a pulsed field up to 80 kOe. The aligned green compacts are further compacted either by uni-axial pressing or iso-static pressing up to 2000 bar. The alignment and compaction are carried out in argon (or nitrogen) environment.

The sintering process is preferably carried out in vacuum or argon gas atmosphere at temperatures from 1040–1130°C for 1 hour followed by rapid cooling in a cooling chamber. The sintered samples are given a post sintering heat treatment for 1 hour at 550–650°C and cooled rapidly. For HD powder compacts, desorption of hydrogen during sintering involves three stages. First, hydrogen is released by the matrix phase at about 200°C and subsequently by the \( \text{Nd} \)-rich intergranular material at 250°C and 600°C.

### 2.10.1 Powder Blending

Powder blending is an alternate method of varying the composition of an alloy prior to sintering, having distinct advantages compared to the compositional modification of the starting alloy at the pre-casting stage.

Otsuki et al. reported first in 1990 that powder blending was a suitable process for magnet production. Otsuki blended stoichiometric \( \text{Nd}_2\text{Fe}_{14}\text{B} \) with \( \text{Nd}_{30}\text{Fe}_{64}\text{B}_6 \) – the composition of the liquid phase during sintering [48]. The powders were mixed after rough milling but before fine milling. This process, often referred to as co-milling
causes the alloys to be broken up together, a degree of mechanical alloying may also occur. An enhancement in alignment of the matrix phase was noticed with this process and that the pickup of oxygen was also lower than with the standard processing route. Miao et al. (1996) also produced magnets by mixing Nd$_2$Fe$_{14}$B with HD liquid phase composition powder prior to fine milling [49]. These magnets showed higher remanence and squareness than those produced by the conventional method. Again domain observation showed good alignment of the matrix phase and an energy product of 43 MGOe (340kJ/m$^3$) was reported. Velicescu (1995) blended other additives with NdFeB powders [50]. Annealed powder of NdFeB was blended with Nd$_3$Co, Nd$_3$Co$_2$ and Dy$_{1.5}$Nd$_{1.5}$Co$_2$. All powders were milled independently to 3.5 $\mu$m size before mixing. The Co phase was found to be distributed homogeneously through the matrix phase where it affects intrinsic properties such as the Curie temperature. Ahmad, Mottram and Harris (2001) used PrFeCoB alloys with composition ranging from Pr$_{13}$Fe$_{80.5}$B$_{6.5}$ to Pr$_{16}$Fe$_{76}$B$_8$ for blending with Co in the range of 0-10 atomic percent [51]. Al, Co, Cu, Nb and V were blended with Nd$_{16}$Fe$_{76}$B$_8$ and their distribution through the microstructure was studied. Nd and Dy hydrides were blended with the lower rare earth containing powders. The magnets produced by blending were indistinguishable from those produced by the traditional alloying route.

These studies indicate that powder blending is an effective production technique. The most distinct feature of powder blending is that a wide range of compositions can be assessed rapidly using a single starting alloy and a range of additives.

2.11 Microstructure and Corrosion of $R_2$Fe$_{14}$B Magnets

The sintered NdFeB permanent magnets are characterized with a complex multiphase microstructure. There are in fact three stable ternary phases i.e. Nd$_2$Fe$_{14}$B ($\phi$) matrix phase, the Nd-rich grain boundary phase - Nd$_5$Fe$_2$B$_6$ ($\rho$) and the boride phase - Nd$_{1+\varepsilon}$Fe$_4$B$_4$ ($\eta$) embedded in the grain boundary phase. Electrochemically, the Nd$_5$Fe$_2$B$_6$ ($\rho$) phase has the highest potential followed by Nd$_{1+\varepsilon}$Fe$_4$B$_4$ ($\eta$) phase and the matrix phase. This multiphase structure is highly susceptible to corrosion due to the formation of galvanic cells among the phases.

![Fig. 2.10 Schematic illustration of preferential corrosion of grain boundary phases and subsequent disintegration of sintered NdFeB magnetic material](image)
The minor phases, \( \text{Nd}_5\text{Fe}_2\text{B}_6 (\rho) \) and \( \text{Nd}_{1+\varepsilon}\text{Fe}_4\text{B}_4 (\eta) \) become anodic to the major phase \( \text{Nd}_2\text{Fe}_{14}\text{B} (\phi) \). The unfavourable area ratio with large area of the major phase (cathodic phase) in contact with the small area of grain boundary minor phases (anodic phases) causes accelerated corrosion at the grain boundaries. As a consequence, the intergranular corrosion of Nd-rich phase set in preferentially. The next step is the preferential corrosion of B-rich phase. This intergranular corrosion subsequently leads to the breaking-off of the entire matrix by losing contact with the other phases. The magnetic properties are weakened and the material is turned into powder-like non-useable product. Fig. 2.10 presents schematic illustration of the fragmentation of the NdFeB magnet due to preferential corrosion of grain boundary phases.

### 2.12 Corrosion Control for sintered \( \text{Nd}_2\text{Fe}_{14}\text{B} \) Magnets

Two dimensional efforts have been made to control the corrosion of sintered NdFeB magnets and ensure the designed life in a given environment without affecting the magnetic properties. The first approach is to alter the electrochemical potential of Nd-rich grain boundary phase through alloying additions while the second approach is to provide corrosion protection through barrier coatings.

#### 2.12.1 Through Alloying Additions

Partial substitutions for the rare earth element as well as transition metal have been investigated. Only a few elements marginally improve the corrosion resistance at a sacrifice of magnetic properties [52, 53, 54]. The prominent alloying additions in this regard are partially substituted Dy for Nd [55, 56, 57] and Co for Fe [58, 59, 60]. Besides these substitutions of Al, Cu, Ga, Nb, W, Mo etc. for Fe have also been investigated for microstructural modifications [61, 62, 63].

#### 2.12.2 Through Surface Engineering

Corrosion protection of sintered NdFeB magnets through surface engineering techniques is more suitable, effective and economically feasible. The usefulness of surface engineering techniques has been promising in a number of cases [64, 65, 66, 67]. Since corrosion resistance of sintered NdFeB permanent magnets is poor even in mildly aggressive environments so coating or plating is generally recommended. In this contest organic and metallic coatings are common but each coating has its own benefits and limitations.

The organic coatings comprising mainly of epoxy and/or urethanes are non-hermetic i.e. they do restrict the environmental species to react with the NdFeB magnet but do not seal against moisture and environmental oxygen. The “Spray Epoxy” and “Electrophoretic Epoxy” generally known as “E-Coat” are widely used for less critical applications.

Among the metallic coatings Al, Zn and Ni are common. Aluminium plating by hot dip method is sensitive to the temperature. If the temperature is too low, the coating will...
not adhere to the magnet, conversely if too high, it will fully react with the magnet and produce a rough coating surface [68]. Aluminium is also reported to form intermetallic compounds with the NdFeB substrate and the nature of the intermetallic depends upon the microstructure of the magnet and thus affect the magnetic properties as well [69]. Aluminium plating is also non-hermetic and needs conversion coating to provide a good seal to the substrate from the environment. Combined together they make a thicker layer that imposes a reasonable decrease in the magnetic flux density. However, conversion coating plus Aluminium top layer is quite expensive too.

Zinc plating is yet again non-hermetic and the single elemental deposit marginally improves the corrosion protection characteristics. A conversion coating is needed in conjunction with the zinc plating to seal the substrate from the air and moisture. Nevertheless, zinc is anodic to the NdFeB magnet and as such provides galvanic protection to the substrate.

Electrolytic nickel is hermetic in nature and seals the substrate but has poor performance in the salt and acidic environmental conditions. Electroless nickel though fully covers the internal diameters of the holes, threads and crevices yet it is less protective to the NdFeB substrate. Another approach is to use nickel plating plus an organic overcoat that offers improved resistance to salt spray plus protection from air and moisture but still the organic overcoat has limited protection life. Another limitation of nickel is that it provides even poorer protection against the sulphate ions compared to the chloride ions. This makes the nickel coating more susceptible to corrosive attack in industrial environment that mainly comprise of sulphate ions. Moreover, nickel is cathodic to the NdFeB substrate and any damage or discontinuity in the nickel coating during the service life will expose the anodic NdFeB magnet to the air and moisture. The anodic substrate with smaller surface area in presence of partially damaged cathodic coating with larger surface area will then corrode rapidly due to unfavourable area effect. This poses a serious threat to all cathodic coatings regardless the substrate is a magnet or else.

It therefore instigated the efforts and research work with dual layer or multiple layer coatings either with a single coating technique or with combination of two or more coating techniques. Several combinations are being investigated and the most successful one is the Ni-Cu-Ni triple layer coating for the NdFeB permanent magnet. In a recent report I. Rampin et al. [70] showed that the Ni/Cu/Ni coated NdFeB magnets had a better corrosion resistance in chlorides atmosphere compared to the one containing sulphides. The magnetic properties Ni/Cu/Ni coated NdFeB magnets remained unchanged after exposure to the aggressive environment. It is for this reason that Ni/Cu/Ni coating is assumed to be one of the best for NdFeB magnets and is being considered as a reference coating by different researchers investigating other coatings.

It is important to note that most of the investigations are based on electrolytic, electroless, spray and dip coatings whereas scant reports are available on sol-gel, thermally evaporated and/or PVD coating techniques employed for synthesizing protective coatings on substrates comprising of sintered NdFeB permanent magnets.
The challenge therefore remains to synthesize a coating for the sintered NdFeB permanent magnets that is corrosion resistant in mild as well as aggressive environments comprising either of chlorides or sulphates.

2.13 References

[45] P. Weiss, J. Phys. 6 (1907) 661

As the name suggests, the chapter briefly describes the experimental procedures and the setup used to deposit metallic, ceramic and composite coatings on the sintered NdFeB permanent magnets. It also provides information about the different techniques employed for the characterization of coating substrate systems.
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3.1 The NdFeB Magnets Studied

The sintered NdFeB magnets were used for the present study. The chemical composition of the sintered NdFeB magnets determined through wet analysis using “Inductively Coupled Plasma” (ICP) technique is given in section 4.1. Some of the samples were disc shaped with having 12 mm diameter and 2.5 mm thickness where as some samples were square shaped (10mm × 10mm) having 5 mm thickness.

3.2 Characterization Techniques used

3.2.1 Sample preparation

The sectioning of samples was carried out with the help of a “Slow Speed Diamond Cutter” to minimize the damage by wear and frictional heat. The sectioned samples were then cold mounted in epoxide. Wet grinding technique was employed to grind the samples followed by polishing with diamond paste and synthetic cloths with polishing speed in the range of 150 – 200 rpm. The samples were then ultrasonically cleaned and etched chemically in 2% Nital to reveal the grain boundaries and general structure.

3.2.2 Metallography

The microstructural studies were carried out using optical as well as scanning electron microscopes.

Fig. 3.1 shows the Olympus BX51 Optical Microscope that was used to study the microstructure of the prepared samples. Different objective lenses with magnification 5x, 10x, 20x, 50x and 100x were used with an eye-piece of 10x magnification. The microscope was equipped with DP12 Digital Camera to capture the photomicrographs. “Olysia” Image analysis software, was used to measure the coating thickness.
### 3.2.3 Composition – EDX Analyses

The chemical composition of different phases and features in the magnetic samples was determined with the help of EDX 7274 analyzer equipped with the scanning electron microscope (SEM) employing micro-probed energy dispersive spectroscopy. For low atomic number elements like Boron, Inductively Coupled Plasma (ICP) was used to determine their weight percentage.

### 3.2.4 SEM Secondary Electron Imaging

The JEOL JSM 5910 LV Scanning Electron Microscope shown in Fig. 3.2 was used to study the microstructures of the samples up to 10,000x with 20 kV excitation voltage. The samples for SEM were prepared by standard metallographic techniques.

### 3.2.5 Phase Analyses by X-Ray Diffraction

The diffraction patterns were scanned with the help of Siemens D-500 Diffractometer shown in Fig. 3.3, employing Fe-filtered Co-kα radiations.
Chapter 3 | Experimental and Characterization Techniques

The 2θ range scanned was 25º to 100º with a step size of 0.1º. The intensity as counts per second was plotted as a function of Bragg’s angle 2θ, with the help of “ORIGIN50” software. The data was statistical treated to minimize the noise effects and make the ordinates comparable with each other. The phases were identified in accordance with Henawalt Method and the data cards provided by Joint Committee on Powder Diffraction (JCPD).

3.3 Surface Engineering

Electrodeposition of nickel and copper was carried out with the Watt’s solution and copper sulphate bath respectively. A nickel strike layer was deposited followed by the copper interlayer and again nickel layer above all. The coated surfaces were buffed before intermediate shifting between the baths and after final layer of nickel.

Besides this, Cathodic Arc Physical Vapour Deposition (CAPVD) was used to deposit Titanium Nitride coating on the sintered NdFeB magnets. Short descriptions for these processes are as under.

3.3.1 Electrodeposition of Nickel

The sintered NdFeB substrates were polished and ultrasonically cleaned before nickel plating in Watt’s solution. The bath composition is given in Table 3.1. The electrodeposition setup is shown schematically in Fig. 3.4. The coating variables like current density, pH, coating time and bath temperature were optimized to deposit a dense layer of nickel electrodeposits having thickness in the range of 2-5 µm.

First a nickel strike layer was electrodeposited followed by electrodeposition of copper and an overcoat of nickel electrodeposits.

![Fig. 3.4 Schematic representation for electrodeposition of nickel](image-url)
### Table 3.1 Baths composition and conditions used for electrodeposition of Copper and Nickel

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<th>Copper Plating</th>
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</tr>
<tr>
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**Parameters**

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<tr>
<td>pH</td>
<td>5</td>
<td>2</td>
</tr>
</tbody>
</table>

#### 3.3.2 Electrodeposition of Copper

Copper electrodeposits were used as a protective interlayer between the two nickel plates. The sintered NdFeB substrates with nickel strike layer were buffed and ultrasonically cleaned before copper plating in acid plating bath. The bath composition is given in Table 3-1. The electrodeposition setup is shown in Fig. 3.5. The operating variables were varied and optimized to deposit thick and dense copper electrodeposits with thickness in the range of 10-13 µm.

![Electrodeposition of Copper](image)

Fig. 3.5 Schematic representation for electrodeposition of copper

#### 3.3.3 Cathodic Arc Physical Vapour Deposition of Titanium Nitride

DREVA RC 400 Coating plant was used to deposit Titanium Nitride films on the samples.

![CAPVD coating plant](image)

Fig. 3.6 CAPVD coating plant used for depositing titanium nitride film on the sintered magnets
The prepared substrates were mounted on a rotary sample holder at an angle of 30° with the normal to the cathode. The coating set up shown in Fig. 3.6 had a disc shaped cathode (titanium target) mounted on water cooled copper stage. The anode was also a disc, fixed at a perpendicular distance of 300 mm on top of the cathode. A double walled stainless steel jacket was used to enclose the whole assembly. The hollow cathode argon plasma discharge was used to clean the chamber after evacuation. Grounded copper wire was used to trigger the arc. Automatic microprocessor controlled feeding system was used to introduce nitrogen into the chamber with controlled partial pressure. The coating parameters such as coating current, coating bias voltage, argon partial pressure and coating time were studied and optimized in an attempt to deposit a thick and dense coating with low density of permeable defects. Multilayer coating was deposited by repeating the coating cycles of 40 minutes each for 2, 3 and 4 times giving a total coating time of 80, 120 and 160 minutes respectively.

3.4 Corrosion Testing

Accelerated electrochemical corrosion testing was carried out to evaluate the coating-substrate system in different simulated environments. Aerated 3.5 wt.% NaCl (ASTM D-1141 Artificial Sea Water) and 0.5 Molar Na₂SO₄ aqueous solutions were used to simulate marine and industrial environment respectively. Besides these the effect of acidic environments like HNO₃, containing oxidizing compounds were also studied so as to cover the range of environments. Following electrochemical tests were carried out;

3.4.1 Exposure to Humid Environment – Environmental Chamber

The BAS Environmental Chamber equipped with microprocessor temperature controller and humidity controller was used to expose the sintered NdFeB magnets to 95% relative humidity at 38°C in the laboratory as per ASTM standard D 2247 – 02 [71] to study the corrosion mechanism in the multiphase microstructure of sintered NdFeB magnets.

3.4.2 Electrochemical Polarization – Tafel Extrapolation

The electrochemical polarization technique provides a rapid estimation of the corrosion rate of a metal in an electrolytic solution. The technique is based on the following relationship,

\[ i_{app} = i_{corr} \left[ e^{2.3(E - E_{corr})/\beta_a} - e^{-2.3(E - E_{corr})/\beta_c} \right] + C \left( \frac{dE}{dt} \right) \quad \ldots[72, 73] \]

Where

- \( i_{app} \) = applied current density based on surface area,
- \( i_{corr} \) = corrosion current density,
- \( E \) = applied potential,
- \( E_{corr} \) = free corroding potential or open circuit potential,
- \( C \) = interfacial capacitance associated with the electrochemical double layer[74],
- \( \beta_a \) = Tafel coefficient related to slope of the polarization curve in the anodic region,
- \( \beta_c \) = Tafel coefficient related to slope of the polarization curve in the cathodic region,
- \( \frac{dE}{dt} \) = scan rate or rate of change of applied potential
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Cell current readings are taken during a very short, slow sweep of the potential thus the second term i.e. $C \left( \frac{dE}{dt} \right)$ approaches zero. The sweep typically is from -250 to +250 mV relative to open circuit potential ‘$E_{OC}$ or $E_{Corr}$’.

The graphical output of the experiment is a plot of $\log(i_{app})$ versus potential (E) as shown in the Fig. 3.7 (redrawn from ASM Metal Handbook, Vol. 13). Extrapolating the applied current from either the anodic or cathodic Tafel region to the open circuit potential or position of zero over potential leads to the determination of the corrosion current density ($i_{Corr}$). Analysis of the curve can yield the following types of information:

a. Corrosion potential  
b. Corrosion current and corrosion rate  
c. Kinetic information (Beta coefficients) for the anodic and cathodic reactions

At potential well away from the corrosion potential, the current density reflects the kinetics of only one of the reactions. Extrapolating the linear portions of the polarization curve found at potential well away from $E_{Corr}$ leads to an intersection at $E_{Corr}$. This intersection corresponds to the corrosion current density ($i_{Corr}$). Assuming uniform dissolution across the surface, Faraday’s law can be used to convert it to penetration rate for engineering design. Extrapolation to the reversible potentials can be used to determine the exchange current densities for the two reactions [75]. The generation and analysis of polarization curve data was carried out with the help of EG&G Princeton Applied Research Potentiostat, Model-273A as shown in Fig. 3.8.

Fig. 3.8 EG&G Princeton Applied Research Potentiostat Model-273 used for electrochemical polarization and cyclic potentiodynamic polarization of bare and coated NdFeB magnets
The system has been designed in such a way that only an extremely small current can flow between the working electrode and the reference electrode. The current needed to polarize the working electrode is supplied through auxiliary or counter electrodes. The Potentiostat actually contains an operational amplifier to provide the feedback of the current necessary for maintaining the fixed potential between the working and the reference electrode. The potential can be applied in ramp fashion, stepped as a function of time or kept at a fixed level. The saturated calomel electrode (SCE) with potential of +0.242 V/SHE was used as a reference electrode. The schematic arrangement is shown in the Fig. 3.9 (redrawn from ASM Metal Handbook, Vol. 13). After determining the value of \( i_{\text{corr}} \), the corrosion rate can be calculated as:

\[
\text{Corrosion Rate} = \frac{i_{\text{corr}} \cdot k \cdot EW}{\rho \cdot A} \quad \ldots\ldots\ldots\ldots\ldots\ldots
\]

Where; \( \rho = \text{density (g/cm}^3) \); \( A = \text{surface area (cm}^2) \); \( k = 1.288 \times 10^5 \) when \( CR \) is in mills per year (mpy) or \( k = 3272 \) when \( CR \) is in millimeters per year (mpmy) and \( EW = \text{Equivalent weight} \)

The experimental procedure adopted for electrochemical polarization study is best described in ASTM G3-89 [76, 77, 78]. The assumption of a steady-state system is implicit for all the discussion of polarization curves. The difference between a steady state and equilibrium is that, no corroding system can be in equilibrium; if it were, it would not be corroding. Corrosion is a non equilibrium process that may occur at steady state. Steady state corrosion occurs when the rate of corrosion does not change with time. Knowledge that a given system is and will remain in steady state is a great value. The most popular means of monitoring the approach to steady state of a corrosion system is the measurement of the corrosion potential with time. Generally, the \( E_{\text{corr}} \) changes most rapidly at the beginning of immersion. As the conditions at the metal/solution interface approaches steady state, the time-rate of change in \( E_{\text{corr}} \) decreases. A reasonable criterion for steady state would be a change of less than 5mV over a 10 minute period.

Even the most skilled interpretation of electrochemical data is akin to the best photograph in that it contains only a portion of the available information. Correlation of electrochemical measurements to as many varied measurements as possible is good practice. So the estimation of corrosion behavior based on Tafel extrapolation was correlated to other possible measurement methods.

Fig. 3.9 Schematic arrangement of the polarization and reference cells
3.4.3 Cyclic Polarization

The cyclic potentiodynamic polarization technique is used to examine the overall corrosion behaviour of a system. The technique is based on the idea that corrosion can be predicted by measuring the response of a material at steady state to a controlled upset. The applied voltage or current is used to create the upset. Usually, voltage is ramped in a cyclic manner starting from \( E_{\text{Corr}} \) or some active potential with respect to \( E_{\text{Corr}} \) and the current generated as a response is measured to depict the corrosion behaviour. The voltage is applied between the working electrode (metal under study) and the inert counter electrode(s) with the help of a potentiostat. The voltage increase in the positive or noble direction is termed as the “Forward Scan” where as the voltage scan in the negative or active direction is called “Reverse Scan”. The scan is terminated at some active potential with respect to \( E_{\text{Corr}} \). The test procedure is detailed in ASTM standard G61-86 [79]. The structure of the polarization scan depicts the corrosion behaviour. The propensity for localized corrosion is characterized by \( E_{\text{Pit}} \) – Pitting potential and \( E_{\text{Prot}} \) – Protection or Repassivation potential [80]. These parameters are not fundamental properties of the material rather these are empirical in nature and the experimental variables like scan rate and point of reversal do alter their values or relative position. Nevertheless, the technique remains useful for practical corrosion screening even with its empiricism. So it should be ensured that the experimental variables have been selected carefully and the differences among polarization scans are related to the actual corrosion behaviour. Thus, the technique is useful for qualitative and comparative study and must not be used for quantitative estimation of corrosion rates. The applicable features are shown in the Table-3.2.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Quality or Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pitting potential</td>
<td>Potential favouring pitting/corrosion</td>
</tr>
<tr>
<td>Repassivation or Protection Potential</td>
<td>Potential favouring passivation of protection</td>
</tr>
<tr>
<td>Potential of anodic-to-cathodic transition on reverse portion of scan</td>
<td>Potential favouring the transition</td>
</tr>
<tr>
<td>Active-Passive Transition</td>
<td>Present or absent</td>
</tr>
<tr>
<td>Hysteresis</td>
<td>Positive, none, negative</td>
</tr>
</tbody>
</table>

Proper consideration of the above mentioned features can help to deduce the propensity of localized corrosion in the form of pitting and/or crevice corrosion. The relative positions of \( E_{\text{Pit}} \) and \( E_{\text{Prot}} \) with respect to the \( E_{\text{Corr}} \) are important and the appearance of hysteresis leads to valuable depictions such as:

- In case \( E_{\text{Corr}} \) lies between \( E_{\text{Pit}} \) and \( E_{\text{Prot}} \), the preformed pits or crevices will activate and grow
- In case \( E_{\text{Corr}} \) is cathodic (active) with respect to \( E_{\text{Prot}} \), pitting would not occur and the material is expected to resist localized corrosion

As a rule-of-thumb, when \( E_{\text{Corr}} \) is ~200 mV more active than \( E_{\text{Prot}} \), the risk of pitting or crevice corrosion is negligible. The \( E_{\text{Pit}} \) in that case, is either missing or some what 100-
200 mV nobler than \( E_{\text{Prot}} \). The hysteresis refers to a feature of the polarization scan in which the forward and reverse scans trace different paths i.e. for the same potential; the current density is different during forward and reverse scans. The increase in potential disrupts the passivation chemistry of the surface and during reversal the surface tends to restore its passivation with decreasing potential. The hysteresis can be negative or positive. The negative hysteresis refers to a lack of resistance to localized corrosion or pitting. In this case, the decrease in current density during reverse scan is much slower indicating difficulty in surface repassivation. In case of a positive hysteresis the current density decreases rapidly with decreasing potential during the reverse scan indicating an ease of repassivation and resistance to localized corrosion or pitting. The “anodic-to-cathodic transition potential” refers to the potential at which the current density changes from anodic to cathodic during the reverse scan.

3.4.4 Electrochemical Impedance Spectroscopy (EIS)

The Potentiostatic EIS technique was used to characterize an electrochemical interface which was held at a fixed potential. The technique involves the application of a small amplitude sinusoidal potential perturbation (usually 10mV) to the working electrode at a number of discrete frequencies. As a result sinusoidal current waveform appears at each of the frequency that is out of phase with the applied potential by a certain angle. The phase sensitive AC response of the interface is measured as the frequency of the excitation signal is varied, as described in ASTM G106-89 [81].

EIS is a particularly powerful tool for the study of coated metal corrosion. It is also useful in almost every other area of electrochemistry, including research in batteries, electrode kinetics, and industrial electrolysis [82, 83, 84, 85]. For executing an EIS experiment on bare metal same type of working electrode can be used as used for DC Electrochemical technique. A small signal AC potential excitation is applied to an electrochemical cell. The phase sensitive AC response of the interface is measured as the frequency of the excitation signal is varied.

EIS is a particularly powerful tool for the study of coated metal corrosion. It is also useful in almost every other area of electrochemistry, including research in batteries, electrode kinetics, and industrial electrolysis.

The output of an EIS experiment is a complex impedance spectrum. The term complex is used in its mathematical sense -- containing both real and imaginary terms. An EIS spectrum is usually graphed as either a Bode plot (Impedance magnitude and phase plotted versus frequency) or a Nyquist plot (imaginary impedance plotted versus real impedance). Analysis of the impedance spectrum can lead to the following information:

a. Polarization Resistance
b. Double layer capacitance
c. Solution Resistance
d. Coating defect parameters
e. Mechanistic and kinetic information
3.4.5 Equivalent Circuit Model

The EIS300 includes a powerful nonlinear least squares curve fitting tool. Normally the tool is used to fit equivalent circuit models to impedance spectra. However, it can be used to fit any model that can be expressed in a standard mathematical form. The EIS300 is supplied with equivalent circuit models for a few of the more common electrochemical situations. However, these do not approach the enormous number of models required to describe real world electrochemical cells.

Because of this, the EIS300 also includes a graphical model editor. This editor is used to modify the standard EIS300 models or to create completely new equivalent circuit models. Models are built up using resistors, capacitors and inductors, all of which are familiar to electrical engineers. Less common components can also be added to a design e.g. “Warburg and Gerischer Impedances” which describe diffusion and the “Constant Phase Elements” that describe non-ideal capacitors.

3.5 Electrochemical Frequency Modulation

In electrochemical frequency modulation technique the corroding system is perturbed by two voltage sine waves having different frequencies. Due to the non-linear nature of the corrosion process the resulting alternating current response consists of harmonics at multiples of both frequencies. The EFM has been satisfactorily used in semiconductor research [86, 87]. Applications of EFM in electrochemistry have also been explained by different researchers [88, 89, 90].

In other words, EFM is an electrochemical technique in which two sinusoidal potential signals are summed and applied to a corrosion sample through a potentiostat. The resulting current is measured and the time-domain data is converted to the frequency domain to measure the signal at the applied fundamental frequencies, at harmonics of the fundamental frequencies, and at intermodulation frequencies. By the appropriate mathematical manipulation, EFM gives the corrosion engineer a great deal of useful information, including:

1. Corrosion Rate
2. Tafel Constants
3. A causality factor to validate the data

Unlike Polarization Resistance experiments, Tafel Constants are not needed to calculate the corrosion rate with EFM. The measurement of Tafel Constants during the EFM experiment is a bonus that can have significant implications. For example, by monitoring the Tafel Constants, it may be possible to determine if the mechanism of corrosion is changing during a long-term corrosion study, such as inhibitor evaluations [91,92]. Since the amplitude of the AC voltage waveform is only 10-20 mV, EFM is considered to be a non-destructive technique. In this respect, EFM is similar to Polarization Resistance and Electrochemical Impedance Spectroscopy.
EFM started with the Butler-Volmer equation, so EFM is well-founded in established corrosion theory. EFM was developed at the University of Leuven by Dr. Walter Bogaerts and his students [93, 94]. Unlike EIS, two sinusoidal waves at different frequencies are simultaneously applied to the cell. As current is a non-linear function of potential, the system responds in a non-linear manner to the applied potential excitation. The resulting current is measured and the time-domain data is converted to the frequency domain to measure the signal at the applied fundamental frequencies, at harmonics of the fundamental frequencies, and at intermodulation frequencies [95, 96].

### 3.6 Adhesion of Coatings by Scratch Testing

The scratch tester is a common method that is generally accepted for assessing the adhesion strength of coatings to substrates [97, 98, 99]. The scratch tester equipment used for present study as shown in Fig. 3.10 had a small diamond stylus to test the adhesion of coatings. The diamond with a radius of 200µm was scratched across the coated surface of a substrate at a constant velocity whilst a load was applied with a constant loading rate. The load on the diamond caused stresses to be increased at the interface between the coating and the substrate that could result in delaminating or chipping of the coating to occur. The load at which the coating first delaminates is called the critical load. Coating failure is attributed to different methods such as;

- Measuring the change in friction with the help of a load cell
- Recording the acoustic emission and/or
- Microscopic observation of the scratch channel

The test method does not measure the fundamental adhesion strength of the bond between the coating and the substrate. Rather, the test method gives an engineering measurement of the practical (extrinsic) adhesion strength of a coating-substrate system, which depends on the complex interaction of the test parameters i.e. stylus properties and geometry, loading rate, displacement rate, etc. and the coating/substrate properties i.e. hardness, fracture strength, modulus of elasticity, damage mechanisms, microstructure,
flaw population, surface roughness, and so forth. The definitions and detailed procedure of the test method is covered in ASTM C 1624 – 05 [100].

3.7 Magnetic Hysteresis
The magnetic properties of the coated and uncoated NdFeB permanent magnets were measured with the help of METIS HyM Pulse magnetometer.

The instrument has a “Capacitor Bank” that discharges the stored energy to a coil that in turn generates the pulse of equivalent magnetic energy. Coils capable of generating different magnetic energy are available i.e. 4 to 10 tesla. The output results are displayed in the form of two overlapping hysteresis loops i.e. B vs H and M vs H loops. The results can be reviewed with the help of software known as the “Metis Result Viewer”. The SI or CGS units can be selected as per requirement during the measurement as well as post measurement review. Option for four or two quadrant display is also available. Up to ten hysteresis loops can be overlaid for a comparative study.

3.8 References

The chapter covers the study of the microstructural features, their morphologies, elemental and phase analyses of different deposits on the sintered NdFeB permanent magnets. The corrosion characteristics of bare sintered NdFeB magnets and coating-substrate systems have been evaluated in simulated environments with different electrochemical techniques according to the standard testing procedures. The adhesion and magnetic properties of the sintered magnets with different deposits have also been compared.
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Part – 1
Microstructure, Magnetic Properties and Corrosion Mechanism in Sintered NdFeB Permanent Magnets

4.1. **Composition of the Sintered NdFeB Magnets**
The chemical analysis showed that the magnets were composed of 32.90±0.35 wt% Nd, 1.26±0.14 wt% B and remaining Fe. The equivalent atomic percentage turned out to be Nd$_{15}$Fe$_{77}$B$_8$.

4.2. **Microstructure of the Sintered NdFeB magnets**
The microstructure of sintered NdFeB permanent magnet is shown in Fig. 4.1. Three types of distinct features can be identified i.e. the grains of different shapes and sizes that constitute the matrix phase known as the $\phi$-phase having 2:14:1 composition [101]. The phase around the grain boundaries i.e. the grain boundary phase known as the $\rho$-phase that has been reported to have more Nd compared to the matrix phase and therefore termed as the Nd-rich grain boundary phase with 5:2:6 composition [102].

![Fig. 4.1 SEM secondary electron image of sintered NdFeB permanent magnet material](image)

The third one is the $\eta$-phase with 1+:4:4 composition and is known as the boride phase [103], which is found embedded mainly in the grains of matrix phase and also at the grain boundary regions. Among these phases the 2:14:1, $\phi$-phase, is the hard magnetic phase responsible for the high coercivity and large energy product of the bulk magnet.

The Nd being the lanthanide element has more electrochemical potential compared to the transition element Fe, therefore the Nd-rich paramagnetic phase [104] is electrochemically more active compared to the matrix phase that has lower Nd content. Similarly, the boride phase is also electrochemically more active than the $\phi$-phase. It means that the sintered NdFeB permanent magnet has multi-phase microstructure that can form galvanic couples between the Nd-rich phases and the matrix phase under electrochemical conditions and lead to the preferential corrosive attack on the anodic phases.
4.3. **XRD Analysis of Sintered NdFeB**

The diffraction pattern of the sintered NdFeB is shown in Fig. 4.2. The major peaks have been indexed with the tetragonal Nd$_2$Fe$_{14}$B phase as per JCPD card number 80-0870 with lattice parameters; a= 8.792 °A and c=12.17 °A [105].

A few low intensity peaks remained un-indexed that might belong to some impurities or the minor phases having very low volume fraction in the bulk sintered magnet. The XRD technique, however, did not detect the other two phases mentioned in section 4.2 i.e. the boride and the Nd-rich grain boundary phases. The obvious reason is their small volume fractions compared to the matrix phase.

4.4. **Sintered NdFeB Exposed to Humid Environment**

The magnets were exposed to 95% relative humidity at 38°C in the Laboratory Environmental Chamber as per ASTM standard D 2247 – 02 [71] to study the corrosion mechanism in the multiphase microstructure of sintered NdFeB magnet material. The corrosion mechanism for the material is illustrated in the Fig. 4.3.

The process starts with general oxidation, scale formation and pitting, see Fig. 4.3a. Some blisters are also formed that ruptured with time thereby exposing the underlying grains. The enlarged view of a ruptured blister is shown in the Fig. 4.3b where cracks in the ruptured blister skin can be seen. In Fig. 4.3c inter-granular corrosion and grain disintegration are the prominent features. These stages were observed during the exposure time of first 24 hours.
After 48 hours exposure, the grain boundary phase almost disappeared and the matrix grains showed a covering of oxide layer that appears to be eating up the grains of matrix phase as their size has decreased appreciably and the inter-granular region has widened up considerably, see Fig. 4.3d. It means that besides the preferential dissolution of grain boundary phases the matrix phase is also corroding at its own pace and the whole stock is being converted to powder form.

![Fig. 4.3 Corrosion of sintered NdFeB magnet material in humid environment a) pitting and blister formation and rupturing after 24 hours exposure b) enlarged view of ruptured blister c) inter-granular corrosion and grain disintegration d) dissolution of grain boundary phase with eating up of matrix grains after 48 hours exposure](image)

Fig. 4.4 Corroded NdFeB magnet material after 72 hours humidity exposure in environmental chamber a) dark brown semi loose oxide powder b) higher magnification of same powder

![Fig. 4.4 Corroded NdFeB magnet material after 72 hours humidity exposure in environmental chamber](image)
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After 72 hours exposure time in the environmental chamber, the exposed surface was completely covered with dark brown semi-loose powder as shown in the Fig. 4.4a. The higher magnification revealed the flakes like morphology similar to an onion covering on the grains of the matrix phase, see Fig. 4.4b.

![Image](image_url)

Fig. 4.5 EDX area analyses of features in corroded NdFeB magnet material a) features inside the ruptured blister b) feature outside the ruptured blister

The features of the corroded samples were also analyzed with the help of EDX so as to assess the differences in their elemental nature. The results of EDX area analyses are shown in Fig. 4.5. It can be inferred that the feature regarded as the blister skin (spectrum 1 in Fig. 4.6a) is an oxide layer that is rich in Nd, indicating that both Fe and Nd oxidize during exposure to humid environment but during early stages the oxidation of Nd supersede that of the Fe. Similar results were obtained from spectrum 2 of Fig. 4.5a, indicating that the semi-loose material at the periphery of ruptured blister is actually the broken blister skin. Spectrum 3 and 4 are more or less similar and the lower oxygen content indicate that the inner material has started oxidizing after being exposed due to the rupturing of the blister. On the outer side of the blister, the semi-loose material is also oxides of Nd and Fe (spectrum 2, 3 and 4 in Fig. 4.5b) where as far from the ruptured blister there is some surface area that has not yet been oxidized, probably the electrochemically cathodic area in the galvanic coupling of microstructural phases.
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<table>
<thead>
<tr>
<th>Spectrum Label</th>
<th>O</th>
<th>Fe</th>
<th>Nd</th>
<th>Total</th>
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<tr>
<td>Spectrum 1</td>
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</tr>
<tr>
<td>Spectrum 4</td>
<td>3.62</td>
<td>14.95</td>
<td>81.43</td>
<td>100.00</td>
</tr>
</tbody>
</table>

**a) Inter-granular corrosion**

Fig. 4.6 EDX area analyses of corroded NdFeB magnet material a) Inter-granular corrosion b) Overall oxidation after 72 hours humidity exposure

The spectrum 4 in Fig. 4.6a shows that the nodular particles are mainly the corrosion product of Nd-rich grain boundary phase. A unique observation in the oxidation process is that it proceeds in a manner that converts the grains and the grain boundary material to small spherical particles. In general, the spherical particles with grey contrast are Nd-rich oxides whereas particles with whitish contrast are Fe-rich oxides. After 72 hours of humidity exposure the surface constitutes mostly as Fe-rich oxides as shown in Fig. 4.6b. It indicates that at the later stages the oxidation of Fe dominates since most of the Nd oxidized during the early stages of exposure and it is the left over Fe that is oxidized to finish it out.

**4.5. Microstructure and Magnetic Properties of Sintered NdFeB Magnets before Corrosion**

Fig. 4.7 shows the microstructure and hysteresis loops of sintered NdFeB permanent magnet before exposure to humid environment. The magnetic properties measured from the hysteresis loops were 13.88 kG, remanence ($B_r$), 17.05 kOe, coercivity ($H_C$) and 47.08 MGOe, maximum energy product ($BH_{max}$).
4.6. Microstructure and Magnetic Properties after 24 hours Corrosion

The microstructure and the magnetic properties were studied again after 24 hours of exposure in the humid environment. Fig. 4.8 shows the 24 hours exposed microstructure and the corresponding hysteresis loops for the sintered NdFeB permanent magnet.

The exposed microstructure shows the broken and delaminated surface oxide film with inter-granular corrosion. The inter-granular material is being converted to spherical particles indicating that the reversion of sintered material to the starting powder form has begun during the 24 hours exposure.

The accompanying magnetic properties measured from the hysteresis loops decreased slightly and came out to be 12.67 kG, remanence ($B_r$), 16.31 kOe, coercivity ($H_C$) and 38.29 MGOe, maximum energy product ($BH_{\text{max}}$).
4.7. **Microstructure and Magnetic Properties after 48 hours Corrosion**

The microstructural degradation carried on and after 48 hours exposure in the humid environment the surface was completely covered with spherical particles as shown in the Fig. 4.9. The surface oxide covering has also transformed to folded flakes with whitish contrast compared to the greyish nodular particles that are rare earth rich oxides.

The accompanying magnetic properties measured from the hysteresis loops decreased further and came out to be 11.12 kG, remanence ($B_r$), 15.61 kOe, coercivity ($H_C$) and 29.92 MGOe, maximum energy product ($BH_{max}$).

4.8. **Microstructure and Magnetic Properties after 72 hours Corrosion**

After 72 hours the bulk sintered NdFeB permanent magnet turned completely to powder form and lost its shape as shown in Fig. 4.10. The magnetic properties of the shapeless powder could not be measured with pulsed field magnetometer.
4.9. **Comparison of Microstructures and Magnetic Properties before and after Corrosion**

Fig. 4.11 shows the comparison of the microstructures and the accompanying magnetic properties before exposure and at intermediate stages of exposure to humid environment. The magnetic properties deteriorated along with the microstructural degradation until the bulk magnet transformed to the powder form.

It can be observed from the Fig. 4.12 that the associated changes in the magnetic properties including remanence, coercivity and energy product declined with degrading microstructure due to corrosion in the humid environment.

It can therefore be deduced that corrosion leads to microstructural damage with the loss of hard magnetic $\phi$-phase that in turn decreases the magnetic properties for the sintered NdFeB permanent magnets.
The corrosion mechanism can thus be summarized as,

- General corrosion, pitting and blistering – oxidation of Nd-rich and Fe-rich phases take off simultaneously
- Preferential oxidation of anodic phases – rate of oxidation of Nd-rich phases surpass that of the Fe-rich phases forming spherical oxide particles
- Inter-granular corrosion and grain disintegration
- Eating up of grains – conversion of matrix grains to spherical Fe-rich oxide particles
- Finishing up with semi-loose to loose powder with negligible magnetism

The NdFeB permanent magnets have become important technological materials due to the exceptionally advantageous magnetic properties [106, 107, 108]. At ambient temperature, the NdFeB magnets have highest energy product [109, 110, 111] and thus known for the efficient utilization of electrical energy [112, 113, 114]. Over the years, NdFeB magnets have occupied a leading position among the strong permanent magnetic materials for variety of engineering applications, namely computer peripherals, automation, automobile, aerodynamic, magnetic resonance, biomedical, acoustics and consumer electronics [115, 116]. However, the presence of electrochemically active phases in the microstructure of the sintered NdFeB magnets [117] deteriorate their magnetic efficiency [118] as they corrode during exposure to various environments [119, 120]. Efforts have been made to control the corrosion of sintered neo magnets either by alloying additions to alter the electrochemical potential of active microstructural phases [121, 122, 123, 124] or by tailoring the surface to incorporate mechanical barrier coatings like epoxy, metallic or alloy coatings [125, 126, 127]. Improving corrosion resistance by alloying additions did not serve the purpose as only a few alloying elements marginally improved the corrosion resistance at a substantial compromise of magnetic properties [128, 129, 130].
4.10. **Schematic Corrosion Model**

The Fig. 4.13 shows the schematic degradation model for the corroding sintered NdFeB permanent magnet material under active environment. When sintered NdFeB magnets are exposed to electrochemically active environment such as the humid environment, the Nd-rich grain boundary phases become anodic against the matrix phase thereby resulting in their preferential dissolution. The overall effect is the inter-granular corrosion that leads to the grain disintegration and the solid magnet loses its shape and is converted into useless powder form. Besides their higher electrochemical potentials, the preferential dissolution of grain boundary phases is also favoured by their much smaller anodic area compared to the larger cathodic area of matrix phase.

![Fig. 4.13 Schematic degradation model for corroding NdFeB sintered magnet](image)

4.11. **Corrosion Protection for Sintered NdFeB Permanent Magnets**

Among the two types of remedial measures (see 2.12) to avoid structural changes due to corrosion, “Surface Engineering” was opted for the present study. The cathodic arc physical vapour deposition (CAPVD) technique was used to deposit di-titanium nitride (Ti$_2$N) compound on the sintered NdFeB permanent magnets. The CAPVD is a physical vapour deposition technique in which an electric arc is used to vaporize material from a solid cathode (target). The material is vaporized in a vacuum chamber, transported as “Macros” across the chamber to the substrate. The vaporized material then condenses on the substrate surface, forming a thin film. The technique is used to deposit metallic, ceramic, and composite films. The advantageous features of the CAPVD process are:

- It is clean, efficient and a turn-key process.
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- It employs a multiple rotation system for the substrates in an attempt to avoid non-uniformity of films and obtain a relatively even distribution of the deposit.
- It gives the best “Ionisation Rate” of any PVD process which ensures excellent coating adhesion and structure.
- It is flexible to include reactive processes that form a coating compound on the substrate’s surface.
- The substrate’s temper condition is retained as its temperature remains within 200 to 450°C during the process.
- No distortion of the high melting substrates contrary to the Aluminium alloys that distort due to softening during the process.
- Environmental friendly compared to the polluting galvanic methods.

The selection of titanium nitride (TiN) as a mechanical barrier for the protection of sintered NdFeB is based on the following properties:

- It is chemically resistant, thermally stable (oxidizes at 800°C under normal atmospheric conditions) and excellent diffusion barrier that is electrically conductive [131].
- It has 1:1 stoichiometry however, TiNₓ with 0.5≤x≤1.1 are thermodynamically stable [132].
- It is non-toxic, insoluble in water and reacts with hot concentrated acids.
- Electrical resistivity is 20 ±10 μΩ·cm.
- Magnetic susceptibility is +38×10⁻⁶ emu/mol.
- High Young’s modulus of 600 GPa relative to titanium alloys (100 GPa).
- It forms molecular bond with the substrate material [133].

The major applications of TiN are:

- For edge retention and corrosion resistance on machine tooling, such as drill bits and milling cutters, often improving their lifetime by a factor of three or more.
- Because of TiN’s metallic gold color, it is used to coat costume jewelry and automotive trim for decorative purposes.
- TiN is non-toxic, and is being used as coating for medical implants and devices such as scalpel blades and orthopedic bone saw blades where sharpness and edge retention are important [134], as well as aerospace and military applications. Such coatings have also been used in implanted prostheses especially hip replacement implants.
- As a coating to protect the sliding surfaces of suspension forks of bicycles and motorcycles as well as the shock shafts of radio controlled cars.

The application of CAPVD titanium nitride coating to sintered NdFeB permanent magnets, the microstructural, mechanical, electrochemical and magnetic
characterization of the coating-substrate system is therefore supposed to be the useful incremental scientific and technological information for the community, since it is being explored for the first time through the present work.

The surface treatments such as electrodeposited nickel or zinc, electroless nickel, electroless nickel-phosphide or nickel-cobalt-phosphide, hot dip zinc, aluminizing, electrophoresis, chromate passivated aluminium coating are known corrosion-proofs for neo magnets but each has its own limitations particularly in moist and humid environments [135]. In recent times, ceramic and composite coatings like TiO$_2$, Ni-P/Ti$_2$O and CAPVD Ti$_2$N coatings [136, 137] are emerging as new developments to cater the corrosion protection of sintered neo magnets.
4.12. CAPVD Titanium Nitride – Ceramic Coating

Principally, besides the coating geometry there are four major parameters that control the structure and properties of the coating laid through the Cathodic Arc Physical Vapour Deposition (CAPVD) process. These include coating arc current, coating bias voltage, coating time and the nitrogen partial pressure. Among these the coating arc current was kept constant at 80 amperes and the nitrogen partial pressure was automatically adjusted through the microprocessor at ≥ 0.8 Pa relative to the base pressure that was set at 10⁻² Pa. Table 4.1 shows the cleaning as well as the coating parameters.

Table 4.1 Coating parameters for CAPVD dititanium nitride coating on sintered NdFeB magnets

<table>
<thead>
<tr>
<th>CAPVD Ti₂N Coating Parameter</th>
<th>Value for present coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure</td>
<td>10⁻² Pa</td>
</tr>
<tr>
<td>Cleaning arc current</td>
<td>90 A</td>
</tr>
<tr>
<td>Cleaning bias voltage</td>
<td>200 V</td>
</tr>
<tr>
<td>Cleaning time</td>
<td>600 s</td>
</tr>
<tr>
<td>Coating arc current</td>
<td>80 A</td>
</tr>
<tr>
<td>Coating bias voltage</td>
<td>80 - 180 V</td>
</tr>
<tr>
<td>Coating time</td>
<td>40 - 160 minutes</td>
</tr>
<tr>
<td>Nitrogen partial pressure</td>
<td>≥0.8 Pa of base pressure</td>
</tr>
</tbody>
</table>

The effects of coating bias voltage on the resulting coating thickness are shown in Fig. 4.14a.

![Graph showing variation of coating thickness with coating bias voltage](image-url)
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It is unexpected to note that the coating thickness increased by increasing the bias voltage but decreased after 150V. The probable reason for that could be vaporization of bigger and heavier “Macros” that could not reached the substrate surface with the existing geometrical arrangement in the coating chamber.

The effects of the coating time on the resulting coating thickness are shown in the Fig.4.14b.

![Graph showing variation of coating thickness with coating time](image)

**Fig. 4.14b: The plot showing variation of coating thickness with coating time.**

The coating thickness increased with the coating time till 120 minutes but remained more or less stable after 120 minutes. This is again un-expected and the plausible reason could be related to the vapour pressure thermodynamics in the coating chamber that might have approached to some sort of equilibrium after 120 minutes of coating time and with other prevailing parameters.

X-ray diffraction patterns after different coating durations at constant bias voltages were also used for the optimization of coating parameters as shown in the Fig. 4.15. Each coating cycle was carried for 40 minutes and multilayer ceramic coatings were laid by 2 to 4 coating cycles.
In order to obtain a coating thickness ≥1.6 µm, the coating bias voltage and the coating time should be ~150 V and ≥120 minutes respectively.

4.12.1. Structure of CAPVD Titanium Nitride – Ceramic Coating

Fig. 4.16 shows the diffraction pattern of the CAPVD titanium nitride coated sintered NdFeB magnet with 150 V coating bias potential and 120 minutes coating time. The diffraction pattern shows an additional peak at the Bragg's angle of 42.4° compared to the one shown in Fig. 4.2. This additional peak is indexed with Ti$_2$N tetragonal phase vide JCPDS card number 17-0386 with lattice parameters a=4.9452 Å and c=3.0342 Å [138]. The remaining peaks belong to the substrate.

![Graph showing diffraction patterns at different coating times](image-url)
material that is, the sintered NdFeB magnet. The single diffraction peak indicates that the CAPVD titanium nitride coating is textured with (200) planes oriented parallel to the substrate surface. The (200) orientation in PVD titanium nitride coatings has been reported by different researchers [139, 140, 141]. The development of texture is controlled by the nucleation of the coatings as well as by the way in which they subsequently grow. Movchan and Demchishin [142] identified three distinct zones in thin-film microstructures as a function of the homologous temperature $T/T_m$, where $T$ represents the substrate surface temperature and $T_m$ represents the coating melting point.

- Zone-1 Structure – The microstructure consists of tapered columns with domed tops due to low adatom mobility at low temperature ($T/T_m < 0.25-0.3$).
- Zone-2 Structure – The microstructure consists of straight columns with a smooth surface topography due to more surface diffusion at temperature ($T/T_m = 0.3-0.5$).
- Zone-3 Structure – The microstructure consists of equiaxed grains, as are observed in re-crystallized metals, as the bulk diffusion becomes a dominant process at temperature ($T/T_m > 0.5$).

It means that in vapor deposited coatings the solid material is distributed in an array of fairly closely packed columns that run perpendicular to the substrate. So the columnar microstructure is developed as the thin films are formed from a flux of atoms that approaches the substrate from a limited range of directions. Thus there are many boundaries running perpendicular to the interface that can act as planes of weakness e.g. as short-circuit diffusion paths.


The microstructural morphology of ceramic Ti$_2$N coating shows uneven deposit that comprises of nodular particles embedded in the surface grains and forming a continuous covering on the substrate surface, see Fig. 4.17. The deposit is actually a spray of physical vapours i.e. the particles or macros of Ti$_2$N land onto the surface grains or the grain boundary phase and stick there to form the film or coating. The

![Fig. 4.17 SEM micrograph of CAPVD titanium nitride coated sintered NdFeB permanent magnet material a) superficial view b) sectioned view](image-url)
substrate is moved slowly so as to allow the vapour flux to cover the substrate completely. Fig. 4.17b shows the sectioned view of Ti$_2$N coating and the resolution is not enough to depict the nature of bonding. The nature of bonding in PVD or CAPVD deposits has been reported to be the molecular bonding [129, 143]. Other important features observed in the CAPVD Ti$_2$N Ceramic Coating are shown in the Fig. 4.18. These features are termed as “Crater” and “Nodules”. The crater represents the portion with chipped-off coating having thin covering or lean deposit that may provide access for the environmental species to substrate surface.

![Fig. 4.17b shows the sectioned view of Ti$_2$N coating and the resolution is not enough to depict the nature of bonding.](image)

Besides these, there are other diffusion paths such as shown in the Fig. 4.18b, that make the CAPVD Ti$_2$N Ceramic Coating inherently “Non-encapsulating” i.e. the nature of deposit is such that it can not provide complete capsulation to the substrate [144, 145]. In order to understand the role and contribution of these structural features to the protection against corrosion they were subjected to EDX analyses.

4.12.3. **Superficial EDX Analyses of different Features of the Ceramic Coating**

The EDX spectrum of the “Crater” (1) shows that it does have a thin covering of Ti$_2$N ceramic coating that is transparent to the electron beam as it gives energy peaks of Fe and Nd that in fact is the substrate material, see Fig. 4.19. On the other hand the “Nodule” (2) is Ti$_2$N particle that is rich in titanium. The third spectrum in the Fig. 4.14 is from the coating ground bed (3), showing major energy peaks of Ti with very low energy peaks of Fe and Nd. It means that the substrate is overall covered with the Ti$_2$N ceramic coating but there are some lean deposit areas or portions called “Craters” and contrary to craters there are heavy deposit areas or portions in the form of “Nodules” that seem to be embedded in the coating ground bed. The lean deposit areas appear to be weak portions that can act as the coating holidays thereby providing access for the environmental gases, fluids or moisture to the substrate material.

![Fig. 4.18 SEM micrograph showing inherent defects in the CAPVD titanium nitride coated sintered NdFeB permanent magnet material (sectioned view)](image)
The vapour deposited transition metal nitride coatings normally have microscopic defects such as pores, pin holes and/or voids \([146, 147]\) that provide path for the environmental species to access the substrate surface. Such permeable defects can not be completely eliminated but their size and density can be reduced by depositing thicker coatings \([148, 149]\), by incorporating noble and dense interlayer \([150]\), by interrupting columnar growth with multilayered coatings \([151]\) or by post deposition sealing of defects with polymeric deposits \([152]\).

### 4.13. Electrodeposited Nickel Coating with Copper Interlayer

The electrodeposition of nickel was carried out in Watt's solution where as copper sulphate bath was used for copper electroplate. The bath compositions are mentioned in Table 3.1. The coating parameters were optimized through experimentation by selecting a fixed value of current density and measuring the rate of deposition with different bath temperatures and pH values. Fig. 4.20 shows the plot of deposition rate as a function of bath pH for both nickel and copper. For nickel plating the rate of deposition increases with increasing the bath pH, reaches a maxima at 5 pH and then starts decreasing by further increase in the pH value. On the other hand, the rate of deposition for copper is highest at low pH values and
increasing the pH decreases the rate of copper deposition. It can be seen that for nickel plating the highest deposition rate was obtained at a pH value of 5 where as for copper, the highest deposition rate was at a pH value of 2. The rate of deposition was measured as the mass deposited per unit area for a fixed duration of current flow time i.e. number of milligrams per square centimetre of the substrate for every 5 seconds of current flow.

![Graph](image1)

**Fig. 4.20 Effect of bath pH on deposition rate of Ni and Cu on sintered NdFeB permanent magnet**

Similarly, the effect of bath temperature on the rate of deposition for both copper and nickel are shown in Fig. 4.21. For both types of plating, the rate of deposition increases with increasing bath temperature, reaches a maximum and then starts declining by further increase in the bath temperature depending upon the favourable reaction thermodynamics. The optimum bath temperatures for copper and nickel plating are 50°C and 60°C respectively.

![Graph](image2)

**Fig. 4.21 Effect of bath temperature on deposition rate of Ni and Cu on sintered NdFeB permanent magnet**
4.13.1. **Structure of Nickel Coating with Copper Interlayer**

Fig. 4.22 shows the diffraction pattern of the NiCuNi multilayer coating on sintered NdFeB permanent magnet.

![Diffraction pattern of electrodeposited Ni with Cu interlayer on sintered NdFeB permanent magnet](image)

There are four major diffraction peaks or reflections from the crystal planes. These peaks were indexed with the Hanawalt method \[153\] and belong to two different phases. First one is the pure “Nickel” to which the major intensity peaks belong and the second one is the Cu\(_{3.8}\)Ni phase expected to be formed at the interface between the top nickel layer and the copper interlayer.

4.13.2. **Morphology of Nickel Coating with Copper Interlayer**

The above mentioned structure can be best explained with the help of sectioned view of the NiCuNi multilayer coating as shown in Fig. 4.23.

![Optical and SEM micrograph showing sectioned view of electrodeposited Ni with Cu interlayer on sintered NdFeB permanent magnet](image)
There are three distinct layers and the EDX analyses showed that the top and third layer is rich in nickel whereas between the two nickel rich layers is the copper rich interlayer.

The NiCuNi multilayer coating was deposited for the comparative study i.e. to compare the characteristics and corrosion protection performance of the Ti2N ceramic coating with NiCuNi multilayer coating, that was taken as a reference because nickel coating with copper interlayer is known as the best for corrosion protection of the sintered NdFeB permanent magnets particularly in the humid environment [154, 155].

4.14. **Ni/Ti2N Composite Coating**

Since the CAPVD Ti2N ceramic coating was found to have certain inherent features that make it non-encapsulating for the substrate, so there appears to be room for some innovative solutions. Apparently, the two feasible innovative solutions are:

- Incorporation of a metallic strike layer or an undercoat for the CAPVD Ti2N ceramic coating
- Post deposition sealing of the CAPVD Ti2N ceramic coating with some polymeric material

So, a nickel strike layer or an undercoat was electrodeposited on the sintered NdFeB permanent magnet followed by CAPVD Ti2N deposit to make the novel Ni/Ti2N composite coating. A nickel strike i.e. a thin interlayer of nickel was electrodeposited on sintered NdFeB magnets prior to the CAPVD process to produce a composite Ni/Ti2N coating. The selection of nickel interlayer was based on the better adhesion to the substrate compared to Cr or Cu, that too need an undercoat of nickel prior to plating [156]. It is important to mention that the nickel is cathodic to the ferrous substrate and any crack or holiday in the nickel coating will rapidly corrode the substrate owing to the unfavourable area effect for the galvanic corrosion. Similar trend has been reported in the literature157. This is the reason that nickel is coated with a copper interlayer i.e. NiCuNi coating. It is therefore, necessary to simultaneously study and compare the anticorrosion characteristics of NiCuNi, Ti2N and Ni/ Ti2N coatings.


Fig. 4.24 shows the comparison of diffraction patterns of the composite and the ceramic coating on the sintered NdFeB permanent magnet. The lower most diffraction pattern is for the bare or uncoated NdFeB magnet material. The intermediate one is for the Ti2N ceramic coated NdFeB magnet and the upper most is the Ni/Ti2N composite coated NdFeB magnet. Compared to the bare NdFeB, the diffraction pattern of Ti2N ceramic coating has only one additional peak, that is from (200) planes of tetragonal Ti2N phase (see section 4.7.1). Besides this additional
peak, other peaks are all the same as for the bare NdFeB but with reduced or suppressed intensities. This intensity suppression is due to the fact that the NdFeB is not bare rather it is covered by the ceramic coating. The upper most diffraction pattern is completely different from the two lower ones. It has three major diffraction peaks. One of these diffraction peak belongs to the (200) planes of Ti$_2$N phase that is the same as in the ceramic coated NdFeB. The other two peaks belong to the (111) and (200) planes of pure "Nickel" and these were reflected from the strike layer or the undercoat. In this diffraction pattern, there is no peak from the substrate material i.e. the sintered NdFeB permanent magnet.

It therefore, indicates the facts that;

- The Ni/Ti$_2$N composite coating is thick and or dense enough to restrict the x-rays to approach the NdFeB substrate and get diffracted back to the detector
- The substrate is completely encapsulated by the Ni/Ti$_2$N composite coating

4.14.2. **Morphology and EDX analyses of Ni/Ti$_2$N Composite Coating**

The structural morphology of the Ni/Ti$_2$N composite coating is shown in Fig. 4.20a. It appears to have similar features as observed in the ceramic coating but the EDX analyses of features revealed the differences. The "Crater" has a thin covering of Ti$_2$N but in this case it has energy peaks of Ni instead of Nd and Fe energy peaks. It means that even at the craters there is no substrate effect. The nickel strike layer or the undercoat together with the thin Ti$_2$N covering, form a composite layer that is sufficiently dense to isolate the substrate from the incident electron beam.

![X-ray diffraction patterns showing comparison of sintered NdFeB permanent magnets with and without coatings](image-url)
The intermediate EDX spectrum in the Fig. 4.25a, taken from the ground bed of Ni/Ti$_2$N composite coating shows major energy peaks of Ti and very low energy peaks of Ni. Again there is no substrate effect, whereas for the ceramic coating the substrate effect was present in the form of Nd and Fe energy peaks from the coating ground bed. However, for “Nodules” the EDX spectrum is very similar to the one taken from the ceramic coating. The nodules remained the Ti rich Ti$_2$N thick and dense particulate deposits, impinged in the coating ground bed.

Fig. 4.25a SEM micrograph and EDX spectra showing different features of the Ni/Ti$_2$N composite coating on sintered NdFeB permanent magnet

Fig. 4.25b shows the sectioned view of the Ni/Ti$_2$N composite coating on the sintered NdFeB permanent magnet.

Fig. 4.25b SEM micrograph showing sectioned view of the Ni/Ti$_2$N composite coating on sintered NdFeB permanent magnet
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The coated specimen was sectioned with the help of slow speed diamond cutter and polished metallographically up to 0.5µm Al₂O₃ suspension, ultrasonically cleaned and etched in 0.2% natal. The EDX analysis showed that the top layer was Ti₂N whereas the strike layer or the undercoat is composed of almost pure Nickel. These two layers taken together form the novel Ni/Ti₂N composite coating for the corrosion protection of sintered NdFeB permanent magnets.
4.15. **Electrochemical Polarization in Simulated Marine Environment**

Fig. 4.26 shows the electrochemical polarization curves for the sintered NdFeB permanent magnet material without any coating measured in simulated marine environment i.e. 3.5 wt.% NaCl solution. The fluctuation of current density at the onset of the anodic curve indicates localized electrochemical reactions at the surface of the anode.

![Graph](image)

**Fig. 4.26** Electrochemical polarization of uncoated sintered NdFeB magnet in simulated marine environment

Afterwards the increase in the current density with increasing potential (towards positive) is fairly smooth. The Tafel extrapolation data revealed the anodic slope “βa” to be 0.0621 V/decade that is lower than the “βc” that is 0.1013 V/decade. It means that the electrochemical corrosion of anode i.e. the sintered NdFeB permanent magnet material will continue till any change in the prevailing conditions or till the material is completely corroded and converted into the corrosion product. The free corroding potential (FCP) or \( E_{\text{Corr}} \) for the NdFeB magnet turned out to be \(-0.8514 \) volts relative to saturated calomel electrode (SCE) and the estimated corrosion rate came out to be \( \approx 9 \) mpy (mills per year), that is fairly high for the engineering applications. The obvious reason is the complex microstructure of the sintered NdFeB permanent magnet material as explained in section 4.2 and 4.3 [143].

The electrochemical polarization curves for the Ti\(_2\)N ceramic coated NdFeB magnet system is shown in Fig. 4.27.
It is interesting to note that the free corroding potential (FCP) or $E_{Corr}$ of the coating-substrate system is -0.6816 volts relative to SCE that is ~20% more positive or noble compared to the bare NdFeB magnet. The value of corrosion current, $I_{Corr}$ is 8.584 $\mu$A/cm$^2$ that is less than the half of the bare or uncoated NdFeB magnet (18.53 $\mu$A/cm$^2$). It means that the Ti$_2$N ceramic coating is providing adequate protection to the sintered NdFeB substrate. The corrosion rate decreased from 9 mpy, for the uncoated NdFeB, to 4 mpy for the coating-substrate system. However, the fluctuations of current density in the anodic polarization curve are attributed to coating holidays as described in section 4.7.2 (Fig. 4.13).

Fig. 4.28 shows the electrochemical polarization curves for the NiCuNi coated NdFeB permanent magnet.

![Diagram](image-url)
The free corroding potential (FCP) or $E_{\text{Corr}}$ for the coating-substrate system is -0.4485 volts versus SCE. This value is ~47% and ~34% more positive or noble than uncoated NdFeB and Ti$_2$N coated NdFeB respectively. The value of $I_{\text{Corr}}$ is 2.64 $\mu$A/cm$^2$ and the estimated corrosion rate is 1.12 mpy. So, the electrodeposited NiCuNi multilayer coating provides better protection to sintered NdFeB permanent magnets than the CAPVD Ti$_2$N ceramic coating. It was expected that the Ti$_2$N being a ceramic should have behaved better than the NiCuNi coating, that is metallic in character, but the results came in reverse.

It was realized that the inferior corrosion protection was not due to the electrochemical character of the Ti$_2$N ceramic rather it was attributed to the non-encapsulating nature of the CAPVD deposit [144], as shown in Fig. 4.18 section 4.7.2. So, the innovative approach of Ni/Ti$_2$N composite coating, mentioned in section 4.9 was investigated likewise.

Fig. 4.29 shows the electrochemical polarization curves for the Ni/Ti$_2$N composite coated NdFeB in simulated marine environment. Remarkable improvement was observed in the electrochemical properties.

The $E_{\text{Corr}}$ is -0.2588 volts versus SCE that is ~62% more positive or noble than the Ti$_2$N ceramic coated NdFeB and ~42% more positive or noble than the NiCuNi coated NdFeB. The value of $I_{\text{Corr}}$ has also decreased to 0.8575 $\mu$A/cm$^2$ that is only about 10% of the Ti$_2$N ceramic coated NdFeB. The estimated corrosion rate is 0.4 mpy that is negligible compared to the 9 mpy and 4 mpy for uncoated and Ti$_2$N ceramic coated NdFeB sintered magnets respectively.

Fig. 4.30 shows the overlay of the four polarization curves discussed above. It can be seen clearly that the novel Ni/Ti$_2$N composite coating provides the highest level of corrosion protection to the sintered NdFeB permanent magnets in the simulated marine environment.
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The current density is the lowest and the $E_{\text{Cor}}$ is the most noble to NiCuNi coated, Ti$_2$N ceramic coated and the uncoated NdFeB permanent magnet [158]. So, the innovative approach of the composite coating appears to hold promise for providing excellent corrosion protection to the sintered NdFeB permanent magnets nevertheless, the same has to be investigated in the simulated industrial environment and also by employing different electrochemical techniques.

4.16. Electrochemical Polarization in Simulated Industrial Environment

Fig. 4.31 shows the electrochemical polarization curves for the sintered NdFeB permanent magnet material without any coating measured in simulated industrial environment i.e. 0.5M Na$_2$SO$_4$ solution. The Tafel extrapolation data revealed the anodic slope “$\beta_a$” to be 0.0809 V/decade that is lower than the “$\beta_c$” that is 0.1037 V/decade.

![Comparison of Coatings in 3.5% NaCl (aq) Solution](image_url)

*Fig. 4.30 Comparison of polarization curves for coated and uncoated sintered NdFeB magnets in simulated marine environment*

![Tafe Extrapolation in 0.5M Na$_2$SO$_4$ (aq) Solution](image_url)

*Fig. 4.31 Electrochemical polarization of uncoated sintered NdFeB magnet in simulated industrial environment*
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The free corroding potential (FCP) or $E_{\text{Corr}}$ for the NdFeB magnet turned out to be $-0.9238$ volts versus saturated calomel electrode (SCE) and the estimated corrosion rate came out to be $\approx 9.6$ mpy (mills per year), that is very close to that in the simulated marine environment and is fairly high for the engineering applications.

The electrochemical polarization curves for the Ti$_2$N ceramic coated NdFeB magnet system is shown in Fig. 4.32. The free corroding potential (FCP) or $E_{\text{Corr}}$ of the coating-substrate system is $-0.622$ volts versus SCE that is $\approx 33\%$ more positive or noble compared to the bare NdFeB magnet.

The value of corrosion current, $I_{\text{Corr}}$ is 8.142 $\mu$A/cm$^2$ that is less than the 50% of the bare or uncoated NdFeB magnet (19.54 $\mu$A/cm$^2$). It means that the Ti$_2$N ceramic coating is providing reasonable protection to the sintered NdFeB substrate. The corrosion rate decreased from $\approx 9.6$ mpy, for the uncoated NdFeB, to $\approx 3.8$ mpy for the coating-substrate system.

Fig. 4.33 shows the electrochemical polarization curves for the NiCuNi coated NdFeB permanent magnet. The free corroding potential (FCP) or $E_{\text{Corr}}$ for the coating-substrate system is $-0.5678$ volts versus SCE. This value is $\approx 38\%$ and about $\approx 9\%$ more positive or noble than uncoated NdFeB and Ti$_2$N coated NdFeB respectively. The estimated corrosion rate is 6.9 mpy. So, the electrodeposited NiCuNi multilayer coating provides better protection to sintered NdFeB permanent magnets than the CAPVD Ti$_2$N ceramic coating. The results are analogous to those obtained in simulated marine environment with minor variations. The electrodeposited NiCuNi multilayer coating provides better protection to sintered NdFeB permanent magnets than the CAPVD Ti$_2$N ceramic coating, not because of the electrochemical character of the Ti$_2$N ceramic but owing to the non-encapsulating nature of the CAPVD deposit.

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**Fig. 4.32 Electrochemical polarization of Ti$_2$N ceramic coated sintered NdFeB magnet in simulated industrial environment**

The electrochemical polarization of Ti$_2$N ceramic coated sintered NdFeB magnet in simulated industrial environment is shown in Fig. 4.32. The free corroding potential (FCP) or $E_{\text{Corr}}$ of the coating-substrate system is $-0.622$ volts versus SCE that is $\approx 33\%$ more positive or noble compared to the bare NdFeB magnet.

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Fig. 4.34 shows the electrochemical polarization curves for the Ni/Ti$_2$N composite coated NdFeB in simulated industrial environment. Again appreciable improvement was observed in the electrochemical properties. The $E_{\text{Corr}}$ is -0.1161 volts versus SCE that is $\sim$81% more positive or noble than the Ti$_2$N ceramic coated NdFeB and $\sim$79% more positive or noble than the NiCuNi coated NdFeB. The value of $I_{\text{Corr}}$ has also decreased to 0.3011 $\mu$A/cm$^2$ that is only about 4% of the Ti$_2$N ceramic coated NdFeB. The estimated corrosion rate is 0.14 mpy that is negligible compared to the 9.6 mpy and 3.8 mpy for uncoated and Ti$_2$N ceramic coated NdFeB sintered magnets respectively.

Fig. 4.34 Electrochemical polarization of Ni/Ti$_2$N composite coated sintered NdFeB magnet in simulated industrial environment

Fig. 4.35a shows the overlay of the four polarization curves discussed above.
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It can be seen clearly that the novel Ni/Ti$_2$N composite coating provides the highest level of corrosion protection to the sintered NdFeB permanent magnets in the simulated industrial environment analogous to that provided in simulated marine environment. The current density is the lowest and the $E_{\text{Corr}}$ is the most noble to NiCuNi coated, Ti$_2$N ceramic coated and the uncoated NdFeB permanent magnet.

![Comparison of coatings in 0.5M Na$_2$SO$_4$ (aq) Solution](image)

**Fig. 4.35a** Comparison of polarization curves for coated and uncoated sintered NdFeB magnets in simulated industrial environment

It means that the composite coating is the best anti-corrosion barrier for the sintered NdFeB permanent magnets in both environments i.e. the simulated marine and the simulated industrial environment. Fig. 4.35b shows the comparison of the Tafel Extrapolation data for the ceramic and composite coatings versus bare NdFeB.

![Tafel Extrapolation data for coated and uncoated sintered NdFeB magnets in simulated industrial environments](image)

**Fig. 4.35b** Tafel Extrapolation data for coated and uncoated sintered NdFeB magnets in simulated industrial environments

Clearly, the composite coated NdFeB magnets have the lowest corrosion rates etc.
The electro-less plating and sol-gel technique has been reported for the synthesis of amorphous NiP/TiO<sub>2</sub> coating with very low value of self corrosion current density in 0.5M NaCl solution [159]. Compared to the tedious electro-less and sol-gel coating processes involving lengthy drying and heat treating cycles, the CAPVD is clean and efficient process. Additionally the CAPVD process gives the best “Ionisation Rate” of any PVD process which ensures excellent coating adhesion and structure with flexibility to include reactive processes that form a coating compound on the substrate's surface.

4.17. Electrochemical Polarization in Acidic Environment

![Fig. 4.36a Effect of concentration of HNO<sub>3</sub> on electrochemical polarization of Ni/Ti<sub>2</sub>N composite coated sintered NdFeB magnets](image1)

The electrochemical polarization of novel Ni/Ti<sub>2</sub>N composite coated NdFeB magnets were also investigated in different concentrations of nitric acid. Fig. 4.36a shows the polarization curves measured with three nitric acid concentrations. The free corroding potential (FCP) or <i>E</i><sub>Corr</sub> is not affected by the concentration of nitric acid in the range 0.25 M to 1.0 M. However, decrease in the current density with decreasing concentration is an indicator that the corrosion resistance of the composite coating is higher at low concentrations and decreases with increasing the concentration of acid.

![Fig. 4.36b Comparison of Ni/Ti<sub>2</sub>N composite and Ti<sub>2</sub>N ceramic coated sintered NdFeB magnets in 0.5M HNO<sub>3</sub>](image2)
The electrochemical polarization behaviour of the composite coated NdFeB magnet was also compared to that of the NiCuNi coated NdFeB magnet in 0.5 M nitric acid. Fig. 4.36b shows the overlay of polarization curves for the two coating-substrate systems. There is very little difference in the free corroding potentials of the two systems but the current density for the composite coated NdFeB magnet is considerably lower than that of the NiCuNi coated NdFeB magnet.

It means that the novel Ni/Ti$_2$N composite coating provides adequately higher corrosion protection to the sintered NdFeB permanent magnets compared to the NiCuNi coating in the acidic environment. The detailed investigations in different acids with varying concentrations and their subsequent comparison have not been included in the present study.

However, the Ti$_2$N ceramic coating and the novel Ni/Ti$_2$N composite coated NdFeB magnets were further investigated with cyclic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques in the simulated marine and industrial environments to establish the competitiveness of the novel coating-substrate system.

4.18. Cyclic Polarization in Simulated Marine Environment

Fig. 4.37 shows the cyclic polarization curves for the sintered NdFeB magnet in simulated marine environment.

Fig. 4.37 Cyclic polarization of uncoated sintered NdFeB magnet in simulated marine environment

During forward scan the anodic polarization takes off at a brisk rate, i.e. the current density increases rapidly with small increments in the potential, indicating a fast rate of pitting of the anode material. As the potential is increased towards the positive side, the slope of the curve changes and becomes almost vertical indicating the approach of the limiting current density i.e. a negligible increase in the current density with the potential. It means that at positive potentials the pitting process slows down.
During reverse scan, the curve is retraced with the same slope as was observed during the forward scan and the slope changes at potential lower than that for the forward scan and the reverse anodic curve did not intersect the forward anodic curve. The free corroding potential for the reverse scan is at lower potential as compared to the forward scan. It can therefore, be deduced that the pitting of the sintered NdFeB magnet material is inexorable and will continue till all of it is converted to the corrosion product.

Fig. 4.38 shows the cyclic polarization curves for the CAPVD Ti$_2$N ceramic coated sintered NdFeB magnet in simulated marine environment. The slope of the forward polarization curve is steeper compared to the uncoated NdFeB magnet i.e. the increase in the current density needed a relatively higher increment in the potential. In other words, the rate of pitting is slower compared to the uncoated NdFeB magnets. At the apex, the slope is maximum, nearly vertical that means the limiting current density is approached. During the reverse scan, the curve bended at lower current density than that at the apex. It intersected the forward scan curve while descending with limiting current density. The slope of the curve changed abruptly at a potential well below the free corroding potential during the forward scan.

It can be inferred that the rate of pitting of the coating-substrate system has decreased owing to protection provided by the CAPVD Ti$_2$N ceramic coating.

![Cyclic polarization of Ti$_2$N ceramic coated sintered NdFeB magnet in simulated marine environment](image)

Nevertheless, the non-encapsulating nature of the CAPVD deposit has rendered the coating-substrate system vulnerable to the relentless pitting corrosion.

Fig. 4.39 shows the cyclic polarization curves for the NiCuNi coated NdFeB magnet in simulated marine environment. The forward anodic polarization curve shows a couple of small humps and then a nose near the apex. These abrupt changes in the current density with potential are attributed to the make break of some passive film at the interfaces of the inter-layers of the metallic coatings i.e. NiCuNi.
It has been indicated by the XRD pattern (see Fig. 4.21) that at the interface a Cu$_{3.8}$Ni phase is present or in other words there is a solid solution of Cu$_{3.8}$Ni at or close to the interface. Obviously, the electrochemical potential of a solid solution is different than that of a metal and it is this potential difference that appeared in the form of humps in the current density with the potential change. During reverse scan the polarization curve showed a very little decrease in the current density and as such the anode is said to have reached to a limiting current density. It means that some equilibrium has been established, probably due to some corrosion products adsorbed to the surface or a film formation on the surface that is ineffective with the change of potential. All it means is that the NiCuNi coating might endure for a longer period but eventually it will expose the substrate to the environment. Now, after how long, will be found out after studying the rate of degradation of the coating by EIS.

Fig. 4.40 shows the cyclic polarization curves for the Ni/Ti$_2$N composite coating on the sintered NdFeB magnet in simulated marine environment. The forward anodic polarization curve shows non-linear trend with the slope of the curve changing consistently throughout the forward potential scan. The slope of the curve is maximum at the apex, where it is almost vertical, indicating the approach of limiting current density and the establishment of an equilibrium either by the formation of a protective film or by the adsorption of corrosion products at the surface. The reverse scan showed a negligible decrease in the current density with the change of potential. It means that the equilibrium established near the apex was retained throughout the reverse potential scan.
So, the Ni/Ti$_2$N composite coating being chemically inert should have reasonably high resistance to pitting, which is true and reflected by the shifting of the polarization curve towards noble potential and the lower corrosion current density see Fig. 4.41, but the inherent permeable defects and the diffusion paths activate pitting of the nickel undercoat. The limiting current density near the apex may also be attributed to blockage of the diffusion paths with the corrosion products. The Ni/Ti$_2$N composite coating can therefore, resist pitting for an extended period. However, this needs to be confirmed by the study of coating degradation by EIS.

Fig. 4.40 Cyclic polarization of Ni/Ti$_2$N composite coated sintered NdFeB magnet in simulated marine environment

Fig. 4.41 Comparison of cyclic polarization curves of Ni/Ti$_2$N composite coated and uncoated sintered NdFeB magnet in simulated marine environment

Fig. 4.41 shows the overlay of the cyclic polarization curves for the uncoated NdFeB magnet and the Ni/Ti$_2$N composite coated NdFeB magnet. The whole curve is shifted towards left i.e. lower current density side, and towards top i.e. noble potential side due to the Ni/Ti$_2$N composite coating. Hence, the Ni/Ti$_2$N composite coating ensured extended corrosion protection of the sintered NdFeB magnet substrate.
4.19. Cyclic Polarization in Simulated Industrial Environment

Fig. 4.42 shows the cyclic polarization curves for the sintered NdFeB magnet in simulated industrial environment. The curve is very similar to the one obtained in simulated marine environment. During forward scan the anodic polarization takes off at a brisk rate, i.e. the current density increases rapidly with small increments in the potential, indicating a fast rate of pitting of the anode material. As the potential is increased towards the positive side, the slope of the curve changes and becomes almost vertical indicating the approach of the limiting current density i.e. a negligible increase in the current density with the potential. It means that at positive potentials the pitting process slows down. During reverse scan, the curve is almost retraced with the same slope as was observed during the forward scan and the slope changes at potential lower than that for the forward scan and the reverse anodic curve did not intersect the forward anodic curve. The free corroding potential for the reverse scan is at lower potential as compared to the forward scan. It can therefore, be deduced that the pitting of the sintered NdFeB magnet material is unstoppable and will continue till all of it is converted to the corrosion product.

Fig. 4.43 shows the cyclic polarization curves for the CAPVD Ti$_2$N ceramic coated sintered NdFeB magnet in simulated industrial environment. The curve is similar to one shown in Fig. 4.38. The slope of the forward polarization curve is steeper compared to the uncoated NdFeB magnet i.e. the increase in the current density needed a relatively higher increment in the potential. In other words, the rate of pitting is slower compared to the uncoated NdFeB magnets. Slightly higher values of current density were obtained during the reverse scan. The slope of the curve changed abruptly at a potential well below the free corroding potential during the
forward scan. It is clear that the rate of pitting of the coating-substrate system has decreased owing to protection provided by the CAPVD Ti$_2$N ceramic coating.

**Fig. 4.43** Cyclic polarization of Ti$_2$N ceramic coated sintered NdFeB magnet in simulated industrial environment

Fig. 4.44 shows the cyclic polarization curve for the NiCuNi coated sintered NdFeB magnet in simulated industrial environment. It is a unique curve having negative hysteresis between the forward and the reverse potential scans. There are a couple of noses in the forward potential scan. The first nose reflects the make break of passive film on the surface while after second nose the passive state retained till the apex.

**Fig. 4.44** Cyclic polarization of NiCuNi coated sintered NdFeB magnet in simulated industrial environment

During reverse scan a negative hysteresis i.e. with lower current density was observed. The reverse potential scan intersected the forward potential scan twice before the free corroding potential during the forward scan. The forward potential scan was intersected just above the first nose at about 0.16 volts, which is the
“Pitting Protection Potential” or $E_{\text{Prot}}$. It means that the NiCuNi coating will protect the coating-substrate system from pitting in the simulated industrial environment. In this regard the coating behaves much better in the simulated industrial environment compared to the simulated marine environment.

Fig. 4.45 shows the cyclic polarization curve for the Ni/Ti$_2$N composite coated sintered NdFeB magnet in simulated industrial environment. The curve is similar to the one obtained for the NiCuNi coated magnets in the same environment. Unlike the NiCuNi coated magnet, the Ni/Ti$_2$N composite coated magnet does not have any nose during the forward potential scan. The slope of the curve changed a couple of times before gaining a limiting current density with almost a vertical slope.

During reverse scan a negative hysteresis i.e. with lower current density was observed. The reverse potential scan intersected the forward potential scan twice before the free corroding potential during the forward scan. The forward potential scan was intersected at about 0.10 volts, which is the “Pitting Protection Potential” or $E_{\text{Prot}}$. It means that the Ni/Ti$_2$N composite coating will protect the coating-substrate system from pitting in the simulated industrial environment.

This is an exciting and encouraging result as it has confirmed the earlier result obtained through Tafel extrapolation that the Ni/Ti$_2$N composite coating is more protective for the sintered NdFeB magnets than the Ti$_2$N ceramic and the NiCuNi coatings in both the environments. Further, the coating-substrate system composed of the Ni/Ti$_2$N composite coating on NdFeB magnet has a better corrosion resistance in industrial environment compared to the marine environment.
Fig. 4.46 Comparison of cyclic polarization curves of Ni/Ti$_2$N composite coated and uncoated sintered NdFeB magnet in simulated industrial environment

Fig. 4.46 shows the overlay of the cyclic polarization curves for the uncoated NdFeB sintered magnet and the Ni/Ti$_2$N composite coated NdFeB magnets. The curve for the composite coating is shifted towards lower current density and towards more noble potential compared to the uncoated NdFeB magnet. Moreover, the composite has $E_{\text{Prot}}$ at about 0.10 volts versus SCE, which means that pitting will never occur for the coating-substrate system below this potential.
4.20. **EIS of NiCuNi coating in Simulated Environments**

The coatings degradation was measured with EIS at systematic exposure intervals in simulated marine environment that is, aerated 3.5% NaCl aqueous solution at ambient temperature. The sintered NdFeB substrate was made working electrode where as graphite rod was used as counter electrode. The results of the coating’s impedances are shown in Fig. 4.47 as Nyquist plots. The nickel-copper-nickel coating started degrading straight away and collapsed to failure within 24 hours of exposure [137].

![Nyquist plot showing ac impedance curves at systematic exposure intervals for the nickel-copper-nickel coating](image)

**Fig. 4.47** Nyquist plot showing ac impedance curves at systematic exposure intervals for the nickel-copper-nickel coating

4.21. **EIS of Ti$_2$N ceramic coating in Simulated Environments**

The impedance of the multilayered ceramic coating increased with time till 48 hours exposure, see Fig. 4.48. This is an extraordinary result, because ordinarily the coating either maintains its resistance for some time and then start degrading or it starts degrading straight away as exposed to the active environment.
The multilayered structure however, started degrading somewhere between 48 to 72 hours of exposure and collapsed to complete failure after 84 hours exposure, see Fig.4.49.

Fig. 4.48 Nyquist plot showing ac impedance arcs at systematic exposure intervals for the multilayer ceramic coating

Fig. 4.49 Nyquist plot showing ac impedance arcs for post 48 hours exposure of the multilayer ceramic coating

Fig. 4.50 shows the graph of Rp or the polarization resistance as a function of exposure time for the two coatings. The Rp of NiCuNi coating at 10 mHz was 4.28 kohm-cm\(^2\) just after 1 hour of exposure that decreased sharply to 1.61 kohm-cm\(^2\)
during 24 hours of exposure with complete coating failure, while the Rp of ceramic coating increased from 1.68 kohm-cm² to 3.18 kohm-cm² for the same duration of exposure. The Rp of ceramic coating almost remained constant till 48 hours and after that started decreasing till complete failure between 84 to 90 hours of exposure. It means that the rate of degradation of ceramic coating is at least three times less than that of nickel-copper-nickel coating. In other words, the corrosion resistance of the CAPVD multilayered ceramic coating for sintered NdFeB magnets is three times better than the electrodeposited nickel-copper-nickel coating [145].

![Fig. 4.50 Comparison for the rate of change of polarization resistances of two types of coatings on sintered NdFeB magnets](image)

### 4.22 EIS of Ni/Ti₂N composite coating in Simulated Environments

The comparison of EIS data for the composite coating measured after different exposure times in simulated industrial and marine environments is shown in Fig. 4.51. The Nyquist plots show higher values of impedance in the industrial environment compared to the marine environment for the composite coated NdFeB magnets. This is in agreement with the dc polarization results discussed in section 3.3. The comparison is further elaborated in the Fig. 4.52, where EIS data of industrial environment is overlaid on marine environment exclusively after 1, 4, 16 and 128 hours of exposures. In case of industrial environment, the value of Zre was 38.77 kΩ after 1 hour of exposure and increased to 48.0 kΩ after 4 hours of exposure but started decreasing some where between 4 to 16 hours.
After 16 hours, the value of $Z_{\text{re}}$ was 35.29 k$\Omega$ and kept on decreasing gradually to 20.29 k$\Omega$ after 64 hours. However, after 128 hours of exposure the $Z_{\text{re}}$ recovered slightly to 22.65 k$\Omega$. On the other hand, after 1 hour of exposure in marine environment, the value of $Z_{\text{re}}$ was 47.45 k$\Omega$ and instead of increasing it decreased to 7.37 k$\Omega$ after 4 hours of exposure and continued decreasing to 2.44 k$\Omega$ after 64 hours. After 128 hours it improved to 5.94 k$\Omega$ just like the industrial environment. It means that the real component of coating impedance decreases quickly and drastically during prolonged exposure in the marine environment as compared to the industrial environment [145]. In other words, the life of composite coated magnets is more in the industrial environment than the marine environment.
The profile of charge transfer resistance, $R_{ct}$ at 10 mHz, as a function of the exposure time is shown in Fig. 4.53. The overall $R_{ct}$ profile in industrial environment is higher than the marine environment. The trend of $R_{ct}$ degradation with time is similar except for the initial 4 to 16 hours.

![Graph showing $R_{ct}$ profiles](image)

**Fig. 4.53 Rct profiles for the composite coated neo magnets as a function of exposure time in simulated environments**
Chapter 4 | Results and Discussion

It means that the chloride ions are more lethal compared to the sulphate ions[143], probably due to the smaller size or ionic radius of the chloride ions that helps them to penetrate through the crevices and/or coating holidays. Nevertheless, the Ni/Ti$_2$N composite coating did not lose the barrier protection in both the environments as there were no signs of second time constant or Warburg’s impedance in the EIS data even after 128 hours of exposure.

4.23. **Equivalent Electrical Circuit Modelling**

Since the composite coating was conductive in nature and there was no electrical insulation between the substrate and the environment plus the phase angle never reached a value of -90°, so it behaved like a non-ideal capacitor. It means that the coating capacitance was there, but it was not like that of an ideal capacitor. The Nyquist curves for all the spectra indicated that the coating-substrate system followed one time constant throughout the prolonged exposure in the simulated marine and industrial environments and was expected to follow the equivalent electrical circuit model (ECM) as shown in Fig. 4.54.

![Fig. 4.54 Equivalent electronic circuit model (ECM) for the Ni/Ti$_2$N composite coated sintered neo magnets](image)

Besides the solution resistance ($R_s=1 \ \Omega$), the time constant of ECM comprised of the charge transfer resistance ($R_{ct}$) and a constant phase element (CPE), since the measured phase angles were lower than the value for the ideal capacitor. The value of $Z_{re}$ measured at 10 mHz frequency was taken as the $R_{ct}$ and the CPE was calculated from the following equation

$$CPE = \left( \frac{1}{(2\pi f)^{1/\alpha} Z_{im}} \right)^\alpha$$
Chapter 4 | Results and Discussion

Where $\alpha$ is the ratio of the lowest measured phase angle to the phase angle for ideal capacitor. The curves produced through the ECM were fitted on the measured EIS data as shown in Fig. 4.55. The goodness of the fits for 16 hours exposure data in marine and industrial environments are $1.115 \times 10^{-3}$ and $3.055 \times 10^{-3}$ respectively [158].

![Fig. 4.55 Curve fitting for ECM calculated data and measured EIS data for Ni/Ti$_2$N coated sintered neo magnets after 16 hours exposure; a & c) Bode plots, b & d) Nyquist plots](image)

Finally the values of $R_{ct}$ measured through EIS and those calculated through the ECM were plotted as a function of exposure time, as shown in Fig. 4.56 and Fig.4.57 to estimate the rate of coating degradation.

![Fig. 4.56 Rct profiles for EIS measured and ECM calculated for Ni/Ti$_2$N coated NdFeB magnets during prolonged exposure in simulated industrial environment](image)
4.24. **Electrochemical Frequency Modulation**

Fig. 4.58 shows the plot of polarization resistance $R_p$ of the composite coated NdFeB magnet as a function of measuring time for exposure in simulated marine environment for 1 to 144 hours.

![Diagram showing graph of $R_{ct}$ vs. exposure time in 3.5 wt.% (aq) NaCl (hours)](image)

**Fig. 4.57** $R_{ct}$ profiles for EIS measured and ECM calculated for Ni/Ti$_2$N coated NdFeB magnets during prolonged exposure in simulated marine environment

**Fig. 4.58** $R_p$ vs time for Ni/Ti$_2$N coated NdFeB magnets during prolonged exposure in simulated marine environment
Chapter 4 | Results and Discussion

The $R_p$ decreased sharply during first 24 hours of exposure then recovered slightly after 96 hours but declined further till 144 hours exposure. The trend is similar to the one observed for the charge transfer resistance $R_{CT}$ measured with EIS technique as shown in Fig. 4.53. The sharp decrease and then a little increase in the $R_p$ indicates the make break of passivation that is in agreement with the cyclic polarization results shown in Fig. 4.40.

![Electrochemical Frequency Modulation Trend](image)

**Fig. 4.59 EFM for Ni/Ti$_2$N coated NdFeB magnets during prolonged exposure in simulated marine environment**

Fig. 4.59 shows the plot of corrosion rate and corrosion current for the composite coating exposed in marine environment for exposure time of 1 to 144 hours. Generally, the corrosion rate increased with the exposure time but some data points show sharp decrease in the corrosion rate indicating localized passivation. The EFM technique however, determined higher values for the corrosion rate as compared to the Tafel extrapolation technique for the composite coating in simulated marine environment.

Fig. 4.60 shows the plot of polarization resistance $R_p$ of the composite coated NdFeB magnet as a function of measuring time for exposure in simulated industrial environment for 1 to 144 hours. The value of $R_p$ decreased till 96 hours of exposure in the simulated industrial environment but increased appreciably after 120 to 144 hours of exposure.
It clearly indicates the formation of some passivation film which is in agreement to the cyclic polarization results for the composite coated NdFeB magnets shown in Fig. 4.45. However the $R_p$ values determined by EFM are higher compared to the $R_{CT}$ values determined by EIS.

Fig. 4.61 shows the plot of corrosion rate and corrosion current for the composite coating exposed in simulated industrial environment for exposure time of 1 to 144 hours. The corrosion rate after 1 hour exposure was below 1 mpy and decreased further till 144 hours exposure in the industrial environment. The results are in agreement with the Tafel extrapolation results that also determined the corrosion rate of the novel Ni/Ti$_2$N composite coated NdFeB magnets below 1 mpy as shown in Fig. 4.34.
Table 4.2 shows the average values for the corrosion rate and the corrosion current, calculated from the data presented in Fig. 4.59 and Fig. 4.61. The values for the corrosion rates in the marine and industrial environments as a function of exposure time are plotted in Fig. 4.62.

Table 4.2 Corrosion rate and corrosion current from the EFM plots

<table>
<thead>
<tr>
<th>Exposure Time (Hours)</th>
<th>Corrosion Rate (mpy)</th>
<th>Corrosion Current (μA)</th>
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<td></td>
<td>Marine</td>
<td>Industrial</td>
</tr>
<tr>
<td>1</td>
<td>7.01</td>
<td>0.62</td>
</tr>
<tr>
<td>96</td>
<td>10.41</td>
<td>0.15</td>
</tr>
<tr>
<td>144</td>
<td>14.99</td>
<td>0.07</td>
</tr>
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</table>

Fig. 4.61 EFM for Ni/Ti$_2$N coated NdFeB magnets during prolonged exposure in simulated industrial environment

Fig. 4.62 Plot of average values of corrosion rates from EFM data for Ni/Ti$_2$N coated NdFeB magnets in simulated marine and industrial environments
The corrosion rate for the composite coated magnets increased with exposure time in the marine environment whereas it decreased with the exposure time in the industrial environment, an indication of passivation with exposure time.

It can be deduced from the corrosion study of different coatings on the sintered NdFeB permanent magnet substrates with different electrochemical techniques that

- The CAPVD Ti$_2$N ceramic coating provided adequate corrosion protection but due to the inherent short circuit diffusion paths it can not encapsulate the substrate
- The NiCuNi coating is better than the Ti$_2$N ceramic coating in both environments but EIS showed that the coating degrades much faster compared to the Ti$_2$N ceramic coating
- The novel Ni/Ti$_2$N composite coating turned out as the best anticorrosion barrier in both the marine and the industrial environments
- The marine environment is however, lethal compared to the industrial environment as the coatings have lower corrosion resistance and degrade at a faster rate in the marine environment
- The Ni/Ti$_2$N composite coating appeared to passivate in the industrial environment where as the passivation is not attained in marine environment
- The results of different electrochemical techniques were in phenomenal agreement with each other but some techniques showed higher values compared to the other
Part – 5
Coating Adherence of Surface Engineered Sintered NdFeB Permanent Magnets

4.25. **Scratch Test for Adherence of Coatings**
Fig. 4.63, 4.64 and 4.69 show the scratch test results of NiCuNi coated, Ti$_2$N ceramic coated and Ni/Ti$_2$N composite coated NdFeB magnets respectively.

![Fig. 4.63 Scratch test for NiCuNi coated NdFeB sintered magnet](image1)

![Fig. 4.64 Scratch test for Ti$_2$N ceramic coated NdFeB sintered magnet](image2)
Table 4.3 summarizes the scratch test results for the two coatings. The Ti$_2$N coating, though less than one micron in thickness, withstood more normal force ($F_n$) compared to Ni-Cu-Ni coating and the indenter traversed more linear distance ($d_L$) before it pierced through the coating and approached to the base metal [144]. The percentile range of acoustic emission is also more for the titanium nitride coating. The results indicate that the “Critical Scratch Load – $F_n$” i.e. the applied normal force at which well-defined, recognizable damaging event occurred or observed is maximum for the novel Ni/Ti$_2$N composite coating. Similarly the distance traversed by the stylus till the $F_n$ is also maximum for the composite coating.

It means the overall adhesive strength of Ni/Ti$_2$N composite coating is more than the Ni-Cu-Ni and Ti$_2$N coated NdFeB magnets.
4.26. Magnetic Properties of Sintered NdFeB with and without Coatings

One of the objectives of this work was to improve the corrosion resistance without compromising the magnetic properties. The hysteresis loops for the uncoated and coated sintered NdFeB permanent magnets are shown in the Fig. 4.66. There are two loops in each plot. The horizontal loop showing saturation magnetization is the $M$ vs $H$ loop whereas the tilted loop is the $B$ vs $H$ loop with no saturation in the magnetic induction.

Apparently all the hysteresis loops are identical and can hardly be differentiated. However, the overlay of the four hysteresis loops is shown in Fig. 4.67. The second quadrant demagnetizing curves show marginal differences in the magnetic properties.
The novel composite coating (Ni/Ti$_2$N) composed of electrodeposited nickel interlayer plus CAPVD Ti$_2$N ceramic coating proved up to the mark in this regard as the magnetic properties remained comparable [144, 158] as shown in Fig. 4.67 and tabulated in Table 4.4.

Hence, it is safe to deduce that the CAPVD coatings do not have any damaging effect on the magnetic properties of the sintered NdFeB permanent magnets.

Table 4.4 Magnetic properties of coated and uncoated sintered NdFeB magnets

<table>
<thead>
<tr>
<th>Coating-NdFeB</th>
<th>$B_r$ (kG)</th>
<th>$J_{HC}$ (kOe)</th>
<th>$BH_{max}$ (MGOe)</th>
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<tr>
<td>Uncoated NdFeB</td>
<td>12.80</td>
<td>15.99</td>
<td>39.57</td>
</tr>
<tr>
<td>NiCuNi coated</td>
<td>12.61</td>
<td>15.65</td>
<td>37.78</td>
</tr>
<tr>
<td>Ti$_2$N coated</td>
<td>12.77</td>
<td>15.56</td>
<td>38.77</td>
</tr>
<tr>
<td>Ni/Ti$_2$N coated</td>
<td>12.68</td>
<td>16.32</td>
<td>38.31</td>
</tr>
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The objectives of the present study have successfully been achieved and the corrosion resistance of sintered NdFeB permanent magnets has been improved by synthesizing novel Ni/Ti$_2$N composite anticorrosion barrier without any sacrifice of their magnetic properties.
4.27. References


[145] A. Ali, A. Ahmad, K.M. Deen, J. Rare Earths, 27(6), (2009) p1003-1007


CONCLUSIONS

Chapter 5

This chapter provides the “Sum up” of the discussion, carried out in the last chapter based on the experimental results and thereafter the “Conclusions” drawn. Lastly, some important points have been mentioned as “Next to do” for further exploration of the composite coating and to extend the research work presented in the thesis.
5.1 Sum up

The magnetic properties, microstructure and corrosion resistance of uncoated and coated sintered NdFeB permanent magnets have been studied. The complex microstructure of the sintered NdFeB magnets consisting of three thermodynamically stable ternary phases, with different electrochemical potentials, was found susceptible to intergranular corrosion in the active environment. The situation leads to the formation of galvanic couple between the more active and less active phases. The Nd-rich anodic phase around the grains of the cathodic matrix phase, corrode preferentially at a much faster rate due to unfavourable area or volume ratio. Similarly the third phase that is boron-rich phase corrodes preferentially and subsequently the grains of the matrix phase break-off and disintegrate in to powder form. The magnetic properties of the sintered NdFeB magnet declined due to the decreasing volume of the hard magnetic phase with progressive corrosion and ultimately, the magnetic properties disappeared as the magnet material turned to the powder form.

One way to improve the corrosion resistance is the alloy modification that is partial substitution of rare-earth and/or the transition elements but the published reports have shown that only a few elements have marginally improved the corrosion resistance but at the sacrifice of either the coercivity or the remanance.

The alternate solution is the incorporation of a barrier coating through surface engineering. Much has been published on protective coatings for NdFeB magnets such as polymer resins, electroless Ni, electrodeposited Ni, NiP, Zn, Al and so forth but each has its limitations. To this end, it was decided to investigate the titanium nitride ceramic coating deposited by cathodic arc physical vapour deposition and compare its anticorrosion characteristics with the electrodeposited NiCuNi coating. Later an innovative composite coating consisting of titanium nitride top-layer plus nickel undercoat was deposited on the sintered NdFeB magnets.

Different electrochemical techniques were used to characterize the coating-substrate systems including Tafel Extrapolation, Cyclic Polarization, Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Frequency Modulation (EFM) in simulated marine and industrial environments.
The characterization results showed that the composite coating was excellent anti-corrosion barrier for the sintered NdFeB magnets in both the marine and the industrial environments.

5.2 Conclusions

The uncoated sintered NdFeB permanent magnet has a complex multi-phase microstructure with three ternary phases in equilibrium at ambient temperature. This forms galvanic couples between the Neodymium rich phases and the matrix phase and lead to the preferential corrosive attack on the anodic phases resulting in "Inter-granular Corrosion". Besides their higher electrochemical potential, the preferential dissolution of grain boundary phases is also favoured by their much smaller anodic area compared to the larger cathodic area of the matrix phase.

The overall effect of the corrosion is the microstructural degradation resulting in the loss of hard magnetic matrix phase along with proportionate decrease in the magnetic properties. Finally the grain disintegration occurs and the solid magnet loses its shape and is converted into useless powder form. The experimental results showed that all this happens in 48 to 72 hours at 38°C in 95% relative humidity environment. The sintered NdFeB permanent magnets were thus surface engineered to synthesize multilayer “Di-Titanium Nitride” coatings with and without nickel strike layer.

The CAPVD ceramic coating provided adequate protection to the sintered NdFeB by enhancing the corrosion resistance of the coating-substrate system without affecting the magnetic properties.

However, the level of protection with Ti$_2$N ceramic coating was lower than the nickel-copper-nickel coating due to the morphology of CAPVD Ti$_2$N ceramic coating which was inherently incapable of completely encapsulating the substrate.

Nevertheless, the rate of degradation of polarization resistance for the CAPVD Ti$_2$N ceramic coating was lower compared to the nickel-copper-nickel coating.

To overcome the limitation of ceramic coating, an innovative composite coating composed of an under-coat of electrodeposited nickel and a top-layer of CAPVD Ti$_2$N ceramic coating was successfully employed for corrosion protection of sintered NdFeB permanent magnets.

The novel composite coating markedly improved the corrosion protection for sintered NdFeB permanent magnets. The results of dc and ac electrochemical techniques are in agreement with each other and proved that the composite coating provided improved and prolonged protection to the sintered NdFeB magnets compared to the ceramic and the nickel-copper-nickel coatings in simulated marine and industrial environments without affecting the magnetic properties.
Chapter 5 | Conclusions

The Ni/Ti$_2$N composite coating has adequate and better electrochemical impedance than that of Ti$_2$N ceramic coating and is capable of providing prolonged protection to the sintered NdFeB magnets. The simulated marine environment comprising of chloride ions is however, more lethal to the composite coating compared to the simulated industrial environment having sulphate ions.

5.3 Next to do

- The Ni/Ti$_2$N composite coated NdFeB magnets should also be investigated in the synthetic body fluid and saliva since NdFeB magnets are being extensively used in hand held surgical equipment
- The Ni interlayer or undercoat should be replaced with cheaper materials like Al or Cr and characterized accordingly
- Attempt to re-optimize the CAPVD process or experiment with a modified process so as to deposit other Ti$_x$N compounds instead of Ti$_2$N that are chemically more stable and might contribute to the economy
- Experiment with post deposition sealing treatment of the CAPVD Ti$_2$N ceramic coating by PMMA (polymethyl methacrylate) or another suitable polymeric material
Annexure – A

LIST OF PUBLICATIONS
List of Publications from PhD work

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<td>1</td>
<td>Corrosion protection of sintered NdFeB magnets by CAPVD titanium nitride coating</td>
<td>Journal of Materials and Corrosion ISSN: 1521-4176 (online)</td>
<td>Wiley VCH 12205 Berlin, Germany</td>
<td>03/09/2008</td>
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<td><strong>Citation:</strong> A. Ali, A. Ahmad, J. Mater. Corr. 60, 5 (2009) p 372-375</td>
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