STUDIES ON THE MAGNETIC PROPERTIES AND MICROSTRUCTURE OF SINTERED Nd-Fe-B MAGNET

AISHWARYESWAR M (19Y202)

Under the guidance of

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Assistant Professor

Dissertation submitted in partial fulfillment of the requirements for the degree of

BACHELOR OF ENGINEERING

Branch: METALLURGICAL ENGINEERING

of Anna University, Chennai

May 2023

DEPARTMENT OF METALLURGICAL ENGINEERING

PSG COLLEGE OF TECHNOLOGY

(Autonomous Institution)

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EXTERNAL GUIDE

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FACULTY GUIDE

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HEAD OF DEPARTMENT

Certified that the candidate was examined in the viva-voce examination held on ……

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(INTERNAL EXAMINER)

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(EXTERNAL EXAMINER)

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ABSTRACT

Nd-Fe-B permanent magnets are widely used in various applications, including electric motors, generators, and hard sensors due to their excellent magnetic properties. The present study investigates the magnetic properties and microstructure of commercial Nd-Fe-B magnet. The as-received magnet was annealed at 900°C for 2h and subsequently at 500°C for 2h. In the magnetization measurement, the as-received sample shows the coercivity of 1.55 T. However, the decrease in coercivity of 1.38 T was observed in annealed sample. Scanning Electron Microscope analysis in the Back Scattered Electron (SEM-BSE) mode was carried out to understand the microstructure of the as-received and annealed samples. The microstructure of both the as-received and annealed samples show distinct contrast representing the different phases such as matrix phase, grain boundary (GB) phase, triple junction phase (TJP) and secondary phase. After annealing, it was observed that there is substantial grain growth; consequently, the annealed sample shows lower coercivity than the as-received sample.

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CHAPTER 1

INTRODUCTION

Magnetic materials have been used for various purposes for centuries. They have played a vital role in the development of modern technologies such as electricity, electronics, and telecommunication. Magnetic materials are essential for the functioning of various devices such as motors, generators, transformers, and magnetic resonance imaging (MRI) machines. The need for magnetic materials is increasing rapidly due to the rapid advancements in technology and the growing demand for more efficient and reliable devices. This reason is that, magnetic materials possess unique properties that make them essential for various technological applications. The use of magnetic materials in various fields has led to the development of new and innovative products. For instance, the use of magnetic materials in the production of hard disks has enabled the storage of large amounts of data in small devices. The use of magnetic materials in the production of MRI machines has enabled the diagnosis of various diseases in a non-invasive manner. The demand for magnetic materials is expected to increase further due to the growing demand for electric vehicles and renewable energy sources [1].

1.1 Classification of Magnetic materials

The most important property of magnetic materials is their ability to produce a magnetic field. This property arises from the alignment of the magnetic moments of the atoms within the material. Magnetic materials can be classified into three categories based on their magnetic behavior: diamagnetic, paramagnetic, and ferromagnetic [2, 3].

1.1.1 Diamagnetism

Diamagnetism is a type of magnetism that is relatively weak and temporary in nature, and is only present in materials when they are exposed to an external magnetic field. This phenomenon occurs due to changes in the orbital motion of electrons in response to the external field, resulting in the induction of a magnetic moment that is directed opposite to the applied field. Diamagnetism is a universal property of all materials; its effects are imperceptible and can only be detected in the absence of other forms of magnetism.

1.1.2 Paramagnetism

Paramagnetism is a type of magnetism that occurs in certain magnetic materials, whereby the magnetic dipoles within the material tend to align with the direction of an external magnetic field, thereby increasing the overall magnetic field strength. These materials are attracted to a magnet when exposed to a sufficiently strong external magnetic field. However, the magnetic field strength resulting from paramagnetism is typically weak, and the magnetization ceases to exist when the external magnetic field is removed.

1.1.3 Ferromagnetism

Ferromagnetism is a form of magnetism characterized by the organization of magnetic dipoles into domains, where the arrangement of individual dipoles generates strong magnetic fields. When subjected to an external magnetic field, these domains reorient themselves in a manner that enhances the external field, producing a powerful internal magnetic field aligned with the external field. Upon removal of the external field, the majority of domains remain in their newly aligned state, maintaining the magnetic field of the material even in the absence of the external field.

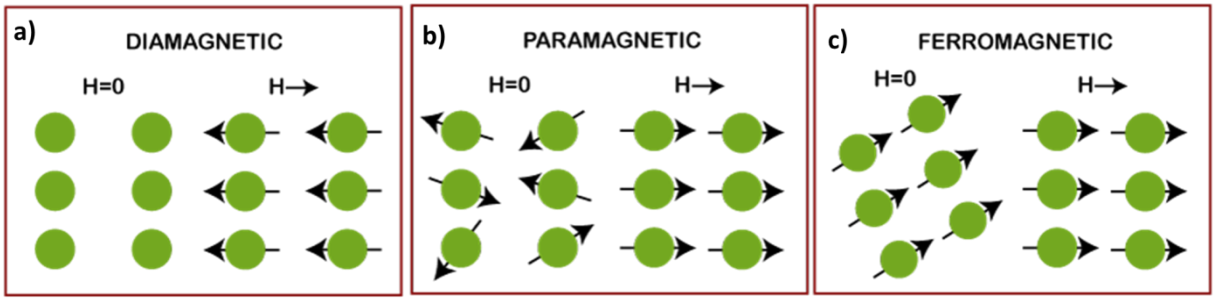

Fig. 1.1. Arrangement of Magnetic Dipoles in a) Diamagnetic, b) Paramagnetic and c) Ferromagnetic materials.
(Courtesy:https://static.javatpoint.com/blog/images/paramagnetic-vs-diamagnetic.png)

1.2 Terminology

In order to attain a comprehensive understanding of magnetic materials, it is essential to be familiar with specific terminology, such as domains, hysteresis, coercivity, remanence, and magnetic saturation. These terms play a crucial role in conducting experiments related to magnetic materials and their properties. By comprehending the meaning and significance of these terms, we can obtain a more profound understanding of the behavior and characteristics of magnetic materials, including their response to magnetic fields, magnetic induction, and the stability of magnetization.

1.2.1 Domain

A domain refers to a localized region within a magnetic material where the magnetic moments of individual atoms or ions are aligned in a particular direction, resulting in a net magnetic dipole moment for the region. The boundaries possessed by domains are known as domain walls, which separate adjacent domains with different orientations of magnetization. The presence of domains in magnetic materials leads to various magnetization phenomena, such as hysteresis and remanence [4].

1.2.2 Hysteresis

Hysteresis in magnetism refers to the phenomenon where the magnetic response of a material lags behind the applied magnetic field due to the existence of magnetic domains in the material. When a magnetic field is applied to a ferromagnetic material, the domains within the material may reorient themselves, resulting in an increase in magnetization. However, when the applied magnetic field is reduced to zero, some domains may remain oriented in their previous direction, resulting in a residual magnetization. The amount of residual magnetization depends on the magnetic history of the material, specifically the maximum magnetic field to which it was previously exposed. This effect is known as hysteresis, and it is a characteristic property of ferromagnetic materials. The hysteresis loop is a graphical representation of this phenomenon, showing the relationship between the applied magnetic field and the resulting magnetization of the material. Figure 1 shows the basic hysteresis curve for magnetic materials [2].

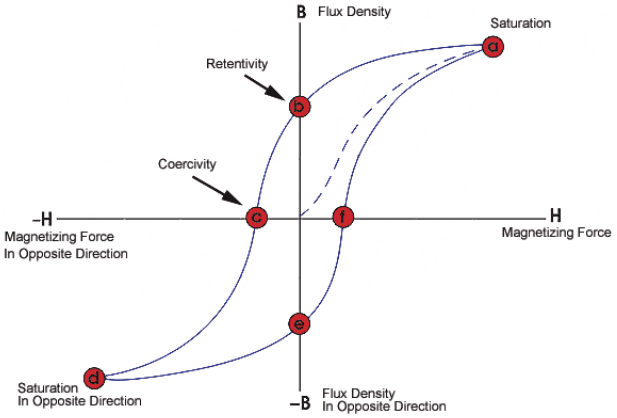

Fig. 1.2. Pictorial representation of hysteresis curve [6].

1.2.3 Remanence

Remanence in magnetism is the measure of the residual magnetization that remains in a ferromagnetic material after an external magnetic field has been removed. The remanent magnetization is a consequence of the existence of magnetic domains within the material, which tend to maintain their orientation even in the absence of an external field. The strength of the remanent magnetization depends on the intensity and duration of the magnetic field to which the material was previously exposed. Remanence is an important property of ferromagnetic materials as it determines their ability to retain magnetic properties over time [2, 4].

1.2.4 Coercivity

Coercivity is a measure of the magnetic field strength required to demagnetize a ferromagnetic material. It is defined as the magnitude of the reverse magnetic field that must be applied to the material to reduce the residual magnetization to zero. The coercivity of a material is a measure of its resistance to demagnetization and depends on the magnetic anisotropy of the material, which determines the preferred direction of magnetization. Coercivity is an important parameter in the design of magnetic materials for specific applications, such as electric vehicle motors and magnetic sensors. High coercivity materials are preferred in such applications as they are less susceptible to unwanted demagnetization, while low coercivity materials are used in applications such as electromagnets where frequent changes in magnetic state are required. Based on their coercivity magnetic materials are classified into two categories, hard and soft [5].

i. **Soft magnetic materials**

Soft magnetic materials, also known as electromagnetic materials, are characterized by their low coercivity, which means they can be easily magnetized and demagnetized. They are typically made from iron, nickel, or cobalt, and are used in a wide range of electrical and electronic devices, including transformers, inductors, motors, and generators. Soft magnetic materials are also used in magnetic shielding to protect sensitive electronic components from external magnetic fields. The magnetic properties of soft magnetic materials can be optimized by controlling their composition, microstructure, and processing conditions.

ii. **Hard magnetic materials**

Hard magnetic materials are characterized by their high magnetic anisotropy and high coercivity, which allows them to retain their magnetization even in the presence of strong external magnetic fields. The most common hard magnetic materials include permanent magnets made from rare earth metals, such as neodymium, samarium, and dysprosium. These materials are used in a variety of applications, including electric motors, generators, magnetic data storage, and magnetic resonance imaging (MRI) machines. The magnetic properties of hard magnetic materials can be tailored by adjusting their composition and microstructure, making them useful for a wide range of industrial and technological applications [7]. The hysteresis curves for soft and hard magnetic materials are shown in Fig. 1.3.

1.2.5 Magnetic Saturation

Magnetic saturation is a state of a ferromagnetic material wherein the material has reached its maximum level of magnetization, and cannot be further magnetized by an external magnetic field. In this state, all the magnetic domains in the material are aligned in the direction of the applied magnetic field, and further increase in the field strength cannot increase the magnetic moment of the material [2].

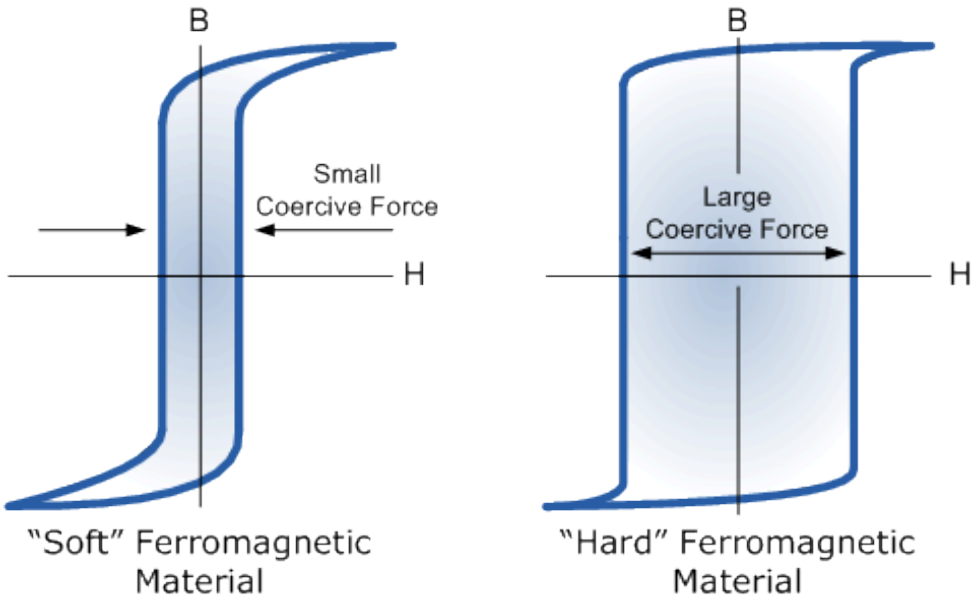

Fig. 1.3. Hysteresis curve for hard and soft magnetic materials [5].

CHAPTER 2

LITERATURE SURVEY

The chapter provided the systematic literature study performed for the better underrating of the fundamental principle and various manufacturing and processing approaches involved in the Nd-Fe-B magnets. In addition, the potential existence of Nd-Fe-B magnets in the various niche applications are also briefed.

Currently, the most high-performance permanent magnets available are based on the $RE_2Fe_{14}B$ (RE: Rare Earth such as Nd, Dy, Tb) system. Two approaches are typically employed within this system to achieve the desired properties, each utilizing a different mechanism to maintain coercivity. In aligned and sintered magnets, microcrystalline $RE_2Fe_{14}B$ is aligned and separated by a thin layer of the paramagnetic rare earth-rich phase. The rare earth-rich phase functions to decouple the grains magnetically and smooth the grain boundaries to prevent reverse domain nucleation, while the fine grain structure pins domain walls. The present chapter will detail the system's fundamentals and describe how it is processed to obtain the desired properties.

2.1 $Nd_2Fe_{14}B$ discovery, crystal structure and properties

In 1984, Croat et al. made a noteworthy discovery of a novel magnetic material that exhibited an energy product of 14 MGOe [8]. The new magnetic material was found while examining rapidly solidified RE-Fe alloys, where an alloy with a composition of $Nd_{0.135}Fe_{0.817}B_{0.048}$ displayed the most superior isotropic magnetic properties at that time. Similarly, Sagawa, Fujimara et al. [9] studied conventional powder metallurgy procedures to process the same material, producing a magnetic material with an energy product of 36 MGOe, from the composition $Nd_{0.15}Fe_{0.77}B_{0.08}$. Subsequent to these discoveries, Rodewald et al. [10] achieved energy products as high as 56 MGOe by carefully managing the composition and processing. Several attempts were made to ascertain the precise stoichiometry of the compound [11-13]. Finally, Herbst et al. utilized neutron powder diffraction studies [14, 15] to accurately determine the crystal structure and stoichiometry, as depicted in Fig. 2.1.

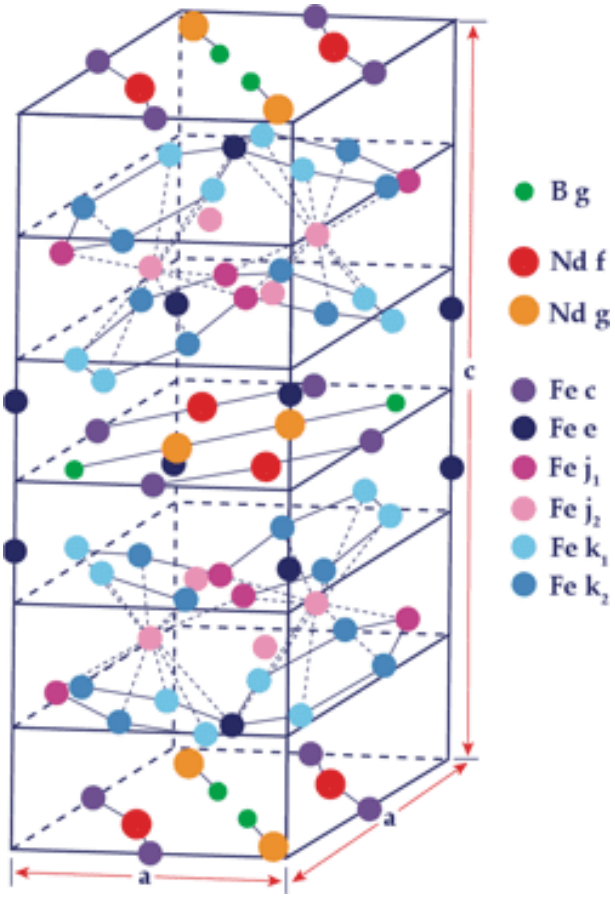

Fig. 2.1. Crystal structure of $Nd_2Fe_{14}B$ [19].

The crystal structure of $Nd_2Fe_{14}B$, which has tetragonal symmetry and lattice parameters of a = 8.80Å and c = 12.20Å reported by J. F. Herbst et al. The unit cell encompasses 68 atoms (4 formula units), consisting of 2 distinct Nd sites, 6 unique Fe sites, and 1 B site. In the structure, the magnetic moments of the 4*f* orbitals of Nd are parallel to the 3*d* orbitals of Fe, leading to a saturation magnetization of approximately 16 kG. Additionally, iron within the lattice forms a networked structure, which results in layered iron within the lattice and a very high uniaxial magneto crystalline anisotropy. This anisotropy leads to the formation of very high coercivities. The system can achieve a maximum possible energy product of 65.6 MGOe due to its high saturation magnetization and the achievable coercivity [16].

2.2 Coercivity Mechanism

One of the critical properties of permanent magnets is their resistance to demagnetization. Coercivity is a property used to describe this behaviour, which is attributed to the material. To enhance coercivity, various microstructural mechanisms utilize domain wall energy to hinder dislocation motion or prevent nucleation. Anisotropy is a requirement for coercivity since it prevents magnetization from merely rotating to the energetically favoured direction due to magnetostatic energy.

$Nd_2Fe_{14}B$ utilizes magnetocrystalline anisotropy, which occurs when certain crystallographic directions require different energies to align the magnetic moments in that direction. $Nd_2Fe_{14}B$ has high magnetocrystalline anisotropy field (73 kOe) [20] due to the large energy difference required to magnetize along the easy and hard axes. Materials with high magnetocrystalline anisotropy are primarily affected by domain processes, with magnetization reversal typically limited by either domain nucleation or domain growth. In materials controlled by domain nucleation, sites where reverse domains nucleate must be removed to maintain coercivity, which can be either chemical or physical defects. A soft magnetic material provides an easy starting point for a reverse domain, leading to low coercivity. Physical defects, such as irregularly shaped grain or phase boundaries, are also sites for demagnetizing fields. Eliminating these sites can significantly increase coercivity. The presence of secondary phases at grain boundaries can help isolate the particles and smooth grain boundaries, as used in sintered Nd-Fe-B magnets. [18]

The second method of improving coercivity is through domain wall pinning. Incorporating defects into the bulk of the material to reduce domain wall motion.

Two methods are typically used for this:

(i) The addition of small particles results in the presence of a second, nonmagnetic phase that interacts with the domain walls, thereby reducing the total domain wall energy and dispersing the particles throughout the structure. These particles must be sized on the order of the domain wall thickness.

(ii) The second method involves the formation of grain boundaries that act as strong pinning sites for domain walls. These grain boundaries can be introduced by adding secondary phases at grain boundaries, which can help to isolate the particles and smooth grain boundaries. [20]

2.3 Nd-Fe-B magnets – Production Methods

There are several routes used for the manufacturing of Nd-Fe-B magnets. The most commonly used routes are given below:

i. **Powder Metallurgy Process:** The most common manufacturing process for Nd-Fe-B magnets is powder metallurgy. In this process, the raw materials are mixed in a specific ratio and melted in a vacuum furnace. The molten alloy is then cast into thin ribbons, which are crushed into fine powder. The powder is pressed into a mold and then sintered at a high temperature. After sintering, the magnets are machined to their final shape.

ii. **Rapid Solidification Process:** The rapid solidification process involves the cooling of a molten alloy at a very high rate to produce a fine-grained structure. The resulting powder is then compacted and sintered to produce the final magnet. The rapid solidification process is a specialized manufacturing route for Nd-Fe-B magnets that is used to produce magnets with a very fine-grained structure.

iii. **Melt spinning:** Melt Spinning is a process in which, the molten alloy consisting of neodymium, iron, and boron is ejected onto a rapidly rotating drum and solidified very quickly to form a thin ribbon of material, which is then ground into a fine powder. The powder is mixed with a binder such as epoxy resin or nylon and then the mixture is compressed into a mold. The magnets are then cured and machined to their final shape.

2.4 Processing of sintered Nd-Fe-B magnets

The raw materials, such as neodymium, iron, and boron, are prepared in powder form. The powders are then milled to achieve a desired particle size and morphology. The Nd-Fe-B powder particles are mixed with a binder material, such as paraffin wax or polyvinyl alcohol, to form a homogenous mixture.

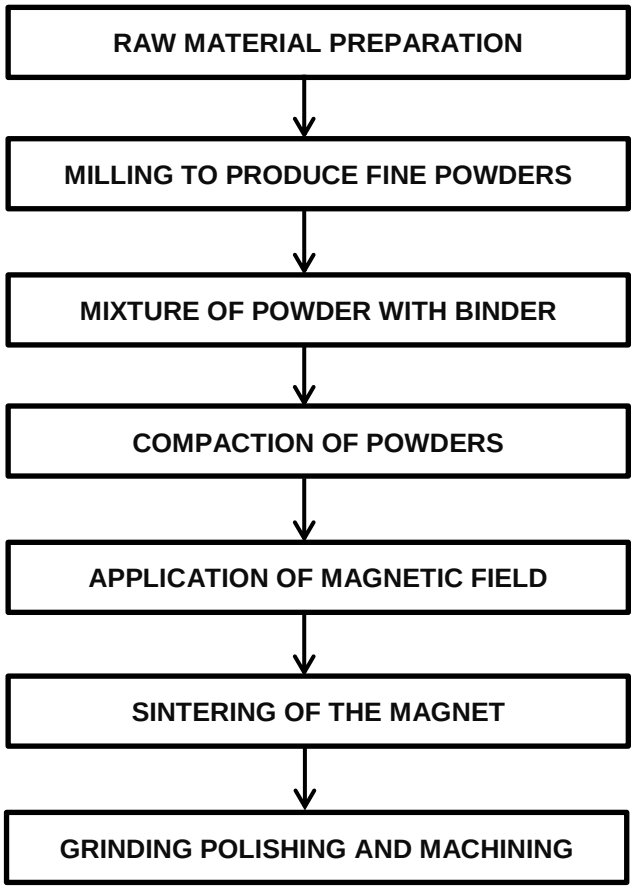

Fig. 2.2. Sintering process of Nd-Fe-B magnets

The mixture is then compacted into a desired shape using a press or a mold under high pressure. During the compaction step, a magnetic field can be applied to achieve magnetic alignment of the particles. The compacted mixture is then heated in a furnace at a temperature near the melting point of Nd-Fe-B. The sintering process takes several hours and involves a gradual increase in temperature to prevent thermal shock. During the sintering process, the NdFeB particles diffuse and bond together to form a solid, dense magnet. A magnetic field is be applied during the sintering process to maintain magnetic alignment. The sintered magnet is then cooled slowly to room temperature to prevent cracking or deformation due to thermal stress. The magnet is then machined to the desired shape and size using various cutting, grinding, and polishing tools [19].

2.5 Applications of Nd-Fe-B

Firstly, Nd-Fe-B magnets have a very high magnetic energy density, meaning they can produce a strong magnetic field relative to their size. This makes them ideal for applications where space is limited, such as in small electronic devices like headphones or hard drives.

Secondly, Nd-Fe-B magnets are very strong and can hold their magnetization for a long time, making them useful in applications where a permanent magnet is needed. Examples of such applications include in electric motors, generators, and magnetic bearings.

Thirdly, Nd-Fe-B magnets have a high resistance to demagnetization, which means they can maintain their magnetization even in the presence of external magnetic fields. This makes them useful in applications such as speakers, where the magnet is exposed to the varying magnetic field produced by the voice coil.

Some important applications of Nd-Fe-B magnets are given below: [3,7].

i. **Electric vehicles**

Nd-Fe-B magnets are used in motorsport applications such as electric bicycles, electric motorcycles, and electric cars. The high power-to-weight ratio of Nd-Fe-B magnets allows for the development of powerful and lightweight electric motors, thus increasing efficiency.

ii. **Robotics**

Nd-Fe-B magnets are used in robotics applications such as grippers, actuators, and sensors. The high magnetic strength and energy density of the magnets make them ideal for use in small and lightweight robotic systems.

iii. **Magnetic Bearings**

Nd-Fe-B magnets are used in magnetic bearing systems to suspend rotating components in machines such as turbines and compressors. This eliminates the need for mechanical bearings, resulting in reduced friction and increased efficiency.

iv. **Magnetic Separation**

Nd-Fe-B magnets are used in magnetic separation equipment to separate magnetic materials from non-magnetic materials. This technique is widely used in industries such as mining, food processing, and recycling.

v. **Magnetic Therapy**

Nd-Fe-B magnets are used in magnetic therapy devices to treat various medical conditions such as pain, inflammation, and arthritis. The magnets are placed on the affected area and produce a magnetic field that penetrates the body and stimulates the healing process.

vi. **Aerospace**

Nd-Fe-B magnets are used in aerospace applications such as navigation systems, altitude sensors, and power generators. The high magnetic strength and stability of the magnets make them ideal for use in harsh environments such as space.

vii. **Magnetic Levitation**

Nd-Fe-B magnets are used in magnetic levitation systems to levitate and move objects without contact. This technique is used in applications such as high-speed trains, magnetic bearings, and magnetic refrigeration. [21]

CHAPTER 3

OBJECTIVES AND METHODOLOGY

3.1 OBJECTIVES

i. To study the fundamentals and the microstructure/phase features of Nd-Fe-B (as-received and thermally treated) samples.

ii. To study the effect of annealing on the coercivity of the sintered Nd-Fe-B magnets.

3.2 SCOPE

i. Studying the microstructure could open up the avenues to tailor the microstructure/ phase by adopting a processing approach to enhance the magnetic properties.

ii. To plot the M-H curve of the Nd-Fe-B magnet in the as sintered and annealed condition and compare them.

3.3 METHODOLOGY

i. Procuring and demagnetizing the sintered Nd-Fe-B magnet
ii. Thermal treatment on the Nd-Fe-B sintered magnet
iii. Preparation of the samples by metallographic polishing process for microstructural analysis.
iv. Understanding the microstructure and phase details of the as-received and annealed samples by SEM analysis.
v. Studying the magnetic properties of the as-received and annealed samples.

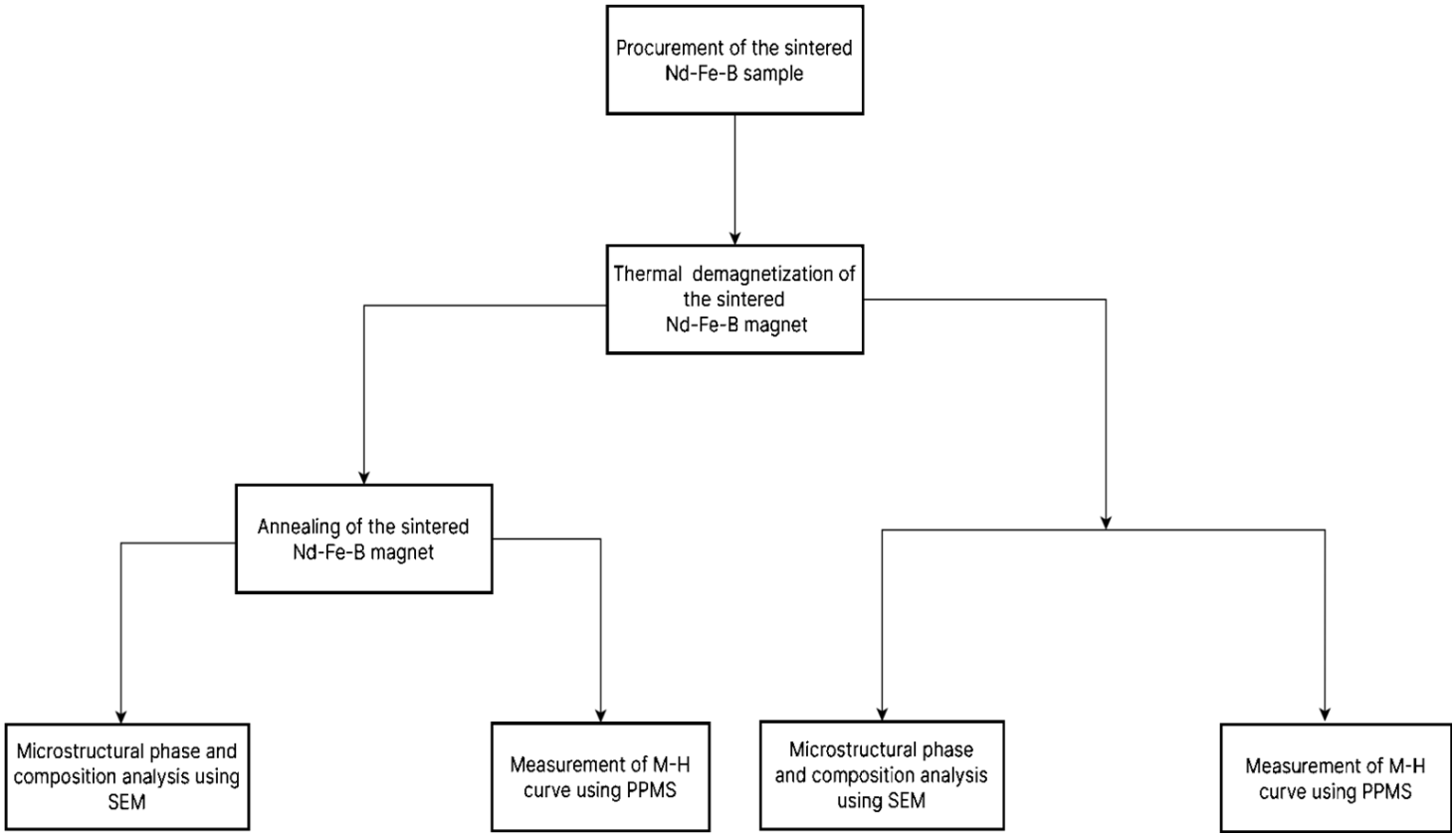

Fig. 3.1 Methodology flowchart

CHAPTER 4

EXPERIMENTAL PROCEDURES

The chapter details the various experimental procedures, principle and instruments involved in the sample preparation, processing and characterization to meet the objectives of the work.

4.1 Thermal demagnetization of the sintered Nd-Fe-B magnets

The commercially available Nd-Fe-B magnet was demagnetized by thermal process. The magnetic sample was first vacuum sealed in a quartz tube and placed in a tubular furnace (Nabertherm GmbH, Germany) as shown in Fig. 4.1. As the Curie temperature of the Nd-Fe-B magnet is around 320^{o}C, the magnet was heat treated at a temperature of 400C for 1 hour in order to remove the remanent magnetization in the sample.

4.2 Annealing of the sintered Nd-Fe-B magnets

The demagnetized sample was then heated at the rate of 10^{o}C/min to a temperature of 900^{o}C. Once the sample had reached the desired temperature, it was held at that temperature for 2 hours.

Fig. 4.1 Picture of tubular furnace

Subsequently, the temperature is lowered to 500^{o}C and kept in the furnace and held for 2 hours and then the sample was allowed to cool gradually inside the furnace. The thermal cycle is graphically presented in Fig. 4.2.

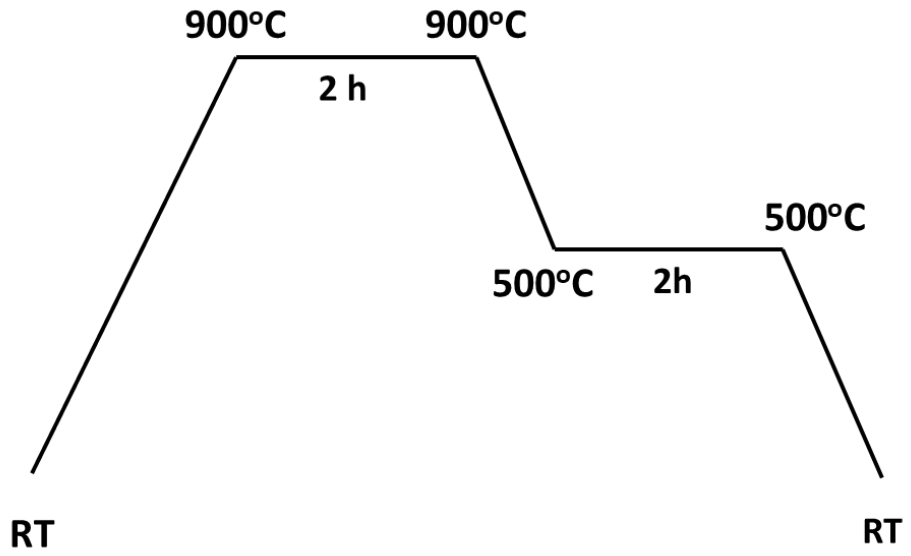

Fig. 4.2. Graphical representation of annealing

4.3 Metallurgical characterization of the Nd-Fe-B alloy

The first step involved the preparation of the sample. The sample was sectioned from the bulk material using a diamond coated blade in a low-speed saw cutter (IsoMet, Buehler, USA), The sample was polished using a series of abrasive papers of Grit sizes P60, P120, P320, P400, P600, P800, and P1200. The purpose of grinding was to remove the surface layer damaged during sectioning and to produce a flat surface perpendicular to the direction of polishing. The next step was to polish the sample using a series of diamond suspensions with decreasing particle sizes. The purpose of polishing was to remove the grinding marks and to produce a smooth and mirror-like surface that was free of scratches, pits, or other surface defects. The sample was then sonicated in acetone for 10 minutes.

The sample was imaged using Scanning electron microscopy (SEM) (Carl Zeiss, Germany). The mode of signal used here was backscattered electrons (BSE). These signals were collected by detectors and used to generate an image of the sample surface. Then the phase fraction analysis was performed to characterize the microstructure. Finally, the results of the SEM analysis were interpreted to understand the microstructural features and composition of the Nd-Fe-B magnet.

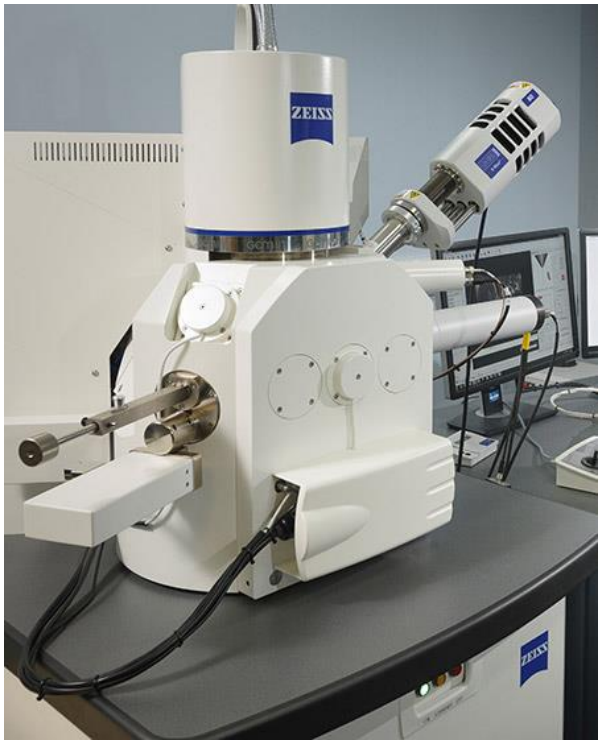

Fig. 4.3 Scanning electron microscope (SEM)

4.4 Calculation of phase fractions and Grain size measurement

The micrograph obtained from the SEM image was analysed using software called ImageJ. The microstructure image was then segregated into distinct phases. This involved setting thresholds to separate the phases based on their grayscale values. Once the microstructure image was segmented, ImageJ was used to calculate the phase fractions. The program can count the number of pixels assigned to each phase and calculate their area fractions.

For measuring the grain size, line intercept method was used. The ASTM standard that covers the line intercept method adhering to ASTM E112-13a was used for estimating the average grain size. Then the estimated grain size is verified with a standard relationship between grain size and the grain size number [22]. The first step involved calibrating the image using a straight line with the help of a scale bar. Thresholding of the image was carried out to distinguish between grains and background. The Multi-point tool was used to mark each intercept of the line with a grain boundary. Then using the Analyze tool the number of intercepts is counted, and the grain size is calculated using the following steps:

First the mean lineal length was calculated using the given formula:

$$N_L = \frac{L*n}{M*Ni} \qquad \text{Eqn.4.1}$$

$$\ell = 1/N_L \qquad \text{Eqn.4.2}$$

Where,

N_L =Number of intercepts per unit length of test line.

N_i = Sum of intercepts or intersections counted on the field

n = Number of intercepts

L = Total test line length in mm

M = Magnification

ℓ = Mean lineal length

The grain size number was obtained by substituting the mean lineal length in the formula:

$$G = -3.2877 - 6.6439\, log10\, \ell \qquad \text{Eqn.4.3}$$

4.5 Physical Property Measurement System (PPMS)

The magnetic properties were measured under the field of ± 9 T using physical property measurement system (PPMS, Dyna-Cool, USA) which is shown in Fig. 4.4.

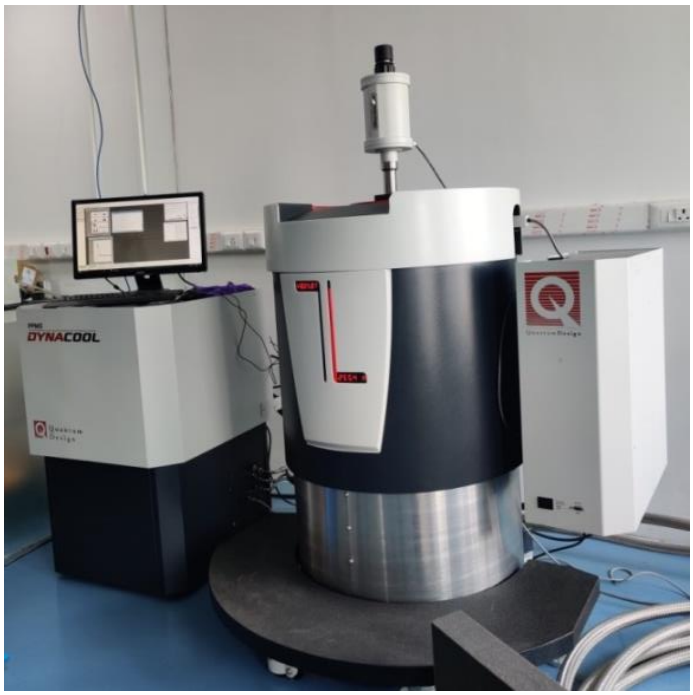

Fig. 4.4. Picture of Physical Property Measurement System (PPMS)

A small piece was sample is cut from the bulk and polished to obtain a flat and smooth surface. The sample was then cleaned using acetone and sonicated for 10 minutes to remove any contaminants or surface debris. The sample holder for measuring coercivity should be selected based on the type and geometry of the sample. The sample holder typically consisted of a non-magnetic material, such as plastic or aluminium, to avoid interference with the magnetic field. The $Nd_2Fe_{14}B$ sample was fixed with GE varnish onto the sample holder, in which the *c*-axis of the magnet was along the magnetic field direction.

CHAPTER 5

RESULTS AND DISCUSSION

The chapter summarizes the detailed discussion arrived from the microstructural evaluation of the as-received and annealed sintered Nd-Fe-B samples. The evolution in the microstructural features and variation in the phases present and its significant role in the magnetic properties are systematically correlated.

5.1 MICROSTRUCTURAL INVESTIGATIONS

The microstructure of the as-sintered sample is observed by SEM as shown in Fig. 5.1. a-b. From the low magnification micrograph, one can observe random grains of various sizes separated by grain boundaries. Along with, there are a few residual phases present in the sample. Further to get more understanding the enlarged micrograph is made for better understanding about the different regions.

The microstructure of both the as received and annealed samples show distinct contrast representing the different phases such as matrix phase, grain boundary (GB) phase, triple junction phase (TJP) and secondary phase. It shows the dark gray region emphasizing the $Nd_2Fe_{14}B$ primary or a matrix phase, and the GB phases are Nd-rich which composed of metallic Nd. There are at least two different contrasts in the secondary phases white and light grey and it could be Nd-O phases. The $Nd_2Fe_{14}B$ grains are magnetic and are the primary source of magnetic properties. They are responsible for the high coercivity and remanence of Nd-Fe-B magnets. Nd-rich and Nd-O phases are non-magnetic and act as binders, holding the $Nd_2Fe_{14}B$ grains together. Triple junctions play an important role in determining the magnetic properties of Nd-Fe-B magnets. They are regions where it shows non-magnetic phases at regions where three or more grains meet that can affect the magnetic behaviour of the material.

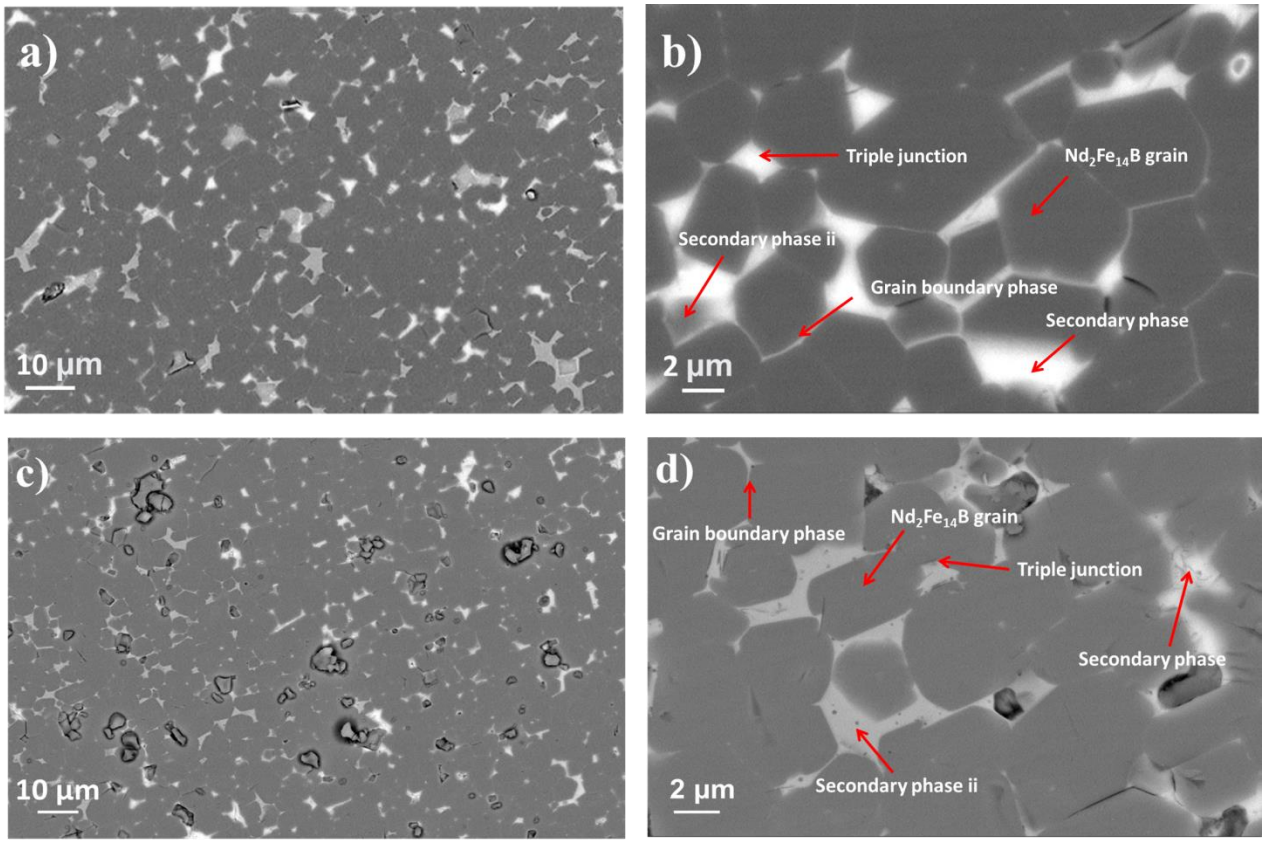

Fig. 5.1. SEM-BSE microstructure of Nd-Fe-B samples of different conditions a) As-received condition and b) enlarge view of grains and grain boundaries region, and c) Annealed condition and b) enlarge view of grains and grain boundaries region.

5.2 PHASE FRACTION ANALYSIS AND GRAIN SIZE MEASUREMENT

The BSE-SEM image and its corresponding phase mapping of the as-received and the annealed are shown in Fig.5.2. The constituent phases such as of $Nd_2Fe_{14}B$ grains and secondary phases are distinctly mapped with different colour contrast of as-received and annealed samples are observed from the Fig.5.2 c-d. The quantification of distinct phases present in the samples are summarized in the Table 1. The as-received sample constitutes 87.6% of the Nd-Fe-B grains and 12.4% of secondary phase. On the other hand, in the annealed sample there could be seen an enhancement in the $Nd_2Fe_{14}B$ phase of 89.1% with noticeable reduction to 10.9% in the Nd-O phase. The secondary phases are lower as compared with the as-received sample which implies grain growth in the annealed sample.

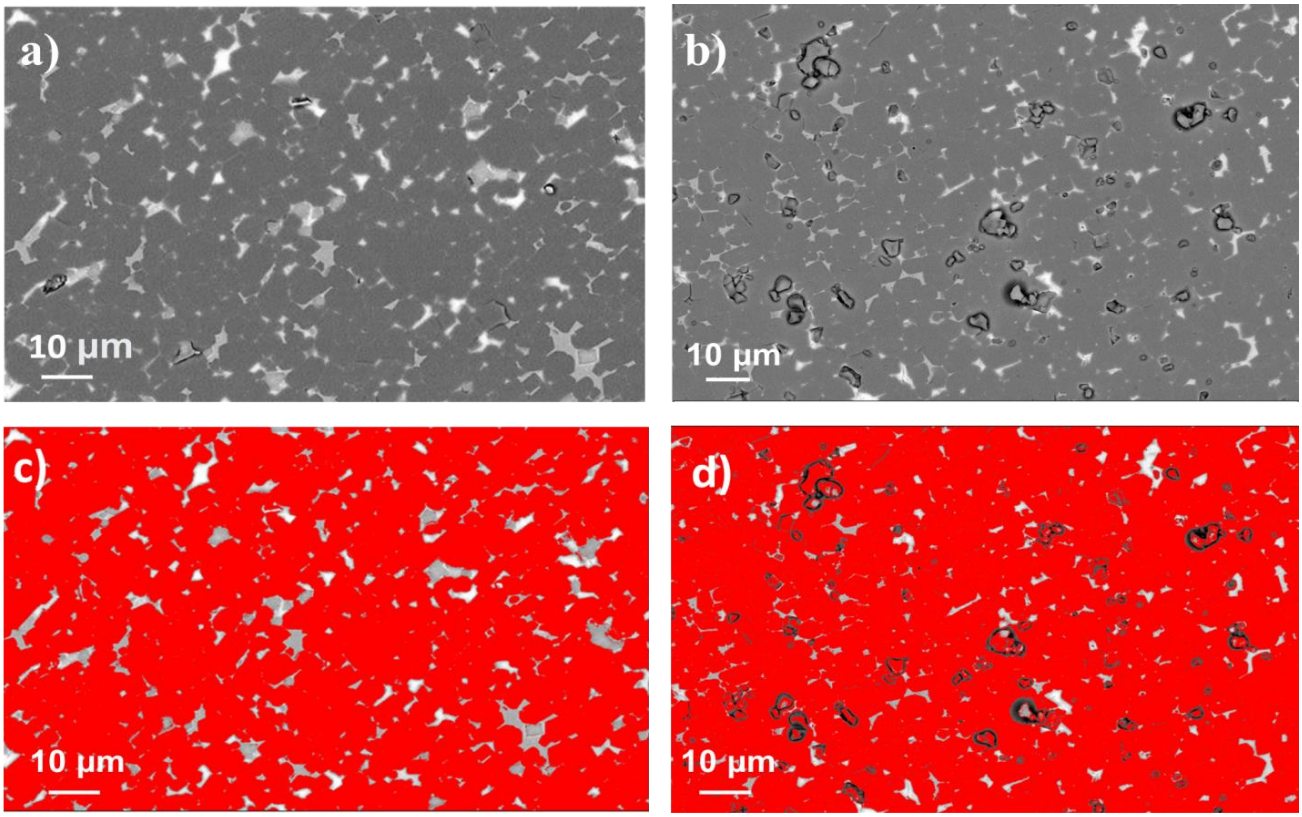

Fig. 5.2 SEM-BSE microstructure of Nd-Fe-B samples of different conditions a) As-received and b) Annealed and Phase mapping in c) As-received and b) Annealed conditions

Table 1. Phase fractions of the as-sintered magnet and annealed magnet

Phases Present	$Nd_2Fe_{14}B$ (Dark grey contrast) (%)	Light (Grey contrast) (%)	White contrast (in %)	Nd-O rich (Grey+ White) (%)	Grain Size (µm)
As sintered magnet	87.6	10.4	2.0	12.4	4.6 ± 0.2
Annealed magnet	89.1	9.2	1.7	10.9	5.0 ± 0.2

Comparing the average grain size measurement, the as-received $Nd_2Fe_{14}B$ grain possessing 4.6 ± 0.2 µm and after the post sintered annealing condition it shows a slight increase to 5 ± 0.2 µm. The growth of $Nd_2Fe_{14}B$ grains is influenced by various factors, such as annealing temperature and annealing time. After annealing, the boundaries between grains become thinner and become non-continuous and as a consequence of thermodynamic activation energy leads to growth. It further leads to have the variation in the phases present i.e. higher fraction of grain with the substantial reduction in the Nd-rich and secondary phases. It is fairly understood that, as the grain size becomes larger, the volume of grain

boundaries decreases which hinders the domain wall motion. Hence the domains in the magnet become more mobile and can diffuse across grain boundaries.

5.3 MAGNETIC PROPERTIES

Using the PPMS (Physical Property Measurement System), the M-H curve of the as-received and the annealed magnets are measured thus determining their magnetic properties like coercivity, remanence, and magnetic saturation. In the magnetization measurement (Fig. 5.3 and 5.4), the as-received sample shows the coercivity of 1.55 T. However, the decrease in coercivity of 1.38 T was observed in annealed sample which is 12% lower than the as-received sample. This is explain with respect to the increase in grain size which in turn decreases the number of grain boundaries and domain walls within the magnet, which in turn reduces the number of pinning sites for the magnetic domains. The pinning sites are defects or impurities that prevent the magnetic domains from moving easily, and they contribute to the coercivity of the magnet. With fewer pinning sites, the magnetic domains are able to move more easily, and the magnet becomes easier to demagnetize, resulting in a decrease in coercivity [23].

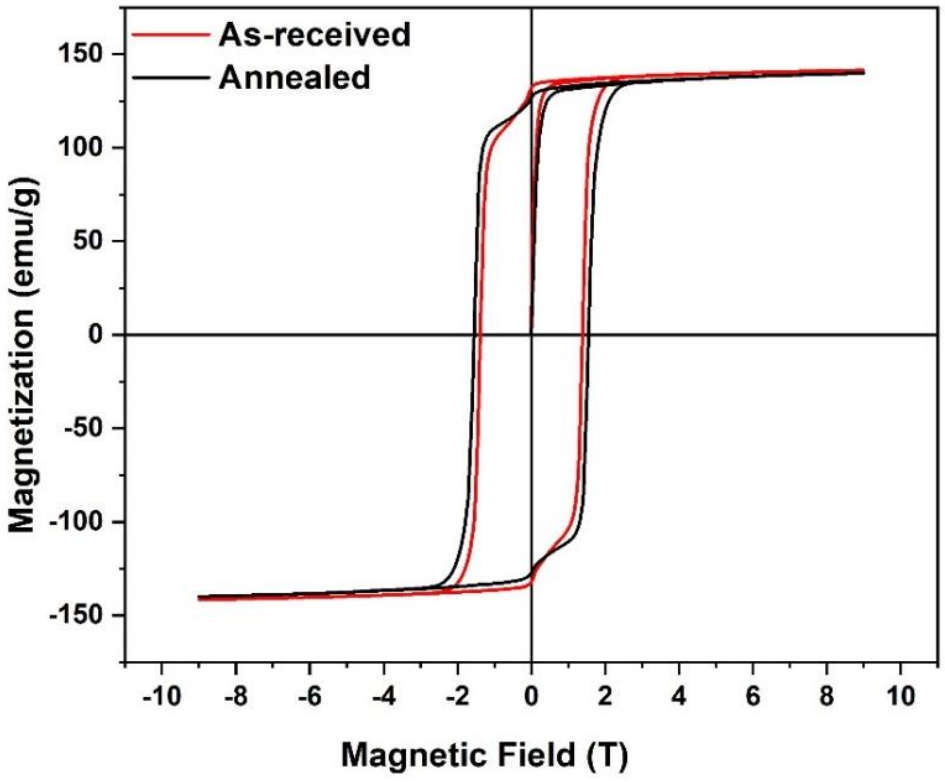

Fig. 5.3 M-H Curve of the as-received and annealed sintered magnet

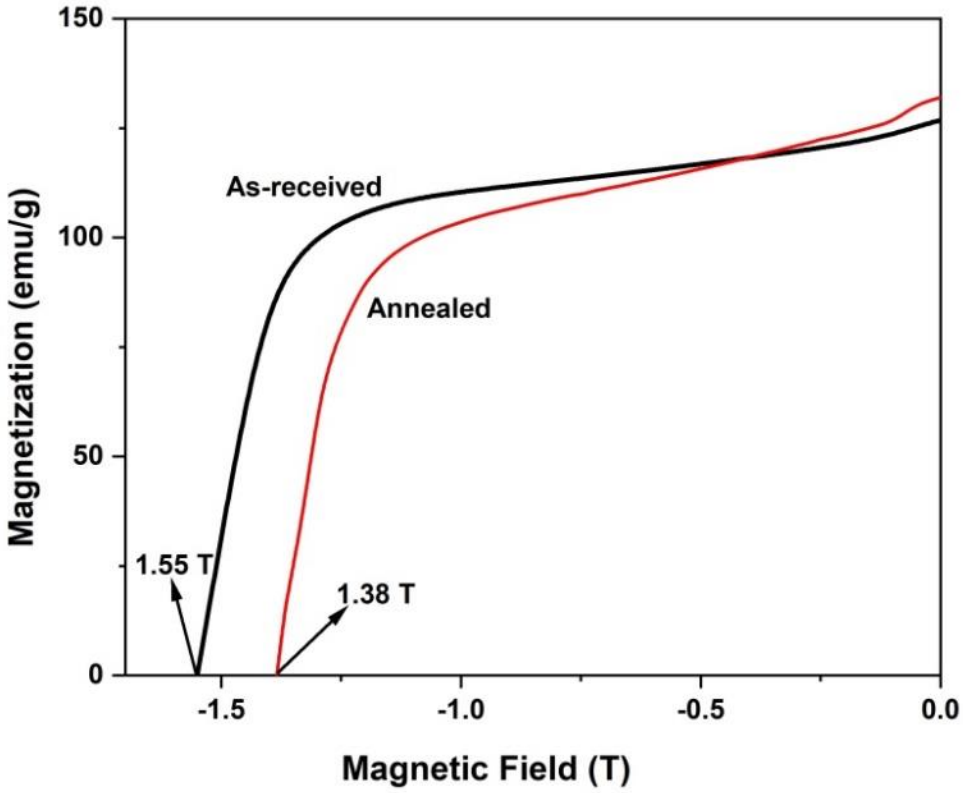

Fig. 5.4 Demagnetization curve of the as-received and annealed samples

Table 2. Magnetic properties of the as-sintered and annealed sample

Magnet	Coercive field (H_c) in T	Saturation magnetization (M_s) in emu/g	Remanent magnetization (M_r) in emu/g	M_r/M_s
As-received	1.55	140	127	0.91
Annealed	1.38	142	132	0.93

Although the coercivity of the magnet appears to decrease, other properties such as remanence and saturation magnetization demonstrates an increasing trend in the annealed magnet compared to the as-received magnet. The observed increase in the remanence and saturation magnetization of Nd-Fe-B magnets with an increase in grain size can be attributed to several underlying mechanisms. Firstly, the annealed magnet exhibits fewer grain boundaries which serve as sites for the pinning of magnetic domain walls, leading to a reduced hindrance to the motion of magnetic domains. Secondly, the annealed magnet tends to exhibit a lower fraction of Nd-rich and Nd-O phases, which have lower magnetic moments

compared to the $Nd_2Fe_{14}B$ phase. Consequently, larger grains have a higher fraction of the $Nd_2Fe_{14}B$ phase, resulting in an enhanced remanence and magnetic saturation [24].

CHAPTER 6

CONCLUSION AND FUTURE WORK

The current study elucidated the evolution in the microstructural and phase features in the as-received and annealed conditions of sintered Nd-Fe-B magnets. SEM characterization evident the microstructural evolution of both the samples and it influences the magnetic properties. The following significant observations are arrived.

(i) The as-received sample exhibits the primary Nd-Fe-B grains of 87.6% with grain boundaries of Nd-rich phase of 12.4%. After annealing the $Nd_2Fe_{14}B$ phase is increased to 89.1% and GB of 9.2%. In both the conditions, Nd-O phase is observed.

(ii) Annealing of Nd-Fe-B magnet influences the increase in the average grain size to 5.0 ± 0.2 from 4.6 ± 0.2 of as-received condition.

(iii) The coercivity of as-received sample shows 1.55 T which has been reduced to the 1.38 T (12% decrease). The reduction is owing to the increase in the average grain size and reduction in the Nd-rich GB phase.

The study further motivates to expand in the following perceptions

(i) The intense study using advanced characterization tools will explore the secondary phases present and absolute quantification of its composition.

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