A STUDY OF THE MAGNETIC PROPERTIES OF SLM-PROCESSED Nd-Fe-B MAGNETS

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UNDER THE GUIDANCE OF

DR. M KAVITHA

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

BACHELOR OF ENGINEERING

Branch: METALLURGICAL ENGINEERING

of Anna University, Chennai

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DEPARTMENT OF METALLURGICAL ENGINEERING

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

(Internal Examiner)	(External Examiner)

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ABSTRACT

Additive manufacturing has revolutionized the production of magnets by offering a more flexible and efficient way of producing net-shaped magnets with complex geometries. Selective Laser Melting (SLM) is a promising technique for producing Nd-Fe-B magnets with high accuracy and repeatability. However, the low coercivity of SLM-produced Nd-Fe-B magnets has been a significant challenge. Selective Laser Melting is a well-established additive manufacturing method that can be used to produce net-shaped Nd-Fe-B magnets. Low coercivity has been one of the drawbacks in the Additive Manufacture processed Nd-Fe-B magnets. In this work, annealing is performed on the additive manufactured Nd-Fe-B sample and the resultant magnetic properties is compared with the Additive manufactured sample and we have tried to demonstrate that the grain boundary diffusion process using low-melting Nd-Cu, La-Ce, Dy-Cu and DyAlCu, alloys to the selective laser melted Nd-Fe-B magnets can result in a substantial enhancement of coercivity. Specifically, annealing is used as a heat treatment process to carryout grain boundary diffusion to improve the magnetic properties of the Nd-Fe-B magnets. Multiple optimizations have been made to the annealing process to achieve the desired results.

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Chapter 1

1.Introduction:

1.1 Nd-Fe-B Magnets

The **Nd-Fe-B magnet** is the strongest permanent magnet in the world. It is a tetragonal crystal formed of **neodymium**, iron, and boron. This kind of magnet is the most commonly used rare earth magnet nowadays and is widely used in electronic products, such as hard drives, mobile phones, earphones, and battery-powered tools. They are from the Rare-Earth magnet family and have the highest magnetic properties of all permanent magnets, stronger than Samarium Cobalt (SmCo), Alnico and Ferrite. In addition to their high magnetic strength, they are relatively inexpensive, making them an ideal choice for a wide range of consumer, commercial, industrial and technical applications.

It is foreseen that the needs for the high-performance Nd-Fe-B based permanent magnets will increases further due to the rapid expansion of applications in green energy sectors such as motors and generators for electric vehicles drones, robots, and wind turbines maximum energy product of Nd-Fe-B is approaching its theoretical limit the important extrinsic properties for permanent magnet application is still far. Physically the coercivity of permanent magnets should scale with the compounds A; however, the typical coercivity values of coming are only around 0.2Ha which is known as Brown's paradox.

1.2 Additive Manufacturing

Additive manufacturing is the process of creating an object by building it one layer at a time. It is the opposite of subtractive manufacturing, in which an object is created by cutting away a solid block of material until the final product is complete. Technically, additive manufacturing can refer to any process where a product is created by building something up, such as molding, but it typically refers to 3-D printing. Additive manufacturing was first used to develop prototypes in the 1980s — these objects were not usually functional. This process was known as rapid prototyping because it allowed people to create a scale model of the final object quickly, without the typical setup process and costs involved in creating a prototype. As additive manufacturing improved, its uses expanded to rapid tooling, which was used to create molds for final products. By the early 2000s, additive manufacturing was being used to create functional products. More recently, companies like Boeing and General Electric have begun using additive manufacturing as integral parts of their business processes. Using computer aided design (CAD) or 3D object scanners, additive manufacturing allows for the creation of objects with precise geometric shapes. These are built layer by layer, as with a 3D printing process, which is in contrast to traditional manufacturing that often requires machining or other techniques to remove surplus material. To create an object using additive manufacturing, someone must first create a design. This is typically done using computer aided design, or CAD, software, or by taking a scan of the object someone wants to print. Software then translates the design into a layer-by-layer framework for the additive manufacturing machine to follow. This is sent to the 3-D printer, which begins creating the object immediately.

AM technologies can be broadly divided into three types. The first of which is **sintering** whereby the material is heated without being liquified to create complex high-resolution objects. Direct metal laser sintering uses metal powder whereas selective laser sintering uses a laser on thermoplastic powders so that the particles stick together. The second AM technology fully melts the materials, this includes direct laser metal sintering which uses a laser to melt layers of metal powder and electron beam **melting**, which uses electron beams to melt the powders. The third broad type of technology is **stereolithography**, which uses a process called photopolymerization, whereby an ultraviolet laser is fired into a vat of photopolymer resin to create torque-resistant ceramic parts able to endure extreme temperatures.

1.3 Additive Manufacturing of Magnetic Materials

Additive Manufacturing (AM) techniques involve printing successive layers of materials from 3D model data to fabricate components, usually possessing complex geometries. AM has recently transformed from a rapid prototyping technology to a manufacturing technology. However, most of this transformation has been only for structural materials and not for functional materials. AM for functional materials development, e.g., AM to produce soft and hard magnets for electric motors/ transformers or other complex components is still in its infancy. Multinational companies, e.g., General Electric (GE), Siemens, HP. Wipro, etc. are developing AM systems and producing complex parts using AM processes. Laser based additive manufacturing is one such promising method for processing components of complex geometry and compositionally graded alloys and components. There are several review papers on the AM of structural materials, however, to date, there is no comprehensive review of AM of magnetic materials. Metamorphic manufacturing, which relies on local optimization of microstructure requires tight control of process parameters to produce complex geometries. Such components with locally optimized properties can be realized using AM. One objective can be, for example, to process a material which is magnetically soft, mechanically strong, and exhibits high electrical resistivity to fulfil the growing demand for high frequency and high-power electric machines operating in extreme conditions. Materials with an optimized combination of mechanical, physical, and functional properties are required in many engineering applications The traditional method of developing new alloys is to prepare a few samples with different alloy compositions and perform extensive characterization and property assessment. This method is costly and time consuming, limiting the opportunity to discover excellent new materials. Hence, accelerated materials development is of high interest. High throughput or combinatorial methods can be used for accelerated discovery of novel materials and to improve the properties of existing materials. These methods require the rapid synthesis of materials over a wide composition range, followed by rapid assessment of the properties. These studies can rapidly reveal compositions with the optimum structure and properties as well as relevant processing parameters. Combinatorial approaches have been extensively used in thin film-based materials. However, less effort has been devoted to techniques for accelerated development of bulk materials.

1.4 Selective laser Melting

Selective laser melting (SLM) is a comparatively newer 3D-printing technology and developed in 1995 by German scientists. Similar to SLA where UV laser is used, a high-powered laser beam is used in SLM to form 3D parts. During the printing process, the laser beam melts and fuses various metallic powders together. As the laser beam hits a thin layer of the material, it selectively joins or welds the particles together. After one complete print cycle, the printer adds a new layer of powered material to the previous one. The object is then lowered by the precise amount of the thickness of a single layer. When the print process is complete, someone will manually remove the unused powder from the object. The main difference between SLM and SLS is that SLM completely melts the powder, whereas in SLS, only partly melted or sintered powdered is used. In general, SLM end products tend to be stronger as they have fewer or no voids. A common use for SLM printing is with 3D parts that have complex structures, geometries and thin walls. The aerospace industry uses SLM 3D printing in some of its pioneering projects. These are typically those which focus on precise, durable, lightweight parts. SLM is quite widespread now among the aerospace and medical orthopedics industries.

Those who invest in SLM 3D printers include researchers, universities, metal powder developers and others, who are keen to explore the full range and future potential of metal additive manufacturing. A SLM process is actually composed of two main steps: powder deposition and laser melting. Each one is critical to the success of the manufacture of the final object, and it strongly depends on both powder properties and laser parameters. SLM is a thermal process which is obviously driven by material and laser properties, but also by the powder properties.

Concerning the material properties, optical absorption at laser wavelength and thermal conductivity will be of utmost importance. Concerning laser parameters, laser power and wavelength will be very important but the waist of the focused beam, and the scanning speed and strategy will also have a strong influence on the result. Finally, grain size distribution and shape and layer thickness will also modify effective thermal conductivity and absorption of the powder material and therefore modify the laser-matter interaction. Thus, to get the best result using a SLM process, it is necessary to get the most homogeneous grain size and shape for the powder, to deposit a homogenous layer thickness of powder, then to optimize laser power and scanning speed and strategy. Powder layer deposition is a critical step since the thickness has to be quite homogeneous on the overall surface.

A change in thickness could induce a change in heat transfer than in material melting. Available SLM machines are commonly based on a powder bed system. The classical setup deals with connected vessels. The first one provides the powder while the second receives the powder to be melted. The substrate is usually deposited in this second vessel, on top of a vertical translation stage which permits the powder layer thickness to adjust and also to stack several melted layers. Finally, a scraping or rolling tool homogeneously spreads the powder before laser melting. Such a setup is very efficient but is quite complex to develop. Laser used in selective laser melting strongly depends on the material to process. As a thermal effect is wanted, CW lasers are the best candidates, but nanosecond pulsed lasers are also suitable. The material determines the laser wavelength as the highest optical absorption is needed to convert laser energy into heat energy. Standard lasers used in YAG (1064 nm). As the material has to be melted, high power lasers are required (several tens of watts).

1.5 Physical Property Measurement System

A Physical Property Measurement System (PPMS) is a versatile tool used in materials science and physics research to investigate various physical properties of materials under different environmental conditions. It is a powerful platform that combines several experimental techniques, allowing for the measurement of a wide range of physical properties such as electrical resistivity, magnetic susceptibility, specific heat, thermal conductivity, and many more.

PPMS typically consists of several components, including a cryogenic refrigerator, a superconducting magnet, a sample holder, and various sensors and probes. The cryogenic refrigerator is used to cool the sample to extremely low temperatures, typically below 4 Kelvin, which is necessary for the measurement of certain properties such as magnetic susceptibility and specific heat. The superconducting magnet provides a strong and stable magnetic field, which is essential for the measurement of magnetic properties such as magnetization and susceptibility.

The sample holder is a critical component of the PPMS, as it allows the sample to be easily mounted and positioned within the system for accurate and precise measurements. The sample holder can accommodate a variety of sample geometries, including thin films, powders, and bulk materials, and can be easily exchanged to facilitate different types of experiments.

The PPMS also includes various sensors and probes that are used to measure the physical properties of the sample. For example, a vibrating sample magnetometer (VSM) is used to measure magnetic properties such as magnetization and susceptibility, while a four-point probe is used to measure electrical resistivity. Other probes include calorimeters, thermometers, and heat capacity sensors, which are used to measure thermal properties such as specific heat and thermal conductivity.

One of the key advantages of the PPMS is its versatility. It allows researchers to perform a wide range of experiments on a single platform, reducing the need for multiple instruments and simplifying the experimental setup. Additionally, the PPMS allows researchers to investigate the properties of materials under different environmental conditions, such as high pressure, low temperature, or in a magnetic field, providing valuable insights into the behavior of materials under extreme conditions.

In summary, the Physical Property Measurement System is an essential tool for researchers in materials science and physics, providing a versatile platform for the measurement of a wide range of physical properties under various environmental conditions. Its versatility and accuracy make it an invaluable resource for researchers studying the properties of materials at the atomic and molecular level.

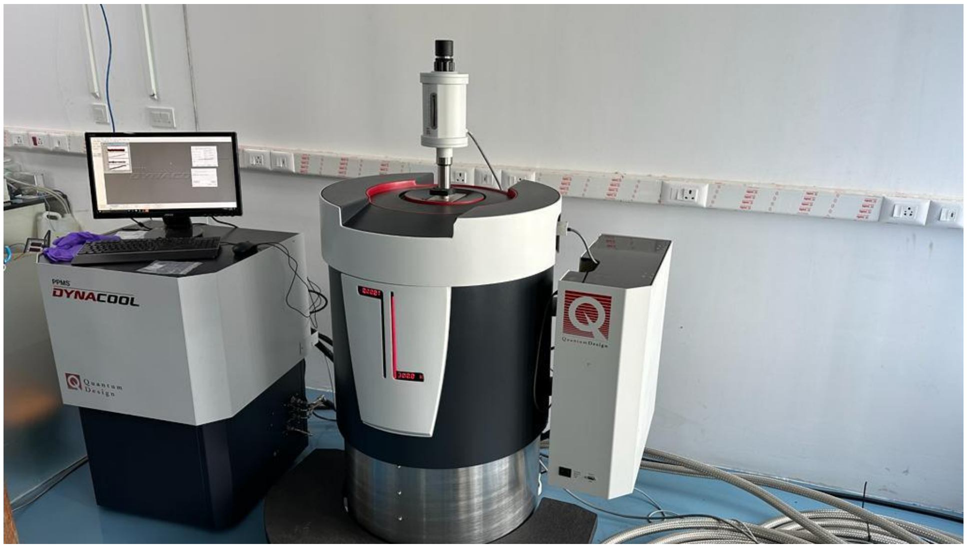


Fig. 1.5 PPMS

1.6 Scanning Electron Microscope

Scanning electron microscopy (SEM) is a powerful imaging technique that uses a focused beam of electrons to create high-resolution images of a sample's surface. The electrons in the beam interact with the atoms in the sample, producing signals that can be detected and used to form an image of the sample's topography and composition. The technique can be used to study a wide range of materials, including metals, semiconductors, polymers, ceramics, and biological specimens. In a typical SEM setup, the sample is placed in a vacuum chamber, and a beam of electrons is generated by an electron source, such as a tungsten filament or field-emission gun. The beam is then focused using electromagnetic lenses and directed onto the surface of the sample. As the electrons interact with the atoms in the sample, various signals are produced, including secondary electrons, backscattered electrons, and characteristic X-rays. These signals are detected and used to create an image of the sample. SEM can provide a wealth of information about a sample's structure and composition. By adjusting the imaging conditions, SEM can be used to generate images at different magnifications, from the micrometer to the nanometer scale. The technique can also be used to study the chemical composition of a sample, either through the detection of characteristic X-rays or by using specialized detectors that can distinguish between different types of electrons.

Chapter 2

LITERATURE SURVEY

2.1 Laser Powder Bed Fusion of Nd-Fe-B and influence of heat treatment on microstructure and crack development

In this work, the influence of different processing parameters and their interactions as well as a subsequent heat treatment on the resulting properties of Nd-Fe-B parts produced by LPBF were investigated. This first-time statistical analysis could show that all three varied parameters have a significant influence on the process outcome with a significant interaction effect of laser power and scanning speed. To sum up it can be stated that the energy input as a calculated measure containing all of the varied parameters can be used to adapt the porosity of additively manufactured Nd-Fe-B parts specifically. It is more effective than a subsequent heat treatment that could not decrease the number of pores or cracks. Cracks caused by internal stresses were the main cause of specimen failure during the building process and could be attributed most effectively by increasing the porosity through implementing higher hatch distances and therefore a lower volume energy density.

Microstructural analysis revealed different phases indicating a non-equilibrium solidification due to rapid cooling rates and a change in solidification mode presumably leading to the formation of soft magnetic phases and therefore weakened magnetic properties. Furthermore, the formation of oxide phases around the cracks after heat treatment could be detected. Regarding this, further investigation of heat treatment methods under argon atmosphere or hot isostatic pressing (HIP) are of future interest. Nevertheless, a further microstructural analysis is inevitable to clearly identify the observed phases and as Nd-Fe-B is used for high performance permanent magnets, the magnetic properties in dependence of the processing parameters and the resulting microstructure will be part of future research.

2.2 Coercivity enhancement of selective laser sintered Nd-Fe-B magnets by grain boundary infiltration

Laser powder bed fusion (LPBF) is a well-established additive manufacturing (AM) method to produce metal high performance metallic parts. Recently, several research groups worked on AM methods for hard or soft magnetic objects. However, low coercivity of Nd-Fe-B magnets processed with LPBF has been one of the draw backs of these magnets. The commercial isotropic Nd-Fe-B powder MQP-S from Magnet quench meets the powder requirements for the LPBF process. For an efficient diffusion of the low melting point alloy, the powder is only sintered and not fully melted during the LPBF process. The printing parameters are optimized in order to produce mechanically stable parts with a similar volumetric mass density as the powder tab density. The coercivity of the sintered parts is with 0.65 T slightly lower than the coercivity of the powder (0.88 T). This low coercivity is a result of the absence of the Nd-rich grain boundary phase which separates nano-sized $Nd_2Fe_{14}B$ grains as well as of the existence of soft α-Fe phase in the microstructure. For the coercivity enhancement of the printed parts, low melting point melt-spun ribbons with compositions of $Nd_{70}Cu_{30}$ $Nd_{80}Cu_{20}$, $Nd_{60}Al_{10}Ni_{10}Cu_{20}$, and $Nd_{50}Tb_{20}Cu_{20}$ are investigated. Diffusion of Nd-Cu alloys and Nd-Al-Ni-Cu alloys increases the coercivity from 0.65 T to 1.0 T. However, use of Nd-Tb-Cu as the diffusion source results in achieving a larger coercivity of 1.5 T in the samples. After diffusion process, the samples showed a full density of above 7.5 g/cm3. Enrichment of Tb at the surface of $Nd_2Fe_{14}B$ grains increases magneto crystalline anisotropy field at the interfaces hindering nucleation of reversed domains at the interfaces resulting an increase in the coercivity

2.3 Laser powder bed fusion of Nd-Fe-B permanent magnets

In this work, we used laser powder bed fusion (LPBF) to produce Nd-Fe-B permanent magnets from commercially available Nd-lean powder with spherical morphology (MQP-S from Magnequench). A suitable process window was identified by careful optimization of LPBF parameter.

The resulted magnetic properties, remanence J, of 0.63 T. coercivity H. of 885 kA/m and maximum energy product (BH_{max}) of 63 kJ/m^3, overcome published reference values significantly and represent the actual benchmark for additive manufacturing of permanent magnets. Furthermore, the magnetic performance of LPBF-fabricated samples is comparable to or exceeds conventional polymer bonded permanent magnets. It was found that the general processability is mainly determined by the area energy input during LPBF and a stable process is possible for an area energy between 0.6 and 2.3 J/mm^2. For lower values, low consolidation through sintering is observed, while higher energy leads to delamination. Magnetic properties and density show a similar behavior of enhancement as laser power is increased or scan velocity or hatch spacing is decreased. However, the trend is limited by the maximum allowed energy input for LPBF for this material. A first phenomenological model considers the impact of LPBF parameter on coercivity. Since an unexpectedly high coercivity for Nd-lean precursor can be obtained by LPBF, this technology offers new opportunities for resource-efficient production of permanent magnets. Furthermore, LPBF seems to be able to create different magnetic properties in one sample directly during magnet shaping by a proper choice of process parameters, without further post treatment. This is not possible with any other available processing technology for permanent magnets. Investigations to clarify the interplay between processing, microstructure and resulting magnetic properties are in progress.

2.4 Additive manufacturing of soft and hard magnetic materials used in Electrical appliances

This paper presented the magnetic performance of soft and hard magnetic components built by both FF and cold spray. It was shown that magnetic performance can be improved by careful selection of the powder feedstock and binder. More specifically it was shown that a smaller binder size is the most determining factor in the optimization of the hard-magnetic volume fraction in the cold spray process. An Al-Nd-Fe-B composite containing more than 70% of magnetic phase was obtained leading to remanence value of 0.5 T. Soft magnetic composite materials were successfully deposited using cold spray. High density was obtained leading to high overall DC performance (permeability and B12000) which are similar to what can be obtained with compacted SMC. However, even with the usage of high resistivity FeSi powder, the losses were significantly higher than compacted SMC, limiting, at this point of development, their usage for low frequency applications.

For FFF, it was determined that the increasing stiffness of the filament, when magnetic powder is added, limits the magnetic material volume fraction. In this study, filament containing 45% of both soft and hard magnetic powders were successfully produced. However, due to the lack of fusion between the successive layers, a volume fraction of only 30% was reached in the 3D printed magnetic parts. Further development would be required to use this type of material as the main core or magnet in electrical machines.

Finally, a new electric motor design that exploits the advantages of the cold spray processes was developed and shows the possibility of achieving enhanced performance compared to that of standard electric motors that are using higher performance magnetic materials. The presence of the aluminum binder led to magnet losses. However, optimization of the original design led to overall losses similar to that of a standard motor.

2.5 Additive Manufacturing of Magnetic materials

The fabrication of a variety of magnetic materials using various AM techniques has been reviewed in this paper. The ongoing activities in research groups around the world indicate that AM using a feedstock consisting of either blended elemental powders, or pre-alloyed powders, or metallic powders blended in a suitable polymer, is a viable manufacturing process to develop magnetic parts.

AM can produce near net-shape magnets with improved magnetic properties and reduced processing costs. Many soft magnetic materials such as Fe-Ni, Fe-Co, Fe-Si, ferrites, magnetic composites, and high entropy alloys have been successfully fabricated using AM, especially using SLM and LENS type processes. The effect of process parameters such as laser speed, laser power, and heat treatment on the microstructure, mechanical properties, and magnetic properties has been discussed. AM processed bonded Nd-Fe-B permanent magnets exhibit better or equivalent magnetic properties compared to conventionally processed magnets. Two AM methods; i.e., binder jetting and big area additive manufacturing have been successfully used to print such bonded magnets. AM machines equipped with controlled magnetizing tools may be useful to print anisotropic hard magnets. Thus, there is a bright future for additive manufacturing of magnetic materials and components. Additionally, AM will very likely enable the implementation of novel and radical design concepts for magnetic components, such as functionally graded components with tailored site-specific magnetic properties. The future of AM technology will include integrated systems coupling (i) thermal sensors which can provide in-situ diagnostics during printing, (i) temperature controlled building platform which can control the thermal gradient during printing, (iii) robotic arms for removing the support materials and surface finishing, (iv) high temperature furnace which can be used for post printing heat treatments an automated manner, and most importantly and (v) an improved interface between hardware and software to control every step of the 3D printing process. Such an integrated system can substantially accelerate AM usage for magnetic material processing.

2.6 Defects in using AM technique

There are several defects associated with components produced by AM techniques

•Porosity can arise from several factors such as the quality of powder particles, processing parameters, and the nature of the solidification process

•The quality of the powders largely depends on the techniques used to make them. The most common techniques are gas atomization, rotary atomization, plasma atomization, and plasma rotating electrode process (PREP)

•The pores induced by the AM process are usually formed when the supplied energy is insufficient for the complete melting of the powder particles.

• Un-melted powder is one of the reasons for decrease in mechanical strength

•Cracking may arise during solidification or subsequent heating; the presence of pores can also lead to cracking.

2.7 Effect of process parameters on various defects and magnetic properties

- **Defects can occur when process parameters are not optimized:**
- The density of the laser-based AM processed components can be tuned by scan rate, laser power, hatch spacing, layer thickness and type of gas used in the chamber
- A component prepared using a low energy density can have high porosity which can results in low permeability, a lower magnetization per unit volume and a higher demagnetizing field
- A component prepared using a high energy density can have high density possibly together with cracking which can result in low mechanical strength.
- The thermal gradient varies with time and position inside the melt pool, which can influence solidification rate, scale of microstructure, grain growth. The larger the grains the smaller the coercive force
- Cooling rate has a direct influence on the liquid-solid and solid-solid phase transitions, grain structure and hardness. The cooling rate is controlled by travel speed, the input power, thermal conductivity of the material and the substrate etc.

- Microstructural related features such as grain size, texture, porosity, cracks etc. influence the coercivity and permeability

2.8 Hysteresis loop and magnetic properties

A hysteresis loop is a graphical representation of the magnetic behavior of a ferromagnetic material, such as iron, nickel, or cobalt. It is obtained by measuring the magnetic field (H) as a function of magnetization (B). There are various terms associated with a hysteresis loop, they are given below

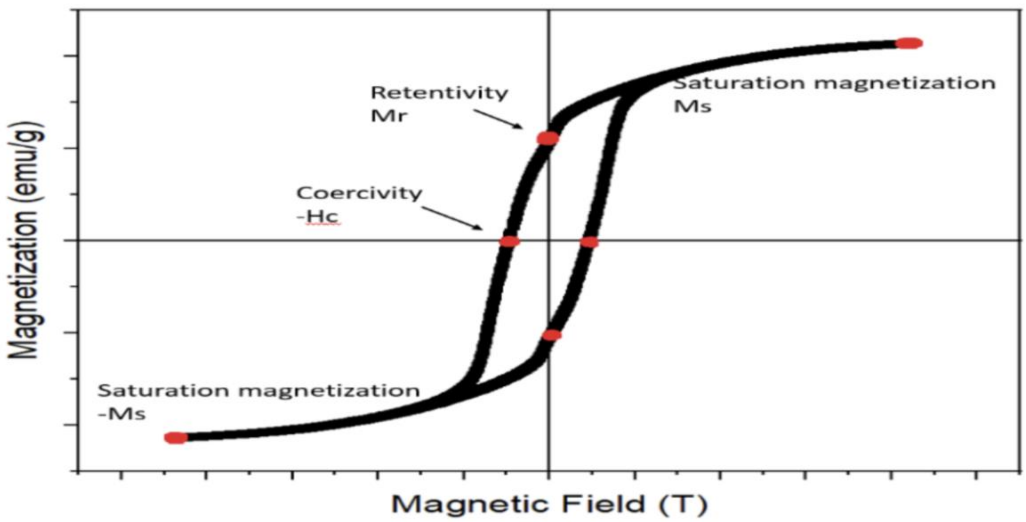


Fig 1.1 Hysteresis loop

- Saturation magnetization (Ms): It refers to the maximum magnetic moment per unit volume that a material can achieve when exposed to an external magnetic field.
- Coercivity (Hc): It is the resistance to the demagnetizing field, or the magnetic field required to drop magnetization from maximum to zero value.
- Remanence (Br): it is the magnetization remains in a ferromagnetic material after removing the magnetic field.
- Energy product (BH)max: The maximum magnetic energy density that can be stored in a ferromagnetic material. It is the area enclosed by the hysteresis loop and represents the maximum amount of energy that can be extracted from

the material. magnetization (Ms): It refers to the maximum magnetic moment per unit volume that a Saturation magnetization (Ms): It refers to the maximum magnetic moment per unit volume that a material can achieve when exposed to an external magnetic field.

2.9 Grain boundary diffusion process (GBD)

The magnetic properties of selective laser-melted Nd-Fe-B magnets are influenced by microstructural-related features such as grain size, cracks, and porosity. To improve the magnetic properties, especially the coercivity of such magnets, the grain boundary diffusion process (GBD) is a promising route. This process involves annealing treatment using low melting point alloys containing rare earth as diffusion sources. The advantage of using low melting point alloys is their ability to melt at relatively low temperatures and diffuse into the deeper interior of the magnets, forming $(Nd\ RE)_2Fe_{14}B$ structured shells that strengthen the surface of $Nd_2Fe_{14}B$ grains. Furthermore, the use of low melting point alloys can also enhance the thermal stability and corrosion resistance of the magnets, which is important for certain applications. Microstructural-related features such as grain size, cracks, and porosity have an influence on the coercivity and other magnetic properties of selective laser-melted Nd-Fe-B magnets. The grain boundary diffusion process is the best route to enhance the magnetic properties, especially the coercivity of such magnets. Low melting point alloys containing rare earth are used as diffusion sources in this process. GBD is usually carried out via annealing treatment and low melting point alloys are employed as diffusion sources because of their ability to be melted at relatively low temperatures. GBD leads to the diffusion of these alloys into the interior of the Nd-Fe-B magnet from the surface which will strengthen the surface of $Nd_2Fe_{14}B$ grains by forming $(Nd,RE)_2Fe_{14}B$ structured shells. Low-melting-point diffusion source alloy is always advantageous to diffuse into the deeper interior of the magnets possibly. In addition, the use of low melting point alloys can improve the thermal stability and corrosion resistance of the magnets which can be important factors for certain applications. Microstructural-related features such as grain size, cracks, and porosity have an influence on the coercivity and other magnetic properties of selective laser-melted Nd-Fe-B magnets. The grain boundary diffusion process is the best route to enhance the magnetic properties, especially the coercivity of such magnets. Low melting point alloys containing rare earth are used as diffusion sources in this process. GBD is usually carried out via annealing treatment and low melting point alloys are employed as diffusion sources because of their ability to be melted at relatively low temperatures. GBD leads to the diffusion of these alloys into the interior of the Nd-Fe-B magnet from the surface which will strengthen the surface of $Nd_2Fe_{14}B$ grains by forming $(Nd,RE)_2Fe_{14}B$ structured shells. Low-melting-point diffusion source alloy is always advantageous to diffuse into the deeper interior of the magnets possibly.

2.10 Why do we use low-melting alloys Nd-Cu and La-Ce powders to anneal Nd-Fe-B magnets and increase magnetic property?

To improve their magnetic properties, annealing treatment using low melting point alloys containing rare earth can be employed. Nd-Cu and La-Ce powders are used for annealing Nd-Fe-B magnets because they can easily diffuse into the interior of the magnet during the grain boundary diffusion process, which occurs during annealing, leading to the enhancement of the magnetic properties. The melting of Nd-Cu is 520°C and LaCe is 500-550°C. To densify the Nd-Fe-B magnets we do annealing at high temperature in which grain growth occurs. So, to avoid that we are using low-melting eutectics like Nd-Cu and LaCe which will melt at low temperature of 500-600°C and densify the magnets and enhance the magnetic property fills up the pores and increasing the density and magnetic property of the Nd-Fe-B magnet.

Other alloys containing rare earth, such as Dy-Cu alloys, have also been used for annealing Nd-Fe-B magnets. However, the use of strip-form eutectics like Dy-Cu alloys has been found to be difficult to diffuse into the samples. On the other hand, using eutectics in powder form, as in the case of Nd-Cu and La-Ce powders, allows for smooth diffusion of the eutectic into the magnet interior, leading to considerable improvements in the magnet's magnetic properties.

Chapter 3

OBJECTIVES AND SCOPE OF THE PROJECT

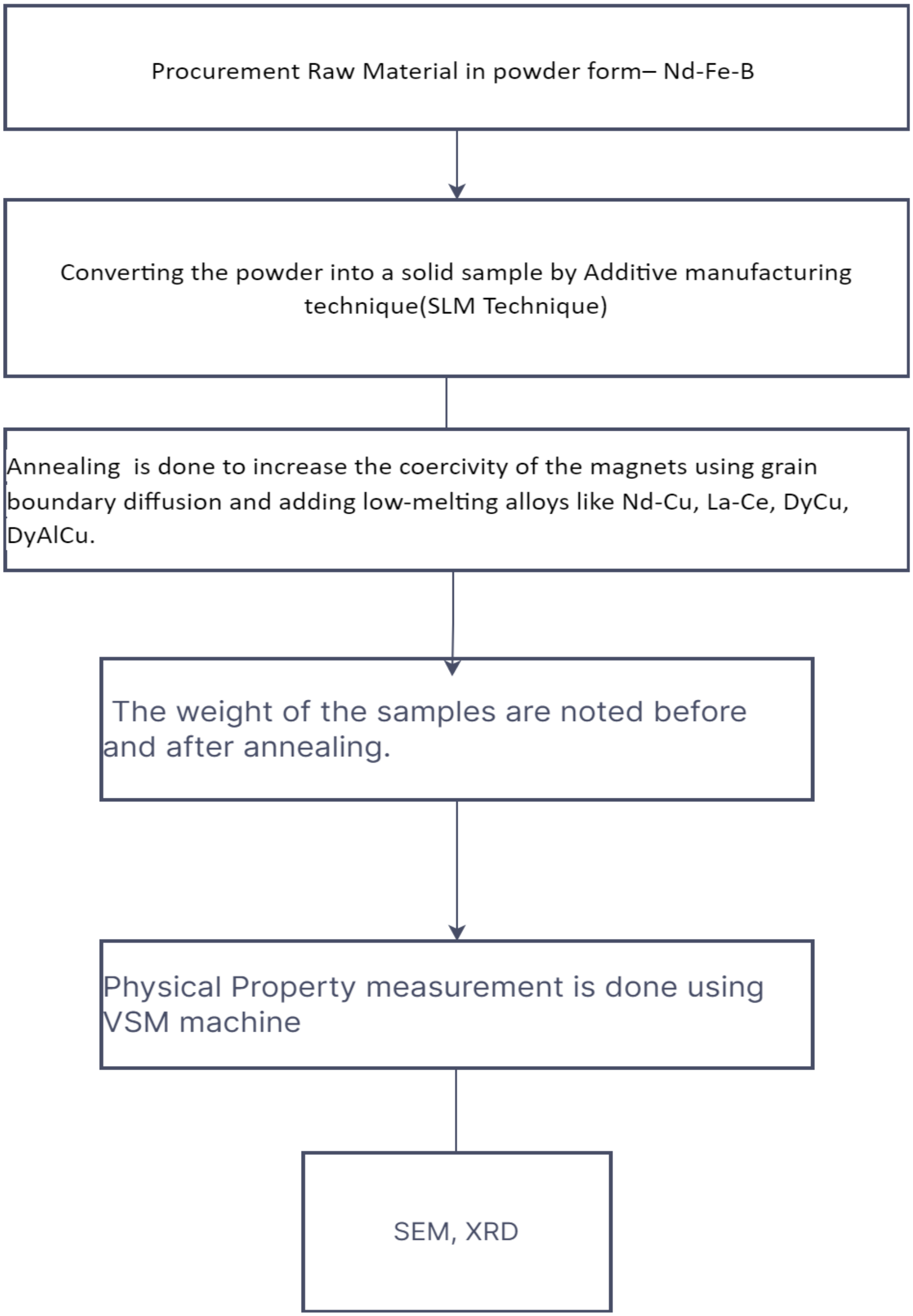
3.1 Objectives

- To manufacture a Nd-Fe-B Magnet using Selective laser Melting technique and enhance the magnetic property.
- To study the micro-structural and magnetic properties changes of these Nd-Fe-B magnets under Heat-Treated condition.
- To carry out the process low melting point alloys containing rare earth elements will be used and these alloys will be made to diffuse through the grain boundaries of AM-processed Nd-Fe-B magnets using an annealing treatment
- This will allow this project to explore the effects of annealing treatment using different low melting point alloys on the magnetic properties and microstructure of Nd-Fe-B magnets.

.3.2 Scope

- To develop near-nut shape magnetic materials by Selective laser melting technique.
- To enhance the coercivity of the AM processed Nd-Fe-B magnets by annealing using low melting point alloys to carry out microstructural analysis.

3.3 Methodology



Chapter 4

MATERIALS AND METHODS

For the experimentation, Nd-Fe-B magnets produced through SLM were used. The SLM process was performed using the SLM 280HL model machine from SLM Solutions GmbH, which features a 400W fiber laser with spot sizes ranging from 80-115 µm. The processing speed can reach up to 10m/s with the help of Vario-scan. The build area of the machine is 280×280 and the z-axis can go up to 365mm. The layer thickness ranges from 20-100µm, and the platform is heated up to 200°C.

4.1 Annealing using low melting point alloys

Selective Laser Melting (SLM) is a popular technique for producing Nd-Fe-B magnets due to its ability to fabricate complex geometries and high precision parts. However, the as-produced magnets may have limitations in their magnetic properties, such as lower coercivity and remanence. To enhance these properties, an annealing process is carried out on the SLM-produced Nd-Fe-B magnets. The annealing process involves grain boundary diffusion, which is facilitated by using various low melting point alloys. This process allows for the formation of a thin film on the grain boundaries, resulting in improved magnetic properties. Vibration Sample Magnetometer (VSM) analysis is used to determine the magnetic properties of the samples before and after the annealing process. By conducting VSM analysis before and after annealing, the changes in magnetic properties such as coercivity, remanence, and energy product can be studied. The results of these analyses can provide valuable insights into the effectiveness of the annealing process in enhancing the magnetic properties of SLM-produced Nd-Fe-B magnets.

4.1.1 Annealing using LaCe powder and crushed ribbons with compositions of Nd-Cu

A boat-shaped crucible is used to contain two SLM-processed Nd-Fe-B magnets, weighing 0.0438g and 0.2064g, respectively. Fine particles of LaCe (in powder form) and Nd-Cu (in low melting point melt-spun ribbons) are prepared using a motor and pestle and deposited separately on the magnets in a mass ratio of 20 to 1. The crucible containing the samples is subjected to vacuum pumping and annealed at a temperature of 600°C for a duration of 2 hours. After the annealing process, a small portion is extracted from two of the samples and their magnetic properties are measured using Vibration Sample Magnetometer (VSM).

4.1.2 Annealing using DyCu strips

The experiment involves placing two samples of unknown material, weighing 0.6691g and 0.5936g, into crucibles shaped like boats. Four strips made of DyCu are selected as a diffusion source, which are carefully polished using an emery sheet and cleaned with acetone using sonication. Once the strips are prepared, they are placed on the top and bottom sides of the two magnets. The samples with the strips are then placed in a vacuum chamber and annealed at a high temperature of 600°C for 2 hours to promote the diffusion of DyCu into the samples. Following annealing, the magnetic properties of the magnets are evaluated using a VSM. The VSM measures the magnetic moment of the samples, allowing the magnetic characteristics of the samples to be analyzed, such as coercivity, magnetic anisotropy, and magnetic susceptibility. By comparing the magnetic properties before and after annealing, the effect of DyCu diffusion on the magnetic properties of the samples can be determine

4.1.3 Annealing using DyAlCu and DyCu strips

Two small samples, one weighing 0.1782g and the other 0.4621g, were placed separately in a crucible shaped like a boat. Additionally, four metal strips (two DyAlCu and two DyCu) were prepared using iso-met machine and polishing them with emery sheets and cleaning them with acetone through sonication. The strips were then attached to the upper and lower ends of two magnets using fevi-quick adhesive and secured with tantalum wires. Next, the samples were subjected to vacuum pumping and annealing, which involved heating them to 900°C for 2hrs hours, followed by a 2-hour annealing at 550°C (a two-step annealing process). Finally, the magnetic properties of the magnets were determined using VSM.

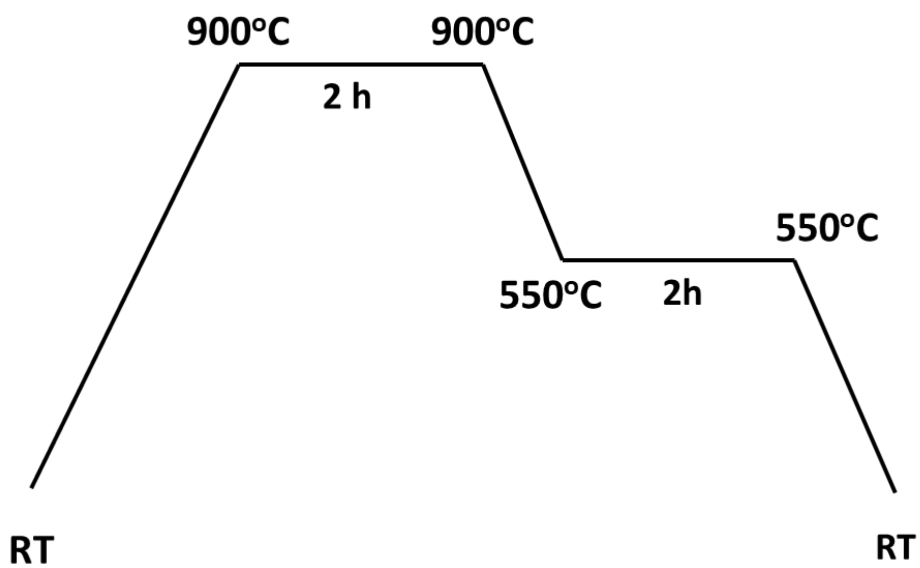


Fig. Two-step annealing Process

Fig. 4.4 Samples in crucible with DyCu, DyAlCu strips tied with Tantalum wires

4.1.4 Annealing using $(CeLa)_{70}Cu_{30}$ and Nd-Cu powders

In an experiment, two small samples weighing 0.4039g and 0.2451g were placed into a crucible shaped like a boat. To enhance the process of diffusion, low melting point alloys such as $(CeLa)_{70}$ Cu_{30} and Nd-Cu powders were used as sources. To ensure proper deposition of the alloys onto the samples, a layer of fevi-quick adhesive was applied to the samples before depositing the alloys separately on each one. The samples were then exposed to high vacuum pumping and subjected to annealing at a temperature of 600°C for a duration of 2 hours. Afterward, the magnetic properties of the samples were measured using a VSM.

4.2Microstructural investigations using FE-SEM

A microstructural analysis of the Nd-Fe-B magnets was conducted using an FSEM instrument, both before and after the process of annealing.

Chapter 5

Experimental data

5.1 Nd-Fe-B (B3) samples (LaCe) powder and crushed ribbons (Nd-Cu)

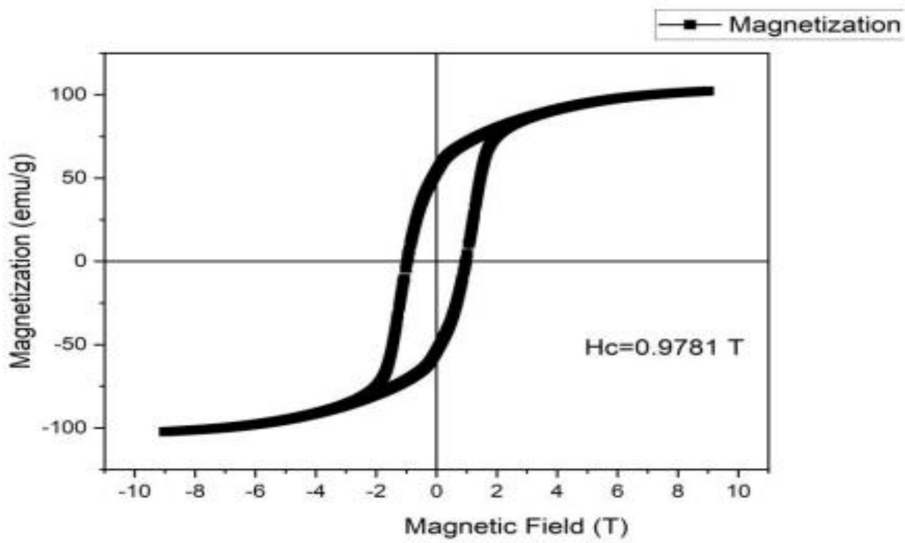


Fig 5.a Hysteresis loop of Nd-Fe-B (B3) sample before annealing

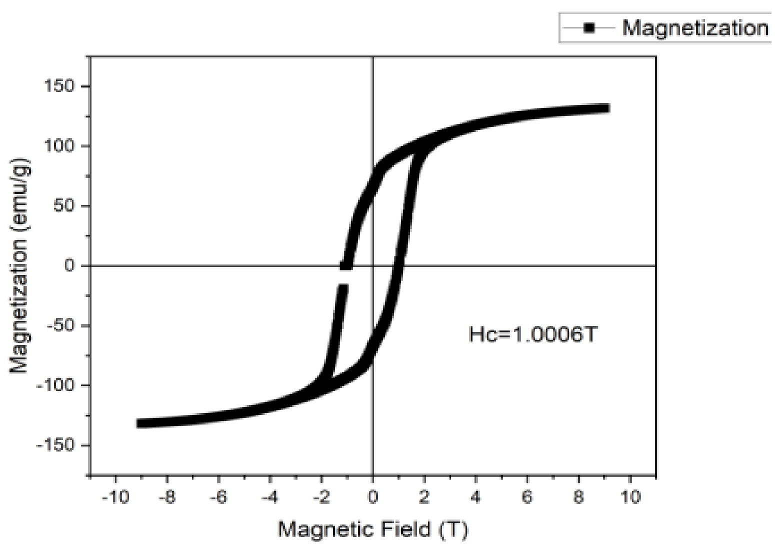


Fig 2.b Hysteresis loop of Nd-Fe-B (B3) sample after annealing with La-Ce powder

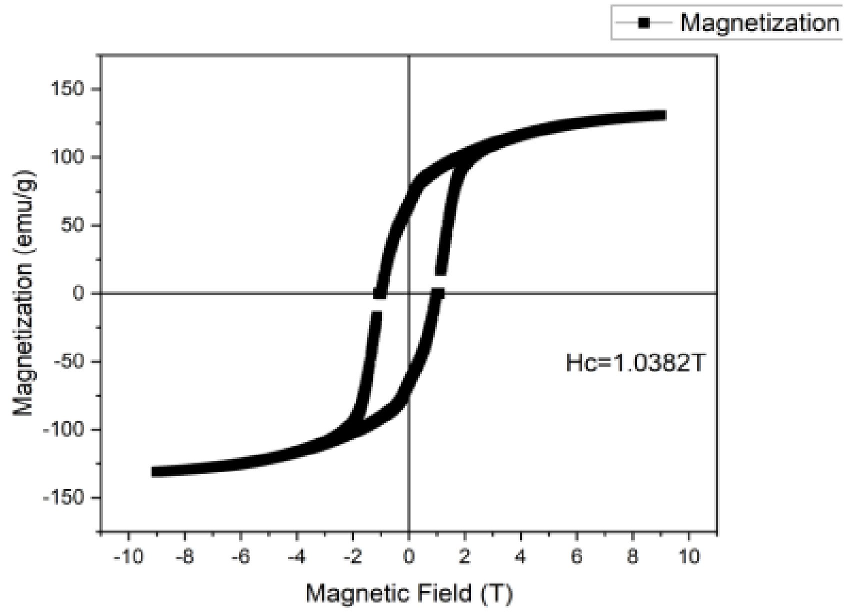


Fig.5.c Hysteresis loop of Nd-Fe-B (B3) sample after annealing with crushed ribbons having the compositions of Nd-Cu

TABLE 5.1 Magnetic properties of the Nd-Fe-B (B3) samples before and after annealing

Sample name	Magnetic property	Before annealing	After annealing(600°C-2hr)	
			LaCe powder	Crushed ribbons (NdCu)
B3	Coercivity(Hc)	0.9781 T	1.0006T	1.0382 T
	Saturation magnetization(Ms)	102.30 emu/g	131.72 emu/g	130.92 emu/g
	Remanence (Mr)	53.97 emu/g	66.15 emu/g	65.76 emu/g
	Remanence ratio (Mr/Ms)	0.5276	0.5022	0.5023

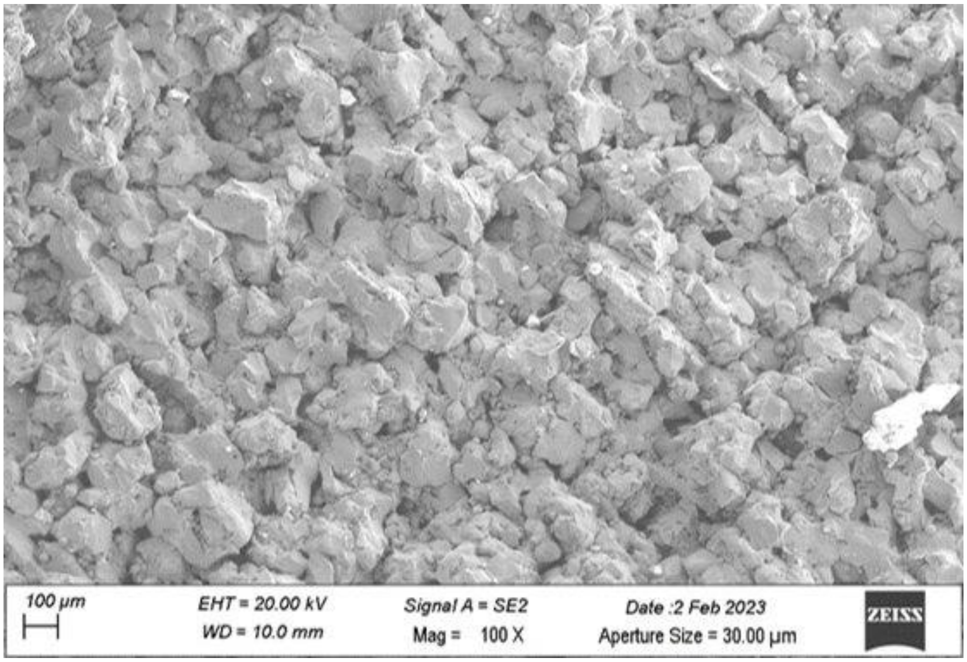


Fig 5.D FE-SEM image of Nd-Fe-B (B3) sample before annealing

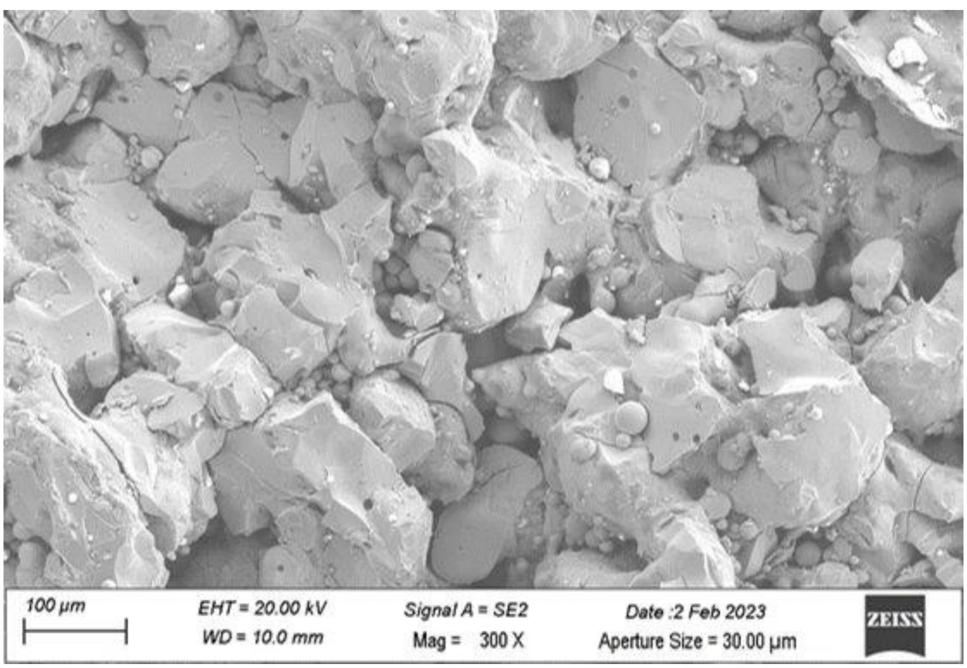


Fig 5.E FE-SEM image of Nd-Fe-B (B3) sample before annealing

5.2 Nd-Fe-B (A1) sample (DyCu strips)

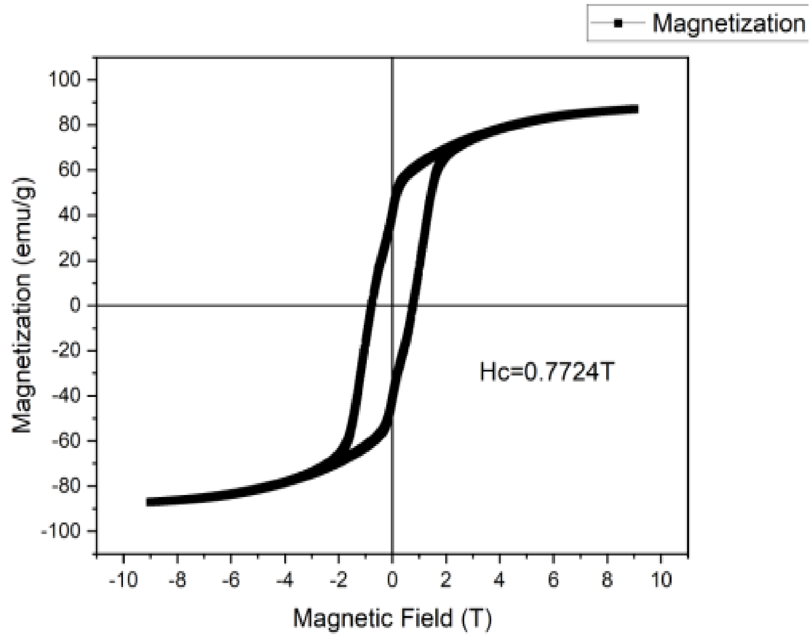


Fig 5.F Hysteresis loop of Nd-Fe-B (A1) sample before annealing

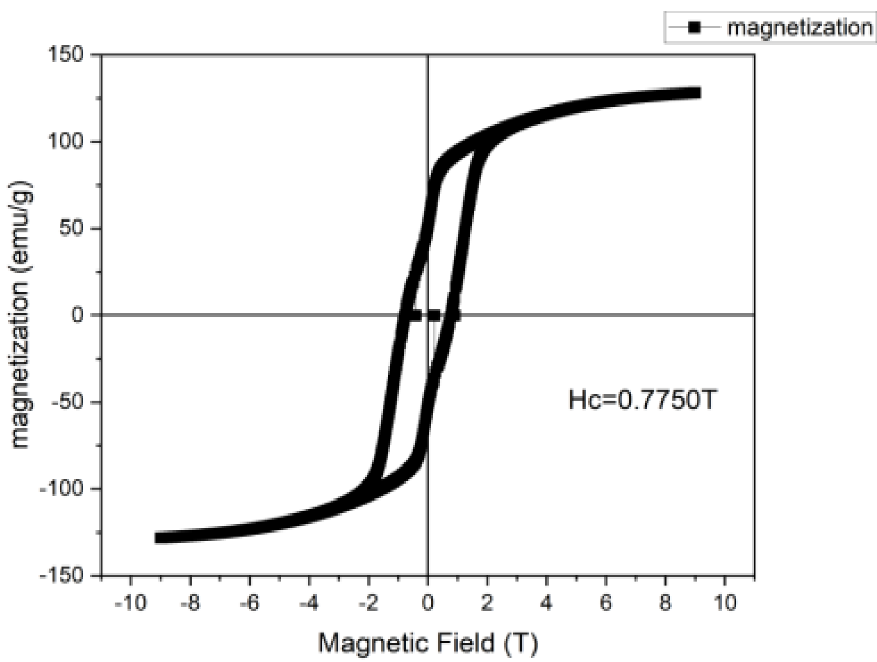


Fig 5.G Hysteresis loop of Nd-Fe-B (A1) sample after annealing with DyCu strips

Sample name	Magnetic property	Before annealing	After annealing (600°C-2hr) DyCu strips
A1	Coercivity (Hc)	0.7724 T	0.7750 T
	Saturation magnetization (Ms)	86.96 emu/g	128.18 emu/g
	Remanence (Mr)	41.02 emu/g	51.35 emu/g
	Remanence ratio (Mr/Ms)	0.4717	0.4006

TABLE 5.2 Magnetic properties of Nd-Fe-B (A1) sample before and after annealing

5.3 Nd-Fe-B(B3) sample (DyAlCu strips)

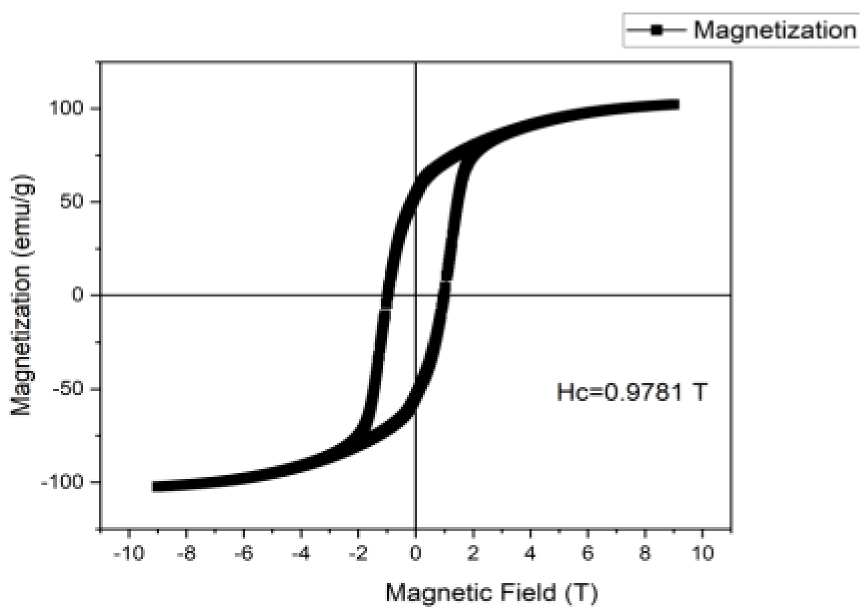


Fig 5.H Hysteresis loop of Nd-Fe-B (B3) sample before annealing

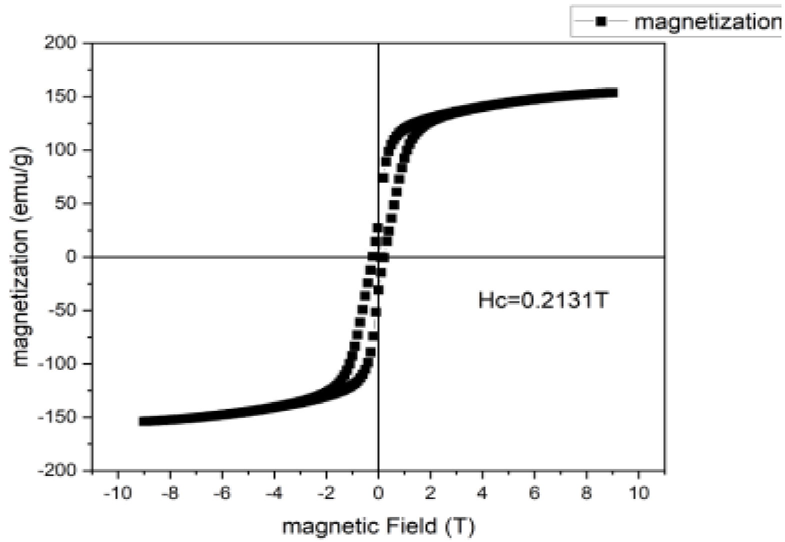


Fig 5.I Hysteresis loop of Nd-Fe-B(B3) sample after annealing with DyAlCu strips

TABLE 5.3 Magnetic properties of the Nd-Fe-B (B3) sample before and after annealing

Sample name	Magnetic property	Before annealing	After annealing(600°C-2hr) DyAlCu strips
B3	Coercivity(Hc)	0.9781 T	0.2131T
	Saturation magnetization (Ms)	102.30 emu/g	153.70 emu/g
	Remanence (Mr)	53.97 emu/g	26.03 emu/g
	Remanence ratio (Mr/Ms)	0.5276	0.1693

5.4 Nd-Fe-B (A1) samples (La-Ce and Nd-Cu powder)

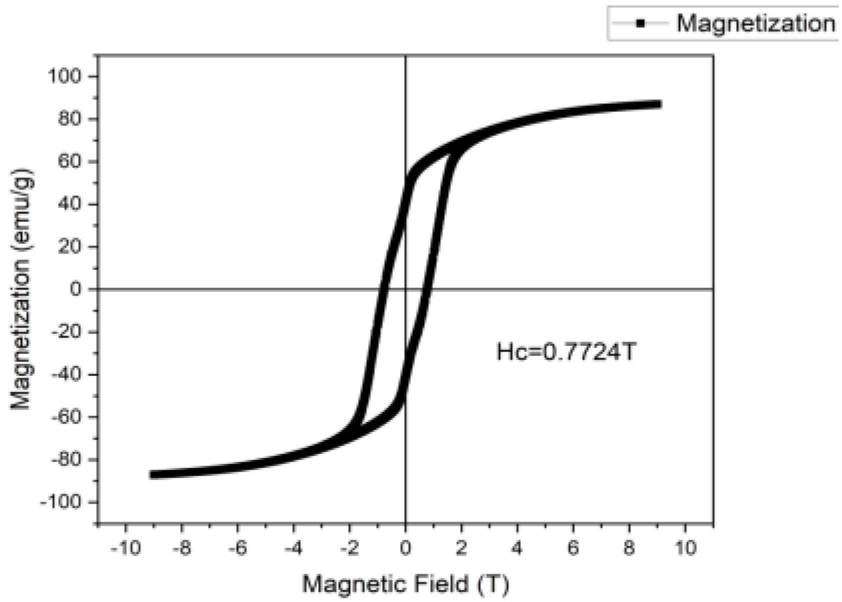


Fig 5.J Hysteresis loop of Nd-Fe-B (A1) sample before annealing

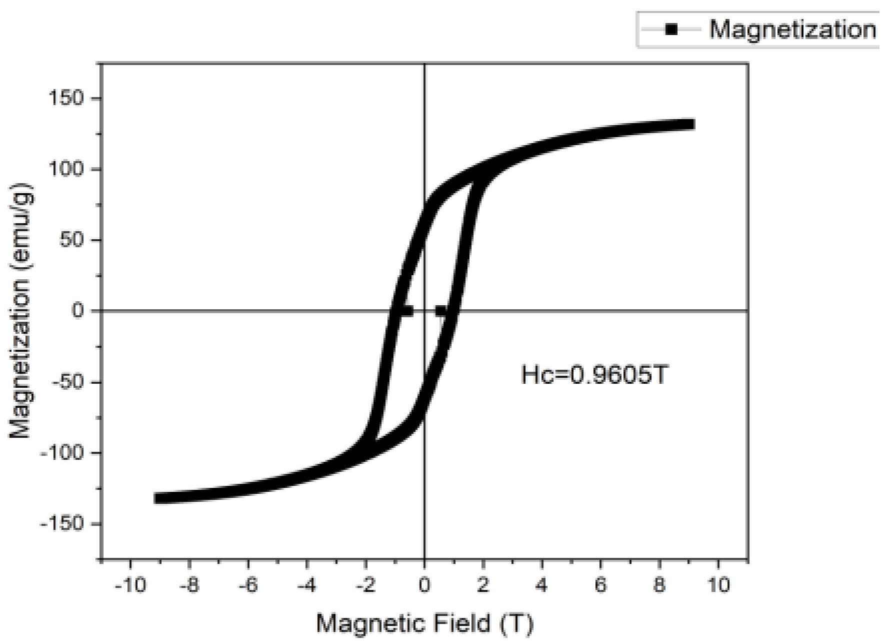


Fig 5.K Hysteresis loop of Nd-Fe-B (A1) sample after annealing with LaCe powder

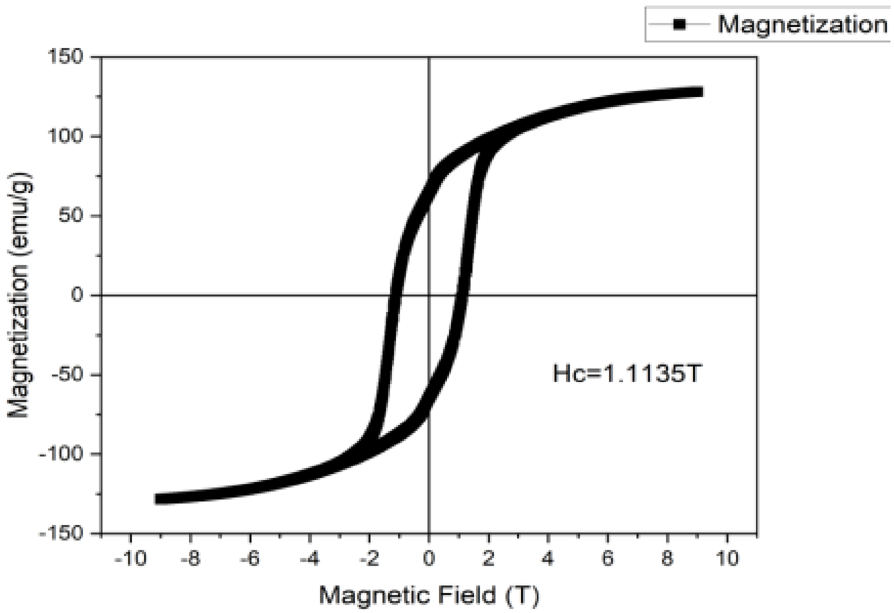


Fig 5.L Hysteresis loop of Nd-Fe-B (A1) sample after annealing with Nd-Cu powder

Sample name	Magnetic property	Before annealing	After annealing (600°C-2hr)	
			LaCe powder	NdCu powder
A1	Coercivity(Hc)	0.7724T	0.9605T	1.1135
	Saturation magnetization (Ms)	86.96 emu/g	131.91 emu/g	128.18 emu/g
	Remanence(Mr)	41.02 emu/g	61.20 emu/g	64.43 emu/g
	Remanence ratio (Mr/Ms)	0.4717	0.4639	0.5026

TABLE 5.4 Magnetic properties of Nd-Fe-B (A1) sample before and after annealing

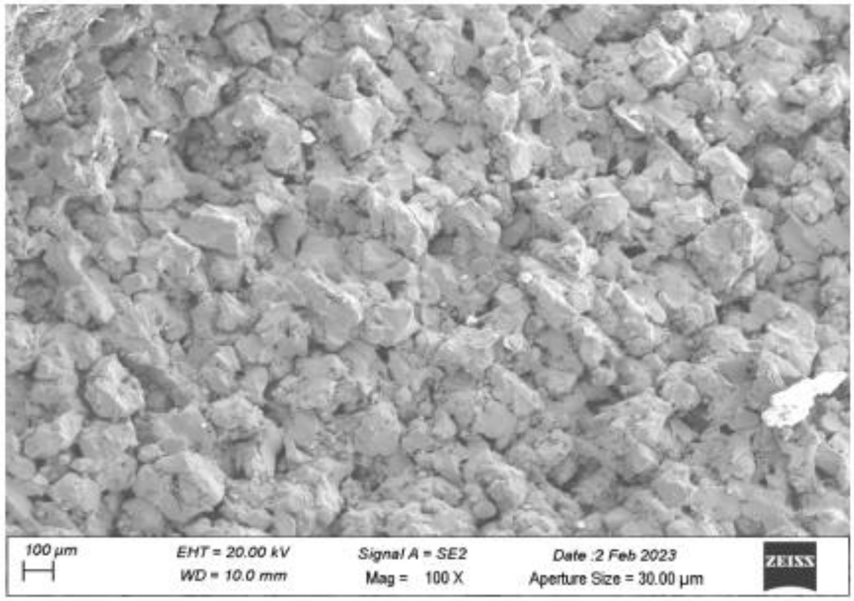


Fig 5.M FE-SEM image of Nd-Fe-B (A1) sample before annealing

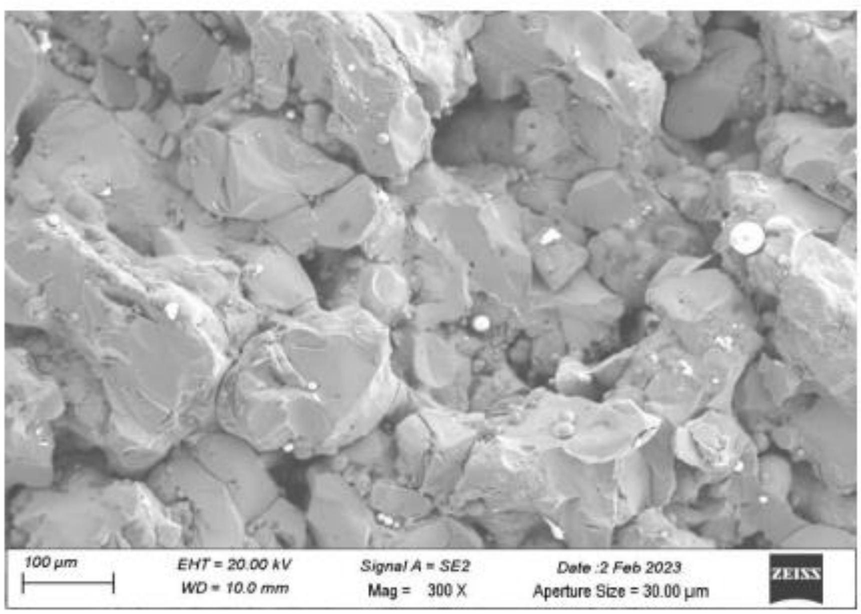


Fig 5.N FE-SEM image of Nd-Fe-B (A1) sample before annealing

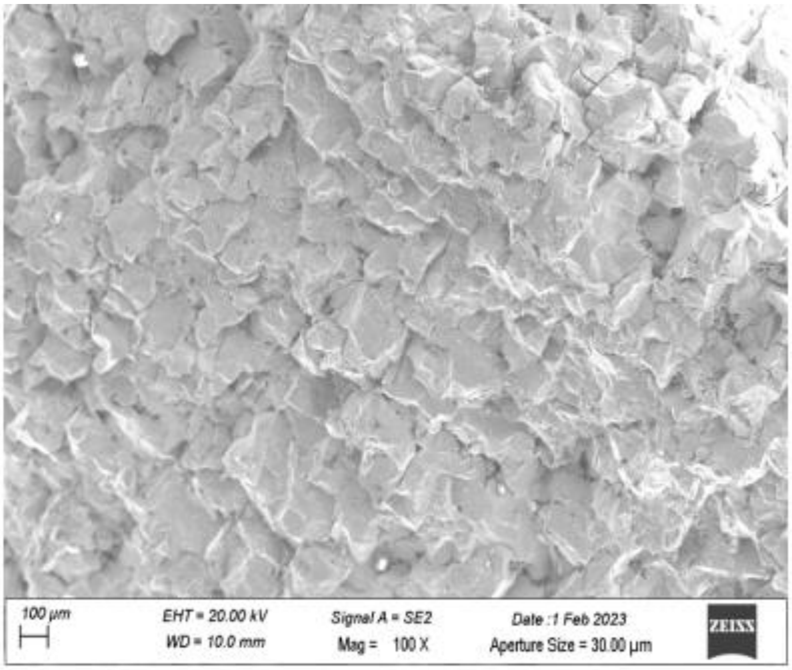


Fig 5.0 FE-SEM image of the Nd-Fe-B(A1) sample after annealing with Nd-Cu powder

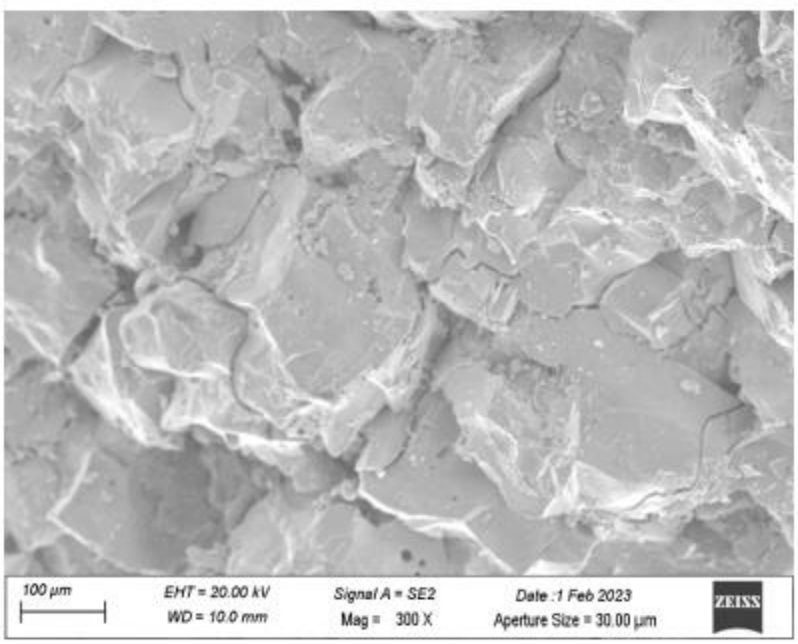


Fig 5.P FE-SEM image of the Nd-Fe-B (A1) sample after annealing with Nd-Cu powder

Chapter 6

Results and Discussion

This project aims to study and enhance the magnetic properties of additive manufactured Nd-Fe-B magnets, focusing on coercivity by the grain boundary diffusion process. The SEM images revealed the presence of defects such as cracks and pores that had a negative impact on the magnetic properties of the samples. In order to improve the magnetic properties, annealing was carried out using different eutectics.

Firstly, the hysteresis loops of the **Nd-Fe-B (B3) (Fig-5. a)** sample were compared before and after annealing with LaCe powder and crushed ribbons (Fid-5. b) (with the compositions of Nd-Cu). The coercivity, saturation magnetization, and remanence were found to have slightly improved after annealing, due to the diffusion of low melting point alloys (LaCe and Nd-Cu) into the grain boundaries of the Nd-Fe-B magnets. The magnetic properties of the initial and final (annealed) B1 samples were listed in (Table 5.1). Although this improved the magnetic properties, it was necessary to significantly enhance the properties for better applications. Therefore, annealing was conducted using other eutectics. To ensure proper placement of the eutectics on the sample strip, shaped eutectics were utilized, and annealing was carried out. DyCu alloys were chosen as they possess high magnetic moment and curie temperature. The hysteresis loops of the **Nd-Fe-B (A1) (Fig.5.F)** sample before and after annealing **(Fig.5.G)** using DyCu strips were compared. It was evident that the coercivity was almost the same for samples before and after annealing, but other magnetic properties such as remanence and saturation magnetization had significantly improved. However, a two-stage annealing process was suggested to solve the problem of less diffusion of DyCu strips into the sample.

A two-stage annealing process using DyAlCu strips was applied to an Nd-Fe-B (B3) sample, but the resulting coercivity was observed to have decreased as a consequence of enlarged grain size. On the other hand, other magnetic properties, such as saturation magnetization, were found to have improved. The coercivity, saturation magnetization, and remanence were significantly improved for Nd-Fe-B (A1) samples after annealing with LaCe and Nd-Cu powder.The coercivity, saturation magnetization, and remanence were significantly improved for Nd-Fe-B (A1) samples after annealing with LaCe and Nd-Cu powder. The hysteresis loops of the sample before (Fig 5.J) and (Fig 5.K) and (Fig 5.L) after annealing with LaCe and Nd-Cu powders were compared. and the coercivity had significantly enhanced. This was due to the proper diffusion of the eutectics into the interior of the sample, achieved by the proper deposition of the eutectic on the sample using fevi-quick.

Huber et al. were able to achieve comparable improvements in coercivity through their own experimentation with GBD. They were able to increase coercivity from 0.65 T to 1 T by using Nd-Cu alloy and achieved an even greater improvement, up to 1.5 T, by using Nd-Tb-Cu alloy. Zeng et al. also utilized GBD techniques, utilizing LaCe alloys, and were able to increase coercivity from 1.24 T to 1.29 T.

The FE-SEM images (Fig 5.0) and (Fig 5.P) of the sample after annealing showed that the sample had densified after the annealing treatment. Further microstructure analyses and characterizations like XPS will be carried out on the annealed samples in the future, as an investigation in this direction is worth exploring

In summary, the study investigated the effect of annealing on the magnetic properties of Nd-Fe-B magnets made using selective laser melting. The presence of defects such as cracks and pores in the samples negatively impacted their magnetic properties. To improve the magnetic properties, annealing was carried out using different eutectics. The results showed that annealing with LaCe and Nd-Cu powder significantly enhanced the coercivity, saturation magnetization, and remanence of the samples. Further microstructure analyses and characterizations like XPS will be carried out on the annealed samples in future because an investigation in this direction is worth exploring.

Chapter 7

Conclusion

Selective Laser Melting (SLM) is a highly effective method of fabricating Nd-Fe-B magnets, but microstructural defects can negatively impact their magnetic properties. Therefore, improving the magnetic properties of SLM-processed Nd-Fe-B magnets is essential to make them more suitable for various applications. Annealing with various low melting point alloys, which contain rare earth elements, can facilitate grain boundary diffusion and improve magnetic properties. Several eutectics were used during the annealing process to improve the magnetic properties of SLM-processed Nd-Fe-B magnets. The annealing process involves the diffusion of the alloys into the interior of the magnets, resulting in enhanced magnetic properties. The coercivity and other magnetic properties of samples annealed with LaCe powder and crushed ribbons (comprised of Nd-Cu) were slightly improved, with coercivity increasing from 0.97T to 1T. However, for further improvements, annealing can be carried out using other eutectics.

Although the magnetic properties of samples annealed with DyCu alloys (in strip form) improved with respect to remanence and saturation magnetization, there was no improvement in coercivity. Diffusion of strip-form eutectics into the samples was found to be challenging. However, using eutectics in powder form can help solve this problem, allowing for the smooth diffusion of eutectics into the sample interior, leading to significant improvements in magnetic properties. Proper deposition of the eutectics is crucial during annealing, as improper deposition can make diffusion difficult. In one experiment, significant enhancement of coercivity from 0.7T to 1.1T was observed when LaCe and Nd-Cu powders were uniformly deposited on the samples using fevi-quick during annealing. It is always better to use eutectics in powder form, as this facilitates the smooth diffusion of the eutectic into the sample interior, leading to the considerable enhancement of various magnetic properties.

In conclusion, annealing using various eutectics can significantly improve the magnetic properties of SLM-processed Nd-Fe-B magnets. Employing eutectics in powder form is preferable to strip form, as the latter is challenging to diffuse into the sample. Proper deposition of eutectics during annealing is also critical to achieving the desired improvements in magnetic properties. Overall, enhancing the magnetic properties of Nd-Fe-B magnets through annealing can significantly improve their suitability for various applications.

Chapter 7

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