Microwave processing of Nd-Fe-Co-B magnetic materials

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**NANYANG
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UNIVERSITY**

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**MICROWAVE PROCESSING OF Nd-Fe-Co-B MAGNETIC
MATERIALS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

MICROWAVE PROCESSING OF Nd-Fe-Co-B MAGNETIC MATERIALS

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Date

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.....
Tan Xiao

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

Chapter 4 is published as X.Tan, H.Parmar, Y.Zhong, V.Chaudhary, and R.V. Ramanujan, Microwave-Based Chemical Synthesis of Co-Alloyed Nd-Fe-B Hard Magnetic Powders, *IEEE Magnetics Letters* **8**, 1-5(2017). DOI: 10.1109/LMAG.2017.2746039

The contributions of the co-authors are as follows:

- Prof R.V. Ramanujan provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. H. Parmar, Y. Zhong, and Dr. V. Chaudhary.
- I designed the study with Prof R.V. Ramanujan and performed all the laboratory work in School of Materials Science and Engineering in Nanyang Technological University. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Y. Zhong assisted in the laboratory work and interpretation of microscopy data.
- Dr. H. Parmar and Dr. V. Chaudhary assisted in the collection and provide guidance in the interpretation of the magnetic measurement data.

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- Prof R.V. Ramanujan and I designed the initial project plan and Prof R.V. Ramanujan edited the manuscript drafts.
- I performed all the laboratory work in School of Materials Science and Engineering in Nanyang Technological University. I prepared the manuscript drafts.
- All microscopy, including sample preparation, was conducted by Y. Zhong and me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr. H. Parmar and Dr. V. Chaudhary provide guidance in the interpretation of the magnetic measurement data. The manuscript was revised by Dr. H. Parmar, Y. Zhong and Dr. V. Chaudhary.

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- Dr. H. Parmar and Dr. V. Chaudhary assisted in interpretation of the magnetism study. They also edited the manuscript.

Abstract

Numerous studies have been performed in the field of Nd-Fe-B based permanent magnets since they possess excellent hard magnetic properties. The magnetic properties are closely related to the structure, phases present, processing route etc. High performance hard magnets can obtain their desired large energy product by interaction of magnetic moments at the nanoscale. Therefore, developing nanostructured Nd-Fe-B based magnets requires the study of novel synthesis techniques, microstructure and properties. Conventional physical techniques have limitations of inhomogeneity, contamination, poor control of microstructure and high cost due to the use of elemental rare earth metals. On the other hand, bottom-up chemical methods offer better control of structure at the nanoscale. The use of metal salts as precursors significantly reduces the cost. Hence, a cost-effective, bottom-up, microwave synthesis method is promising to produce homogenous particles by uniform microwave heating. The main objective of this project is the study of the microwave synthesis of Nd-Fe-B based magnets. The processing parameters, reaction mechanisms, characterization and property evaluation of these materials were carried out.

Nanostructured Nd-Fe-B particles were prepared by microwave combustion and reduction diffusion. Microwave combustion resulted in a transformation from metal salts to mixed metal oxides consisting of CoFe_2O_4 , NdFeO_3 , Nd_3FeO_6 and Fe_2O_3 . $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ nanoparticles were obtained by the reduction diffusion process, in which the mixed metal oxide was reduced by CaH_2 . The effects of processing parameters on properties and structure were studied. It was found that the structure and magnetic properties can be controlled by the microwave power. Higher microwave power resulted in larger grain size. The coercivity of the particles increased from ~ 6 kOe to ~ 9 kOe when the grain size increased from ~ 20 nm to ~ 60 nm. A range of reduction-diffusion annealing times was also tested. The highest energy product was obtained for reduction diffusion at 800°C for 2 h. The CaO byproduct was removed by different chemicals. The optimum chemical was found to be NH_4Cl (dissolved in methanol), which eliminated the use of water, thus avoiding the vigorous reaction between CaO and water.

A novel one pot microwave processing technique was proposed and developed to synthesize $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ exchange coupled nanoparticles. Nd-Fe-Co-B mixed oxides were obtained from metal nitrates *via* microwave combustion followed by microwave reduction of these oxides, to form hard magnetic $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ powder, in the same microwave chamber. The maximum energy product reached a value of 11.4 MGOe, it is the largest value among the reported values in chemical synthesis of $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanoparticles. The conventional use of a furnace for oxide reduction was eliminated. The reaction mechanisms for both microwave combustion and microwave reduction were studied for the first time. During the formation of mixed oxides, boron oxide formed first. Iron and cobalt oxides subsequently formed, followed by the formation of neodymium iron oxide. The $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ alloy formed through several steps. At 350 °C, iron, cobalt and boron oxides were reduced. At 740 °C, the partial reduction of neodymium oxide to NdH_5 took place. After heat treatment at 800 °C for 2 hours, the desired $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ and $\alpha\text{-Fe}$ phases were formed.

Heavy rare earths such as Dy enhance coercivity and improve thermal stability by increasing magnetocrystalline anisotropy. Hence, $(\text{Nd}_{15-x}\text{Dy}_x)\text{-(Fe}_{67}\text{Co}_{10})\text{-B}_8$ ($x=0, 3, 6, 9$) alloys were studied. The influence of Dy substitution on the magnetic properties were investigated. $(\text{BH})_{\text{max}}$ was found to be as high as 12.6 MGOe for the $(\text{Nd}_{12}\text{Dy}_3)\text{-(Fe}_{67}\text{Co}_{10})\text{-B}_8$ alloy. As Dy content increased from $x=0$ to $x=9$, coercivity increased significantly, from 8 kOe to 14.5 kOe. The thermal stability increased for higher Dy content. Analysis of the temperature dependent magnetic properties and comparison with modeling results showed that the dominant coercivity reversal mechanism was nucleation of reversed magnetic domains.

This microwave synthesis technique was shown to successfully synthesize Nd-Fe-B base hard magnets. A range of parameters were studied to optimize the performance of the material. The reaction mechanism was determined. Dy could be readily alloyed to increase the thermal stability of the material.

Lay Summary

Energy resources are being continuously depleted, leading to climate change, with irreversible consequences. Therefore, there is ever-increasing attention to improving efficiency of energy use. Magnetic materials can play a vital role in increasing the efficiency and performance of various energy systems and devices. Due to their superior magnetic properties, Nd-Fe-B based permanent magnets are the most widely used high performance hard magnet. Applications range from electric motors, wind turbines, power generators and many other emerging applications.

The magnetic properties of the high performance nanostructured permanent magnets depend on the composition, phases, microstructure, crystal size. Bottom-up chemical methods offer better control of structure at the nanoscale to overcome limitations such as contamination, poor microstructure control and expensive raw materials in physical techniques. The use of metal salts as the precursors significantly reduce the cost.

Therefore, the major aim of this thesis is the development of high performance, nanostructured Nd-Fe-Co-B based hard magnetss via a cost effective microwave processing method. To achieve these objective, three aspects were studied (1) Optimization of processing parameters to improve the magnetic properties (2) Determination of the reaction mechanisms of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ phase formation by microwave processing (3) Alloying additions of Dy to $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ to increase thermal stability and to study coercivity reversal mechanisms in the synthesized nanoparticles.

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Abbreviations

DCD	Direct Current Demagnetization
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
HDDR	Hydrogenation Disproportionation Desorption Recombination
HRTEM	High Resolution Transmission Electron Microscopy
IRM	Isothermal Remnant Magnetization
PPMS	Physical Properties Measurement System
RD	Reduction Diffusion
SCS	Solution Combustion Synthesis
SEM	Scanning Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
VSM	Vibrating Sample Magnetometry
XRD	X-ray Diffraction

Chapter 1

Introduction

There is ever-increasing attention to improving the efficiency of energy use. Magnetic materials can play a vital role in increasing efficiency and performance of various energy systems and devices. Nd-Fe-B based permanent magnetic materials are the most commonly employed high-performance permanent magnets. Applications range from electric motors, wind turbines, power generators and many other emerging applications. However, expensive raw materials and geographically limited availability of rare earth metals limits the use of Nd-Fe-B magnetic materials to high end devices. Hence, the aim of the project is the development of high performance, nanostructured Nd-Fe-Co-B based hard magnets via a novel and cost-effective microwave based chemical processing route. This chapter describe the motivation of the work undertaken in this thesis for developing Nd-Fe-Co-B based magnetic materials. Current unmet needs in Nd-Fe-B materials are listed and the chemical synthesis approach is described. The objectives, hypothesis and scope of the work are provided. The novelty and significance of the project is also illustrated.

1.1 Hypothesis/Problem Statement

Many unpredictable and alarming consequences have emerged due to the excessive exploitation of fossil fuel energy resources, e.g., global warming, oil price volatility and air pollution. Numerous scientists, politicians and researchers have urged the development of green and renewable energy to support future development[1]. The development of renewable energy requires efforts from various technologies. Developing high performance hard magnets is one important sectors [2].

One of the figures of merit in the characterization of permanent magnets is the maximum energy product, i.e. $(BH)_{\max}$, defining as the maximum magnetic energy that can be stored in a magnet. Materials with higher $(BH)_{\max}$ can furnish the same field and flux with smaller volume and weight, leading to higher performance. As Nd-Fe-B based magnets possesses the highest $(BH)_{\max}$ among all known permanent magnets, they have attracted most attentions in the area of high performance permanent magnets [3-5]. However, expensive raw materials and geographically limited availability of rare earth metals has limited the use of Nd-Fe-B magnets to high end devices. The mostly commonly used magnets in today's markets are still the low cost, low performance ferrites. **Reducing the cost of Nd-Fe-B based magnets by the use of microwave processing is a challenging subject and is a key driving force for this thesis.**

High performance hard magnets obtained their large energy product through interaction of magnetic moments in nanoscale. Nd-Fe-B based exchange coupled magnets have attracted high interest. Such magnets consist of magnetically interacting nanoscale hard and soft phases. Coey predicted an enormous energy product for such materials[6]. **However, experimental results are still much lower than this prediction. The structure of the nanomagnetic materials needs to be optimized to achieve effective coupling.**

In exchange coupled magnets, the nano-sized hard phase is magnetically coupled with the nano-sized soft phase. A large energy product is expected due to the large coercivity value obtained from the hard phase and the high magnetization value obtained from soft phase

[6]. To achieve efficient coupling, the soft magnetic grain need to be in the nanometer size and around twice the domain wall width of the hard magnetic phase, which is ~ 10 nm[7]. Conventional methods to produce such magnets include multiple top-down steps: casting from expensive elemental metal, pulverizing the ingot to powder and compacting the powder by a hot press. Such physical methods have very little control over the microstructure and hence it is difficult to achieve the desired exchange coupling nanostructures. Physical methods, including melt spinning, ball milling and hydrogenation disproportionation desorption recombination (HDDR) are commonly used in synthesizing nanocrystalline Nd-Fe-B magnets [8-12]. Some shortcomings of these physical methods include contamination, inhomogeneity and long processing time. Physical methods also share a common shortcoming which is the high cost due to the use of high purity rare earth metals.

On the other hand, chemical synthesis can solve these problems as it is a bottom-up process. It is promising to use chemical methods for obtaining homogeneous and desirable structures for the intimate mixing of multiple phases. Alloying elements can also be readily incorporated. In chemical methods, usually the starting materials are low cost metal salts or metal oxides. Since the reduction potential of Nd is considerable large, it is hard to reduce the rare earth (Nd, -2.43 eV) and the transition metal (Fe, -0.057 eV) at the same time. An advance in the chemical synthesis of the NdFeB was the reduction diffusion (RD) technique 1987[13, 14]. This technique used Ca/CaH₂ to reduce the metal oxide precursors. Ca has higher oxygen affinity (-2.87eV) than Nd, and can be used to reduce rare earths. Since the Nd-Fe-B particle size can be turned by varying the oxide size, the desired nanocrystalline structure was not achieved due to the large size of the precursor materials available at that time. Therefore, many recent efforts have been devoted to synthesizing Nd-Fe-B nano particles by preparing nano-sized oxide precursors using chemical methods, followed by the RD method. Some chemical methods to process nano-sized oxide powders include the sol-gel approach, auto-combustion approach and solution based synthesis [15-20]. **However, these techniques are mostly lab-based, difficult to scale up, require long processing time and are associated with limited magnetic properties.** Hence, there is

an urgent need to develop and study a novel, low-cost, scalable processing technique for the production of nanostructured Nd-Fe-B alloys.

In the past decade, growing interest was observed in green synthesis approaches, hence, microwave based synthesis has gained increasing interest. Heating using microwaves is useful for introduction of energy directly into polar reactants in chemical syntheses and transformations. In many of the published examples, microwave heating has been shown to dramatically reduce reaction times, increase product yield and enhance product purity by reducing unwanted side reactions compared to conventional heating methods [1]. Thus microwave processing is an energy efficient (green) process[21]. It has been scaled up and widely used in food processing, the drying industry, industrial synthesis of thermoelectric materials, etc[22-24]. Microwave combustion processing is a well-developed approach in various materials, including ceramics[25, 26], catalyst[27-29], silicides[30-32] and intermetallic compounds[33-36]. For magnetic materials, ferrites with relatively good magnetic properties were processed by such methods [37-40], demonstrating that mixed oxide nanoparticles can be prepared by microwave combustion. As a bottom-up chemical process, the processing parameters can be controlled, leading to the desired microstructure. The use of metal salts instead of elemental metal powders significantly reduces the precursor cost. The effective dielectric heating induced by microwave irradiation significantly reduces processing time and this technique is scalable. A calculation of the cost of raw materials to synthesize 1 kg of $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$ was carried out and was compared with that of the physical methods (table 1.1). It can be seen that the cost reduced by more than half when using the microwave approach. **Therefore, a major hypothesis is that this cost-effective synthesis method can be used to successfully prepare nanostructured Nd-Fe-Co-B based permanent magnets.**

Table 1.1 Cost comparison for raw materials to produce 1 kg of $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$ by the conventional process and the microwave chemical process

	Conventional Processing				Microwave Processing					Commercial Sintered $\text{Nd}_2\text{Fe}_{14}\text{B}$
Precursors	Nd	Fe	Co	B	$\text{Nd}(\text{NO}_3)_3$	$\text{Fe}(\text{NO}_3)_3$	$\text{Co}(\text{NO}_3)_2$	H_3BO_3	CaH_2	
Cost* (SGD/kg)	2100	330	1000	22000	970	140	150	160	830	
Amount/kg $\text{Nd}_2\text{Fe}_{14}\text{Co}_2\text{B}$	266	616	108	16	388	620	238	8	1560	
Cost* (SGD/kg $\text{Nd}_2\text{Fe}_{14}\text{Co}_2\text{B}$)	6120				2814					3516

Although microwave combustion and reduction diffusion has been reported for the synthesizing nanostructured Nd-Fe-B [41], the relationship between processing parameters and microstructure as well as the optimization of the process parameters to obtain good magnetic properties has not been well studied. Our study of the formation mechanism enables us to address these issues. Despite the importance of the reduction diffusion process in developing Nd-Fe-B materials, issues regarding removal of the CaO byproduct without deterioration of the magnetic properties are not well understood, hence these studies have been carried out.

Nd-Fe-B has limited use in high temperature applications since it has low Curie temperature (T_c) and limited operating temperature. T_c of $\text{Nd}_2\text{Fe}_{14}\text{B}$ is $\sim 310^\circ\text{C}$, and its operating temperature is usually $\sim 80^\circ\text{C}$ [42], which is below the ideal operating service temperature of some energy converter devices. **There is an urgent need to improve T_c and operating temperature of Nd-Fe-B type magnets.** The T_c is proportional to the magnitude of exchange energy integral (J_{ex}). The Bethe-Slater curve (figure 1.1), shows the J_{ex} vs r_a/r_{3d} , where r_a is the radius of an atom while r_{3d} is the radius of the 3d shell of electrons. $J_{\text{ex}} > 0$ represents the parallel alignment of magnetic spins. When $J_{\text{ex}} > 0$, J_{ex} is proportional the Curie temperature, spins are parallelly aligned due to strong exchange forces. These spins can only be disordered by sufficient thermal energy [43]. Since Co has the highest positive J_{ex} , in this project, powders of Co-alloyed NdFeB have been synthesized to increase the T_c of the material.

Although Co can increase the T_c of $\text{Nd}_2\text{Fe}_{14}\text{B}$, it can reduce the coercivity and has limited influence on the temperature stability [42, 44]. The thermal stability of Nd-Fe-B can be enhanced by Dy alloying, thus expands the operating temperature of Nd-Fe-B and is necessary for some of the more challenging automotive applications [45]. Heavy rare earths such as Dy can enhance the coercivity by increasing the magnetocrystalline anisotropy field (H_A). H_A of $\text{Dy}_2\text{Fe}_{14}\text{B}$ is $\sim 12577 \text{ kA/m}$ (158 kOe), which is more than twice the value of $\text{Nd}_2\text{Fe}_{14}\text{B}$ ($\sim 5570 \text{ kA/m}$ (70 kOe))[46]. Therefore, Dy was added to increase coercivity. Thus, the substituting Nd by Dy and Fe by Co at the same time can simultaneously increase thermal stability and enhance coercivity. Dy magnetic moments align antiparallel to Fe and Nd magnetic moments. Therefore, Dy alloying may decrease saturation magnetization and energy product [47, 48]. Furthermore, the geographical availability of Dy is limited and the cost of Dy alloyed magnets rise dramatically. Hence, achieving excellent magnetic properties and good thermal stability by the minimum amount of heavy rare earths is essential.

Figure 1.1 Bethe-Slater curve (schematic)[42]

1.2 Objectives and Scope

The major objective of this research is the study of Nd-Fe-Co-B based hard magnets, including the processing, characterization and property evaluation of the relevant magnetic nanostructures (figure 1.2). Detailed objectives are listed below:

- (a) Synthesis, characterization and magnetic property evaluation of Nd-Fe-Co-B magnetic particles by microwave combustion and the RD process. The processing parameters in microwave combustion and in the RD process was studied and optimized to produce Nd-Fe-Co-B particles with the highest performance.
- (b) Synthesis, characterization and magnetic property evaluation of Nd-Fe-Co-B magnetic powders by a novel one pot microwave synthesis process. In a single microwave chamber, the synthesis of Nd-Fe-Co-B mixed oxides *via* microwave combustion and microwave reduction of these oxides to hard magnetic $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ powder were completed. The conventional use of a furnace for oxide reduction was eliminated.
- (c) The reaction mechanisms and kinetics of the microwave combustion process as well as the RD process were studied. Experimental data and thermodynamic models were used to address this objective.
- (d) One of the advantages of this chemical approach is the facile alloying addition elements. Alloying by Dy was carried out. The effects of Dy on the microstructure as well as the magnetic properties were evaluated. A coercivity mechanism of the synthesized particles was determined.

Figure 1.2 Scope and workflow of the project

1.3 Dissertation Overview

This thesis includes 7 chapters,

Chapter 1 is the rationale for this thesis. The problem statement/hypothesis, objectives and scope, dissertation overview and findings and outcomes are stated.

Chapter 2 is the literature review, including the theory of magnetism, background of permanent magnets, especially nanostructured NdFeB based magnets. The synthesis techniques for NdFeB nanomaterials has been presented.

Chapter 3 illustrates the processing methodology and the characterization techniques employed in this research. The working principles and parameters of these techniques are also explained.

Chapter 4 provides the results and the discussion of the synthesis of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ nano particles through microwave combustion and RD. The synthesis results of each step are presented and discussed. Discussion of the impact of process parameters on the micro structure as well as magnetic properties are also discussed.

Chapter 5 provides the results and discussion of a novel one-pot microwave processing technique to process $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ nano particles. The microstructure and magnetic

properties are presented and discussed. The mechanism of both microwave combustion and microwave reduction were studied by experimental methods and by thermodynamic models.

Chapter 6 provides the results and discussion of the microwave synthesis of Dy substituted $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ nano particles by microwave chemical processing. This chapter also analyzes the influences of Dy addition on the microstructure and magnetic properties. The room temperature and temperature dependent magnetic properties are discussed. The coercivity mechanism for the nanoparticles was investigated.

Chapter 7 draws together the threads and provides the summary of this thesis. Furthermore, this chapter also provide the author's reflections, opportunities and strategies for future work.

1.4 Findings and Outcomes/Originality

Coercivity, magnetization and $(\text{BH})_{\text{max}}$ are extrinsic properties that can be tuned via processing. In physical techniques, such as melt spinning, ball milling and Hydrogenation Disproportionation Desorption Recombination (HDDR), contamination is inevitable. This can result in reduction in exchange coupling, leading to low magnetization and energy product. In the absence of contamination, more uniform nanostructures are expected. This will give rise to a smooth demagnetization curve in the 2nd quadrant of the M-H loop. Chemical methods, as a bottom-up technique, are promising to obtain such homogeneous nano structures. Therefore, microwave combustion followed and RD process were employed in this project to synthesize Nd-Fe-B based nanostructured hard magnets. The novelty, along with a brief description of this work is indicated in Table 1.2.

Table 1.2 Summary of Novelty

Area	Novelty
Microwave chemical approach+ Reduction diffusion	No previous report of Co alloyed Nd-Fe-B by this approach Processing parameters: 1. Microwave power 2. RD duration 3. Removal of byproduct
One pot microwave processing	No previous report of the synthesise of Nd-Fe-B by this approach 1. Magnetic properties and microstructure 2. Microwave combustion reaction mechanism 3. Microwave reduction reaction mechanism
Dy addition in Nd-Fe-Co-B NPs	No previous report of Dy,Co co-substitution Nd-Fe-B nanoparticles 1. Dy effects on microstructure 2. Dy effects on magnetic properties 3. Coercivity mechanism

Several novel outcomes are obtained by this research:

1. Studying for the first time the reaction mechanisms for both microwave combustion and reduction-diffusion.
2. Establishing processing parameters - microstructure - magnetic properties relationships of the Nd-Fe-Co-B magnetic powders.
3. Developing a novel one-pot microwave synthesis approach to synthesize high energy product $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ hard magnetic nanoparticles. This method is cost effective, facile and energy efficient. The $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ exchange coupled nanoparticles display a high energy product.
4. Dy,Co co-substitution by microwave processing. The impact of Dy on the micro structure and magnetic properties of these nanoparticles were investigated for the first time. The coercivity mechanism in these nanoparticles was analyzed, which can contribute to the ongoing debate of the coercivity mechanisms in Nd-Fe-B based nanoparticles.

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Chapter 2

Literature Review

The superior magnetic properties of Nd-Fe-B based hard magnets arise from their crystal structure, microstructure, processing route etc. This chapter first describes magnetism in permanent magnets. The microstructure, magnetic properties, alloying effects are reviewed. Such information is beneficial to understand magnetism in Nd-Fe-B magnets. Achieving the desired microstructure and magnetic properties, synthesis by conventional physical techniques and by emerging chemical methods are discussed. The limitations of conventional methods in synthesizing nanostructured magnetic particles are discussed. The emergence of cost-effective microwave synthesis is highlighted. Finally, the contribution of this thesis to the literature is presented.

2.1 Fundamental Magnetism in Permanent Magnets

The superior magnetic properties of permanent magnets arise from their crystal structure, microstructure, composition etc. Therefore, understanding of the fundamental magnetism is needed to develop a permanent magnet. In this section, an overview of the fundamentals of magnetism will be provided. The terminologies and important concepts in magnetism will be introduced, including the origin of the magnetic moment, magnetic anisotropy, magnetic domains and domain walls. After that, a description of the magnetization process and the hysteresis loop will be elucidated. The important properties of permanent magnetism will be introduced.

2.1.1 Magnetic Moment

Magnetism of materials arises from the magnetic moment induced by two sources: (1) spin: intrinsic angular momentum of electron (2) orbital: orbital angular momentum (figure 2.1).

Figure 2.1 Magnetic moment associated with (a) Orbital angular momentum and (b) intrinsic angular momentum of electron[1]

The magnetic moment associated with the orbital motion of electrons can be expressed using the Bohr model[1, 2]:

$$\mu(\text{orbit}) = \frac{neh}{4\pi m} \text{ (SI units)} \quad 2.1$$

The magnetic moment induced by the motion of spin is termed as the Bohr magneton and is expressed as[1, 2]:

$$\mu(\text{spin}) = \frac{eh}{4\pi m} \text{ (SI units)} = 9.27 \times 10^{-24} \text{ A m}^2 \quad 2.2$$

The vector addition of the magnetic moment of all electrons in determines the net magnetic moment in an atom. As a result, two cases are expected: (1) the sum of all the magnetic moments of all electrons cancel with each other, leading to zero net magnetic moment, which is called diamagnetism. (2) the sum of magnetic moments of all electrons is partially canceled, leaving a non-zero net magnetic moment of the atom. In this case, materials are classified as paramagnetic, ferromagnetic, antiferromagnetic, or ferromagnetic, depending on the exchange interactions (figure 2.2).

Figure 2.2 Types of magnets. (a) Paramagnets (b) Ferromagnets (c) Antiferromagnets (d) Ferrimagnets[3]

- (a) Paramagnets, atoms possess permanent magnetic dipole moments. However, the net magnetic moments of the electrons is zero due to the random orientation of their moments.
- (b) Ferromagnets: atoms possess permanent magnetic dipole moments. The magnetic moment of neighboring atoms are aligned parallel with one another due to exchange interactions. Typical ferromagnetic materials includes Fe, Co, Ni etc.

- (c) Antiferromagnets: atoms possess permanent magnetic dipole moments. They possess a zero net magnetic moment as the magnetic moments of neighboring atoms aligned antiparallel to each other. Typical antiferromagnetic materials includes MnO, FeO, CoO, NiO etc.
- (d) Ferrimagnets: As in the case of antiferromagnets, the atoms possess permanent magnetic dipole moments and the magnetic moments of neighboring atoms are aligned antiparallel to each other. However, magnitude of the moment of one direction is different from that of the opposite direction. Hence, a non-zero net magnetic moment exists. Typical examples includes Fe₃O₄, Fe₂O₃ and spinel ferrites.

2.1.2 Exchange Interaction

The exchange interactions originate from two main types of interactions: (a) intra-atomic exchange interactions and (b) inter-atomic exchange interactions. Intra-atomic exchange interactions determine the atomic magnetic moment and favor parallel spins, according to Hund's rule. Inter-atomic exchange interactions affect the exchange interaction of neighboring atoms. Heisenberg interactions are commonly considered to be inter-atomic exchange interactions, and can be expressed as[2]:

$$E_{ex} = -2J_{ex}S_1 \cdot S_2 = -2J_{ex}S_1S_2\cos\theta \quad 2.3$$

where J_{ex} is the exchange integral, θ is the angle between two neighboring spins S_1 and S_2 .

When $J_{ex} > 0$, E_{ex} is at minimum when the spins are aligned in a parallel fashion ($\theta = 0^\circ$), which is the case of ferromagnetic ordering below the Curie temperature (see section 2.1.6).

When $J_{ex} < 0$, E_{ex} is at a minimum when spins are antiparallely aligned ($\theta = 180^\circ$), which is the case of antiferromagnetic ordering.

2.1.3 Magnetic Anisotropy

Magnetic anisotropy refers to the fact that in ferromagnetic or antiferromagnetic materials, the saturation magnetic field differs from one direction to another. The direction along which the maximum field is needed is called the hard axis, while the direction along which the minimum field is needed is called the easy axis. Magnetic anisotropy has significant influence on magnetization and coercivity. In permanent magnetic materials, strong easy axis anisotropy is favored, whereas in soft magnetic materials, minimum anisotropy is favored. Energy is required to rotate magnetization away from the easy direction, which is termed as the anisotropy energy [3]:

$$E_a = K_1 V \sin^2 \theta \quad 2.4$$

Where θ represents the angle between direction of magnetization (M) and direction of easy axis, K_1 represents the anisotropy constant, V represents the magnetic volume.

There are three major types of anisotropies contributing to the overall magnetic anisotropy[4]:

(a) Magnetocrystalline anisotropy (b) Shape anisotropy and (c) Induced anisotropy.

(a) Magnetocrystalline anisotropy originates from the spin-orbit coupling effect of the electrons in a crystal structure. The spin moments of electrons tend to reorient themselves in the presence of a magnetic field. The orbital moments tend to rotate as well but are strongly bound to the crystal structure, resisting the reorientation of spins. Hence, the energy to overcome this spin-orbit interaction and reorient the spin from the easy axis direction is termed as anisotropy energy. Hence, magnetocrystalline anisotropy is an intrinsic property and is strongly associated with crystal symmetry and the microstructure of a material. Magnetocrystalline anisotropy is temperature dependent, it usually decreases as temperature is increased and vanishes at the Curie temperature.

- (b) The shape of the magnets may result in shape anisotropy, which is extrinsic property derived from the demagnetization effect. The demagnetization effect is intensified in small particles, in which the free poles at the surface of the particles align opposite to the external magnetic field. For large samples, internal flux closure destroys shape anisotropy.
- (c) Induced anisotropy derived from texture in the sample. For example, strain created by stress, annealing under a magnetic field etc.

2.1.4 Magnetic Domains and Domain Walls

Magnetic domains were proposed by James Ewing[5] and the principles of domain theory were established by Lev Landau and Evgenii Lifschitz in 1935[6]. According to the Weiss theory, ferromagnetic materials consist of many regions, such that in each region, the direction of spontaneous magnetizations differs from one another. Each region is called a domain. The net magnetic moment of the whole magnet is zero due to the random magnetization of each domain. Domain wall refers to the interfaces between the domains. One may imagine a drastic change of spins between domains, as shown in figure 2.3(a). However, exchange energy is minimum when adjacent spins are parallelly aligned in a ferromagnet. This abrupt change in spin will induce large exchange energy. Therefore, a gradual change of spin direction is expected in the domains (figure 2.3(b)) [1].

Within the domain wall width, rotation of the magnetization is observed. The magnetization direction rotates from one direction of the easy axis of one domain to the other easy direction of another domain. Figure 2.3(b) shows an example of domain wall that contains a 180° wall existing between two domains with an antiparallel alignment. However, the spins in figure 2.3(b) deviate from the easy directions for both the adjacent domains, leading to high crystal anisotropy within the walls. The exchange energy favors thick domain walls with minimum angles between adjacent spins, while crystal anisotropy favors a thin domain wall with minimum number of spins directed towards the non-easy

directions. The competition between the two effects results in a non-zero thickness of the domain walls.

In an unit area, the energy of a 180 ° Bloch wall can be expressed as[2]:

$$\gamma = \delta K_I + \delta A_{ex} \left(\frac{\pi}{\delta} \right)^2 \quad 2.5$$

Where A_{ex} is the exchange constant, δ is the thickness of the wall, K_I is the magneto-crystalline anisotropy constant. At equilibrium, $\frac{d\gamma}{d\delta} = 0$. Hence, the equilibrium thickness, δ_m , of a 180 ° Bloch wall is expressed as:

$$\delta_m = \pi \sqrt{\frac{A_{ex}}{K_1}} \quad 2.6$$

The equilibrium domain wall energy γ_m is expressed as:

$$\gamma_m = 2 \pi \sqrt{\frac{A_{ex}}{K_1}} \quad 2.7$$

Figure 2.3 (a) Hypothetical 180 ° domain wall with zero thickness (b) Schematic of domain wall between 180° domains[1]

2.1.5 Magnetization Process and Hysteresis Loop

In a ferromagnetic material with many domains, the magnetization $\mathbf{M}$ responded to the magnetic field $\mathbf{H}$ in a non-linear fashion. This response is represented by the hysteresis loop, a standard method of characterization of magnetic materials. A typical hysteresis loop is represented as figure 2.4.

During characterization, the magnetic sample was first subjected to an external field from zero to a specified field. The magnetic moments aligned gradually with the direction of the external field. The magnetization M increased as H increased until the material reached the saturated state (curve from point o to point a), all the moments were aligned with the external field. The magnetization at this stage is termed as the saturation magnetization M_s . After that, the field decreased to zero, the value of M decreased with the decreasing H , following a different curve (a to b) compared to the original curve (o to a). A non-zero magnetization remains at this zero field and is termed as remnant magnetization M_r . To achieve zero magnetization of the magnet, an opposing magnetic field was needed, termed as the intrinsic coercivity H_c (b to c). Apart from M_s , M_r and H_c , the maximum energy product $(BH)_{max}$ is also an important property of a permanent magnet. $(BH)_{max}$ represents the energy stored in a magnet within a defined volume. The value of $(BH)_{max}$ is calculated using maximum area under the B-H curve in the second quadrant.

Figure 2.4 Typical B-H and M-H hysteresis loops of permanent magnets[7]

2.1.6 Curie Temperature and Thermal Properties

In spite of good room temperature magnetic properties, there is a drawback of Nd-Fe-B magnets, i.e., the thermal stability is relatively poor compared to Sm-Co based magnets.

The Curie temperature of NdFeB is 312 °C and magnetic properties deteriorate rapidly at temperatures in excess of ~ 150 °C. Apart from the Curie temperature, the thermal stability is represented by temperature coefficients and irreversible or reversible magnetic losses.

Thermal stability of the permanent magnet in a temperature range between T_0 - T can be characterized by the temperature coefficient of remanence (α) and temperature coefficient of coercivity (β), which can be expressed as:

$$\alpha = \frac{J_r(T) - J_r(T_0)}{J_r(T_0)(T - T_0)} \times 100\% \quad 2.8$$

and

$$\beta = \frac{j^{Hc}(T) - j^{Hc}(T_0)}{j^{Hc}(T_0)(T - T_0)} \times 100\% \quad 2.9$$

A smaller absolute value of the coefficient indicates a better thermal stability. Liu et al. studied the thermal stability of nanocrystalline NdFeB based magnets. Their results showed that nanocomposites were more thermally stable than single phase RE-rich nanocrystalline alloys and that smaller grain size is beneficial to thermal stability[8, 9].

2.2 Permanent Magnets

This section first provides the background to different generations of permanent magnets. After that, the literature review focuses on the magnetic properties of Nd-Fe-B magnets and their origin in the crystal structure and microstructure. (1) The large coercivity arises from high anisotropy owing to the layered uniaxial lattice. (2) The large magnetization is a result of Fe-Nd exchange interactions. (3) The energy product is enhanced by exchange coupling through control of the microstructure. (4) To analyze inter-particle interactions and the coercivity reversal behavior, approaches, such as Henkel plot and models of coercivity mechanisms are introduced.

2.2.2 Crystal Structure of Nd-Fe-B Magnet

Understanding the crystal structure of Nd-Fe-B is important as the intrinsic magnetic properties are closely correlated with crystal structure. Figure 2.5 (a) presents the crystal structure of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ unit cell. The space group of $\text{Nd}_2\text{Fe}_{14}\text{B}$ is $P4_2/mmm$, which is structure No. 136 and belongs to the tetragonal structure. Each unit cell consists of 68 atoms, which consists of four sets of $\text{Nd}_2\text{Fe}_{14}\text{B}$ formula units. It can be found that Nd and B atoms occupied the $z = 0$ and $z = 0.5$ planes (figure 2.5 (a)). Only 4 Fe atoms occupy the $z = 0$ and $z = 0.5$ plane. Other Fe atoms are located between these two planes and are connected with each other *via* hexagonal nets. The B atoms are located in the center of trigonal prisms formed by 6 Fe atoms (figure 2.5 (b)). It is evident from figure 2.5 (a) that the Fe arrangement and environment are very different in the c -axis direction and perpendicular to the c direction [10, 11].

Figure 2.5 (a) $\text{Nd}_2\text{Fe}_{14}\text{B}$ unit cell (b) Trigonal prism containing a boron atom in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ structure[16].

The intrinsic crystalline anisotropy is strongly related to this unique layered arrangement in the tetragonal structure. The lattice parameters of $\text{RE}_2\text{Fe}_{14}\text{B}$ obey the phenomenon of lanthanide contraction. Table 2.1 shows information of typical $\text{RE}_2\text{Fe}_{14}\text{B}$ lattices and

intrinsic magnetic properties. It can be seen that the variation of c is large while the variation of a is small.

Table 2.1 Lattice parameter and intrinsic magnetic properties of $R_2Fe_{14}B$ type magnets[12]

	Lattice parameters		M_s		$\mu_0 H_a$		T_c
	a_0	c_0	kAm^{-1}	kOe	T	kOe	K
$Pr_2Fe_{14}B$	0.882	0.885	1233	15.5	8.7	80.7	564
$Nd_2Fe_{14}B$	0.882	1.224	1281	16.1	6.7	67	585
$Sm_2Fe_{14}B$	0.880	1.215	1201	15.1	12.5 (Planar)	125	612
$Y_2Fe_{14}B$	0.877	1.204	1144	14.4	2.0	20	565
$Dy_2Fe_{14}B$	0.875	1.200	572	7.2	15.4	154	602

2.2.1 Overview of Permanent Magnets

The first known permanent magnet is the lodestone, which was used in compasses by the Chinese, they are mostly made of ferrimagnetic Fe_3O_4 . Their coercivity values are usually in the tens of Oe and saturation magnetization is ~ 0.4 T (4 kOe). A vital finding was the discovery of Alnico (Al–Ni–Co–Fe alloy) in the 1930s. A significant improvement of coercivity (~ 600 Oe) was observed. However, the saturation magnetization reduced, leading to a maximum $(BH)_{max}$ of 1 MGOe. Later, the discovery of hexagonal ferrites increased the energy product from 1 MGOe to 3 MGOe[13]. However, ferrite possesses low magnetization and Curie temperature. In the 1960s, the crucial finding of rare-earth-based PMs in the form of RCO_5 took place. The energy product increased dramatically to 30.2 MGOe, which was ten times larger than the previous generation of PM. Following this, the discovery of $Nd_2Fe_{14}B$ magnets further increased the energy product of rare-earth-based magnets to 49 MGOe, the large percentage of Fe makes this material much more economical than RCO_5 [14]. Nowadays exchange coupled $Nd_2Fe_{14}B/Fe$ magnets, which are proposed to have an energy product of 120 MGOe, have attracted great attention. However, though enormous work has been done, recently reported results still display a big gap from these predictions[15]

Figure 2.6 The development of permanent magnets in the 20th Century. $(BH)_{\max}$ has improved dramatically, $1 \text{ MGOe} = 7.96 \text{ kJ/m}^3$ [16]

2.2.3 Magnetic Properties of Nd-Fe-B based Magnet

This section will describe the important magnetic properties of Nd-Fe-B based magnets. With high coercivity and high remanent magnetization, Nd-Fe-B possesses the largest $(BH)_{\max}$ among all permanent magnets. The effect of alloying especially of Co and Nd, will also be presented, as they are used in this project.

2.2.3.1 Magnetic Properties of $\text{Nd}_2\text{Fe}_{14}\text{B}$

The attractive Nd-Fe-B magnetic properties originates from the following points:

- Large uniaxial crystalline anisotropy ($K_u = +5 \times 10^6 \text{ J/m}^3$) resulting from the layered tetragonal structure
- Large magnetization as a result of Fe-Nd exchange interactions

- (c) The stable 2-14-1 phase allows us to develop a microstructure where the 2-14-1 phase can be separated by Nd-rich and B-rich phases, which will decouple the 2-14-1 magnetic phases.

Three types of exchange interactions contribute to the overall magnetic properties in $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets, namely RE-RE, RE-Fe and Fe-Fe interactions. The exchange constant for RE-Fe is $\sim -1.22 \times 10^{-22}$ J. The magnetic moments of Nd and Fe in $\text{Nd}_2\text{Fe}_{14}\text{B}$ align, achieving a magnetization of 1.61 T (16.1 kOe) at room temperature, which is the highest in rare earth based magnets[17, 18]. The exchange constant for RE-Fe varies by a factor of 2 when comparing different RE elements, which is a result of lanthanide contraction (more details will be discussed in section 2.3.3.2). The energy product and remanence of NdFeB reaches 56 MGOe and 15.14 kOe[19].

As discussed in section 2.1.2, the Curie temperature is determined by exchange interactions, specifically the net effects of RE-RE, RE-Fe and Fe-Fe interactions. The ferromagnetic exchange interactions, i.e., the Fe-Fe interactions are the lowest among all. The strength of the Fe-Fe interactions dominant the Curie temperature. Fe-Fe interactions depend on the inter-atomic spacing. Thermal expansion will weaken the interactions. Thus, weak interactions between Fe results in a relatively low Curie temperature of 585 K[14, 20].

The strong magnetic anisotropy of $\text{Nd}_2\text{Fe}_{14}\text{B}$ is as a result of the asymmetry of the crystal structure and the Nd orbital angular momentum. The anisotropy of RE is very strong, K_1 is of the order of 10^6 J/m³, while the corresponding value of Fe is 5×10^4 J/m³. At room temperature, $\text{Nd}_2\text{Fe}_{14}\text{B}$ are uniaxial ferromagnets, the easy axis is the [001] direction. The easy axis deviates from the [001] direction for higher temperatures[21].

2.2.3.2 Effect of Substitution

For improving the performance of Nd-Fe-B magnets, two approaches are commonly employed, namely (a) compositional modification and (b) microstructure optimization. In this section, the compositional effect will be discussed.

Alloying can be categorized into three major aspects as (Nd,S1)-(Fe,S2)-B-(M1,M2), where S1(Ce, Pr, Sm, Tb, Dy, etc.) and S2(Cr, Ni, Co, etc.) elements substitute for Nd and Fe, respectively in the 2-14-1 phase (figure 2.7)[22]. M1 (Cu, Zn, Ga, Al, Ge, In, etc.)[23] and M2 (Nb, Ti, V, Zr, W, Mo, etc.)[24] will form M1-Nd-Fe or M1-Nd phases and M2-Fe-B or M2-B phases, respectively. M1 and M2 can change the intrinsic properties, such as T_c , saturation/remanent magnetization and coercivity. M1 and M2 can also tune coercivity and corrosion resistance[25, 26].

Substitutions and Dopants
(Nd,**S1**)-(Fe,**S2**)-B-(**M1,M2**)

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Rn		Rf	Db	Sg	Bh	Hs	M									

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Figure 2.7 Alloying in (Nd,S1)-(Fe,S2)-B-(M1,M2). S1, S2: substituting for Nd and Fe, respectively. M1, M2: Forming additional intergranular Nd-containing phase and borides, respectively.[25]

In this work, Co was used to substitute for Fe to increase the Curie temperature. Researchers have studied most of the transition elements to substitute Fe to increase T_c and improve thermal stability. Al, Si and Ga alloying in NdFeB can enhance thermal stability. However, only Co can substitute for the entire composition range of Fe and also maintain the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase [19]. Co is also the only element that can have a significant effect on the magnetic ordering temperature. Alloying Co in NdFeB has been studied [27-35]. Table 2.2 presents the results for $\text{Nd}_{16}\text{Fe}_{77-x}\text{Co}_x\text{B}_7$. T_c increases with greater cobalt content. In

this work, it was found that Co atoms favors to locate at the k_2 and j_2 sites in the tetragonal structure (the corresponding sites are labeled in figure 2.5). The k_2 , j_2 and j_1 sites play a vital role in determining the Curie temperature. The j_2 site has 12 neighboring atoms, leading to strong positive exchange interaction. Hence, the occupation of Co on the j_2 sites contribute to strong positive interactions $J_{\text{Co-Co}} > J_{\text{Co-Fe}} > J_{\text{Fe-Fe}}$. The distance between the j_1 - k_2 and j_1 - j_1 sites are 0.240 nm and 0.243 nm, respectively. These values are smaller than the critical length of the transition between positive and negative exchange interactions (0.245 nm). Hence, j_1 and k_2 sites contribute to negative interactions. Therefore, the occupation of Co on the k_2 site decreases the negative j_1 - k_2 interaction. Overall, the Co atoms enhance positive exchange interactions and raise the Curie temperature.

Table 2.2 Magnetic properties of $\text{Nd}_{16}\text{Fe}_{77-x}\text{Co}_x\text{B}_7$ studied in literature[27]

Cobalt content, x	B_r/T	jH_c/kAm^{-1}	jH_c/kOe	$T_c/^\circ\text{C}$
0	1.26	811.72	10.2	318
0.05	1.23	987.84	12.4	374
0.1	1.22	373.23	4.7	433
0.2	1.11	344.58	4.3	490
0.3	1.08	289.67	3.6	553

* B_r : remanence magnetization, jH_c :coercivity, $(BH)_{\text{max}}$: energy product, T_c : Curie temperature

The j_2 sites have strongest planar anisotropy. The influence of Co on the anisotropy is more than that of Fe, hence the preferential location of Co on the j_2 sites increases the anisotropy in the direction which is perpendicular to c-axis. Consequently, the total uniaxial anisotropy decreases. The coercivity is decreased when alloying with Co. Another element, Dy has also been used to replace Nd to increase coercivity and thermal stability. H_A of $\text{Dy}_2\text{Fe}_{14}\text{B}$ is $\sim 12577 \text{ kA/m}$ (158 kOe), which is more than twice the value of $\text{Nd}_2\text{Fe}_{14}\text{B}$ ($\sim 5570 \text{ kA/m}$ (70 kOe)) [36]. Hence, Dy can enhance coercivity by increasing H_A . Chen et al studied the effects of Dy concentration on coercivity. The coercivity first increased with increasing Dy content until a maximum value and then decreased [37]. The decrease of coercivity with higher Dy content was due to the larger grain size and weak exchange interactions. However, the high cost of Dy leads to a dramatic increase of cost of $\sim 50\%$

even when the Dy substitution is only ~ 10% [36]. Hence, reducing Dy or decrease the cost of the Dy content source is urgently needed.

2.2.3.3 Magnetic Properties of Nanostructured Nd-Fe-B

In nanocrystalline NdFeB magnets, the grain size varies from a few nanometers to few hundreds of nanometers. The magnets can be isotropic or anisotropic and are usually prepared from powders. Some common fabrication approaches include melt spinning, HDDR (Hydrogenation Disproportionation Desorption Recombination) and wet chemistry methods. The nanostructuring gives rise to novel properties.

Table 2.3 shows some important parameters that define the magnetic properties of permanent magnets. One can see that nanostructured magnetic materials have dimensions in the range of several characteristic lengths. Therefore, these magnets will show properties different from those of conventional permanent magnets.

Table 2.3 Magnetic characteristic lengths[38]

Feature	Length scale
Domain size	10 -10 ⁴ nm
Domain wall width	~ 1 - ~10 ² nm
Exchange length	~ 1 - ~10 ² nm
Exchange interaction range	~10 ⁻¹ - ~1 nm
Superparamagnetic diameter	~ 1 - ~10 ² nm

The Stoner-Wohlfarth theory proposed that there is a critical size below which coherent rotation demagnetization is predominant. This critical size should be at the same range of the single domain particle. Above this size, demagnetization via moment rotation is not favored as the formation of domain walls is involved. The critical size of the single domain is expressed as [39]:

$$R_c = \frac{36\sqrt{A_{ex}K}}{\mu_0 M_s^2} \quad 2.10$$

Where μ_0 is the permeability of empty space, A_{ex} is the exchange constant, K is magneto-crystalline anisotropy constant. According to this equation, the critical size for $\text{Nd}_2\text{Fe}_{14}\text{B}$ is 107 nm and geometry dependent. The Stoner-Wohlfarth theory also predicted that the remnant magnetization (M_r) of a permanent magnetic material should be half the value of saturation magnetization (M_s), i.e., $M_r = 1/2 M_s$ in a material with randomly oriented crystallites. Therefore, the energy product of modern RE magnets is generally limited by the remanence: $(BH)_{\max} \leq (2\pi M_s)^2$. However, some researchers have shown that the remnant magnetization can be enhanced to above the $0.55 M_s$ when refining the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain size. This effect is referred to remanence enhancement [40]. The remanence of melt spun $\text{Fe}_{70.6}\text{Nd}_{13.2}\text{B}_6\text{Si}_{1.2}$ with a grain size of 40 nm was progressively enhanced by exchange coupling.

The physics of exchange coupling was investigated by various researchers. Kneller and Hawig propounded the exchange coupling theory, they proposed that remanence can be enhanced without a loss of coercivity [6]. Coehoorn et al [41]. demonstrated an enhancement of remanence of 85% of saturation magnetization in NdFeB based magnets. In this system, the main phases are the soft FeB phase and a hard phase of $\text{Nd}_2\text{Fe}_{14}\text{B}$, a small content of α -Fe also present. Later, Skomski and Coey [20] theoretically predicted an energy product of 120 MGOe in a nanostructured $\text{Sm}_2\text{Fe}_{17}\text{N}_3/\text{FeCo}$ composite magnet. They also proposed that, to achieve effective coupling, nano size of both phases are required and the size of the soft magnetic grains should be limited to smaller than double the domain wall length of the hard magnetic phase. Nd concentration was reduced in exchange coupled Nd-Fe-B magnets, leading to enhanced corrosion resistance and reduced cost.

In such exchange coupled magnets, the hard magnetic phase has high anisotropy while the soft magnetic phase has high magnetization (2.8). When the two grains are intimately contacted, magnetic moments interactions occurs at the interface of two grains [41]. Demagnetization was initiated from the soft magnetic grains, propagating to the hard magnetic grains. The induced rotation of magnetic moment in the hard phase lowered the coercivity of the magnet. When soft phase size was doubled to that of the domain wall

thickness of the hard phase, the hard phase stiffens the direction of magnetic moments in the soft phase. Hence, a higher field is needed for the nucleation of reversal of demagnetization, leading to high remanence and coercivity[42-47].

Figure 2.8 Exchange coupled magnet hysteresis loop. Exchange coupled magnet possess the advantages of large magnetization of the soft magnetic phase and high coercivity of the hard magnetic phase. The red line represents the soft magnetic hysteresis loop, the blue line represents the hard magnetic hysteresis loop. Dashed line represents the exchange coupled magnetic hysteresis loop.

To obtain effective exchange coupling, both the size of the two phases should be in the range of the hard magnetic domain wall length. Hence, the ideal structure should be a homogenous distribution of nanosized $\text{Nd}_2\text{Fe}_{14}\text{B}$ and soft magnetic phase (e.g., $\alpha\text{-Fe}$, FeCo , FeB)[30, 48-50].

2.2.4 Analysis of Inter-particle Interactions: Henkel Plot

To analyze the inter-particle interactions of ultrafine magnetic particles, remanence curves are commonly used [51-55]. The hysteresis loop of a magnetic material consists of both irreversible and reversible processes. The remanence is a result of irreversible process. Therefore, the remanence curve is an effective tool to separate the irreversible and

reversible contributions to the magnetization process. The Henkel plot is obtained by two magnetization measurements.

- (a) Isothermal remanent magnetization (IRM) measurements. In this process, an external field (H) is applied to a completely demagnetized sample for some time and then switched off. The remanence $M_r(H)$ is measured. A second magnetic field (H), which is larger than the previous field, is then applied and a second $M_r(H)$ is obtained. The process is repeated with increasing H , until the sample is saturated, the saturation value is denoted as $M_r(\infty)$.
- (b) DC demagnetization (DCD) measurement. It is a similar experiment to that of the IRM, but with a magnetic field opposing to the direction in IRM. Each remanence $M_d(H)$ is measured after the application of H in the opposing direction.

The remanence from IRM and DCD measurements can be related by the equation below:

$$M_d(H) = M_r(\infty) - 2 M_r(H) \quad 2.11$$

According to the Stoner-Wohlfarth model, a straight line of $M_d(H)/M_r(\infty)$ vs $M_r(H)/M_r(\infty)$ should be observed for noninteracting particles. Any deviation from this relation is attributed to particle interactions[51, 56, 57].

$$\delta M = \left[\frac{M_d(H)}{M_r(\infty)} \right] - \left[1 - 2 \frac{M_r(H)}{M_r(\infty)} \right] \quad 2.12$$

δM can be arise from[61]:

- (a) non-uniaxial anisotropy
- (b) incoherent rotation
- (c) particle interactions

A typical Henkel plot of NdFeB exchange coupled magnets is shown in figure 2.9 [59, 60]. At low fields, $\delta M > 0$ indicates intergrain exchange coupling, while at large fields, the value of negative δM indicates the dominance of magnetostatic interactions[61].

Figure 2.9 δM vs H plot for $\text{Nd}_8\text{Fe}_{86}\text{B}_6$ (b) δM vs H plot for $\text{Nd}_4\text{Fe}_{77}\text{B}_{19}$ [61]

2.2.5 Coercivity Reversal Mechanism

In multidomain ferromagnets, the coercivity reversal mechanism is usually the nucleation of domain walls and domain wall pinning. When external magnetic is applied to a uniform structure, domains aligned in favorite directions to the external field grow, while domains aligned in unfavorable directions shrink at the same time. Hence, domain walls start to propagate. As discussed, the domain wall energy is determined by anisotropy constant and exchange interaction. In non-uniform regions, e.g., lattice defects, non-magnetic inclusions and external surfaces, there is a local variation in anisotropy and exchange interactions, leading to a change of wall energy when these defects are encountered. These defects can be barriers to domain wall propagation. To force the domain walls to pass through these barriers, extra energy/field is required. If the energy/field is insufficient, the walls will be pinned at defects. Similarly, in the nucleation mechanism, the defects or inclusions have different values of exchange and anisotropy fields, resulting in the formation of sites where formation of new domains are preferred. Hence, the defects can reduce coercivity [62-65].

Researchers have studied the coercivity mechanism in Nd-Fe-B magnets and found that the coercivity mechanism for sintered Nd-Fe-B magnets was controlled by the nucleation mechanism[66], while domain wall pinning was the dominant process for melt-spun Nd-Fe-B magnets [67]. However, the coercivity mechanism of Nd-Fe-B nanoparticles is still not clear.

The coercivity value H_c is highly sensitive to microstructure. For sintered Nd-Fe-B magnets, the coercivity value can be described using Brown's equation based on a nucleation type mechanism. From the temperature behavior of these nanoparticles, a modified expression of Brown's equation is employed to describe the temperature dependence of coercivity. If the demagnetization of these samples are governed by the nucleation field [68-71].

$$\mu_0 H_c(T) = \alpha_K \mu_0 H_N^{\min}(T) - N_{\text{eff}} M_s(T) \quad 2.13$$

Where $H_c(T)$ is the coercivity at different temperatures, $H_N^{\min}(T)$ is the minimum nucleation field, α_K and N_{eff} are microstructure related parameters, $M_s(T)$ is the spontaneous magnetization at different temperatures [72].

The shape of the initial susceptibility curves suggests that a more complex coercivity mechanism should be associated with these samples. Hence, we tested the fitting pinning dominated model put forward by Gaunt [73], as shown below.

$$\left(\frac{H_c}{H_0}\right)^{1/2} = 1 - \left(\frac{75k_B T}{4bf}\right)^{2/3} \quad 2.14$$

where H_c : coercivity, H_0 : the critical field without the thermal activation effect, $4b$: the interaction range between pins, which equals to the domain wall length, k_B : Boltzmann constant, f : maximum force stored for one pin.

2.3 Synthesis of Nd-Fe-B based magnet

Relating the microstructure, magnetism and magnetic properties of Nd-Fe-B based magnets, one can conclude that microstructure and composition plays a vital role in enhancing magnetic properties. Therefore, synthesizing Nd-Fe-B with the desired microstructure and composition is a promising direction for improving magnetic properties. This section describes the development of Nd-Fe-B based magnetic materials, including traditional physical methods and novel chemical methods, with the focus on the latter. The limitations of the physical methods are emphasized and how to overcome these limitations by chemical methods are described.

2.3.1 Physical Processing

After the discovery of $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets, various approaches were employed to fabricate these materials. In conventional physical fabrication of Nd-Fe-B magnets, precursors consisting of elements are formed into ingots by casting in molds. Crushing and sintering are usually followed to generate bulk samples. Such top-down methods cannot obtain the ideal nano structure.

Mechanical techniques, including melt spinning, ball milling and hydrogenation disproportionation desorption recombination (HDDR) approaches are also used. In physical techniques, the starting materials are the expensive rare earth elements, resulting in a high raw material cost. Furthermore, homogeneity is difficult to achieve, and contamination is inevitable in these techniques. In melt spinning, a liquid alloy was ejected *via* an orifice to a fast rotating substrate, allowing the liquid to be cooled and solidify rapidly on the surface of the substrate [74-77]. Nanocrystalline NdFeB magnets with composition near $\text{Nd}_2\text{Fe}_{14}\text{B}$ can be obtained. However, an inhomogeneous microstructure is induced by non-uniform cooling between the surface and inner regions. Atomization has a high production rate and can produce particles with uniform spherical particles. However, this technique is limited in composition range due to the low quenching rate [19]. The HDDR process is well known for making NdFeB material with ultrafine equiaxed and highly textured grains. $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains show strong texture, but thermal stability is limited in these alloys [19, 78]. Mechanical alloying can produce nanocomposite powder but has the drawback of low yield (70%). Nowadays, ball milling is also used to produce Nd-Fe-B. This process can tremendously improve the magnetic properties of Nd-Fe-B permanent magnets because of the high anisotropy induced during milling [79-85]. Fully dense microcrystalline magnets maybe abstained by sintering *via* conventional powder metallurgy techniques, such as cold/hot press, sintering or hot deformation. Ball milling commonly consists of long milling time and multiple processing steps, leading to low productivity and efficiency.

2.3.2 Solution Based Chemical Processing

Conventional mechanical methods, e.g., melt spinning, ball milling and HDDR methods are highly non-equilibrium. A series of processing steps i.e., homogenization at high temperature, melting, casting, milling followed by annealing are necessary to obtain the final product. These multiple steps require large amounts of energy. In addition, these methods use high purity rare earth elements as their starting material. Usually an excess amount of Nd is used to compensate for evaporation loss. Hence, the cost of production is increased. Besides, these conventional techniques have difficulties in obtaining nanoparticles and controlling the microstructure. Therefore, chemical synthesis has attracted significant research interest due to the possibility of better control of particle size. Solution based chemical synthesis has been employed to produce nanostructured FePt, SmCo, CoPt and Nd-Fe-B magnets.

Researchers have attempted to use the wet chemical approach to synthesize $\text{Nd}_2\text{Fe}_{14}\text{B}$ [86-88]. Inspired by the borohydride reduction of transition metals, NaBH_4 was utilized to reduce Nd and Fe salts in aqueous solution. However, as a result of the high negative reduction potential of Nd, most of the attempts failed. For example, in 1997, Lin et. al achieved reduction of Fe ions by NaBH_4 to form only FeB[87]. The source of Nd was obtained from the RD process, which will be discussed later in section 2.4.4. Later in 2005, Haik and others synthesized Nd-Fe-B NPs by this method[88]. The reduction process was performed at 0 °C along with ultrasonication. Nd-Fe-B NPs with particle size ranging from ~20 – to ~60 nm was achieved. However, the product is amorphous since the synthesis temperature is below the glass transition temperature. This leads to superparamagnetic properties with negligible coercivity. Besides, the mechanism of borohydride reduction is not well understood, and the composition of the end product is not very predictable.

Inspired by the self-assembly process of FePt, the thermal decomposition approach was also attempted[89]. NdFeB-oleate complexes were obtained by heating of an organic solvent at 70 °C for 4 h. NdFeB NPs were formed from thermal decomposition of the complex. TEM showed that the particle size was precisely controlled; monodispersed NPs

with particle size of 6-10 nm were observed. However, EPMA data shows a high concentration of C and oxygen arising from the oleate used. There are also limitations which need future improvement in chemical synthesis of Nd-Fe-B based magnetic materials. Usually the chemical techniques are mostly lab-based, difficult to scale up and are associated with limited magnetic properties caused by impurities.

2.3.3 Reduction Diffusion

Inspired by the chemical synthesis of Sm-Co magnets, researchers attempted to employ the wet chemical approaches to synthesize $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles [86-88]. However, most of the attempts failed because of Nd's the large negative reduction potential ($\text{Nd}^{3+} \rightarrow \text{Nd}$, -2.4 eV). Some of the commonly used reducing agents and their reduction potentials are listed in table 2.4. Polyols have a mild reducing potential and hence it cannot reduce the rare earth ions. Alkalides, such as Li, Na and K anions stabilized by the organic crown are powerful reducing agents to reduce rare earths. Na and K naphthalides are also strong reducing agents for the reduction of rare earths. However, these metal naphthalides are very unstable and difficult to handle since they are extremely air-sensitive and moisture-sensitive.

Table 2.4 Standard reduction potential of elements[90]

Oxidation state	Reduced state	Standard reduction potential
Nd^{3+}	Nd	+1.2
Co^{2+}	Co	-0.27
Fe^{2+}	Fe	-0.47
Fe^{3+}	Fe	-0.037
Sm^{3+}	Sm	-2.304
Nd^{3+}	Nd	-2.43
Dy^{3+}	Dy	-2.295
Li^+	Li	-3.05
Na^+	Na	-3.71
K^+	K	-2.93
Ca^{2+}	Ca	-2.87

A vital advance in synthesizing Nd-Fe-B powder is the Reduction Diffusion (RD) technique. Intensive efforts have been devoted in this research area [87, 91-99]. Ca has a high reduction potential of -2.87 eV ($\text{Ca}^{2+} \rightarrow \text{Ca}$, -2.87 eV). In the RD process, Ca or CaH_2 was used to reduce the metal oxides to obtain alloys. Later, the CaO byproduct needs to be removed. Okajima et al employed the RD method to prepare rare-earth based alloys[91]. The final particle size depends on the starting materials, e.g., Nd oxides or Nd salts. Synthesis of micro-size Nd-Fe-B using Nd_2O_3 by the RD process was first reported by Ghandehari [100]. NdCl_3 was also used as the source of Nd [91, 92]. The reactions involved are shown below. In the latter case, CaCl_2 has a high solubility in water, the disintegration process was completed faster during removal of the CaO byproduct by water. CaCl_2 prevents excessive temperature rise, which avoids melting and adhesion of adjacent raw materials. Therefore, the chloride salt content influences the morphology of the final particles. One of the advantages of the RD technique is the low raw material cost as it uses the low cost rare earth oxide/salts as the starting materials rather than the high cost pure metal.

The synthesized sample was obtained in powder form without the need for ball milling. However, in the early demonstrations, the size of the particles were in the micron range. Hence, researchers devoted their effort to synthesizing nano-sized Nd-Fe-B particles by preparing nano-sized precursors by chemical methods, followed by the RD method. Some of the approaches will be discussed in section 2.4.4.

In these preparation methods, the major byproduct was CaO. This is a non-magnetic phase that need to be removed. Several washing agents have been tried to remove CaO [101]. It was found that the deterioration of coercivity was inevitable because of the formation of $\text{Nd}_2\text{Fe}_{14}\text{BH}_x$ phase or a magnetic dead layer during washing by aqueous solution[102]. The reason is considered to be oxidation on the nanoparticles surfaces by the exothermic

reaction between CaO and water. One of the objectives of this work is to investigate methods which can remove CaO without deterioration of the magnetic properties.

2.3.3.1 Reaction Mechanism in Reduction Diffusion

Calcium/calcium hydride has a strong affinity for oxygen and is employed as a reducing agent to reduce the metal oxide to form metal [103-105]. The reaction mechanism of reduction of metal oxide by CaH₂ has been studied by Meerson et al[106]. They have shown that the primary reducing agent in CaH₂ is Ca rather than hydrogen. Tanabe *et al.* studied the reaction mechanism of LaNi₅ formation by reducing La₂O₃ in the presence of Ni. An intermediate product, CaNi₅, is found to form prior to the replacement of Ca by La[104].

It is found that the Ca-Fe phase is not favored in rare-earth transition alloys. Therefore, the formation mechanism differs from that of LaNi. Sidhu *et al.* suggest rare earth oxide was first reduced to the metallic state and the metals diffused across the transition metal particle surface, allowing reaction with the transition metal to form the alloy[95]. Deheri et al. studied the reaction mechanism in the formation of the Nd-Fe-B alloy by RD. Three stages were observed [107].

At 300 °C

At 620 °C

At 692 °C

2.3.4 Solution Based Chemical Processing Followed by Reduction Diffusion

As discussed, the Nd-Fe-B particle size is dependent on the oxide precursor size, hence a recent research trend is to prepare nano-size NdFeB oxides by soft chemistry from the precursors, followed by RD to obtain alloy particles. Solution based chemical processing has been widely used to prepare metal oxide nanoparticles. The large surface area of the nanoparticles is more amenable compared to coarse particles for the reduction of the oxides to form alloys. Nd-Fe-B oxide nanoparticles were prepared by several solution based processes using the techniques shown in table 2.5 [15, 88, 89, 107-114].

Table 2.5 Particle/Grain size, Coercivity, Saturation magnetization (M_s), and remanent magnetization (M_r) of NdFeB based magnets synthesized by chemical approaches.

Synthesis route	Composition	M_s (emu/g)	M_r (emu/g)	H_c (kOe)	Grain/particle size (nm)	$(BH)_{max}$	Ref.	Year
Microwave combustion	Nd ₂ Fe ₁₄ B	95	50	~4	80	-	[111]	2013
Microwave combustion	Nd ₂ Fe ₁₄ B / α -Fe	~70	~135	9	~62	5.2	[115] Co-author work	2017
Sol-gel	Nd ₂ Fe ₁₄ B	102	50	3.9	50	-	[107]	2010
Sol-gel	Nd ₂ Fe ₁₇ / α -Fe	118	76	1.8	~200	-	[116]	2016
Auto-combustion	Nd ₂ Fe ₁₄ B	~80	69	~3.3	~44	-	[114]	2015
Thermal decomposition	Nd ₂ Fe ₁₄ B / α -Fe	71	45	12	25/10	-	[112]	2014
Sol-gel	Nd _{15-x} Dy _x Fe _{77.5} B _{7.5}	-	-	11.8	~60	-	[117]	2017
Soapnut extraction	Nd ₂ Fe ₁₄ B	-	-	0.0022	15-30	-	[118]	2018
Thermal decomposition	Nd ₂ Fe ₁₄ B / Fe ₃ B	~80	42	11.1	25/10	-	[119]	2016
Thermal decomposition	Nd ₂ Fe ₁₄ B	~50	~35	5.4	980 (with CaO)	1.9	[120]	2016

As mentioned, most of the borohydride reduction processes failed to reduce Nd³⁺ due to its high reduction potential. Researchers attempted to reduce Fe iron, Nd ions by borohydride

to form FeB along with Nd oxides. In the RD step, Nd oxides was reduced, Nd atoms diffuse into the transition metal to form Nd-Fe-B particles. The size of the Nd-Fe-B particles thus was determined by the size of the transition metal[96]. However, the magnetic properties were soft with low coercivity. The end product is also not reproducible.

Nd-Fe-B oxide precursors was also prepared by sol-gel[107, 108], solvothermal decomposition[89, 113] auto-combustion[110, 114] and microwave synthesis approaches[111].

The sol-gel technique converts monomers into a colloidal solution precursor for gelation. In the gelation process, polymeric units link and form a continuous network. Porous material containing mixed oxide nanoparticles or oxide nanoparticles embedded in an amorphous matrix can be obtained by dehydration of the gels. This sol-gel technique, followed by the RD technique shows the capability of making nano-size Nd-Fe-B particles with hard magnetic properties. The synthesized Nd-Fe-B magnetic particles show a particle size ranging from 50-200 nm [107]. Alloying of other elements to Nd-Fe-B magnets is possible by this processing technique[117]. With alloying of Dy, the coercivity was found to reach a value of 1663.9 A/m (21kOe).

In the solvent thermal decomposition method, monodispersed α -Fe nanoparticles were firstly prepared by $\text{Fe}(\text{CO})_5$ thermal decomposition. The α -Fe nanoparticles were then injected into a solution containing organic Nd, Fe and B precursors. The solution was then heat treated at 300 °C to produce an α -Fe and Nd-Fe-B mixed composite, followed by RD. Exchange coupled $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ was obtained [112]. A similar method was then used to synthesis the core-shell $\text{Nd}_2\text{Fe}_{14}\text{B}/\text{Fe}_3\text{B}$ nanocomposite[119]. This method produces uniform size $\text{Nd}_2\text{Fe}_{14}\text{B}$ nanoparticles.

Auto-combustion followed by the RD method was also studied. A nitrate salt solution of Nd, Fe and B was heated to remove water. Glycine or citrate acid was used to stabilize the metals by forming complexes with metal ions. At the same time, glycine/citrate acid reacts with NO_3^- , releasing large amount of heat, leading to auto combustion, which generates

nano-size Nd-Fe-B oxide powder [110, 114]. The microstructure and final phases can be controlled by various processing parameters in the combustion process, e.g., metal to fuel ratio, nature of the heating, heating rate etc.

The mixture of metal nitrates and glycine can also be heated by microwave irradiation. Microwave heating is more homogenous owing to dielectric heating, the heating and mixing of precursors is at molecular level. These methods facilitate a more uniform product [111, 115]. Details of microwave combustion will be discussed in section 2.3.5.

2.3.5 Microwave Processing

In this work, a microwave system was used as the source of energy to ignite auto combustion. Microwave heating employed the phenomenon of dielectric heating. Polar molecules that have a net electrical dipole moment align with the electromagnetic field. The microwave has an oscillating electric field. As the field alternates, molecules reverse their directions to chase the electric field. Molecules rotate, pull/push or collide, releasing heat. Hence, heating is at molecular level. Processing needs less time and consumes less energy. Therefore, this is a promising method for obtaining homogenous product.

2.3.5.1 Reaction mechanism in Solution Combustion Synthesis

Solution combustion synthesis (SCS) is synthesis accomplished in a solution containing fuel and oxidizer. The redox reaction between the oxidizer and the fuel is highly exothermic, the heat released is sufficient to maintain a self-propagated chemical reaction. A common oxidizer is hydrated metal nitrates and fuels can be chosen from a broad range, e.g., urea, citric acid, glycine. As a consequence of the exothermic reaction, the solution temperature increases, leading to the increase of reaction rate. Hence, the process becomes self-accelerating. The process finishes only when all the reactants transform into products.

In a glycine – metal nitrate system, metals (Me), carbon (C), and hydrogen(H) are considered as reducing elements. Oxygen(O) is considered as the oxidizing element. The

gaseous products are assumed to be H_2O , CO_2 , and N_2 . Hence the reaction is as follows[121]:

There are two modes of SCS, i.e., self-propagating combustion and thermal explosion (or volume combustion). In the first case, a small volume of solution/gel is heated until reaction is ignited, the flame wave then propagates towards the rest of the volume. In the second case, the entire volume is uniformly heated to the boiling temperature of the solvent (figure 2.10, stage I), followed by evaporation of the free and a portion of the bounded water in stage II. In stage III, the temperature increases to the ignition temperature (T_{ig}) and drastically increases to a maximum temperature (T_{m}) in stage IV[122]. Since microwave combustion belongs to volume combustion, this section focus on the fundamentals and literature of volume combustion mode.

Figure 2.10 Temperature–time profile for synthesizing Fe_2O_3 powder using $\text{Fe}(\text{NO}_3)_3$ - glycine solution via the volume explosion mode[122]

Semenov determined that the critical condition for volume combustion mode to occur is when the heat release rate from the reaction is larger than the heat exchange rate with the

environment[123]. Phase transformation, e.g., melting or evaporation and decomposition typically results in a sharp increase in the reaction rate. In these cases, the critical temperature of volume combustion is identified to be the phase transition temperature, it is weakly related to other system parameters. Strong evidence showed that chemical transitions induced the self-sustaining solution combustion in the case of the iron nitrate–glycine system[122]. Figure 2.11 represents results of the thermogravimetric and differential thermal analysis (TGA/DTA) of iron nitrate. Two major conclusions are: (i) the temperature for system ignition is in the range of 125–150 °C, which fits with the nitrate decomposition temperature and (ii) T_{ig} is independent of the initial mixture composition. Deshpande et al. suggested that at T_{ig} , either HNO_3 or its decomposition products react exothermically with glycine to trigger the self-combustion reaction[122]. Thus, T_{ig} of glycine - iron nitrate is related to the phase transformation temperature, i.e., decomposition temperature of the oxidizer.

Figure 2.11 Thermogravimetric and differential thermal analysis for iron nitrate decomposition and its combustion characteristics with glycine [122]

The mechanism of SCS implies information of the elementary stages of the process, kinetics of each reaction and the formation sequence of the intermediate and final phases. The studies are based on DTA, TGA and differential scanning calorimetry (DSC) results

of the precursors[122]. More sophisticated analysis also involves the thermodynamics of SCS, the mass spectrometry and X-ray diffraction [124].

The mechanisms of combustion reactions in nickel nitrate–glycine solution was studied based on the TGA/DTA results[124]. Combining with previously work[125], the authors concluded that glycine started to decompose at ~ 243 °C, the main product of this stage is NH_3 . In the temperature range of 312 °C – 457 °C, the main decomposition product were CO and HNCO. There were several stages in the decomposition of nickel nitrate hexahydrate as well. In the temperature range of 37 °C – 77 °C, water evaporated. In the temperature range of 147 °C – 187 °C, nickel nitrate partially decomposed to form $\text{Ni}(\text{NiO}_3)(\text{OH})_{0.25} \cdot \text{H}_2\text{O}$, which decomposed in the third stage (257 °C –297 °C) according to the following reaction:

Figure 2.12 summarizes the reaction mechanism. The authors showed that, if the gases that trigger the combustion were removed, combustion did not take place. If the system is heated at a sufficiently slow rate, the flame did not occur. This was due to the time to heat the solution to ignite temperature was long enough that all the responsible gases escape from the system.

Figure 2.12 Schematic of combustion synthesis for metallic nickel[124]

2.3.5.2 Fundamentals of Microwave Processing

Microwave are electromagnetic waves with frequencies ranging from 300 MHz to 300 GHz. The most commonly used frequency is 2.45 GHz. Both the electric and magnetic components of the wave contribute to the interaction with the materials. Loss tangent, expressed by equation 2.20, is used to characterize the efficiency of the absorption of the materials and conversion of the energy to heat.

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad 2.24$$

Where ϵ' is the relative dielectric constant and ϵ'' is the relative loss factor indicating the ability of the materials to transform the energy from electromagnetic energy to heat[126]. δ is the phase difference between the oscillating electric field and the polarization in the materials.

Another important parameter is the power penetration depth, D_p , which indicates the depth at which the power density is reduced to $1/e$ (37%) of the value of the surface.

$$D_p = 1/\alpha \quad 2.25$$

$$A = 2\pi f \left(\frac{\mu_0 \mu_r' \epsilon_0 \epsilon_r'}{2} \right)^{1/2} [(1 + (\tan \delta)^2)^{\frac{1}{2}} - 1]^{1/2} \quad 2.26$$

Where f is the microwave frequency, μ_0 is the permeability of empty space, ϵ_0 is the permittivity of empty space, μ_r' is the relative permeability, ϵ_r' is the relative dielectric constant. For good conductors, such as metals, the penetration depth is very low.

The use of microwave energy induces direct heating of materials within the penetration depth, leading to a near instantaneous temperature rise, eliminating the need to heat the container. The penetration depth increases with increasing thickness, resulting in a uniform temperature profile in the volume.

The microwave applicator consists of two major types, multimode and single mode. In a multimode applicator, the cavity is larger than the incident wavelength. Hence the resonant cavity can contain numerous electromagnetic fields. The field profile inside the cavity is

the superimposition of different waves propagating in various directions because of the reflection from the chamber walls. The homogeneity in this kind of cavity is poor and rotation of the sample plate is needed to enhance homogeneity. The advantage of this kind of system is the possibility of high volume production. In single mode cavity, a well-defined spatial configuration of the field exists. At least one of the chamber's dimensions is of the same order as the length of the microwave. This mode has more uniform field profile in the chamber.

2.3.5.3 Microwave and Solution Combustion Processing

Solution combustion synthesis (SCS) ignited by a microwave can be categorized by the type of fuel, oxidizer and solvent. Some of the most frequently used components in microwave combustion are summarized in table 2.6. The dielectric properties are also presented. It can be seen that the dielectric properties are comparable or higher than that of water, making these reaction systems suitable for microwave combustion.

Table 2.6 Commonly used reactants in the synthesis of reactive mixtures by solution combustion processing. The loss tangent at 2.45 GHz and room temperature is reported [121, 127-130].

Oxidizer	$\tan \delta$	Fuel	$\tan \delta$	Solvent	$\tan \delta$
Metal nitrate/metal nitrate hydrate	1.10-1.23 ^a	Urea	n/a	Water	0.123
Ammonium nitrate	<0.015-0.005	Glycine	n/a	kerosene	0.0045
Nitric acid	~1.6 ^b	Sucrose	0.09 ^c , ~0.4 ^d	Benzen	n/a
		Glucose	~0.14 ^e	Ethane	0.941
		Citric acid	n/a	Methanol	0.659
		Carbohydrazide	n/a	Furfuryl alcohol	n/a
		Oxalyldihydrazide	n/a	2-Methoxyethanol	0.41
		Hexamthylenetetramine	n/a	Formaldehyde	n/a
		Acetyl acetone	n/a		

^a For $\text{Al}(\text{NO}_3)_3$, $\text{Cr}(\text{NO}_3)_3$ and $\text{Fe}(\text{NO}_3)_3$, concentration of 500 mM in water at 20 °C; ^b Nitrate concentration of 0.2M; ^c pure sucrose; ^d 20% (w/w) of sucrose in water at 24 °C; ^e 10%(w/w) of D-glucose in water at 20 °C; n/a= not available.

In microwave heating, the entire reaction mixture interacts with the microwave. It is easier to have a volumetric ignition of SCS, this ignition is similar to the thermal explosion mode in solid state combustion, assuring a homogenous reaction in the entire volume. Different heating rates also result in a range of microstructures. For example, microwave ignition of water solution of magnesium nitrate and urea results in a nanosheet structured MgO, while traditional heating result in a cubic structure[131]. A recent work on the preparation of LaFeO₃ by microwave SCS in single mode applicator revealed that a higher maximum combustion temperature was obtained in microwave combustion, which explains the larger particles obtained in microwave combustion.

Microwave combustion processing is a well-established technique in some materials, such as ceramics[132, 133], catalyst[134-136], silicides[137-139] and intermetallic compounds[140-143]. In the synthesis of magnetic materials, various ferrites with relatively good properties were processed by such approaches[144-147], demonstrating that mixed oxide nanoparticles can be prepared by microwave combustion. Swaminathan et al. successfully synthesized Nd-Fe-B nanomaterials from Nd-Fe-B oxides by a microwave assisted heating method[111]. However, the microwave applicator was a domestic microwave, where temperature monitoring is not possible, and power is controlled by switch on-off time. The relationship between process parameters, morphology and property of final product have yet to be systematically understood.

2.3.5.4 Microwave and Solid Reactions

The microwave initiated synthesis of solid reactants can be dated back to the work of Dalton *et al.*[148], which focused on ceramic materials, especially carbides. Carbides have excellent capability of absorbing microwave energy. The heating of metal by microwave was thought to be impossible at that time, until Roy et al. use the microwave for combustion synthesis between pure metallic materials[140, 149]. As mentioned in 2.4.5.1, the multi-mode applicator suffered from non-uniformity of microwave, hence a hybrid heating was invented [149]. In hybrid heating, microwave susceptor elements were used, leading to combined heating of microwave and conventional heating. Table 2.7 shows the processing

of solid reactants by microwave heating. In the field of permanent magnetic materials, many attempts were carried out to sinter ferrites powders to form bulk magnets[150-152]. Higher density or shorter sintering duration was observed. Gjoka et al. attempted sintering of Nd-Fe-B powders by microwave, and experimental evidence of sintering of Nd-Fe-B powder was provided[153]. However, there is no previous report on the synthesis of Nd-Fe-B through microwave induced solid state reaction. A reduction of TiO_2 and B_2O_3 by Mg as shown in table 2.7 was reported. Inspired by work, processing of Nd-Fe-B through RD induced by microwave energy was performed.

Table 2.7 Selected research results on microwave and combustion synthesis from solid state reactants carried out by multimode applicators

Combustion reaction	Microwave power Frequencies Heating type	Ref
$26\text{Al} + 3\text{Fe}_2\text{O}_3 + 3\text{Co}_2\text{O}_3 + 3\text{Ni}_2\text{O}_3 + 6\text{CuO} \rightarrow 4\text{FeCoNiCuAl} + 11\text{Al}_2\text{O}_3$	Not specified	[154]
$\text{MoO}_3 + 3\text{Zn} \rightarrow \text{Mo} + 3\text{ZnO}$	850 W, 2.45GHz; hybrid heating (SiC block susceptor)	[155]
$\text{Co} + \text{Si} \rightarrow \text{CoSi}$, $\text{Co} + 2\text{Si} \rightarrow \text{CoSi}_2$	0-3000 W, 2.45GHz; hybrid heating (SiC block susceptor)	[156]
$8\text{Al} + 3\text{Fe}_2\text{O}_3 \rightarrow 2\text{Fe}_3\text{Al} + 3\text{Al}_2\text{O}_3$	1400 W, 2.45GHz, pure microwave heating	[157]
$13\text{Al} + 3\text{ZrO}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Al}_3\text{Zr}$	800 W, 45GHz; hybrid heating (SiC powder susceptor)	[158]
$\text{TiO}_2 + \text{B}_2\text{O}_3 + 5\text{Mg} \rightarrow \text{TiB}_2 + 5\text{MgO}$	850 W, 2.45GHz; hybrid heating (SiC block susceptor)	[159]
$\text{MoO}_3 + 3\text{Zn} + 0.5\text{C} \rightarrow 0.5\text{Mo}_2\text{C} + 3\text{ZnO}$	850 W, 2.45GHz; hybrid heating (SiC block susceptor)	[160]

2.4 Questions to Answer Based on the Literature

As discussed in the literature review, great progress has been seen in the development of Nd-Fe-B based hard magnets. Various methods have been attempted to improve magnetic properties and to achieve the desired nanostructured magnets. Nevertheless, some questions still need to be addressed.

Based on the literature review above, the following questions/gaps still remains and need to be answered. Firstly, how to reduce the cost of processing Nd-Fe-B based hard magnets

due to the use of rare earth elemental powders. Secondly, the poor temperature stability makes it undesirable to use the Nd-Fe-B magnets at elevated temperatures. Heavy rare earths, such as Dy, Tb, are currently used to improve the thermal stability. However, this further increases the cost. Hence, minimum use of heavy rare earth and cost-effective processing approaches remains another question and challenge. Thirdly, solution based chemical synthesis followed by RD has been reported, which successfully synthesized $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic powders. However, there is still a large gap between the experimental results of magnetic properties and theoretically predicted values. Therefore, synthesis and optimization of the nanostructure to enhance magnetic properties remains a challenge. Furthermore, previous chemical synthesis of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and exchange coupled $\text{Nd}_2\text{Fe}_{14}\text{B}$ requires long processing time and uses multiple equipment. How to synthesize $\text{Nd}_2\text{Fe}_{14}\text{B}$ chemically with relatively simple and short processing is another challenge. The understanding of the reaction mechanisms and influence of microwave processing parameters on the magnetic properties of $\text{Nd}_2\text{Fe}_{14}\text{B}$ still remains to be a question and needed to be investigated.

2.5 Summary of the Thesis' Contribution to Literature

The focus of this thesis is the synthesis of Nd-Fe-Co-B based permanent magnetic materials. We developed a novel microwave chemical processing method to synthesize Nd-Fe-Co-B nanoparticles with enhanced magnetic properties. **The contributions of this thesis to the literature are:** The influence of microwave processing parameters on the structure and magnetic properties was studied. The reaction mechanisms were determined. The structure, magnetic behaviour and magnetic properties were investigated. The detailed conclusions of the thesis are:

(1) Nd-Fe-Co-B mixed oxides, with crystal sizes ranging from 20 nm to 60 nm, were synthesized by microwave assisted combustion. $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ nanoparticles, with crystals, in the same size range as these oxide powders, were obtained by reduction of these oxides. The microwave energy resulted in the evaporation of water. Subsequently, in microwave initiated auto combustion step. N-H , COO^- and NO_3^- ions took part in self-

propagating combustion reaction. This combustion led to the formation of CoFeO_4 , NdFeO_3 , Nd_3FeO_6 and Fe_2O_3 . Higher microwave power led to higher combustion temperature, which led to larger crystal size of Nd-Fe-Co-B oxide. The crystal size of $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ followed the same trend as that of the oxide. The coercivity of $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ particles increased from 6.2 kOe to 8.8 kOe when the crystal size increased from 21 nm to 63 nm.

(2) $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$ hard magnetic nanoparticles were successfully synthesized by low cost, green, one-pot microwave synthesis. The heating source was only by microwave irradiation using a single microwave chamber. The use of a vacuum furnace is eliminated. We investigated the structural and magnetic properties of the heavy rare earth free $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$ exchange coupled nanoparticles. The formation mechanism of these nanoparticles were also studied for both oxide and alloy formation. The magnetic properties of the $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$ nanoparticles were highly sensitive to magnetic alignment. After alignment, M_r/M_s increased from 0.56 to 0.88. With a high remanence of 99 emu/g, the maximum energy product of these hard-magnetic nanoparticles reached a value of 11.4 MGOe, which is the highest for $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanoparticles synthesized by chemical approaches.

(3) This work reports for the first time the room temperature and temperature dependent behaviour of $\text{Dy}_x\text{Nd}_{15-x}\text{Fe}_{67}\text{Co}_{10}\text{B}_8$ ($x=0, 3, 6, 9$) hard magnetic nanoparticles. The effect of Dy substitution on the microstructure and magnetic properties were studied. With increasing Dy content, the unit cell of $(\text{Nd},\text{Dy})_2(\text{Fe},\text{Co})_{14}\text{B}$ contracted and uniform distribution of Dy within the particle was observed. The coercivity increased from 7.9 kOe to 14.5 kOe when the Dy content increased from $x=0$ to $x=9$. It was found that the particles can be crystallographically aligned by an external magnetic field. After alignment, remanence and $(\text{BH})_{\text{max}}$ were significantly enhanced. For the composition corresponding to $x=3$, the highest $(\text{BH})_{\text{max}}$ of 12.6 MGOe was obtained due to minimum reduction of remanence and strong exchange coupling effects. Thermal coefficients improved with increasing Dy content. The coercivity mechanism was investigated by studying the temperature dependent magnetic properties. It was found that the controlling mechanism is the nucleation of reverse domains.

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Chapter 3

Experimental Methodology

In this chapter, the experimental procedures for the synthesis, characterization and property evaluation are discussed. The synthesis of Nd-Fe-Co-B based nanostructured magnetic materials by the microwave chemical processing approach is described. The rationale for the selected methodology is described. Characterization techniques utilized for thermal, structural and property measurements are described in this chapter. These techniques include X-ray diffraction (XRD), Rietveld refinement, transmission electron microscopy (TEM), Scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), vibrating sample magnetometry (VSM) and Physical properties measurement system (PPMS). The working principle and parameters used are stated.

3.1 Rationale for Selection of Methods and Material

Following the discovery of $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets, several relevant approaches were employed to fabricate these high performance magnets. In the conventional methods, precursors consisting of elements are cast in molds to form ingots. Crushing and sintering are followed to generate bulk materials. This approach has limited control of the microstructure. Other physical techniques include melt spinning[1-4], sintering[5-7], hydrogen–disproportionation–desorption–recombination (HDDR)[8-10] and mechanical alloying [11]. However, in these physical methods, contamination, inhomogeneity and long processing time are inevitable. Moreover, the high purity elements, especially rare earth metals, used in these methods are expensive, leading to high production cost. The bottom-up chemical approaches are expected to produce more homogeneous particles. Additional elements can be easily alloyed by adding them in the precursor solution [12]. The precursors used in chemical methods are usually metal salts, which leads to significant reduction in cost. Some of the chemical processing methods for Nd-Fe-B includes borohydride reduction [13], thermal decomposition [14], sol-gel [15], auto-combustion [16] etc. In this work, microwave based chemical synthesis was employed for synthesizing Nd-Fe-Co-B powders. Some distinct advantages of the microwave approach includes: (a) The metal ions were homogeneously mixed at a molecular level. (b) Homogeneous heating was achieved by volumetric microwave heating, leading to better control over the microstructure and better homogeneity. (c) The sol gel and auto-combustion methods need overnight heating and multiple-stage heat treatment [16-19], on the other hand microwave combustion is completed in less than 10 min without a preheating stage. Thus, microwave processing is more energy efficient and yields improved productivity.

The major limitation of Nd-Fe-B magnetic materials are their low T_c (~ 585 K) [20-22]. Al, Si and Ga alloying in NdFeB can enhance thermal stability [23]. However, only Co can replace Fe for the entire Fe content and meanwhile retain the $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystal structure [24]. Co is also the only element that can significantly change the magnetic ordering temperature. Alloying Co in NdFeB magnet has been studied by several researchers [25-33]. T_c increases with increasing cobalt content. However, adding Co can also reduce

coercivity[24, 34]. Hence, 10% of Co is substituted to improve T_c while retaining the coercivity [35]. Heavy rare-earth, e.g., Dy, can enhance coercivity by increasing the magnetocrystalline anisotropy field (H_A) since H_A of $Dy_2Fe_{14}B$ (~ 12580 kA/m) doubles the H_A of $Nd_2Fe_{14}B$ (~ 5570 kA/m)[36]. Therefore, Dy was added to increase coercivity. Thus the simultaneous replacement of Nd by Dy and Fe by Co can simultaneously increase thermal stability and enhance coercivity.

3.2 Synthesis of Nd-Fe-Co-B based Magnetic Materials

In this section, the synthesis of Nd-Fe-Co-B based magnetic particles by microwave combustion, RD and by-product removal are described. The procedure for magnetic alignment of the synthesized particles is also described. Spark plasma sintering of particles to form bulk material is also described.

3.2.1 Synthesis of Nd-Fe-Co-B Based Magnetic Particles – Microwave Combustion Followed by Reduction Diffusion

3.2.1.1 Microwave Combustion

Commercially available $Nd(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9%), $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma Aldrich, 98+%), $Co(NO_3)_2 \cdot 6H_2O$ (Alfa Aesar, 98%), H_3BO_3 (Alfa Aesar, 99.8%) and $Dy(NO_3)_3 \cdot 5H_2O$ (Sigma Aldrich, 99.9%) were used as precursors in the microwave combustion process. Glycine (Sigma Aldrich, purity $\geq 99\%$) was used as the fuel. All precursors were weighed according to the nominal compositions and dissolved in Millipore water. For synthesizing 2 g of powder, 25 ml deionized water and 1 ml Nitric acid was used to dissolve the salts. Glycine was also dissolved in the solution, the amount of glycine is according to the molar ratio of 1:1 (salt: glycine). The solution was manually stirred until a red homogenous solution was obtained. The solution was loaded into a 250 ml quartz beaker. Microwave combustion was carried out in the microwave processing system (Dawnyx Technologies Pte Ltd, HTVF-3). The quartz beaker was placed at the center of the base of the microwave chamber. The maximum microwave output is 2.8 kW.

The solution temperature can be detected by pyrometers attached to the microwave. The solution was heated until ignition by microwave irradiation using a range of microwave power (1.2 kW, 1.8 kW, 2.4 kW and 2.8 kW) until ignition. Under the influence of microwave induced heating, water and other volatiles gradually evaporated, resulting in a red viscous gel. Further heating resulted in combustion between nitrate salts and glycine. After combustion, Nd-Dy-Fe-Co-B oxide nanoparticles were obtained. The powder was collected from the quartz beaker and transferred to a mortar for grinding.

3.2.1.2 Reduction Diffusion

To synthesize the Nd-Fe-Co-B particles, the synthesized mixed oxide powders were reduced in the RD process by the use of a reducing agent CaH_2 (Alfa Aesar, purity 92%). To reduce 1 g of mixed oxide, 1.5 g of CaH_2 was manually ground and mixed with the oxide obtained by microwave combustion. A hydraulic press was used to compact the mixture. The compacted pellet was then heat treated in a vacuum furnace under a high vacuum (better than 10^{-5} torr). It is found that the formation of Nd-Fe-B alloy occurred at 800°C [18]. Therefore, RD was performed at 800°C for a range of durations (0.5 h, 2 h and 4 h). The sample was removed after furnace cooling to room temperature. Figure 3.1 shows a flow chart of the synthesis route described in section 3.2.2.1 and section 3.2.2.2.

Figure 3.1 Microwave based chemical synthesis consisting of microwave combustion, followed by RD in a vacuum furnace

3.2.2 Synthesis of Nd-Fe-Co-B based Magnetic Particles – One Pot Microwave Processing

One pot microwave processing consists of two steps, microwave combustion and microwave reduction. Microwave combustion processing has been described in section 3.2.1.1. The oxides obtained by microwave combustion was mixed with reducing agent CaH_2 in the same ratio as described in 3.2.2.2. The pellet of this mixture was formed by cold pressing. This pellet was placed back into the same microwave chamber as that of microwave combustion. The set-up of this microwave reduction is shown in figure 3.2. SiC has an excellent capability to absorb microwaves, it can be heated to high temperatures by the microwave[37]. Hence, a 250 ml quartz beaker filled with SiC powder was prepared as a microwave susceptor. This susceptor was placed inside a thermal insulator (alumina silicate refractory ceramic fibers). The sample was placed on top of the SiC powder bed. An opening of 3 cm diameter at the center of the lid of the thermal insulator allowed the infrared thermometer to detect sample temperature. Evacuation of the microwave chamber was carried out until vacuum reached a level of 10^{-2} mbar and the chamber was filled with Ar to 1 atm, this process was carried out 3 times. This is to ensure that an inert atmosphere was created to accomplish the reduction diffusion process. The sample was heated by microwave irradiation to 800 °C by a heating rate of 5 °C/min. The heating rate was controlled by the microwave synthesis system, in which microwave power were modulated by the program set inside the microwave synthesis system. The sample was heat treated at 800 °C by microwave for 2 h, followed by cooling down with the microwave chamber. Figure 3.3 shows a schematic diagram of the flow chart of this one pot microwave synthesis.

Figure 3.2 Schematic of the microwave reduction setup

Figure 3.3 One-pot Microwave chemical synthesis route consists of microwave combustion, followed by microwave reduction

3.2.3 Synthesis of Nd-Fe-Co-B based Magnetic Particles – Byproduct Removal

The resulting powders after reduction contain CaO by-product. The nonmagnetic CaO has to be removed to increase magnetization. The reaction between CaO and water is highly exothermic, which may lead to surface oxidation of the particles. Therefore, several approaches have been used to remove the CaO byproduct, such as the use of dilute acetic acid, glycerol, EDTA and NH_4Cl /methanol. Details of these methods are listed (table 3.1). After the removal of byproduct, the sample was vacuum dried to obtain dried powder.

Table 3.1 Methods and agents for byproduct removal

Agent	
A	Diluted acetic acid (0.1vol % in DI water)
B	Glycerol and methanol mixture(volume ratio 1:1)
C	EDTA dissolve in mixture of triethanolamine and methanol(volume ratio 1:1)
D	2 gram NH_4Cl dissolve in 100 ml methanol

3.2.4 Synthesis of Nd-Fe-Co-B based Magnetic Particles – Magnetic Alignment

The magnetic particles were aligned by an external magnetic field. A small amount of powder (less than 2 mg) was suspended in an adhesive (Yamayo super glue, Singapore) and sonicated for 5 min. The suspension was then dropped onto a glass slide and placed on an electromagnet (Field control electromagnet, model: DXSB-178, China). The sample was subjected to a 2 T (20 kOe) external uniform magnetic for 20 min during the drying of the adhesive. Figure 3.4 shows the magnetic alignment experimental set-up.

Figure 3.4 Set up of powder sample alignment by an electromagnet

3.3 Materials Characterizations

Phase transformation during microwave combustion, reduction and spark plasma sintering were examined by X-ray, SEM, TEM and FTIR techniques. Property evaluation was carried out by VSM and PPMS techniques. It is important to understand the working principles of these techniques to correctly and fully use of these instrumentations.

Therefore, the working principles of these characterization techniques are briefly discussed in this section.

3.3.1. X-ray Diffraction

X-ray diffraction (XRD) is an important non-destructive analytical tool for materials characterization to obtain information in the level of atomic scale for both crystalline and amorphous materials [38]. XRD has acted as the cornerstone of twentieth century science. In 1912, Max von Laue first discovered the crystal diffraction phenomenon of X-Ray. In 1913, W. H. Bragg and his son W. L. Bragg successfully applied the technique to structure determination of crystalline materials such as metals, alloys, minerals, inorganic and organic materials. Subsequently, the XRD technique was used to quantify crystalline phases, determine precise lattice parameters, determine crystallite size and strain, etc[39].

When an individual atom is hit by a beam of X-rays, the electrons of that atom oscillate around its mean position. The X-ray photon is absorbed by the atom and another photon with the same energy emitted, this process is known as scattering. For many atoms arranged in a solid material, the scattered waves from all atoms interfere with each other. If the scattered waves are coherent (in phase), the waves are constructive and diffracted beams are obtained in specific directions. Figure 3.5 shows the working principle of the X-ray diffractometer. When a beam of incident X-rays interact with the crystal lattice, interference patterns will be generated. When the interference patterns are constructive and the diffraction angle θ satisfies Bragg's law, the signals will be picked up by the XRD detector[40]. To derive Bragg's law, each plane of atoms in the material is assumed to partially reflect the incident wave like a half-silvered mirror. Consider an incident beam at an angle θ , the criterion for the constructive wave is that the scattered X-rays should all be in phase across a wavefront, YY'. The path lengths from wavefront XX' to YY' for the rays should differ by exactly an integral number (n) of wavelengths λ . Hence, the path difference δ must be

$$\delta = n \lambda \quad 3.1$$

Since lines AB and AC are also wavefronts,

$$\delta = BD + CD = 2 CD \quad 3.2$$

From elementary trigonometry,

$$\delta = 2 CD = 2 AD \sin \theta \quad 3.3$$

Since AD is the interplanal distance d, therefore

$$\delta = 2d \sin \theta \quad 3.4$$

By combining equation 2.1 and 2.4,

$$n \lambda = 2d \sin \theta \quad 3.5$$

The XRD measurement were performed by the Bruker D8 Advance X-ray diffractometer, which used the Cu-K α radiation ($\lambda = 0.154$ nm). Identification of the phases was performed by the MATCH program. To quantitatively analyze the phases, scanning was done in the 2θ range of 10-120 ° with a low scan rate at 0.1 °/s and a step size at 0.01 °. The analysis of the mass fraction of each phase and the studies of crystal structure was achieved by using Rietveld refinement, which was facilitated by the TOPAS 4.1 program.

Figure 3.5 Working principle of X-ray diffractometer

3.3.1.1 The Rietveld Method

The conventional powder X-ray diffraction approach is ideal for identification of compounds. However, it has several limitations; it is difficult to determine the structural parameters when multiple phases exist in the sample due to the overlap of peaks. In the Rietveld method, the crystal structures information is analyzed by fitting the entire diffraction profile to a calculated profile. The contribution of the individual phases to the

overlapping peaks can be distinguished by fitting to suitable structural models. Thus, the structural information can be determined [41, 42].

The Rietveld analysis of the structural information is obtained by minimizing the difference between a suitable crystal model and the experimental measured data. The theory for the Rietveld refinement is the least-squares minimization refinement algorithm (equation 2.6). Crystallographic information including crystal symmetry, atomic coordinates, lattice parameters and site occupancies can be determined by the model[43].

$$M = \sum_{i=1}^n w_i (y_i(\text{obs}) - y_i(\text{cal}))^2 \quad 3.6$$

Where $y_i(\text{obs})$ is the intensity measured at point i after background correction, w_i is the weight related to standard deviation, $y_i(\text{calc})$ is the calculated intensity.

The Topas 4.1 program was used to perform the Rietveld refinement. A pseudo-Voigt peak profile, which combines both the Lorentzian (size broadening effect) and the Gaussian (strain broadening effect) functions, was utilized to model the experimental diffraction peak shape[44].

The refinement starts with fitting the full scale experimental XRD pattern using a polynomial function of degree 1-2, zero error correction, and refinement of scale factors and lattice parameters. All parameters were systematically refined until the refinement was converged with a GOF (goodness of fitting) less than 2.

3.3.2. Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an efficient and versatile technique to obtain detailed microstructural information via generating high magnification and high resolution images. It can investigate the crystal structure, orientations and the chemical compositions of samples by diffraction pattern, X-ray and electron energy analysis techniques. The magnification may be up to 1,000,000x and the resolution can be ~ 1 nm. This technique

allows us to investigate the symmetry, crystal structure and the orientation of the crystals in the sample [45].

In 1925, Louis de Broglie suggested that electrons had wave-like characteristics. It did not take long for Knoll and Ruska (1932) to propose the idea of an electron microscope, for which Ruska received the Nobel Prize. The TEM was developed for commercial use four years later, the first commercial TEM was a Metropolitan Vickers EMI[46]. The major reason for using a TEM is its high resolution. The resolution of a TEM means the smallest separation at which two points can be distinguished, the resolution can be expressed by the following equation [47]:

$$d = \frac{0.61 \lambda}{n \sin(\alpha)} \quad 3.7$$

Where λ represents the wavelength of the electrons, n represents the refractive index and α represents the aperture angle.

As electrons have a much smaller de Broglie wavelength ($\lambda = \frac{h}{\sqrt{2meV}}$) compared to light, the resolution is much higher than that of a light microscope. TEM images are generated *via* 2 stages. In stage A (figure 3.6), the incident electron beam is scattered by a specimen. The scattered radiation passes through an objective lens and is then focused by the objective lens to form the primary image. A diffraction pattern is produced at the back focal plane. The diffraction pattern is the Fourier transform of the scattered electron wave. The primary image is formed by Fourier transform of the diffraction pattern. In stage B, the primary image is magnified by additional lenses, forming a highly magnified image[48].

High resolution TEM images (HR-TEM) and selected area diffraction (SAED) patterns were employed to investigate the crystal structure of Nd-Fe-Co-B based nanoparticles. The TEM images are also used to determine the particle size and morphology. The inter-planar distance of the crystal lattice obtained by HR-TEM images was used to validate the crystal structure. The energy dispersive spectrum (EDS) and the corresponding element map from the scanning transmission electron microscopy (STEM) mode was used to identify the

elemental composition and distribution within the particles. Powder samples were first dispersed in ethanol and sonicated for 10 min. The particle/ethanol dispersion was then dropped onto a copper grid and vacuum dried. JEOL 2010 or JEOL 2100 F TEM at an operating voltage of 200 kV and under a vacuum better than 10^{-5} torr were used for TEM imaging [49].

Figure 3.6 Working principle of Transmission Electron Microscopy [49]

3.3.3 Differential Scanning Calorimeter

Differential Scanning Calorimetry (DSC) was used to study the reaction mechanism, reaction kinetics and activation energy of the microwave combustion and reduction process. DSC is a thermal analytical tool which can record heat flow in isochronal or isothermal conditions. In the isochronal condition, the heat flow is detected by the temperature difference between the sample and a reference (figure 3.7(a))[50]. The temperature of the sample holder is increased linearly. The temperature difference between the sample and

the reference can be detected and recorded. The heat flow is usually due to chemical reactions, physical phase changes, etc, resulting in a peak or a dip in the heat flow versus temperature profile (figure 3.7(b)) [51, 52] . For a process that releases heat, such as crystallization or an exothermic chemical reaction, an upward peak can be observed. For a process that absorbs heat, such as melting or endothermic chemical reactions occurs, a downward dip can be observed. The temperature of the peak/dip indicates the temperature at which the reaction/phase transformation take place. The activation energy can be evaluated by the Kissinger model:

$$\ln \frac{b}{T_p^2} = -\frac{E_a}{RT_p} + C_1 \quad 3.8$$

Where b is the heating rate, T_p is the temperature of the peak/dip, E_a is the activation energy, R is the ideal gas constant, C_1 is a constant.

Figure 3.7 (a) Schematic set of Differential Scanning Calorimetry (b) typical Differential Scanning Calorimetry output [50]

The activation energy can be calculated by the shift in the peak position as a function of heating rate [53, 54]. In this project, an SDT Q600 DSC was used to determine the reactions temperature and the overall activation energy during microwave combustion and reduction. These activation energies were the average energies of nucleation and growth of multiple reactions since (a) in RD, DSC was not able to distinguish between the energy change induced by the nucleation and growth process. (b) Several chemical reactions can occur at the same temperature, DSC was unable to separate these reactions. Measurements were

performed under argon environment. Heating rates and maximum temperature were varied according to the purpose of the studies.

3.3.4 Thermal Gravimetric Analysis (TGA)

A thermogravimetric analyzer instrument was used to perform thermogravimetric analysis. TGA measures the amount of weight change in the sample as a function of temperature or time in a controlled environment. This technique can be used to identify the sample composition and to predict the thermal stability of the samples. Weight change can be triggered by decomposition, oxidation, dehydration etc. Hence, the technique can be applied to estimate the lifetime, decomposition kinetics, determination of moisture/volatiles content of the materials etc. Figure 3.8 shows a set-up of a TGA with a standard furnace[55].

A standard TGA contains a precise balance and a sample pan located inside a furnace. The temperature is programmed by a computer. The atmosphere inside the furnace can be controlled by purging different gases. When the temperature increases, a thermal reaction may occur at a certain temperature and atmosphere. The change in weight will be measured and displayed as a plot of weight change versus temperature or time. The first derivative of the TGA curve can be used to determine the points at which the reaction occurs [56].

In this thesis, SDT Q600 DSC/TGA was used to determine the temperatures at which combustions occurred and the temperatures at which reduction occurred. This information is important to analyze the reaction mechanisms in microwave combustion and RD. Measurements for the microwave combustion were performed under ambient atmosphere, while the measurements for RD were performed under Ar gas atmosphere.

Figure 3.8 Schematic set up in Thermal Gravimetric Analysis[57]

3.3.5 Fourier-transform Infrared Spectroscopy (FTIR)

The wave number of infrared wave ranges from 12800 to 10 cm^{-1} . Scientists have used infrared absorption spectroscopy to determine the molecular structures since the discovery of infrared light. Fourier-transform infrared spectroscopy (FTIR) is the third generation of infrared spectrometer. This generation has the following advantages: (1) high signal to noise ratio (2) improved accuracy of wavenumber with error within $\pm 0.01 \text{ cm}^{-1}$ (3) shorter scan time (4) high resolution of 0.1 to 0.05 cm^{-1} (5) wide scan range of 1000 to 0 cm^{-1} [55]

When sample molecules are subjected to infrared radiation, the molecules can selectively absorb infrared irradiation at specific wavelengths which can lead to a change of dipole moment of these molecules. The vibrational energy of the molecule is then promoted from the ground level to an excited level. The frequency of the absorbed infrared radiation should be equal to the gap of the two vibrational levels. The profile of the absorption peaks is associated with vibrational degrees of freedom and the change in dipole moment. Therefore, structural information and functional groups of the molecules can be identified[55]. The technique can be used for gas, liquid and solid samples. Commonly

used FTIR have a scan range of 4000 to 400 cm^{-1} since the absorption range of most of the inorganic ions and organic compounds lie within this range [55].

In this thesis, Perkin-Elmer FTIR (Perkin Elmer Spectrum FTIR spectrometer) was used to analyze the molecular structure of ions and molecules of the viscous gel before the gel was ignited by microwave heating. The samples were mixed with KBr and pelletized. The pellet was subjected to 25 scans and the results were averaged. The scanning range is between 400 – 4000 cm^{-1} .

3.3.6. Vibrating Sample Magnetometer (VSM)

A vibrating sample magnetometer (VSM) is an instrument for measuring magnetic properties. The basic instrument is illustrated in figure 3.9. The sample is vibrated perpendicular to the field applied by an electromagnet. The oscillating magnetic field in the vibrating sample generates a voltage, which is collected by stationary pick-up coils. The magnetic properties of the specimen are derived from the voltage signals [58, 59]. The magnetic properties of some samples were measured by a VSM (Lakeshore VSM3.1) at a maximum applied field of 1.45 T (14.5 kOe) at room temperature. The VSM magnetometer was calibrated using a pure nickel standard sample. ~ 10 mg of powder was wrapped in Teflon tape and placed into the powder sample holder, then rigidly screwed onto the end of the sample rod.

Figure 3.9 Schematic set up of vibrating sample magnetometer[58]

3.3.7 Physical Property Measurement System

A physical property measurement system (PPMS) (EverCool-II, Quantum Design Inc., USA), with a VSM head was used to measure the magnetic properties of powder samples and the aligned samples. The PPMS is a sensitive and fully automated DC magnetometer for magnetic properties measurement. The working temperature of PPMS ranges from 1.9 K to 400 K, the maximum magnetic field is up to 5 T (50 kOe and has a sensitivity of $\sim 10^{-6}$ emu.

The VSM mode contains a VSM linear motor (head) to vibrate the sample in a perpendicular direction, a coil set puck for signal detection, electronics for driving the linear motor transport and detecting the response from the pickup coils. A software (MultiVu) is used to control and program the measurement. During measurement, the sample is fixed to the end of a sample holder rod which is sinusoidally oscillated. The sample oscillation will induce a changing magnetic flux and can be picked up by the pickup coil. According to Faraday's law, a voltage will be induced by this changing magnetic flux which will be detected by the VSM detection module[60].

When sample is located in the uniform magnetic field, dipole moments can be induced in the material proportional to the product of the sample susceptibility and the applied field. If the sample is made to undergo sinusoidal motion, an electrical signal will be induced as a result of the flux changes near the specimen.

The time-dependent induced voltage in coil can be described by the equation below[60]:

$$V_{\text{Coil}} = \frac{d\phi}{dt} = \left(\frac{d\phi}{dZ}\right)\left(\frac{dZ}{dt}\right) \quad 3.9$$

Where ϕ is the magnetic flux, Z is the vertical position of the sample respect to the pickup coil and t is the time.

For a sinusoidally oscillating sample position (typical oscillating mode in VSM), the induced voltage can be re-written as[60]:

$$V_{\text{Coil}} = 2\pi f C m A \sin(2\pi f t) \quad 3.10$$

where C is a coupling constant, m is the DC magnetic moment of the sample, A is the oscillation amplitude and f is the oscillation frequency.

Figure 3.10 shows a typical setup of a VSM mode in PPMS. The sample is inserted in the sample holder between the poles of the electromagnets. A sample rod with a transducer assembly is used for sample mounting. The rod passes along a driving coil center. An oscillator drives the power amplifier, which then drives the transducer. The transducer is driven by a power amplifier which is itself driven by an oscillator. The sample vibrates only along the vertical axis, inducing signals in the pickup coils. The magnitude of these signals depend on the sample's magnetic properties. A pair of stationary coils can pick up the resulted electrical signals. The output of the sample coil is fed to the differential input of a lock-in amplifier. The signal from the amplifier is proportional to the magnetic moment of the sample. The magnetic moment vs the applied magnetic field can now be plotted into a graph.

Figure 3.10 Operating principle of the physical property measurement system (PPMS) using the vibrating sample magnetometer (VSM) mode [60]

In this project, the room temperature magnetic hysteresis loops of all samples were measured at room temperature under an applied magnetic field of up to 5T. The temperature

dependent magnetic hysteresis loops of selected samples were measured from 300 K to 400 K in the same field.

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Chapter 4

Synthesis of $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ Powders by Microwave Combustion followed by Reduction Diffusion

In this chapter, the synthesis, characterization and property evaluation of Co substituted Nd-Fe-B magnetic nanoparticles is reported. Microwave combustion and reduction diffusion in a vacuum furnace was employed to synthesize Nd-Fe-Co-B magnetic nanoparticles. Nd-Fe-Co-B mixed oxides were produced by microwave combustion. The crystal size was controlled by processing parameters. $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ powders, with similar crystal size, were synthesized by reduction diffusion of the microwave synthesized oxides. The effect of processing parameters on microwave combustion and the reduction diffusion processes were investigated and optimized. The reaction sequence in the reduction diffusion process was investigated.

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4.1 Introduction

In this chapter, the microwave synthesis method was used. There are several advantages of this method. Due to the dielectric heating of the microwave, homogenous and fast heating can be achieved. The heating time was typically less than 10 mins, which is quick and energy efficient. Volumetric heating by microwave irradiation provides homogenous particles. In addition, by tuning the process parameters, the nanostructure of the particles can be controlled. The use of metal salts as precursors can reduce production costs. For example, the cost of 100 gram neodymium ingot is ~320 USD (99.9% Alfa Aesar), while the cost of 100 gram neodymium nitrate is only ~90 USD (99.9% Alfa Aesar). The microwave assisted combustion technique was studied by Swaminathan et al.[2] and single phase hard magnets and exchange-coupled Nd-Fe-B magnets were successfully synthesized[3]. However, the formation mechanism and effects of processing parameters on the structure was not well understood. The microwave power used was also limited due to the use of a domestic microwave. In this work, a study was carried out to synthesize Nd-Fe-B based particles using a commercial microwave synthesis system. One of the limitations of Nd-Fe-B magnets is low Curie temperature. Hence, Co was also alloyed to Nd-Fe-B to increase the Curie temperature. The formation mechanism of Nd-Fe-Co-B powders and the effect of processing parameters on the nanostructure and magnetic properties were studied. The as-synthesized Nd-Fe-Co-B nanoparticles possessed a crystal size ranging from 20-60 nm, with coercivity ranging from 6.2 kOe to 8.8 kOe. The magnetization of the nanoparticles ranged from 73 emu/g to 106 emu/g. The coercivity of the synthesized nanoparticles is nearly double that of the coercivity observed in particles synthesized by sol gel methods [4-6]

4.2 Synthesis of $\text{Nd}_x\text{Fe}_{82-x}\text{Co}_{10}\text{B}_8$ Powders by Microwave Combustion followed By Reduction Diffusion (RD) Technique

4.2.1 Nd-Fe-Co-B Oxide Synthesis

This section describes the results and the mechanism of microwave combustion. Liquid sol containing the metal nitrate precursors and glycine fuel was subjected to microwave irradiation at a microwave power 1.2 kW for different times, ranging from 180 s to 560 s. The IR spectra of the precursor liquid (Figure 4.1) and the dried sol/gel (Figure 4.1(b) to Figure 4.1(d)) revealed absorption bands at a wavenumber of 3196 cm^{-1} and 1620 cm^{-1} , corresponding to N-H bond stretching and anti-symmetrical and symmetrical vibration of COO^- in glycine, respectively [7]. The absorption bands located at 1384 cm^{-1} and 3410 cm^{-1} correspond to stretching of anti-symmetric NO_3^- and the stretching of the O-H bond in water, respectively [8].

Figure 4.1 IR spectra of samples taken out during microwave combustion synthesizing (a) liquid precursor, microwave irradiated for (b)180s (c)360s (d)540s, (e)as-synthesized powder

The IR spectra were identical for sol/gel samples removed after different microwave irradiation times. Thus, the main function of microwave irradiation is to evaporate water from the sol precursor. Ignition of the gel occurs at 560 s. Figure 4.1(e) shows the IR spectra of the as-synthesized powders. The absorbance bands of 3196, 1620 and 1384 cm^{-1} disappeared, indicating that N-H, COO^- and NO_3^- ions participated in the self-propagating combustion reaction. The as synthesized powder was then heat treated at 800 $^{\circ}\text{C}$ for 1h. Figure 4.1(f) shows the IR spectrum of this heat treated sample. The small peaks near 1500 cm^{-1} (figure 4.1(e)) disappeared, indicating these peaks arise from residual organic materials. The absorbance at 570 cm^{-1} was attributed to stretching vibration of tetrahedral ferrite[8]. The as-synthesized powder was further characterized by XRD (figure 4.2), which showed that the product consists of CoFe_2O_4 , NdFeO_3 and Nd_3FeO_6 . Boron oxide was not detected by XRD due to its low mass fraction (less than 3%).

Figure 4.2 X-ray diffraction pattern of the synthesized mix oxides prepared by auto-combustion assisted by microwave heating. 1, CoFe_2O_4 ; 2, NdFeO_3 ; 3, Nd_3FeO_6

The as-synthesized oxide powder was further characterized by TEM (Figure 4.3), the diffraction pattern shows a good match with CoFe_2O_4 , which is the dominant phase (~68% mass percent).

Based on the above discussion, the overall chemical reaction is as follows:

During the combustion process, the gaseous product, i.e., N_2 , CO_2 and steam, inhibited agglomeration of the crystals and created a porous product[9]. The morphology of the as-synthesized product was foamy and fluffy, with low density. As mentioned earlier, XRD was not able to detect the boron oxide due to the low mass fraction of boron. Hence, the above equation does not include boron.

Figure 4.3 TEM of the as-synthesized mixed oxide powder, the diffraction pattern shows a good match with CoFe_2O_4

4.2.2 Synthesis of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ Alloy

It is found that Nd-Fe-B phase formed at 800 °C[6]. Hence, the desired $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ nanocrystalline alloy was formed by reduction and annealing at 800 °C for a range of annealing times (0.5 h, 2 h and 4 h).

Figure 4.4 shows the XRD pattern of the synthesized $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ before(a) and after(b) byproduct removal. The product from this RD process consisted of the desired $\text{Nd}_2(\text{FeCo})_{14}\text{B}$ phase and the byproduct CaO (Figure 4.4(a)). The presence of $\text{Ca}(\text{OH})_2$ in the XRD patterns was due to absorption of moisture by CaO during the XRD scan. NH_4Cl dissolved in methanol was used to remove CaO. CaO was leached out as CaCl_2 , which has high solubility in methanol (29.2 g/ 100 g at 20 °C)[10]. This choice of organic solvent was to avoid the exothermic reaction between CaO and water. Thus, CaO was successfully removed (Figure 4.4(b)). Figure 4.5(a) shows a high resolution TEM image of the $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ after removal of CaO. The lattice spacing of 0.633 nm, 0.328 nm and 0.316 nm was assigned to the (110), (212) and (220) planes of $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$, respectively. (b) The bright field TEM micrograph of $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$ nanoparticles prepared by microwave combustion followed by RD is also shown in 4.5(b).

Figure 4.4 XRD analysis of Nd-Fe-Co-B magnet by microwave combustion and reduction diffusion (a)as-synthesized $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$ and $\text{CaO}/\text{Ca}(\text{OH})_2$ (b)after removal of CaO by NH_4Cl (dissolved in methanol). α , $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$; ϵ , CaO ; ϕ $\text{Ca}(\text{OH})_2$

Figure 4.5 HRTEM image of $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$ nanoparticle (b) bright field TEM micrograph of $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$ nanoparticle synthesized via microwave combustion and reduction diffusion

The reaction sequence of this RD was analyzed. The isochronal DSC thermogram of a mixture of Nd-Fe-Co-B oxides and CaH_2 is shown in figure 4.6. These results show two exothermic peaks, at temperatures of $\sim 350^\circ\text{C}$ and $\sim 740^\circ\text{C}$, indicating that the RD reaction occurred in two major steps. Hence, heat treatment was performed at these temperatures for 2 h. The resulting phases were subsequently analyzed by the XRD technique (figure 4.7)

Figure 4.6 DSC thermogram of Nd-Fe-Co-B oxides and CaH_2 mixture

Figure 4.7 XRD of samples heat treated at 340 °C, 740 °C, of CaO removed Nd-Fe-Co-B powders prepared via microwave combustion and reduction diffusion. 1, CoFe_2O_4 ; 2, NdFeO_3 ; 3, Nd_3FeO_6 ; α , $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$; β , α -Fe; δ , Nd_2O_3 ; χ , NdH_2

The thermodynamics of the RD process was studied. To calculate the Gibbs free energy change, thermodynamic data were obtained from the HSC chemistry data base. The free energy change (ΔG) values of the relevant reduction reactions were calculated (Table 4.1).

There is no standard Gibbs free energy, enthalpy or entropy information available for Nd_3FeO_6 in the literature, Nd_3FeO_6 is treated as a mixture of NdFeO_3 and Nd_2O_3 (1:1).

Table 4.1 Chemical reactions and Gibbs free energy change (ΔG) in the RD process

Reaction No.	Reaction	ΔG (kJmol ⁻¹) at 350°C	ΔG (kJmol ⁻¹) at 740°C
1	$2\text{NdFeO}_3 + 3\text{CaH}_2 = \text{Nd}_2\text{O}_3 + 2\text{Fe} + 3\text{H}_2(\text{g}) + 3\text{CaO}$	-705	-868
2	$\text{NdFeO}_3 + 3\text{CaH}_2 = \text{NdH}_2 + \text{Fe} + 3\text{CaO} + 2\text{H}_2(\text{g})$	-362	-458
3	$\text{NdFeO}_3 + 3\text{CaH}_2 = \text{Nd} + \text{Fe} + 3\text{CaO} + 3\text{H}_2(\text{g})$	-251	-408
4	$0.75\text{CoFe}_2\text{O}_4 + 3\text{CaH}_2 = 1.5\text{Fe} + 0.75\text{Co} + 3\text{CaO} + 3\text{H}_2(\text{g})$	-737	-876
5	$\text{B}_2\text{O}_3 + 3\text{CaH}_2 = 2\text{B} + 3\text{CaO} + 3\text{H}_2(\text{g})$	-320	-454
6	$\text{B}_2\text{O}_3 + 3\text{CaH}_2 = \text{B}_2\text{H}_6(\text{g}) + 3\text{CaO}$	-167	-221
7	$\text{B}_2\text{O}_3 + 3\text{CaH}_2 = 2\text{BH}(\text{g}) + 3\text{CaO} + 2\text{H}_2(\text{g})$	440	230
8	$\text{Nd}_2\text{O}_3 + 3\text{CaH}_2 = 2\text{Nd} + 3\text{CaO} + 3\text{H}_2(\text{g})$	203	52
9	$\text{Nd}_2\text{O}_3 + 3\text{CaH}_2 = 2\text{NdH}_2 + 3\text{CaO} + \text{H}_2(\text{g})$	2.4	-49

Comparing ΔG values, the most thermodynamically favored reduction at 350 °C is reaction 4, where CoFe_2O_4 was reduced to Fe and Co. This was substantiated by the XRD results, which showed Fe and Co formation and no CoFe_2O_4 (figure 4.7).

The reaction of NdFeO_3 with CaH_2 (reaction 1, 2 and 3) can occur at 350 °C (as suggested by the ΔG value). Reaction 1 was thermodynamically more favorable than reaction 2 and 3. In reaction 1, Fe was reduced, however Nd was not reduced due to its high reduction potential. Instead, Nd remained as Nd_2O_3 . The XRD results were in accordance with this calculation. Besides, NdH_2 and Nd formation was also feasible at 350 °C, with NdH_2 formation more favorable than Nd formation. However, neither NdH_2 nor Nd was present in the XRD data(figure 4.7), indicating that reduction of Nd did not occur at this temperature, perhaps due to kinetic reasons. However, a small amount of NdFeO_3 remains, as suggested by the XRD data, which may be due to kinetic reasons.

Reaction 8 was not feasible either 350 °C or 740 °C for the reaction of Nd_2O_3 with CaH_2 . Reaction 9 was only feasible at 740 °C. The XRD (figure 4.7) results also supported this prediction by revealing small peaks of Nd_2O_3 and the presence of NdH_2 .

For B_2O_3 reduction, at 350 °C, the positive values of Gibbs free energy (ΔG) indicates that reaction 6 and 7 were not feasible. The Gibbs free energy of B and B_2H_6 showed that the

generation of elemental boron (reaction 5) was more favorable than boron hydride. Crystallization of boron occurs at 1800 °C. Here, boron was not detectable due to its low atomic number and amorphous nature.

The Nd-Fe-Co-B phase was also detected in the XRD data of heat treated samples at 740°C for 2 h. The DSC peaks were present at ~350 °C and 740 °C, suggesting that the reaction:

occurred at 740 °C after the formation of NdH₂.

Based on the above calculations and experimental observations, the following reaction sequence is proposed:

At ~350 °C:

At ~740 °C:

4.2.3 Influence of Nd content

The influence of Nd content on the microstructure and magnetic properties of Nd-Fe-Co-B powder synthesized by microwave technique followed by the RD process were studied. Figure 4.9 shows the room temperature VSM properties of sample of nominal composition of Nd_xFe_{82-x}Co₁₀B₈ (x = 15, 25, 35 denoted by ND15, ND25, ND35 respectively) after removal of CaO byproduct. The coercivity increases with Nd content. Table 4.2 also summaries the mass fraction of the phase and crystal sizes of these three compositions. The phase fraction and crystal size information were obtained through Rietveld refinement (figure 4.8). The crystal size (volume weighted mean crystal size, L vol-IB) determined by

Rietveld refinement of XRD data was found to be 78-99 nm throughout the composition range (Table 4.2).

Figure 4.8 XRD pattern and Rietveld refinement of $\text{Nd}_x\text{Fe}_{82-x}\text{Co}_{10}\text{B}_8$ ($x = 15, 25$ and 35)

Table 4.2 Phases fraction and crystal sizes of $\text{Nd}_x\text{Fe}_{82-x}\text{Co}_{10}\text{B}_8$ ($x = 15, 25$ and 35)

Sample	$\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$		Fe		Nd_3Co	
	Content (%)	Size (nm)	Content (%)	Size (nm)	Content (%)	Size (nm)
ND15	95.2	78	4.8	53	-	-
ND25	83.5	99	-	-	16.5	38
ND35	56.9	92	-	-	43.1	44

Room temperature M-H curves for the three compositions are shown in figure 4.9. It is observed that, for ND35 and ND25, there is one additional NdCo_3 phase, which is undesirable in the Nd-Fe-Co-B system. The intermetallic compound Nd_3Co is a

ferromagnet with Curie temperature $T_c \sim 27$ K. Due to the low curie temperature, Nd_3Co have a low magnetization (M_s) at room temperature. Therefore, as the Nd_3Co content increases, the magnetization(M_s) of the synthesized Nd-Fe-Co-B decreases[11]. Both Nd-Fe,Co-B and the Fe phases exist only in ND15. M_r/M_s for ND15 is calculated to be $47/87=0.54$, which is greater than 0.5, indicating that exchange coupling is present in this material.

Figure 4.9 Room temperature M-H of $\text{Nd}_x\text{Fe}_{82-x}\text{Co}_{10}\text{B}_8$ ($x = 15, 25$ and 35) for various nominal compositions synthesized by the microwave technique and RD process. ND15, ND25 and ND35 refers to $\text{Nd}_{15}\text{Fe}_{67}\text{Co}_{10}\text{B}_8$, $\text{Nd}_{25}\text{Fe}_{57}\text{Co}_{10}\text{B}_8$ and $\text{Nd}_{35}\text{Fe}_{47}\text{Co}_{10}\text{B}_8$, respectively.

4.3 Study of Processing Parameters

4.3.1 Effect of Microwave Power

Room temperature M-H curves for the three compositions are shown in figure 4.9. It is observed that, for ND35 and ND25, there is one additional NdCo_3 phase, which is undesirable in the Nd-Fe-Co-B system. The intermetallic compound Nd_3Co is a ferromagnet with Curie temperature $T_c \sim 27$ K. Due to the low curie temperature, Nd_3Co have a low magnetization (M_s) at room temperature. Therefore, as the Nd_3Co content increases, the magnetization(M_s) of the synthesized Nd-Fe-Co-B decreases[11]. Both Nd-

Fe,Co-B and the Fe phases exist only in ND15. Mr/Ms for ND15 is calculated to be $47/87=0.54$, which is greater than 0.5, indicating that exchange coupling is present in this material.

4.3.1.1 Effect of Microwave Power on Nd-Fe-Co-B Oxides Formation

Figure 4.10 shows the temperature versus time profile for the synthesis of Nd-Fe-Co-B oxides for a range of microwave power. It can be observed that, in each profile, there was a sharp peak, the sudden temperature increase indicated ignition of the combustion reaction. The peak temperature was interpreted as the combustion temperature. The temperature drops rapidly after the peak temperature was achieved, indicating that self-propagating combustion was a fast process, which was completed in a few seconds. The increase in temperature was observed after combustion as a result of heating of the as-synthesized metal oxides by the microwave irradiation. After the microwave power was switched off, the temperature declined exponentially.

Figure 4.10 Recorded Temperature (°C) profile as a function of time(s) during microwave combustion using different powers. ↓ marks indicated the point at which microwave power were removed

It can be seen that microwave power had a significant influence on combustion behavior. The flame temperature increased from ~ 200 °C to 410 °C by an increase of microwave power from 1.2 kW to 2.8 kW, while the time to ignite the combustion reaction decreased from 450 s to 330 s. Initially, most of the microwave power was absorbed by water (section 4.2.1), leading to water evaporation. At a later stage, as water content decreased, more microwave energy was absorbed by the glycine and nitrates. Higher microwave power resulted in greater heating rate, leading to higher combustion temperature and shorter time for ignition. Figure 4.11 shows the Rietveld refinement analysis of the product phases and the mass fraction of the phases for different microwave power. All powders are crystal, and the CoFe_2O_4 and NdFeO_3 are the major phases in all the samples. Figure 4.12 shows the crystal size and combustion temperature as a function of microwave power. The crystal size was also determined by Rietveld refinement. The crystal size of the two major oxide phases increased with microwave power as a result of greater crystal growth at higher combustion temperatures.

Figure 4.11 Rietveld refinement of Nd-Fe-Co-B oxides prepared by auto-combustion induced by microwave irradiation. Microwave power of 1.2 kW, 1.8 kW, 2.4 kW, 2.8 kW. 1, CoFe_2O_4 ; 2, NdFeO_3 ; 3, Nd_3FeO_6 ; 4, Fe_2O_3 .

Figure 4.12 Combustion temperature and crystal size as a function of microwave power for various oxide phases (a) CoFe_2O_4 (b) NdFeO_3 (c) Nd_3FeO_6

For higher power, i.e., 2.4 kW and 2.8 kW, there was an additional phase, i.e., Fe_2O_3 was present. The mass fraction of the Fe_2O_3 phase increased with increasing microwave power (Figure 4.11). Comparing 1.8 kW and 2.4 kW in figure 4.11, the mass fraction of CoFe_2O_4 reduced by ~5% while the mass fraction of Fe_2O_3 increased by ~5%. Comparing 2.4 kW and 2.8 kW in figure 4.11, the mass fraction of CoFe_2O_4 reduced by ~9% while the mass fraction of Fe_2O_3 increased by ~10%. This result indicates that higher combustion temperature induced further oxidization of the Fe^{2+} in CoFe_2O_4 into Fe_2O_3 .

4.3.1.2 Effect of Microwave Power on Microstructure and Magnetic Properties of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$

XRD was performed to obtain the $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ alloy from the oxide powders prepared in the earlier step. The oxide powders were prepared over a range of microwave powers. The powders were individually mixed with CaH_2 and pressed into pellets. The pellets were annealed at 800 °C for 2 h in a vacuum furnace. When the annealing temperature is below 800 °C, good hard magnetic properties were not obtained, as the majority phase was the soft magnetic α -Fe phase [2]. Annealing for 0.5 h at 800 °C resulted in incomplete reduction, while annealing for 4 h at 800 °C resulted in α -Fe as the majority phase (see section 4.2.2). Figure 4.13 shows the Rietveld refinement analysis of $\text{Nd}_2(\text{FeCo})_{14}\text{B}$ powders synthesized at different microwave powers before removal of the byproduct. The crystal size of the $\text{Nd}_2(\text{FeCo})_{14}\text{B}$ alloy increased for greater microwave power, which was similar to the increase in oxide powder size with higher microwave power.

Figure 4.13 Rietveld refinement of as-synthesized $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$ alloy before removal of byproduct α , $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$; ϵ , CaO ; ϕ $\text{Ca}(\text{OH})_2$

Figure 4.14 shows the room temperature M-H curve of the samples processed at different microwave power. The coercivity increased for larger crystal sizes. Removal of the CaO

byproduct can reduce the structure and coercivity of $\text{Nd}_2(\text{FeCo})_{14}\text{B}$. Therefore, the crystal size and coercivity were measured for the as-synthesized samples. The relationship between crystal size and coercivity can be related to the mechanism of nucleation of reverse domains. The smaller grain size implies a larger grain boundary area, resulting in more defects on the surfaces of the grains. These defects can act as nucleation sites for reverse domains, hence a smaller grain size can lead to easier reversal[12]..

Figure 4.14 Hysteresis loops at room temperature for $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$ nanoparticles prepared by microwave assisted combustion by different microwave powers and followed by RD Microwave power: (a)1.2 kW, (b)1.8 kW, (c)2.4 kW, (d)2.8 kW. Black lines: before CaO removal, red lines: after CaO removal

The byproduct (CaO) present in the powders obtained by the RD process were subsequently removed by NH_4Cl dissolved in menthol. As shown in Table 4.3, the coercivity decreased to the range of 4.6 kOe to 7.9 kOe, which may be due to degradation of the $\text{Nd}_2(\text{FeCo})_{14}\text{B}$ nanostructure. On the other hand, magnetization increased to the

range of 73 emu/g - 106 emu/g when the CaO magnetic phase was removed. It was observed that the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase dispersed in the nonmagnetic CaO matrix segregated after the RD process[6]. The CaO phase detached from the $(\text{Nd}_2\text{FeCo})_{14}\text{B}$ phase, which can lead to defects on the surface of the $\text{Nd}_2(\text{FeCo})_{14}\text{B}$ phase. These defects can act as nucleation sites for the reversal mechanism, resulting in a decrease in coercivity. It is reported that rare earth atoms at particle surfaces are prone to oxidation[13]. Due to the large surface area of the nanosized $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ particles, the possibility of oxidation of rare earths on the surfaces is higher, leading to a decreased value of coercivity. In an earlier report of the microwave synthesis method, a domestic microwave with a maximum power of 800 W was used and the highest obtained coercivity value was 4 kOe. In this project, a microwave with a maximum microwave power of 2.8 kW was used and the highest coercivity value is nearly twice that of the value obtained in the earlier report[2].

Table 4.3 Summary of magnetic properties and grain sizes of Nd-Fe-Co-B obtained in this project

Composition	Microwave Power (kW)	Magnetization (emu/g)		Coercivity (H_c) (kOe)	Average grain size (nm)	Remarks
		Mr	Ms			
$\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$ CaO	1.2	13	25	6.2	21	With CaO
	1.8	15	24	7.7	34	With CaO
	2.4	17	28	8.2	46	With CaO
	2.8	17	26	8.8	63	With CaO
$\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$	1.2	56	106	4.6	44.3	CaO removed
	1.8	59	100	5.8	69.9	CaO removed
	2.4	48	82	7.2	63.2	CaO removed
	2.8	46	73	7.9	71.5	CaO removed

4.3.2 Effect of Reduction Diffusion Time

It has been reported that RD temperatures below 800 °C did not provide good hard magnetic properties, as the majority phase was the soft magnetic α -Fe phase[2]. Reduction diffusion was performed in a vacuum tube furnace at 800 °C for different heat treatment times of 0.5 h, 2 h and 4 h. Table 4.4 summarizes the phase fraction and crystal sizes for these three heat treatment times. The phase content and crystal size information were

obtained through Rietveld refinement (figure 4.15). The crystal size (volume weighted mean crystal size, Lvol-IB) was determined by Rietveld refinement of XRD data.

Figure 4.15 Rietveld refinement for different RD time: 0.5 h, 2 h, and 4 h

Table 4.4 Phase fraction and crystal size for different RD time

Reaction duration	Nd ₂ Fe ₁₂ Co ₂ B		Fe		NdH ₂	Nd ₂ O ₃
	Content	Size (nm)	Content	Size (nm)	Content	Content
30 min	95%*	52*	-	-	5%*	-
2 hr	95%#	80#	5%#	53	-	-
4 hr	49%	144	45%	94	-	6%

For all time spans, Nd₂Fe_{14-x}Co_xB was formed. It is observed that, for 30 min heat treatment time, ~5% Nd³⁺ was partially reduced to NdH₂ instead of Nd. For 2 h, Nd was completely reduced and no NdH₂ phase was present. As the heat treatment time was increased to 4 h, Nd was oxidized to Nd₂O₃ again, suggesting that Nd was oxidized during annealing. This leads to Fe diffusing out from Nd-Fe-Co-B phase to form α -Fe. The crystal size were observed to increase from around 50 nm $\rightarrow$ 80 nm $\rightarrow$ 140 nm.

Figure 4.16 shows the room temperature M-H curve of Nd-Fe-Co-B alloy RD at different time after removal of CaO byproduct. As the RD time increased from 0.5 h to 2 h, the complete reduction of the 5% NdH₂ to Nd and the mass fraction of the Fe phase increased. Crystal size also increased. A large coercivity decrease was observed when the reaction time was increased from 2 h to 4 h. This is due to evaporation and oxidation of Nd and a dramatic increase in Fe content. As a result of the Fe content, the magnetization increased to 95 emu/g. Highest energy product (4.4 MGOe) was obtained at 2 h reaction time as the Fe exchange coupled with the hard Nd-Fe-Co-B phase. The energy product of 0.5 h and 4 h annealing was 3 MGOe and 3.8 MGOe, due to the existence of NdH₂ and Nd₂O₃.

Figure 4.16 M-H curves for the synthesized Nd-Fe-Co-B powder using different reduction diffusion durations: 30 min, 2 h, and 4 h

4.3.3 Effect of Byproduct Removal Methods

In the RD process, CaH₂ was used to reduce Nd-(Fe-Co)-B oxide powders. Following the RD process, CaH₂ was converted to CaO byproduct. Several chemical agents to remove CaO have been studied [2, 14-16]. However, the coercivity was reported to be dramatically reduced after removal of byproduct by aqueous solution due to the formation of Nd₂Fe₁₄BH_x. Therefore, removal of CaO byproduct with minimum loss in coercivity was studied. In this work, 4 chemicals were used to remove the byproduct, i.e., dilute acetic

acid, mixture of glycerol and methanol, EDTA (dissolved in organic solvent) and NH_4Cl (dissolved in methanol). Table 4.5 summarizes these approaches.

Table 4.5 Removal of byproduct and sample properties before and after removal of byproduct.

Sample	Agent	CaO residue?	Coercivity		Magnetization	
			Before	After	Before	After
			(Oe)	(Oe)	(emu/g)	(emu/g)
A	Diluted acetic acid (0.1vol % in aqueous solution)	no	5123	1144	38	113
B	Glycerol and methanol mixture with volume ratio of 30:100	yes	5123	786	38	55
C	2g EDTA dissolved in a mixture of 50ml triethanolamine and 30ml methanol	no	5912	3559	34	100
D	2g NH_4Cl dissolved in 100ml methanol	no	5929	4741	33	77

In sample A, byproduct was removed by dilute acetic acid and no CaO phase was found in the XRD analysis (figure 4.17). However, dissociated hydrogen gas diffuses into the Nd-Fe-B matrix. $\text{Nd}_2\text{Fe}_{14}\text{B}$ peaks shift to lower angles, indicating an increase in d spacing of the crystal. $\text{Nd}_2\text{Fe}_{14}\text{BH}_5$ peaks were observed in the XRD pattern, this led to a decrease in magnetic properties [17]. In this study, coercivity decreased dramatically from 5123 Oe to 1144 Oe, as shown in table 4.5.

Figure 4.17 XRD analysis before and after removal of CaO by diluted acetic acid

Hence, removal of byproduct by organic solvents, which does not bring about severe exothermic reaction between water and CaO, was attempted. According to the work of León-Reina, glycerol reacts with CaO to form calcium glyceroxide according to the following equation[18].

Thus, glycerol and methanol solution was one of the candidates. In sample B, a solution of glycerol and methanol were used. However, XRD shows that CaO was not completely removed (figure 4.18(a)) and the coercivity decreased significantly to that of a soft magnet (figure 4.18(b)).

Figure 4.18 XRD pattern for Nd-Fe-B synthesis through the microwave combustion and reduction diffusion, the CaO was removed by solution of glycerol and methanol (a) XRD result of alloy after removal of byproduct (b) room temperature M-H curve of alloy before and after removal of byproduct

The third agent used was the EDTA. Ca^{2+} tends to bind with EDTA to form complexants which can be utilized to remove CaO. In sample C, CaO was removed by EDTA (dissolved in the mixture of triethanolamine and methanol), XRD and EDS patterns showed no trace of CaO or Ca (figure 4.19(a) and figure 4.19(b)). VSM shows that magnetization increases from 34 emu/g to 100 emu/g, while coercivity decreased by 40% from 5912 Oe to 3559 Oe (figure 4.19(c))

Figure 4.19 Nd-Fe-B synthesis by microwave synthesis and the RD method, followed by removal of CaO by EDTA (a) XRD result of alloy after removal of CaO (b) EDS result of alloy after removal of CaO (c) room temperature M-H curve of alloy before and after removal of CaO

In sample D, NH_4Cl was dissolved in methanol to remove the byproduct. The idea was inspired by the work of Yamamoto, in which NH_4Cl (dissolved in methanol) was used to remove the byproduct after synthesis of Fe_2Co using CaH_2 [19]. When using NH_4Cl , CaO/Ca was converted to CaCl_2 . CaCl_2 was dissolvable in methanol and hence can be removed. XRD and EDS shows no trace of CaO or Ca (figure 4.20(a) and 4.20(b)). VSM shows that the magnetization increased from 33 emu/g to 77 emu/g, while coercivity decreased by 19%, from 5929 Oe to 4741 Oe. This is the best removal method among all the approaches tried in this research work, as it has the lowest decrease in coercivity. The TEM micrograph shows that the $\text{Nd}_2\text{Fe}_{14}\text{B}$ powder particles were equiaxed (figure 4.21).

Figure 4.20 Nd-Fe-B synthesis by the microwave synthesis and RD method, followed by removal of CaO by NH_4Cl (a) XRD result of alloy after removal of CaO (b) EDS result of alloy after removal of CaO (c) room temperature M-H curve of alloy before and after removal CaO.

Figure 4.21 (a) High resolution transmission electron microscopy (HRTEM) image of $\text{Nd}_2\text{Fe}_{12}\text{Co}_2\text{B}$ nanoparticles, byproduct removed by method D (b) bright field TEM micrograph of Nd-Fe-B alloy after removal of byproduct by NH_4Cl

4.4 Conclusions

Microwave combustion, followed by the RD technique, was successfully employed to chemically synthesize $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ powders, with crystal size in the nano range. The reaction sequence of microwave assisted combustion and RD were identified. Phase formation of Nd-Fe-Co-B oxide powders by microwave combustion and phase formation of $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ by RD process were studied by FTIR, XRD and DSC techniques. Initially, the microwave energy resulted in the evaporation of water. Subsequently, the microwave energy initiated auto combustion. N-H , COO^- and NO_3^- ions all took part in this self-propagating combustion reaction. This combustion led to the formation of CoFeO_4 , NdFeO_3 , Nd_3FeO_6 and Fe_2O_3 . For the RD process, the reaction sequence was: Co and Fe oxides were first reduced to Fe and Co at $\sim 350^\circ\text{C}$. Nd oxides was partially reduced to NdH_2 at $\sim 350^\circ\text{C}$ and finally to Nd at $\sim 740^\circ\text{C}$, when the desired $\text{Nd}_2(\text{Fe},\text{Co})_{14}\text{B}$ phase was also obtained. The effect of Nd composition were studied. $\text{Nd}_x\text{Fe}_{82-x}\text{Co}_{10}\text{B}_8$ ($x = 15$) was found to have the largest energy product, as exchange coupling was observed for this composition.

The effects of processing parameters were studied,

- (a) Microwave power: Greater microwave power led to higher combustion temperatures, which led to larger crystal size of Nd-Fe-Co-B oxide. $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ crystal size followed the same trend. The coercivity of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ was found to increase from 6.2 kOe to 8.8 kOe when the crystal size increased from 21 nm to 63 nm.
- (b) RD time: It was found that a temperature of 800 °C was required to form the $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ phase. The highest energy product were obtained for RD treatment at 800 °C for 2 h.
- (c) Byproduct removal: The CaO byproduct was removed by 4 chemicals, i.e., dilute acetic acid, mixture of glycerol and methanol, EDTA (dissolved in organic solvent) and NH_4Cl (dissolved in methanol). The use of NH_4Cl (dissolved in methanol) eliminated the use of water and thus avoided the vigorous reaction between CaO and water. It was found that the method of NH_4Cl (dissolved in methanol) led to least reduction of coercivity.

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Chapter 5

One-pot Microwave Synthesis of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ Exchange Coupled Powders

A novel one pot microwave synthesis technique was developed to produce hard magnetic exchange coupled $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ nanoparticles. Nd-Fe-Co-B mixed oxides were synthesized from metal nitrates via microwave combustion followed by microwave reduction of these oxides to hard magnetic $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ powder in the same microwave chamber. The conventional use of a furnace for oxide reduction is eliminated. This method is cost effective, facile, energy efficient and widely applicable to a variety of materials. The reaction mechanisms of both microwave combustion and microwave reduction was studied for the first time. The synthesized $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ nanoparticle have a narrow size distribution with 60% in the size range of 35 nm - 45 nm. The maximum energy product of these hard magnetic nanoparticles reached a value of 11.4 MGOe, which is the highest among the values reported for $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanoparticles synthesized by chemical approaches.

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5.1 Introduction

The chemical synthesis of metallic and intermetallic particles is of broad interest [2-4]. Among the synthesis techniques developed for the production of such particles, the microwave based technique has considerable potential for commercial applications [5-7]. However, this technique has rarely been used to produce metallic and intermetallic particles. Hence, we developed the synthesis of hard magnetic intermetallic powders produced by one pot microwave processing. As discussed, there is high demand for high performance permanent magnets, allowing devices to become more energy efficient and with smaller volume and lighter weight attracted much attentions. Due to the superior magnetic properties, exchange coupled Nd-Fe-B magnets have attracted intense interest. Such magnets consist of magnetically interacting nanoscale hard and soft phases. To achieve efficient coupling, nanosized grains of the soft magnetic phase are needed and the grain size should be around twice the domain wall length of the hard magnetic phase, which is ~ 10 nm[8].

A novel one-pot microwave method was developed to synthesize $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ exchange coupled nanoparticles. The method consists of (a) preparation of Nd-Fe-Co-B mixed oxides from metal nitrates by microwave combustion and (b) formation of intermetallic nanoparticles by microwave reduction of these oxides. In both cases, sample heating was only by microwave irradiation. For the first time the synthesis of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ exchange coupled hard magnetic intermetallic nanoparticles was achieved by this novel one-pot microwave synthesis. In the previous chapter, synthesis of NdFeB based materials was accomplished by microwave combustion, followed by RD in a vacuum furnace. In this chapter, the same microwave was used to accomplish both the combustion and reduction processes, eliminating the use of a vacuum furnace. Some advantages of this method include (1) Lower energy consumption compared to conventional heating methods, such as vacuum furnace heating. (2) The entire process can be completed using a single processing equipment. (3) The method can be easily modified so that there is no need to transfer the intermediate compounds between two different

chambers. The detailed reaction mechanism of microwave combustion as well as microwave RD was also studied for the first time.

Based on the literature, an initial composition of $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$ was chosen[9]. To increase the Curie temperature while retaining reasonable coercivity, the composition was tuned by replacing 10% of Fe by Co to produce $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ [10]. We have successfully synthesized $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ exchange coupled hard magnetic nanoparticles. Transmission electron microscopy (TEM) indicated that the average size of the particles was ~40 nm. A narrow size distribution from ~20 nm to 60 nm was observed, with 60% lies in the range of 35 nm to 45 nm. High-resolution transmission electron microscopy (HRTEM) indicated that the particles possessed the desired $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ exchange coupled structure. The reported values of saturation magnetization for chemically synthesized Nd-Fe-B is usually low (<105 emu/g). In this work, with a high remanence of 99 emu/g and high saturation magnetization of 112 emu/g, the maximum energy product of these hard magnetic nanoparticles reached a value of 11.4 MGOe, which is the highest among the values reported for $\text{Nd}_2\text{Fe}_{14}\text{B}/\alpha\text{-Fe}$ nanoparticles synthesized by chemical approaches.

5.2 Microstructure and Magnetic Properties

Based on the results of chapter 4, an initial composition of $\text{Nd}_{15}\text{Fe}_{67}\text{Co}_{10}\text{B}_8$ was chosen owing to its largest energy product. This section reports the microstructure and magnetic properties of the $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ synthesized by our two-step process, i.e., microwave combustion and microwave RD. Both these processes were carried out in the same microwave chamber. CaO was removed by a solution of NH_4Cl and methanol. Rietveld refinement (Figure 5.1) of the resultant powder showed that the product consisted of 88.9 wt% of crystalline $\text{Nd}_2\text{Fe}_{10}\text{Co}_4\text{B}$ ($c=12.16$ nm, $a=8.78$ Å), possessed the desired tetragonal crystal structure, as well as 11.1 wt% of $\alpha\text{-Fe}$ ($a=2.87$ Å). The grain size of the $\text{Nd}_2\text{Fe}_{10}\text{Co}_4\text{B}$ and $\alpha\text{-Fe}$ phases, calculated by Rietveld refinement, were ~26.6 nm and ~21.1 nm, respectively.

Figure 5.1 XRD pattern and Rietveld refinement of *Nd-Fe-Co-B* powder prepared by microwave combustion, followed by microwave RD. (a) as reduced powder, (b) After removal of *CaO*. Black curves are from XRD results, red curves are calculated by Rietveld refinement.

Bright field TEM micrographs of the powder (after byproduct removal) (figure 5.2(a)) indicated that equiaxed particles were presented, with particle sizes ranging from 20 to 60 nm. The average size of the nanoparticles was ~40 nm, the size distribution is shown in the inset graph of figure 5.2(a). 60 % of the particles were in the size range of 35 nm - 45 nm. A HRTEM image of this $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ two phases structure is shown in figure 5.2(b). The value of 0.202 nm were indexed to the (110) plane of $\alpha\text{-Fe}$, while the values of 0.303 nm, 0.633 nm, 0.311 nm and 0.328 nm were indexed to the (004), (110), (220) and (212) planes of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$, respectively. The $\alpha\text{-Fe}$ phase was uniformly distributed in the $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ matrix. The diffraction pattern (Figure 5.2(b) inset) can be indexed to that of the desired $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ nanocomposite.

Figure 5.2 (a) Bright field transmission electron image (TEM) (inset: particle size distribution of 120 particles) and (b) High Resolution TEM of $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$ (the selected area diffraction pattern (SADP) is indexed to $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$).

The room temperature M-H curves of the randomly oriented powder is shown in figure 5.3(a)(black points). The coercivity (H_c), remanence (M_r) and saturation magnetization (M_s) are 4.9 kOe, 65 emu/g and 116 emu/g respectively. These measurements were performed at magnetic field up to 5 T (50 kOe) magnetic field, however, about 8 T (80 kOe) field is needed for saturation for Nd-Fe-B based magnets [11]. Hence, the M vs $1/H$ curve was plotted and extrapolated to 8 T (80 kOe) to obtain the M_s value. The M_s for the randomly oriented powder sample was found to be 116 emu/g. The reduced remanence ratio for the random powder is ~ 0.56 , above the minimum value of 0.5 required for an exchange coupled magnet.

The randomly oriented powders were suspended in super liquid glue(Yamayo super glue, Singapore) and this mixture was dropped on a glass slide. The slide was placed in an electromagnet (Field control electromagnet, model:DXSB-178, China). A field of 2 T (20 kOe) was applied during solidification of the mixture. After this alignment, the magnetic properties of the aligned sample were separately measured in direction perpendicular (figure 5.3(a), blue points) and parallel to the alignment direction (figure 5.3(a), red points). The saturation magnetization and squareness were found to be highly

sensitive to the magnetic alignment. After alignment, M_r increased from 65 emu/g to 100 emu/g, while the value of M_r/M_s increased dramatically from 0.56 to 0.88. We calculated the energy product of the randomly oriented sample and the aligned sample assuming a theoretical density of Nd-Fe-B (7.5 g/cm^3) [9, 12, 13]. The energy product $(BH)_{\max}$ was obtained by plotting the demagnetization B-H curves for the randomly oriented samples and aligned samples. Interestingly, a large variation in energy product was observed (figure 5.3(b)). The $(BH)_{\max}$ is highest (11.36 MGOe) for the easy axis (0°), while $(BH)_{\max}$ is lowest (3.7 MGOe) for the hard axis (90°). The energy product of our powder is as high as 11.36 MGOe. This high energy product is due to the high saturation magnetization and squareness induced by alignment of the nanoparticles in the easy axis. As proposed by Fernengel et al [11], the degree of alignment of the nanoparticles was calculated by the term of average misorientation angle $\varphi = \tan^{-1}(\frac{2M_r^\perp}{M_r^\parallel})$. The misorientation indicates the angle between the easy directions of each grains (c-axes) and the easy direction of magnetization macroscopically. The φ value was found to be $\sim 48^\circ$, a similar value was found in the work of Liu et al [14]. Since the average misalignment angle decreases with increasing grain size of the particles, our higher φ value is due to the smaller grain size of our samples [14].

Figure 5.3 (a) M-H loops of randomly oriented samples and aligned samples. Blue line: measured 90° to the alignment direction, red line: 0° to the alignment direction (b) Second quadrant of B-H curve and maximum energy product $(BH)_{\max}$

Figure 5.4 XRD of (a) randomly oriented powder and (b) field-aligned $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ powders // to the c-axis

The XRD pattern of the randomly oriented and the aligned $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$ particles is shown in figure 5.4(a) and 5.4(b). It can be seen that after the powder was aligned under a 2 T (20 kOe) magnetic field, crystallographic alignment was observed as an enhanced hkl reflections with a larger l value when measured // to the c-axis was observed. This observation is similar to that of Meisner and Zhong[15-17], which indicated that the $\text{Nd}_2\text{Fe}_{14}\text{B}$ based particles can indeed be crystallographically aligned by an external applied magnetic field.

5.3 One-pot Microwave Synthesis of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$: Reaction Mechanism

Isochronal DSC (SDT TA Q600) were performed in air and Ar atmosphere to investigate the mechanism of mixed oxide formation as well as $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ intermetallic formation. For oxide formation, the mixed metal nitrate solution was heated in the microwave for 2 h at temperatures corresponding to peaks in the DSC curves. The power was controlled by the program, in which the microwave power was modulated so that the heating rate was kept at $5^{\circ}\text{C}/\text{min}$ until the temperature reached the desired temperature. The microwave

power was then modulated so that the temperature is kept at the desired temperature for 2 hours. Each metal nitrate solution was also heat treated in a box furnace for 10 h at temperatures corresponding to peak temperatures observed in the DSC results. XRD results showed that 10 h heat treatment in a box furnace was needed to form crystalline phases while 2 h heat treatment was sufficient for microwave heating. The product of thermal decomposition of the metal nitrates was investigated by the XRD technique. A similar approach was applied to the RD process. Nd-Fe-Co-B mixed oxide powders synthesized by microwave combustion were mixed with CaH_2 for isochronal DSC measurements under Ar atmosphere. The reaction mixture were heated by the microwave for 2 h in Ar atmosphere at the peak temperatures observed in the DSC curves, and analyzed by the XRD technique.

5.3.1 Reaction Mechanism in Microwave Combustion

As described above, Nd-Fe-Co-B oxide was synthesized by microwave combustion. Microwave combustion has been used for the synthesis of oxide based magnetic materials, ceramics and thermoelectric materials etc[18-24]. However, the formation mechanism has not been well studied. The reaction mechanism of single element metal oxide has been reported[25]. However, no report has previously discussed the reaction mechanism by microwave combustion for the formation of multicomponent Nd-Fe-B. This section will discuss the reaction mechanism of microwave combustion to form Nd-Fe-B mixed oxides.

In microwave irradiation, dipolar molecules rotate and ions move to align with the oscillating field, resulting in heating of the material. Before ignition, microwave heating led to evaporation of water and other volatile species[26, 27]. After ignition, reaction between metal nitrates and glycine led to self-sustaining combustion. The reaction can be described as [28]:

Where v is the valence of the metal, ψ is the fuel to oxidizer ratio, M represents the elemental metal ($M = \text{Nd, Fe, Co}$).

It is well-known that thermal decomposition of metal nitrates leads to the formation of the corresponding oxides. Manukyan et al studied the reaction mechanism for Ni oxide formation by the nitrate-glycine combustion process[25]. However, the reaction mechanism of mixed metal oxides e.g., Nd-Fe-Co-B mixed oxides during combustion has not been previously reported. To reveal the reaction sequence of mixed oxide formation, we first investigated the decomposition process of each metal nitrate. The TGA-DSC analysis results of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and H_3BO_3 are shown in figure 5.5(a1),(b1),(c1),(d1). Each salt was heated at temperatures corresponding to the peak temperatures observed in the DSC-TGA results. The product at intermediate temperatures were identified by the XRD technique (figure 5.5(a2),(b2),(c2),(d2)). From the DSC-TGA and XRD results, one can see that H_3BO_3 decomposed to form boron oxide at $\sim 130^\circ\text{C}$, followed by the formation of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at 160°C , the formation of oxides from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at 200°C and finally oxide formation from $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at 480°C (table 5.1). The TGA-DSC results for glycine showed that glycine started to decompose intensively at $\sim 240^\circ\text{C}$ (figure 5.6), which coincided with the results of glycine decomposition obtained earlier[29]. Glycine decomposed below 300°C to form solid glycylglycine (dipeptide) and 2,5-piperazinedione, simultaneously releasing NH_3 , CO_2 and H_2O [25].

Figure 5.5 TGA-DSC analysis of (a1) $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, (b1) $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (c1) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and (d1) H_3BO_3 . Each metal nitrate and boric acid were separately heat treated in a box furnace at responsible temperatures observed in the DSC-TGA results. XRD analysis of the oxide formation process for (a2) $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, (b2) $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (c2) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and (d2) H_3BO_3

Table 5.1 Precursor, oxide formation temperatures and product

Precursor	Oxide formation temperature (°C)	Product
H_3BO_3	130	B_2O_3
$Fe(NO_3)_3 \cdot 9H_2O$	160	Fe_2O_3
$Co(NO_3)_2 \cdot 6H_2O$	200	Co_3O_4
$Nd(NO_3)_3 \cdot 6H_2O$	480	Nd_2O_3
Mixture $Nd(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ $Co(NO_3)_2 \cdot 6H_2O$ H_3BO_3	150	$Nd(NO_3)_3 \cdot 6H_2O, Fe_2O_3$
	200	$Nd(NO_3)(OH)_2, Fe_2O_3$
	290	$NdFe_2O_4, Fe_2O_3$

Figure 5.6 DSC-TGA graph of the thermal decomposition of glycine

To study the phase evolution of the metal nitrate mixtures, $Nd(NO_3)_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and H_3BO_3 were dissolved in water and stirred thoroughly. TGA-DSC analysis of this solution was performed (Figure 5.7). It was found that there are three major endothermic peaks at 150 °C, 200 °C and 300 °C, indicating major reactions at these temperatures. The solution was then heated by microwave for 2 h at temperatures corresponding to the peak temperatures observed in DSC/TGA.

Figure 5.7 (a) DSC-TGA graph of heating of mixed metal nitrates (b)XRD pattern of mixed metal nitrates microwave heated at 150 °C, 200 °C and 290 °C for 2 h. *The peaks of Fe₂O₃ and CoFe₂O₄ cannot be distinguished in the XRD pattern, these peaks are indicated as Fe₂O₃ in the XRD patterns.

XRD analysis of the product revealed that:

- (a) At 150 °C, $Fe(NO_3)_3 \cdot 9H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ peaks disappeared; small peaks of $Fe_2O_3/CoFe_2O_4$ were observed, indicating formation of $Fe_2O_3/CoFe_2O_4$.
- (b) At 200 °C, $Nd(NO_3)_3 \cdot 6H_2O$ partially decomposed to $Nd(NO_3)(OH)_2$.
- (c) At 290 °C, $Nd(NO_3)(OH)_2$ decomposed and transformed to $NdFe_2O_4$.

A schematic representation of the formation mechanism is presented in Figure 5.8. The following reaction sequence emerges from the above results:

First, water bound to iron nitrate hydrate was released at ~105 °C (figure 5.6 (b1)). At 150 °C, iron and cobalt nitrate decomposed to form $Fe_2O_3/CoFe_2O_4$. At ~200 °C $Nd(NO_3)_3 \cdot 6H_2O$ lost bound water and released NO_x, partially decomposing to $Nd(NO_3)(OH)_2$. At 250 °C, glycine decomposed, releasing NH₃, CO₂ and H₂O. At the same time, $Nd(NO_3)(OH)_2$ gradually released NO_x. The exothermic reaction between NH₃ and NO_x contributes to the combustion[25], further increasing the temperature. This high temperature resulted in the complete decomposition of $Nd(NO_3)(OH)_2$ to form NdFe₂O₄.

The reaction between NO_x , released during decomposition of the metal nitrate, and NH_3 , released along with glycine decomposition, resulted in the high combustion temperature. Due to the low weight percentage of boron species (<3%), boron was not detected in XRD. However, we can predict that boron oxide formed at $\sim 130^\circ\text{C}$ (figure 5.5(d1) and (d2)) during the combustion.

Figure 5.8 Schematic of the mechanism for microwave combustion of metal nitrates to synthesize Nd-Fe-Co-B mixed oxides.

5.3.2 Reaction Mechanism in Microwave Reduction

The second step of the synthesis of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ was microwave RD of a mixture of these oxide powders and CaH_2 . The synthesis of Nd-Fe-B based intermetallic powders by RD has been reported [8, 11, 29-35]. However, these reports performed the RD in vacuum or argon atmosphere based furnace. On the other hand, in our work, RD was carried out in the same microwave chamber which was used to synthesize Nd-Fe-Co-B oxides.

As shown in figure 3.2, SiC acted as a microwave susceptor and was placed below the sample to facilitate sample heating. The mechanism of reduction of metal oxide by CaH_2 has been suggested by Meerson et al [38]. The reduction reaction can be considered to be ($M = \text{Nd, Fe, Co, B}$):

We studied the reaction sequence for the reduction of mixed Nd-Fe-Co-B oxides. The mixed oxide was mixed with CaH_2 for isochronal DSC measurements. The DSC curves show two exothermic peaks at 350 °C and 740 °C (figure 5.9(a)). The reaction mixture were heated at these two temperatures by microwave irradiation for 2 h under Ar atmosphere and analysed using the XRD technique (figure 5.9(b)). The XRD analysis showed that reduction of Fe and Co oxides occurred at 350 °C. The reduction of neodymium oxides occurred at 720 °C and resulted in the partial reduction of Nd oxides to the NdH_5 phase. After annealing at 800 °C for 2 h under microwave irradiation, the desired $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ and $\alpha\text{-Fe}$ phases (and CaO by product) were formed (Figure 5.1(a)). For the reduction of B_2O_3 , XRD was not able to detect the boron signal due to the small amount used (<3%). Therefore, a theoretical prediction was made by Gibbs free energy calculations (Table 5.2). At 350 °C, the most negative value of Gibbs free energy for reaction 1 suggested that B_2O_3 will be reduced to B at 350 °C, Deheri et al reported a similar result[30].

Figure 5.9 (A) DSC-TGA graph of the heating of a mixture of mixed oxide and CaH_2 (B)XRD pattern of a mixture of oxide and CaH_2 subjected to microwave heating at (a)350 °C and (b)740 °C for 2 h.

Table 5.2 Gibbs free energy of reactions during reduction diffusion at 350 °C and 740 °C

Reaction No.	Reaction	ΔG at 350°C (kJ/mol)	ΔG at 740°C (kJ/mol)
1	$\text{B}_2\text{O}_3 + 3\text{CaH}_2 \rightarrow 2\text{B} + 3\text{CaO} + 3\text{H}_2$	- 319	- 453
2	$\text{B}_2\text{O}_3 + 3\text{CaH}_2 \rightarrow 2\text{B}_2\text{H}_6 + 3\text{CaO} + 3\text{H}_2$	- 166	- 220
3	$\text{B}_2\text{O}_3 + 3\text{CaH}_2 \rightarrow 2\text{BH} + 3\text{CaO} + 2\text{H}_2$	440	230

* ΔG stands for Gibbs free energy, thermodynamic data from Barin[39].

Based on the above experimental results and thermodynamic calculations, the reaction sequence in the microwave reduction is proposed as follows:

At 350 °C:

At 740 °C:

At 800 °C:

5.3.3 Kinetics and Activation Energy for One pot Microwave Synthesis of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$

The activation energy (E_a) can be calculated by the Arrhenius equation:

$$k = Ae^{-E_a/(RT)} \quad 5.11$$

Where A is the frequency factor, R is the gas constant, k is the reaction rate constant, T is the absolute temperature, E_a is the activation energy

From the above equation, E_a was calculated by chemical reaction temperature peak (T_p) shift caused by different heating rate for both oxide formation and RD. Two limitations of this method are that the (a)DSC result was unable to distinguish between the energy change due to nucleation and the continual particle growth, (b)Several chemical reactions may occur at the same temperature, DSC was unable to separate these reactions.

The well-known Kissinger model was used to determine the activation energies for the reactions:

$$\ln \frac{b}{T_p^2} = -\frac{E_a}{RT_p} + C \quad 5.12$$

Figure 5.10 (a) and (b) show the isochronal DSC-TGA data of the combustion process at different heating rates. Large exothermic peaks were observed in the DSC curves at 170 - 180 °C for all the heating rates. The corresponding weight loss (50 to 62%) were observed in the TGA curves in the same temperature range for each heating rate. Therefore, the peaks at 170 - 180 °C correspond to combustion of the mixture. The increase in mass before the large weight loss was attributed to combustion. Another exothermic peak in each DSC

curve, apart from the combustion peak, was due to burning of the residual organic species. The overall activation energy (E_a) for the above equation was determined from the slope of the plot of $\ln \frac{b}{T_p^2}$ vs $\frac{1}{T_p}$ (Figure 5.10 (c)). The calculated E_a for the combustion reaction was 205 kJ/mol.

Figure 5.10 (a) DSC plots of the combustion at a range of heating rates (b) TGA plots of the combustion at a range of heating rates (c) plot of $\ln \frac{b}{T_p^2}$ as a function of $\frac{1}{T_p}$, black dots: calculated from experiment, red line: linear fit of the black dots.

Figure 5.11 (a) shows the isochronal DSC data of the RD process at a range of heating rates. As mentioned earlier, there were two peaks in the DSC curve, at 350 °C and 740 °C. Similarly, the overall activation energy (E_a) for the reactions at the two temperatures were determined from the slope of the plot of $\ln \frac{b}{T_p^2}$ vs $\frac{1}{T_p}$ (Figure 5.11 (b) and (c)). The calculated activation energies were 146 kJ/mol and 335 kJ/mol for the reactions at 350 °C and 740 °C,

respectively. The overall activation energy for reactions (5) (6) and (7) was 146 kJ/mol, while the overall activation energy for reaction (8) was 335 kJ/mol. E_a obtained by Deheri et al for samples synthesized by the sol-gel method was 870 kJ/mol, which is much higher than the value obtained in this work[30].

Figure 5.11 (a) DSC trace of the reduction-diffusion process, (b) $\ln \frac{b}{T_p^2}$ vs $\frac{1}{T_p}$ graph for temperature ~ 350 °C, (c) $\ln \frac{b}{T_p^2}$ vs $\frac{1}{T_p}$ graph for the temperature ~ 740 °C, black dots: calculated from experiment, red line: linear fit of the black dots in (b) and (c).

5.4 Conclusions

$\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$ hard magnetic nanoparticles were successfully synthesized by a novel and low cost, green, one-pot microwave synthesis technique. The heating source for the entire process was only by microwave irradiation using a single microwave chamber. We investigated the structural and magnetic properties of the heavy rare earth free $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$ exchange coupled nanoparticles. The formation mechanism of these nanoparticles were also studied for both oxide and alloy formation:

(1) Nd-Fe-Co-B mixed oxides were prepared from metal nitrates *via* microwave combustion. During the formation of the mixed oxides powder, boron oxide formed first. Iron and cobalt oxides formed subsequently, followed by the formation of neodymium iron oxide.

(2) In the microwave RD process, $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}$ alloy formed through several steps. At 350 °C, iron, cobalt and boron oxides were reduced. At 740 °C, the partial reduction of

neodymium oxide to NdH_5 took place. After annealing at 800 °C for 2 hours, the desired $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}$ and $\alpha\text{-Fe}$ phases were formed.

(3) The magnetic properties of the $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$ nanoparticles were highly sensitive to magnetic alignment. After alignment, M_r/M_s increased from 0.56 to 0.88 while the energy product increased from 3.7 MGOe to 11.36 MGOe.

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Chapter 6

Microwave Synthesis of Dy Alloyed $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ Powders

Heavy rare earths such as Dy can enhance the coercivity and improve thermal stability by increasing the magnetocrystalline anisotropy field (H_A). The H_A of $\text{Dy}_2\text{Fe}_{14}\text{B}$ ($H_A=12576.8$ kA/m (158 kOe)) is much larger than that of $\text{Nd}_2\text{Fe}_{14}\text{B}$ ($H_A=5572$ kA/m (70 kOe)). However, the higher cost for Dy compared to Nd leads to a dramatic increase of cost of $\sim 50\%$ even when the substitution of Dy is $\sim 10\%$. Hence, reducing Dy content or decrease the cost of Dy precursor source is urgently needed. The influence of Dy substitution on both room temperature and temperature dependent magnetic properties were investigated. For $(\text{Nd}_{12}\text{Dy}_3)-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ alloy, $(BH)_{\max}$ was found to be as high as 12.6 MGOe. Coercivity increased significantly, from 8 kOe to 14.5 kOe, as Dy content increased from $x=0$ to $x=9$. Analysis of the temperature dependent magnetic properties and comparison with modeling results showed that the dominant coercivity reversal mechanism of these particles was nucleation of reversed magnetic domains.

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6.1 Introduction

As a bottom-up chemical technique, the microwave based synthesis technique reported in this thesis is promising to obtain homogeneous nanostructures in fewer steps. Alloying additions can also be readily incorporated. The use of lower cost metal salts as precursors can also reduce production cost. In chapter 4, Co alloyed Nd-Fe-B powders by a microwave based chemical method was discussed. In this chapter, the same technique was used to synthesize Dy substituted Nd-Fe-Co-B powders with improved properties.

One of the limitations of Nd-Fe-B magnets is the low Curie temperature (~ 585 K)[2-4]. Hence, Co was added to Nd-Fe-B to increase the Curie temperature [5-9] (chapter 4 and 5). However, adding Co can reduce coercivity[9, 10]. Heavy rare earths such as Dy can enhance the coercivity by increasing the magnetocrystalline anisotropy field (H_A) [11]. Therefore, Dy was added to increase coercivity. It is also a common practice to use Dy alloying to increase the thermal stability of Nd-Fe-B based magnets. Thus the simultaneous substitution of Nd by Dy and Fe by Co can simultaneously increase thermal stability and enhance coercivity. Dy magnetic moment is aligned antiparallel to Fe and Nd magnetic moments. Therefore, Dy alloying can decrease remanence and energy product[12, 13]. Moreover, availability of the heavy rare earth elements is very limited and the cost of these magnets rises drastically. Hence, obtaining good magnetic properties and thermal stability using the minimum amount of heavy rare earths is required.

In the current study, a microwave based chemical approach was used to synthesize Dy,Co substituted Nd-Fe-B magnetic powders. A broad range of Dy content was examined, according to the composition set of $\text{Nd}_{15-x}\text{Dy}_x\text{Fe}_{67}\text{Co}_{10}\text{B}_8$ ($x=0, 3, 6, 9$). Samples with a large range of Dy content were synthesized to analyse the effect of Dy on the microstructure, magnetic properties and coercivity mechanism. Room temperature and temperature dependent magnetic properties were investigated as a function of Dy content. The influence of Dy substitution on $(BH)_{\text{max}}$ and thermal stability were determined. The coercivity mechanism of these nanoparticles were investigated by studying the temperature dependent magnetic properties of these alloys.

6.2 Effect of Dy on the Microstructure

Chapter 4 and 5 reported the synthesis of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ nanoparticles via microwave chemical synthesis. To further improve the magnetic properties and study the effects of Dy content, sample sets with compositions of $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ ($x=0, 3, 6, 9$) were synthesized using similar approach as discussed in chapter 4. Figure 6.1(a) shows the diffraction pattern and Rietveld refinement of the powders with various Dy content, after RD and removal of CaO byproduct. It can be seen that all compositions successfully formed the desired tetragonal 2-14-1 crystal structure. The positions and relative intensities of the powders matched well with the peaks of the standard diffraction patterns of $\text{Nd}_2\text{Fe}_{14}\text{B}$ [PDF#01-089-3547]. The zoomed in XRD patterns are shown in figure 6.1(b). With increasing Dy content, the diffraction peaks were shifted to higher 2θ angles. According to Bragg's law, $\lambda=2d\sin\theta$ (λ , wavelength = 1.5406 Å, d is the crystal plane distance, and θ is the angle of diffraction), 2θ angles shift towards higher angles, indicating a decrease of d -spacing values of the crystal. The actual lattice constants (a and c) of the particles were calculated by Rietveld refinement (table 6.1). A decrease of lattice parameters of a , c and unit cell volume were observed. The contracted tetragonal cell is due to the lower ionic radius of Dy compared to Nd[14].

Figure 6.1 (a) XRD pattern of $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ nanoparticles for a range of Dy compositions, $x=0, 3, 6, 9$. The diffraction peaks for $(\text{Dy,Nd})_2(\text{Fe,Co})_{14}\text{B}$ are shown by the symbol ‘*’ (b) zoomed in X-ray diffraction patterns of $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ ($x=0, 3, 6, 9$). Black curves are the observed data, red curves are the calculated data from Rietveld refinement. The small diffraction peaks marked by ‘?’ were not identified.

Table 6.1 $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ ($x=0, 3, 6, 9$) Lattice parameters, calculated by Rietveld refinement from X-ray diffraction analysis.

x	a (Å)	c (Å)	v (Å ³)	Grain size $L_{\text{vol-IB}}$ (nm)	R_{bragg}
0	8.794	12.182	942.09	46.6	0.84
3	8.787	12.150	940.25	57.6	0.82
6	8.779	12.152	936.56	58.5	1.27
9	8.760	12.072	926.38	42.8	0.83

A representative bright field TEM image of the $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ ($x=3$) nanoparticles is shown in figure 6.2. The samples possessed an average particle size of ~ 60 nm, similar to the value obtained in our previous work. The particle size ranges from ~ 10 nm to ~ 120 nm, the size distribution of the particles are also shown (figure 6.2 inset). To investigate the distribution of Dy in the $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ particles, TEM EDS

maps of Fe, Nd and Dy were obtained from selected samples (figure 6.3(a) for $x=3$ and figure 6.3(b) for $x=9$). The selected peaks of the EDS spectrum for the map are Fe $L\alpha$, Nd $L\alpha$ and Dy $L\alpha$. The EDS maps of the $\text{Nd}_6\text{Dy}_9\text{Fe}_{67}\text{Co}_{10}\text{B}_8$ nanoparticles shows a homogenous distribution of Dy and no evidence of Dy segregation.

Figure 6.2 Bright field transmission electron micrograph of $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ particles after by-product removal, inset: particle size distribution of $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ particles after by-product removal

Figure 6.3 Elemental distribution map, obtained by scanning transmission electron microscopy, of $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ (a) $x=3$ (b) $x=9$.

6.3 Effect of Dy on the Room Temperature Magnetic Properties

Figure 6.4(a) shows the room temperature M-H loops of $(\text{Dy}_x\text{Nd}_{15-x})\text{-(Fe}_{67}\text{Co}_{10})\text{-B}_8$ powder for a range of Dy content ($x=0, 3, 6, 9$). It can be seen that the coercivity increased continuously, from 7.9 kOe to 14.5 kOe, with larger Dy content. The saturation magnetization decreased due to antiferromagnetic coupling between the Dy and the Fe atoms. The continuous increase of coercivity (figure 6.4(b)) can be explained by the larger value of intrinsic anisotropy field. The intrinsic coercivity of RE-Fe-B magnets can be expressed as [15, 16]:

$$H_c = cH_A - nM_s \quad 6.1$$

Where H_A and M_s are the anisotropy field and saturation magnetization of $\text{RE}_2\text{Fe}_{14}\text{B}$, respectively. c and n are parameters related to the microstructure.

It can be seen from equation 6.1 that H_c is limited by H_A . The H_A of $\text{Dy}_2\text{Fe}_{14}\text{B}$ (158 kOe) is much higher than that of $\text{Nd}_2\text{Fe}_{14}\text{B}$ (75 kOe), hence an increase in coercivity is expected. Specifically, H_A of Dy substituted $\text{RE}_2\text{Fe}_{14}\text{B}$ can be estimated by the rule of mixtures [17]:

$$H_A = \frac{H_A^{\text{Nd}} \times [\text{Nd}]}{[\text{Nd}] + [\text{Dy}]} + \frac{H_A^{\text{Dy}} \times [\text{Dy}]}{[\text{Nd}] + [\text{Dy}]} \quad 6.2$$

Where H_A^{Nd} and H_A^{Dy} are the anisotropy field of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $\text{Dy}_2\text{Fe}_{14}\text{B}$, respectively. $[\text{Nd}]$ and $[\text{Dy}]$ are the atomic percentage of Nd and Dy in the material, respectively. This equation assumes a uniform distribution of Nd and Dy (figure 6.3). According to equation 6.2, every 3 at% replacement of Nd by Dy will result in an increase of anisotropy field by 1.66 kOe. Therefore, increased Dy content results in higher local magnetocrystalline anisotropy field, hence there was an increase in coercivity.

The M-H curves were measured at magnetic field up to 50 kOe. However, about 80 kOe magnetic field is needed for Nd-Fe-B magnets to saturate [18]. Therefore, extrapolation

was performed of the M versus $1/H$ plot up to 80 kOe magnetic field. It can be observed in figure 6.4 that both saturation magnetization and remanence decrease with increasing Dy content. However, the remanence does not decrease much for the $x=3$ Dy composition. This indicates that the synthesis of Dy-substituted Nd–Fe–B nanoparticles using 3% Dy can enhance coercivity without much reduction in remanence.

Figure 6.4 Magnetic hysteresis (M - H) curves of $(Dy_xNd_{15-x})-(Fe_{67}Co_{10})-B_8$ particles ($x = 0, 3, 6, 9$) after by-product removal, at room temperature. (b) Room temperature value of coercivity, remanence and saturation magnetization of $(Dy_xNd_{15-x})-(Fe_{67}Co_{10})-B_8$ particles.

In our previous research, it was found that the magnetic properties of the $Nd_2(Fe,Co)_{14}B$ particles were highly sensitive to magnetic alignment. In this chapter, alignment of powders were also carried out. $(Dy_xNd_{15-x})-(Fe_{67}Co_{10})-B_8$ ($x=0,3,6,9$) particles were suspended in a liquid adhesive and aligned under an external field of 18 kOe during solidification of the adhesive. Figure 6.5 shows the room temperature MH loops for the aligned sample measured in the direction // to the alignment direction (red lines) and randomly oriented powder (black lines). It can be seen that the shape of the MH curve is sensitive to the alignment. The remanence versus saturation magnetization value (M_r/M_s) increased by $\sim 26\%$.

Figure 6.5 Room temperature M-H magnetic hysteresis loop for $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ particles (a) $x = 0$, (b) $x = 3$, (c) $x = 6$, (d) $x = 9$ measured for randomly oriented powders (black curves) and // to the magnetic alignment c-axis direction (red curves)

The maximum energy product $(\text{BH})_{\text{max}}$ of both the randomly oriented sample and the aligned samples were calculated by assuming a theoretical density of Nd-Fe-B (7.5 g/cm^3) [19-21]. The demagnetization B-H curve was plotted for the randomly oriented samples and aligned samples to determine the $(\text{BH})_{\text{max}}$ for all samples. A summary of $(\text{BH})_{\text{max}}$ for randomly oriented samples and the aligned samples is shown in figure 6.6. For the same Dy content, $(\text{BH})_{\text{max}}$ for the aligned samples were enhanced significantly compared to the randomly oriented powder, especially for $x=0$ and $x=3$, where the $(\text{BH})_{\text{max}}$ almost doubled. The high energy product of the aligned samples are due to the saturation magnetization and squareness induced by alignment of the along the easy axis. Comparing the $(\text{BH})_{\text{max}}$ for a range of Dy content, it can be seen that, the largest $(\text{BH})_{\text{max}}$ of 12.6 MGOe occurs at $x=3$.

Figure 6.6 Maximum energy product calculated for randomly oriented powders (black curve) and aligned samples (red curve) of $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ ($x=0, 3, 6, 9$)

Since interparticle interactions affect magnetic properties, the coercive force and magnetic properties were also analyzed by the Henkel plot. The isothermal remanent magnetization ($M_r(H)$) values and DC demagnetization ($M_d(H)$) were measured for samples with different Dy content. The Henkel plot was plotted according to:

$$\delta M = M_d(H)/M_r(\infty) - \{1 - 2 \times [M_r(H)/M_r(\infty)]\} \quad 6.3$$

Where $M_r(\infty)$ is the remanence after the sample is saturated. In the Henkel plot, δM equal to zero represents noninteracting single domain particles[22].

Positive δM indicates intergrain exchange coupling, while a negative δM indicates dominant magnetostatic interactions. Higher positive δM peak indicates stronger exchange coupling effect between the grains[23, 24]. Figure 6.7 shows the Henkel plots for a range of Dy content. The positive peaks suggest exchange coupling for all compositions. The exchange coupling effect increases below $x=3$ composition and decreases beyond $x=3$ composition. This trend agrees with the $(BH)_{\max}$ trend shown in figure 6.6. Therefore, the

variation in the $(BH)_{\max}$ with increasing Dy content can be understood by a change in the magnitude of exchange coupling interactions.

Figure 6.7 Henkel plots of $(Dy_xNd_{15-x})-(Fe_{67}Co_{10})-B_8$ ($x=0, 3, 6, 9$) particles

6.4 Effect of Dy on Temperature Dependent Magnetic Properties

It is well known that Dy alloying can improve the temperature stability of Nd-Fe-B based magnets. Therefore, the temperature dependent magnetic properties were investigated. MH loops were measured at a range of temperatures (from 300 K to 400 K) for selected samples, e.g., $x=0, 3$ and 9 . The $x=0$ sample is selected as a reference since does not contain Dy, while $x=3$ sample exhibited the largest $(BH)_{\max}$ and the $x=9$ sample displayed the highest coercivity. Figure 6.8(a)(b) and (c) shows the demagnetization curve for the $x=0, 3$ and 9 samples, respectively. It is clearly that both H_c and M_r increased with temperature decreased from 400 K to 300 K, due to thermal effects.

Figure 6.8 M-H demagnetization curves for $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ particles, at a range of temperatures from 300 K to 400 K. (a) $x = 0$ (b) $x = 3$ and (c) $x = 9$

Figure 6.9 shows the coercivity and remanence as a function of temperature. It is found that for these Dy compositions, H_c and M_r decreased with increasing temperature. A higher rate of decrease can be observed at ~ 360 K. The thermal stability was obtained by calculating the thermal coefficient of remanence (α) and coercivity (β) according to the equations below:

$$\alpha(M_r) = \frac{M_r(T_2) - M_r(T_1)}{M_r(T_1)(T_2 - T_1)} \times 100\% \quad 6.4$$

$$\beta(H_c) = \frac{H_c(T_2) - H_c(T_1)}{H_c(T_1)(T_2 - T_1)} \times 100\% \quad 6.5$$

Where T_1 refers to the start temperature and T_2 refers to the end temperature of interest. For the temperature range from 300 K to 400 K, the α values of $x=0, 3, 9$ were found to be -0.59%, -0.37% and -0.34%, respectively. The β values of $x=0, 3, 9$ are -0.89%, -0.83% and -0.74%, respectively. These β values are comparable to the room temperature value of commercial Nd-Fe-B magnets. It can be seen that higher Dy content improved the thermal stability of the magnetic nanoparticles.

Figure 6.9 (a) Coercivity – temperature curves for $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ ($x = 0, 3, 6, 9$) particles, at temperatures ranging from 300 K to 400 K. (b) Remanence – temperature curves for $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ ($x = 0, 3, 9$) particles, at temperatures ranging from 300 K to 400 K.

6.5 Coercivity Mechanism in $(\text{Dy,Nd})_2(\text{Fe,Co})_{14}\text{B}$ nanoparticles

The coercivity mechanism of Nd-Fe-B magnets has been previously investigated, the coercivity mechanism of sintered Nd-Fe-B magnets is the nucleation mechanism while that of melt spun Nd-Fe-B magnets is dominated by domain wall pinning [25] [26]. For the Nd-Fe-B nanoparticles, the coercivity mechanism is still unclear. Therefore, the coercivity mechanism analysis was performed by studying the temperature dependence of the magnetic properties of Nd-Fe-B nanoparticles.

From the initial magnetization curve (virgin magnetization curve), two qualitative different kinds of magnetization behaviour can be observed as shown in figure 6.10[27]. [1]. Generally, these are classified into nucleation type and pinning type behaviors. In a nucleation-type magnet, the initial curve is steep and the saturation of magnetization is reached under a field much lower than, while in a pinning-type magnet, a field of the same order of coercivity is required to saturate the magnetization of the specimen from the initial state [28]. In this work, from figure 6.4(a), one can observe that the behaviour of the initial curves were between the pinning type and nucleation type curves, indicating an combination of the two mechanisms. Hence, further study of the coercivity mechanism was carried out based on the temperature dependent magnetic properties.

Figure 6.10 Different models for coercivity reverse mechanism[27]

The temperature dependence of the intrinsic magnetic properties causes a reduction in coercive field with temperature. This dependence can be expressed by Brown's equation, based on a nucleation type coercivity reversal mechanism [29-31].

A simplified version of the Brown's equation was employed to analyze the temperature dependence of H_c .

$$\mu_0 H_c(T) = \alpha H_A(T) - n M_s(T) \quad 6.6$$

Where α and n constants related to microstructure[25, 32], $H_A(T)$ is the temperature dependent anisotropy field and $\alpha H_A(T)$ can be interpreted as the nucleation field of the reverse domain. $M_s(T)$ is the temperature dependent saturation magnetization and $n M_s(T)$ indicates local demagnetization effects. Since Dy was found to be uniformly distributed, $H_A(T)$ of the Dy substituted $R_2Fe_{14}B$ phase can be calculated according to the rule of mixtures, as in equation 6.2.

This equation is usually assumed to provide support for a nucleation-controlled mechanism[26]. From this equation, the plot of $\frac{\mu_0 H_c(T)}{M_s(T)}$ vs. $\frac{\mu_0 H_A(T)}{M_s(T)}$ should yield a straight line, with a slope of α and an intercept on the y axis of $-n$. Figure 6.11 (a) shows a plot of

$\frac{\mu_0 H_c(T)}{M_s(T)}$ vs. $\frac{\mu_0 H_A(T)}{M_s(T)}$ for the synthesized powder with composition $x=0, 3, 9$. The temperature ranges from 300 K to 400 K. It can be observed that all alloys have a good linear fitting with the theoretical line, suggesting a nucleation controlled coercivity mechanism for the particles. Values of the microstructure constants are listed in the inset of Figure 6.11 (a). The value of α was 0.45, 0.38, 0.51, respectively; and N is 1.84, 2.00, 6.64, respectively. The value of α does not vary much for the various samples, indicating that grain size does not change much with Dy content, which is consistent with the results tabulated in Table 6.1. The difference in the demagnetization parameter N suggests that the smoothness of the grain boundary and local stray fields were influenced by Dy substitution. Detailed studies are needed to identify the effect of Dy substitution on the grain boundary related magnetic properties.

Further analysis was performed for the pinning dominated mechanism using the model of Gaunt [33].

$$\left(\frac{H_c}{H_0}\right)^{1/2} = 1 - \left(\frac{75k_B T}{4bf}\right)^{2/3} \quad 6.7$$

where H_c is the coercivity, H_0 is the critical field in the absence of thermal activation, k_B is Boltzmann constant, $4b$ is the interaction range of a pin equating with the domain wall width and f is the maximum restoring force per pin. In this model, since H_0 , k_B , b and f are all constants, a linear relationship between $(H_c)^{1/2}$ and $(T)^{2/3}$ is expected for the pinning controlled coercivity mechanism. In figure 6.11 (b), $(H_c)^{1/2}$ vs $(T)^{2/3}$ were plotted for samples with compositions of $x=0, 3, 9$, a linear fit was observed. However, the experimental data points deviate to some extent from linear behavior. These findings suggest that strong pinning of domain walls may also take part in the coercivity reversal process. Comparing the fits in figure 6.11 (a) and 6.11 (b), better linear fit is revealed in figure 6.11(a), suggesting that the process is dominated mainly by nucleation-control.

Figure 6.11 (a). Plots of $\frac{\mu_0 H_c(T)}{M_s(T)}$ vs. $\frac{\mu_0 H_N^{\min}(T)}{M_s(T)}$, (b) Plot of $(H_c)^{1/2}$ vs. $(T)^{2/3}$ for $(\text{Dy}_x\text{Nd}_{15-x})-(\text{Fe}_{67}\text{Co}_{10})-\text{B}_8$ ($x = 0, 3, 9$) particles.

6.6 Conclusions

This chapter reports the room temperature and temperature dependent behaviour of $\text{Dy}_x\text{Nd}_{15-x}\text{Fe}_{67}\text{Co}_{10}\text{B}_8$ ($x=0, 3, 6, 9$) hard magnetic nanoparticles. The effects of Dy substitution on the microstructure and magnetic properties were studied. With increasing Dy content, the unit cell of $(\text{Nd,Dy})_2(\text{Fe,Co})_{14}\text{B}$ contracted and a uniform distribution of Dy within the particle was observed. The coercivity increased from 7.9 kOe to 14.5 kOe when the Dy content increased from $x=0$ to $x=9$. It was found that the particles can be crystallographically aligned by an external magnetic field. After alignment, remanence and $(\text{BH})_{\max}$ were significantly enhanced. For the composition of $x=3$, the highest $(\text{BH})_{\max}$ of 12.6 MGOe was obtained due to minimum reduction of remanence and strong exchange coupling effects. Thermal coefficients were improved with increasing Dy content. Through a study of the temperature dependent magnetic properties, the coercivity mechanism was investigated. It was found that the controlling mechanism is the nucleation of the reverse domains.

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Chapter 7

Summary and Future Work

Increasing attention is being paid to improve energy usage efficiency. As an important part of energy materials, magnetic materials play a vital role to increase the efficiency and performance of various energy related applications. Due to the superior magnetic properties, Nd-Fe-B based permanent magnets are widely used. The increasing demand for higher performance and the high cost of rare earth materials provides significant motivation to develop a cost effective method to produce Nd-Fe-B materials. Nanostructured Nd-Fe-B alloys have been predicted to have high energy product and hence have drawn much attention. Hence, a bottom-up chemical synthesis approach was developed to produce Nd-Fe-B based alloys. This chapter summarizes the main findings and suggests future work.

7.1 Summary

In this work, two cost-effective chemical processing approaches were employed for the synthesis of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ nanoparticles: (a) microwave combustion followed by RD in a vacuum furnace and (b) one pot microwave processing. $(\text{Dy,Nd})_2(\text{Fe,Co})_{14}\text{B}$ alloys were prepared. The effect of Dy on the microstructure and magnetic properties were investigated. The coercivity reversal mechanisms were studied by the use of appropriate models.

Microwave assisted combustion, followed by the RD technique, was successfully employed to chemically synthesize $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ powders with crystal size in the nano range.

- (a) In the microwave combustion process, the microwave energy initially resulted in the evaporation of water. Subsequently, microwave initiated auto combustion. The N-H, COO^- and NO_3^- ions all took part in this self-propagating combustion reaction. This combustion led to the formation of CoFeO_4 , NdFeO_3 , Nd_3FeO_6 and Fe_2O_3 .
- (b) In the RD process, Co and Fe oxides were first reduced to Fe and Co as the temperature reached $\sim 350^\circ\text{C}$. Nd oxides was partially reduced to NdH_2 at $\sim 350^\circ\text{C}$ and finally to Nd when the temperature reached $\sim 740^\circ\text{C}$. At this temperature the desired $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ phase was also obtained. The effect of Nd composition was studied. $\text{Nd}_x\text{Fe}_{82-x}\text{Co}_{10}\text{B}_8$ ($x = 15$) was found to have the largest energy product, exchange coupling was observed.
- (c) The effects of processing parameters were studied,
 - Microwave power: Greater microwave power led to higher combustion temperatures, which led to larger crystal size of Nd-Fe-Co-B oxide powder particles. The crystal size of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ followed the same trend as that of the oxide powders. The coercivity of the desired $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ magnetic particles was found to increase from 6.2 kOe to 8.8 kOe when the crystal size increased from 21 nm to 63 nm.

- Reduction diffusion time: It was found that a temperature of 800 °C was required to form the $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ phase. The highest energy product was obtained for RD treatment at 800 °C for 2 h; less than 2 h resulted in incomplete reduction of Nd, while longer than 2 h resulted in the formation of a large amount of Fe (45%) and Nd_2O_3 (6%).
- Byproduct removal: The CaO byproduct has to be removed after RD. Four chemicals were tested to remove the byproduct, namely dilute acetic acid, mixture of glycerol and methanol, EDTA (dissolved in organic solvent) and NH_4Cl (dissolved in methanol). The use of NH_4Cl (dissolved in methanol) eliminated the use of water and thus avoided the vigorous reaction between CaO and water. It was found that the method of NH_4Cl (dissolved in methanol) led to least reduction of coercivity.

A novel and low cost, green, one-pot microwave synthesis technique was used to successfully synthesize $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$ hard magnetic nanoparticles. The heating source for the entire process was only by microwave irradiation using a single microwave chamber. We investigated the structural and magnetic properties of the heavy rare earth free $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$ exchange coupled nanoparticles. The formation mechanism of these nanoparticles were also studied for both oxide and alloy formation:

- (a) The synthesized $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}/\alpha\text{-Fe}$ nanoparticle have a narrow size distribution with 60% in the size range of 35 nm - 45 nm. The magnetic properties of the $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}/\alpha\text{-Fe}$ nanoparticles were highly sensitive to magnetic alignment. After alignment, M_r/M_s increased from 0.56 to 0.88 while the energy product increased from 3.7 MGOe to 11.36 MGOe.
- (b) Water bound to iron nitrate hydrate was released at ~105 °C. At 150 °C, iron and cobalt nitrate decomposed to form $\text{Fe}_2\text{O}_3/\text{CoFe}_2\text{O}_4$. At ~200 °C $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ lost bound water and released NO_x , partially decomposing to $\text{Nd}(\text{NO}_3)(\text{OH})_2$. At 250 °C, glycine decomposed, releasing NH_3 , CO_2 and H_2O . At the same time, $\text{Nd}(\text{NO}_3)(\text{OH})_2$ gradually released NO_x . The exothermic reaction between NH_3 and NO_x contributed to the combustion, further increasing the temperature. This high temperature resulted in

the complete decomposition of $\text{Nd}(\text{NO}_3)(\text{OH})$ to form NdFe_2O_4 . The reaction between the NO_x released during decomposition of the metal nitrate, and the NH_3 released along with glycine decomposition, resulted in high combustion temperature.

- (c) In the microwave RD process, $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}$ alloy was formed through several steps. At 350°C , iron, cobalt and boron oxides were reduced. At 740°C , the partial reduction of neodymium oxide to NdH_5 took place. After annealing at 800°C for 2 h, the desired $\text{Nd}_2(\text{Fe}_{10}\text{Co}_4)\text{B}$ and $\alpha\text{-Fe}$ phases were formed.

Dy alloying additions to Nd-Fe-B based alloys were studied. Room temperature and temperature dependent behaviour of $\text{Nd}_{15-x}\text{Dy}_x\text{Fe}_{67}\text{Co}_{10}\text{B}_8$ ($x=0, 3, 6, 9$) hard magnetic nanoparticles were reported in this thesis. The effects of Dy substitution on the microstructure and magnetic properties were studied.

- (a) With increasing Dy content, the unit cell of $(\text{Nd,Dy})_2(\text{Fe,Co})_{14}\text{B}$ contracted and an uniform distribution of Dy within the particle was observed. The coercivity increased significantly from 7.9 kOe to 14.5 kOe when the Dy content increased from $x=0$ to $x=9$.
- (b) It was found that the particles can be crystallographically aligned by an external magnetic field. Remanence and $(\text{BH})_{\text{max}}$ were significantly enhanced after alignment. For the composition of $x=3$, the highest $(\text{BH})_{\text{max}}$ of 12.6 MGOe was obtained due to minimum reduction of remanence and strong exchange coupling effects.
- (c) Thermal coefficients were improved with increasing Dy content. Through a study of the temperature dependent magnetic properties, the coercivity mechanism was investigated. It was found that the controlling mechanism was the nucleation of the reverse domains.

7.2 Proposed Future Research

The main focus of the thesis was a study of Nd-Fe-Co-B based nanoparticles by the microwave synthesis method. We presented microwave synthetic strategies to produce Nd-Fe-B based permanent magnetic nanoparticles. This chemical approach offers a convenient approach to synthesize Nd-Fe-B based permanent magnetic nanoparticles and provides an opportunity for tuning the phase content and crystal structure.

However, challenges still remain for future development of the chemical approach to prepare nanostructured rare earth based permanent magnetic materials. For example, defects are often present at the grain boundaries of the nanoparticles and the morphology of the nanoparticles is relatively difficult to control compared to non rare earth based magnetic nanoparticles. The as-synthesized nanoparticles are very reactive. Future work to decrease the reactivity of the nanoparticles needs to be investigated, e.g., coating of the nanoparticles or high vacuum compaction of the nanoparticles.

As alloying elements can be readily incorporated by adding metal salts in the precursor, this process provides the opportunity to easily tune the chemical composition of the magnets. The concern of the high cost of heavy rare earth elements is minimized by the use of metal salts. Therefore, further improvement of magnetic properties can be carried out by alloying other elements. Although single-phase Te-, Pr- based magnets exhibit either small moment or a low magnetic anisotropy, the addition of those elements in Sm- or Nd-based magnets may dramatically increase the $(BH)_{\max}$ of magnets.

Nd-Fe-B permanent magnets have a range of life cycles, depending on the applications. The life cycle varies from as short as 2–3 years in consumer electronics to 20–30 years in wind turbines. The size of Nd-Fe-B magnets can be as large as 1000–2000 kg in the generators of modern wind turbines, hence efficient recycling processes for Nd-Fe-B sintered magnets are required from the viewpoint of resource scarcity. The microwave chemical process describe in this thesis can be modified for the recovery of rare earth based magnets.