UNIVERSITI PUTRA MALAYSIA

INFLUENCE OF PROCESS-INDUCED MICROSTRUCTURE AND ADDITIVES (Co, Al, Ti, C) ON MAGNETIC PROPERTIES OF Nd-Fe-B BASED ISOTROPIC HARD MAGNETIC MATERIALS

RAHIM SABBAGHIZADEH

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By

RAHIM SABBAGHIZADEH

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
Fulfilment of the Requirements for the Degree of Doctor of Philosophy

February 2015

DEDICATION

With great respect, I would like to dedicate my dissertation work to my family. A special feeling of gratitude to my loving parents, Iraj Sabbaghizadeh and Fatemeh Mahmoodi, whose words of encouragement and push for tenacity ring in my ears, for all their love, sacrifices and faith. My Brother, Hadi, has never left my side and is very special person for me.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chair: Associate Professor Mansor Hashim, PhD

Faculty: Institute of Advanced Technology

Nanocrystalline permanent magnets offer original magnetic features as a result of surface or interface consequences which are different from properties of bulk or microcrystalline materials. The main reason for this is the grain size and the presence or absence of intergranular stages. Most of the NdFeB research literature has only very superficially dealt with the question of how to improve the magnetic properties of the NdFeB materials. The literature has covered in great detail the answers for the case of Rare Earth-Iron-Boron-based materials obtained from high amounts of rare earth material. Thus, this work was a fresh attempt to critically track the influence of process-induced microstructure, additives and annealing temperature on magnetic properties of (Nd, Pr)-(Fe, Ti, C, Co, Al)-B isotropic nanocomposite alloys with unique compositions, containing medium amounts of boron and lesser amounts of rare earth material.

Various routes were used to organize them, such as direct quenching with different roll rates, devitrification of amorphous over-quenched ribbons by annealing at different temperature ranges and mechanical alloying technique. The results of a methodical analysis of the relationship between microstructure and magnetic properties in isotropic nanocrystalline (Nd,Pr)-(Fe,Ti,C,Co,Al)-B permanent magnets were provided in the present study. The first section explains how microstructure and magnetic properties of (Nd,Pr)-(Fe,Ti,C)-B Melt-spun ribbons are dependent on the solidification rate (quenching wheel speed). Based on these results, the lower speeds were shown to increase the magnetic properties. Thus, we can develop a uniform $Nd_2Fe_{14}B/Fe_3B$ nanocomposite structure with fine soft grains at an optimum 5m/s quenching wheel speed. Moreover, it was shown that increasing quenching wheel speed results in reduced grain size and higher amount of amorphous phase.

The second section, presents the impact of Titanium, Carbon, Cobalt and Aluminum additions on the crystallization behavior, microstructure and magnetic properties of (Nd,Pr)-Fe-B alloys with different compositions. It was shown that additions of Ti and C improved the glass forming ability and raised the temperature of crystallization. Ti addition led to considerable refinement of grain size as a result of the formation of amorphous grain boundaries enriched with Ti. Further C addition led to the enhancement of Ti enrichment in the grain boundary stage that increased coercivity and maximum energy product. The best magnetic properties were obtained from the samples which contain 3 atomic percentages of Titanium and Cobalt. In addition, it was shown that additions of Co increase the temperature of crystallization. Additionally,

substitution of Co enhances the generation of 2:14:1 phase that leads to a considerable increase in coercivity of the ribbons. The appropriate substitution of Co makes intergranular exchange coupling of the grains stronger and results in the improvement of the remanence and energy product for the $(Nd,Pr)_2(Fe,Ti,C)_{14}B/Fe_3B$ type ribbons. The best magnetic properties were achieved for ribbons with Co_3. Nevertheless, small aluminum addition improves coercivity. The Al and Co combination leads to Nd_3Co and $Nd(Fe,Al)_2$ formation at the grain triple points after heating and results in better magnetic isolation of grains. Also, the uniform grain boundary distribution and increasing anisotropy field of the alloys improve alloy coercivity. The third section investigates the effects of different annealing temperatures on the magnetic properties and structure of Nd-Fe-B nanocomposite permanent magnetic alloys with different compositions. Generally, it has been shown that the amorphous alloys' crystallization behavior is strongly dependent on the temperature of heat treatment and the size and volume fraction of α-Fe and $Nd_2Fe_{14}B$ can be manipulated by subsequent thermal processing. Furthermore, magnetic properties are highly dependent on the grain size of the hard and soft magnetic phase. Hence, the increase and decrease of annealing temperature will increase and decrease the magnetic properties. Finally, the best magnetic properties in type (E) and type (F) were achieved at 720 ^{o}C and 700 ^{o}C annealing temperatures respectively, with the $(BH)_{max}$=60.48 KJ/m^3 in type (F) ribbons.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENGARUH PROSES INDUKSI MIKROSTRUKTUR DAN PENAMBAH (Co, Al, Ti, C) KE ATAS SIFAT MAGNETIK Nd-Fe-B BERDASARKAN KEKERASAN ISOTROPIK MAGNET

Oleh

RAHIM SABBAGHIZADEH

Februari 2015

Pengerusi: Profesor Madya Mansor Hashim, PhD

Fakulti: Institut Teknologi Maju

Magnet kekal nanokristal menawarkan keaslian sifat magnet sebagai hasil dari kesan permukaan atau antara muka yang berbaza berlainan dari sifat bahan pukal atau mikrokristal. Faktor utama berlakunya sedemikian adalah wujudnya saiz butiran dan keujudan atau tidak peringkat ikatan antara butiran. Kebanyakan kaji selidik literatur NdFeB membincangkan secara ringkas mengenai persoalan bagaimana untuk meningkatkan sifat magnet bahan NdFeB. Literatur terdahulu telah memberi banyak informasi dan jawapan bagi kes sifat bahan berasaskan nadir bumi-Ferum-Boron yang disediakan dengan jumlah terkini bahan nadir bumi yang tinggi. Oleh itu, kaji selidik ini adalah suatu usaha mengkaji lebih mendalam tentang mikrostruktur yang dipengaruhi oleh proses persediaan, penambahan, dan suhu sepuh lindapan pada sifat magnet nanokomposit aloi isotropic (Nd Pr)-(Fe, Ti, C, Co, Al)-B dengan komposisi unik, mengandungi jumlah boron yang sederhana dan sedikit nadir bumi. Pelbagai cara sudah digunakan contohnya, pelindapan pantas pada kadar guling yang berbeza, devitrifikasi reben amorfus lampau-lindap dengan suhu lindapan yang berbeza dan teknik pengaloian mekanik. Hasil dari kaedah analisis mengenai perhubungan antara mikrostruktur dan sifat magnet yang terdapat didalam nanokristal isotropik (Nd,Pr)-(Fe,Ti,C,Co,Al)-B magnet kekal telah dibekalkan dalam kaji selidik ini. Bahagian pertama menerangkan bagaimana mikrostruktur dan sifat magnet reben lebur-putar (Nd,Pr)-(Fe,Ti,C)-B bergantung pada kadar pemejalan (kelajuan pemejalan). Berdasarkan keputusan, semakin perlahan kelajuan pemejalan, semakin meningkat sifat magnet. Oleh itu, struktur nanokomposit $Nd_2Fe_{14}B/Fe_3B$ yang seragam dengan butiran yang halus pada kadar kelajuan pemejalan yang optimum, 5 m/s dapat disediakan. Selain itu, kaji selidik ini telah menunjukkan peningkatan kelajuan kadar pemejalan menghasilkan pengurangan saiz butiran dan peningkatan jumlah fasa amorfus. Bahagian kedua, menunjukkan kesan penambahan Titanium, Karbon, Kobalt and Aluminium pada sifat pengkristalan, mikrostruktur dan sifat aloi (Nd,Pr)-Fe-B pada komposisi yang berbeza. Ini menunjukan pertambahan unsur Ti dan C telah meningkatkan kebolehan pembentukan kaca dan suhu pengkristalan. Pertambahan Ti memberi kesan kepada saiz butiran sebagai hasil dari pembentukan sempadan butiran amorfus yang kaya dengan Ti. Pertambahan C telah membawa kepada unsur Ti dalam pengkayaan sempadan butiran, yang meningkatkan koersiviti dan produk tenaga maksimum. Sifat magnet yang yang terbaik diperolehi dari sampel yang mempunyai 3 peratus atom titanium dan kobalt. Sebagai tambahan, kajian menunjukan pertambahan Co telah meningkatkan suhu pengkristalan. Selain itu, penggantian unsur Co meningkatkan pembentukan fasa 2:14:1 yang membawa kepada peningkatan koersiviti reben. Penggantian Co yang sesuai telah memberi gandingan pertukaran ikatan antara butiran menjadi lebih kukuh dan penambahbaikan hasil remanen dan produk tenaga bagi reben $(Nd,Pr)_2(Fe,Ti,C)_{14}B/Fe_3B$. Sifat magnet yang paling baik tercapai adalah bagi reben dengan $Co_{3.}$ Namum, sedikit pernambahan aluminium meningkatkan koersiviti. Kombinasi Al dan Co membawa kepada pembentukan Nd_3Co dan $Nd(Fe,Al)_2$ pada suhu tiga titik butiran selepas dipanaskan dan menghasilkan pengasingan butiran magnet yang lebih baik. Disamping itu, pengagihan sempadan butiran meningkatkan medan anisotropi dan meningkatkan koersiviti aloi. Bahagian ketiga menyiasat kesan suhu penyelindapan yang berbeza terhadap sifat magnet dan struktur aloi nanokomposit magnet kekal Nd-Fe-B dengan komposisi yang berbeza. Secara amnya, menunjukkan sifat pengkristalan amorfus aloi bergantung pada suhu pemanasan dan saiz pecahan isipadu bagi α-Fe dan $Nd_2Fe_{14}B$ yang boleh dimanipulasi dari proses haba. Sebagai tambahan, sifat magnet adalah bergantung pada saiz butiran fasa magnet keras dan lembut. Oleh itu, peningkatan dan pegurangan suhu penyelindapan akan meningkatkan atau mengurangkan sifat magnet. Akhir kata, sifat terbaik magnet pada jenis (E) dan jenis (F) akan dicapai pada suhu penyelindapan 720 ^{o}C dan 700 ^{o}C masing-masing, dangan $(BH)_{max}$=60 KJ/m^3 dalam reben jenis (F).

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Countless of people contribute to this thesis; mentors and /or supervisors, family, friends and even some strangers have set off trains of thought and spark ideas or understandings. This means that, by mentioning names, I would be omitting someone. Never the less, my unreserved appreciation goes to my able supervisor Associate Professor Dr. Mansor Hashim for his guidance and suggestions, without which, this work would not have been a success. This thesis is, but a fraction of evidence reflecting his vast insight into magnetism and magnetic materials. I am highly indebted and eternally grateful. To my co-supervisors, Dr. Khamirul Amin Matori and Assoc. Prof. Dr. Jumiah Hassan, I thank them for keeping me right on track. Their contributions would forever remain indelible in my memories.

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APPROVAL

I certify that a Thesis Examination Committee has met on 24/2/2015 to conduct the final examination of Rahim Sabbaghizadeh on his thesis entitled "INFLUENCE OF PROCESS-INDUCED MICROSTRUCTURE AND ADDITIVES (Co, Al, Ti, C) ON MAGNETIC PROPERTIES OF Nd-Fe-B BASED ISOTROPIC HARD MAGNETIC MATERIALS", in accordance with the University and University Colleges Act 1971 and the Constitution of the University Putra Malaysia [P. U. (A) 106] 15 March 1998. The committee recommends that the student be awarded the Doctor of Philosophy.
Members of the Thesis Examination Committee were as follows:

Mohd. Nizar Hamidon, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Abdul Halim b Shaari, PhD
Professor
Faculty of science
Universiti Putra Malaysia
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Faculty of science
Universiti Putra Malaysia
(Internal Examiner)

Ramaswamy Murugan, PhD
Professor
Department of Physics
Pondicherry University
(External Examiner)

Zulkarnain Zainal, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 15 April 2015

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirements for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Mansor Hashim, PhD

Associate Professor
Institute of Advanced Technology
Universiti Putra Malaysia
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Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

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Associate Professor
Faculty of Science
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Declaration by the student

I hereby confirm that:

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- the research conducted and the writing of this thesis was under our supervision;
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Name of Chairman of Supervisory Committee: Mansor Hashim, PhD

Signature: ____________________

Name of Member of Supervisory Committee: Jumiah Hassan, PhD

Signature: ____________________

Name of Member of Supervisory Committee: Khamirul Amin Matori, PhD

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LIST OF ABREVIATIONS

2θ	2 theta degree
d_m	mean grain diameter
σ_R	Specific remanent magnetization
σ_S	Specific saturation magnetization
θ_C	Curie temperature
θ_N	Néel temperature
γ	magnetic domain wall energy proportional
a.u	Arbitrary unit
AFM	Atomic force microscopy
BPR	Ball-to-powder weight ratio
$(BH)max$	Maximum Energy Product
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
H	Magnetic field strength
H_C	Coercivity
hkl	Miller indices
M	Mass magnetization
MA	Mechanical alloying
M_R	Remanent magnetization
M_S	Saturation magnetization
M_{sm}	magnetization per unit mass
M_{sv}	magnetization per unit volume
MUT	Material under test
NdFeB	Neodymium- Iron – Boron
VCM	Voice Coil Motor

SEM	Scanning Electron Microscopy
TEM	Transmission electron microscopy
VSM	Vibrating sample magnetometer
wt %	Weight percent
χ	Magnetic susceptibility
XRD	x-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

A permanent magnet refers to a ferromagnetic material, produced in a metastable condition in which it retains some net magnetisation. Thus, a magnet could be as an energy-storage material that supplies a magnetic field in a specific space volume. The history of permanent magnets comes from a naturally occurring stone, lodestone. This unique stone was discovered mostly in the State of Magnesia in Macedonia, from where the phrase “magnetism” was derived. The primary record of magnetic materials and also the first application as a compass had been in China about 200 B. C. (Muth and Parker, 1990). The initial scientific experimental exploration of magnetism had been by Gilbert in 1600 on lodestone (Fe_3O_4). He analysed terrestrial magnetism and magnetic induction and discovered that magnets lose their own magnetism when heated. In 1825, Sturgeon developed the electromagnet and observed the magnetic field, which is produced by an electric current via coils. In 1880, Warburg demonstrated the primary hysteresis loop intended for iron. Additionally developments related to magnetic phenomena have occurred since the 19th centuries: the connection among an internal and external magnetic field in ferromagnetic materials was discovered by Weiss, magnetostriction by Joule, the Curie law by Curie and hysteresis by Ewing. In the 20th century, scientists developed the physical concept of magnetism; involving quantum mechanics with theories of electron spin in addition to exchange forces, to describe the phenomena of magnetism. During this time period, Néel discovered ferrimagnetism. Wonderful advances in permanent magnet technology took place at the start of the 20th century. Several new magnetic materials were identified and the maximum energy product (BH)*max* enhanced noticeably with the development of each material. The sequential development of the different magnetic materials is connected with their energy product, (BH)*max*.

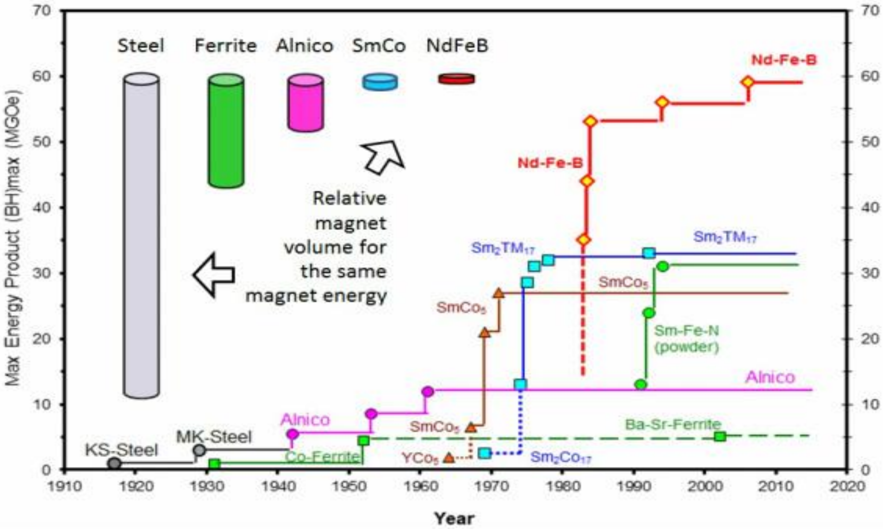

Figure 1.1 Variation of (BH)*max* with time via various types of magnetic material (Magnet Energy Corp, 2014).

The primary magnet found out with a valuable energy product in the last section of the 20th centuries was carbon steel. An important development of this magnet showed in 1917, while Honda and Shimizu (1903) replaced 35% of cobalt into tungsten steel magnets. These types of cobalt steel magnets enhanced the (BH)*max* to ~8kJm^{-3} (Honda and Shimizu, 1903). The subsequent major progress was the improvement of Alnico magnets. Alnico magnets were produced through cobalt magnets in 1932 by Mishima (Livingston, 1990). Alnico alloys consist largely of aluminum, nickel in addition to cobalt (hence the term al-ni-co) with the addition of iron, copper and, occasionally, titanium. They could be magnetized to generate permanent magnetic fields. Alnico alloys have Curie points about 800°C (Chikazumi, 1982). From the beginning 1950s, Ba-ferrite having a hexagonal magnetoplumbite type composition was observed.

The initial Ba-ferrite presented an increased energy product of 32 kJ/m^3. These kinds of ferrites were the 1st main illustration of material that used magnetocrystalline anisotropy for the reason as the basis for their coercivity. This simplicity of processing, without necessity for a protective coating, and also the low cost of the raw materials create this ferrite magnets cost effective to make (Stijntjes and Van Loon, 2008). Within the next ten years, materials with intrinsically higher anisotropy were being produced by hexagonal structured rare earth (RE)-transition metal alloys. Within 1967, Karl Strnat generated the 1st commercial practical RE-based hard magnetic material, $SmCo_5$, which has a maximum energy product of 160 kJm^{-3} (Vieira-Nunes, 1999). Thus far, SmCo5 contains the greatest uniaxial magnetocrystalline anisotropy, accomplished by very careful control of the microstructure as well as additions including iron, copper along with zirconium. Throughout 1970s, as a result of several political as well as prices problems concerning cobalt, scientists started to take into consideration some other raw materials to dropcobalt from the manufacturing of the magnets. Within the late 1970s, a study into boron stabilized Nd-Fe chemical substances by a Ruskies team started the development of the NdFeB ternary compound.

1.2 Nd-Fe-B permanent magnets

Within 1983, Sumitomo Special Metals of Japan and, individually, General Motors of the USA acknowledged the important compound as Nd2F14B and designed appropriate processing tracks to create permanent magnets (Robinson, 1987). Both the various routes for making the particular Nd-Fe-B alloy were the powder metallurgy route manufactured by Sumitomo, along with a nano-crystalline melt spinning method acquired by General Motors. Sagawa claimed a maximum energy product of 290 kJm-3 for sintered magnets (Sagawa, et al., 1984). The properties of Nd-Fe-B based magnets were being enhanced more via optimizing processing variables as well as small alloy additions to the starting material. Following several enhancements in both the heat treatment and also control of Nd-Fe-B based alloys, permanent magnets which has a report maximum energy product of 474 kJm-3 (Br=1. 555T, HcJ=653kA/m) were developed (Xie, et al., 2006). The modern Nd-Fe-B permanent magnets have magnetic properties more advanced than various other magnetic materials at room temperature. It has made them favorite for several purposes, gradually exchanging ferrite- and Sm-type magnets. Nevertheless, the effective use of Nd-Fe-B permanent magnets is restricted to low operating temperatures and non-humid surroundings due to its low Curie temperature (312°C), weak corrosion resistance and poor temperature coefficients of coercivity and remanence.

1.3 Nd-Fe-B permanent magnets Applications

Following NdFeB magnet after it was developed, several new applications including voice coil motors (VCM) for hard disc drives (HDD) and magnetic resonance imaging (MRI) equipment appeared, with a large market developed during the past twenty years. Several new applications which use the NdFeB sintered magnets appear in cars, commercial motors and electrical appliances today. Figure 1.2 demonstrates application of NdFeB magnets in 1999 and 2004. The share of using these kinds of magnets considerably changed between 1999 and 2004. NdFeB magnets for VCM motors had the highest application share and their share in the market was 50% in 1999. On the other hand, the marketplace share of magnets for motors increased to 35% in 2004, compared to that of the VCM magnets which was 32%.

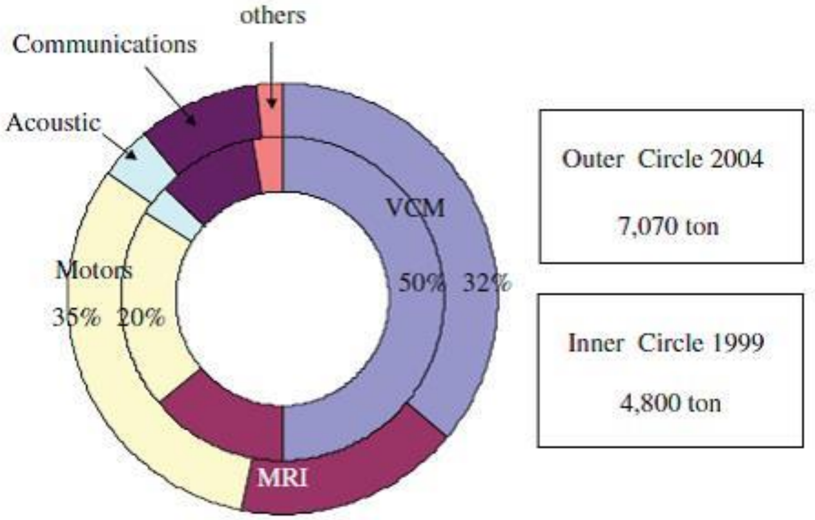

Figure 1.2 Application share of NdFeB sintered magnets (Matsuura, 2006).

1.3.1 Automobile and electric appliances

Nowadays, NdFeB magnets are used on the magnetic motors of automobiles including traction motors in hybrid electric automobiles and electric power steering motors (Gieras, 2002). Magnets are employed at high temperatures and in huge reverse magnetic fields that originate in the stator coils in most of the mentioned applications. These kinds of applications need coercive force magnets and greater magnetic flux compared to standard, traditional, applications. Saving energy and performance are regarded as serious problems for cars and electric devices. NdFeB high-performance sintered magnets can certainly have an extremely critical role in these types of applications. There are several instances of the latest motor applications; compressor motor of air conditioner uses NdFeB magnets. Introduced permanent magnet rotor is utilized due to greater performance compared to a surface mounted rotor in a compressor motor. Hybrid electric vehicle motors and electric power steering motors (EPS) added to the latest extension of motor marketplace.

1.3.2 Magnetic Recording Media

Functionality and assemblage of magnetic nanoparticles have attracted wonderful consideration because of the prospective application in ultrahigh-density magnetic recording (Poudyal, et al., 2007). Continued enhancement within the areal density of hard disk drive is going to be restricted to thin film media where each bit of data is saved over numerous grains. Self-assembled nanoparticle media and patterned media, in which info are stored in a range of single-domain magnetic particle have been recommended as methods to defeat this restriction and to make it possible for recording density approximately 1 Tbit inch-2 (Ross, 2001). In such ultrahigh-density media, as a consequence of high recording density, a smaller material grain and thin size submission are required. To acquire both high signal-to-noise and thermal stability of the media, isolated, non-interacting or very regular interacting nanoparticles with quite high magnetic anisotropy energy Ku are essential (Li, 2007).

1.3.3 Biomedical Applications

Magnetic nanoparticles have been offered for biomedical applications for many years (Pankhurst, et al., 2003). Nowadays, nanotechnology has developed to a level that enables us to generate, characterize and specifically target the functional properties of nanoparticles for applications. This is considerably promising for biomedical and diagnostic field applications such as hyperthermic treatment for malignant cells, targeted drug delivery, and magnetic resonance imaging (MRI) (Willard, et al., 2004).

1.4 Problem Statement

In research on Nd-Fe-B permanent magnets, researchers have neglected a fundamental line of investigation over the past three decades: What are the relationships between composition and microstructure at varying intermediate sintering conditions as the morphology and the properties of material evolve parallel to each other? Do the changes of microstructure affect the magnetic properties of the materials? How do magnetic properties evolve with changes of the microstructure? How do manufacturing techniques affect the magnetic properties in Neodymium Iron Boron magnets? How does wheel speed affect the microstructure and magnetic properties in the melt-spinning method? Thus a line of inquiry has been designed to begin answering these questions using focused objectives as following section.

1.5 Objectives

The main purpose of this study is an investigation on the effect of the manufacturing technique employed, alloy composition and sintering temperature on the magnetic properties and microstructure of isotropic nanocrystalline (Nd,Pr)-Fe-B permanent magnets. Consequently, one important move is to synthesize the NdFeB Permanent Magnets using melt-spinning and mechanical alloying method as well as tracking the evolution of magnetic properties parallel to the microstructural changes. Another investigation is meant to reveal how addition of a small amount of Cobalt, Titanium, Carbon and Aluminium would refine the microstructure, which should result in realization of high magnetic properties.Thus, This research work embarks on the following objectives:

1) To prepare different Nd-Fe-B permanent magnets compositions using melt-spinning and mechanically alloying methods.

2) To determine the optimum composition and processing condition for obtaining the best combinations of magnetic properties by direct quenching.

3) To identify new nanocomposites processed by over quenching and annealing that show good combinations of iHc and (BH)*max*.

4) To study the effect of the (Co, Ti, C, Al) additives and annealing temperature on the microstructure and magnetic properties of Nd-Fe-B permanent magnets

1.6 Thesis Outline

The thesis consists of 6 chapters which contain introduction, literature review, theory, experimental methods, results and discussion, and then conclusion. Chapter 1 presents some briefing about the research background, motivation and objectives. Chapter 2 describes the development of permanent magnets from early history until the discovery of novel nanocomposite permanent magnetic alloys. The subsequent chapter specifies some of the significant principles in magnetism and magnetic materials which are connected directly to the current studies. Chapter 4 refers to materials fabrication and characterisation techniques. The discussion of the acquired results and the microstructure-magnetic properties relationship forms chapter five. Chapter six summarizes and concludes the research information, together with several suggested recommendations. The list of the author's publications is attached right at the end of the thesis, preceded by the references and author's biography and appendices respectively.

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9. Sabbaghizadeh, R., Hashim, S. Kanagesan, N. Shourcheh, N. Deyhimi 2014, Effects of a partial substitution of Fe by Al on nanostructure and Magnetic properties of (Nd,Pr)-(Fe,Co)-B alloys prepared by mechanical alloying. (Submitted)

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