Cobalt-based Magnetic Nanoparticles: Design, Synthesis and Characterization

A Dissertation

By

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ABSTRACT

The ever-increasing desire for more energy attainable from a smaller volume of matter has driven researchers to explore advanced materials at the molecular or even atomic size scale. Magnetic materials at the nanometer size scale have been the subject of enormous research effort worldwide for more than half a century. Different magnetic nanoparticles have shown different behavior in the absence and presence of an external magnetic field, which has led them to be categorized as soft (easy to demagnetize) or hard (resistive against demagnetization) magnets. Applications range from medical and biomedical devices to magnetic recording media and magnetic sensing have emphasized the importance of this class of materials. Soft magnetic phases have found application in power generation and magnetic targeted drug delivery, while hard magnets have been subject of extensive research for application as energy storage media. Discovery of the exchange-coupling phenomenon between the spins of two adjacent hard and soft magnetic phases which means taking advantage of both high magnetic moment of the soft phase as well as high coercivity of the hard phase has attracted scientists to develop advanced materials for energy storage with no usage of fossil fuels: clean energy.

In this Dissertation, synthesis of pure phase, soft FeCo nanoparticles with high magnetic moment and hard phase Co\textsubscript{x}C nanoparticles possessing high coercivity is reported. The polyol method (chemical co-precipitating at polyhydric alcohol as reducing agent) is used to make FeCo and Co\textsubscript{x}C nanoparticles and the
effects of important reaction kinetics parameters on the structure and magnetic properties of the products are studied. Careful analysis of correlations between these parameters and the properties of the magnetic particles has made synthesis of FeCo and Co₅C nanoparticles with desired properties possible. Fabrication of MnAlC-FeCo heterostructures as a rare earth-free alternative for high-performance permanent magnet is also reported. To synthesize MnAlC-FeCo, mechanical alloying and dry mixing of MnAlC and FeCo nanoparticles are accomplished followed by annealing in a furnace. Morphological and magnetic properties of the nanoparticles are obtained by scanning electron microscopy (SEM), x-ray diffractometry (XRD), vibrating sample magnetometry (VSM) and physical property measuring system (PPMS) magnetometry, respectively. Overall, the achieved results in this work enable synthesis of high moment FeCo and high coercivity Co₅C with desired structure and magnetic properties obtained through polyol method. In particular, this Dissertation provides the technique to fabricate cobalt carbide nanoparticles without using rare earth elements as a catalyst or as heterogeneous seed nuclei at any stage: pre-processing, synthesis and post-processing.

Although the experimental results of this work suggest successful fabrication of desired materials, there are many unanswered questions and unresolved challenges regarding reaction mechanism and optimizing the magnetic properties of these materials. Therefore, some recommendations are provided at the end of this Dissertation for further studies and future work. It should be noted that, implementing first principal calculations on these particles will provide
better explanations and enable prediction of structure and magnetic properties of the nanoparticles and facilitate designing more complex heterostructures.
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1.0 INTRODUCTION

1.1 Motivation

Magnetic nanoparticles (MNPs) have been the object of increasing research since the 1950s. Their broad application range covers areas from magnetic recording media and permanent magnetism to biomedical applications [1 & 2]. With the development of new preparation techniques, magnetic nanoparticles with sizes well below 10 nm with narrow size distributions and different compositions can be fabricated by means of a variety of methods. Magnetic particles with nanometer sizes possess interesting new properties that can be attributed either to extrinsic properties of the individual particles, such as finite-size and surface effects or with characteristics of the nanoparticles agglomerates, such as dipole-dipole interactions and exchange coupling between the particles. An interesting magnetic nanoparticle system is that of heterostructured nanoparticles in which the ferromagnetic phase is in contact with either a nonmagnetic, antiferromagnetic, or ferro/ferri-magnetic phase. Among these different types of heterostructures systems, a bimagnetic one, where phase 1 is a soft ferromagnetic and phase 2 is a hard magnet is of particular importance since it is well known that at the vicinity of a soft and a hard magnet the coupling between two phases’ spins induces an exchange anisotropy producing a broadening in the hysteresis loop that has been attributed to the “exchange-coupling” or “exchange spring” phenomenon.

Exchange-coupled hard-soft nanomagnets based on the exchange-spring mechanism have attracted many recent investigations specifically due to the
prediction of energy product values almost twice those achieved for the strongest
magnet made yet; Nd₂Fe₁₄B; as high as 120 MGOe [1]. However, rare-earth
elements are very expensive and prone to corrosion, in addition to the drawback
in using them (severe cost limitations as well as supply chain challenges to
commercial industries). On the other hand, the alternatives to rare-earth metals,
AlNiCo and ceramics ferrites, are either brittle and possess much lower energy
product compared to their rare earth-contained counterparts. In order to obtain
materials with high energy product one could utilize the combination of the high
saturation magnetization of a soft phase and the high coercivity of a hard one.
This kind of matter also shows higher resistance to eddy currents in microwave
applications by reduction in the skin depths.

The exchange coupling phenomenon is a direct coupling between hard and
soft magnetic phases at their interface which make them behave like a single-
phase material during magnetization reversal processes, hysteresis loop, making
these nanocomposites special among magnetic structures. This effect has been
extensively studied in the past decades and progress has been made in its
understanding, though it should be noted that it is not completely understood yet
because of the intrinsic inhomogeneity in the parameters characterizing the
bimagnetic structures, such as particle size, shell thickness, anisotropy constants
and easy axis directions.

In general, the maximum energy product tends to increase both with
increasing coercive field \( H_C \) and saturation magnetization \( M_S \). However, for
materials with sufficiently high $H_C$ values, the theoretical limit for the energy product is limited only by $M_S$ and is given by:

$$ (BH)_{\text{max}} \leq \frac{J_S^2}{4 \mu_0} \quad (1) $$

where $J_S = \mu_0 M_S$ and $\mu_0$ is the permeability in vacuum.

Therefore, we explore the hypothesis that a heterostructure consisting of a soft and a hard phase possesses high saturation magnetization, high permeability as well as high energy product. In keeping with this hypothesis, the overall goal of this Ph.D. Dissertation is to fundamentally understand, design and synthesize soft and hard magnetic nanoparticles, and also to fabricate rare earth-free, high-performance permanent magnets made of inexpensive constituents.

1.2 Overview of research

In this Dissertation, FeCo has been chosen as the soft magnetic phase since this binary alloy possesses the highest saturation magnetization among the 3d-transition metals and also shows one of the highest Curie Temperatures; $950^0\text{C}$. Cobalt carbide, a recently discovered hard magnetic material, has been chosen due to its inexpensive constituents and lack of a thorough study to understand the effect of kinetic parameters on structural and magnetic properties of this system. Synthesis of heterostructures of MnAlC-FeCo as high-performance, rare earth-free permanent magnets has also been attempted and the experiments have shown promising results.
Overall, synthesis of these nanoparticles has been explored by examining the effect of these parameters: (1) reaction temperature; (2) reaction duration; (3) precursors’ concentrations; (4) surface active/capping agents; and (5) reducing potential of the solvent. In this work, also the effect of exposure of the synthesized particles to ambient air has been studied since FeCo nanoparticles have high affinity to react with oxygen which in turn has deteriorate effect on magnetic moment of the particles.

To approach the industrial demand for the magnetic nanoparticles, attempts have been made to scale the production of the materials up to higher amounts. Therefore, in this Dissertation, production of 10 grams FeCo and 5 grams CoxC per batch has been reported with minimum decrease in magnetic properties such as coercivity and saturation magnetization.

1.3 

**Organization of Dissertation**

This Dissertation consists of 6 chapters: (1) Introduction; (2) Critical Literature Review; (3) Experimental Methods and Techniques; (4) Results and Discussions; (5) Conclusions and Summary; and (6) Outlook and Recommendations for Future Work. Chapter 2 of this Dissertation reviews the basic knowledge of magnetism, magnetic materials and permanent magnets and provides the reader with the fundamentals of chemical synthesis methods with the focus on polyol technique. It also reviews and critiques the work done on fabrication of FeCo and CoxC nanoparticles and their magnetic and structural properties. In Chapter 3, the experimental procedures used in this work have been
explained and the equipment and techniques used to characterize the structural and magnetic properties of the samples have been briefly discussed. Chapter 4 contains the experimental results of the synthesized nanoparticles; FeCo in Section 4.1, Co₈C in Section 4.2 and MnAlC-FeCo in Section 4.3, and the effect of each parameter on the properties of the particles has been reported, accompanied by discussing the trends and behavior of systems observed during the course of this Dissertation. Chapter 5 has summarized the experimental results and concluded the overall achievements of this work and finally, in Chapter 6, some recommendations have been provided for future studies.
2.0 CRITICAL LITERATURE REVIEW

This chapter on critical literature review has three main sections. The first section is Section 2.1 which reviews the fundamental knowledge of the magnetic materials at nanometer scale sizes and their distinct properties with special attention paid to permanent magnets and exchange-coupled permanent magnets, followed by reviewing different processing techniques in fabricating these classes of materials. Applications of the permanent magnets are also summarized.

Section 2.2 contains a summary of literature reports on the fabrication of iron-cobalt binary alloys with different chemical techniques. Finally, Section 2.3 briefly reviews the fabrication of a newly discovered cobalt-carbide particles and their potential utilization as an alternate to rare earth-contained permanent magnets.

2.1 Magnetic nanoparticles and their applications

The fundamental understanding of chemical, electrical, optical and magnetic properties of nanomaterials (materials with dimensions less than 100 nm) has been of significant importance over the past two decades [1,2]. Magnetic nanoparticles are a specific class of nanomaterials, composed of at least one magnetic element. These materials could be used in a variety of forms including: in solution as ferrofluids for audio speakers [2], as particle arrays in magnetic storage media [3-8], as surface functionalized particles for biosensing applications [9-17], as powder compacts for power generation, conditioning and conversion [2], in medical applications including magnetic targeted drug delivery [18-23] and contrasting agents in magnetic resonance imaging [24-28].
The study of magnetic properties of nanomaterials is an important area for the advancement of nanoscience and nanotechnology mostly because of the fact that the nanoscale magnetic properties differ from their bulk counterparts.

Based on the response to an applied magnetic field, materials can be divided into diamagnetic, paramagnetic, ferromagnetic, ferrimagnetic and antiferromagnetic.

2.1.1 Introduction to magnetism

In each atom, every electron possesses an intrinsic form of angular momentum; “spin” that is equivalent to the strength of the magnetic field (magnetic moment) of that electron. Electrons are arranged in energy states of successive order, and according to Pauli’s exclusion principle, for each energy state there can be only two electrons of opposite spins. The other source of magnetization is the orbital motion of an unpaired electron around the nucleus. The magnetic moment of each electron pair in an energy level is opposite in direction and consequently, whenever an energy level is completely full, the net magnetic moment is zero. In most of the elements, the unpaired electron is in the valence shell and can interact with valence electrons of neighboring atoms leading to the cancellation of the net magnetic moment in the material. However, certain elements such as cobalt and iron have an inner energy level that is not completely filled, thus each atom in the metal has a permanent magnetic moment equal in strength to the number of unpaired electrons [29].
**Diamagnetism**

Diamagnetism appears in all materials, and is the tendency of a material to oppose an applied magnetic field, and therefore, to be repelled by a magnetic field. However, in a material with paramagnetic properties (that is, with a tendency to enhance an external magnetic field), the paramagnetic behavior dominates [30] Thus, despite its universal occurrence, diamagnetic behavior is observed only in a purely diamagnetic material. In such material, there are no unpaired electrons, so the intrinsic electron magnetic moments cannot produce any bulk effect. Wilhelm Weber and Paul Langevin theorized that an applied field acts on a single electron orbit to reduce the effective current of the orbit, in turn producing a magnetic moment that opposes an applied field [31]. Examples of diamagnetic materials are water, wood, most organic compounds and copper [29].

**Paramagnetism**

In a paramagnetic material there are unpaired electrons. While paired electrons are required by the Pauli’s exclusion principle to have their intrinsic ('spin') magnetic moments pointing in opposite directions, an unpaired electron is free to align its magnetic moment in any direction [32]. These uncompensated moments tend to align, in the same direction with the applied field; however, thermal energy keeps them from total alignment.

**Ferromagnetism**

A ferromagnet, like a paramagnet, has unpaired electrons. However, in addition to the electrons' intrinsic magnetic moment's tendency to be parallel
to an applied field, there is also in these materials a tendency for these magnetic moments to orient parallel to each other to maintain a lowered-energy state. Thus, even when the applied field is removed, the electrons in the material maintain a parallel orientation [33].

**Antiferromagnetism**

In another kind of magnetic material, there is a tendency for the intrinsic magnetic moments of neighboring valence electrons to point in opposite directions. When all atoms are arranged in a substance so that each neighbor is 'anti-aligned', then the substance is called “antiferromagnetic”. Antiferromagnets have a zero net magnetic moment, meaning no field is produced by them. They are less common compared to other types of magnetic behaviors, and are mostly observed at low temperatures.

**Ferrimagnetism**

In an antiferromagnet, if two atoms have anti-parallel magnetization of unequal magnitude a resultant magnetization remains in the direction of the stronger magnetic moment and applied field. This is referred to as ferrimagnetism. (See Figure 1)
Figure 1. Different types of magnetism in materials. Blue Arrows indicate the direction of the extern applied field. Blue arrows in the black circle signify the direction of the electron spin [29]
2.1.2 Chemical synthesis methods of magnetic nanoparticles

Like other types of inorganic materials, magnetic nanoparticles should be produced with controlled properties based on manipulation of processing parameters. For magnetic nanoparticles to be incorporated into magneto-bio-electronic devices, the chemical processing has to control the composition, microstructure, phase purity and morphology of the particles which include controlling the particle size, reducing the aggregation of particles and size distribution. For reliable reproducibility, knowledge of the most sensitive processing parameters to the formation of particles of the preferred phase is essential. Also, control of the processing conditions is needed to manipulate the structural characteristics of the particles allowing control of the intrinsic magnetic properties [2].

The three most common approaches used to produce magnetic nanoparticles are: physical vapor deposition [34], mechanical attrition [35 & 36], and chemical routes from solution [37-40]. In both the vapor phase and solution routes, the particles are formed from individual atoms. Alternatively, mechanical alloying involves the fracturing of larger bulk materials to form nanostructures [2]. In this section, the focus will be on chemical methods of producing magnetic nanoparticles due to their enhanced homogeneity from the molecular level design of the materials, cost effectiveness of the bulk quantity production, controlling the particle size and size distribution, morphology and agglomerate size. Also, surface modification as well as post-synthesize is easily accomplished, providing additional functionality of the nanoparticles.
Turkevich established the first reproducible standard procedure for the preparation of metal colloids [41]. He also proposed a mechanism for the stepwise formation of nanoclusters based on nucleation, growth, and agglomeration [42 & 43]. His model was modified later by data from modern analytical techniques and results obtained from thermodynamic and kinetic studies and is still valid today (Figure 2). According to this model, the metal salt is first reduced to give zero-valent metal atoms. These atoms collide in solution to give a stable ‘seed’ nucleus which its formation is irreversible. It predicts that to initiate nucleation, the concentration of metal atoms in solution must be high enough to reach a specific concentration called ‘supersaturation’ [44 & 45]. However, it was LaMer and coworkers [46] who were the first to propose that nucleation from supersaturated solutions occur as a sudden burst. The point, at which the concentration of free material no longer increases and eventually starts to decrease, is termed the critical supersaturation point. At this point the stable nuclei begin to grow. The growth follows diffusion kinetics and Ostwald ripening (formation of larger nuclei at the expense of smaller ones) [47] and the model also stated that monodispersity is a consequence of carefully separating the nucleation step from the subsequent growth step (see Figure 3). For metal particles, nucleation is the result of a complicated interplay of factors such as the difference between the reduction potentials of the metal salt and the reducing agent and the reaction conditions including the rate of addition, the rate of removal, the reaction temperature, the reaction duration and even the stirring rate. To achieve a monodisperse sample, the nucleation step must be complete before the growth
step begins. As a rule, short nucleation times are the prerequisite for monodisperse particle formation. [48 & 49]

Figure 2. (a) Schematic illustration of the LaMer model: separate nucleation and growth for the synthesis of monodisperse nanoparticles; (b) a typical “hot-injection” set-up to achieve the burst nucleation in (a) [45]

As a result of attractive van der Waals forces and the tendency of the system to minimize the total surface or interfacial energy, nanostructured particles often form agglomerates which can happen during any of the synthesis, drying, handling and/or post-processing. To impede agglomeration of particles,
surfactants (any substance that affects the surface or interfacial tension of the medium in which it is dissolved) can be used [50] to control the dispersion during chemical synthesis by reducing the interparticle interaction through an increase in repulsive forces. Capping or stabilizing agents may also be used to help control the particle size and shape.

Figure 4 shows the chemical synthesis techniques used for the formation of magnetic nanoparticles. Some techniques are frequently used together or in a series of reactions, as noted by the cross-hatching between fields in the figure. The dotted line indicates the demarcation between syntheses using organic and those using aqueous solutions. It’s worth mentioning that generally, sol–gel and hydrothermal reactions produce oxide nanoparticles due to their production in an aqueous solution without a source of reduction.
Figure 3. LaMer crystallization model. 3-step crystallization model for homogeneous nucleation and growth: I. Pre-nucleation period, II. Nucleation and III. Growth [46]
Figure 4. Schematic diagram showing chemical synthesis techniques for magnetic nanoparticles: crosshatched regions indicate common combinations of synthesis techniques [2] PPC: precipitation; H: hydrothermal; HR: hydride reduction; M: micellar or microemulsion; T(OM): thermolysis– organometallic decomposition; T(CO): thermolysis– carbonyl decomposition; UV: photolysis; S: sonolysis; SG: sol–gel; P: polyol; EC: electrochemical; ED: electrodeposition; MSP: multisynthesis processing [46]
2.1.2.1 Precipitation

One of the oldest techniques for the synthesis of particles is the precipitation of products from solutions. Kinetically, the metal precursors are dissolved in a solvent (commonly water) and a precipitating agent is added to form an insoluble solid. In most cases, a further reduction step is required, either in solution after synthesis (such as borohydride reduction) or to the collected precipitate, (i.e. heat treatment in hydrogen gas) as seen in Figure 5. Many magnetic nanoparticles can be synthesized using these aqueous precipitation reactions. These reactions can generate a wide range of magnetic materials including spinel ferrites, perovskites, metals, and alloys with the advantage of large quantities of particles, but the particle size distribution is usually broad [2]. Figure 6 shows magnetic FePt particles 6 nm in diameter synthesized by precipitation in hexane/octane solution.

However, requiring higher activation energy and affinity to react with dissolved oxygen in water are two main reasons to use other solvents. The polyol method, in which a polyol (a polyhydric alcohol, see Figure 7) acts as solvent, reducing agent, and surfactant, is a suitable method for preparing nanoscale size particles with well-defined shapes and controlled particle sizes. [50-55].

Polyols are interesting solvents because they have relatively high permittivity, making them ideal for dissolving ionic and even inorganic solids [56-60]. Nanocrystalline powders of different metals such as Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Sn, Re, W, Pt, Au, or their alloys such as (Fe,Cu), (Co,Cu), (Co,Ni),
and (Ni,Cu), (Fe,Co) and (Fe,Ni) were synthesized using different salt precursors by this method [61-64].

Figure 5. Wet chemical formation of nanostructured metal colloids [29]
Figure 6. TEM micrograph of a 3D assembly of 6-nm as-
synthesized Fe$\textsubscript{50}$Pt$\textsubscript{50}$ particles deposited from a hexane/
octane (v/v 1/1) dispersion onto a SiO-coated copper
grid. (B) TEM micrograph of a 3D assembly of 6-nm
Fe$\textsubscript{50}$Pt$\textsubscript{50}$ sample after replacing oleic acid/oleyl amine
with hexanoic acid/hexylamine. (C) HRSEM image of a
180-nm-thick, 4-nm Fe$\textsubscript{52}$Pt$\textsubscript{48}$ nanocrystal assembly
annealed at 560 °C for 30 minutes under 1 atm of N\textsubscript{2}
gas. (D) High-resolution TEM image of 4-nm Fe$\textsubscript{52}$Pt$\textsubscript{48}$
nanocrystals annealed at 560 °C for 30 minutes on a Sm
coated copper grid [48]
Polyols, like alcohols, are mild reducing agents therefore the reactions can occur between room temperature and the boiling point of the solvent (up to 450 °C for light polyethylene glycols). Fievet et al. [65] have reported fabricating isolated metallic nanoparticles of different metals such as; gold, palladium, iridium, copper, silver, nickel, cobalt, lead, and cadmium via polyol reduction, in ethylene glycol as media. However, they reported that in absence of additional stabilizers to control the growth of the nanoparticles, the particles were highly agglomerated and the particle size distribution was broad with irregular shapes.
The polyol method was modified later by different noble strategies to overcome this deficiency; for example, by varying the temperature of the reaction or using a precursor that is partially soluble, which gives rise to an insoluble solid phase that acts as a kind of reservoir. Alternately, kinetically controlled reactions by using heterogeneous nucleation seeds to slow the nucleation step can also be employed for better dispersed metal nanoparticles. Also, employing long-chain polyols that can act as protective agents (surfactants) or the use of additional protective agents (e.g., PVP) allows controlling the particle growth, which is crucial in case of magnetic metals that have higher tendency to agglomerate.

PVP (PolyVinylPyrrolidone), a water soluble polymer, was found to be a suitable surfactant because the reduction of nobler metal salts by polyols in the presence of other surfactants often resulted in non-homogenous particles. By reducing the precursor to PVP ratio, it is possible to generate metal particles sizes of few nanometers. These colloidal particles are prone to oxidizing because samples washed with the solvent and dried in the air are not any more pyrophoric.

### 2.2 Permanent magnets

A figure of merit of permanent magnets (magnets which maintain a large magnetic flux in the absence of a magnetizing field) is calculated as the optimal product of the remanence (remanent magnetic flux in the absence of external magnetic field; $B_r$) and the coercivity (resistance to demagnetization; $H_c$) manifest in the second quadrant of the (B-H) hysteresis loop (see Figure 8) and is called the ‘maximum energy product’. This quantity is an extrinsic property of the magnet since it is dependent on the magnetic materials’ microstructure and is defined at
the temperature of interest. On the other hand, ‘intrinsic’ magnetic properties are those determined by the crystal structure and composition of the material, and independent of the microstructure of the material. Saturation magnetization $M_s$, the ferromagnetic Curie temperature $T_C$ and its antiferromagnetic counterpart, the Neel temperature $T_N$ (temperature at which the ambient thermal energy becomes sufficiently large to cancel the effective magnetic ordering out within the material) are some examples of important intrinsic magnetic properties.

Figure 8. The second quadrant of the intrinsic magnetic (B-H) hysteresis loop, identifying important parameters such as magnetic remanence $(B_r)$, intrinsic coercivity $(H_{ci})$, and maximum energy product $(BH)_{max}$ that quantifies the energy stored, or the strength, of a permanent magnet [67]
The magnetocrystalline anisotropy energy $E_A$, which is determined by the local interatomic bonding environment surrounding a magnetic atom, specifies the energy per unit volume necessary to direct the magnetization from the easy axis to the hard axis in a crystal and is approximated in a uniaxial system as a power series of the form

$$E_A = \sum_n K_n \cdot \sin^{2n} (\theta) \tag{2}$$

Where $K_n$ represents the uniaxial anisotropy constant for nth direction in the crystal and $\theta$ is the angle between the magnetization vector and the easy axis [67]. Generally, first term is sufficient for calculating the magnetocrystalline anisotropy energy and it becomes:

$$E_A = K_1 \sin^2 (\theta) \tag{3}$$

Assuming that magnetization reversal only occurs via rotation of the magnetic vector between easy axes against the magnetocrystalline anisotropy, maximum coercivity becomes:
Thus, maximum energy product would be ideally equal to:

\[ (BH)_{\text{max}} = \frac{(4\pi M_s)^2}{4} \quad (5) \]

Equation (5) predicts that the maximum energy product corresponds to an ideal rectangular hysteresis loop. Therefore, research has focused on developing new high-anisotropy materials with high saturation magnetization \( M_S \) and high operating temperature \( T_C \). These materials are usually a binary or ternary rare earth (RE) transition metal intermetallic, boride or nitride compounds such as SmCo5, Sm2Co17, Nd2Fe14B and Sm2Fe17N3 [2]. In these materials, the giant anisotropy arises mostly from the crystal-field interaction of the aspherical rare earth 4f shells while the TM (usually Fe or Co) contribute to higher \( M_S \) and \( T_C \) [68]. Thus, new permanent magnetic compounds will ideally be transition metal-rich to enhance saturation magnetization. The high cost of rare earth metals, due to very low concentrations in their ores which makes mining the rare earth metals very expensive and their high affinity to oxidizing were the main driving forces to develop rare-earth-free permanent magnets [67].
Figure 9. World production, reserves and U.S. imports of rare-earth elements [69]

Table 1. Rare Earth Elements: World Production & Reserves [69]

<table>
<thead>
<tr>
<th>Country</th>
<th>Mine Production (metric tons)</th>
<th>% of total</th>
<th>Reserves (106 metric tons)</th>
<th>% of total</th>
<th>Reserve Base (106 metric tons)</th>
<th>% of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>none</td>
<td></td>
<td>13.0</td>
<td>12</td>
<td>14.0</td>
<td>9.3</td>
</tr>
<tr>
<td>China</td>
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<td>95</td>
<td>55.0</td>
<td>50</td>
<td>89.0</td>
<td>59.3</td>
</tr>
<tr>
<td>Russia</td>
<td>2200</td>
<td>2.0</td>
<td>19.0</td>
<td>17</td>
<td>21.0</td>
<td>14</td>
</tr>
<tr>
<td>Australia</td>
<td>2800</td>
<td>2.5</td>
<td>3.1</td>
<td>2.8</td>
<td>1.3</td>
<td>1.0</td>
</tr>
<tr>
<td>India</td>
<td>250</td>
<td>0.22</td>
<td>Small</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Malaysia</td>
<td>280</td>
<td>0.25</td>
<td>Small</td>
<td></td>
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<tr>
<td>Other</td>
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<td></td>
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<tr>
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<td>111,000</td>
<td></td>
<td>110.0</td>
<td></td>
<td>154</td>
<td></td>
</tr>
</tbody>
</table>
Permanent magnets can be broadly classified into three categories: besides rare earth-3d transition metal intermetallic, there are AlNiCos (alloys of primarily iron with nickel, cobalt and copper and sometimes titanium) and ceramic magnets which are typically strontium-doped barium hexaferrites. Their applications include: devices with tractive and repelling exertions such as magnetic separators, torque drives and bearings, to convert energy as generators, alternators, motors and actuators. They can also be applied in radiofrequency, microwave and millimeter-wave devices such as isolators, circulators, phase shifters and ion pumps as well as cathode ray tubes and cyclotrons [70].

2.3 Exchange-coupled permanent magnets

Magnetic particles with nanometer sizes possess interesting new properties that can be attributed either to intrinsic properties of the individual particles, such as finite-size and surface effects or with characteristics of the nanoparticles agglomerates, such as dipole-dipole interactions and exchange coupling between the particles. An interesting magnetic nanoparticle system is that of two-phase hetero-structured nanoparticles in which a ferromagnetic material is in contact with either a nonmagnetic, antiferromagnetic, or ferro/ferri-magnetic material. Among these different types of binary systems, a bimagnetic one, where one layer is a soft ferromagnetic (a magnet with coercivity less than 100 Oe) and the other is a hard magnet (a magnet with coercivity larger than 1000 Oe) is of particular importance since it is well known that at the vicinity of a soft and a hard magnet the coupling between two phases’ spins induces an exchange anisotropy producing a broadening in the hysteresis loop that has been termed “exchange
coupling” or “exchange spring”. Exchange-coupled hard-soft nanomagnets based on the exchange-spring mechanism have attracted many recent investigations specifically due to the prediction of energy product values almost 2 times that achieved for the strongest magnet made yet; Nd$_2$Fe$_{14}$B; as high as 120 MGOe [68]. However, as noted before, rare-earth elements are very expensive, prone to corrosion and pose severe cost limitations as well as supply chain challenges to commercial industries. On the other hand, the alternatives to rare-earth metals; AlNiCo and ceramics ferrites, are either brittle and possess much lower energy product compared to their rare-earth counterparts. In order to obtain materials with high energy product one could utilize the combination of the high saturation magnetization of a soft phase and the high coercivity of a hard one. This kind of matter also shows higher resistance to eddy currents in microwave applications by reducing in their skin depths.

The exchange coupling phenomenon is a direct coupling between hard and soft magnets at their interface which make them behave like a single-phase material within magnetization reversal processes, making these nanocomposites special among magnetic structures. This effect has been extensively studied in the past decades and progress has been made in its understanding, though it should be noted that it is not completely understood yet because of the intrinsic inhomogeneity in the parameters characterizing the two-phase structures, such as particle size, layer thickness, anisotropy constants and easy axis directions.

For a heterostructure material with uniaxial anisotropy and the easy axes of the hard and soft phases being collinear, the coercivity modified to [68]:

\[ H_{\text{c, mod}} = H_{\text{c, hard}} - H_{\text{c, soft}} \]
\[
H_c = 2 \left( K_H f_H + K_S f_S \right) / \left( M_H f_H + M_S f_S \right) \tag{6}
\]

where;

- \( K_H \): anisotropy constant of the hard phase
- \( K_S \): anisotropy constant of the soft phase
- \( M_H \): saturation magnetization of the hard phase
- \( M_S \): saturation magnetization of the soft phase
- \( f_H \): volume fraction of the hard phase
- \( f_S \): volume fraction of the soft phase

The exchange coupling at the interface is mediated by the exchange field \( H_{ex} \), which essentially determines the nucleation field of the soft phase. Goto et al. [71] derived an expression for \( H_{ex} \) for layered systems consisting of a perfectly rigid hard layer and a zero-anisotropy soft layer:

\[
H_{ex} = \pi^2 A_s / \left( 2 M_S t_S^2 \right) \tag{7}
\]
where

\( A_S \): exchange constant

\( M_S \): saturation magnetization

and

\( t_S \): thickness of the soft layer

However, experimental results for SmCo/Fe and SmCo/Co bilayers indicate that the value for \( H_{\text{ex}} \) in SmCo (200 Å) / Co (200 Å) is about three times larger than that of SmCo (200 Å) Fe (200 Å). The difference in \( H_{\text{ex}} \) for both systems cannot be explained by equation (8), which suggests that the anisotropy of the soft phase is not necessarily a negligible factor in real materials. It was also observed that the value of \( t_S \) for single-phase-like magnetization reversal at room temperature for SmCo/Fe bilayers is between 25 and 100 Å, but is 200 Å for SmCo/Co which contradicts the statement that \( t_S \) should be less than twice the domain wall thickness of the hard phase irrespective of the properties of the soft material [68].

This proposal focuses on fabricating exchange coupled hard-soft magnetic composites consisting FeCo as the soft phase and Co\(_{3}\)C as the hard phase.

2.4 FeCo nanoparticles

Iron-cobalt based alloys exhibit interesting magnetic properties including:
high Curie temperatures, high saturation magnetizations (\( M_S =2.4 \) T, for the bulk alloy at room temperature, the highest among binary alloys, see Figure 10), high
permeability, low magnetic losses at high frequencies and being relatively strong [72-74]. This fact makes this binary alloy the best candidate as the soft component in making a rare earth-free exchange coupled permanent magnet. Since first report of fabrication of FeCo as soft magnetic material by Elmen in 1929 [75] there has been lots of research done to understand the physics of magnetism and improve their properties [76-80].

Although the maximum saturation magnetization occurs at 35% cobalt content, equiatomic compositions offer a considerable enhanced permeability for an almost similar saturation (see Figure 11).

![Slater-Pauling curve](image)

Figure 10. The Slater-Pauling curve showing the mean atomic moment for binary alloys of transition metals as a function of their composition [76]
Equiatomic FeCo alloys have a b.c.c (Body Centered Cubic) structure ($\alpha$ in figure 12) below 980 °C, with a lattice parameter given by [82]:

$$a_\alpha/\text{nm} = 0.28236 + 6.4514 \times 10^{-5}[\text{at}\%\text{Fe}]$$ \hspace{1cm} (8)

$$a_\alpha/\text{nm} = 0.28250 + 6.4231 \times 10^{-5}[\text{at}\%\text{Fe}]$$ \hspace{1cm} (9)

and a f.c.c one ($\gamma$ in figure 12) above this temperature, with a lattice parameter given by:
\[ a_\gamma / \text{nm} = 0.35438 + 1.0233 \times 10^{-4} [\text{at}\% \text{Fe}] \] (10)

Figure 12. The FeCo binary diagram as given in. \( T_C \) denotes the Curie temperature [83]

Various methods have been used to correlate magnetic properties changes and the disorder-order transition. Measurements of the saturation moment show
an increase of just about 4% upon chemical ordering [64-67] as shown in Figure 13.

![Graph showing the variation of the saturation magnetization of iron cobalt alloy as a function of temperature.](image)

**Figure 13. The variation of the saturation magnetization of iron cobalt alloy as a function of temperature [88]**

Since both iron and cobalt have a high affinity to oxidization, an organic alcohol should be used as the solvent during nanoparticles synthesis to minimize the oxygen concentration in the solution. Fievet et al [71] used ethylene glycol as the solvent to make copper, cobalt, and nickel and iron nanoparticles. According to the proposed mechanism the polyol serves both as a solvent (first step) and as a reducing agent (second step). On the other hand, Kodama and coworkers [89] reported the important role of the hydroxyl ions. They suggested that the hydroxyl...
ion provides the sites for nucleation and subsequent growth of the metals. By changing the amount of salt to metal precursor ratio between 1 to 40 they could make particles with magnetic moments up to 220 emu/g (see Figure 14). Particle sizes were tuned by controlling the metal-ion concentration while the hydroxyl ion concentration and also the relative concentration of the metal precursors were kept constant, (as in Figure 15).

Figure 14. The hysteresis loop of the Fe$_{68}$Co$_{32}$ alloy showing the maximum magnetization at room temperature [89]
Figure 15. Transmission electron micrographs illustrating particle size variation of the Fe$_{68}$Co$_{32}$ alloy synthesized with metal-ion concentrations of a) 0.07 b) 0.03, and c) 0.015 molL$^{-1}$ [89]

Viau et al. synthesized FeCo alloy particles in polyol in 1996 for the first time [90]. They reported that these reactions consist of disproportionation of iron hydroxide in organic media with the concomitant reduction of other metal hydroxides such as Co and Ni in the original process. They also claimed that the polyol process does not apply to iron as it is more electropositive than Ni or Co and ethylene glycol is too weak to reduce ferrous ions. On the other hand, Joseyphus et al. [91] disagreed by reasoning that if iron is synthesized through disproportionation, equal quantities of metallic iron and magnetite should be obtained. They also showed that the polyol can reduce iron and thus synthesis of iron metal as well as low-temperature synthesis of Fe-based noble and transition metal alloys in the polyol is feasible.
Jeyadevan and coworkers [92] studied the polyol process extensively and proposed that reduction of metal hydroxide to metals takes place through dehydration reactions in ethylene glycol as:

\[
2 \text{CH}_2\text{OH}-\text{CH}_2\text{OH} \rightarrow 2 \text{CH}_3\text{CHO} + 2 \text{H}_2\text{O} \quad (11.\text{a})
\]

\[
2 \text{CH}_3\text{CHO} + \text{M} (\text{OH})_2 \rightarrow \text{CH}_3\text{COCOCH}_3 + 2 \text{H}_2\text{O} + \text{M} \quad (11.\text{b})
\]

They claimed that the hydroxyl ion concentration plays an important role in determining the nucleation rate and were able to control the number of nuclei formed in any system by changing the hydroxyl ion concentration, see Figure 16.

Figure 16. SEM micrographs of the FeCo alloy nanoparticles (right) Fe_{73}Co_{27}, (middle) Fe_{74}Co_{26}, and (left) Fe_{57}Co_{43} synthesized in ethylene glycol [91]
2.5 Co$_x$C nanoparticles

There has been a huge amount of research devoted to making alternates to rare earth magnets since these metals are expensive and prone to corrosion and, as such, severe cost limitations as well as supply chain are more challenges to commercial industrial utilization. Although much attention has been paid to carbon-containing magnetic materials which include carbon-coated magnetic-metal nanocrystalline materials [93], M$_n$C (M = Fe, Co, Ni, Cu, n = 1-6) nanoclusters [94] and Co-C granular films [95-97], these studies did not explore magnetic properties. The focus of these studies was the fabrication of carbon-related composites mostly for biomedical applications and cancer remediation therapies [98].

Historically, cobalt carbide was studied because of its formation during Fischer-Tropsch (FT) synthesis of methane [81] which can be described as a polymerization reaction of adding C$_1$ (simple alkyl chain) unit to a growing chain. Several mechanisms were proposed for these reactions based on the C$_1$ unit. In any case, the surface of the catalyst always consists of a wide range of carbon-containing molecules; and each of them interacts with the catalyst differently. Therefore, it is reasonable to expect that carbon is a possible cause of deactivation of the catalysts, by forming inactive species: carbides [81, 99-103]. Hofer et al. and Dureux and coworkers [104 & 105] utilized x-ray diffraction (XRD) as the most commonly used technique to detect bulk carbides; however, cobalt carbides were found to be metastable especially in the presence of H$_2$ [104-106]. Hofer
also found out that cobalt crystallites subjected to pure carbon monoxide at 226-230 °C slowly form cobalt carbide corresponding to Co$_2$C.

Fukumiya et al. [107] studied the thermal stability of metastable co-sputtered Co-C composites alloy films in terms of the concept of formation enthalpy. They also reported the mechanical hardness of the alloy films and found it to decrease almost linearly with increasing fraction of carbon content in the film, concluding that this carbon content can be used as the measurement of hardness to monitor the film qualities. Furthermore, they showed that the hardness of metastable phase is greater than the alloy films. However, Lavrentiev’s results [108] showed formation of Co-C$_{60}$ polymeric chains as the major product of co-deposition of Co and fullerene instead of metastable carbide phases. Upon annealing at 300 °C, the growth of diamond and single-wall carbon nanotubes was observed. Wang [109] also reported fabrication of carbon-coated cobalt nanocapsules by the chemical vapor condensation process (see figure 17). The core-shell phases (onion-shape alternate bilayers) were composed of fcc-Co, hcp-Co and cobalt carbides regardless of the condensation temperature. They also studied the magnetization behavior of the samples; however, CoC nanocapsules were soft magnets with $M_r/M_s$ of 0.3.
Figure 17. XRD patterns of Co(C) nanoparticles prepared at different condensation temperatures (a) 400 °C, (b) 500 °C, (c) 700 °C, (d) 800 °C (f) 1100 °C [109]

There are a few published articles on electronic structure of cobalt carbides [110-113]. Among them, Yong-Hui et al. [114] studied the structural and electronic properties of Co$_2$C and its surface stability by density functional theory calculations. They found that the formation of Co$_2$C phase is exothermic with the
formation energy of 0.81 eV/Co$_2$C with respect to Co under the presence of CO and H$_2$ gas stream. But they concluded that the cobalt carbide is a paramagnetic phase.

![Figure 18](image_url)

Figure 18. (a) unit cell of Co$_2$C (b) same unit cell stack of bulk Co$_2$C as in (a) but from 001 view (c) stack of bulk hcp type Co. Dashed frame in (b) and (c) ABAB...stacking of Co. The grey and blue balls represent C and Co atoms, respectively [114]

Chemical techniques were not the only route to synthesize cobalt carbides. There have been some attempts to fabricate Co$_x$C materials by mechanical alloying as well [115 & 116]. Patroni and coworkers prepared non-equilibrium, f.c.c. CoC solid solutions supersaturated with carbon to above 7 at.%. By increasing the carbon content to 10 at.%, the f.c.c. phase began converting to metastable Co$_3$C with an orthorhombic structure. By further increasing the carbon content, milling time and heat treating the powders at different temperatures, they successfully reported fabrication of Co$_2$C and Co$_3$C; however, no magnetic
studies were performed. Diaz Barriga-Arceo et al. used the same technique to prepare cobalt carbide, although their objective was synthesis of carbon nanofiber by decomposition of carbide phase by heating at 800 and 1000 °C. To fabricate Co₃C, ball milling in an Argon atmosphere for 15 hours was performed with ball to powder ratio of 20:1. A bright field TEM of the as-made cobalt carbide and XRD patterns of the samples are shown in Figures 19 and 20, respectively.

Figure 19. (a) Bright field electron transmission micrograph of cobalt carbide produced by mechanical alloying [116]
Figure 20. XRD patterns of elementary and mechanically alloyed powders (a) the f.c.c. and hcp structure of cobalt. (b) The carbon soot presenting a cubic structure and an amorphous region. (c) XRD pattern of as-milled powders for 15 h. An orthorhombic structure is present, and cobalt carbide is formed with a stoichiometry Co$_3$C. XRD patterns of heat-treated samples at 800 °C (d) and 1000 °C (e), where carbon soot and cobalt are separated [115]
Following early studies by Chinnasamy et al. [117] Harris and coworkers [70] reported a ferromagnetic material based upon nanoscale cobalt carbide particles that showed promise as a rare earth-free alternative to high performance permanent magnets. They fabricated cobalt carbide nanoparticles using polyol reduction chemistry in a single step process. Particles were acicular in morphology and room temperature coercivities reached 3.4 kOe and maximum energy products greater than 20 kJm\(^{-3}\) which is comparable with AlNiCo and ferrites as illustrated in Figure 21.

![Figure 21. Energy products versus intrinsic coercivity of cobalt carbide nanoparticle powders compared with powders of AlNiCo and ceramic ferrite systems. Values of (BH)\(_{\text{max}}\) of Co\(_x\)C were calculated with corrected magnetization values][70]

The particles of Harris’s studies were consisted of admixture of Co$_2$C and Co$_3$C phases. It was shown that the volume of each phase, particle size and particle morphology all play important roles in determining permanent magnets properties. The large room temperature coercivities were assumed to originate from dipolar and magnetocrystalline anisotropies of carbide phases.

![Graph showing hysteresis loop](image)

**Figure 22.** Room temperature hysteresis loop of representative sample having $M_s$ of 73 emu g$^{-1}$ and an $H_c$ of 3.1 kOe. The $(BH)_{max}$ is 20.7 kJm$^{-3}$ [70]
Recently, Carroll and coworkers [118] reported synthesizing well-characterized carbide nanoparticles and investigated atomic structures of each phase by first principles calculations and demonstrated how the magnetic moment and the energy product of the nanocomposite material vary with the size of the assembled nanoparticles. They also determined how the incorporation of carbon into cobalt lattice increases the anisotropy of the individual phases. It has been shown that cobalt carbide forms due to a surface reconstruction/diffusion of carbon atoms into the cobalt structure [119 & 120], therefore this diffusion and the particle growth are competing events. By controlling growth dynamics via synthesis parameters highly coercive carbides particles were fabricated. Furthermore, by using elevated temperature x-ray diffraction (ETXRD), it has been revealed that Co$_3$C decomposed to $\alpha$-Co while Co$_2$C transitioned to $\alpha$ and $\beta$-Co phases at 325 $^\circ$C and 275 $^\circ$C respectively. Based on their studies, Carroll et al. proposed that Co$_2$C forms by $\beta$-Co and Co$_3$C forms by $\alpha$-Co as depicted in Figure 23.

Synthesized cobalt carbide particles of their study possessed an average secondary particle diameter around 300 nm which TEM revealed them as agglomerates of particles with 15-50 nm sizes (see Figure 24).
Figure 23. Proposed mechanism for the formation of Co$_3$C and Co$_2$C in Tetraethylene glycol, 1- Cobalt nucleates to form α-Co (top) and β-Co (bottom) in boiling TEG, 2- TEG is catalytically decomposed on the faces of Co particles, 3- Free carbons travel through the interstitial sites in the Co lattice and form Co$_3$C (top) and Co$_2$C (bottom) and 4- at elevated temperatures the carbon atoms diffuse out of the carbide and decomposes into the original metallic cobalt phases [118]
Figure 24. Bright field TEM images of (a) Co$_3$C particles, (b) Co$_3$C particle surface showing the presence of a glycolate layer and fine crystallites, indicated by arrows, (c) HRTEM of Co$_3$C particles showing glycolate layer and inset FFT corresponding to Co$_3$C (010) zone axis [70]
3.0 CHARACTERIZATION TECHNIQUES

The overall goal of this Dissertation is to understand and develop magnetic nanoparticles including soft and hard magnetic phase and to tune the structure and magnetic properties of the materials by changing the reaction parameters. The chosen soft phase magnetic material is the iron-cobalt binary alloy and the hard phase is the cobalt-carbide nanoparticles, a recent candidate as a rare earth-free permanent magnet.

3.1 Chemical, structural and magnetic characterization

The following section will review some basic principles of the characterization techniques used in this research. Interested readers will find additional information in the referenced material at the end of this Dissertation.

3.1.1 Introduction to X-ray diffractometry

X-ray diffractometry is used for phase identification, determining the crystallinity of particles and purity of the samples. By comparing the position of the peaks in the diffracted beam to the standards provided by the Joint Committee on Powder Diffraction Standards (JCPDS) and the International Center for Diffraction Data (ICDD) the unknown phases present in each sample were identified.
Figure 25. Schematic illustrating the process of a collision of an accelerated electron and the resulting x-ray emissions by electrons filling the ejected electron hole [122]

X-rays are produced by a beam of energetic electrons bombarding a metal target in an evacuated tube. The energetic electrons excite the target atoms, which subsequently emit high frequency electromagnetic radiation as they decay back to their ground states. The emitted x-rays are characteristic for the target material and usually consist of a few strong lines. Cu and Mo are the most widely used target metals; however, other anodes are also used. The resulting beam is then filtered by using a monochromating crystal, which allows the passage of the $K_{\alpha 1}$ and $K_{\alpha 2}$ x-rays with wavelengths of 1.5405 Å and 1.544 Å respectively. The
intensity ratio for the $K_{\alpha_1}$ and $K_{\alpha_2}$ x-rays is approximately 2:1 and the weighted average of the radiation is 1.5418 Å. [122-125]

Figure 26. Figure illustrates that each energy level emits a characteristic x-ray by the relaxation process [123]
3.1.1.1 Bragg’s Law

X-rays are a form of electromagnetic radiation that is characterized as having high energies and short wavelengths. When a beam of x-rays hits a material, a portion of the beam will be scattered from the material and constructively interfere in distinct directions based upon the symmetry of the repeating crystal structure associated with the material (Figure 25). The angles where the peaks in the x-ray diffraction spectrum occur obey the Bragg's law:

\[ n \lambda = 2 d_{(hkl)} \sin (\theta) \quad (13) \]

Where \( \lambda \) is the wavelength of the x-ray beam, \( d_{(hkl)} \) is the spacing between the (hkl) crystallographic planes contributing to the diffraction peak, \( \theta \) is the angle of diffraction, and \( n \) is an integer. The Bragg condition indicates the angular positions at which only constructive interference can be found. If the Bragg conditions are not satisfied, then the interference will be nonconstructive and will yield a very low intensity diffracted beam. In a typical x-ray diffraction study, a range of \( \theta \) is scanned to identify the Bragg reflection angles and determine the lattice spacing (Figure 26).
After determining the phase of the material, the XRD patterns were used to investigate the structural nature of the material, for example, the size and crystallinity of the particles. A material’s structural nature can be either crystalline or amorphous. Crystalline materials have sharp constructive diffraction lines in their XRD patterns and have minimal microstrain associated with the peaks, while amorphous materials have more diffuse diffraction lines due to a lack of atom-to-atom long range ordering. There are also many factors that may contribute to the broadening of diffraction lines, which makes the analysis of XRD patterns difficult. For example, instrumental broadening, microstrain (lattice strain), powder inhomogeneity, and temperature are a few contributions that can convolute a diffraction pattern. Broadening in the diffraction pattern can also
occur with a reduction in particle or crystallite size. Peak width varies inversely with crystallite size. So as the crystallite size gets smaller, the peaks get broader. Paul Scherrer, who is most famous for his equation for crystallite broadening, first realized this in 1918; [125]

\[
B(2\theta) = \frac{K \lambda}{L \cos(\theta)}
\]  \hspace{1cm} (14)

In his equation, B refers to the peak width, typically referred to as the full width at half maximum (FWHM) of the diffraction peak. B is inversely proportional to the crystallite size L. K is the Scherrer constant, typically 0.94 for spherical particles with cubic symmetry, \( \lambda \) is the wavelength of irradiation, and \( \theta \) is half the diffraction angle. Crystallite broadening is most pronounced at large angles of \( 2\theta \); however, lattice strain and instrumental broadening is largest at a larger \( 2\theta \). In addition, to make this more difficult, peak intensity is usually the weakest at these larger angles.

### 3.1.1.2 X-ray diffractometer

The diffractometer used to obtain x-ray diffraction patterns for this work was made by Rigaku. A copper anode was used as the source of x-rays with a current of 44 mA at an accelerating voltage of 40 kV. As described previously, the copper source emits x-rays with \( K_{\alpha 1} \) and \( K_{\alpha 2} \) wavelengths of 1.5405 Å and
1.544 Å respectively. A continuous scan mode is employed, in which the x-ray source and the x-ray detector continuously repeat the 2θ range, utilizing a Bragg-Brentano scattering geometry. The dried powder samples were gently ground using a mortar and pestle and then pressed onto a low background, low volume holder using a Fisherbrand pre-cleaned microscope slide. The sample holder was then placed in the instrument for XRD analysis. Upon completion of the run, the data were analyzed in the Jade program, which has a built-in diffraction library to compare the sample’s diffraction pattern to the diffraction patterns in the JCPDS-ICDD database.

3.1.2 Vibrating Sample Magnetometry (VSM)

Room temperature vibrating sample magnetometry (VSM) was used in this work to determine the magnetic properties of materials. A Lakeshore model 7300 vibrating sample magnetometer was used for all room temperature analysis. The measuring field was oriented either parallel or perpendicular to the plane of the sample depending on the sample shape (for example pellets were oriented parallel, while powders were oriented perpendicular). To describe VSM in the most basic sense, a sample is placed in a uniform constant magnetic field. If the sample is magnetic, this constant magnetic field will magnetize the sample by aligning the magnetic domains or magnetic spins with the field. If the sample vibrates in a sinusoidal motion, an electrical signal can be induced between two coils (pick-up coils). This signal has the same frequency of vibration and the
amplitude is proportional to the magnetic moment of the material. Figure 25 shows a typical VSM.

Figure 28. A typical VSM magnetometer used to measure magnetic properties of the nanoparticles [126]

3.1.3 Physical property measurement system (PPMS)

In order to obtain magnetic properties of the samples as a function of temperature and also to investigate the effect of applied magnetic field on the magnetic response of the samples, physical property measurement system (PPMS)
was used. It can reach temperatures as low as 5 K and high as 500 K. Also magnetic fields up to 10 T are attainable by PPMS. Figure 26 depicts a typical PPMS equipped with helium tank for cryogenic measurements.

Figure 29. Typical PPMS equipped with a helium tank for low temperature measurements

3.1.4 Scanning electron microscopy (SEM)

Development of electron microscopes was due to the limitations of optical microscopes were limited in spatial resolution due to the wavelength of light. Electron microscopes use a beam of electrons for imaging surfaces [127]. The
first type of electron microscopes was transmission electron microscope (1931) in which a focused electron beam passes through the specimen. Scanning electron microscope (SEM) was developed later and became commercially available in 1965. In SEM, energetic electrons (1-30 keV) are focused by magnetic lenses to form a beam of 2-10 nm in diameter. This beam reaches the specimen surface and the electrons ionize nearby atoms, creating secondary electrons. Some of the generated secondary electrons would leave the surface and be collected and counted by a positively charged detector. The specimen should be conductive enough to dissipate the charge of electrons. Large depth of field in SEM allows for imaging into deep vertical features [128].

3.1.5 Energy-Dispersive x-ray spectroscopy (EDXS)

The scanning electron microscope, which is closely related to the electron probe, is designed primarily for producing electron images. But it can also be used for element mapping and even point analysis, if an X-ray spectrometer is added. Energy-dispersive x-ray spectroscopy (EDXS) makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. All elements from atomic number 4 (Be) to 92 (U) can be detected in principle, though not all instruments are equipped for 'light' elements (Z < 10). Qualitative analysis involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. Quantitative analysis (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration standards of known composition [129].
By raster scanning the beam and displaying the intensity of a selected x-ray line, element distribution images or 'maps' can be produced. Also, images produced by electrons collected from the sample reveal surface topography or mean atomic number differences according to the mode selected [130].
4.0 RESULTS AND DISCUSSION

In this chapter, results obtained in this Dissertation, on fabrication of iron-cobalt and cobalt-carbide nanoparticles and MnAlC-FeCo composites are discussed.

4.1 Fabrication of pure-phase iron-cobalt nanoparticles

The design of novel ferromagnetic alloys of metallic nanoparticles has been of significant interest over the past decade. FeCo-based alloys have specifically attracted interest due to high saturation magnetization along with a high Curie temperature (~900 °C), good permeability and good mechanical strength [131 & 132].

One of the oldest methods to synthesize nanoparticles is the precipitation of products from solutions. In such reactions, metal precursors are first dissolved in a solvent which is usually water or an organic solvent. A precipitating agent then is then added to the solution. Sometimes the solvent serves as reducing agent as well. Most magnetic nanoparticles can be synthesized with this kind of reactions. However, in the case of materials with high affinity to oxygen like iron, solvents other than water should be used. One such solvent is a polyol which is a polyhydric alcohol which was used in this Dissertation.

Physical properties of the synthesized magnetic nanoparticles, and especially their magnetic moment, are function of the reduction rate of the metals; r. The reduction rate of the metal governs the shape, size and structure of the particles. This reduction rate may be expressed as [133 & 135]
\[ r = r \left( P_r, C_{\text{metal}}, C_{\text{OH}}, T, t \right) \quad (15) \]

Where \( P_r \) is the reduction potential of the polyol, \( C_{\text{metal}} \) and \( C_{\text{OH}} \) are the concentration of metals and hydroxyl ions in the solution, respectively. \( T \) is the temperature and \( t \) is the reaction duration.

In this section, experimental results of synthesis of pure-phase iron-cobalt and the approaches to do so are presented. The effects of important parameters such as reaction time, hydroxyl ion concentration and reaction temperature on the size, composition and magnetic properties of iron-cobalt nanoparticles are reported followed by reports of synthesizing large amount of particles (>10 grams per batch) and study the effect of ‘ageing’ (exposure to ambient air) on the magnetic properties of the particles.

4.1.1 Effect of initial solution temperature

The effect of initial solution temperature was studied by adding the metal precursors at different temperatures. In all experiments, fixed amounts of NaOH (5 g) was added to 100 mL ethylene glycol and then a constant amount of cobalt acetate and iron chloride \([\text{[Co]} + [\text{Fe}] = 0.1 \text{ M}]\) were added to the solution at temperatures ranging from 25 °C to 200 °C. The saturation magnetization trend suggests that addition of reactants to the low temperature solution gives the particles with lower than expected saturation magnetization (as in Figure 30). As the temperature increases, the saturation magnetization also increases and the
highest moments were attained when the metal precursors were added at highest temperature: boiling point of the solvent. On the other hand, coercivity was highest when the initial temperature was low and as the temperature reached the boiling point of the solvent, the coercivity decreased to values less than 100 Oe.

X-ray diffraction patterns confirmed existence of some secondary phase peaks between 20 0 and 35 0 in 2θ, which are attributed to oxides of iron and cobalt. The reason for this behavior to happen is, as the temperature elevates, the dissolved oxygen in the ethylene glycol decreases exponentially according to solubility of gases in the solvent which inhibits oxidation of cobalt and iron and reduces the thickness and volume fraction of the oxide layer around the particles. Therefore, decreasing the temperature lowers the magnetic moment and enhances the coercivity of the particles because of high coercivity of the oxides compared to iron and cobalt nanoparticles.
4.1.2 Effect of surfactant on magnetic properties of FeCo nanoparticles

It’s been well known that using surface active compounds; “surfactants”, control the shape and size of the particles by limiting the size of the particles and encapsulate them in their long polymer chains. Liu and coworkers [61] reported synthesis of monodispersed FeCo nanoparticles by using hexadecanediol. Other surfactant such as oleic acid [133 & 134], PVP [134] and oleylamine [136] were used successfully to fabricate monodisperse FeCo nanoparticles. However, due to presence of the surfactant layer around the particles, their magnetic moment per unit weight decreases substantially. In fact the upper limit found in the literature for FeCo particles synthesized with using surfactants is 207 emu/g by [135]
compared to 221 emu/g reported by Zamanpour et al. [137] On the other hand, Kodama et al. hypothesized and later verified that ethylene glycol can serve as surfactant as well as solvent and reducing agent in formation of FeCo nanoparticles [138]. Our studies are in agreement with this hypothesis, hence, to maximize the magnetic moment of the samples no further surfactant were used, as shown in Figure 31. Figures 32 and 33 show a typical hysteresis loop for a sample synthesized in the absence of surfactants and a SEM image of that sample, respectively. Note on the SEM image that, formation of clusters of particles is clearly observed because of very high magnetization of the FeCo which makes it difficult to find individual particles’ images.

![Figure 31. Change in magnetic moments of FeCo nanoparticles with respect to surfactant concentration](image-url)
Figure 32. Hysteresis loop for a sample without using surfactant with saturation magnetization of 195 emu/g

Figure 33. SEM image of the sample shown in Figure 32
4.1.3 Effect of reaction Temperature on magnetic and structural properties of FeCo nanoparticles

Arrhenius equation predicts that with increasing the temperature, all the reaction rates increase rapidly. In the case of nanoparticle formation, if reaction temperature goes up, then both nanoparticle formation and oxidation speed up. By operating the reactions at different temperatures it was realized that higher temperature was indeed in favor of FeCo particle formation while the oxidation is still minor. Kodama and coworkers [138] was able to synthesize FeCo nanoparticles at temperatures as low as 130 °C. But in order to obtain particles with desired properties, they increased the reaction time to 2 hours. On, the other hand, to minimize the oxidation, PVP was used as a surfactant. In this research, the temperature range between 150 °C and 200 °C were investigated. At 150 °C, as expected, the reactions were sluggish and the resultant nanoparticles were very low in both quantity (less than 1/5 of the yield at 200 °C) and quality (See Figure 34). As the temperature raised, the yield and the saturation magnetization increased and reached its maximum value at 200 °C which was the boiling point of the solvent.
Figure 34. Effect of reaction temperature on saturation magnetization of the nanoparticles. Both yield and the magnetic moments enhanced sharply by increasing the reaction temperature to boiling point of the solvent.

4.1.4 Effect of reaction time on magnetic and structural properties of FeCo nanoparticles

LaMer describes three steps involved in the growth of monodispersed particles in a solution [46]; formation of nuclei, growth of the particles, and growth saturation. In order to investigate the effect of reaction duration on magnetic properties of the particles, same experiments were done by changing the reaction time. In all the experiments 0.014 M of cobalt acetate and 0.056 M iron
chloride were mixed with 1.2 M sodium hydroxide and reacted for various times from 1 min to 60 min. As seen in Figure 35, when reaction takes place for less than 15 minutes, the nanoparticles possess very low room-temperature saturation magnetization. This unexpected behavior is indicative of “raw” particles that are below the superparamagnetic diameter. After 15 minutes of reaction time the particles become sufficiently large to exhibit ferromagnetism with high room-temperature saturation magnetization. The trend of increasing magnetization continues to increase with reaction time until $t = 40$ min; at this reaction time the magnetization sharply decreases. This decrease in magnetization at longer reaction times is attributed to the formation of an oxide layer surrounding the particles resulting from a long exposure time to dissolved oxygen in the solution.
Figure 35. Magnetic moments of the iron-cobalt powder versus the reaction time. Until 15 min reaction particles’ size are beyond the single domain values. As the reaction continues, the single domain particles grow and the moment increases until they reach their maximum at 30 min reaction and drop at larger sizes.

X-ray diffractometry revealed formation of iron and cobalt oxides at elongated reactions. As one can see on Figure 36, all the particles are pure-phase iron-cobalt before $t = 40$ min, although a large portion of the particles formed earlier at $t \leq 15$ min are superparamagnetic and have low magnetic moments which were confirmed by particle size analysis by using Scherrer formula; see Equation 13, the results are depicted in Figure 36. It is noteworthy that as reaction
further continues to 60 minutes, the only iron-oxide peak remaining is the 110 peak and all other detected peaks belong to oxides of iron and cobalt.

Figure 36. Particles sizes versus reaction time. Sharp increase in particles diameters attributed to the formation of oxide layer around the
Figure 37. XRD patterns of FeCo nanoparticles formed at various reaction times (top) before 40 min and (bottom) 40-60 min. Note that secondary phase peaks (red circles) observed at long reactions and short reactions yielded pure-phase nanoparticles. FeCo plane indices are shown on top figure. Detection of unreacted cobalt peaks are because of low OH in the solution [137]
4.1.5 The Effect of hydroxyl ion on magnetic and structural properties of FeCo nanoparticles

Kodama et al. [138] hypothesized that hydroxyl ions \([\text{OH}]^-\) provide nucleation sites for FeCo nanoparticles during the polyol synthesis. Therefore, [OH] concentration plays an important role in the formation and properties of the particles. After fixing the reaction time, metal concentrations, reaction temperature and initial reaction temperature, by changing the salt concentration, the magnetic and structural properties of the nanoparticles can be tuned and optimized.

By systematically increasing different amounts of [NaOH] / [Fe+Co] concentration ratios from 1 to 40 the role of hydroxyl ions on the overall reactions was measured. Figure 38 indicates that a [NaOH] / [Fe+Co] concentration ratio equal to 12:1 yields particles with an overall low saturation magnetization that is attributed to insufficient nucleation sites. Increasing this ratio to 24:1 yielded nanoparticles with room-temperature saturation magnetization of 221 emu/g. Further increases in the salt: metal ratio beyond 27:1 causes magnetization to decrease sharply to below 200 emu/g likely due to the presence of excessive oxygen in the solution and subsequent oxidation. It is also observed that the particles diameter do not change significantly until the formation of oxides around the particles.

X-ray diffraction studies confirm the presence of an oxide phase, potentially in the form of a FeCo/oxide core-shell nanostructure. The secondary peaks indicated by color circles in the figure 36 are iron and cobalt oxides peaks.
Figure 38. Saturation magnetization and the particles sizes for samples with different amounts of sodium hydroxide [137]
Figure 39. XRD patterns of the samples with different amounts of NaOH salts. Salt: metal concentration ratios are shown on each diffraction line. Numbers in brackets indicate iron cobalt peaks indices. Red circles indicate oxide peaks.

Figure 40. SEM image of clusters of FeCo nanoparticles [137]

Figure 41. SEM image of an individual FeCo nanoparticle [137]
SEM images (Figures 40 & 41) clearly show that particles found in the form of clusters and aggregates because of high magnetic moments of the individual particles.

Energy-Dispersive x-ray Spectroscopy (EDS) analysis was used to investigate the chemical composition of the powders. It was observed that the as-synthesized nanoparticles’ stoichiometry is almost identical to that of designed as shown in Figure 42.

![EDS spectrum](image)

**Figure 42.** Energy dispersive X-ray spectrometry (EDS) analysis reveals powders of equiatomic concentration, the designed composition was Fe$_{50}$Co$_{50}$ and the EDS result was Fe$_{46}$Co$_{54}$
4.1.6 Effect of ‘ageing’ on the magnetic properties of FeCo nanoparticles

As time passes, since the particles are usually exposed to ambient air, they are in direct contact with the oxygen and the oxidation is unavoidable. The extent the particles lose their magnetic moment with respect to time is called ‘particle ageing’. To determine this effect and the percentage particles lost their magnetization, the saturation magnetization of the as-synthesized samples were measured at 10 kOe using a vibrating sample magnetometer (VSM) at room temperature. This process was repeated for several weeks and it was realized that the magnetic moments of the particles dropped 25% on average. It was noted that for the FeCo nanoparticles of this study the ageing time takes about 2 months and after that time there is no further significant (less than 2%) decrease in magnetic moment of the particles (See table 2)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decay of magnetic moment (%)</td>
<td>19</td>
<td>29</td>
<td>20</td>
<td>17</td>
</tr>
</tbody>
</table>

Table 2. Decay of saturation magnetization of particles after 2 months [137]
Figure 43 depicts the decrease in saturation magnetization for different samples within 8 weeks. It should be noted that after 8 weeks the magnetic moments of the samples reached the steady values and didn’t change afterwards. It signifies that, after 8 weeks, a passive layer of oxide coated the nanoparticles and prohibited further oxidation and as a result the magnetization kept constant.

Figure 43. Effect of aging on particles’ saturation magnetization after 8 weeks [137]
4.1.7 Large-scale synthesis of FeCo nanoparticles

After determining the best conditions for the synthesis of high-saturation magnetization FeCo nanoparticles, the process was scaled to yield 10 grams per batch. The results are sufficiently promising for the purpose of making large batches of magnetic nanoparticles with magnetizations > 200 emu/g as in Figure 44. With utilizing a 10 L reaction vessel, 10 grams single-phase iron-cobalt was synthesized with saturation magnetizations up to 229 emu/g. Particle size analysis using Scherrer formula indicated that the produced particles are 27 nm in diameter (See figure 44). X-ray diffractograms also indicate synthesizing pure-phase iron-cobalt nanoparticles in large-scale (See Figure 45).

Figure 44. Hysteresis loop of the large batch FeCo nanoparticles

with $M_s = 229 \text{ emu/g}$ and $H_c = 123 \text{ Oe}$
Figure 45. An example of calculation of particle size by using Scherrer formula done by Jade software for a large-batch experiment. In this case, the particles were 27.3 nm in diameter.
Figure 46. X-ray diffractometry pattern of the scaled up batch. No secondary phase peaks or unreacted cobalt or iron ions were detected

4.2 Synthesising $\text{Co}_x\text{C}$ nanoparticles

Permanent magnets found numerous applications including; electronics, automobile and hybrid engines, communication, and information technologies. Most of the permanent magnets contain rare earth elements enabling them to provide the highest energy products. However, these materials are expensive to manufacture and are prone to corrosion. Although it’s alternatives; AlNiCo and ceramic magnets, have been designed; however, these materials have a much lower energy products. Despite this drawback, AlNiCo and Ceramics have grown as
viable global permanent magnet materials. Since late 1980s, very few advances have been made to create more efficient magnets. Moreover, the need for the design of rare earth-free 3d-transition metal permanent magnets has increased because of undesired dependence on foreign resources. This section discusses a ferromagnetic material based upon nanoscale cobalt carbide particles that provides a rare earth-free alternative to high performance permanent magnets.

In the second step of this research, fabricating cobalt-carbide nanoparticles was studied. It has been shown that cobalt-carbides consist of two exchange-coupled phases [70], Co$_2$C and Co$_3$C in which Co$_2$C has lower magnetic moment but higher coercivity. Carroll et al. [80] hypothesized the reaction mechanism of formation of Co$_x$C in tetraethylend glycol, TEG. They suggested that it consists of 4 steps; 1- dissociation of cobalt salt to form cobalt ions, 2- nucleation and growth of Co particles, 3- decomposition of TEG on cobalt surface and 4- carbon diffusion into cobalt lattice. They further predicted that α-cobalt results in formation of Co$_3$C and β-cobalt yields Co$_2$C and Co$_3$C. By changing the reaction temperature, reaction duration, hydroxyl ion concentration and surfactant concentration, reaction mechanism, structural and magnetic properties and chemical composition of the resulted cobalt-carbides was studied.

The chemical process is polyol method, in which tetraethylend glycol was served as solvent and reducing agent. Different surfactants and catalysts were tested as well as different reaction conditions.
4.2.1 Effect of reaction time on magnetic and structural properties of Co₃C

As we discussed in Section 4.1, the rate of reduction of the particles, and therefore the shape, size and properties of them is a function of the kinetic parameter. One of the most important parameters is the reaction time. By implementing the reaction for various times, volume fraction of each carbide phase and formation of secondary phases can be controlled since the last step of the reaction; the extent carbon diffuses into cobalt lattice, can determine the fraction of each cobalt-carbide phase. On one hand, long reactions produces metallic cobalt and carbides, and on the other hand, short reaction time can inhibit complete diffusion of carbon into cobalt lattice and results in cobalt-carbide-carbon core-shell nanostructure.

In most of the experiments, unless stated otherwise, different amounts of cobalt acetate tetrahydrate, sodium hydroxide and polyvinylpyrrolidone (PVP) were added to 100 mL of tetraethylene glycol (TEG) (99.9%, Sigma Aldrich) at room temperature. The mixture then stirred mechanically for 20 min to become homogenized. The heat was turned on and the solution was reached and stayed at 120 °C to evaporate the water content in metal salt and the solvent. After 20 min, the mixture was heated to the reaction temperature (usually 290-310 °C) and allowed to react for different reaction times. The solution then cooled down to room temperature by removing the heat source and the black solid precipitated by using a rare earth magnet. After removing the supernatant, the concentrated solution was rinsed by reagent alcohol (90% ethanol, 5% methanol and 5% isopropyl alcohol)
and centrifuged numerous times. Drying the black solid in air overnight was the last step to get the powders.

The composition of the particles was analyzed by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS, Zeiss Supra 25), while the morphology of the particles was analyzed by using scanning electron microscopy (SEM, JSM 6510 LV). The nature of the crystal structure was determined by x-ray diffraction (XRD, Rigaku, Ultima III, CuKα radiation) and the magnetic properties of the samples were measured at room temperature using a vibrating sample magnetometer (VSM, LakeShore Model 7400) and a Physical Property Measurement System (PPMS, Quantum Design, Model 6000).

To study the effect of reaction time, raw materials were reacted for different periods of time between 5 minutes to 150 minutes. As seen in Figure 47, at short reaction times the moment and coercivity both were low. By increasing the reaction time, the coercivity enhanced and reached its maximum at 1400 Oe at 45 minutes reaction, but decreased sharply and fell below 500 Oe after 90 minutes. Meanwhile, the magnetic moment started at more than 100 emu/g, which later confirmed by XRD to be cobalt particles. According to the proposed reaction mechanism discussed earlier, after injecting the cobalt salt to the solution, it dissociates to cobalt ions which form nuclei instantaneously. By increasing the concentration of these nuclei, cobalt particles form. Subsequently, by dissociation of the TEG into carbon, cobalt particles being coated by a layer of nonmagnetic carbon. The sharp drop in the moment of the samples to 30-40 emu/g is attributed to fromation of these species that lasted until carbon began to diffuse into cobalt lattice. Upon
completion of this step, the coercivity reached its maximum while saturation magnetization didn’t change significantly, but again hiked to 90 emu/g at longer times. X-ray diffractometer shows that by increasing the reaction time to over 90 minutes, some part of the cobalt-carbide decomposed to metallic cobalt and as a result, the moment jumped but the coercivity decreased dramatically.

**Figure 47.** Change in saturation magnetization and coercivity of cobalt carbides with respect to reaction time. Blue curve shows the saturation magnetization and red curve indicates the coercivity of the cobalt carbide nanoparticles
4.2.2 Effect of reducing agent on magnetic and structural properties of Co$_x$C

Reducing potential of the polyol family member strongly depends on the molecular weight/chain size. The bigger the polyol chain, the stronger the polyol is in reducing metal salts. The polyols studied in this Dissertation are the most widely used ones; Ethylene glycol and tetraethylene glycol. In both cases, all conditions were the same. After measuring the resultants, it was shown that the reaction involving smaller polyol; ethylene glycol did not produce carbide. X-ray diffractograms show formation of cobalt by ethylene glycol while tetraethylene
glycol produced cobalt carbide nanoparticles. Table 3 compares both cases. It can be concluded that although both solvents were able to dissociate the metallic salt and precipitate cobalt, to provide carbon for synthesizing cobalt carbide, bigger alkyl chain (more carbon) was necessary.

Table 3. Comparison of resulted particles by different polyols

<table>
<thead>
<tr>
<th></th>
<th>Ethylene glycol (EG)</th>
<th>Tetraethylene glycol (TEG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction Temperature (°C)</td>
<td>200</td>
<td>300</td>
</tr>
<tr>
<td>Saturation Magnetization (emu/g)</td>
<td>104</td>
<td>46</td>
</tr>
<tr>
<td>Coercivity (Oe)</td>
<td>143</td>
<td>1500</td>
</tr>
</tbody>
</table>

4.2.3 Effect of reaction temperature on magnetic and structural properties of Co₄₋₆C

After determining the reaction time and choosing the appropriate solvent for synthesis of cobalt carbide, next studied parameter was the reaction temperature. It has been known that temperature plays a very important role in formation of metallic particles in polyols [2]. Therefore, in this section, the results of
experiments that were designed to determine the temperature at which the desired reactions occur are presented.

![Graph showing coercivity and saturation magnetization of cobalt carbide nanoparticles with respect to temperature reaction. Blue curve shows magnetic moment and red line indicates coercivity of the samples.](image)

**Figure 49.** Coercivity and saturation magnetization of cobalt carbide nanoparticles with respect to temperature reaction. Blue curve shows magnetic moment and red line indicates coercivity of the samples.

Temperature of the reaction was changed between 240 and 310 °C, which is the boiling point of the solvent, tetraethylene glycol. Magnetic and structural studies showed that metastable cobalt carbide formation starts at 270 °C but at
highest operating temperature, the coercivity decreased from 1.6 kOe to 1.21 kOe which was attributed to partial decomposition of cobalt carbides into cobalt-carbon core-shell structures. Thermal analysis (Figure 50) studies by Elevated Temperature X-ray Diffraction (ETXRD) [50, 80] revealed decomposition of Co₃C to hcp and fcc-Cobalt at 325 °C.

Figure 50. Decomposition of Co₃C to α–Co begins at 325 °C [118]
4.2.4 Effect of hydroxyl ion and carbon on magnetic and structural properties of Co$_x$C

As mentioned earlier, it’s been hypothesized that OH ions provide the nucleation sites for formation of metallic nanoparticles in the solution. Therefore, hydroxyl concentration plays a crucial role in structural and compositional properties of the products. In this section, the experimental results of effect of carbon concentration and hydroxyl ions are presented.

In order to investigate the effect of OH concentration of carbide formation, the OH:Co ratio was changed, keeping the Co content and the volume of the solution (C content) were kept constant. For studying the effect of carbon concentration, for more accuracy in implementing the experiments, the same volume of solution was utilized while the amount of metal was changed and OH:Co ratio was also changed accordingly to keep the OH:Co constant and change the carbon content.

Here, the results of the OH:Co ratio and carbon content on saturation magnetization are presented. The initial cobalt content was 0.3 g and increased by 0.15 g increments until 0.75 g. Figure 51 depicts the saturation magnetization of the nanoparticles versus hydroxyl ion concentration and cobalt content of the solution. The overall trend is increase in the saturation magnetization and a sharp decrease after reaching a maximum value. Although the moment fluctuates afterwards, but it never recovers. It should be noted that the maxima take place at different hydroxyl to cobalt ratios for different solutions but it usually shifts to larger ratios as the
cobalt content increases, except for 0.75 g cobalt at which no absolute maximum is distinguished.

The trend in coercivity of the particles suggests better explanation of the behaviour of the system. In figure 52 one can see that the coercivity of the particles also possess an absolute maximum at for each cobalt concentration and there is another exception in this case too; the 0.3 grams cobalt. Figure 53 (top) shows a hysteresis loop of sample containing 0.3 gram cobalt. It sigmoidal shape and low coercivity indicate soft magnetic behaviour of the particles. To shed more light on these trends, x-ray diffractography (Figure 53, bottom) was performed. As seen, there were no carbide peaks detected by x-ray. Based on these magnetic and structural results in can be concluded that at very low cobalt concentration, upon formation of small amount of cobalt nuclei, the subsequent particles grow rapily resulting in large particles.
Figure 51. The effect of hydroxyl ions and carbon content on saturation magnetization of the particles for different amounts of cobalt.

Carbon layer did not have enough time to diffuse into the cobalt lattice, resulting in formation of carbon-coated cobalt particles. Existence of this nonmagnetic carbon layer was accounted for lower than expected saturation magnetization, while coercivity did not enhanced due to absence of carbide phase.
Figure 52. The effect of hydroxyl ions and carbon content on coercivity of the particles for different amounts of cobalt.
Figure 53. (top) Hysteresis loop and (bottom) XRD pattern for a sample containing 0.3 grams cobalt as metal precursor and OH:Co ratio of 22:1. \(H_c= 440 \text{ Oe}\) and \(M_s= 45 \text{ emu/g}\)
As more amount of cobalt added to the solution, the number of cobalt nuclei increased, inhibiting growth of the particles and formation of very large ones. This sluggish growth phase favors coating metallic particles by carbon layer formed from dissociation of solvent, followed by diffusion into cobalt lattice which leads to formation of cobalt carbide magnetic nanoparticles. Synthesising cobalt cabde phase enhances the coercivity at in the expense of lower saturation magnetization.

In each of the experiments sets, as the hydroxyl ion to cobalt ratio increased, more nucleation sites became available for cobalt particles, paving the path to diffusion of carbon into smaller metallic particles and formation of carbide phase. One the other hand, ample amount of OH deterirated the magnetic properties of the samples. This was mostly because of the large number of cobalt nuclei that made the solution carbon deficient. The carcon deficiency led to uncarbonized cobalt particles with soft magnetic properties. In overall, the optimum magnetic properties of the particles were realized at OH:Co range 20:1 to 26:1 in all the experiments sets, but generally, the more the cobalt consecnt of the solution, the narrower that optimum ratio “window” was. Top part of Figure 54 depicts hysteresis loop for a hard-phase cobalt carbide sample with coercivity 2.3 kOe and saturation magnetization 47 emu/g. X-ray studies (Figure 54, bottom) revealed existence of equal volume fraction of Co$_2$C and Co$_3$C species in the sample. It should be noted that no secondary phase was observed on x-ray pattern.
Figure 54. (top) Hysteresis loop and (bottom) XRD pattern for a cobalt carbide sample with saturation magnetization 47 emu/g and coercivity 2.3 kOe [138]
4.2.5 **Effect of surfactant on magnetic and structural properties of Co₄C**

It has been known that some specific organic compounds by lowering surface tension between molecules control the shape and size of the products. Common active agents or surfactants include PVP, Oleylamine (OA) and CTAB (cetyl trimethylammonium bromide). First two surfactants were chosen to investigate the effect of surfactant on magnetic properties of the cobalt carbide nanoparticles.

Although cobalt in metallic form shows high affinity to get oxidized, during the course of this Dissertation all the cobalt carbide samples were found oxide-free which indicates the ability of the solvent; tetraethylene glycol, to serve both as reducing agent and capping agent/surfactant. To further control the size of the particles however, PVP and Oleylamine (OA) were studied. In all experiments 0.6 grams cobalt were added to 150 mL TEG and reacted for 45 minutes. The results of magnetic properties of the particles are shown in Figure 55. While there was not detected a significant different between the size of the particles (see Table 4), TEG proved to be the best surfactant because of very low magnetic moment of the particles synthesized in presence of PVP as surfactant as well as below the hard magnetic phase threshold coercivity of cobalt carbides fabricated with oleylamine presented as active agent. It’s worth noting that both OA and TEG show similar pattern of change in $H_c$ and $M_s$, but particles formed in presence of OA behave different trend.
Figure 55. The effect of surfactant of (top) Saturation magnetization and (bottom) coercivity of the cobalt carbide particles.
Table 4. Particle Size ($D_p$ in nanometer) of Co$_x$C as a function of surfactant

<table>
<thead>
<tr>
<th>OH: Co</th>
<th>TEG</th>
<th>PVP</th>
<th>OA</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>33</td>
<td>32</td>
<td>37</td>
</tr>
<tr>
<td>22</td>
<td>29</td>
<td>35</td>
<td>26</td>
</tr>
<tr>
<td>24</td>
<td>22</td>
<td>33</td>
<td>33</td>
</tr>
<tr>
<td>26</td>
<td>18</td>
<td>34</td>
<td>26</td>
</tr>
</tbody>
</table>

4.3 MnAlC-FeCo nanocomposites as rare earth free permanent magnets

As mentioned in early chapters, there has been a huge effort to design and fabricate rare earth-free permanent magnets comparable in performance to their rare earth-contained counterparts. One method to achieve this objective is to synthesize a composite consists of a hard magnet (to utilize its high coercivity) and a soft magnetic phase (to improve the remanent magnetization) with enhanced $(BH)_{max}$. In this section the results of attempting to fabricate MnAlC-FeCo doped nanocomposites are presented.

The best available hard magnetic materials have a lower saturation polarization $J (=\mu_0M_s)$ compared to many soft magnetic materials. Furthermore, they are chemically very reactive (easily oxidisable) and also expensive. These limitations and drawbacks have driven researchers to develop permanent magnets
of composite materials consisting of two suitably dispersed ferromagnetic and mutually exchange-coupled phases, one of which is hard magnetic in order to provide a high coercive field, while the other is soft magnet to provide a high saturation, and should surround the hard phase regions to minimized their oxidation. Exchange interactions cause the magnetization within the soft magnetic grains to be aligned parallel to the direction of the magnetization in the neighboring hard magnetic particles [139].

The demagnetization curve (second quadrant in B-H curve) becomes highly reversible, since the magnetization within the soft phase can rotate out of its preferred direction in the absence of an external field without inducing an irreversible switching of the hard magnetic grains. Although, the high amount of soft magnetic phases reduces the coercive field as compared to isotropic, single-phase magnetically hard materials, a reasonable energy-density product can be obtained in a magnet even with no rare-earth content, if the composition and the microstructure of the hard and soft phases are carefully adjusted and engineered to obtain the desired properties [140].
The specific spin configuration for such a system will depend on the relative strengths and directions of the anisotropies, as well as the exchange interaction between the magnetic layers phases and the orientation of applied magnetic field. The spin configuration is then determined by the energy minimization, taking into account the various magnetic contributions in the system as a whole.

To study the exchange-coupling phenomenon, MnAl was chosen as hard magnetic phase and FeCo as soft magnetic phase.
Figure 57. Schematic of demagnetization curves, MH (Left) Exchange spring magnet composed of a hard magnetic phase and a soft magnetic phase and (Right) Conventional single ferromagnetic phase magnet. Note the difference between the reversible and irreversible demagnetization regions. [141]

Presence of the metastable magnetic τ-phase MnAl, which is obtained by heat-treatments has attracted a lot of attention as a potential high performance hard magnet. Carbon-doped MnAl has shown enhanced magnetic stability during heat-treatment by inhibiting the diffusion of the Mn and the Al atoms and by preventing the decomposition of the magnetic phase into nonmagnetic (Mn) and Al Mn phases [142-147]. Mechanically alloyed MnAlC was heat-treated to obtain τ-MnAl and was used as the hard magnetic phase in MnAlC-FeCo nanocomposite.
Figure 58. Mn-Al phase diagram. Note the $\tau$ phase region [148]

$\tau$-MnAlC with unit formulae Mn$_{54}$Al$_{43}$C$_3$ were mixed by 10 wt. % FeCo nanoparticles, ball-milled and annealed. Table 5 compares the magnetic properties of the MnAlC and mechanically alloyed MnAlC-FeCo nanocomposites. As expected, doping with a soft magnet increased the saturation magnetization, while decreased the coercivity. In overall, the figure of merit of the permanent magnets; $(BH)_{\text{max}}$ was decreased by 21%.
Table 5. Magnetic properties of the MnAlC and as-synthesized MnAlC-FeCo nanocomposites [149]

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_s$ (emu/g)</th>
<th>$M_r$ (emu/g)</th>
<th>$M_r/M_s$</th>
<th>$H_c$ (Oe)</th>
<th>$(BH)_{max}$ (MGOe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnAlC</td>
<td>70</td>
<td>45</td>
<td>0.64</td>
<td>3477</td>
<td>1.38</td>
</tr>
<tr>
<td>MnAlC-FeCo</td>
<td>76</td>
<td>43</td>
<td>0.57</td>
<td>2873</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Annealing the as-synthesized MnAlC-FeCo particles were done at 500 °C for 30 minutes under Argon gas flow. Annealed powder was then pressed uniaxially at 2 T/cm$^2$ and a compacted powder with density 4.8 g/cm$^3$ was obtained. The compact then was measured by PPMS at room temperature and the observed coercivity was 3420 Oe for a sample with saturation magnetization 95 emu/g (See Figure 59). This leads to maximum energy product value of 1.56 MGOe for an exchange-coupled hard-soft permanent magnet, which is 43% higher than as-synthesized sample and 13% more than pure phase MnAl alloy.
Figure 59. Hysteresis loop for annealed MnAlC-FeCo compacted nanocomposites indicates the existence of an exchange-coupled permanent magnet. Inset shows the coercivity of the sample at magnified scale. Measured values for magnetic properties are: $M_s = 95$ emu/g, $H_{ci} = 3420$ Oe, $B_r = 2460$ Oe and $(BH)_{max} = 1.56$ MGOe [149]
5.0 CONCLUSIONS & SUMMARY

The overall goal of this Ph.D. Dissertation is to understand, design and synthesize FeCo and CoxC magnetic nanoparticles as well as to study and fabricate exchange-coupled hard-soft magnetic heterostructures as permanent magnets and to tune the magnetic and structural properties of the materials by changing the parameters of reaction kinetics. Chosen soft phase magnetic material was iron-cobalt binary alloy as strongest magnetic binary alloys of 3d elements and the hard phase was cobalt carbide nanoparticles, a recently discovered candidate as a rare earth-free permanent magnet.

These goals were achieved as follows: (a) Developing pure phase, oxide-free iron-cobalt nanoparticles and optimizing their magnetic properties by tuning the operation conditions such as the temperature, reaction time etc. via modified polyol process. (b) Developing cobalt-carbide nanoparticles and understanding their morphological and magnetic properties as functions of their crystalline structure, and (c) Fundamental understanding, design and demonstrating exchange-coupled nanocomposites consisting of a hard and a soft magnetic phase.

The experimental results in Section 4.1 showed that the highest saturation magnetization of FeCo particles fabricated by polyol method can be achieved at hydroxyl to metal precursor concentration ratio of 27:1 and reaction time 45 minutes. Pure phase FeCo nanoparticles with high saturation magnetizations up to 229 emu/g were fabricated. It was shown that chemical synthesis of nanoparticles via polyol method does not require using surfactant to minimize oxidation, which increases the saturation magnetization by eliminating the adverse effect of presence
of nonmagnetic surfactant layer around the magnetic particles. Production was then scaled-up to more than 10 grams FeCo powders per batch without losing magnetization compared to small batch. Aging the particles, the effect of exposure of the particles to the ambient air over time, was also studied and it was shown that the particles’ oxidation terminates after 8 weeks of exposure to air and the magnetic moment loses about 30% of its initial value. The reason for terminating the oxidation is the oxide layer itself, since it acts as a resistive layer against more oxidation, forming a passive layer around the particles.

In Section 4.2, synthesizing a newly discovered hard magnet: CoxC, was achieved via modified polyol method using tetraethylene glycol (TEG) as solvent and reducing agent. Although previous studies [70] suggested that rare earth metals are required to synthesize cobalt carbide and it was postulated that they act as catalyst in formation of the carbides, but in this Ph.D. Dissertation we have successfully fabricated cobalt carbide without need to utilize precious rare earth elements. Effect of different reaction kinetics parameters were studied and cobalt carbides particles with magnetic moment 28 emu/g and coercivity as high as 2.3 kOe were fabricated. The temperature and reaction time found to be the most important parameters in determining properties of the final products. PVP and Oleylamine were used as surfactants and found to deteriorate magnetic properties of the particles, while TEG proved to serve as both reducing agent and surfactant with minimum adverse effect on coercivity and saturation magnetization.

Finally in Section 4.3, exchange-coupled nanostructures consisting of FeCo particles as soft phase and MnAlC as hard phase were synthesized through dry
mixing followed by heat treatment. The heat-treated MnAlC-FeCo nanocomposites proved to be exchange-coupled at room temperature with remanence magnetization 2.46 kOe and intrinsic coercivity 3.42 kOe. The energy product of the particles was promising value of 1.56 MGOe; 12.8 kJ/m³. This value compared to AlNiCo and Ferrites is significant and can compete with soft ferrites.
6.0 OUTLOOK AND RECOMMENDATIONS FOR FUTURE WORK

In this Dissertation, binary alloys of FeCo and Co$_x$C magnetic nanoparticles and heterostructures of MnAlC-FeCo were synthesized by modified polyol and dry mixing, respectively. By changing reaction kinetics parameters such as: the temperature, precursors’ concentrations, the reaction time and the capping agents, the magnetic properties of the materials were optimized and pure phase, size and shape-controlled nanoparticles were fabricated. Exchange-coupled MnAlC-FeCo structures also fabricated and room temperature ($BH)_{max}$ more than 1.5 MGOe was achieved. Despite these achievements in this Dissertation, the results leave many open questions to be answered thoroughly, namely;

1- Can first principal calculations explain the trends seen in synthesizing FeCo and Co$_x$C nanoparticles?

2- What is the exact role of rare earth elements in synthesizing Co$_x$C? Do they change the reaction path? Are they playing the catalyst role or heterogeneous seed for nucleating cobalt carbide?

3- What is the effect of impurity, nonmagnetic and magnetic, in magnetic properties of cobalt carbides?

4- What would be the optimized ($BH)_{max}$ value for MnAlC-FeCo? What is the ideal size and content of each phase for this optimal ($BH)_{max}$?
Beside the results provided in this Ph.D. Dissertation, this chapter contains some guidelines and recommendations to help answering the above mentioned questions. These recommendations could facilitate understanding the physical explanations for the different phenomena observed throughout this Dissertation.

Recommendation 1: In-situ investigating of the nucleation and growth of the FeCo and Co₅C particles

Experimental results in Section 4.1 and 4.2 clearly show the impact of reaction time on structure and magnetic properties of cobalt carbide and iron cobalt particles. In order to fully understand, predict and design the desired nanoparticles with specific properties, real-time knowledge of nucleation and growth phase of formation of particles is highly desired. Understanding the nucleation and growth conditions enables us to synthesize desired particles by terminating/promoting the appropriate reaction phase. Elevated Temperature X-Ray Diffractometry (ETXRD) and transmission electron microscopy (TEM) analysis can shed more light on our understanding of the reaction mechanisms in formation of particles in solution.

Recommendation 2: Investigating the effect of rare earth elements in formation of Co₅C

Although, it was suggested [70] that samarium plays an important role in formation of cobalt carbide particles in TEG, it was not clear whether it acts as catalysis and facilitate synthesis of CoxC or was a heterogeneous seed/substrate for formation of cobalt carbides. However, the experimental results in this Dissertation demonstrated synthesis of cobalt carbide in the absence of rare earth elements in all
the processes including: preparation, reaction and post-processing. The difference in shape of the cobalt carbide species: spherical particles versus acicular particles formed with and without using rare earth metals, respectively, suggest possibility of different reaction mechanisms and paths for two cases. Also, it is highly recommended to study the effect of other rare earth metals such as Nd and Dy on the structure and magnetic properties of the particles.

Recommendation 3: Conducting first principal calculations to explain the results provided in this Dissertation

This Dissertation reported experimental results that should be explained theoretically. Conducting density functional theory (DFT) studies aiming to understand the behavior of FeCo and Co₅C systems will help to predict and design the particles with desired properties. Our results indicate coexistence of two carbide phases in the system; Co₂C and Co₃C. There are ambiguities regarding the role and extent of impact of each phase in determining the magnetic properties of the system. Using DFT enables modelling the system which could be verified by experimental results. To date, computational studies mainly focused on structure and electronic properties of the cobalt carbides as a nonmagnetic material and to the best of our knowledge, there has been no micromagnetics study on cobalt carbides yet. Let alone the exchange interactions between different carbide species which is a crucial parameter in explaining the magnetic behavior of the cobalt carbide system.
Recommendation 4: Investigating, experimentally and computationally, the exchange-coupled behavior observed in MnAlC-FeCo in this Dissertation

Although the exchange-coupling reported in Section 4.3 of this Dissertation for MnAlC-FeCo shows a high value of energy product and intrinsic coercivity, it was a demonstration as the first result and need a thorough study. Knowing the correlation between the hard and soft magnetic phase by changing the composition and size of each phase as well as computational studies will lead to synthesis of high-performance and inexpensive permanent magnets free of expensive and readily oxidasable rare earth-contained counterparts. The effect of each constituent, volume fraction of each phase and impact of reaction kinetics parameters on structure and magnetic properties of the final heterostructures should also be studied. Other synthesis techniques can be used and studied to determine the best route to produce high-performance exchange-coupled permanent magnets.
7.0 NOMENCLATURE

\( a \) \quad \text{In-plane unit cell lattice constant, Å}

\( A_s \) \quad \text{Exchange Stiffness constant, J/m}

\( \text{AF} \) \quad \text{Antiferromagnetic}

\( B \) \quad \text{Peak width, degrees}

\( \text{BCC} \) \quad \text{Body-centered cubic unit cell}

\( (\text{BH})_{\text{max}} \) \quad \text{Maximum energy product, kJ/m}^3, \text{MGOe}

\( c \) \quad \text{Out-of plane unit cell lattice constant (in-plane), Å}

\( C \) \quad \text{Concentration, mol/L}

\( c/a \) \quad \text{Lattice distortion}

\( d \) \quad \text{Crystallite size, nm}

\( \text{DFT} \) \quad \text{Density Functional Theory}

\( \text{DSC} \) \quad \text{Differential Scanning Calorimetry}

\( \text{EDS} \) \quad \text{Energy Dispersive x-ray Spectroscopy}

\( \text{EG} \) \quad \text{Ethylene glycol}

\( E_a \) \quad \text{Activation energy, J/mol}

\( f_{\text{Hf}} \) \quad \text{Volume fraction of the hard phase}
f_s Volume fraction of the soft phase

FFT Fast Fourier Transformation

FM Ferromagnetic

FWHM Full Width at Half Maximum, degrees

H Applied magnetic field, T

HCP Hexagonal Closed-Pack

hkl Miller indices

HRTEM High Resolution Transmission Microscopy

ICDD International Center for Diffraction Data

JCPDS Joint Commission on Powder Diffraction Standards

k Scherrer Constant, 0.94 for spherical particles

K_H Anisotropy constant of the hard phase, J/m^3

K_n Uniaxial anisotropy constant for nth direction in the crystal, J/m^3

K_S Anisotropy constant of the soft phase, J/m^3

M Magnetization, emu/g

M_r Remanence, emu/g

M_s Saturation magnetization, emu/g
OA  Oleylamine

PPMS  Physical Property Measurement System

PVP  Poly-Vinyl-Pyrrolidone

SEM  Scanning Electron Microscopy

t  Time, min

T  Temperature, K

TEG  Tetra-Ethylene-Glycol

TEM  Transmission Electron Microscopy

$T_b$  Blocking temperature, K

$T_c$  Curie temperature, K

$T_N$  Neel temperature, K

$t_S$  thickness of the soft layer

VSM  Vibrating Sample Magnetometer

XRD  X-ray Diffraction

$\theta$  Angle between the magnetization vector and the easy axis, degrees
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