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Surface and Interface Effects of Magnetoimpedance Materials at High Frequency

Tatiana M. Eggers
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Surface and Interface Effects of Magnetoimpedance Materials at High Frequency

by

Tatiana M. Eggers

A dissertation submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy
Department of Physics
College of Arts and Sciences
University of South Florida

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Keywords: amorphous alloys, magnetoimpedance, magnetic anisotropy, surface magnetic domains

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DEDICATION

To my father, for giving me patience;
To my mother, for giving me confidence;
To my husband, for giving me support;
And to my son, for giving me strength.
ACKNOWLEDGEMENTS

This body of work could not have been completed without the mentorship of my major advisor, Dr. Manh-Huong Phan. His encouragement, wisdom, and enthusiasm has left me with a set of skills and perspectives that I will carry for a lifetime. Along with my co-major advisor Dr. Hariharan Srikant, my advisors have created opportunities for me to build my skills as a scientist, collaborator, and professional. Their unwavering commitment to student mentorship has created a strong research group that benefits not only their students, but their colleagues, collaborators, and the Physics department at USF. I would also like to thank all of the past and present FML/Sensor Lab coworkers for being there to motivate me, lend a helping hand, and provide warm support during the past five years.

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ABSTRACT

Amorphous and nanocrystalline transition metal magnetic alloys (TMMAs) have been the subjects of fundamental and applied study due to their unique structure. The lack of long-range order in these materials sets the stage for their soft magnetic properties to be tuned for a variety of technological applications, such as sensitive magnetic field sensors, high frequency transformers, and stress sensors. Fundamental investigation of the magnetic and structural properties of these materials is also motivated by their unique amorphous or nanocrystalline-embedded amorphous matrix morphology, which has consequences on both the magnetism seen from both the atomic and macro-scale. The surfaces of these materials become important to their high frequency applications, where the skin depth of the excitation field is distributed near the surface. In conjunction with high frequency magnetoimpedance measurements, surface sensitive probes of magnetism and structure must be employed to provide a complete picture of the relationship between the surface and dynamic magnetism. This dissertation focuses on the surface impact of chemical composition, annealing conditions, and coatings on TMMAs on their magnetoimpedance response through multiple surface sensitive techniques such as atomic/magnetic force microscopy, magneto-optical Kerr effect, and scanning/transmission electron microscopy. These tools provide a view into the relationship between the nanostructure, microstructure and soft magnetic properties that make these materials highly desired for fundamental study and technological application.
1. INTRODUCTION

1.1. Motivation

Sensors based on magnetotransport phenomena appear in all aspects of modern technology [1,2]. In particular, sensors based on the giant magnetoimpedance (GMI) effect in soft ferromagnetic ribbons and wires have spurred much study over the past 20 years due to exciting opportunities for its use as sensitive magnetic field sensors for a variety of applications [3]. MI-based sensors have potential for use in applications such as magnetic recording, geomagnetic sensing, position sensing, torque and stress sensing, and also appear in the biomedical field for the detection of magnetic nanoparticles [4–7]. The GMI effect is also a useful tool due to the close relationship between the impedance, penetration depth, and magnetic permeability. When coupled with surface sensitive tools such as the magneto-optical Kerr effect, the unique intrinsic and extrinsic magnetic properties of magnetoimpedance materials can be explored.

The magnetoimpedance materials in this dissertation are transition-metal amorphous alloys (TMAAs). These are rapidly quenched magnetic glasses with soft magnetic properties stemming from their high permeability and weak magnetic anisotropy. The amorphous phase of transition metal alloys also has a higher resistivity than their crystalline counterparts, which is beneficial to high-frequency transformer applications. Their plasticity is not dislocation mediated, so they exhibit a high elastic limit as well as no microstructural continuities, such as grain boundaries, which can pin domain walls. Appropriately annealed TMAA’s have a unique nanocrystalline phase embedded in an amorphous matrix, thus they are sometimes called nanocomposites. These nano-sized crystalline grains, typically less than 10 nm in size, are much smaller than the ferromagnetic exchange length, therefore, soft magnetic behavior is preserved.
The first groups to consider GMI for technological application were chiefly concerned with sensitive changes in magnetic impedance at excitation frequencies less than 10 MHz \cite{8,9}. They described the impedance change as the classical consequence of the (magnetic) skin effect, where the distribution of an ac current of frequency, $f$, in a soft magnetic conductor of conductivity, $\sigma$, flows near the surface at a depth $\delta = (\pi \sigma f \mu_t)^{-1/2}$. The large and sensitive transverse magnetic permeability, $\mu_t$, of soft ferromagnetic conductors (i.e. ribbons) is the key to unlocking giant changes in impedance. Accordingly, what governs $\mu_t$ is the frequency and field dependent dynamic magnetization reversal mechanism in the ferromagnetic conductor, which can have contributions from domain wall motion, magnetization rotation, and/or ferromagnetic resonance depending on the frequency of the probe current. However, the desire for increasing speed and frequency of modern electronics fuels the need for understanding of the dynamic properties of magnetic materials at higher frequencies towards gigahertz \cite{10}, where ferromagnetic resonance (FMR) and other magnetic-microwave absorption phenomena are involved in driving impedance changes. Despite a number of previous studies \cite{11–27}, a clear understanding of effects of the surface magnetic domain structure, magnetization process, and surface roughness on the high frequency magnetoimpedance response of the materials has remained elusive.

The theme of this Ph.D. work is to use the magnetoimpedance (MI) effect RF and microwave frequencies to study surface and interface effects on the dynamic permeability of ferromagnetic ribbons and microwires, both research-fabricated and commercially available. Surface magnetic domain structure, magnetization, and surface condition of the materials are characterized by atomic/magnetic force microscopy (A/MFM) and magneto-optical Kerr effect (MOKE). The consequences of material composition, shape, fabrication methods, annealing treatments, and surface coatings on the high frequency MI and its association with the MFM and MOKE are ultimately evaluated to support the integration of these materials into today’s microwave technology.
1.2. Dissertation Overview

This dissertation consists of nine chapters. Chapter One presents the motivation for the work and the organization of the dissertation.

In Chapter Two the fundamental concepts of magnetically soft, amorphous transition metal alloys are given. After an introduction to the amorphous character of these alloys and their nanocrystallization kinetics, the relevant energy densities comprising the free energy of function of amorphous and nanocrystalline transition metal alloys. The complex domain structure of negative magnetostrictive microwires is given along with the mechanisms of magnetization reversal at dc and higher frequency.

Chapter Three outlines the principles and methods behind the experiments performed in this dissertation, including a brief outline of the fabrication method. Chapter Three also features an extensive overview of the high frequency magnetoimpedance phenomena and its sensitive relationship to the measurement apparatus, a network analyzer.

Chapter Four begins the original work performed in this dissertation with the effect of Joule annealing on the magnetoimpedance of FeCo alloy ribbons with varying glass former content. In this work, the surface domain structure observed by magnetooptical Kerr effect is linked to the magnetoimpedance behavior. The mechanism of induced anisotropy is discussed in terms of the mobility of the magnetic elements under the self-induced magnetic field generated by the annealing current.

In Chapter Five, the impact of layered amorphous and crystalline magnetic materials on the magnetoimpedance is investigated in two different systems. The first is an amorphous NiFe ribbon coated with Co. The surface magnetic anisotropy is examined and the effect of the Co-coating on the magnetoimpedance is discussed through the components of the complex impedance through inductance formalism. In the second system, an amorphous/nanocrystalline bilayer ribbon is studied to understand the impact of a mixed-phase ribbon system on the magnetoimpedance. Magneto-optical Kerr effect hysteresis loops were taken with a high frequency current passing through the ribbon.
Chapter Six shows high-resolution magnetic force microscopy on melt-extracted Co-rich amorphous microwires with varying Zr content from 0-4 at. %. The model for the surface domain structure is given and related to the magnetic gradient contrast in the normal direction that is measured by magnetic force microscopy. Periodic bamboo domains are imaged and the periodicity was found to change with Zr content. This effect was related to the uniaxial wall spacing theory and the anisotropy change with Zr content is elucidated.

Chapter Seven presents the unique relationship between an amorphous/nanocrystalline phase separation and the core-shell domain model of melt-extracted Co-rich amorphous microwires. The radially dependent phase separation is induced by a stepped Joule annealing procedure. The phase separation is seen as a function of maximum annealing current by cross sectional scanning electron microscopy. The magnetoimpedance response is related to the phase separation by the skin effect.

Chapter Eight concludes this dissertation with the summary and conclusions on research of amorphous and nanocrystalline soft magnetic materials with the magnetoimpedance effect and related surface phenomena.

1.3. References


2. FUNDAMENTAL ASPECTS OF SOFT AMORPHOUS AND NANOCRYSTALLINE MAGNETIC ALLOYS

In this Chapter, important aspects of the structure and magnetism in rapidly quenched, soft magnetic materials are given. First, the relevant length and time scales of the magnetic phenomena probed in this work are overviewed. Then, the phenomenology of the magnetic anisotropy and magnetic domain structure in rapidly quenched, amorphous magnetic materials is presented. Finally, the mechanisms behind the magnetization reversal process in magnetic materials, with emphasis placed on those classified as "soft magnetic", are given.

2.1. Magnetic Transition Metal Amorphous Alloys

The amorphous magnetic materials that are of interest to technological applications are made up of late transition (TL) metals Fe, Ni, and Co as the magnetic constituents. Transition metal amorphous alloys (TMAA) also include early transition metals (TE) such as Zr and Nb and metalloids (M) such as B and Si, which are used to stabilize the amorphous state. The TE and M elements are also referred to as glass formers. The general composition that permits room temperature magnetism is TL\(_{1-x}(TE,M)_x\), where \(x = 10-40\%\) and (TE,M) represent some combination early transition metals and metalloids. The nanocrystalline phase of TMAA is also technologically important. The nanocrystalline phase is achieved with optimized annealing procedures. It is characterized by grain sizes ranging from 1-50 nm embedded in an amorphous matrix. In addition to the TE and M elements in the TL\(_{1-x}(TE,M)_x\) system, small amounts ranging from 1-4 at. % of noble metals (NM) such as Cu serve as nucleating agents for a nanocrystalline phase. TMAAs annealed with the intention of transformation into the nanocrystalline phase are often called nanocomposites.

The TMAAs studied in this dissertation are given in Table 2.1.
Table 2.1 Transition metal amorphous alloys studied in this dissertation

<table>
<thead>
<tr>
<th>Composition</th>
<th>Family</th>
<th>Morphology</th>
<th>Origin</th>
</tr>
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<tbody>
<tr>
<td>(Fe&lt;sub&gt;65&lt;/sub&gt;Co&lt;sub&gt;15&lt;/sub&gt;)&lt;sub&gt;x&lt;/sub&gt;B&lt;sub&gt;13&lt;/sub&gt;Nb&lt;sub&gt;x&lt;/sub&gt;Si&lt;sub&gt;2&lt;/sub&gt;Cu&lt;sub&gt;1.5&lt;/sub&gt; (x = 0-4)</td>
<td>HITPERM variant</td>
<td>2 mm wide/20 μm thick</td>
<td>Melt-spinning ribbon</td>
</tr>
<tr>
<td>(Fe&lt;sub&gt;50&lt;/sub&gt;Ni&lt;sub&gt;30&lt;/sub&gt;)&lt;sub&gt;x&lt;/sub&gt;B&lt;sub&gt;12&lt;/sub&gt;Nb&lt;sub&gt;7&lt;/sub&gt;</td>
<td>FeNi-based</td>
<td>6 mm wide/25 μm thick</td>
<td>Planar flow casting ribbon</td>
</tr>
<tr>
<td>(Co&lt;sub&gt;69&lt;/sub&gt;Fe&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;x&lt;/sub&gt;Si&lt;sub&gt;13&lt;/sub&gt;B&lt;sub&gt;13.5&lt;/sub&gt;TE&lt;sub&gt;x&lt;/sub&gt; x = 0-4 at. %, TE = Zr,Nb</td>
<td>Co-based</td>
<td>40-60 μm diameter</td>
<td>Melt-extraction wires</td>
</tr>
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</table>

The most important property of the TMAAs listed above is their soft magnetism, which is a consequence of their small magnetic anisotropy due to the lack of magnetocrystalline anisotropy. All of these materials can have a transverse magnetic domain structure either resulting directly from fabrication conditions or through a proper annealing treatment with stress or magnetic field. The transverse easy axis of magnetization is transverse relative to the current direction in a longitudinal magnetoimpedance measurement geometry (i.e., along the induced magnetic field direction from the alternating current). This domain configuration is important for a large transverse (or circumferential, for microwires) ac permeability, which increases the magnetoimpedance effect due to its relationship with the skin effect. Another important property these materials share is a near-zero magnetostriction coefficient. This is also a reason for their soft magnetic property but also important to their use in applications. A near-zero magnetostriction constant means their magnetic properties do not change under tensile or compressive stress.
2.1.1. Amorphous and Nanocrystalline Structure

Immediately after solidification by rapid quenching, the TMAAs that are the subject of this dissertation are in their amorphous phase. Their local atomic arrangements are thought to resemble the liquid melt frozen in place by the high cooling rate ($10^5$-$10^6$ K/s). Crystalline metals are modeled by close packed hard spheres with parameters such as the interplanar distance ($d$) that is constant over long length scales. This is illustrated in Fig. 2.1 (a). In contrast, silica glass is covalently bonded with fixed bond length, but they are arranged in a randomly oriented network (Fig. 2.1(b)). The local atomic structure of an amorphous metal is modeled by random, quasi-densely packed spheres pictured in Fig. 2.1 (c). Their short range atomic order is similar to the stable crystalline phase of the composition. This can be illustrated by an X-ray diffraction scan of an amorphous Co-based ribbon. Although periodically spaced parallel planes do not exist in the Co-based amorphous ribbon, a broad peak in the scattered intensity of the X-rays is evident near $2\theta = 44^\circ$, which corresponds to where one or more diffraction peaks would occur in crystalline Co.

Figure 2.1 Schematics of (a) crystalline structure, (b) amorphous covalently bonded structure, (c) amorphous metallic and (d) nanocrystalline phase.
An annealed TMAA or nanocomposite has a two-phase structure typically consisting of a nanocrystalline phase embedded in an amorphous matrix as shown in Fig 2.1(d). The grain size of the nanocrystalline phase can range from 1 nm – 50 nm, depending on the temperature and duration of the annealing procedure. The structure and magnetic properties of the nanocrystalline phase and amorphous matrix both impact the magnetic and mechanical properties. One key structural aspect permitting the soft magnetic property of amorphous and nanocrystalline magnetic alloys is maintaining a structural correlation length that is much less than the ferromagnetic correlation length.

2.1.2. Thermodynamics

This section will briefly outline the critical temperatures, crystalline products, and related magnetic properties of the TMAA’s after annealing. In Table 2.2, the crystallization temperature and crystalline products are presented for the materials studied in this dissertation.

There is a lot of detailed work on the crystallization kinetics of HITPERM-variant Fe_{65}Co_{35} amorphous alloy conducted by Refs. [1–3]. The combined works show that the primary crystalline product ($T_x = 375-450 \, ^\circ C$) of the alloy is ferromagnetic BCC $\alpha$-FeCo, with the ratio of Fe:Co being 70:30, which is slightly higher than the bulk ratio of 65:35. This is attributed to the higher mobility of Fe than Co. Therefore, the formation of $\alpha$-FeCo leaves behind the glass formers along with a composition richer in Co as compared to the nominal Fe:Co ratio. Upon further heating to $T \sim 550 \, ^\circ C$, the second phase to form from the amorphous matrix is BCC (Fe,Co)$_{23}$B$_6$. Depending on the ratio of Fe:Co, this boride phase may be a hard magnet or nonmagnetic at room temperature.

Fe$_{50}$Ni$_{50}$-based amorphous alloys crystallize into FCC FeNi at $T_{x1} = 463 \, ^\circ C$, which is a soft ferromagnet at room temperature. This turns into the BCC phase when the Fe:Ni ratio leans toward Fe. Similar to the FeCo-alloys, the secondary crystallization is the so-called 23-6 boride phase. The boride phase is generally a hard magnet.
Table 2.2 Crystallization temperature and crystalline products of annealed transition metal amorphous alloys

<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystallization Temp.</th>
<th>Crystalline Products</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>((Fe_{65}Co_{35})<em>{83.5-x}B</em>{13}Nb_{x}Si_{2}Cu_{1.5}) ((x = 0-4))</td>
<td>(T_{x1} = 375-450 , ^{\circ}C)</td>
<td>(\alpha)-FeCo</td>
<td>[1,3]</td>
</tr>
<tr>
<td></td>
<td>(T_{x2} = 500-700 , ^{\circ}C)</td>
<td>((Fe,Co)<em>{23}B_6 &amp; (Fe,Co)</em>{2}B_1)</td>
<td></td>
</tr>
<tr>
<td>((Fe_{50}Ni_{50})<em>{83}B</em>{12}Nb_{7})</td>
<td>(T_{x1} = 463 , ^{\circ}C)</td>
<td>FCC FeNi</td>
<td>[4][5]</td>
</tr>
<tr>
<td></td>
<td>(T_{x2} = 604 , ^{\circ}C)</td>
<td>((Fe,Ni)_{23}B_6)</td>
<td></td>
</tr>
<tr>
<td>((Co_{69}Fe_{4})<em>{74}Si</em>{13}B_{13.5-x}TE_x) (x = 0-3 , \text{at.} , %), (TE=Zr,Nb)</td>
<td>(T_{x1} = 530-548 , ^{\circ}C)</td>
<td>FCC Co</td>
<td>[6][7]</td>
</tr>
<tr>
<td></td>
<td>(T_{x2} = 693-670 , ^{\circ}C)</td>
<td>CoSi, CoB</td>
<td></td>
</tr>
<tr>
<td>((Co_{x}Fe_{1-x})<em>{81}Nb</em>{7}B_{12}) (x = 0.75-1)</td>
<td>(T_{x1} = 415-441 , ^{\circ}C)</td>
<td>FCC Co</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>(T_{x2} = 627-676 , ^{\circ}C)</td>
<td>CoB, ((Co,Fe,Nb)_{23}B_6)</td>
<td></td>
</tr>
</tbody>
</table>

Co-rich amorphous alloys can crystallize into their HCP or FCC phases depending on the annealing temperature [9,10]. Using the standard technique of differential scanning calorimetry at ~ 10 K/min, the primary crystallization phase is found around \(T_{x1} = 465 \, ^{\circ}C\) for Co-rich CoFeBSi. The addition of early transition metal Zr or Nb increases the primary crystallization temperature. The secondary crystallization products are cobalt boron-silicate compounds, which are non-magnetic at room temperature.

### 2.2. Energetics of an Amorphous or Nanocrystalline Ferromagnet

The interpretation of a domain pattern or hysteresis loop of a magnetic material is based on thermodynamics. The main principle utilized is the minimum energy principle, where the equilibrium orientation of the magnetization vector, \(M\), is determined by the minimum free energy with the constraint that the magnitude of the magnetization vector remains conserved (i.e. \(M^2 = 1\)). Some magnetic energy terms depend on their local environment while others do not depend on the local values of \(M\). In Chapter 2.2, the contributions to the total free energy of a ferromagnet are reviewed with special attention paid to the unique conditions posed by an amorphous or nanocrystalline ferromagnetic ribbon or wire. Refs. [11–13] are referenced in this section.
2.2.1. Exchange Energy

The fundamental property of a ferromagnet is parallel spin alignment at equilibrium. The exchange energy for a pair of atoms $i$ and $j$ with spin $S$ is represented as:

$$ E_{ex} = -2JS^2 \cos \theta_{ij} \quad (2.1) $$

where $J$ is the exchange constant and $\theta_{ij}$ is the angle between the two spins. For a positive exchange constant, $J$, a parallel alignment of spins reduces the overall energy. The exchange energy itself is not typically included in a macroscopic assembly of the free energy, however, it is encompassed within the magnetocrystalline anisotropy energy. The strength of the exchange interaction at a microscopic level becomes important in the analysis of magnetic domain walls (see section 2.3.6), where there is a transition area between antiparallel magnetic domains. The continuum expression of the exchange energy is

$$ E_{ex} = -2A \cos \left( \frac{d\theta}{dx} \right), \quad (2.2) $$

where $A$ is the exchange stiffness constant and $x$ is unit length. In the continuum expression for exchange energy, the microscopic quantities $J$ and $S$ are combined into $A$. Magnetic materials with larger $A$ have a higher energy cost for deviation from parallel alignment than those with small exchange stiffness. The exchange stiffness, $A$, is always taken to be constant for a given material (crystalline or amorphous) and is regarded as isotropic. Typical values of $A$ range between $10^{-11}$-$10^{-12}$ J/m for soft ferromagnets at room temperature [14,15].

2.2.2. Magnetostatic Energy

The magnetostatic energy is considered a non-local, i.e. long range, contribution to the total free energy. This energy arises due to the discontinuity of the normal component of the magnetization across an interface such as the sample’s surface. Consider the cross section of a rectangular magnetic sample that is uniformly magnetized such as in Fig. 2.2, where the magnetization is represented by the blue arrows pointing up. At the surfaces of the sample, there is a discontinuity of the internal magnetization, which is
represented by a fictitious magnetic “charge” or pole. The positive and negative magnetic charges set up their own field, shown as the black arrows in the figure.

Figure 2.2 Schematic of the magnetostatic energy contribution to the free energy.

The field lines that pass through the interior of the sample is called the demagnetizing or “demag” field. For a thin sample, the demag field is constant and for a thick or bulk sample the strength of the field drops off toward its middle. In this dissertation, the thickness (diameter) of the ribbons (wires) range from 30-60 μm, so we take the demag field to be constant throughout the thickness (radius). Typically, the magnetostatic energy contribution has uniaxial symmetry with the axis of symmetry being along the short axis of the sample. The magnetostatic energy is expressed as:

\[ E_{ms} = -\mathbf{M} \cdot \mathbf{H}_d = -MH_d \cos(\theta), \]  

(2.3)

where \( \mathbf{M} \) is the magnetization vector, \( \mathbf{H}_d \) is the demag field vector, and \( \theta \) is the angle between the two vectors. This energy contribution is often called “shape anisotropy” since it depends on the sample geometry.

2.2.3. Magnetic Anisotropy Energy

In crystalline and nanocrystalline magnetic alloys, the dominant contribution to the free energy is from the intrinsic magnetocrystalline anisotropy. The magnetocrystalline anisotropy originates from the
interaction between the crystal lattice and spin-orbit coupling as well as the exchange interaction. For crystalline alloys, the symmetry of the anisotropy takes on the same symmetry as the crystal. In a textured polycrystalline alloy, there can be a distribution of magnetic anisotropies that can be well defined. In the case of nanocrystalline magnetic materials, the magnetocrystalline anisotropy is averaged out since each nano-sized grain is of random orientation. Of course, in amorphous ferromagnets, the magnetocrystalline contribution is not considered due to the lack of long-range order. The most common function for magnetic anisotropy energy \((E_a)\) has uniaxial symmetry:

\[
E_a = K_U \sin^2 \theta, \quad (2.4)
\]

where \(K_U\) is the uniaxial anisotropy constant and \(\theta\) is the angle between the magnetization and easy axis.

The magnetoelastic energy has its origin in the same crystal field/spin-orbit coupling as the magnetocrystalline. It is possible for a magnetic object to physically deform due to a magnetic interaction. Such a deformation is called the magnetoelastic interaction and it is typically very small and isotropic in ferromagnets. However, there is a second-order interaction that is very relevant in amorphous and soft magnetic materials and that is a strain-dependent magnetoelastic coupling called magnetostriction. In this effect, an external stress on a magnetic body can shift the preferred magnetization direction. Amorphous magnetic materials are considered isotropic with respect to the magnetoelastic energy since there is no long range atomic order. The contribution to the free energy is of the form:

\[
E_{me}^{iso} = \frac{3}{2} \lambda_s \sigma \cos^2 \theta, \quad (2.5)
\]

where \(\lambda_s\) is the saturation magnetostriction constant, \(\sigma > 0\) is the tensile stress (\(\sigma < 0\) is compressive), and \(\theta\) is the angle of the magnetization with respect to the easy axis.

### 2.2.4. Zeeman Energy

The Zeeman energy represents the potential energy of a magnetic moment in an external field. It is simply the dot product of the magnetization with the external field:
\[ E_z = -M \cdot B. \quad (2.6) \]

The negative sign ensures that there is a reduction of total free energy when the magnetization and external field align. The Zeeman energy can present a competing force to intrinsic magnetic properties of an amorphous magnetic alloy, especially in layered systems or systems with low anisotropy energy and dominant exchange energy contributions such as nanocrystalline materials. The Zeeman energy also plays an important role in magnetic field annealing of amorphous alloys when the Curie temperature is greater than the annealing temperature.

2.2.5. \textit{Induced Anisotropy by Joule Annealing}

The magnetic anisotropy in an amorphous ferromagnet can be induced or tailored by conventional annealing, applied stress, and/or by application of a current. The latter is termed Joule annealing and it was exclusively used to tailor the magnetic anisotropy of the wires and ribbons in this dissertation. Joule annealing is a desirable method to treat rapidly quenched amorphous materials due to the combination of heat and self-induced circumferential or transverse magnetic field. The induced magnetic field by the annealing current has been shown to align the domain walls along the same direction; what’s more is that the transverse (for planar ribbons) or circumferential (for wires) induced magnetic field is also the magnetically easy direction with regards to the ac magnetic field produced by the ac driving current in magnetoimpedance measurements. There are several proposed mechanisms for induced magnetic anisotropy by Joule annealing:

1. Induced atomic pair ordering of the magnetic components
2. Structural relaxation i.e. rearrangement of free volume
3. Alignment of magnetic crystallites within the amorphous matrix

In this dissertation, the target temperature for Joule annealing is below the crystallization temperature and Curie temperature. Even at these temperatures, there is sufficient thermal energy to allow some short-range atomic mobility. As a result, the thermal motion of the atoms is susceptible to bias of temperature or magnetic field gradients. This still results in an amorphous phase but now there is some
additional short-range atomic order or even a long-range correlation of a small percentage of the atoms. However, upon cooling, the atomic positions mostly relax into their original arrangement. Annealing in an incremental or step-wise fashion is explored to combat that relaxation and retain the long-range correlation induced. The addition of metalloids into the alloy promotes induced anisotropy because of their high mobility and strong chemistry with transition metals.

2.3. Magnetic Domains and Domain Walls

Magnetic domains form as a result of the dipole fields set up at the surface of a magnetic material (see section 2.2.2). The size and shape of magnetic domains reflect an arrangement that minimizes the magnetostatic energy and therefore is an extrinsic property of the magnetic body. A domain wall is a region that separates two magnetic domains. While a domain is a region of uniform magnetization within a magnetic body, the magnetic domain wall contains moments which gradually change from one magnetization orientation to another. This section focuses on the model for the domain and domain wall structure of a negative magnetostrictive amorphous micron-sized wire.

2.3.1. Core-shell Domain Structure of Negative Magnetostriction Amorphous Wires

The model for the magnetic domain structure of a negative magnetostriction amorphous wire, such as a Co-rich metallic glass microwire, was first proposed by Panina et al. in [16] and dubbed a “core-shell” or “bamboo-like” domain pattern. Panina and coworkers suggested that a radial dependence of the quenching rate put the surface layer of the wire under circumferential or axial compression while toward the region near the center of the wire was under tension. Due to the negative magnetostriction, the circumferential or axial compression would act to create a circumferential easy axis near the surface and a longitudinal or axial easy axis near the core as seen in Fig. 2.3.
At the time, this model of the domain structure was adequate considering only a few observations of the surface domain structure existed. Later, it was argued by Usov et al. [17] that the proposed radial symmetry of the wire and residual stresses from fabrication would result in no magnetic “charges” or poles at the surface of the wire and therefore the magnetostatic energy at the surface would be negligible. Thus, without the need to minimize the magnetostatic energy, no domains should form at all. This did not agree with experimental observations, so Usov et al. supposed that a deformation (break in radial symmetry) of the wire was a possible origin for the bamboo-like domain structure. However, Chen et al. [18] argued that physical deformation was not enough to change the domain structure and that not only was an axial core domain energetically unfavorable, but also suggested that a bamboo-like surface domain structure is most likely a metastable state. Basically, the problem boiled down to knowledge of the stress distribution of the wire. In contrast to previous works where thermal stress during rapid quenching was thought to directly influence the residual stress patterns, Chen et al took the residual stresses ($\sigma$) acting on the wire to be instead from a nonuniform density distribution resulting from the rapid quenching. This distinction changed the scaling of the resultant stresses from $\sigma \propto (T_g - T_0)$ to $\sigma \propto (T_m - T_g)$, where $T_g$, $T_0$, and $T_m$ refer to the glass transition temperature, room temperature, and molten alloy temperature, respectively.

![Figure 2.3 A cartoon of the core-shell model of negative magnetostrictive microwires (courtesy of S. Jiang from HIT).](image)

The revised core-shell domain model from Chen et al. [18], taking into account the aforementioned factors, results in a circular anisotropy for the outer shell and the same ratio of $r_c$ to $r_0,$
$r_c/r_0 = 0.75$, just as in previous models. The difference has to do mainly with the core domain structure, which, according to the revised model, is thought to be of helical symmetry with directions +/- 30° from the circular direction. This revised core-shell model also has implications for the magnetization process of the Co-rich microwire. In Co-based wires, the technical magnetization should take place by irreversible rotation of the domain magnetization in the core region.

2.3.2. Domain Walls

This section will outline the general theory of domain walls in magnetic materials with uniaxial symmetry. Soft magnetic amorphous alloys fit in this category. The domain wall structure in bulk amorphous and nanocrystalline alloys is understood through a balance of the exchange energy and the leading term of the anisotropy energy. Domain walls called Bloch walls the simplest type of magnetic domain wall and are characterized by a 180° rotation of the magnetization vector within the wall, as pictured in Fig. 2.4.

![Figure 2.4 A cartoon of a 180° Bloch wall from [12].](image)

Domain walls in general are continuous transition regions between two anti-parallel domains, however, the wall thickness can be estimated for the simple case of a uniform magnetic material with uniaxial symmetry [11]:

$$
\delta_{dw} = \pi \frac{A}{\sqrt{K}}, \quad (2.7)
$$

where $A$ is the exchange stiffness constant and $K$ is the uniaxial energy constant (from any origin).
2.4. Magnetization Reversal Mechanisms

2.4.1. Quasi-static Magnetization of a Single Uniaxial Domain

The magnetization process of a single domain magnetic body with uniaxial anisotropy is a canonical example of magnetization reversal by coherent rotation of domain spins [11]. When the applied field is along the hard axis of the material, the magnetization process is reversible and hence little energy is lost. This is usually the first order approximation for the reversal mechanism of a magnetic material with domain walls that are immobile due to either defects or eddy currents. Minimization of the total free energy with respect to the magnetization direction provides an analytical solution in the case where the applied magnetic field, $H$, is perpendicular to the easy axis (EA), as pictured in Fig. 2.5. The hard axis magnetizing field is the field configuration for longitudinal giant magnetoimpedance measurements of ribbons and wires (outer shell).

Figure 2.5 A schematic representation of the hard axis magnetization field configuration and the resulting M-H loop of a single domain particle.
The free energy density in this configuration is:

\[ E = K_u \cos^2(\theta) - M_s H \cos(\theta), \quad (2.8) \]

where \( K_u \) is the uniaxial anisotropy constant \( (K_u > 0) \), \( M_s \) is the saturation magnetization, \( H \) is the applied field, and \( \theta \) is the angle between the magnetization and applied field. By taking the derivative of Eq 2.8 with respect to \( \theta \), the energy minimum can be found:

\[ (-2K_u \cos(\theta) + M_s H) \sin(\theta) = 0. \quad (2.9) \]

However, the solution to Eq. (2.9) is not stable unless the second derivative is positive:

\[ -2K_u \cos^2(\theta) + M_s H \cos(\theta) > 0. \quad (2.10) \]

The first solution is \( \theta = n\pi \) where \( n = 0, 1, 2, \ldots \). These solutions correspond to the saturated state, where \( M=M_s \cos \theta \) would be parallel or anti-parallel to the applied field, \( H \). This solution is an obvious one and does not provide any insight into the magnetization process. The second solution is given by:

\[ 2K_u \cos(\theta) = M_s H, \quad (2.11) \]

which is the equation of motion for the magnetization below saturation.

The stability condition of Eq. 2.10 states that the saturation states \( \theta = 0 \) and \( \theta = \pi \) are only stable if \( H > 2K_u/M_s \) and \( H < -2K_u/M_s \), respectively. The stability condition allows one to define the field that saturates the magnetic body as the anisotropy field, \( H_K = 2K_u/M_s \). Substitution of \( \cos(\theta) = m = M/M_s \) and \( h = H/H_K \) gives simply \( m = h \). Therefore, the \( M(H) \) loop normalized to the saturation magnetization and anisotropy field is linear between the saturated states. This general equation of the magnetization process still holds even if domain walls exist (parallel to the EA) and are free to move. Since there is no energy difference across the domain wall in the hard-axis configuration, the walls behave as pinned.

The contribution to the total dc permeability from domains with easy axes perpendicular to the applied field can also be determined:
\[ \mu_{rot} = \mu_0 \frac{H + M}{H} = \mu_0 \left(1 + \frac{M_s^2}{2K_u}\right) \approx \mu_0 \frac{M_s^2}{2K_u}. \quad (2.12) \]

2.4.2. Frequency-dependent Permeability

The permeability of a magnetic material refers to the ease or difficulty of the magnetization response to an applied magnetic field. Depending on the magnitude and frequency of the alternating magnetic field, the magnetic material may be more or less permeable. There are many contributions to the permeability of an amorphous soft magnet, for example, domain wall displacement, irreversible and reversible magnetization rotation, and meeting the ferromagnetic resonance condition. Each of these are both frequency and field dependent. In this dissertation, the giant magneto-impedance effect is employed as an indirect probe of the permeability. The impedance (in the high frequency limit) of a magnetic wire conductor is related to the permeability of the material through the skin depth [20,21]:

\[ Z = \frac{r R_{dc} (1 + i)}{2 \delta}, \quad (2.13) \]

where \( r \) is the wire radius, \( R_{dc} \) is the dc resistance, \( i \) is the imaginary unit, and

\[ \delta = \left( \frac{\mu_0}{\mu_{eff}} \right)^{1/2} \delta_0, \quad (2.14) \]

where \( \mu_0 \) is the permeability of free space and \( \mu_{eff} \) is the effective ac permeability considering all possible contributions. From Eqs. 2.13 and 2.14, it can be seen that the \( Z \sim (\mu_{eff})^{1/2} \).

For a negative magnetostrictive wire with circumferential domain structure near the surface, the ac magnetic field in longitudinal magnetoimpedance is an easy axis field. Therefore, at frequencies below 1 MHz, the magnetic permeability mainly arises due to movement of domain walls and rotational permeability. At around \( f = 1 \text{ MHz} \), the permeability relaxes due to the induced eddy currents that act to freeze domain wall movements. The relaxation frequency at which this occurs depends greatly on the resistivity of the material. Higher resistivity materials such as amorphous materials (about 3-5 times
greater resistance than their crystalline counterparts) are desirable for high kHz applications such as transformers for this reason.

Once domain wall motion is damped, the remaining contribution to the permeability is rotation of domain magnetization, which decreases with increasing frequency as it becomes harder for the magnetization to follow the rapidly changing field. As the frequency reaches the GHz range, the gyromagnetic effect becomes important and the permeability can suddenly increase as ferromagnetic resonance conditions are met. This usually occurs in regions of the magnetic material where the magnetization is saturated. Another consequence of increasing frequency is the decrease of the penetration depth of the ac current. As the skin depth decreases, less of the bulk properties are sampled and the surface magnetic structure plays a greater role. As mentioned in section 2.3.1, some amorphous magnetic materials have different domain structures at their surface than in the bulk.

2.5. References


[3] S. Kernion, V. Keylin, J. Huth, M.E. McHenry, Secondary crystallization in (Fe_{65}Co_{35})_{79.5+x}B_{13}Nb_{4-x}Si_{2}Cu_{1.5} and (Fe_{65}Co_{35})_{73}B_{10}Nb_{x}Si_{2}Cu_{1} nanocomposite alloys, J. Appl. Phys. 111 (2012) 07A329. doi:10.1063/1.3677830.


3. EXPERIMENTAL METHODS

This chapter describes the techniques and methods behind the preparation, measurement, and interpretation of the samples in the following chapters. First, the rapid quenching method for preparation of the amorphous ribbon and microwire samples, their coatings and their bilayer structures is given. The methods used to determine the structural properties of the samples, such as X-ray diffraction and electron microscopy are reviewed. The relevance of surface-sensitive quasi-static hysteresis loops and microscopy of the domains conducted with magneto-optical Kerr effect microscopy is given. The dynamic magnetic measurements using the magnetoimpedance effect in a transmission line, along with detailed analysis of the measurement results, are provided.

3.1. Sample Fabrication

The amorphous magnetic ribbons and wires studied in this dissertation were fabricated by various rapid quenching processes. Also known as rapid solidification, this fabrication technique can be broadly defined as the rapid extraction of heat or thermal energy inducing the phase transition from a high temperature liquid to room temperature solid. To be considered rapidly quenched or rapidly solidified, the cooling rate should exceed $10^5$ K/s. In this section of Chapter 3, the two rapid quenching methods used to manufacture the materials studied in this work will be briefly overviewed. A current review on rapid solidification techniques can be found in Ref. [1].

3.1.1. Melt-spinning and Planar Flow Casting

Melt spinning (MS) and planar flow casting (PFC) are very similar rapid quenching techniques that involve the process of directing a nozzle feeding an alloy melt to a chilled moving surface. The distance between the nozzle and substrate is the main difference between MS and PFC. A cartoon of the two processes is diagrammed in Fig. 3.1. As can be seen from the figure, the nozzle is much closer to the cooled surface or substrate than in MS. Contact between the melt and highly thermal conducting surface
ensures ultra-fast cooling rates on the order of $10^5$-$10^8$ K/s. In general, PFC can produce ribbons of varying widths ranging from 0.5-200 mm wide. In both cases, ribbons produced are 20-40 μm thick and can be made continuous for over 100 m.

The (Fe$_{65}$Co$_{35}$)$_{83.5-x}$B$_{13}$Nb$_x$Si$_2$Cu$_{1.5}$ ($x = 0$-$4$ at. %) ribbons researched in this dissertation were fabricated by melt-spinning at Carnegie Mellon University (CMU) in Pittsburgh, PA, USA. These are compositional variants of a commercialized alloy designated HTX-002.

The (Fe$_{50}$Ni$_{50}$)$_{81}$B$_{12}$Nb$_7$ and CoSiB/CoFeNbB ribbons were produced by planar flow casting by collaborators at Slovak Academy of Sciences, Bratislava, Slovakia. The bilayer ribbons in this study were fabricated by two-nozzle planar flow casting. The system for fabricating bilayer ribbons with two different compositions is identical to PFC with an additional nozzle directly adjacent to the first. More information about bilayer ribbon fabrication can be found in Ref. [2,3]. The (Fe$_{50}$Ni$_{50}$)$_{81}$B$_{12}$Nb$_7$ ribbon was coated with Co by RF magnetron sputtering.

3.1.2. Melt Extraction

The technique used to prepare the wires in this dissertation is melt extraction. In melt extraction, a sharp V-shaped wheel edge, rotating at high speed, makes contact with a molten puddle thereby extracting and cooling a continuous wire. A diagram and photo of the apparatus is shown in Fig. 3.1 (a,b). During melt extraction, the solidification rate is one of the highest among rapid quenching techniques. It can produce long, continuous wires as seen in Fig. 3.2 (c). A review of the melt extraction technique can be found in Ref. [4].
All of the \((\text{Co}_{94}\text{Fe}_{6})_{72.5}\text{Si}_{12.25}\text{B}_{14.25}\text{X}_{y}\) \((\text{x} = \text{Nb, Zr and} \ y = 0-3 \text{ at. %})\) wires researched in Chapters 6 and 7 of this dissertation were manufactured by our collaborators at Harbin Institute of Technology, China.

3.2. Structural Characterization

3.2.1. X-ray Diffraction

X-ray diffraction (XRD) is a non-destructive characterization technique used to probe periodic atomic structures of a sample. From an XRD diffractogram, or pattern, structural information such as the crystal structure, degree of crystallinity, and phase of the material can be inferred. A Bruker AXS D8 Focus Diffractometer operating at characteristic wavelength of Cu Kα \((\lambda = 1.54056 \ \text{Å})\) was used to perform the XRD measurements in this work. Figure 3.3 (a) diagrams the diffractometer as operated in locked-coupled mode. In this mode, the source is stationary, and the sample and detector move in tandem to scan the desired 2θ range (typically 20°-80°) such that the incident angle \(\theta\) is always equal to the half of the diffracted angle, 2θ. This is also referred to as a symmetric scan. In Fig. 3.1 (a), θ represents the
incident angle of the x-ray beam, ω is the angle between the sample and the incident beam, and 2θ is defined as the diffracted angle.

Bragg’s Law is a model of the interference patterns of x-rays scattered by crystals. Bragg reflections, or observed intensity peaks of scattered x-rays, occur in an XRD scan when the following two conditions are true: (1) the incident angle of the x-rays was equal to the scattering angle and (2) the path length difference of the x-rays was integer multiples of their wavelength. These two conditions form a simple equation relating an integer multiple of the wavelength, nλ, and the angle of the scattered x-ray, θ, to the spacing between the planes of a periodic lattice, d by:

\[ n\lambda = 2d\sin(\theta) \] (3.1)

When Eq. 3.1 is satisfied, a diffraction pattern, or Bragg reflections, are observed. However, if the sample is amorphous, there is no long-range or periodic atomic order. As a consequence, an XRD pattern of an amorphous material should yield no pattern at all. However, as mentioned in Ch. 2.1.1., there exists some short range order in amorphous materials on the atomic length scale. In fact, XRD of an amorphous
sample does reveal a wide peak near the $2\theta$ position of the stable crystalline phase. Figure 3.3 (b) demonstrates XRD patterns for an amorphous (Fe$_{50}$Ni$_{50}$)$_{81}$B$_{12}$Nb$_7$ ribbon as quenched and after two different annealing treatments. The appearance of sharp peaks indicates crystallization.

### 3.2.2. Scanning and Transmission Electron Microscopy

Diffraction limits of visible light restrict the resolution of optical microscopy to a few hundred nanometers. This observation was discovered by Ernst Abbe in 1873. The wavelength, $\lambda$, of light travelling in a medium with refractive index, $n$, and converging to a point with half-angle $\theta$ will form a spot size with radius, $r$, no smaller than [5]:

$$r = \frac{\lambda}{2n\sin(\theta)}. \quad (3.2)$$

This relationship is known as the Abbe diffraction limit. For example, using 635 nm red light and a numerical aperture ($n\sin\theta$) of 1, the Abbe diffraction limit is roughly $\lambda/2$ or about 0.3 $\mu$m (317 nm).

To overcome this limitation so that nanometer scale microscopy is possible, deBroglie matter waves (electrons) can be used instead of light waves (i.e. photons). This type of microscopy is called electron microscopy. For example, by accelerating an electron with 10 keV of energy, its (deBroglie) wavelength, $\lambda$, is only

$$\lambda = \frac{h}{p} = 0.01 \text{ nm}, \quad (3.3)$$

where $h$ is Planck’s constant and $p$ is the momentum of the traveling electron. Therefore, high resolution images can be achieved using an electron microscope such as a scanning electron microscope (SEM) or transmission electron microscope (TEM). Both microscope systems utilize a concentrated electron beam produced from a source located at the top of a series of electromagnetic lenses. Analogous to optical lenses, these electromagnetic lenses finely tune parameters of the electron beam before it makes contact with the sample under investigation. The specimen under investigation should be able to withstand vacuum conditions and high energy electron bombardment. All metallic alloys studied in this dissertation met such requirements.
Between the two techniques, SEM has a lower resolution. Under optimal conditions, 1-10 nm features can be resolved. The principle of image formation by a SEM is based on two phenomena: the elastic scattering of the electron beam reflected from the sample, called back-scattered electrons, and the emission of secondary electrons from the sample surface. The back-scattered electrons come from deeper within the sample surface, therefore these electrons are primarily used to illustrate contrast in the microscopy image. Secondary electrons emitted from near the sample surface are valuable for providing highly resolved morphology and topography of the sample surface.

The generation of characteristic X-rays is another consequence of high energy electron beam bombardment. Measurement of the number and energy of these photons can provide element-specific information about the sample under investigation. This analytical technique which normally accompanies SEM observation is called energy dispersive X-ray spectroscopy (EDS or EDX). Characteristic X-rays are emitted due to the inelastic collisions between the electron beam and electrons inside discrete orbitals of an atom. When an electron from the ground state of an inner shell is excited to a higher orbital, an electron hole is left behind. An electron from a higher energy shell fills the electron hole and as a result an X-ray photon of specific energy (equal to the difference in energy between the outer and inner shell) is emitted. Correlating characteristic X-ray energies to the theoretical energy difference allows identification and quantification of elements within the sample.

In TEM, the transmitted intensity of an electron beam through the sample is the principle behind image construction. The electron beam is focused onto a sample causing an enlarged image to appear on a fluorescent screen or captured by a charge-coupled device (CCD) camera. For TEM to be successful, the sample must be thinned to at most 100 nm. The TEM samples were thinned using a Gatan 691 ion beam thinner for 3–5 h at a voltage of 3.5 kV until the sample thickness was reduced to a few nm. Two ion beams, an upper and a lower beam, are aligned with a tilt angle of 7° and 8°, respectively. More details of this procedure can be found in Ref. [6].

For more information and reading about electron microscopy, please see Ref. [7].
3.2.3. Atomic Force Microscopy

Atomic force microscopy (AFM) is a characterization technique with the ability to quantify interatomic forces as small as $10^{-18}$ N and provide detailed topographical images with high scale resolution. Developed in 1986 [8], AFM was shown [9] to produce three dimensional images a vertical resolution of 0.1 nm and lateral resolution of 20-30 nm. The basic working principle of AFM is centered around perturbation of a vibrating cantilever at or near resonance as pictured in Fig. 3.4. The cantilever is comprised of an atomically sharp-tipped probe mounted on a piezoelectric transducer. As the tip of the cantilever is brought close to a sample, interatomic forces such as Van der Waals or Coulomb forces disturb the amplitude and frequency of the cantilever’s vibration. A heterodyned laser interferometer is responsible for measuring the amplitude of the vibration. Image contrast is given by a surface mapping either the amplitude, resonance frequency, or phase change of the vibrating cantilever.

3.2.4. Magnetic Force Microscopy

Magnetic force microscopy (MFM) [10] operates on the same principle as AFM. When a magnetic probe is brought close to a sample the stray magnetic fields emanating from the surface are responsible for cantilever perturbation. The direction of the remnant magnetization of the probe tip will determine which component of the stray field is measured. For example, MFM probes are typically constructed of AFM probes sputter coated with CoCr. Due to the sharp point at the end of the probe and thickness of the film, the magnetic anisotropy of the CoCr sputter coating ensures a remnant magnetization that can be well approximated to be along the $z$-direction, as seen in Fig. 3.4. Therefore, MFM images produced in this way will image surface stray magnetic fields along the +/- $z$-direction.
The A/MFM images and data presented in this dissertation were taken by collaborators at the Harbin Institute of Technology (HIT), China.

3.3. Quasi-static Magnetic Characterization

3.3.1. Vibrating Sample Magnetometry

The working principle of a vibrating sample magnetometer (VSM) is based on Faraday’s law of induction. Faraday’s law states that a voltage can be induced in a pick-up coil if there is a changing magnetic flux within the coil. Thus, a vibrating magnetic sample placed between the pick-up coils is responsible for any induced voltage in the coils. In this manner, a magnetic sample is moved sinusoidally in and out of the sensing coil region at a known frequency, which produces a constant amplitude, time-dependent sinusoidal voltage in the pick-up coils. The amplitude and phase of the induced voltage is then measured by lock-in (or phase sensitive) detection and a previously calibrated coupling constant is used to quantify the magnetic moment of the sample under investigation in units of $emu$.

The VSM measurements in this work were conducted by Physical Property Measurement System (PPMS) from Quantum Design at USF and HIT.
3.3.2. Magneto-optical Kerr Effect

A magnetometer based on the magneto-optical Kerr effect (MOKE) measures the change in polarization state of light upon reflection from a magnetic surface. The change in polarization state by rotation of the plane of polarization or induced ellipticity of polarized light is assumed to be proportional to the magnetization through the magneto-optic coupling constant, $Q$. Details about the quantum mechanical/microscopic origin of the Kerr effect can be found in Ref. [11,12].

MOKE is generally introduced with three geometries that categorize the Kerr effect: polar, longitudinal, and transverse. They can each be visualized in Figure 3.5 (a)-(c), respectively. The orientation of the magnetization vector, $M$, with respect to the surface of the sample and to the optical plane of incidence defines whether rotation of the polarization and/or an induced orthogonal component occur upon reflection.

![Figure 3.5 A cartoon diagram of the Kerr effect geometries: (a) polar geometry (b) longitudinal geometry, and (c) transverse geometry.](image)

The geometrical characterization of MOKE can be misleading as it is important to note that for a sample with an unknown direction of $M$, a combination of these three effects can exist in a measurement. For example, Ref. [13] derived the reflection coefficients of MOKE for a typical measurement scheme consisting of a light source, two polarizers, and a photodetector as seen in Fig 3.6. This scheme is also used in the homemade MOKE setup constructed by the author of this dissertation. The light source is a linearly polarized diode laser (5 mW, 655 nm) with polarization in the $s$ or $p$ direction, referring to the
direction perpendicular or parallel to the plane of incidence, respectively. The polarizers are set in a nearly crossed arrangement. The reflection coefficient $r_{ps}$ then represents the induced $p$ component upon reflection of $s$-polarized light. The matrix element of the combined MOKE reflection coefficients is given for the detection of the induced $s$ component with incident $p$-polarized light:

$$
\vec{r}_{sp} = -\vec{r}_{ps} = \frac{i\mu_0\mu N \cos \theta_1 (m_y \sin \theta_2 + m_z \cos \theta_2) Q}{(\mu_0 N \cos \theta_1 + \mu \cos \theta_2)(\mu \cos \theta_1 + \mu_0 N \cos \theta_2) \cos \theta_2} \quad (3.4)
$$

where $i$ is the imaginary unit, $\mu_0$ and $\mu$ are the permeability of free space and of the magnetic material, respectively, $N$ is the index of refraction of the magnetic material, $\theta_1$ is the angle of incidence and $\theta_2$ is the angle of refraction in the magnetic medium, $m_y$ and $m_z$ represent the normalized magnetization vector in the $y$- and $z$- direction, respectively, and $Q$ is the magneto-optic coupling constant.

![A photo of the homemade MOKE apparatus. The top left inset shows the non-specular reflection from the radius of curvature of a microwire sample. The top right inset shows the vector components of the magnetization. The optical components of the homemade Kerr effect setup: LD-laser diode, P1-polarizer, S-sample, L-lens, P2-polarizer, PD-photodetector.](image)

The main feature of this large equation is the coexistence of two magnetization directions, one in the plane of the magnetic sample and one out of plane, in the induced orthogonal component to the incident polarization state. Therefore, in this measurement scheme both components of the magnetization
may be detected. This aspect as it pertains to amorphous ribbons and sputtered coatings on ribbons is discussed in detail in Ch. 5.

A planar sample, such as a ribbon or thin film, provides a mostly specular reflection of the light and can enter the second polarizer and photodetector unassisted. However, when measuring MOKE in a microwire sample with diameter less than the spot size of the laser, one must account for the diffuse or non-specular reflection with a collimating lens. This reduces the overall light intensity somewhat but it is still detectable.

### 3.4. RF Magnetoimpedance Effect

#### 3.4.1. Maxwell’s Equations and the Landau-Lifshitz-Gilbert Equation of Motion

The electromagnetic framework [14,15] guiding the interpretation of the dc magnetic field dependence of the RF impedance of a ferromagnetic conductor is presented. The macroscopic formalism of classical electrodynamics in continuous media is used since the penetration depth of the RF field and domain width of the soft ferromagnetic materials is much larger than atomic length scales. At the same time, there are no displacement currents ($D$) resulting from free charges ($\rho_f$) in a ferromagnetic conductor, so Gauss’ law ($\nabla \cdot D = \rho_f$) in Maxwell’s equations in matter is not used. There are two other material relationships relating to a ferromagnetic conductor that can be inserted into the remainder of Maxwell’s equations. The first is Ohm’s law, $J = \sigma E$ or $E = \rho J$, and the second is the relationship between magnetic flux ($B$) and magnetization ($M$) and external field ($H$), $B = \mu_0 (H + M)$. The three remaining Maxwell’s equations along with the substitutions mentioned above give:

\[
\nabla \times \mathbf{H} = J \quad (3.5)
\]

\[
\nabla \times \mathbf{J} = -\mu_0 \sigma (\dot{\mathbf{H}} + \dot{\mathbf{M}}) \quad (3.6)
\]

\[
\nabla \cdot (\mathbf{H} + \mathbf{M}) = 0. \quad (3.7)
\]

By taking the curl of Eq. 3.5 and substituting $\nabla \times \mathbf{J}$ and $\nabla \cdot \mathbf{H}$ for equations Eq. 3.6 and 3.7, Maxwell’s equations give:

\[
\nabla^2 \mathbf{H} - \nabla (\nabla \cdot \mathbf{H}) = \mu_0 \sigma (\dot{\mathbf{H}} + \dot{\mathbf{M}}). \quad (3.8)
\]
A rigorous approach to the RF magnetoimpedance framework requires the dynamic response of the magnetization to be solved simultaneously with the above equation. The Landau-Lifshitz equation of motion

$$\dot{M} = \gamma M \times H_{\text{eff}} - \left( \frac{\alpha M_s}{M_s^2} \right) M \times \dot{M} \quad (3.9)$$

where $\gamma$ is the gyromagnetic ratio, $M_s$ is the saturation magnetization, $H_{\text{eff}}$ is the effective field and $\alpha$ is the Gilbert damping parameter, describes the dynamic response of the magnetization to the exciting field and other external fields present. The effective field, $H_{\text{eff}}$, is calculated from minimization of the free energy of the system and includes all the macro- and microscopic energy contributions such as the Zeeman energy, magnetostatic energy, exchange energy, and anisotropy energy.

### 3.4.2. Impedance of a Magnetic Conductor

To relate the field configuration to the impedance, the geometry of the sample and measurement scheme must be identified. Consider a ferromagnetic conductor in a wire geometry and placed in a static magnetic field $H_z$ directed along the wire axis. The wires in this dissertation were $r \sim 40 \, \mu m$ in radius and $l = 1 \, cm$ long, so it can be assumed that the axial demagnetizing field is negligible in $H_{\text{eff}}$. A sinusoidal electric field, $e$, (i.e. current) is applied and enters a sample/microstrip line in a quasi-TEM mode. The microstrip line ensures that, to a good approximation, the propagation direction, $k$, of the electromagnetic field is along the axial direction and the electric ($e$) and magnetic ($h$) fields are mutually perpendicular along the radial and circumferential directions, respectively. The wavelength, $\lambda$, of the excitation frequency, $f$, should be at least 4 times the length of the sample to consider the electric field as constant over the length of the wire, e.g. $l \ll \lambda/4$.

The impedance of a TEM wave propagating in a cylindrical conductor can be defined in terms of the $e$ and $h$ fields, assuming the current density is independent of sample length:

$$Z = \frac{V_{ac}}{I_{ac}} = \frac{le_z(S)}{2\pi r h_{\phi}} = \frac{l}{2\pi r} Z_s \quad (3.10)$$
where \( V_{ac} \) is the ac voltage across the sample, \( e_z(S) \) is the sinusoidal electric field at the surface, \( I_{ac} = 2\pi rh_\phi \) is the current resulting from the sinusoidal magnetic field \( h_\phi \) and \( Z_s \) is the surface impedance of an electromagnetic wave in a cylindrical conductor:

\[
Z_s = k\rho \frac{J_0(kr)}{J_1(kr)}, \quad (3.11)
\]

where \( k = (1+i)\delta \) and \( J_0, J_1 \) are the zero and first order Bessel functions, respectively. The skin depth, \( \delta \), is

\[
\delta = \sqrt{\frac{\rho}{\pi \mu_\phi f}}, \quad (3.12)
\]

where \( \rho \) is the resistivity, \( \mu_\phi \) is the circumferential permeability, and \( f \) is the excitation frequency. The sensitivity of the skin depth to the circumferential (or transverse, for planar geometry) permeability is the primary actor of the giant magnetoimpedance effect. For magnetic materials with large permeability, such as amorphous soft wires and ribbons, the skin depth can change significantly, with dc magnetic field.

### 3.4.3. Wave Guides and Transmission Line Theory

The impedance of a conductor can be measured in a straightforward manner using current-voltage techniques and understood through circuit theory at frequencies below 10 MHz. However, at higher frequencies, traditional circuit architecture fails because current and voltage are no longer well defined quantities over the length of the circuit. In the case of excitation frequencies in the MHz, GHz and beyond, current and voltage are treated as propagating electromagnetic waves. Reliable transmission of high frequency electromagnetic waves requires a waveguide, such as a transmission line, to direct their propagation from a source to a destination or load with minimal loss.

Transmission lines are waveguides that can support a special mode of wave propagation called transverse electromagnetic or TEM. In this propagation mode, the components of the electric and magnetic field are mutually perpendicular and perpendicular to the propagation direction. The field configuration of two ubiquitous transmission lines, the coaxial and microstrip line, are visualized in Fig. 3.7, respectively. Unlike the coaxial line, which supports a pure TEM mode, the asymmetric microstrip line does not actually support a pure-TEM mode and instead is referred to as quasi-TEM. The mode of
wave propagation in a waveguide is determined by solving Maxwell’s equations with appropriate boundary conditions for the components of the electric field, $E$, and magnetic field, $B$. Unlike a single hollow conductor with $E = 0$ inside, the addition of a center conductor in a coaxial transmission line permits a wave propagation mode with $E_z = 0$ and $B_z = 0$. With these parameters, the solutions to Maxwell’s equations reduce to the classic electro/magnetostatic solutions of an electric and magnetic field from an infinitely long line charge and infinitely long straight current, respectively. Examples of this procedure are given in several undergraduate texts [16–18].

![Figure 3.7 A drawing of the field lines in (a) a coaxial transmission line and (b) microstrip transmission line.](image)

A transmission line is characterized by its intrinsic or characteristic impedance, $Z_C$. The characteristic impedance represents the impedance to the incident electromagnetic wave in the transmission line if it were of infinite length. Consider the transmission line segment in Fig. 3.8. Let a voltage and current wave of known frequency, $\omega$ or wavelength, $\lambda$, and amplitude be introduced to the center conductor.

It can be shown starting from either Kirchhoff’s circuit analysis or Maxwell’s field analysis that the voltage $V(z)$ and current $I(z)$ along any two-conductor transmission line obeys respective linear homogenous differential equations arising from the wave equation:

39
\[
\frac{d^2V(z)}{dz^2} - \gamma^2 V(z) = 0 \quad (3.13a)
\]
\[
\frac{d^2I(z)}{dz^2} - \gamma^2 I(z) = 0 \quad (3.13b)
\]

where

\[
\gamma = \alpha + j\beta \quad (3.14)
\]

is the complex wave propagation constant composed of a real component \(\alpha\) (attenuation) and imaginary component \(\beta = 2\pi/\lambda\) (phase shift). The complex propagation constant is also related to the following familiar circuit parameters:

\[
\gamma = \sqrt{(R + j\omega L)(G + j\omega C)}, \quad (3.15)
\]

where \(R\) is the resistance of the electromagnetic wave due to the finite conductivity of the two conductors in the transmission line; \(\Omega\) per unit length, \(L\) is the total self-inductance of the two conductors; \(H\) per unit length, \(C\) is the shunt capacitance due to the proximity of the two conductors; \(F\) per unit length, and \(G\) is the dielectric loss due to the material between the two conductors.

The respective solutions for the voltage and current waves are the superposition of two waves travelling along opposite directions:
\[ V(z) = V_0^+ e^{-\gamma z} + V_0^- e^{\gamma z} \]  
\[ I(z) = I_0^+ e^{-\gamma z} + I_0^- e^{\gamma z}, \]

where \( V_0^+/\) and \( I_0^+/\) represent the amplitude of the voltage and current wave travelling in the positive and negative \( z \) directions, respectively. From this solution and its derivatives with respect to \( z \), the characteristic impedance of the general two-conductor transmission line, \( Z_c \), can be derived as (the full derivation can be found in Refs. [16,17,19]):

\[ Z_c = R + j\omega L = \sqrt{\frac{R + j\omega L}{G + j\omega C}}. \]  

3.4.4. Working Principle and Calibration of a Scalar Network Analyzer

The input impedance, \( Z_{in} \), is the actual impedance measured by the network analyzer. As the name suggests, the \( Z_{in} \) can vary depending on where along the transmission line it is measured. Generally, the material under test (MUT) is incorporated into a waveguide (transmission line), collectively called the test cell, which is itself connected to another transmission line some distance away from the analyzer. Therefore, the sinusoidal electromagnetic wave sent out by the analyzer can meet with several interfaces, or boundary conditions, before entering the test cell. Ideally, an experimentalist would want the input impedance to be measured just before the test cell. Achieving this requires careful calibration of the analyzer.

![Figure 3.9](image)

Figure 3.9 A terminated transmission line with load impedance \( Z_L \) and the location the input impedance is measured.

Before considering the loss of power and other unwanted effects of multiple transmission line segments, the working principle of the HP 4191A scalar network analyzer is outlined with a single transmission line segment of length \( l \), terminated with a load of impedance \( Z_L \) at \( z = 0 \). The HP4191A
sends an incident electromagnetic wave of the form $V_0^+ e^{j\gamma z}$ with known amplitude. The ratio of voltage to current in the line ($z > 0$) is $Z_C$ but at $z = 0$ the ratio must be $Z_L$. Using the total voltage and total current from Eqs. 3.16 and 3.17,

$$Z_L = \frac{V(z = 0)}{I(z = 0)} = \frac{V_0^+ + V_0^-}{V_0^+ - V_0^-} Z_C. \quad (3.19)$$

By rearranging Eq. 3.19 to solve for $V_0^-$, one obtains:

$$V_0^- = \frac{Z_L - Z_C}{Z_L + Z_C} V_0^+. \quad (3.20)$$

The scalar network analyzer takes the ratio of the reflected wave, $V_0^-$, to the incident wave, $V_0^+$, in what is called the voltage reflection coefficient:

$$\Gamma(z = 0) = \frac{V_0^-}{V_0^+} = \frac{Z_L - Z_C}{Z_L + Z_C}. \quad (3.21)$$

With this identity, the total voltage and current waves on the line can be given as:

$$V(z) = V_0^+ \left( e^{-j\gamma z} + \Gamma e^{j\gamma z} \right) \quad (3.22)$$

$$I(z) = \frac{V_0^+}{Z_C} \left( e^{-j\gamma z} - \Gamma e^{j\gamma z} \right). \quad (3.23)$$

It is apparent by the positive argument in the exponential term that the voltage and current are oscillatory as a function of position. Therefore, the reflection coefficient is also a function of position. The reflection coefficient can be generalized to any point $z$ along the transmission line by:

$$\Gamma(z) = \frac{V_0^- e^{-j\gamma z}}{V_0^+ e^{j\gamma z}} = \Gamma(z = 0) e^{-2j\gamma z}. \quad (3.24)$$

This relationship and its many variations are used to transform the effect of a load mismatch ($Z_C \neq Z_L$) to anywhere down the segment of transmission line. The input impedance, $Z_{in}$, as seen looking toward the load ($z = -l$) can now be defined:

$$Z_{in} = \frac{V(z = -l)}{I(z = -l)} = 1 + \frac{\Gamma e^{-2j\gamma l}}{1 - \Gamma e^{-2j\gamma l} Z_C}. \quad (3.25)$$

Systematic errors in the impedance measurement are measured and accounted for by calibration of the instrument using the short, open, and 50 $\Omega$ standards. The calibration takes place at the end of the
coaxial transmission line, just before it connects the waveguide to the impedance analyzer, denoted as $z = l_1$ in Fig. 3.10.

Figure 3.10 A schematic of the waveguide used in impedance measurements. The sample is placed as the center conductor of an airline. The signal from the impedance analyzer passes through at least two transmission lines before it encounters the sample.

3.5. References


4. EFFECT OF JOULE ANNEALING ON MAGNETOIMPEDEANCE OF FECO-BASED RIBBONS WITH VARYING GLASS FORMER CONTENT

In this chapter, we present the results of a comparative study of the magnetoimpedance response of two annealed melt-spun ribbons with and without glass former Nb. The role of the glass former in the formation of the induced magnetic anisotropy of low current intensity Joule annealing is examined through the surface sensitive magneto-optical Kerr effect (MOKE) and magnetoimpedance effect. MOKE microscopy showed a longitudinal magnetic anisotropy and the ribbon with 4 at. % Nb glass former had a nearly transverse anisotropy. The transverse ac permeability inferred from magnetoimpedance measurements proved to be higher than the ribbon without glass former Nb. This established a correlation between the surface domain structure, induced anisotropy, and high frequency magnetoimpedance in the ribbons.

4.1. Introduction

The discovery [1] of a giant magneto-impedance (GMI) response in soft ferromagnetic amorphous ribbons and wires has spurred much study over the past 20 years due to exciting opportunities for its use as sensitive magnetic field sensors for a variety of applications [2]. The first groups to consider GMI for technological application were chiefly concerned with sensitive changes in electrical impedance at excitation frequencies less than 10 MHz [3,4]. They described the impedance change as the classical consequence of the skin effect, where the distribution of an ac current of frequency, \( f \), in a soft magnetic conductor of conductivity, \( \sigma \), flows near the surface at a depth \( \delta = (\pi \sigma f \mu_r)^{-1/2} \). The large and sensitive transverse magnetic permeability, \( \mu_r \), of soft ferromagnetic conductors is the key to unlocking giant

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1 Portions of this chapter have been previously published in a peer-reviewed journal article (Eggers et al., Journal of Alloys and Compounds 682, 799, 2016) and have been reproduced with permission from the respective publishers.
changes in impedance. Since its discovery, magneto-impedance (MI) has become a common tool used to probe the ac transverse permeability of many magnetic materials [5–7].

FeCo alloys have previously been studied for their use in power conversion applications which utilize their excellent bulk magnetic properties of high saturation magnetization and magnetic softness [8,9]. The high permeability of these alloys also makes them interesting from the standpoint of high-frequency MI, where small magnetic fields can induce large variations in transverse permeability, thus large changes in impedance through the skin depth [10]. At excitation frequencies greater than 100 MHz, the skin depth is small; $\delta \sim 4 \mu m$ at 100 MHz using bulk resistivity and permeability values found in [11]. Therefore, considering the magnetic behavior of the surface is essential for interpreting the MI response at high frequency.

Melt-spun Fe-rich FeCo ribbons, such as those in this study, are amorphous and have quenched-in stresses that are a dominant source of their magnetic anisotropy. The as-quenched domain configuration is generally inhomogeneous over the ribbon surface and thickness, making the large distribution of magnetic anisotropy in ribbons unfavorable for high-frequency sensor applications. Thermomagnetic treatments such as transverse magnetic field annealing (TMF) can nucleate nanocrystalline phases within the amorphous matrix, providing a source for well-defined magnetocrystalline anisotropy in the bulk ribbon [11,12]. Previous work using TMF has found that the induced anisotropy of the ribbon can be controlled through nanocrystallization by adding Nb as a growth inhibitor, which suppresses crystallite size and increases bulk permeability values [13,14]. While field crystallization succeeds at reducing the random anisotropy distribution caused by internal stresses trapped by rapid solidification, bulk crystallization of FeCo-based ribbons causes embrittlement, which makes the ribbon difficult to realize in applications [8]. Besides TMF annealing, Joule annealing (JA) by application of a dc current also has the benefit of an applied magnetic field during the thermal treatment. With low current intensities and long annealing times, it is possible to relax the frozen-in stresses via interatomic diffusion while staying below the
crystallization temperature. The self-induced magnetic field has the potential to act as the driving force for interatomic diffusion, where it can interact locally with the magnetization of a microscopic region (a domain or grain or crystallite) [15]. Upon cooling, however, the current is shut off and the magnetic field disappears. Thus, the magnetic structure set up by the guided diffusion could deteriorate.

In this work, the surface domain structure, surface anisotropy and high frequency magneto-transport of Fe-rich FeCo ribbons with (4 at. %) and without (0 at. %) growth inhibitor Nb are examined. The as-cast ribbons were Joule annealed at low current amplitudes to see how the growth inhibitor influences the surface anisotropy when bulk crystallization is intentionally avoided. Surface sensitive techniques like magneto-optical Kerr effect and high-frequency magneto-impedance were employed to determine the effect of the Nb addition on the surface magnetic properties of the ribbons before and after annealing. The results obtained provide important understandings of the role of growth inhibitor Nb in Fe-rich FeCo ribbons in regard to their prospective use in high frequency MI-based sensors.

4.2. Materials and Methods

Amorphous ribbons of composition (Fe_{65}Co_{35})_{83.5-x}B_{13}Nb_xS_{13}Cu_{1.5} (x = 0 and 4) (denoted throughout this work as Nb0 and Nb4, respectively) were prepared by melt-spinning [14]. The thickness of the ribbons was 30 µm and they were 2 mm wide. The ribbons were cast in very long strands from which 4 cm sections were cut and subject to a dc Joule heating treatment of 500 mA (1.25 x 10^7 A/m^2) for

![Figure 4.1 X-ray diffraction of the as-cast and annealed ribbons showing no major crystallization.](image)
3 h. The steady state temperature measured by thermocouple on the surface of the ribbons reached 80 °C. Due to high radiative losses at the ribbon surface, the annealing temperature is expected to be higher than 80 °C, but still much less than the crystallization temperature of 380-440 °C [11].

X-ray diffraction (XRD) was performed on the as-cast and annealed ribbons. The XRD scans (Fig. 4.1) showed no evidence of bulk crystalline formation. Bulk magnetic properties were measured by vibrating sample magnetometry (VSM) with a Helmholtz field applied along the ribbon length. MOKE microscopy was conducted to image the domain structure on the surface of the ribbons. Longitudinal magneto-optical Kerr effect (L-MOKE) hysteresis loops were taken using a homemade setup with a 5 mW (655 nm) laser source with a spot size ~1.5 × 1.5 mm²; about nine times larger than the field of view of the microscope.

Magneto-impedance was measured as a function of applied field ($H_{\text{max}}=300$ Oe) along the length of the ribbon at high frequency (100-1000 MHz) using an HP 4191A impedance analyzer. The HP 4191A determines the complex reflection coefficient, $\Gamma$, of a high frequency signal sent down a terminated transmission line. An airline [16] made of a 2 cm section of ribbon suspended over a Cu ground plane served as the transmission line, which was terminated with a 50 Ω standard that matches the input impedance of the analyzer. The complex reflection coefficient at the beginning of the ribbon airline was measured and converted to complex impedance ($Z$) by

$$Z = 50 \frac{1 - \Gamma}{1 + \Gamma} = R + jX, \quad (4.1)$$

where $R$ is the resistance, $X$ is the reactance, and $j$ is the imaginary unit. In this work, the magneto-impedance ratio is defined as

$$\frac{\Delta Z}{Z}(\%) = \frac{Z(H) - Z(H = 0)}{Z(H = 0)} \times 100\%, \quad (4.2)$$
where $Z(H)$ is the impedance (or resistance, reactance) at field $H$. The impedance ratio is normalized by $Z(H=0)$.

Inductance formalism is generally used to connect complex impedance measurements directly with ac magnetic phenomena [17]. The transformation that takes place between $Z$ and complex inductance, $L$, is simple but leads to a crossover between the real and imaginary components. Therefore the real part of $Z$ is proportional to the imaginary part of the inductance, and vice versa. The complex inductance, in turn, is directly proportional to the complex permeability by a scalar geometrical factor. Thus, $R$ is related to the imaginary component and $X$ to the real component of the complex permeability. Furthermore, the nature of the ac magnetization process can be interpreted by the examination of the real and imaginary parts of the permeability, where, at frequencies greater than 100 MHz, the real part represents reversible rotation processes (imaginary part of the impedance) and the imaginary part represents dissipative processes such as the rotation of pinned domain spins.

4.3. Interpretation of Surface Domain Structure and Static Magnetic Properties

Several MOKE microscopy images were made on the air side of as-cast Nb0 and Nb4 ribbons along the ribbon length. Selected MOKE images are presented in Fig. 4.2 (a,c). For both compositions, the inhomogeneous distribution of quenched-in stresses from fabrication gives rise to a complicated domain structure. The Nb4 ribbon sample in particular had layered domain patterns where tightly-wound regions of high anisotropy overlay wide planar domains. These fingerprint-like domain patterns are evidence of perpendicular magnetic anisotropy with respect to the ribbon surface [18]. The rounded L-MOKE hysteresis loops of the as-cast ribbons (dashed lines in Fig. 4.2 (e,f)) also reflect a large distribution of in-plane anisotropy near the surface.

The surface domain structure changed dramatically with the 3 h Joule annealing (JA) treatment. The Nb0 and Nb4 ribbon, Fig. 4.2 (a,c), both developed wide planar domains as a result. The absence of the
‘fingerprint’-type domain patterns indicates that the JA treatment reduced the layered stresses quenched in during melt spinning. Interestingly, the Nb0 ribbon sample developed stripe-like domains along the ribbon axis, while the Nb4 sample developed an anisotropy ~30° from the transverse axis. The hysteresis loops, measured by a separate MOKE setup, show strikingly different switching behavior at the surface as a result of the 3 h JA treatment. The annealed Nb0 ribbon sample developed a square hysteresis loop clearly indicating the longitudinal easy axis found in the microscopy images. The hysteresis loop of the annealed Nb4 ribbon shows a hard axis magnetic behavior, confirming the microscopy images showing the domain easy axis roughly ~60° away from the longitudinal measuring axis.

Bulk magnetometry from VSM (Fig. 4.3 (a)) shows both Nb0 and Nb4 compositions with nearly equal and vanishing coercivities and characteristic soft ferromagnetic behavior. The saturation magnetization ($M_S$) is lower for the Nb4 ribbon, which can negatively impact the MI response, especially at lower frequencies where the skin depth reaches deep into the bulk. From Fig. 4.3 (b) it can be seen that after a 3 h and 500 mA JA treatment, the bulk coercivity of the Nb0 composition increased from $H_c = 0.22$ Oe to $H_c = 0.65$ Oe and the Nb4 ribbon increased slightly from $H_c = 0.25$ Oe to $H_c = 0.41$ Oe. Overall, there is little
indication of the bulk magnetic properties being affected by the JA technique. This could imply that the bulk of the ribbon did not reach temperatures high enough to begin bulk crystallization.

4.4. Influence of Joule Annealing on Magnetoimpedance

High-frequency MI was examined to probe the field dependence of the ac rotational (transverse) permeability near the surface of the ribbons. The real and imaginary components of the complex impedance were measured as a function of applied dc field at frequencies ranging from 100 to 1000 MHz. At these excitation frequencies, the ac magnetic field penetrates about 1-2 orders of magnitude deeper than the light probe in MOKE experiments and covers a much larger surface area. The field dependence

![Figure 4.3 (a) M-H loops from vibrating sample magnetometry at room temperature on 6 x 1mm² section of ribbon before and after 3h JA treatment. The magnetic field was applied along the ribbon axis. (b) Zoom in of the small coercivity of all samples.](image-url)
of the MI ratios (Fig. 4.4) displays a typical high-frequency double-peak behavior; an assurance that there is negligible contribution to the ac permeability from domain wall motion. Thus, the increase in MI ratio from $H_{DC} \sim 0$ is attributed to the decrease in skin depth from a rise in ac rotational permeability transverse to the current direction (i.e. along the ac field, $h_{ac}$, direction). The increase in ac rotational permeability with $H_{DC}$ can be understood by considering the competition between $H_{DC}$ and the anisotropy field, $H_k$, of a single domain with uniaxial anisotropy. Increasing $H_{DC}$ can compensate the anisotropy field, which makes the ac rotational magnetization process is easier, thus increasing the rotational permeability until it reaches a maximum at a field close to $H_k$. As the $H_{DC}$ exceeds $H_k$, more domain magnetizations couple to $H_{DC}$, thereby lowering the ac rotational permeability causing the decrease in the MI ratios.

The magneto-resistance, magneto-reactance, and magneto-impedance ratios ($\Delta R/R$, $\Delta X/X$, & $\Delta Z/Z$) at 100 MHz, 400 MHz, and 1000 MHz of the as-cast ribbons are presented in Fig. 4.4 (a-i) (dashed lines).

![Figure 4.4 The magnetoresistance ($\Delta R/R$), magnetoreactance ($\Delta X/X$), and magnetoimpedance ($\Delta Z/Z$) ratios measured at $f = 100$ MHz (a-c), 400 MHz (d-f), and 1000 MHz (g-i). As quenched ribbons are dashed lines and solid lines are after a 3 h JA treatment.](image-url)
Examining the first column of Fig. 4.4, all the ratios of the as-cast Nb0 and Nb4 ribbons have similar field dependent behavior, e.g. similar $H_k$ values and anisotropy distributions, at the lowest measured frequency of 100 MHz. As the ac frequency is increased, the MI probes closer to the surface of the ribbon and a greater distinction between the different compositions of ribbon are apparent. At 400 MHz, second column of Fig. 4.4, the $\Delta R/R$ and $\Delta X/X$ ratios of the Nb4 ribbon begin to overtake those of the Nb0 ribbon, especially in the anisotropy field regime. At the highest measured frequency of 1000 MHz, third column, the similarities between the Nb0 and Nb4 ratios continue to diverge at $H_{DC}$ fields much lower than $H_k$.

The MI ratios at 100 MHz of each ribbon after 3 h annealing (Fig. 4.4 (a-c), solid lines) show that the JA protocol had an impact on the MI of both compositions of ribbon. The $\Delta R/R$ ratio of annealed Nb0 ribbon (black line) increases significantly from the as-cast state, while the $\Delta X/X$ ratio shows only a slight improvement. As compared to the Nb0 ribbon, the annealed Nb4 composition shows a more marked improvement in both ratios as a result of the JA treatment, especially in $\Delta X/X$. Considering the connection between the reactance, $X$, and real part of the permeability via inductance formalism, the enhancement of $\Delta X/X$ by the JA treatment had a greater impact on the reversible ac permeability of the ribbons with the growth inhibitor Nb. This is connected to the domain structure depicted in MOKE images of the annealed ribbons in Fig. 4.2 (b,d), which shows the development of stripe-like domains at different orientations with respect to the transverse direction. The preferential direction of the surface anisotropy for the Nb4 ribbon is aligned much closer (~30 degrees) to the transverse direction, which supports reversible ac rotational permeability.

The maximum change in MI, $[\Delta Z/Z]_{\text{max}}$, of the field-dependent $\Delta Z/Z$ curves (Fig. 4.4) occurs when the transverse permeability $\mu_t(H_{DC})$ takes its highest value. The frequency dependence of $[\Delta Z/Z]_{\text{max}}$ is presented in Fig. 4.5 (a). The JA treatment increased $[\Delta Z/Z]_{\text{max}}$ of both ribbons over the entire test frequency regime as compared to their as-cast counterparts. In the higher frequency region, however, the
improved $[\Delta Z/Z]_{\text{max}}$ of the sample with growth inhibitor Nb persists at high frequencies where the values of $[\Delta Z/Z]_{\text{max}}$ of the ribbon without Nb approach the as-cast value. This also implies the JA had a greater impact on the ac transverse permeability of the ribbon with growth inhibitor Nb. The JA treatment also caused a shift of the $[\Delta Z/Z]_{\text{max}}$ peak to lower frequencies as compared to the as-cast state. A broad peak in $[\Delta Z/Z]_{\text{max}}$ can be seen near 200 and 400 MHz for the as-cast Nb0 and Nb4 ribbon, respectively, where upon annealing the peaks shift to < 100 MHz and ~200 MHz, respectively.

Another interesting feature of Fig. 4.5 (a) concerns a cross over that takes place between the $[\Delta Z/Z]_{\text{max}}$ of the Nb0 and Nb4 compositions, an indication that at lower frequencies Nb0 has higher MI ratios. Indeed, as the MI probe frequency is decreased, the skin depth undoubtedly samples a larger portion of the ribbon and thus bulk magnetic properties have a greater contribution to the MI. This is further supported by the larger bulk $M_S$ of the ribbon without the Nb growth inhibitor. Considering the consequence of the skin effect, as the frequency increases the bulk properties that once promoted MI at lower frequencies make less of an impact. Since it is clear from the near-transverse anisotropy of the annealed Nb4 ribbons that its $\mu_r$, hence $[\Delta Z/Z]_{\text{max}}$, is higher at larger excitation frequencies, it is possible

Figure 4.5 (a) Maximum change in $\Delta Z/Z$ as a function of frequency for the as-cast (open symbols) and annealed (closed symbols) ribbons. (b) The anisotropy field ($H_K$) as a function of frequency.

Another interesting feature of Fig. 4.5 (a) concerns a cross over that takes place between the $[\Delta Z/Z]_{\text{max}}$ of the Nb0 and Nb4 compositions, an indication that at lower frequencies Nb0 has higher MI ratios. Indeed, as the MI probe frequency is decreased, the skin depth undoubtedly samples a larger portion of the ribbon and thus bulk magnetic properties have a greater contribution to the MI. This is further supported by the larger bulk $M_S$ of the ribbon without the Nb growth inhibitor. Considering the consequence of the skin effect, as the frequency increases the bulk properties that once promoted MI at lower frequencies make less of an impact. Since it is clear from the near-transverse anisotropy of the annealed Nb4 ribbons that its $\mu_r$, hence $[\Delta Z/Z]_{\text{max}}$, is higher at larger excitation frequencies, it is possible
that crossover could represent the skin depth where the near transverse surface anisotropy of Nb4 outweighs the higher bulk $M_S$ of the Nb0 ribbon.

The corresponding field point of $[\Delta Z/Z]_{\text{max}}$, defined as $H_k$, is presented in Fig. 4.5 (b). The effect of annealing is obvious as the $H_k$ values are greatly reduced across the excitation frequency range. This is linked to the increase in $[\Delta ZZ]_{\text{max}}$ since $H_k$ is inversely proportional to $\mu_r$ when considering the simple case of reversible rotational magnetization process of a single domain with uniaxial anisotropy [19,20].

The $H_k$ values for the as-cast ribbons (open symbols) are similar at low frequencies but noticeably diverge from each other near 500 MHz. Interestingly, upon annealing, the $H_k$ values (closed symbols) of the two different ribbons have a similar behavior, however, now the divergence begins at a much lower frequency of $\sim$100 MHz.

4.5. Conclusions

The melt-spun Fe-rich FeCo alloy ribbons with and without crystallite growth inhibitor Nb were Joule annealed at low current intensity to avoid bulk crystallization. The effect of the Nb doping on the surface magnetic properties of the ribbons was investigated with MOKE and high-frequency MI. The surface of the Nb0 ribbon (0 at. % Nb) developed a longitudinal anisotropy as a result of the Joule annealing treatment, while the Nb4 ribbon (4 at. % Nb) developed an anisotropy 30 ° from the transverse direction. The $H_k$ of both ribbons decreased after annealing, indicating an increase in transverse ac permeability. The near transverse anisotropy at the surface of Nb4 is evident in MI measurements by a higher $[\Delta Z/Z]_{\text{max}}$ as compared to Nb0 at frequencies greater than 200 MHz. A good understanding of the correlation between the magnetic domain structure and MI in soft ferromagnetic thin films [21,22] and microwires [23] has provided useful guidance on tailoring their MI properties for high-performance magnetic sensors, and our study presented in this article also serves the same purpose.

4.6. References


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5. SURFACE MAGNETIC ANISOTROPY AND MAGNETOIMPEDANCE OF CO-COATED NIFE-BASED RIBBON

This chapter presents the results of a comparative study of the surface magnetization and GMI effect in an uncoated and 120 nm Co-coated \((\text{Fe}_{0.5}\text{Ni}_{0.5})_{81}\text{Nb}_{7}\text{B}_{12}\) nanocrystalline ribbon through MOKE and MI experiments. In full agreement with the MOKE results, MI measurements indicated an increase in anisotropy field in the excitation frequency range 100-1000 MHz in the Co-coated ribbons. Noticeably, the Co-coating improved the MI ratio by 15 % at fields near and below the anisotropy field. The large improvement of the low-field MI response by the coating encourages the use of magnetic coatings to improve MI-based sensors for technological applications. Our study also yields important insights into the effects of negative magnetostrictive coatings on the MI behavior in soft magnetic ribbons.

5.1. Introduction

Understanding the relationship between the surface magnetic properties, microstructure and giant magneto-impedance (GMI) effect in soft ferromagnetic ribbons is essential for the development of sensitive magnetic field sensors for a variety of applications \([1]\). While a large GMI effect, on the order of hundreds of percent, has been demonstrated optimized Fe-rich \([2]\) and Co-rich \([3,4]\) microwires at high frequency (a current review on the subject is given in \([5]\)), the GMI effect is generally low in the ribbon geometry. Since the platform shape of a ribbon or film is highly desirable to the application of GMI to biomagnetic \([6]\) or flexible stress \([7]\) sensors, there is still effort put toward research into the effects of post-processing techniques to increase the GMI effect in ribbons by way of annealing \([8]\) and coating \([9–14]\).

Some works have reported a significant enhancement of the GMI effect upon coating ribbons with other magnetic layers. For example, an increase in the GMI ratio at 2.6 MHz was observed when a...
nanocrystalline Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ (FINEMET) ribbon was coated with (130 – 500 nm) Ni$_{80}$Fe$_{20}$ film [10]. The magnetic exchange interaction and low stress between layers due to a lattice match between the Ni$_{80}$Fe$_{20}$ film and the Fe$_{73.5}$Cu$_1$Nb$_3$Si$_{13.5}$B$_9$ ribbon was suggested to promote the GMI enhancement. In another study conducted by Laurita et al. [15], the authors found that sputter deposition of a 50 nm Co film enhanced both the GMI ratio and sensitivity of a HITPERM ribbon at frequencies of 10 MHz and below. The enhancement was attributed to the reduction of stray fields and an improved magnetic flux path closure at the ribbon’s surface. At excitation frequencies below 10 MHz, the effective permeability change with magnetic field is governed by magnetization reorientation of the film/ribbon bulk, while at higher frequencies, the skin depth approaches its minimum value and more of the surface and interface of the film/ribbon system is sampled. A clear understanding of how a magnetic coating affects the effective permeability and the GMI response at high frequency ($f > 100$ MHz) of the ribbon is not well understood.

Since amorphous ribbons with a domain structure or anisotropy transverse to the current direction are excellent candidates for GMI based sensors due to high GMI ratios [16,17], it would follow that the magnetic coating should be capable of supporting a transverse anisotropy [14,15,18–21]. From a structure-magnetic property perspective, Co is chosen as the coating layer since it has a negative magnetostriction. It has been shown that isothermally annealed FeNi-based ribbons contract along their length [22], therefore could be a source of a stress-induced transverse anisotropy in the Co coating. Annealing these ribbons at 500 °C achieves uniform, nanosized crystalline grains and thus soft magnetic behavior beneficial to the GMI effect. In a nanocrystallized system, the local magnetocrystalline anisotropy of the nanograins embedded in the amorphous matrix is randomly averaged out by their exchange interaction resulting in a small net anisotropy [23].

5.2. Materials and Methods

In this work, we aim to investigate the impact of a 120 nm polycrystalline Co coating on two sides of an amorphous (Fe$_{50}$Ni$_{50}$)$_{81}$Nb$_7$B$_{12}$ ribbon, which was subsequently annealed along with a control ribbon to achieve a nanocrystalline morphology. Using magneto-optical Kerr effect to measure and image
the low field dc surface magnetization, the positive and negative effects of the Co coating layer with a transverse anisotropy on the magnetoimpedance of the ribbon are assessed. Amorphous ribbons of composition $(\text{Fe}_{50}\text{Ni}_{50})_{81}\text{Nb}_{7}\text{B}_{12}$ were prepared by planar flow casting with master alloys prepared from elements with purity better than 99.95% [26]. Both sides of a 4 cm section of as-quenched ribbon were coated with 120 nm of Co by RF magnetron sputter deposition. The coated ribbon, along with an uncoated control ribbon, was annealed for 1 h at 500°C under high vacuum in order to achieve a low coercive field and soft magnetic behavior [24]. X-ray diffraction (XRD) of the coated and uncoated ribbons was conducted using Cu Kα radiation. Longitudinal magneto-optical Kerr effect (L-MOKE) hysteresis loops were taken using a homemade setup with a 5 mW (635 nm) laser source. The applied magnetic field was oriented in two directions, along the length of the ribbon and perpendicular to the length of the ribbon. MOKE microscopy was conducted by Magneto-optical Kerr Microscope (EVICO Magnetics), also in the longitudinal geometry, to image the domain structure on the surface of the coated and uncoated ribbons with the magnetic field applied along the ribbon axis.

Magneto-impedance was measured as a function of applied field ($H_{\text{max}}=110$ Oe) along the length of the ribbon at high frequency (100-1000 MHz) using an HP 4191A impedance analyzer. The HP 4191A determines the complex reflection coefficient, $\Gamma$, of a high frequency signal sent down a terminated transmission line. An airline [24] made of a 2 cm section of ribbon suspended over a Cu ground plane served as the transmission line, which was terminated with a 50 $\Omega$ standard that matches the input impedance of the analyzer. The complex reflection coefficient at the beginning of the ribbon airline was measured and converted to complex impedance ($Z$) by

$$Z = 50 \frac{1 - \Gamma}{1 + \Gamma} = R + jX, \quad (5.1)$$

where $R$ is the resistance, $X$ is the reactance, and $j$ is the imaginary unit. In this work, the magnetoimpedance ratio is defined as
\[ \frac{\Delta Z}{Z} (\%) = \frac{Z(H) - Z(H_{\text{max}})}{Z(H_{\text{max}})} \times 100, \]

(5.2)

where \( Z(H) \) is the impedance (or resistance, reactance) at field \( H \). The impedance ratio is normalized by \( Z(H=H_{\text{max}}) \).

Figure 5.1 XRD patterns of (a) the nanocrystalline control ribbon annealed at 500 °C and (b) the ribbon with 120 nm Co. (c) TEM of nanocrystalline uncoated ribbon and (d) SEM of coated ribbon cross section.

5.3. Structural Properties

Figure 5.1 (a),(b) shows XRD patterns of the control \((\text{Fe}_{50}\text{Ni}_{50})_{81}\text{Nb}_{7}\text{B}_{12}\) ribbon and Co-coated ribbon after annealing at 500 ° C for 1 h, respectively. The nanocrystallized control ribbon shows a hump near \(2\theta=43.9^\circ\), which corresponds to the fcc(111) reflection of bulk \(\text{Fe}_{0.5}\text{Ni}_{0.5}\) and an additional peak at \(2\theta=50.79^\circ\) identified as (200) reflection of the fcc phase. This agrees with prior research on these
FeNiNbB ribbons [24]. The XRD pattern of the annealed Co-coated ribbon shows the development of a shoulder near 44.5°, which is likely due to the presence of Co hcp(002) and/or Co fcc(111), which have very close lattice spacings [28,29]. Figure 5.1 (c) shows the nanocrystalline surface microstructure of the control FeNi ribbon after the 1 h, 500 °C annealing treatment. Figure 5.1 (d) is a cross sectional SEM image of the clean interface between the 120 nm layer of Co on the FeNi ribbon. This image shows the Co-coating was continuous and mechanically solid interface was formed between the Co layer and the ribbon.

5.4. Surface Magnetization

Kerr microscopy was used to image the low-field domain structure of the ribbons after the 1 h anneal at 500 °C. Figures 5.2 (a-b) show the domain patterns on the air side of the uncoated FeNi-based ribbon with increasing magnetic field (0<|H_{DC}|<0.5 Oe). The corresponding images consist of wide planar domains oriented predominantly in the transverse direction with respect to the ribbon axis. A marked change of this simple domain structure after application of low magnetic field (0 → 0.5 Oe) is typical of the soft magnetic behavior of these ribbons after an annealing treatment that achieves nanocrystallization. The MOKE patterns in Fig. 5.2 (c-d) show the domain structure of the 120 nm Co coating on top of the crystallized FeNi ribbon with increasing field from 1→5 Oe. There is evidence of two types of domains; wide, planar transverse domains and high anisotropy narrow, river-like domains. This complicated domain structure is less responsive to small changes of magnetic field, which is related to the magnetic hardening of the surface layer due to Co-deposition. Also evident from the microscopy is the rough crystalline surface.

MOKE hysteresis loops were taken in the longitudinal geometry (L-MOKE) to examine the dc magnetization of the surface on the air side of the coated and uncoated ribbons. The samples used in L-MOKE were measured with respect to two different orientations: \( H_{DC} \) parallel and perpendicular to the ribbon casting direction. Figure 5.3 (a) shows L-MOKE on the air side of the uncoated ribbon in the two measuring directions. A super soft easy axis with a coercive field (\( H_C \)) of about 0.2 Oe. A hard axis
hysteresis loop is found when the air side of the ribbon was rotated 90° (perpendicular to the casting direction/ribbon length) and Kerr effect measured. The anisotropy field can be roughly estimated from the saturation field of the hard axis if it is assumed the anisotropy is uniaxial. The anisotropy field estimated from MOKE of the uncoated ribbon is around 3 Oe. Meanwhile, the Co-coated ribbon has a square hysteresis loop when measured in the perpendicular field orientation, while a hard axis is evident in the parallel orientation (Fig. 5.3 (b)). This is a clear indication of a transverse (easy axis transverse to the ribbon length) magnetocrystalline anisotropy attributed to the polycrystalline Co-coating. The coercive field of about 50 Oe is typical for a 120 nm Co film annealed at 500 °C [29,30].

The hard axis MOKE curve of Fig. 5.3 (b) is atypical, but the humped features around zero field are an artifact of the Kerr effect measurement geometry. When measuring MOKE in the longitudinal geometry, there are two possibilities for the magnetization direction in the sample that would be in the plane of incidence of the experimental setup. Longitudinal magnetization (in plane of the sample) and
polar magnetization (out-of-plane of the sample) can both contribute to the polarization rotation or ellipticity change in the plane of incidence. Due to the rough surface of the Co coating, evidenced by microscopy, it is likely that some polar contribution to the magnetization is being measured when the magnetization vector happens to lie in the plane of incidence. The polar signal is not seen in Fig. 5.3(a) because the light intensity change due to the polarization rotation along the easy axis overwhelms the small polar signal.

In Fig. 5.3 (c), L-MOKE hysteresis loops from the air and wheel side are compared. The external field was applied perpendicular to the ribbon axis. On the wheel side, which is typically the rougher side, a split hysteresis loop is seen indicating a hard axis. It is worth mentioning that the rougher wheel side of a rapidly quenched ribbon could have multiple local anisotropies at the surface. In Fig. 5.3 (d), the Co-
coated ribbon shows an increased coercivity and wider switching distribution on the wheel side as compared to the air side. This also points toward increased roughness on the wheel side of the ribbon.

5.5. Analysis by Components of the Magnetoimpedance

The field dependence of the $\Delta R/R$, $\Delta X/X$, and $\Delta Z/Z$ ratios are presented in Fig. 5.4 (a-c) for selected frequencies of 100, 400, and 900 MHz. At frequencies less than 400 MHz, the $\Delta R/R$ of the coated ribbon shows a beneficial increase while at higher frequencies the coating had a negative effect. The increase in $\Delta R/R$ is seen over a large field range. Conversely, the $\Delta X/X$ of the coated ribbon shows a reduction between $|H_{DC}| < \sim 50$ Oe. Since the resistance contributes mostly to the impedance at this frequency range, the $\Delta Z/Z$ of the coated ribbon ultimately has a beneficial increase up until 400 MHz. The frequency dependence of the maximum change in $\Delta R/R$, $\Delta X/X$, and $\Delta Z/Z$ is presented in Fig. 5.4 (d-f), respectively. The field value of the maximum change in the impedance is given in the following Fig. 5.5 (a-c). At excitation frequencies less than 400 MHz, the benefit of the Co coating is seen in the $\Delta R/R$ and $\Delta Z/Z$.

Examination of the real and imaginary components of the impedance can provide insight into the effect of the Co-coating on the ac magnetic behavior of the ribbons. Fig. 5.4 (a) shows that the Co-coating had a beneficial effect on the $\Delta R/R$ over a large dc field range at frequencies near $f = 400$ MHz. The change in reactance decreased from $\sim -50$ Oe $< H_{DC} < \sim 50$ Oe over all frequencies. This behavior can be understood through inductance formalism [31], which allows one to connect the impedance to a magnetic quantity. Inductance formalism relates the real (imaginary) part of the impedance to the imaginary (real) part of the permeability via a geometrical constant. In this formalism, the real part of the impedance (imaginary part of the permeability) is related to dissipative magnetization processes that contribute to the permeability, such as domain wall movement, irreversible rotation, etc., and the imaginary component of the impedance (real part of permeability) is related to conservative magnetic process such as reversible
spin rotation [32]. Therefore, the increase in $\Delta R/R$ due to the coating could indicate an increase in lossy ac magnetization processes contributing to the impedance. However, since the increase in $\Delta R/R$ is over the entire field range, it is more likely the beneficial increase in $\Delta R/R$ is due to the lower resistivity of the Co.

However, the $\Delta X/X$ was reduced at fields between +/- 50 Oe. This could be evidence of some form of magnetic interaction between the Co layer and FeNi ribbon. The high degree of anisotropy evidenced in the Co layer could be strong enough to restrict the magnetization process of FeNi ribbon near the Co/FeNi interface, which would suppress reversible magnetization processes until the Co anisotropy field is reached, leading to a reduction in $\Delta X/X$ between +/- 50 Oe. The symmetric peaks in amplitude and field position as seen in Fig. 5.4 (a-c) does not indicate a presence of magnetostatic coupling, as observed in thin film layered systems [33,34]. Typically, magnetic film ($t > 100$ nm)/ribbon structures do not exhibit any features of magnetostatic or exchange coupling in their GMI curves at $f < 20$

Figure 5.4 $\Delta R/R$ (a), $\Delta X/X$ (b), and $\Delta Z/Z$ (c) at selected excitation frequencies as a function of $H_{DC}$. Open symbols denote control ribbon and closed symbols denote 120 nm Co coated ribbon. (d) Maximum change in resistance, (e) maximum change in reactance, and (f) maximum change in impedance of the control and coated ribbon.
MHz [11,12,16,17]. On the other hand, asymmetric peaks and hysteresis of the GMI curve is observed in the Co(15 nm)/Co-rich ribbon system of Ref. [14] at $f = 10$ MHz.

5.6. Frequency-dependence of $H_K$ and Surface Domain Structure

The GMI peak position is the field value that makes the effective permeability a maximum and therefore the dc field that makes the $Z$ a maximum is called the effective anisotropy field, $H_K$. In Fig. 5.5, $H_K$ is extracted from the peaks in $R(H)$, $X(H)$, and $Z(H)$. The $H_K$ from $R$ (Fig. 5.5 (a)) is at most increased by 4 Oe due to the Co coating in the frequency range 100-1000 MHz. The $H_K$ from $X$ (Fig. 5.5 (b)) also increased due to the Co coating. Overall, the anisotropy field was only modestly increased by the addition of the Co coating as seen in $H_K$ from $Z$ (Fig. 5.5 (c)). This is expected due to the fact that most of the current is still flowing through the ribbon.

It is of interest to those in the field to correlate the $H_K$ field from GMI to critical field values of the dc magnetization process such as coercive field and anisotropy field. Depending on the excitation frequency, the $H_K$ field from GMI may be related to the $H_K$ estimated from dc hysteresis loops. In general, at frequencies in the tens of MHz and below, it has been shown that the $H_K$ fields from GMI are close to the bulk anisotropy field of the sample [25,26]. As the exciting frequency reaches into the hundreds of MHz and GHz, however, the $H_K$ field is pushed to higher values where some or all of the Co/ribbon structure is uniformly magnetized. Therefore, it is not straightforward to correlate critical fields from the dc magnetization process to $H_K$ from GMI at high frequencies.

At a frequency of 100 MHz, $H_K$ from $Z$ (Fig. 5.5 (c)) of the uncoated and coated ribbon are both 6 Oe, indicating that at $f = 100$ MHz the ribbon contributes mainly to the GMI response. Comparing these values to $H_K$ extracted from MOKE of the uncoated ribbon, the $H_K$ from GMI at $f = 100$ MHz is slightly larger; $H_K^{100\text{MHz}} = 6$ Oe as compared to $H_K^{\text{MOKE}} = 3$ Oe. It is important to note that MOKE is a localized measurement; the spot size used in this research is roughly 1 mm in diameter, while GMI is an average over the length of the ribbon. This could be a reason for the small difference in $H_K$ value. There is no attempt to correlate the $H_K$ estimated from the MOKE of the Co-coated ribbon ($H_K^{\text{MOKE}} \sim 100$ Oe) since
the surface effect of MOKE is sampling, at most, the top 20 nm of the 120 nm-thick Co coating, while the penetration depth of the current is estimated to be on the order of microns and flowing mostly within the ribbon.

![Figure 5.5 Anisotropy field, $H_K$, extracted from the peaks in field dependent resistance (a) reactance (b) and impedance (c) of the nanocrystalline control ribbon (open symbols) and Co coated ribbon (closed symbols).](image)

**5.7. Conclusions**

In conclusion, a comparative study of the surface magnetization and magnetoimpedance effect in an uncoated and 120 nm Co-coated (Fe$_{0.5}$Ni$_{0.5}$)$_{81}$Nb$_7$B$_{12}$ nanocrystalline ribbon was conducted. The impact of the transverse anisotropy of the Co coating, evident from MOKE, was to increase the $\Delta Z / Z$ by a
majority contribution from the $\Delta R/R$. However, the high anisotropy of the Co layer reduced $\Delta X/X$ and increased the dc field where $\Delta X/X$ is a maximum. This could point to a coupling or interaction of the hard Co layer and the soft FeNi ribbon, which acts to reduce the reversible rotational permeability. The $H_K$ fields of the coated ribbon increased by only a few Oe at frequencies less than 600 MHz, where there is an increase in $\Delta Z/Z$, implying that the skin depth in this region is still contains the majority of the FeNi ribbon bulk.

5.8. References


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6. MAGNETIC FORCE MICROSCOPY ON MELT-EXTRACTED MICROWIRES: 
CORRELATION OF DOMIAN PERIODICITY TO MAGNETOIMPEDANCE RESPONSE

In this chapter, the relationship between the surface conditions as measured by magnetic force microscopy and giant magneto-impedance (GMI) in Co-rich melt-extracted microwires is explored. The surface magnetic domain structure parameters of ~45 μm diameter Co_{69.25}Fe_{14.25}Si_{13}B_{13.5-x}Zr_x (x = 0, 1, 2, 3) microwires, including the magnetic domain period (d) and surface roughness (Rq) as extracted from the magnetic force microscopy (MFM) images, have been correlated with GMI in the range 1-1000 MHz. It was found that substitution of B with 1 at. % Zr increased d of the base alloy from 729 to 740 nm while retaining low surface roughness. A tremendous impact on the GMI ratio was found, increasing the ratio from ~360 % to ~490 % at an operating frequency of 40 MHz. Further substitution with Zr decreased the high frequency GMI ratio, which can be understood by the significant increase in surface roughness evident by force microscopy. This study demonstrates the application of the domain period and surface roughness found by force microscopy to the interpretation of the GMI in Co-rich microwires.

6.1. Introduction

Co-rich melt-extracted amorphous microwires have been recognized as an exciting magnetic material involved in various applications [1–5], including geomagnetic detection sensors [6], magnetic induction hyperthermia [7,8], and detection of magnetically labeled biomolecules [9]. Amorphous microwires possess super soft magnetic properties that exhibit fascinating magnetic phenomena such as the giant magneto-impedance (GMI) effect [10,11]. As it is well known, the longitudinal dc magnetization process of Co-rich amorphous microwires, especially near zero magnetic field, is mainly determined by domain wall movement and rotational magnetization. The latter mechanism is closely related to high

1 Portions of this chapter have been previously published in a peer-reviewed journal paper (Eggers et al., Nature: Scientific Reports 7, 46253, 2017; AIP Advances 7, 056643, 2017) and have been reproduced with permission from the respective publishers.
frequency magneto-impedance, since at frequencies below \(\sim 10\) MHz, eddy currents damp domain wall motion.[11] Both processes, however, are closely associated with the surface magnetic domain structure (SMDS), which is essential for interpreting the GMI effect at high frequencies.

Recently, there has been some discussion regarding the stability or presence of the so-called bamboo surface domain structure in negative magnetostrictive Co-based microwires [12,13]. In current literature, magneto-optical methods have detected such a SMDS in magnetic microwires [14–16]. One method is via magneto-optical Kerr effect (MOKE) microscopy [17], which is an optical technique that measures the change in polarization of light after it is reflected from the surface of a magnetic material. In addition, the Faraday effect has been used to image magnetic domains in wires through a technique called the magneto-optical indicator film (MOIF) method [18,19]. However, there have been some magneto-impedance and EMF measurements [20,21] and theoretical calculations [22] with implications that the bamboo SMDS is metastable, i.e., not present in a ‘perfect’ negative magnetostrictive microwire (and that the SMDS of such a wire is single domain), and that the origin of a bamboo SMDS could be due to a surface anisotropy induced by surface irregularities [22,23].

Since its development from atomic force microscopy (AFM) in 1987 [24], magnetic force microscopy (MFM) has been accepted as an effective technique in detecting surface micro-magnetic information [25–27]. Consequently, MFM images have also detected the presence of a bamboo domain structure in Co-rich microwires [28–33] while AFM has been used to detect surface defects and deformations. However, there has been no attempt to quantitatively correlate the observed surface roughness and bamboo domain structure with GMI measurements. In this work, we relate the high frequency longitudinal GMI measurements to the surface roughness and bamboo SMDS period imaged by AFM and MFM. The correlation of these measurements on Zr-substituted \(\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.25}\text{B}_{15.25-x}\text{Zr}_x\) microwires \((x = 0 - 3)\) have allowed us to address this issue, while also giving good guidance on optimization of the high frequency GMI responses of Co-rich microwires for advanced sensor applications.
6.2. Magnetic Force Microscopy Image Processing and Analysis

Soft magnetic materials can be imaged with great sensitivity using CoCr thin film-coated silicon tips with Q values between 100-200.\cite{34} An MFM image is measured by mapping the varying resonance condition of a cantilever with a perpendicularly magnetized tip during its interaction with the normal component of the stray field of the magnetic material, as seen in Fig. 6.1(a).

Figure 6.1 (a) Diagram of the MFM measurement on the surface of a microwire with core-shell domain structure. (b) Optical image of the MFM probe from top down.

It was found that the image of the amplitude and phase change of the cantilever gave identical features, with the former providing a greater contrast. The average value of the magnetic field near the probe is measured instead of discrete values and it shows the negligible influences on the MFM image.
when the lift height is larger than the size of probe. In this study, the microwire sample was fixed to a horizontal substrate before it was placed under a CoCr-coated silicon probe as shown in a top down view in Fig. 6.1(b). The tip profile is shown as an inset in Fig. 6.1(b), with a tip height of 15 ± 2 μm, radius 0.50 ± 5 nm, and force constant of 3 N/m. The MFM image is 128 px × 32 px and scanning rate is 0.996 Hz.

Figure 6.2 Flow chart of MFM image processing including (a) original image (b) linear background subtraction (c) Gaussian-low pass filter (d) mean filter and (e) Butterworth-high pass filter. Inset of (a) and (b) are the side view of 3-D MFM images, inset of (c) and (e) are the low pass and high pass function images, respectively, and the inset of (f) shows the 2D MFM image and definition of a domain period.
Figure 6.2 (a-f) illustrates the image processing steps taken to transform an initial 3D MFM image of a Co$_{68.15}$Fe$_{4.35}$Si$_{12.25}$B$_{14.25}$Nb$_1$ microwire into the restored image used to extract the surface domain period, $d$. In an effort to be transparent with our method of determining the domain period, we chose the Co$_{68.15}$Fe$_{4.35}$Si$_{12.25}$B$_{14.25}$Nb$_1$ microwire since it had a very uniform domains structure. In the following section, the details of the image processing steps are given. Over the course of a long scan, thermal and mechanical induced drift affects the MFM image by imposing a linear background as shown in the side view of Fig. 6.2(a). This image becomes normal after the linear background is fit and subtracted out (side view of Fig. 6.2(b)). Since the signal of surface stray field is mainly in the very low frequency region, high frequency noise present in the image can be removed without affecting the magnetic data. Therefore, a Gaussian-Lowpass filter was applied to smooth Fig. 6.2(b) in order to enhance the signal noise ratio (SNR), which ultimately aids in the extraction of the magnetic parameter $d$. Since the Gaussian transfer function (illustrated in the inset of Fig. 6.2(c)) is a single-valued function with rotational symmetry, the local characteristics of the image edge are not distorted by the process. Fig. 6.2(c) shows stripe-like noise along the wire axis from the scanning pattern of the probe still present in the image. To reduce the contribution from the stripe noise to the parameter extraction, a mean, or convolution, filter is used to further smooth Fig. 6.2(c) and the results are shown in Fig. 6.2(d). The size of the discrete convolution sliding window was chosen to be 5 px $\times$ 5 px or 0.609 $\mu$m$^2$. In order to restore detail to image features that were lost by application of the mean filter, a high-pass filter is applied. The final image used for parameter extraction is shown in Fig. 6.2(e).

MFM measurements on a series of Co$_{68.15}$Fe$_{4.35}$Si$_{12.25}$B$_{15.25}$Zr$_x$ microwires were conducted as a function of transition metal Zr substitution ($x = 0 - 3$). Figure 6.3(a-d) shows 3D AFM and MFM images of the Zr-doped wires along with one MFM scanline down the wire axis used to determine the average value of the domain period, $d$. For the base composition of wire ($x = 0$), the average surface roughness and domain period was found to be $R_q = 1.14$ nm and $d = 729$ nm, respectively. With increasing Zr
content, both surface roughness and domain period increased with $R_q = 3.29$ nm and $d = 740$ nm for Zr$_1$; $R_q = 9.86$ nm and $d = 756$ nm for Zr$_2$; and $R_q = 15.6$ nm and $d = 863$ nm for Zr$_3$.

![Image](image_url)

Figure 6.3 3D AFM (left) and MFM (right) images of (a) Zr0, (b) Zr1, (c) Zr2, (d) Zr3 microwires. Below each pair of images is a single MFM scan line.

### 6.3. Model of Surface Domain Structure by MFM

According to the core-shell model of negative magnetostrictive Co-rich amorphous microwires[11], the magnetic moments of the surface domains are nearly aligned in the circumferential direction. As one can see in Fig. 6.4 (a)-(c), there are two potential sources of surface stray fields according to this picture[35]: one is generated by the domain magnetization and the other by the domain wall. Consequently, there is no stray field in the normal direction due to domain magnetization. However, the Bloch wall has a stray field normal component that is detected by MFM. The stray field from the Bloch walls will generate a magnetic flux leakage field and thus the surface position of the domain wall can be determined by these intense magnetic field lines. The basis for the contrast in the MFM image is
that positive (negative) magnetic charges produced at a surface/domain wall interface interacts with the MFM probe in the following way: The probe is magnetized to be in a negative remanent state, such that the magnetic force \( \vec{F}_z \) gradient along the \( z \)-axis is a minimum if the surface stray field flows out of the surface normal. This corresponds to the wave trough as shown in Fig. 6.4 (a-c).

Figure 6.4 Model of the relationship between the MFM image and surface domain structure; (a) is a 3D MFM image (b) shows a diagram of the MFM scan lines, (c) is the core-shell model of surface domain structure with Bloch walls separating adjacent magnetic domains.
The wave crest corresponds to a repulsive force, where $\vec{F}_z$ maximum. However, based on the above analysis, it is not possible to estimate either the width of the domain or domain wall; only the combined width of the domain and wall can be determined by extracting the average period from crest-to-crest or trough-to-trough, marked as $D$ in Fig. 6.4(a). We can consider $d = D/2$ to represent the domain period as shown in Fig. 6.4(b).

![Figure 6.5 Evolution of the GMI effect in the microwires with (a) Zr0, (b) Zr1, (c) Zr2, and (d) Zr3.](image)

6.4. Magnetoimpedance Effect
Magnetoimpedance measurements at the intermediate frequency range of 20-1000 MHz were conducted on all the microwires. Figure 6.5(a-d) shows the field and frequency evolution of the change in impedance, $\Delta Z/Z$, for the microwires with 0, 1, 2, and 3 at. % Zr, respectively. The 1 at. % Zr doping shows a beneficial increase of $\Delta Z/Z \sim 490 \%$ at a frequency of 40 MHz over the other compositions. Further substitution past 1 at. % suppresses the $\Delta Z/Z$ ratio at higher frequencies, as seen by the flat regions in dark blue in Fig. 6.5(c) and (d). Figure 6.6(a) presents the maximum change in impedance, $[\Delta Z/Z]_{\text{max}}$, of the base composition and Zr-doped wires over the measured frequency range. It is apparent that 1 at. % Zr substitution boosts the maximum impedance change over the whole frequency range while any further doping of Zr brings $[\Delta Z/Z]_{\text{max}}$ down to and below $x = 0$, depending on the excitation frequency. At frequencies below $\sim 140$ MHz, $[\Delta Z/Z]_{\text{max}}$ of $x = 2$ is roughly similar to the $x = 0$ wire, while at higher frequencies $[\Delta Z/Z]_{\text{max}}$ values drop steadily lower.

The DC magnetic field also modifies the skin depth through the circumferential (AC) permeability. Since the circumferential permeability is at its highest value at $H_{\text{DC}} = H_K$, the skin depth is a minimum at this field for any given frequency. At $H_{\text{DC}} = H_{\text{max}}$, the circumferential permeability is at its lowest value and the skin depth is a maximum. A simple model can be used to determine the penetration depth of the skin effect based on the assumption that the real part of the impedance change is due only to changes in effective cross-sectional area[36]. With this assumption, Fig. 6.6(c) can represent not only the maximum change in resistance, $[\Delta R/R]_{\text{max}}$, but also the maximum change in skin depth at any given frequency. Figure 6.6(d) presents the maximum change in reactance, $[\Delta X/X]_{\text{max}}$, for the microwires. This component of the impedance is generally analyzed through inductance formalism, where the imaginary part of the impedance undergoes a simple geometrical transformation to the real part of the inductance.[37] The real part of the inductance is then proportional to the real part of the complex permeability, which represents conservative magnetization processes such as reversible magnetization rotation.
Energetically, one can determine the equilibrium domain period based on minimization of the magnetostatic energy and domain wall energy contributions as done in Ref.[22]. The magnetostatic contribution depends on wire radius and cross-sectional shape, while the domain wall energy term depends on the thickness of the outer shell and anisotropy and exchange constants. With increasing shell thickness and ellipticity of wire cross section, the domain period is found to increase, while the domain period decreases with increasing surface anisotropy. We consider the substitution of transition metal Zr for B to mainly affect the stress induced during fabrication by removal of the amorphous component B

6.5. Uniaxial Wall Spacing

Figure 6.6 Maximum change in impedance (a), anisotropy field (b), maximum change in resistance (c), and maximum change in reactance (d) of the microwires where the square, circle, triangle, and inverted triangle refer to Zr0, Zr1, Zr2, and Zr3 compositions, respectively. The inset of (a) shows the correlation between the surface roughness and domain period. The inset of (b) shows \( H_K \) from 1-200 MHz. The surface roughness (stars) are shown on the right axis in (c) and (d) for comparison.
and introducing more crystallite nucleation sites with Zr[4], since all fabrication parameters were held constant for all the microwires. This could have the impact of increasing/decreasing the thickness of the outer shell, inducing irregular surface morphologies, and/or affecting the induced surface anisotropy. This seems a reasonable assumption considering the positive correlation of the average surface roughness and domain period in the wires, as seen in the inset of Fig. 6.6(a).

Figure 6.6(a)(b) shows that substitution with \( x = 1 \) at. \% has the highest \( \frac{\Delta Z}{Z} \)\textsubscript{max} and lowest \( H_K \) over the majority of the spectrum. Considering this, it can be concluded that the slight increase of domain period in the \( x = 1 \) at. \% could originate from a reduction of induced surface anisotropy. With Zr substitution of 2-3 at. \%, the \( H_K \) increases dramatically over the whole frequency range especially at high frequencies where the penetration depth is close to the surface. This might suggest an increase in induced surface anisotropy, however the domain period at the surface is observed to increase as well. It is likely then that the anisotropy is not responsible for the domain period increase in this case, and the observed roughness increase by a factor of 3 could point to a deformity in wire cross section or an increase in shell thickness, since these factors can increase the domain period[22].

Fig. 6(c)(d) show that the resistance is the major contributor to the impedance over all frequencies, while the maximum change in reactance drops to near zero percent at \( f > 600 \) MHz. This behavior is expected at this frequency range as the experimental conditions approach that of ferromagnetic resonance, where the real part of the impedance continues to climb until resonance is reached while the imaginary part approaches zero. However, the near zero percent change in the reactance is simply a consequence of the definition (Eq. 2); the applied field at which the reactance is a maximum for \( f > 600 \) MHz has shifted beyond \( H_{\text{max}} = 110 \text{ Oe} \).

It is apparent that the reduction of \( \frac{\Delta Z}{Z} \)\textsubscript{max} as Zr substitution is increased to 2 and 3 at. \% is greatly affected by the surface roughness increase, which plays a crucial role at high frequencies where the skin depth is small.[38,39] The large \( H_K \) and wide field-dependent GMI curves (Fig. 6.5 (c)(d)) at frequencies greater than 600 MHz indicate a much larger surface anisotropy distribution than \( x = 0 \) or 1
%. This suggests an increase in fluctuations of local magnetic anisotropy and saturation magnetization at the surface and is well known to negatively impact $[\Delta ZZ]_{\text{max}}$ along with surface defects that can immobilize surface spins and reduce the GMI ratio$^{[23],[40]}$.

6.6. Conclusions

In summary, the Zr-substitution of B in Co$_{68.15}$Fe$_{4.35}$Si$_{12.25}$B$_{15.25}$-$x$Zr$_{x}$ microwires was conducted to establish the relationship between the surface roughness, MFM and the GMI effect. Both AFM and MFM images were observed and standard image processing techniques were used to extract surface magnetic parameters meaningful to the analysis of the GMI effect. By linking the observed MFM to the core-shell model of negative magnetostrictive microwires, the magnetic domain period could be established. Coupled with the average surface roughness and qualitative observations, AFM/MFM images are significant tools capable of quantitative analysis of the influences of domain structure changes on the GMI effect, especially changes which are subtly induced by chemical substitution.

6.7. References


7. THE RELATIONSHIP BETWEEN PHASE SEPARATION INDUCED BY STEPPED JOULE ANNEALING AND THE BAMBOO DOMAIN STRUCTURE IN MICROWIRES

In this chapter, amorphous microwires are annealed using a stepped joule annealing protocol. After each successive step, the wire was subjected to tensile loading until fracture. The cross-sectional scanning electron microscopy revealed the development of an unusual two-phase core-shell microstructure with increased annealing current. Transmission electron microscopy of the surface of the wire was also conducted. In conjunction with surface sensitive probes like magnetic force microscopy, magneto-optical Kerr effect, and magnetoimpedance, the nature of the core-shell structure and its benefits to the giant magnetoimpedance effect are examined.

7.1. Introduction

Rapidly quenched ferromagnetic microwires are being targeted as multifunctional elements in a variety of exciting applications ranging from ultrasensitive magnetic sensors [1], MRAM [2], biomagnetic sensors [3], magnetic hyperthermia cancer treatment [4] and self-monitoring smart composites [5]. In particular, melt-extracted CoFeSiB-variant microwires have much to offer these applications as they have been shown to have exciting mechanical and magnetic properties such as high room temperature strength and high magnetic permeability. These beneficial properties to modern application are a direct result of the high solidification rates ($10^5$-$10^6$ K/s) during rapid quenching [6–8]. Like all good things, there is a trade-off. The temperature and stress gradients experienced during fabrication can have negative consequences such as poor ductility and inhomogeneous magnetic structure [6,9]. However, simple post-processing techniques such as Joule annealing hold promise for not only overcoming these limitations but offer a way to tailor the microwire to suit specific applications.
Joule annealing of metallic glass microwires has been explored in detail by those in the magnetism community [10–12]. It is generally concluded that Joule annealing at corresponding temperatures below crystallization yield improvements in soft magnetic properties. Some consider the induced circular magnetic field to play a role in the relaxation of the magnetic structure due to impressive figures of merit for the GMI effect after Joule annealing [7]. But researchers agree that the enhanced magnetic properties by Joule annealing stems from the relaxation of residual stresses trapped during fabrication, while any detriment to the magnetic properties is viewed in terms of devitrification.

However, from the mechanical standpoint, an amorphous matrix with embedded nanocrystalline phase can induce plasticity in the microwire by arresting shear band propagation [6]. Thus, there must be a balance struck between soft, uniform magnetic behavior and robust mechanical property to make these microwires practical for integration into new technologies. In this work, we report the development of a nanocrystalline core-amorphous shell phase separation in $\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.25}\text{B}_{13.25}\text{Zr}_2$ microwires induced by stepped Joule annealing from low to moderate intensity.

We demonstrate the tunable mechanical and magnetic properties of the core-shell phase separation by multiple experiments. First, the two-phase structure is uncovered by scanning electron microscopy (SEM) images of fracture patterns after failure by tensile loading. Then, the devitrification of the metallic glass microwire surface is examined by high-resolution transmission electron microscopy (HRTEM) with each Joule annealing step. To monitor the surface of the microwire, atomic/magnetic force microscopy (A/MFM) was measured in situ during the Joule annealing steps. Finally, to correlate devitrification at different regions of the microwire with the magnetic properties, the giant magneto-impedance effect (GMI) was employed.

### 7.2. Materials and Methods

The high quality as-quenched $\text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.25}\text{B}_{13.25}\text{Zr}_2$ amorphous microwires possess the diameters ranging from 20 to 60 µm in 20-50 cm length were fabricated by melt-extraction described elsewhere [7,8], and saturated magnetostriction with nearly a small negative value (nearly $|\lambda_s| \leq 10^{-6}$) [13].
The uniform and continuous microwire with diameter of $\sim 45 \pm 0.1 \mu m$ and $\sim 26 \text{ mm}$ in length was selected and post-processed by multi-step DC Joule annealing with current amplitudes ranging from 80 mA (current density $\sim 5.03 \times 10^7 \text{ A/m}^2$) to 160 mA ($\sim 10.07 \times 10^7 \text{ A/m}^2$), step value was set as 20 mA and annealing time is 10 min for each stage on this single microwire [7]. The impedance of microwire was measured on an Agilent 4294A precision impedance analyzer, which frequencies of driving current were varied from 1~110 MHz and amplitude of driving current was kept at 20 mA. The samples were placed in a pair Helmholtz coils parallel to the axis of the microwires but transverse to the geomagnetic field. The GMI ratio, $\Delta Z/Z_0$, is defined by the same way as reported in Ref. [14].

The magnetic force microscopy in this work was conducted on a Bruker Dimension Icon in tapping-lift mode with the cantilever driven slightly below its natural resonance frequency to maximize the change in oscillation amplitude. The basic theory and the more details of processing procedure for MFM images are shown in Ref. [15].

The thermal properties associated with glass transition and crystallization were evaluated by differential scanning calorimetry (DSC; TGA/SDTA851E) under a flowing argon atmosphere at a heating rate of 20 °C min$^{-1}$. The measurement of magnetic properties was carried out on a vibrating sample magnetometer (VSM; Lake Shore 7410) and homemade Kerr Effect magnetometer in the longitudinal geometry. The average temperatures of microwires during annealing can be evaluated using the energy conservation law and value iteration as follows [9,16]:

$$\rho_M c \frac{dT}{dt} - Q_E - Q_h - Q_T = 0$$

(7.1)

Simulation data from Fortran programming and Ansys software was used to simulate the thermostatic temperature field distribution of microwires.
The structure information of microwires was examined by scanning electron microscope (SEM; Hitachi S-4700). In addition, the nanostructure of as-quenched and annealed microwires was examined by high-resolution transmission electron microscopy (HRTEM; Tecnai G2F30) and the steps for sample preparation are shown in Ref. [9]. Digital-micrograph software was used to analyze the HRTEM data. Tensile samples were prepared conforming to the ASTM standard D3379-75 with a gauge length of 10 mm and diameter range from 20-50 μm with the annealing current density constant. Micro-tension experiments of microwires with different area reductions were performed using a 10 N Instron 3343 universal testing machine at a constant strain rate of 0.252 mm min⁻¹.

7.3. Structural Properties and Observation of Phase Separation

7.3.1. Nanostructure Evolution with Annealing

In order to correlate simulations with experimental critical temperatures, the microwires were measured by differential scanning calorimetry (DSC) in the as-quenched state and after the 140 mA Joule anneal step. The exothermic peak area of the annealed microwire is larger than the as-quenched microwire due to structural relaxation and enhancement of medium and long range atomic order as seen in Fig. 7.1a. While there is no obvious difference in $T_{\text{tr}}$, after the 140 mA annealing stage, there appears to be a new metastable phase (MS III) made accessible by the annealing step of 140 mA. Based on
electron diffraction, this phase is ascribed to Co$_2$B. The maximum temperature of the microwire at each Joule annealing step was estimated by considering the conservation of energy and iteratively solving for temperature. Figure 7.1b shows that the microwire can reach a steady state temperature in less than a second. However, by Joule annealing the microwires in air and considering their small size, there must be a thermal gradient within the wire. The temperature distribution during Joule annealing at 140 mA is modeled using ANSYS software in Figure 7.1c. It shows only a core region of the wire experiencing high temperatures and the outer shell experiencing relatively low ones when compared to typical crystallization temperatures of Co$_{68.15}$Fe$_{4.35}$Si$_{12.25}$B$_{13.25}$Zr$_2$ products.

Bright field high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) are visual tools for analysis of material morphology as it can provide high-resolution structural and visual information. The microwires samples were thinned using two ion beams on either side in order to thin the selected region enough to reach electron transparency. The ion beam thinning was conducted at low energy and small controllable incident angle in order to manipulate thermal effects.

In the as-quenched state, ultra-fine nanocrystals (~2 nm) are found embedded in an amorphous matrix as seen in the HRTEM image of Fig. 7.2(a). These nanocrystals are surrounded by distorted regions in the yellow rectangle of twin filter inverse fast Fourier transform (IFFT) image below area 2. The distorted regions are thought to be crystal nuclei caused by different rate and type of heat energy exchange and stress inhomogeneity during fabrication [13,17] as shown in red circle of ring filter IFFT area 1 and 2 selected from Fig. 7.2(a). In the corresponding SAED pattern (Fig. 3I), the blurry ring pattern is characteristic of amorphous materials and several diffraction light rings show that the formation of nanocrystals is eutectic crystallization during the solidification process [17].
Figure 7.2 HRTEM images and SAED of the microwire and the corresponding local magnifications: a), b), c), and e) show the HRTEM image of the as-quenched, 100 mA, 140 mA, and 160 mA annealing stages, respectively. Roman numerals I-IV display the corresponding SAED image. Insets 1-7 show the ring- and 8, 9 show twin- filtered IFFT images of local magnification area framed in yellow box and the unlabeled insets below 2, 4, and 6 show a twin filtered IFFT image of the same areas, respectively. Inset D8 and D9 show an estimation of the interplanar distance of the nanocrystal structures observed in insets 8 and 9. d) shows the basis for the ACF calculation, f) shows the results of the ACF along with the average nanocrystal size as a function of current stage. g) the image of (e) with only the nanocrystal clusters showing with white background.
The high melting point of Zr enhances the Gibbs free energy of the liquid alloy which increases the critical radius $r_c$ of as-quenched nucleus by classical nucleation theory. Zr also can serve as nucleation seeds for nanocrystal [7]. Some medium-range order is seen in the as-quenched microwire, about 1.5-2 nm in size. We conclude that the as-quenched microwire is an amorphous phase with small, ~2 nm nanocrystalline precipitates near the surface, as proposed by co-workers in [17].

Figure 7.2(b) shows the HRTEM image after the 100 mA annealing step. Judging by the increased contrast in the image, there has been some short-to-medium range order established with this annealing procedure. The IFFT of selected areas 3 and 5 show the nanocrystal size is relatively the same as the as quenched microwire, about 2 nm. However, areas 4 and 6 of Fig. 7.2(b) highlight regions of medium range order, where the size of the nanocrystal grains has grown to ~3 nm. At the 100 mA stage, the highest temperature is near ~515 °C, which is well below Tg and Tx of any crystalline products seen by DSC. At this temperature ($T_g$-100 °C ~ $T_g$), high temperature structural relaxation occurs through relatively long distance diffusion of defects in the amorphous structure to improve chemical short-range order, while leaving the macroscopic glassy structure intact [18]. At this point, many atomic clusters of subcritical nuclei dimensions (~1 nm) have developed into normal as-quenched nuclei while as-quenched critical nuclei begin growth through fusing with surrounding atoms and nuclei to form larger crystallites and medium-range order atomic cluster.

The IFFT reconstruction of areas 1 & 3, 5 of Fig. 7.2(a) (b) show similar symmetrical patterns of one or two atoms and holes. Such a symmetrical structure is also found in Ref. [19] and there is no doubt that these medium range order structures correspond to the sphere and two fused spheres in three-dimensional space. Based on the quasi-closely packed model [20], the 3D shape of this structure is icosahedron or similar to it. As shown in area 4 and 6, the nanocrystal grain size has grown to ~3 nm, and there is still some as-quenched nuclei nearby to cause lattice distortion to appear (under area 4 and 6, corresponding yellow rectangles).
The HRTEM image in Fig. 7.2(c) was taken after the 140 mA anneal step. Compared to the 100 mA step, the nanocrystals are larger in size and quantity. With a maximum annealing current of 140 mA, the maximum temperature is near ~691 °C, which is past \( T_g \). Nanocrystal and as-quenched nuclei in this temperature region both begin growth through fusing with surrounding atoms and nuclei to form larger nanocrystals and medium-range order atomic clusters. The ring filtered IFFT image of area 7 shows the average size of the nanocrystals have increased to ~5.5 nm. Consequently, the nanocrystal auto-correlation function (ACF) fraction increases to nearly 37.5 %. The twin filter IFFT images of area 8 and 9 display similar phenomenon as before, except the degree of internal lattice distortion has decreased slightly. Based on the calculated interplanar spacing and contrast with PDF cards, we confirm and mask the nanocrystal phase on Fig. 7III. From this figure, the following phases can be identified: CoFe phase is cubic with (110) texture, CoSi and Co\(_2\)B are (210) and (211), which have very close interplanar spacing (1.989 Å, 1.983 Å). The appearance of a small fraction of Co\(_2\)B phase is seen the outermost ring in Fig. 3III, which corresponds to the new crystallization peak (MSIII) from the DSC curve (Fig. 7.1(a)). At this annealing stage, Fig. 7.2(d) was constructed from 64 ACF images corresponding to 64 equally spaced regions of Fig. 3(c), where the red square indicates the standard used to determine the nanocrystal ACF fraction in the scanned area. More details of this procedure are described in previous publications Ref. [7,9].

After the 160 mA annealing step, as is apparent from Fig. 7.2(e) and Fig. 7IV that the nanocrystal size grew to ~9 nm with a strong diffraction ring. On account of the crystal being fully developed, there is almost no lattice distortion or edge dislocation as seen in area 10. Figure 7.2(g) displays the nanocrystals isolated on a white background. Not only is the diameter larger but also the grains can be seen to connect to each other. The average diameter and volume fraction demonstrates a high correlation and the enhancement of ACF increase quickly with each annealing stage as shown in Fig. 7.2(f).
7.3.2. Evidence of Core-Shell Phase Separation

Mechanical fracture experiments were performed on the microwires after each annealing stage. In the as quenched state, the mechanical fracture morphology of the microwire displays a typical vein pattern and slanted mechanical fracture (Fig. 7.3(a)) [6]. There are dimpled defect structures and molten droplets on the surface of the fracture as shown in red framed area 1 and 3 of Fig. 7.3 (b) and (c).

Figure 7.3 (d)-(f) shows the mechanical fracture after the 100 mA annealing step. As is apparent from the figure, thicker multi-shear bands appear after mechanical loading. While the number of multi-shear bands has reduced from the as-quenched microwire, their thickness looks like a shell structure. The main crack nearly disappears and is replaced by a refined alveolate vein pattern [21] and the quality of pinholes and dimple structure is obviously improved. It is generally believed that these multiple structures are generated by Taylor instability and void coalescence [22].

Figure 7.3 (g)-(i) shows the fracture of the 140 mA current annealing stage, in which the fracture changes from slanted to flat and multi-shear bands also disappear. This section of fracture displays a more obviously core/shell-like structure and a clear circular boundary as seen in Fig. 7.3 (h) and (i). Upon further magnification (red boxed area 6), the ~3 µm thick shell still shows a vein pattern characteristic of amorphous fracture. However, the core area displays sector feather-like fracture pattern with many relatively bigger pinholes similar like to the classic crystal material. At this annealing stage the nanocrystalline and amorphous core/amorphous shell phase separation becomes most evident in the fracture images, which suggests that some sort of cooperative diffusion has taken place. With the core experiencing temperatures around Tg, the defects can combine or annihilate each other, while near the surface of the microwire the temperatures may be low enough not to change the population of defects. From the viewpoint of crystal kinematics, primary crystallization of CoFe phase excludes Si and B atoms, while secondary crystallization of CoSi and Co₂B excludes Fe atoms. Therefore, there must be diffusion in front of the growth interface where exclusive atoms move to the front of corresponding phase providing new growth conditions. When temperatures reach Tg, homogeneous nucleation occurs.
concomitantly with some inhomogeneous nucleation and eutectic and polymorphous crystallization both occur.

Figure 7.3 Mechanical fracture images with different magnifications for a-c) as-quenched microwire, d-f) 100 mA annealing stage, g-i) 140 mA annealing stage, and j-l) 160 mA annealing stage. Locations of characteristic region insets are marked in red box.
With annealing current increased to 160 mA, the fracture occurs at a Rayliegh wave region [8]. Thus a bowl-like structure is evident in Fig. 7.3 (j). There is a very thick and smooth shell on the edge of the fracture (Fig. 7.3 (k)) and it appears different from the featureless region of a typical amorphous fracture and more like the area 5 framed in red in Fig. 7.3 (h). There are rounded molten droplets on the core fracture surface and evidence of bigger atom cluster fracture.

7.4. Bulk and Surface Magnetic Properties

The bulk static magnetizations of the melt-extracted microwires were measured by VSM with magnetic field along the microwire axis. As shown in I of Fig. 7.4 (a), the bulk coercivity begins to increase from $H_c = 4$ Oe to $H_c = 8$ Oe after the annealing step 160 mA and the permeability slightly enhance. Meanwhile, the coercivity of the surface (Fig. 7.4 (b)) decreases obviously from 10 to 8 Oe with the 140 mA annealing step. Permeability and coercivity are highly sensitive to the microstructure of a material, which are also key role for the GMI performance. This could indicate some improve of magnetic properties of bulk and magnetic softening of the surface for the microwire during annealing processing.

![Figure 7.4](image_url)

Figure 7.4 a) Normalized magnetization curves from VSM for the as-quenched (blue dash), 140 mA (red), 160 mA (green dash) microwires. The inset (I) shows the direction of external magnetic and (II) shows the coercivity at low field. b) Normalized magneto-optical Kerr effect hysteresis loops in the longitudinal geometry of the microwire surface for the as-quenched wire (red dash), 140 mA-treated (solid blue) and 160 mA-treated (green dash).
Figure 7.5 (a-c) presents the AFM, MFM, and MFM scanlines, respectively, of the same region of microwire during each annealing step. In order to ensure the same area for observation after each annealing step, a surface feature located with AFM (shown in area 1 of Fig. 7.5 (a)) marked the center point of the scans. After 100 mA current annealing, micron-sized atomic clusters appear on the surface as seen in area 2 of Fig. 7.5 (a). In the 140 mA annealing stage, another cluster nucleates (area 3) while prior atomic clusters disappear. As the annealing current increase to 160 mA, larger atomic clusters (area 4 and 5) form on the surface. Figure 7.5 (b) shows MFM images of the surface after annealing in situ. While Joule annealing can reduce the defects in the magnetic domain structure as shown in area 6-8 of Fig. 7.5 (b). At the same time, a connection between adjacent domains is seen forming in corresponding area 9 and 10. This has the impact of increasing the surface roughness, decreasing the leakage field level and destroys the periodicity of the domain structure as shown in Fig. 7.5 (c). The magnetic domain structure observed in Fig. 7.5 appears tilted, resulting in a helical anisotropy.

Figure 7.6 (a) shows the definition of the helical anisotropy angle. Longitudinal MOKE was measured on the as-cast microwire under the influence of a 30 mA bias current in opposite polarities as seen in Fig. 7.6 (b). The black curve is a rectangular hysteresis loop with no bias current. The steepness of the transition indicates that domain wall motion, rather than domain rotation, is responsible for the
magnetization reversal. However, when a bias current of 30 mA is applied in one polarity, there is an asymmetric reversal and the remanence near positive saturation. The curved region marked by “1” is indicative of rotational magnetization. This mechanism is induced by the pinning of the helical domain structure by circumferential magnetic field created by the bias current. When the opposite polarity of bias current is applied, as in Fig. 7.6 (c), the domains are pinned again but in the opposite direction. This time the circumferential field generated by the bias current has a weaker influence on the magnetization reversal. This confirms the helical anisotropy observed by MFM.

Figure 7.6 (a) MFM surface domain structure with definition of helical anisotropy angle, θ. (b) Longitudinal MOKE of the microwire with $i_{dc}=+30$ mA (red dash) and $i_{dc}=−30$ mA (blue dash). (c) Schematic of the circular bias field generated by the bias current.

### 7.5. Magnetoimpedance Effect and Skin Depth

The penetration depth of an ac current in a conductor like copper is around 65 μm at 1 MHz. However, in a ferromagnetic conductor with similar resistivity and a high permeability, the penetration depth of the current can drop by an order of magnitude to just a few microns. Therefore, by applying a small magnetic field to increase the permeability of the ferromagnetic conductor, the skin effect will increase significantly and the majority of the current will be distributed in a thin shell. This is the underlying principle of the giant magneto-impedance (GMI) effect. As an investigative tool, the magneto-
impedance spectra in a frequency range of 1-110 MHz will mainly reflect the skin depth change due to the change in magnetic permeability of rotational magnetization processes, since most domain wall movement is damped in microwires starting in the low MHz. One can correlate high permeability to the amorphous magnetic phase, while a decrease in rotational permeability would correspond to a crystalline magnetic phase.

Figure 7.7 a) The change of impedance ratio relative to zero magnetic field for the microwires after each current annealing stage and the applied external DC magnetic field Hex. The corresponding frequency of the measurement is listed in the figure. b) The sensitivity of the microwire after each annealing stage. The change in resistance c) and change in reactance d) relative to zero magnetic field.

The change in impedance relative to zero magnetic field, $\Delta Z/Z_0$, is plotted at the frequency in which the maximum change is reached, $f_K$, in Fig. 7.7 (a) for each annealing stage. The maximum change
in impedance for the as cast microwire is about 51 % at \( f_k = 25 \) MHz as indicated in Fig. 7.7 (a). When the annealing stage reaches 100 mA or \( \sim 515 ^\circ C \) near the core, the maximum change shifts down to 19 MHz. With subsequent annealing stages, as the core temperature approaches \( \sim 691 ^\circ C \) (140 mA), the maximum value of \( \Delta Z/Z_0 \) reaches \( \sim 567 \) %, which is nearly 10 times the as cast value. However, the value is found to reduce to \( \sim 351 \) % after 160 mA annealing step, or a core temperature \( \sim 801 ^\circ C \). The sensitivity of magnetic field, \( \zeta \), is shown in Fig. 7.7 (b). Similar to the \( \Delta Z/Z_0 \), the sensitivity gradually increases to \( \sim 755 \) %/Oe after 120 and 140 mA annealing and decreases after the 160 mA annealing step. As is apparent from Fig. 7.7 (c) and 7.7 (d) both the resistance and inductive reactance have a similar tendency as the impedance.

Figure 7.8 (a) magnifies the low field region of the magneto-impedance curves presented in Fig. 7.8 (a). What is shown here is the linear detection region increases with each annealing step until the 160 mA step. Figure 7.8 (b) shows that the \( H_K \) field, that is the field location of the maximum change in impedance, gradually increases in magnitude with annealing and is symmetric about zero field. The \( f_k \) decreases also with annealing. In Fig. 7.8 (c), the impedance spectra is presented at \( H=0 \) and \( H=H_K \), at the \( H_K \) fields indicated in Fig. 7.8 (b). The most important feature of this plot is the distinct flattening of the impedance at zero magnetic field, while the maximum impedance is more modestly modified by the annealing current.
Figure 7.8 a) The low-field, linear region of the change in impedance shown in the previous figure. b) The value of the effective anisotropy field, $H_K$, and the excitation frequency where the impedance ratio was a maximum. c) The frequency dependence of the impedance at $H_{ex} = 0$ Oe and $H_{ex} = H_K$ for each annealing stage.
In order to understand how the annealing treatment modifies the penetration depth of the excitation current, the skin depth was calculated based on a simple geometrical model using the dc and ac resistance of the microwires after each annealing step. In Fig. 7.9 (a), the modification of the skin depth at 11 MHz by low magnetic fields is shown in the as cast state and after the 100 mA, 140 mA, and 160 mA annealing steps. The maximum change in skin depth coincides with the maximum change in impedance. In Fig. 7.9 (b), the skin depth value at \( f = 11 \text{ MHz} \) is shown at zero magnetic field (red) and near the \( H_K \) field (blue) of each annealing step. The annealing procedure is shown to significantly modify the skin depth at zero magnetic field while only modestly affecting the minimum skin depth value, which occurs near the anisotropy field, \( H_K \).

We recall that the penetration depth of the ac current, called the skin depth, is:

\[
\delta = \sqrt{\frac{\rho}{\pi \mu_\phi f}}. \quad (7.2)
\]

where \( \rho \) is the resistivity, \( \mu_\phi \) is the circumferential ac permeability, and \( f \) is the excitation frequency. The trend of increasing skin depth at \( H_{ex} = 0 \) until maximum annealing current reaches \( i_{dc} = 140 \text{ mA} \), can mean
the following two things in relation to Eq. 7.2: either the resistivity of the skin depth region is increasing or the circumferential ac permeability at $H_{ex}=0$ is decreasing. It is well known that the resistivity of amorphous materials is about 3-5 x greater than their crystalline counterparts. For the skin depth to increase due to resistivity increase (assuming constant $\mu_0$), the outer shell would have to become less crystalline and/or filled with more metalloid content. The SEM images support this conjecture. If we hold $\rho$ as constant, the increase in skin depth would correlate to a decreasing $\mu_0$ at $H_{ex}=0$. Judging by the TEM images of the surface, the nanocrystals grow to 5 nm grain size at $i_{dc} = 140$ mA and reach up to 10 nm at $i_{dc} = 160$ mA. In general, the initial permeability decreases with increasing grain size due to exchange coupling among grains. So this also supports the trend in skin depth with annealing current at $H_{ex}=0$.

The skin depth as a function of annealing current near $H_{ex} = H_K$ has little change as compared to $H_{ex} = 0$ but in this case the skin depth has the opposite trend by decreasing with annealing current. It is assumed that the resistivity does not change with $H_{ex}$. Therefore, the skin depth decrease with annealing near $H_{ex}=H_K$ reflects enhancements to $\mu_0(H_{ex}=H_K)$. This is supported by the MFM images of the surface. The movement of defects and increased uniformity of the surface domain structure observed by MFM points to an increase circumferential ac permeability at the outermost shell region.

7.6. Conclusions

In this study, we sequentially applied a dc current at temperatures below, near, and above $T_g$ to a ~45 ± 1 μm-diameter Co$_{68.15}$Fe$_{1.35}$Si$_{12.25}$B$_{13.25}$Zr$_2$ microwire at ambient temperature and pressure. The microwire was allowed to cool to ambient temperature before the next step was applied. The large specific surface area of these microwires implies a large heat transfer in the radial direction, therefore non-uniform temperature and cooling rate distributions. By starting the multi-step annealing process with low current intensity, low temperature structural relaxation occurs, which is typically mediated by short-range atomic motion. This has the effect of reducing residual stresses trapped in by fabrication and possibly forming more quenched-in nuclei, while leaving the macroscopic glassy nature intact. As the temperature is increased successively, the existing nanocrystals grow in regions of high temperature ($T >$
While in the cooler areas the crystal growth is slower but more quenched-in nuclei are being created. The temperature and cooling rate distribution becomes more important as the current intensity is increased. In the shell region of the microwire, lower temperatures and higher cooling rates preserve the as-quenched structure, while near the core, high temperatures and slower cooling rates ensure crystallization proceeds. The cyclic nature of this pattern, coupled with ultra-fast heating and a radially-dependent temperature and cooling rate distributions, contribute to a core-shell two phase microstructure induced by the multi-step Joule annealing method.

In conclusion, a core-shell phase separation was observed by examination of the fracture morphology of Joule annealed CoFeBSiZr microwires after tensile loading. Using HRTEM, the average size and phase of the crystallites embedded in the amorphous matrix was found. Increase in the crystallite size of the outer shell when the annealing current was increased to \( i_{dc} = 160 \) mA was found to correlate with decreased soft magnetic property and increase in plastic mechanical behavior. Surface and bulk magnetic measurements provided corroboration to our hypothesis of a unique nanocrystalline core/amorphous shell phase separation. Giant magneto-impedance measurements showed a maximum in \( \Delta Z/Z_0 \) of about 600 \% at \( f = 11 \) MHz when the shell structure was approximately \( \sim 3 \) \( \mu \)m thick as seen by SEM (140 mA). Interestingly, the estimated skin depth of the ac current at this frequency is about \( \sim 2 \) \( \mu \)m at \( H_{dc} = H_k \). The high impedance value at this point, along with the small change in \( H_k \) with annealing steps, indicates a soft magnetic behavior from an amorphous magnetic shell.

### 7.7. References


8. CONCLUSIONS AND OUTLOOK

8.1. Summary

The absence of magnetocrystalline anisotropy in rapidly quenched amorphous and nanocrystalline transition metal metallic alloys (TMMAs) provides a landscape for their soft magnetic properties to be controlled and exploited for many technological applications, such as high frequency transformers and sensors operating on the magnetooimpedance effect. Fundamental investigation of the magnetic and structural properties of these materials is also motivated by their unique amorphous or nanocrystalline-embedded amorphous matrix morphology, which has impacts on both the atomic and macro-scale. The use of these materials in high frequency applications, where the skin depth of the excitation field resides near the surface, necessitates surface sensitive probes of magnetism and structure. Therefore, this dissertation focuses on the impact of chemical composition, annealing conditions, and surface coatings on the structure and magnetic surfaces of these materials through multiple surface sensitive techniques such as atomic/magnetic force microscopy, magneto-optical Kerr effect, transmission electron microscopy, and RF frequency magneto-impedance. These tools provide a view into the relationship between the nanostructure, microstructure and soft magnetic properties that make these materials highly desired for fundamental study and technological application.

The effect of glass former Nb content on the magnetoimpedance properties of melt-spun Fe-rich FeCo alloy ribbons of the HITPERM family was investigated. Joule annealing these ribbons at low current intensity to avoid bulk crystallization was performed and surface hysteresis loops by the magneto-optical Kerr effect (MOKE) were measured. The surface of the ribbon without Nb developed a longitudinal magnetic anisotropy while the ribbon with 4 at. % Nb showed an anisotropy more angled to the transverse direction. The relationship between surface anisotropy evidenced by MOKE and the magnetoimpedance response was established. The highest magnetoimpedance ratios were observed for the Nb 4 at. % ribbon with a near-transverse magnetic anisotropy from Joule annealing, which is attributed in part to the surface domain structure observed by MOKE.
The magnetoimpedance effect is thought to be enhanced by a surface domain structure with anisotropy transverse to the current direction, such as a uniaxial domain structure with easy axis along the width of a ribbon. FeNi-based ribbons have a positive magnetostriction constant, therefore after internal stresses experienced during rapid quenching, the surface domain structure is longitudinal. Despite the longitudinal domain structure, FeNi-based ribbons are magnetically soft and have many desirable magnetic and structural properties. In effort to preserve these properties but increase the magnetoimpedance effect, FeNi-based ribbons were coated on both sides with Co, which permits not only a transverse anisotropy but is a harder magnetic material. Upon annealing the Co/FeNi/Co ribbon structure, the influence of the hard surface ferromagnetic material with easy axis along the transverse direction on the magnetoimpedance effect was examined. First the surface sensitive MOKE confirmed a transverse anisotropy of the 120 nm Co layer. It was found that the magnetoimpedance effect increased for the coated ribbon at frequencies below 300 MHz but the anisotropy field remained relatively unchanged. By analysis of components of the complex magnetoimpedance, it was found that the high anisotropy of the Co layer reduced the change in reactance but the lower resistivity of the crystalline Co layer increased the change in resistance with applied field.

Up until this point, the dissertation work was focused on the engineering of improved magnetoimpedance properties of TMMAs in ribbon geometry through compositional changes, annealing, and coatings. The second half of this dissertation investigated the fundamental magnetic behavior of negative magnetostrictive Co-based microwires through observation of domain structure at the surface using magnetic force microscopy (MFM), MOKE, and magnetoimpedance. In CoFeSiBZr microwires with varying Zr content, the surface domain structure was examined through MFM. A model of the domain structure on the surface was presented and linked to the observations. A domain structure with uniaxial circumferential anisotropy was observed for all wires with varying degrees of uniformity and domain periods. The domain wall period increased with Zr content but the magnetoimpedance response did not show the monotonic tendency with Zr. The substitution of Zr for B reduces metalloid content and
creates more nucleation sites in the wire. The anisotropy field did not substantially increase until \( x = 2 \) at.
\( \% \), where the surface roughness evidenced by AFM was found to jump from a few nm to over 10 nm at \( x = 2 \) and 3 at. \( \% \). The increased surface roughness and magnetostatic contribution was suggested to play a larger role in the deterioration of the magnetoimpedance effect than the increase of domain period due to reduced surface anisotropy. For the \( x = 0 \) and 1 at. \% samples, with similar surface roughness, an increase in domain period was attributed to a decrease in surface anisotropy with the support of high magnetoimpedance ratio and low \( H_K \) over a wide frequency range.

The evolution of the surface nanostructure of negative magnetostrictive \( \text{Co}_{68.15}\text{Fe}_{4.35}\text{Si}_{12.25}\text{B}_{13.25}\text{Zr}_{2} \) microwires after different stages of stepped Joule annealing is examined with transmission electron microscopy in conjunction with MFM images. After tensile loading until fracture, cross-sectional scanning electron microscopy images showed a fracture pattern consistent with a two-phase core-shell microstructure. The mechanism behind the two-phase microstructure was attributed to a radial temperature distribution during Joule annealing which promoted a cyclical pattern where low temperatures and high cooling rates near the surface ensured a primarily amorphous microstructure and higher temperature and slower cooling rates promoted crystalline phase development. When the shell was \( \sim 3 \) \( \mu \text{m} \) thick, magnetoimpedance ratios were their highest. The skin depth, estimated based on the real part of the magnetoimpedance, showed the greatest change from \( \delta = 12 \) \( \mu \text{m} \) at \( H_{ex} = 0 \) to \( \delta = 2 \) \( \mu \text{m} \) at \( H_{ex} = H_K \). This suggested that a two-phase microstructure can promote the magneto-impedance effect if the external dc field drives the penetration depth from a harder crystalline magnetic phase to a softer, amorphous phase.
8.2. Outlook

The demand for room temperature weak magnetic field detection for a variety of applications such as nanomedicine, nanobiology, aerospace, etc. will drive continued research into exploitation of the ultrasoft magnetic properties of TMAAs. However, without more interest from large technology companies, which are mainly concerned with mass production and sale of devices, the vein of research concerning the optimization of magnetic properties of TMAAs will begin to thin out. Co-rich microwires mounted on a chip for geomagnetic field sensing have been commercially available for nearly two decades, but these devices have remained in local Asian markets and have not hit the mainstream. One major challenge to the development of Co-rich microwires for use in ultra-sensitive magnetic field sensing is related to their fabrication. Rapid quenching techniques can produce materials with inconsistent material and magnetic properties on a mass production scale, especially when compared to thin film sputtering. Nonetheless, the magnetoimpedance effect can be a useful tool to probe the magnetization dynamics in a selective region near the surface of a sample. Coupled with other surface-sensitive techniques, such as MOKE and MFM, there remains a landscape rich in fundamental physics and materials science to explore on both the nanoscale and macroscale.
APPENDIX A: List of Publications


APPENDIX B: List of Conference Presentations


APPENDIX C: Patents

1. USF 16B173PRWO.


   Title: “MAGNETO-LC RESONANCE TECHNOLOGY FOR REAL-TIME RESPIRATORY MOTION MONITORING”

   Inventors: Ongard Thiabgoh, Tatiana Marie Eggers, and Manh-Huong Phan

   MBF File No. 210112-9008-US01


   Title: “DETECTING MAGNETIC NANOBiomARKERS USING A SINGLE GIANT MAGNETO-IMPEdANCE MICrowire”

   Inventors: Ongard Thiabgoh, Tatiana Marie Eggers, and Manh-Huong Phan

   Status (in preparation)