Understanding the effects of rapid solidification and ternary alloying additions on chemical order-disorder transformation in FeNi₃

A Thesis Presented

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Abstract

Owing to their unusual thermal expansion behavior and good magnetic permeability characteristics, iron-nickel alloys are often at the cutting-edge of technology. Understanding the chemical order-disorder phase transformation and its effects on the physical properties of these alloy systems have been a longstanding research challenge in materials science and engineering. In keeping with current research, the motivation of this thesis is to study the effect of rapid solidification and ternary alloying additions on the chemical order-disorder phase transformation in the FeNi$_3$ compound. Results obtained from this study will inform factors affecting chemical ordering in specific compositions of iron-nickel alloys which undergo this type of phase transformation.

Chemical ordering in FeNi$_3$ occurs at $T_{OD} = 490 \pm 10$ °C and changes the crystal structure of this compound through short-range diffusion from the A1 structure (chemically-disordered phase in which the iron and nickel atoms can occupy any atomic site in an fcc structure) to the L1$_2$ structure (chemically-ordered fcc phase with specific atomic sites for iron and nickel atoms). Understanding the effect of rapid solidification through the melt-spinning process conducted prior to isothermal annealing as well as the influence of ternary alloying elements on the variation of the degree of chemical ordering in pure FeNi$_3$ are the objectives of this thesis.

Coupled calorimetry and magnetic measurements show that rapid solidification prior to isothermal annealing at $T = 470$ °C does not influence the progression of L1$_2$ phase formation in pure FeNi$_3$. These same studies reveal that addition of both Mn and Cu affects the formation of chemically ordered L1$_2$ phase in FeNi$_3$ during isothermal annealing at $T = 470$ °C; however, this effect is different for each of these elemental substitutions. A larger increase in the degree of chemical ordering, the saturation magnetization, and the saturating filed values as well as a
greater decrease in the susceptibility values of Mn-substituted FeNi$_3$ relative to those of the pure FeNi$_3$ sample upon annealing have been measured in this study. Therefore, it is hypothesized that Mn addition promotes the A1-to-L1$_2$ phase transformation in FeNi$_3$ through replacing the Fe atoms in the lattice structure of this compound and producing partially formed MnNi$_3$-L1$_2$ phase. On the other hand, a smaller increase in the degree of chemical ordering, the saturation magnetization, and the saturating field values as well as a smaller decrease in the susceptibility values measured for Cu-substituted FeNi$_3$ upon annealing compared to those measured for pure FeNi$_3$ ingot sample have been detected. Thus, Cu addition delays the progression of chemical ordering in FeNi$_3$. This effect is tentatively attributed to Cu atoms leaving the FeNi$_3$ lattice during isothermal annealing due to immiscibility of Fe and Cu atoms.
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1.0 INTRODUCTION

The overall goal of this thesis is to examine the role of rapid solidification and ternary alloying elements on the A1-to-L1₂ chemical order-disorder phase transformation in FeNi₃ compound. The FeNi₃ compound is selected as a model system to investigate, understand, and predict the factors affecting chemical order-disorder transformation in the various compositions of iron-nickel alloys which undergo the same phase transformation.

A crystalline chemically-ordered phase is one in which each atom resides at particular specified lattice positions, while chemically-disordered phases are solid solutions in which the probability of finding a particular element at any lattice position is equal to its concentration. FeNi₃ adopts the chemically-ordered face-centered-cubic (fcc) L₁₂ structure that features iron atoms at the corner lattice positions and nickel atoms at the face-centered sites (see Fig. 1(a)). The chemical order-disorder transformation in FeNi₃ occurs at a critical temperature $T_{OD} = 490 \pm 10 \, ^\circ\text{C}$ [1,2], on heating through $T_{OD}$. During this transformation the chemically-disordered fcc A₁-type structure is formed from the L₁₂ phase via short-range diffusion such that the iron and nickel atoms become randomly located in the lattice positions with probabilities equal to their concentrations (Fig. 1(b)).
Figure 1: Schematic representation of FeNi$_3$ in its (a) chemically-ordered L1$_2$ structure, and (b) chemically-disordered A1 structure.

In the research discussed in this thesis, pure and elementally-substituted ingot samples as well as pure ribbons of FeNi$_3$ were synthesized through arc-melting and melt-spinning techniques. Isothermal annealing was then performed at $T = 470$ °C for two weeks (366 h) on all the samples. Evaluation of the A1-to-L1$_2$ phase transformation was done through structural, magnetic and calorimetry measurements of samples in their as-made and annealed states. Comparing the structural, magnetic, and calorimetry results obtained from pure ingot with those of the ribbon sample to study the effect of rapid solidification through melt-spinning on the chemically-ordered phase (L1$_2$) formation in FeNi$_3$ is in the fulfillment of the first objective of this research study. The same measurements have been carried out on the as-arc-melted and annealed pure and elementally-substituted FeNi$_3$ samples to examine the role of ternary alloying additions on the formation of chemically-ordered phase in FeNi$_3$. These results are in satisfaction of the second objective of this thesis project.

Results from experimental studies carried out on the pure ingot and ribbon samples in their as-made and annealed states are summarized here. The XRD patterns of samples have no evidence of chemically-ordered phase (L1$_2$) formation upon annealing which is
likely due to the utilization of Cu-Kα radiation in the laboratory measurement studies. Calorimetry results indicate that isothermal annealing at $T = 470 \, ^\circ C$ for two weeks has an essential role on the formation of L1$_2$ phase in both ingot and ribbon samples. Furthermore, the experimentally-determined enthalpy of the L1$_2$-to-A1 phase transformation indicates that the ingot sample of FeNi$_3$ contains a higher degree of chemical order than the ribbon sample in both as-made and annealed states. Field-dependent magnetic measurements of samples confirmed the calorimetry results by showing larger values of saturation magnetization and anisotropy field ($H_K$) for annealed pure ingot sample compared to those of the annealed ribbons.

Results from investigations of the role of ternary alloying additions of A1-to-L1$_2$ phase transformation in FeNi$_3$ are summarized here. Adding 2 at.% Cu or Mn doesn’t change the structural and magnetic properties of FeNi$_3$ significantly in the as-made state. Coupled calorimetric and magnetic analyses indicate that while Mn-substitution promotes the formation of L1$_2$ phase in FeNi$_3$ during isothermal annealing, Cu-substitution suppresses the formation of this phase.

This thesis consists of seven chapters: (1) Introduction; (2) Critical Literature Review; (3) Objectives; (4) Experimental Procedures and Techniques; (5) Results; (6) Discussion and Conclusions; (7) Recommendations for Future Work; and (8) References. The current chapter, Introduction, provides an introduction to the problem statement and motivation for this research study. Chapter (2) provides the reader with fundamental background regarding different types of order-disorder phase transformations. Chapter (3) presents the objectives of this thesis. In Chapter (4), the experimental techniques used to characterize the chemical, structural, magnetic, and thermal properties of pure and
elementally-substituted FeNi₃ samples are discussed. Experimental results aimed to study the effect of rapid solidification and ternary alloying additions on the formation of L1₂ phase in FeNi₃ are presented in Chapter (5); these results will be then analyzed and discussed in Chapter (6). Recommendations for future experiments are briefly presented in Chapter (7).
2.0 CRITICAL LITERATURE REVIEW

In this thesis, studies focused on understanding the factors influencing the A1-to-L12 phase transformation in FeNi$_3$ compound provides guidance for tailoring chemical ordering phase transformation in this compound, with possible extensions to other compositions of iron-nickel alloys which undergo this type of phase transformation. To this end, this chapter provides a comprehensive review of background information and literature which are relevant to this thesis.

This critical literature review has been divided into 2 primary sections to provide an overview of chemical order-disorder phase transformation in FeNi$_3$ through structural, magnetic, and calorimetric studies of this compound. In the first section (Section 2.1), different types of order-disorder phase transformations will be discussed. Section 2.2 will extend this discussion by addressing an overview of the FeNi$_3$ compound and the factors which can alter the degree of chemical ordering in this system.

2.1 Overview of Order-Disorder Phase Transformations

Two types of ordering phase transformations are discussed in this thesis: magnetic ordering and chemical ordering. Magnetic ordering, Section 2.1.2, describes the coupling of magnetic moments within a material that can result in ferromagnetic behavior. Chemical ordering transformation describes the rearrangement of randomly-distributed atoms in a crystal lattice to form an organized structure in well-defined atomic lattice positions as described in Section 2.1.1.
2.1.1 Magnetic ordering phase transformations

This thesis is concerned with the structural-magnetic properties of FeNi$_3$ as a ferromagnetic material. In a ferromagnetic material, the atomic moments couple to each other to produce a positive net magnetization, $M$, and cooperatively align so that there is a long-range magnetic ordering of the atomic moments [3]. The magnetic phase transition from ferromagnetism to paramagnetism upon heating which is equivalent to a change from magnetic long-range ordering to magnetic disordered is called the Curie transition. The Curie temperature, $T_C$, is the ferromagnetic order-disorder temperature. Magnetic moments in the ferromagnetic materials are coupled and aligned causing a positive net magnetic moment below $T_C$. As the temperature increases towards $T_C$, entropy effects cause disordering of magnetic moments [3].

2.2.1 Chemical ordering phase transformations

Chemical order refers to periodic arrangement of A and B atoms in the specific crystal structure of the solid solution made by these atoms. Chemical ordering in a randomly structured substitutional solid solution of A and B atoms starts at a certain critical temperature, $T_{OD}$, upon cooling and takes place by rearrangement of atoms through short-range diffusion in an orderly periodic manner in the lattice sites.

The conclusive evidence of ordered atomic arrangements, or superstructures as they are called, is furnished by the presence of “superstructure lines” on x-ray diffraction patterns. A periodic arrangement of atoms (superstructure) in AB alloy under examination of an x-ray beam is schematically shown in Fig. 2. Atoms of A and B are arranged in regular array in $\alpha$ and $\beta$ sites respectively. An atom A is called “right” when in an $\alpha$-site and “wrong” when in a $\beta$-site; and similar definitions apply to B atoms. The
occurrence of these superstructure lines in XRD patterns obtained from examining a material is a positive proof of the existence of a superstructure and to some extent their intensity is a measure of its approach to perfection. The x-ray beam, which falls on the perfectly ordered crystal in Fig. 2, is reflected in such a way that its path length difference between two planes of $\alpha$-sites is one wave-length and between adjacent $\alpha$- and $\beta$-planes, one-half wave-length. In this manner, the waves in the outgoing beam scattered by the A atoms will all be exactly in phase with each other and exactly out of phase with those scattered by the B atoms. If the scattering factors of the two kinds of atoms are different, based on Bragg law which is explained in Chapter 4, the opposing waves will not cancel and a line will result on the x-ray plate. Such lines, the occurrence of which is contingent upon the presence of a superstructure, are appropriately known as “superstructure lines”.

![Figure 2: Superstructure and region of superstructure lines](image)

Randomly arrangement of atoms in the unit cell of AB alloy results in equal numbers of A and B atoms upon the $\alpha$-sites and the $\beta$-sites. Therefore, the $\alpha$-sites give rise to scattered waves whose amplitude is the average for A and B atoms and the same
are true of the β-sites. The α and β scattered waves now being equal in amplitude cancel each other completely and no line appears on the plate [4].

This thesis is concerned with the chemical ordering phase transformation (A1→L12) in FeNi3. Since there is only a very slight change in the size of the unit cell and none in the shape upon this transformation, there is practically no change in the positions of the diffraction lines of FeNi3 with chemical ordering. However, the change in the position of the atoms must necessarily cause a change in line intensities which can be determined by calculating the structure factor for each atom arrangement [5]. The atomic scattering factors of a chemically-disordered (a) and a chemically-ordered (b) FeNi3 compound are calculated here:

a) The atomic scattering factor of a chemically-disordered structure of FeNi3 is assumed to be the “average” scattering factor of iron and nickel atoms in this structure.

\[ f_{\text{ave}} = (\text{atomic fraction Fe}) \, f_{\text{Fe}} + (\text{atomic fraction Ni}) \, f_{\text{Ni}} = \frac{1}{4} f_{\text{Fe}} + \frac{3}{4} f_{\text{Ni}} \]  

where:

- \( f_{\text{ave}} \) = Average scattering factor of Fe and Ni atoms
- \( f_{\text{Fe}} \) = Atomic scattering factor of Fe
- \( f_{\text{Ni}} \) = Atomic scattering factor of Ni

There are four “average” atoms per unit cell located at 000, \( \frac{1}{2} \frac{1}{2} 0 \), \( \frac{1}{2} 0 \frac{1}{2} \), and \( 0 \frac{1}{2} \frac{1}{2} \), which results in the structure factor given by:

\[ F = \Sigma f \, e^{2\pi i(hu + kv + lw)} = f_{\text{ave}} \left[ 1 + e^{2\pi i(h+k)} + e^{2\pi i(h+l)} + e^{2\pi i(k+l)} \right] \]

\[ F = 4f_{\text{ave}} = (f_{\text{Au}} + 3f_{\text{Cu}}) \quad \text{for hkl unmixed}, \]

\[ F = 0 \quad \text{for hkl mixed}. \]
Thus, the disordered alloy produces a diffraction pattern similar to that of any face-centered-cubic metal and no reflections of mixed indices are present.

b) Each unit cell of completely ordered FeNi$_3$ contains one Fe atom located at 0 0 0, and three Ni atoms located at $\frac{1}{2}$ $\frac{1}{2}$ 0, $\frac{1}{2}$ 0 $\frac{1}{2}$, 0 $\frac{1}{2}$ $\frac{1}{2}$. Therefore the atomic scattering factor of a chemically-ordered FeNi$_3$ is:

$$F = f_{\text{Au}} + f_{\text{Cu}} [e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}];$$

$$F = (f_{\text{Au}} + 3f_{\text{Cu}}) \quad \text{for hkl unmixed,}$$

$$F = (f_{\text{Au}} - f_{\text{Cu}}) \quad \text{for hkl unmixed.}$$

The chemically-ordered alloy thus produces diffraction lines for all values of hkl, and its diffraction pattern therefore resembles that of a simple cubic substance. In other words, there is a change of Bravais lattice on chemical ordering; the Bravais lattice of the chemically-disordered alloy is face-centered-cubic (fcc) and that of the chemically-ordered alloy simple cubic, Fig. 3.
The chemical ordering process may, in general, be accomplished either by annealing for some time at a steady temperature below the critical ordering temperature or by cooling at a fixed rate through a wide temperature range, for example from just above to well below the critical temperature [1]. The chemical ordering of FeNi₃ has been usually performed by isothermal annealing at $T = 450 \, ^\circ C – 490 \, ^\circ C$ for one to two weeks [7,8], or by slow cooling (0.2 – 0.8 $^\circ C/h$) from $T = 490^\circ C$ to $T = 370 \, ^\circ C$ [1,9,10].

Chemical disordering can be achieved by either performing cold work on the chemically-ordered alloy or by heating it above its ordering temperature. The first effect of increasing the temperature is to increase the amplitude of thermal vibration of the
atoms about their equilibrium positions. When this vibrational amplitude becomes large enough, small groups of atoms gain sufficient energy to break away from their places in the lattice and interchange positions with each other. This interchanging results in a certain number of atoms becoming an A atom on a $\beta$-site or a B-atom on an $\alpha$-site [4].

2.2.1.1 Manifestations of chemical ordering

Thermal and physical properties which are profoundly influenced by the state of chemical order in an alloy can be used to study the chemical order-disorder transformation and deduce the presence of chemically-ordered structures. This indirect evidence can be achieved through measurements of specific heat, electrical resistivity, calorimetry, and magnetic character of an alloy [4].

**Specific heat:** The energy required to move the atoms into wrong positions in opposition to the chemical ordering force, is an excess energy which manifests itself as an “abnormal specific heat”. This excess energy is a heat capacity, in addition to what is predicted on the basis of the Dulong-Petit law for ordinary thermal motion [11], and is associated with the arrangement or configuration of the atoms in the lattice and referred to as “configurational specific heat”. Configurational specific heat increases from zero to a maximum value just below $T_{OD}$, fig. 4. The contribution for $T > T_{OD}$ comes from the local order which continues to require energy for decreasing at higher temperature [4].
In case x-ray diffraction does not detect the superstructure peaks in an alloy, the existence of such specific heat curve can be indirect evidence for existence of a superstructure. Therefore, such a measurement furnishes an important tool for investigating superstructures [4].

**Electrical resistivity:** Electrical resistivity (also known as resistivity, specific electrical resistance, or volume resistivity) is an intrinsic property that evaluates how strongly a given material prevents the flow of electric current [13]. One of the most common methods investigated for estimating the degree of order is measuring the electrical resistivity which is drastically affected by chemical ordering. Unlike measurements of the intensity of the superstructure lines, electrical resistivity measurements can provide a good estimation of the degree of long-range order for a uniformly ordered alloy [4].

Sykes and Jones found the correlation between the degree of chemical ordering and electrical resistivity in AuCu$_3$ compound. They showed that on slow cooling of a quenched specimen of AuCu$_3$ from high temperature, there is a significant drop in
electrical resistivity at the same temperature at which isothermal annealing leads to
detection of the L12 superstructure Bragg peaks [12], Fig. 5.

Figure 5: Electrical resistivity vs. temperature for an
AuCu3 alloy [12].

Magnetic properties: The magnetic properties of ferrous alloys change with the
progression of chemical ordering in such alloys; this change appears in the values of the
saturation magnetization, the magnetocrystalline anisotropy and the Curie temperatures
of these alloys [14], as described in following paragraphs:

a) Saturation magnetization: Saturation magnetization is an intrinsic property of
ferromagnetic and ferrimagnetic materials and is defined as the state reached when an
increase in applied external magnetic field (H) cannot increase the magnetization of the
material further [15]. The magnetic saturation intensity of a ferromagnetic alloy in the
chemically-ordered state is different from that of the chemically-disordered alloy, and may be used, therefore, to examine the degree of order in such an alloy [16–18].

\textbf{b) Curie temperature:} The Curie temperature is the critical temperature at which a material loses its ferromagnetic characteristics and turns to a paramagnetic material [15]. The Curie temperature is another intrinsic magnetic property of ferrous alloys which can be varied by chemical ordering transformation. This variation can result in an enhancement or a reduction of the Curie temperature depending on the alloy and the type of chemical ordering phase transformation [18]–[21].

\textbf{c) Magnetocrystalline anisotropy:} In a crystal lattice, the electron magnetic moment is affected by the interatomic bonds and some orientations of the electron moment may be energetically favorable causing magnetization to occur along particular crystal axes known as the easy axes. This direction dependence of magnetization in a ferromagnetic material is called magnetocrystalline anisotropy. Chemical ordering can have a large effect on the magnetocrystalline anisotropy of some material systems which undergo an order-disorder phase transformation such as Fe-50 at.% Ni or Fe-50 at.% Pd [16–18].

Magnetic measurements along three important crystallographic directions ((111), (110), and (100)) for a ferromagnetic material with face-centered-cubic (fcc) structure is shown in Fig. 6. The field required for a material to reach saturation magnetization (anisotropy field) has a minimum value when measured along the easy axes ((111) direction for fcc structure) and a maximum value when measure along the hard axes ((100) for a fcc structure), as shown in Fig. 6 [15].
Figure 6: Magnetization curve for single crystal of a ferromagnetic material with fcc structure [15].

The directional dependence of the anisotropy can be expressed by the anisotropy energy $E_K$ as a function of the anisotropy constants and directional cosines as shown in equation (2):

$$E_K = K_0 + K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_2 (\alpha_1^2 \alpha_2^2 \alpha_3^2) + \ldots$$  \hspace{1cm} (2)

Where: $K_0, K_1, K_2, \ldots$ = anisotropy constants for a particular material at a particular temperature (erg/cm²)

$\alpha_1, \alpha_2, \alpha_3, \ldots$ = the angles between $M_S$ and the crystal axes (degree)

2.2.1.2 A1-to-L1₂ phase transformation

A1-to-L1₂ phase transformation, which is specifically discussed in this thesis, is a type of chemical ordered-disorder phase transformation that occurs in $AB_3$ compounds such as $\text{AuCu}_3, \text{FeNi}_3, \text{FePd}_3, \text{FePt}_3, \text{MnNi}_3$, etc. The first A1-to-L1₂ transformation was
detected for AuCu$_3$ [23] and SiFe$_3$ [24] by use of x-ray diffraction analysis. During this type of phase transformation a chemically-disordered fcc structured AB$_3$ phase in which atoms are randomly placed in the lattice sites transforms to a chemically-ordered phase in which A atoms are placed in the lattice corners and the B atoms in the face-centered sites of the lattice, Fig. 7.

![Figure 7: Schematic representation of AB$_3$ in its (a) chemically-ordered L1$_2$ structure, and (b) chemically-disordered A1 structure.](image)

Figure 7: Schematic representation of AB$_3$ in its (a) chemically-ordered L1$_2$ structure, and (b) chemically-disordered A1 structure.
2.2 **Overview of the FeNi₃ system**

This thesis is primarily concerned with the A1→L₁₂ phase transformation in the FeNi₃ material system. The specific structural and magnetic properties of A1- and L₁₂-structured FeNi₃ are discussed in the following sections.

2.2.1 **FeNi₃ Phase diagram**

Stability of the L₁₂ phase in the FeNi₃ is examined in the context of the Fe-Ni phase diagram, Fig. 8. The Phase diagram of Fe-Ni alloys exhibits two different solid phases for the Fe-75 at.% Ni composition (FeNi₃) upon cooling from the liquid phase. The first phase which appears at about 1450 °C is the “γ (FeNi₃)” phase with the face-centered-cubic (fcc) structure and is stable to about T = 490 °C. Formation of the chemically-ordered L₁₂, which starts at T = 490 °C, is dependent on the rate of cooling process.

![Figure 8: Calculated Fe-Ni phase diagram](image)

---

**Figure 8: Calculated Fe-Ni phase diagram** [25]
2.2.2 FeNi$_3$ crystal structure

FeNi$_3$ adopts the chemically-ordered face-centered-cubic (fcc) L1$_2$ structure that features iron atoms at the corner lattice positions and nickel atoms at the face-centered sites (see Fig. 1(a)). On heating through a critical chemical order-disorder temperature $T_{OD} = 490 \pm 10 \degree C$ [1,2] the chemically-disordered fcc A1-type structure is formed from the ordered L1$_2$ phase via short-range diffusion such that the iron and nickel atoms become randomly located in the lattice positions with probabilities equal to their concentrations (Fig. 1(b)).

2.2.3 Magnetic properties of FeNi$_3$

FeNi$_3$ is in the vicinity of the permalloy composition (Fe-78 at.% Ni) and possesses similar magnetic properties to this compound. Permalloy is notable for its very high magnetic permeability, which makes it useful as a magnetic core material in electrical and electronic equipment [26]. FeNi$_3$ is a soft magnet (saturation magnetization is achieved in weak applied field) with saturation magnetization values in the range of 110-120 emu/g depending on the utilized fabrication and post-synthesis methods [1,9,27]. It typically possesses a high maximum and initial permeability and a low coercivity close to zero.

2.2.4 Chemical ordering in FeNi$_3$: the A1-to-L1$_2$ phase transformation

The presence of a superlattice in FeNi$_3$ cannot be readily detected due to the similarity in scattering power of Fe (26) and Ni (28). The small difference can be enhanced by using a radiation near to the absorption edge of Fe, since as shown in Fig. 8, in this region the scattering power varies in an anomalous manner with wave-length [8]. Based on the position of each radiation as compared to the absorption edge of Fe shown
in Fig. 9, the most suitable radiations for detecting the superstructure peaks in iron-nickel alloys are Fe-\(K_\beta\), Co-\(K_\alpha\), and Ni-\(K_\alpha\). However, another term that needs to be considered is the mass absorption coefficient of FeNi\(_3\) for these radiations. Table 1 shows the values of mass absorption coefficient of FeNi\(_3\) for various characteristic wavelengths in diffraction [5]; even though Ni-\(K_\alpha\) radiation wavelength is close to the absorption edge of Fe, but, the value of mass absorption coefficient of FeNi\(_3\) for this radiation is a large number. This means that using Ni as radiation source in the X-ray diffraction will cause reduction in intensity of XRD peaks (including the superstructure peaks) in the diffraction pattern of FeNi\(_3\). Thus, Co-\(K_\alpha\) and Fe-\(K_\beta\) radiations are the most suitable ones in detecting the superstructure peaks in iron-nickel alloys. For instance, for Co-\(K_\alpha\) radiation the scattering power of Fe is considerably depressed (by about 4 units) while that of Ni is only slightly affected [9].

![Figure 9: Atomic scattering factors of Fe and Ni as a function of wavelength scale are marked the positions of the \(K_\alpha\)- and \(K_\beta\)-rays from Cu, Ni, Co and Fe [8].](image-url)
Table 1: Values of mass absorption coefficient of FeNi₃ for various characteristic wavelengths used in diffraction [5].

<table>
<thead>
<tr>
<th>Radiation</th>
<th>Mo-Kα</th>
<th>Zn-Kα</th>
<th>Cu-Kα</th>
<th>Ni-Kα</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ = 0.711 Å</td>
<td>391.245</td>
<td>2697.943</td>
<td>997.045</td>
<td>1225.58</td>
</tr>
<tr>
<td>Co-Kα</td>
<td>λ = 1.790 Å</td>
<td>Fe-Kα</td>
<td>Mn-Kα</td>
<td>Cr-Kα</td>
</tr>
<tr>
<td>λ = 1.937 Å</td>
<td>617.429</td>
<td>763.419</td>
<td>651.6</td>
<td>1192.355</td>
</tr>
</tbody>
</table>

Many investigations of the chemical ordering phase transformation in FeNi₃ have been carried out by measurements of characteristic properties such as electrical resistivity, magnetic and thermal properties. Dahl [28] was the first person who suggested the existence of an order-disorder transformation in FeNi₃ (A1→L₁₂) when he observed the similarity in resistivity behavior of quenched and furnace-cooled samples of AuCu₃ with those of FeNi₃ alloy. This observation was a proper educational guess but not a conclusive proof for existence of order-disorder transformation in FeNi₃. Another strong support for superstructure theory occurs in the specific heat measurements of Kaya [29]; he found a sharp maximum in the specific heat results of the furnace-cooled FeNi₃ sample, while for the quenched sample of this compound, the maximum was much lower. He then tried to detect the superstructure using Ni-Kα radiation, but his attempt was unsuccessful due to choosing the inappropriate radiation source.

In another attempt, Haworth used Fe-Kα radiation to detect the superstructure lines in samples containing 70 at.% Ni which had been annealed for 100 hours at T = 425 °C [8], however, could not detect any superlattice peak. He concluded that no superlattice
exists in FeNi$_3$ of sufficiently long range to form an X-ray diffraction pattern. Although
the kind of radiation that he used was suitable enough [8], experiments carried out on
materials of the FeNi$_3$ type containing less nickel show that the transformation becomes
very sluggish as a result of this modification and it is conceivable that the specimen used
by Haworth would not transform sufficiently in any reasonable period of time for
superlattice lines to be observed [9].

Leech was the first one who provided x-ray evidence for existence of superstructure
in FeNi$_3$ using Co-K$_\alpha$ radiation of a sample containing 75.04 at.% nickel which had been
cooled from $T = 490^\circ$C to $T = 370^\circ$C in 150 h (cooling rate of 0.8 °C/h) [9]. He also
showed a big difference in the heat capacity values of furnace-cooled and quenched
samples of this alloy which was an indirect evidence for existence of superstructure in
FeNi$_3$. In the same study, Leech evaluated the effect of annealing time on the degree of
chemical ordering in FeNi$_3$. He performed isothermal annealing on FeNi$_3$ samples at $T =
490^\circ$C for 200 h and 500 h and observed no change in the values of the enthalpy of
chemical disordering considering the measurements’ error for these samples. Thus, he
concluded that chemical ordering phase transformation in FeNi$_3$ is completed after 200 h
annealing of this compound at $T = 490^\circ$C. He measured the enthalpy of chemical
disordering for a perfectly ordered sample of FeNi$_3$ as $13.8 \pm 0.5$ Cal/g ($57 \pm 2$ J/g).
Leech’s report on the enthalpy of chemical disordering of a completely ordered FeNi$_3$
sample is used in order to estimate the degree of chemical ordering in the samples
fabricated in this thesis. Furthermore, Leech observed a feature indicating the magnetic
disordering (Curie temperature) in calorimetry studies of a quenched sample of FeNi$_3$
which also appeared in the calorimetry results of a furnace-cooled sample. Therefore, he
concluded that there is no change in Curie temperature of FeNi$_3$ upon progression of chemical ordering in this compound. Magnetic measurements by Leech showed that saturation magnetization value of a chemically ordered sample of FeNi$_3$ is 5% more than that of the chemically disordered sample of this compound.

McKeehan [10] has measured the magnetic properties of slowly (from 500 °C to 430 °C during 22 days) and rapidly cooled spheroid-shape single crystals of FeNi$_3$ along three main crystallographic directions ((111), (110), and (100)). Results of his measurements revealed that the field required to reach saturation magnetization (anisotropy field) is different when measured along the different crystallographic directions for slowly-cooled FeNi$_3$ sample while it is the same along all the directions for rapidly-cooled sample of FeNi$_3$. Based on this observation, McKeehan concluded that the magnetocrystalline anisotropy of FeNi$_3$ increases upon increase in the degree of chemical ordering in this compound and this can be an indirect evidence of superstructure formation in FeNi$_3$. He also noted that saturation magnetization of slowly-cooled FeNi$_3$ in all the directions is 3% higher than that of the rapidly-cooled sample of this compound.

Grabbe [27] has performed the same measurements as McKeehan on single crystals of iron-nickel alloys with different compositions. He showed that FeNi$_3$ has the maximum change in magnetocrystalline anisotropy and saturation magnetization upon chemical ordering phase transformation in this compound [30].

Iida conducted systematic experiments to study and understand the kinetics of chemical ordering phase transformation in FeNi$_3$ [31–33]. He investigated the chemical order-disorder transitional behavior of FeNi$_3$ by measuring the change in internal energy of samples annealed at $T = 490$ °C for different time durations [31]. He concluded from
this study that development of chemical ordering in FeNi$_3$ starts with formation of short-range order and proceeds to build up the long-range order. Iida then continued his research on FeNi$_3$ with theoretical and experimental studies of progression of the short- and long-range chemical ordering through specific heat studies of this compound. He showed experimental proof for his previous assumption regarding the existence of short-range chemical ordering above $T_{OD}$ which has no critical temperature of formation; On the other hand, formation of long-range chemical ordering has a critical temperature ($T_{OD}$) and it comes into action only below this temperature [32].

Wakelin has studied the structure-magnetism correlations in iron-nickel alloy systems. Results of his study on FeNi$_3$ showed that the Curie temperature of a 50%-80% chemically-ordered FeNi$_3$ sample is about 80 °C higher than that of the chemically-disordered FeNi$_3$. It is noted that Wakelin’s results regarding the change in Curie temperature upon chemical ordering in FeNi$_3$ are no consistent with those of Leech’s study [9]. When an alloy can exist in either an ordered or disordered state, the lattice spacing as measured by x-ray diffraction methods is found to be different in the two cases [1]. The variation in lattice parameter of the quenched and annealed powder samples of iron-nickel alloys which were detected by Wakelin, shows that the maximum difference between the ordered and disordered alloy occurs at Fe-75 at.% Ni (FeNi$_3$) among different compositions of Fe-Ni alloys [1].

Bozorth has measured the anisotropy constant of quenched and furnace cooled iron-nickel alloys containing 30-100 at.% Ni and showed lower (more negative) anisotropy constant especially in the range of composition near FeNi$_3$ at which a deep minimum occurs [34]. In the same study by Bozorth, he also reported on enhancement in anisotropy
constant of FeNi$_3$ with decreasing the cooling rate with which this compound has been cooled from critical ordering temperature, Fig. 10(a) [34]. As reducing the cooling rate leads to increase in the degree of chemical ordering in FeNi$_3$, it can be said that L1$_2$ phase has higher magnetocrystalline anisotropy than A1 in FeNi$_3$. Considering the FeNi$_3$ sample with highest value of magnetocrystalline anisotropy as the 100% chemically ordered sample and the one with anisotropy constant close to zero as the 100% chemically disordered FeNi$_3$ sample, a curve can be extracted from Bozorth’s results on the correlation between magnetocrystalline anisotropy and the cooling rate with which the FeNi$_3$ has been cooled from $T_{OD}$, Fig. 10(b).

Takahashi performed systematic structural, thermal, and resistivity measurements on quenched and annealed samples of FeNi$_3$ to study the chemical order-disorder transformation in this compound [36]. He measured the maximum enthalpy of chemical
disordering transformation as 78 J/mol (45 J/g) for a sample which was annealed at $T = 455 \, ^\circ\text{C}$ for 8 days. He then detected the superstructure lines for annealed FeNi$_3$ samples using Cu-K$\alpha$ radiation. Using Sherre’s formula, he calculated the ordered cluster size for samples annealed at different temperatures and showed that the size of ordered clusters increases (from 80 (Å) to 300 (Å)) with annealing temperature ($T = 400 \, ^\circ\text{C}$ to $T = 500 \, ^\circ\text{C}$).

Dang studied the magnetic and chemical order-disorder transitions in face-centered cubic FeNi$_3$, FeNi, and Fe$_3$Ni by Monte Carlo (MC) simulations using the Ising approximation. He calculated the Curie temperature of the chemically ordered FeNi$_3$ as $T = 907 \, ^\circ\text{C}$ and the chemically disordered FeNi$_3$ as $T = 597 \, ^\circ\text{C}$). Dang’s results show that the Curie temperature of FeNi$_3$ increases upon chemical ordering in this compound which is in agreement with Wakelin’s results but in different from Leech’s conclusions.
2.3 Factors Affecting FCC-to-L12 Phase Transformation in FeNi₃

Creating excess defects and ternary element substitutions have been known as two ways to manipulate the thermodynamic and kinetic parameters that influence the chemical ordering transformation in alloys which undergo this type of phase transformation [18].

2.3.1 Solidification rate

As short-range atomic diffusion in substitutional alloys usually happens via lattice vacancies [37], it has been suggested that engineering an excess of vacancies into the microstructure may facilitate an increase of the rate of the chemical ordering phase transformation [38–41]. The production of excess vacancies via quenching, and its effect on chemical ordering in different alloys, has been widely studied [42–45]. Benci et al. have measured the degree of chemical ordering through resistivity measurements in AuCu₃ specimens which have been subjected to quenching from \( T = 915 ^\circ \text{C} \) prior to annealing [44]; their results showed that quenching prior to isothermal annealing can be effective in achieving higher degree of chemical ordering in less annealing time. Ferro et al. continued the previous work by Benci by investigating the effect of an excess of vacancies introduced by quenching on chemical ordering of FeNi₃ through electrical resistivity measurements [42]; they observed the maximum resistivity change for quenched FeNi₃ samples which have subjected to isothermal annealing at lower temperature range than the usual ordering temperature for this compound. They concluded that quenched FeNi₃ samples should be annealed at \( T < 400 ^\circ \text{C} \) in order to prevent the elimination of vacancies before they can be used as diffusion pathways during isothermal annealing.
2.3.2 Ternary alloying additions

The addition of a small percentage of a third element is known as another way to influence the thermodynamics and kinetics of chemical ordering transformation in binary alloys containing this type of phase transformation [46], [17]. Various reports on the effect of alloying additions on the progression of chemical ordering in FeNi3 have been published. For instance, while several attempts for identifying the L12-FeNi3 superstructure Bragg peaks as a direct evidence for chemical ordering phase transformation in this alloy were unsuccessful, in 1938, Bradley and Tayler were able to detect the superstructure peaks on X-ray photographs of slowly cooled Al-substituted FeNi3 (Ni14Fe5Al) using Co-Kα radiation [47]. Their study had two significant conclusions for FeNi3 system: first, specific type of radiation is needed in order to detect the superstructure peaks in this alloy, and second, Al as a ternary element can facilitate the advancement of chemical ordering in FeNi3 to a high enough degree to be detected by X-ray diffraction. Since then, a variety of elements have been used as ternary additions with the purpose of enhancement in superstructure formation in FeNi3 [48]. It is hypothesized in this study that elements which form L12 phase with either Fe or Ni may improve the advancement of A1→L12 phase transformation in FeNi3. Studies on manganese-nickel binary alloy systems show that this compound undergoes a chemical order-disorder phase transformation (A1-to-L12) in the MnNi3 region [49]. On the other hand, Cu does not form L12 phase with neither Fe nor Ni [50]. Therefore, by choosing Mn and Cu as ternary alloying additions in this study we investigated the effect of an element which forms L12 phase with Ni (Mn) and one which does not. Kaya have measured the resistivity, saturation, and specific heat of alloys with compositions lying in
between MnNi$_3$ and FeNi$_3$ after quenching from various temperatures and annealing to produce the maximum degree of chemical ordering [51]. Their results showed that the saturation magnetization of the alloy containing 10% Mn is higher than either FeNi$_3$ or MnNi$_3$ meaning that Mn can act as an effective ternary element to enhance the degree of chemical ordering in FeNi$_3$. Ravdel has studied the role of Mn and Cu on the chemical ordering transformation in FeNi$_3$ through electrical resistivity measurements and reported on increase in this transformation by adding 4 at.% Mn and reduction by 5 at.% Cu [52].
3.0 OBJECTIVES

As described in Chapter 2.0, iron-nickel alloys around the composition FeNi$_3$ undergo a chemical order-disorder transformation which can be influenced by factors such as fabrication method, heat treatment, alloying additions, etc. Here, FeNi$_3$ serves as a model system to examine the role of rapid solidification and ternary alloying elements on the degree of chemical ordering in specific compositions of iron-nickel systems which undergo this type of phase transformation.

As the first objective of this study, we investigate the effect of rapid solidification on the progression of chemical ordering (A1$\rightarrow$L1$_2$) in FeNi$_3$ by utilizing the melt-spinning technique. To fulfill this objective, coupled magnetic and calorimetric measurements have been performed on ingot and ribbon samples of pure FeNi$_3$. These samples have been synthesized separately and annealed together at $T = 470$ °C for two weeks in order to study the effect of only one variable (fabrication method).

The second objective of this thesis is to study and understand the influence of 2 at.% Mn and 2 at.% Cu as ternary alloying additions on the A1-to-L1$_2$ phase transformation in FeNi$_3$. This study will be conducted through coupled calorimetry and magnetic measurements of the as-arc-melted and annealed ingots with different compositions. Selection of 2 at.% of Cu was based on the Fe-Ni-Cu phase diagram in which L1$_2$ phase in neighborhood of FeNi$_3$ composition is stable up to 5 at.% Cu addition to this compound [53]. In order to change only one variable (type of ternary element), 2 at.% of Mn was also added to FeNi$_3$ to compare the role of same amount of two different ternary alloying elements on the formation of L1$_2$ phase in FeNi$_3$. 
4.0 EXPERIMENTAL PROCEDURES & TECHNIQUES

The experimental details associated with the objectives of this thesis are described in this section. Section 3.1 provides the synthesis and sample preparation methods regarding the fulfillment of the objectives of this study. The chemical composition and homogeneity of samples were verified by scanning electron microscopy energy-dispersive spectroscopy (SEM-EDS) analysis which is detailed in section 3.2. Annealing has been done using a tube furnace as described in section 3.3. The crystal structures were studied using X-ray diffraction (XRD) as presented in section 3.4. Thermal analysis regarding the enthalpic changes of the samples was evaluated by differential scanning calorimetry (DSC) as described in section 3.5. Magnetic characterization was performed using a Quantum Design Versalab Vibrating Sample Magnetometer (VSM) as specified in section 3.6.

4.1 Materials Synthesis and Processing

In this study, we investigate the effect of non-equilibrium solidification as well as ternary additions on the progression of chemical ordering (A1→L12) in FeNi3. The first aim is utilizing the melt-spinning process (prior to isothermal annealing) as a rapid solidification technique and effect of this non-equilibrium solidification on the chemical ordering transformation in FeNi3 during isothermal annealing. To fulfill this objective, an ingot and ribbons of pure FeNi3 have been prepared. An alloy with the starting composition of FeNi3 was synthesized from elemental sources of Fe granules and Ni slubs (Alfa Aesar 99.98%) into a small ~ 5 g ingot through arc-melting in an Ar atmosphere using an Edmund Buhler MAM-1 mini arc-melting system. The ingot sample was melted three times to ensure homogeneity. Following this procedure, the ingot was
rapidly solidified via melt-spinning using an Edmund Buhler GmbH melt-spinner into ribbons of approximately 2 mm in width, 10-20 μm in thickness and 2-20 cm in length; these samples are designated as “as-spun ribbons”. Clear amorphous silica crucibles with a round orifice of diameter of 0.025 inches were used to contain the charge to be melt-spun. The distance from the crucible nozzle to the spinning copper wheel was 8 mm, and the tangential wheel velocity employed was 31 m/s. The sample appearance and the microstructure commonly varies from the ribbon side that solidifies in contact with the wheel (“wheel-side”) and the opposite side (“free-side”) due to rate of heat transfer, so both sides of the ribbon are considered in the microstructural examinations.

The second aim of this study is to study the role of addition of 2 at.% Mn and Cu as two different ternary elements on altering the chemical ordering in FeNi₃. Ingot FeNi₃-based samples with starting compositions of FeNi₃, (FeNi₃)₀.⁹₈Cu₀.₀₂, and (FeNi₃)₀.⁹₈Mn₀.₀₂ were synthesized from elemental sources (Alfa Aesar 99.98%) in an Ar atmosphere using an Edmund Buhler MAM-1 mini arc-melting system; these samples are designated as “as-arc-melted ingots”. The ingot samples were melted three times to ensure homogeneity. The samples containing elemental additions will be henceforth referred to as “substituted” FeNi₃ in this thesis. Prior to characterization the ingot samples were cut into a size compatible with the characterization technique using a diamond saw assembly, and then ultrasonicated for 5 minutes using isopropyl alcohol (IPA) to remove debris.

4.1.1 Operating Principle of Arc-melting

A plasma arc-melter is a furnace that heats materials by means of an argon plasma and is used to form an alloy. In this method a DC current is applied between a tungsten
tip and a water-cooled copper plate in an argon atmosphere to create a sustained plasma arc that reaches a temperature of $T = 3500 \, ^\circ\text{C}$ [54]. Sample material on the copper plate is melted by the argon plasma arc, and solidifies when the plasma arc is removed[55]. The arc melted material forms the charge for melt spinning.

4.1.2 Operating Principle of Melt-spinning

Melt-spinning is a process of rapidly solidification, typically of a metallic sample, from the molten state. Samples that are melt-spun are first homogenized from raw materials into a single bulk ingot (see section 3.1.1). This ingot is then placed in an elongated amorphous silica or boron-nitride 20 crucible. The crucible is manufactured with a round hole or thin slit in the bottom through which the molten alloy can escape. The crucible containing the sample is placed inside a large chamber that is evacuated before being filled with Argon (Ar) gas. Small storage tanks in the melt spinner are also filled with Ar gas to a pressure slightly greater than the pressure contained within the main chamber. The sample is then melted using RF induction with a water-cooled copper induction coil. The surface tension of the molten alloy at the orifice of the crucible prevents the molten metal from dropping out of the crucible. Once the desired temperature has been reached, a valve to the small storage tanks is opened allowing the pressure differential to eject the molten sample out. The sample strikes a water-cooled copper wheel that is spinning rapidly. This procedure helps to draw heat away very quickly and results in an extremely rapid quench of the sample, on the order of $10^6$ degrees/second [56]. Samples produced from this technique typically resemble flat ribbons. Depending on the experiment parameters (orifice size, distance to wheel, etc.) the ribbons can be wide and short or very long and thin [57].
4.2 Composition and Homogeneity Determination Using Energy Dispersive X-ray Spectroscopy (SEM-EDS)

Scanning electron microscope (SEM), Hitachi S4800, equipped with energy x-ray analysis (EDS) was used for compositional analysis and determining the degree of homogeneity of the pure FeNi$_3$, the Mn-substituted, and the Cu-substituted ingots as well as the pure FeNi$_3$ ribbon samples.

Energy-dispersive x-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis of a sample that relies on the interaction of x-rays and the sample. In this technique, a beam of electrons is focused onto the sample that excites an electron in an inner atomic shell, ejecting it from the shell while creating an electron hole. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy and the lower-energy shell will be released in the form of an x-ray. The number and energy of the x-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energies of the x-rays are characteristic of the difference in energy between the two shells and the atomic structure of the emitting element, EDS allows the elemental composition of the specimen to be measured [58]. Fig. 11 shows a schematic representation of the operating principle of EDS.
Figure 11: Schematic representation of energy-dispersive X-ray spectroscopy principles. K, L, and M are the electron shells designations while Kα, Kβ, and Lα are the radiation energies emitted when an electron falls from a higher shell to fill a hole in a lower shell [59].
4.3 Heat Treatment Procedure

In order to induce the chemically-ordered L1₂ phase in FeNi₃, ingot samples of pure and elementally-substituted FeNi₃ were sliced and together with the pure as-spun ribbons were encapsulated in evacuated (1×10⁻⁶ Torr) silica tubes and annealed for 336 h at \( T = 470 \pm 5 \degree C \) followed by controlled cooling with the rate of 1 \degree C /min in the furnace. Annealing is a heat treatment process during which a material is exposed to an elevated temperature for an extended time period to promote diffusion and phase transformation [37]. The chemical ordering process may, in general, be accomplished either by annealing for some time at a steady temperature below the critical ordering temperature or by cooling at a fixed rate through a wide temperature range, for example from just above to well below the critical temperature [1]. The annealing condition for the alloys of this study has been chosen based on literature reports regarding the best heat treatment conditions for L1₂ phase formation in FeNi₃, as described in the Section 2.1.1.
4.4 Structural Characterization Using X-ray Diffraction (XRD)

In this thesis, identification of the crystal structure, crystallite size, lattice parameter, and the phase content of as-made and annealed samples was done using the X-ray diffraction (XRD) technique.

X-ray diffraction is a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline arrangement of the atoms causes a beam of incident X-rays to diffract into specific directions. This technique relies on the dual wave/particle nature of X-ray to obtain information about the structure of crystalline materials.

In laboratory-scale X-ray diffraction, the electrons are boiled off of a cathode and accelerated through a strong electric potential. After reaching a high speed; they collide with a metal plate (commonly copper due to its high thermal conductivity). As a result of this colliding, the parallel beam of x-rays corresponding to the excitation of inner-shell electrons of the metal are generated. This beam passes through a monochromator and radiates on the specimen. X-rays incident on the crystalline sample are elastically scattered by the atoms in certain angles based on the crystal structure of the sample. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg’s law:

\[ n\lambda = 2d \sin \theta \]  

where:
\( d \) = Interplanar spacing (Å)
\( \lambda \) = Wavelength of the incoming radiant (Å)
\( \theta \) = Angle of incident (degrees)
\( n \) = order of reflection (usually taken as one)
The X-ray source orbits the sample so that the path of the x-ray beam is at an angle $\theta$ with the sample surface while the X-ray detector simultaneously rotates to maintain an angle of $2\theta$ (as shown in Fig. 12) and records the intensity of the diffracted X-rays. The collected data of measured intensity as a function of $2\theta$ can be used to determine the phases present in the sample.

**Figure 12: Schematic representation of X-ray diffraction operating principles [60].**

The average crystallite size was calculated according to the Scherrer formula,

$$D (2\theta) = \frac{k\lambda}{B \cos \theta}$$  \hspace{1cm} (2)

where: $D (2\theta) =$ Average grain/particle size (Å)

$k =$ Scherrer constant (taken as 0.9)

$\lambda =$ Wavelength of the Cu K$\alpha$ radiation (1.54056 Å)

$B =$ Full width at half maximum, FWHM, intensity (R)
The XRD peaks were then fitted using a Pseudo-Voigt fitting function. Information regarding the lattice parameters of the crystal structures was obtained using a least squares method for cell parameter refinement based on the Bragg equation, as explained by Novak and Colville [61].
4.5 Thermal Analysis Using Differential Scanning Calorimetry (DSC)

The thermal analysis experiments discussed in this thesis have been carried out to investigate the structural and magnetic phase transformations of pure and elementally-substituted ingots as well as the pure ribbons of FeNi$_3$ using differential scanning calorimetry (DSC). The DSC employed in this thesis is a NETZSCH STA 449 F3 Jupiter instrument with heating capabilities up to 20 degrees/minute [62]. Measurements were collected in an Ar atmosphere in the same condition for all the samples by raising their temperature with a heating rate of 10 °C /min from room temperature to 900 °C and then studied under the same heating and cooling rates.

Differential scanning calorimetry (DSC) is an approach for monitoring the evolution of heat with changes in temperature. The experimental setup of a DSC requires simultaneous heating of a reference and a sample (as shown in Fig. 13). Both the sample and reference are maintained at the same temperature throughout the experiment. The basic principle underlying this technique is that when the sample undergoes a physical transformation such as a phase transformation, more or less heat will need to flow to it than to the reference to maintain both platforms at the same temperature. The difference in the heat flow of the sample and reference is then recorded as a function of temperature (isochronal) or time (isothermal). The reference pan employed is typically an empty aluminum oxide (Al$_2$O$_3$) sample pan.
Figure 13: Schematic representation of the sample and reference pans used during a DSC measurement [63].

This technique allows the detection of processes such as phase transformation, precipitation, or melting, which involve endothermic (heat flowing into the sample) or exothermic (heat flowing out of the sample) processes. Calibration of the DSC equipment for temperature, sensitivity, and thermal-lag was performed using several standard reference materials. The enthalpy of transformation of the materials was found by quantifying the area enclosed by endothermic or exothermic peak via integration of the DSC data with respect to temperature utilizing NETZSCH Proteus® software.

The thermal changes occurring in FeNi$_3$ samples during DSC measurements were determined as the area between the DSC trace and a baseline integrated with respect to time. The data have already corrected for instrumental effects by subtracting thermal data obtained from the measurement of the response of an empty crucible. The errors for heat measurements have been calculated based on the error associated with the calibration scans prior to actual DSC experiments.
4.6 Magnetic Characterization Using Vibrating Sample Magnetometry (VSM)

Vibrating Sample Magnetometry is one of many techniques to characterize the magnetic response of a material. In a vibrating sample magnetometer (VSM) a sample is placed within sensing coils, and is mechanically vibrated. The resulting magnetic flux changes induce a voltage in the sensing coils that is proportional to the magnetic moment of the sample. The magnetic field may be generated by an electromagnet or a superconducting magnet. Magnetic measurements were performed using a Quantum Design Versalab Vibrating Sample Magnetometer (VSM) under fields in the range $-30 \text{kOe} \leq H \leq +30 \text{kOe}$ and at room temperature [64]. Samples were mounted on a straight quartz paddle secured with Kapton tape. The mass was determined by weighing the sample prior to measurement.
5. RESULTS

The results presented here have been divided into two primary sections which address the impact of the fabrication method and of ternary alloying additions on the superstructure formation (L$_{12}$ phase) in FeNi$_3$. Section 5.1 highlights results pertaining to Aim 1 of this thesis: understanding the effects of the melt-spinning process to rapidly solidify FeNi$_3$ compound. Section 5.2 addresses the results associated with Aim 2: quantifying the role of Mn and Cu as ternary alloying additions on the progression of chemical ordering (A1$\rightarrow$L$_{12}$) in FeNi$_3$.

5.1 Understanding the effects of rapid solidification on L$_{12}$ phase formation in FeNi$_3$

This section features the results obtained in fulfillment of Aim 1 of this thesis. The effects of rapid solidification conducted prior to annealing, hypothesized to produce materials defects, on the progression of chemical ordering (A1$\rightarrow$L$_{12}$) in FeNi$_3$ during isothermal annealing have been studied through structural, magnetic, and calorimetric analyses.

5.1.1 Compositional characterization of pure ingot and ribbons of FeNi$_3$

The ingot sample of FeNi$_3$, fabricated by arc-melting, was found to be shiny and did not exhibit any sign of surface oxidation. The ingot was made into ribbons by melt-spinning; the ribbons were of good quality: uniform, free of tears, and roughly 2 mm in width, 10-20 $\mu$m in thickness and 2-20 cm in length. The chemical composition and homogeneity of the as-arc-melted ingot and the as-spun ribbons were verified by scanning electron microscopy energy-dispersive spectroscopy (EDS) analysis. Three measurements were taken on each sample and the average composition is presented in Table 2.
Table 2: Composition analysis of as-made pure FeNi$_3$ in the form of ingot and ribbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>at.% Ni</th>
<th>at.% Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi$_3$ – as-arc-melted ingot</td>
<td>74 ± 1</td>
<td>26 ± 0.5</td>
</tr>
<tr>
<td>FeNi$_3$ – as-spun ribbon</td>
<td>73 ± 1</td>
<td>26.5 ± 0.5</td>
</tr>
</tbody>
</table>

5.1.2 Structural characterization of ingot and ribbons of pure FeNi$_3$

Structural results presented in this section have been achieved by X-ray diffraction (XRD) measurements performed at room temperature utilizing Cu-Kα radiation on as-made and annealed ingot and ribbon samples of pure FeNi$_3$.

5.1.2.1 Structural properties of as-made ingot and ribbon samples

X-ray diffraction results obtained on the as-made ingot as well as from the free side (fs) and from the wheel side (ws) of the as-spun ribbon samples of pure FeNi$_3$ are shown in Fig. 14; the standard XRD pattern for FeNi$_3$ reported by Ahmed [6] is shown for comparison. A face-centered cubic (fcc) phase with sharp Bragg peaks is found for both sides of the as-spun FeNi$_3$ ribbons and a fcc phase with broader Bragg peaks is found for as-arc-melted ingot. The free side of the as-spun ribbons shows Bragg peak positions that match closely to those of the wheel side but with very different peak intensities, confirming the attainment of different textures on free and wheel sides of the as-spun ribbons. No evidence of a superstructure peak associated with the L1$_2$ phase was observed in the XRD patterns of as-made samples.
The (200) Bragg peak from all three samples has been highlighted in Fig. 15 to emphasize the differences in peak position and intensity produced by the melt-spinning process as compared to those produced during ingot casting. The Bragg peaks of the as-arc-melted ingot sample are broad and shift to smaller 2θ angles as compared to those of the free and wheel sides of as-spun ribbons.

Table 3 summarizes the calculated unit cell volumes and crystallite sizes of ingot and ribbon samples as well as those reported for quenched/cold-worked samples of FeNi₃ by Leech [9], Wakelin [1], Lutts [65], and Swartzendruber [25]; these results are plotted in Fig. 15. The unit cell volumes of the phases formed on the free and wheel sides of the melt-spun ribbons are about the same, but both are 0.7% smaller than that of the ingot
sample. Furthermore, it is noted that the unit cell volumes of the phases formed in as-arc-melted ingot sample in this study are close to the values reported by Wakelin [1], Lutts [65], and Swartzendruber [25] for a quenched/cold-worked sample of FeNi$_3$; while the unit cell volumes of the phases formed on the free and wheel sides of the as-spun ribbons are close to that reported by Leech for a quenched sample of FeNi$_3$. The crystallite sizes of the phases formed on the both sides of as-spun ribbon samples are about the same but are larger than that of the as-arc-melted ingot sample.

Table 3: Calculated Lattice parameters and unit cell volumes of as arc-melted pure ingot and as-spun ribbons of FeNi$_3$ as well as the values for quenched/cold-worked samples of FeNi$_3$ reported by Leech [9], Wakelin [1], Lutts [65], and Swartzendruber [25]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter (Å)</th>
<th>Unit Cell Volume (Å$^3$)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi$_3$ – as-arc-melted</td>
<td>3.555 ± 0.002</td>
<td>44.93 ± 0.03</td>
<td>45 ± 1</td>
</tr>
<tr>
<td>FeNi$_3$ – as-spun – fs</td>
<td>3.546 ± 0.006</td>
<td>44.59 ± 0.08</td>
<td>90 ± 2</td>
</tr>
<tr>
<td>FeNi$_3$ – as-spun – ws</td>
<td>3.545 ± 0.006</td>
<td>44.55 ± 0.08</td>
<td>85 ± 1</td>
</tr>
<tr>
<td>Leech – as quenched [9]</td>
<td>3.5470 ± 0.0003</td>
<td>44.63 ± 0.02</td>
<td>-----</td>
</tr>
<tr>
<td>Wakelin – cold-worked [1]</td>
<td>3.5544 ± 0.0002</td>
<td>44.91 ± 0.01</td>
<td>-----</td>
</tr>
<tr>
<td>Lutts – as quenched [65]</td>
<td>3.5556</td>
<td>44.950</td>
<td>-----</td>
</tr>
<tr>
<td>Swartzendruber – as quenched [25]</td>
<td>3.554</td>
<td>44.890</td>
<td>-----</td>
</tr>
</tbody>
</table>
Figure 15: a) Unit cell volumes and b) crystallite sizes of phases formed in the pure FeNi$_3$ ingot and ribbon samples in their as-made states compared to those reported by Leech [9], Wakelin [1], Lutts [65], and Swartzendruber [25].

5.1.2.2 Change in structural properties with annealing

Characterization was also carried out on the annealed samples to investigate the effects of annealing on the structural character of the ingot and ribbon samples of FeNi$_3$. Figure 16 compares the XRD patterns of different states (as-made vs. annealed) for the ingot sample, as well as from the fs and the ws of the ribbon samples. No evidence of a superstructure peak associated with the L1$_2$ phase was observed after annealing. Furthermore, the Bragg peaks of the ingot sample shift to larger 2θ values and become narrower upon annealing. The Bragg peaks obtained from the free side of the ribbons shift to larger 2θ values with no change in peak broadening with annealing, while slight changes in the peak position and in the broadening of the XRD patterns from the wheel side of the ribbons are observed.
The lattice parameters, unit cell volume and crystallite size of each sample before and after annealing, as well as those reported for quenched and furnace-cooled samples of FeNi$_3$ by Leech [9], Wakelin [1], and Lutts [65], have been summarized in Table 4 and plotted in Fig. 17. The unit cell volumes of the phases in all samples in this study, calculated from the data obtained for the ingot and from both sides of ribbons, decrease with annealing, Fig. 17(a). The crystallite size of as-arc-melted ingot sample has doubled after annealing, while those from the free and wheel sides of the annealed ribbons have the same values as those of the as-spun ribbons, Fig. 17(b).
Table 4: Calculated lattice parameters and unit cell volumes of annealed pure ingot and ribbons of FeNi₃ as well as the values for furnace-cooled FeNi₃ samples reported by Leech [9], Wakelin [1], and Lutts [65].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Parameter (Å)</th>
<th>Unit Cell Volume (Å³)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi₃ – annealed ingot</td>
<td>3.552 ± 0.001</td>
<td>44.81 ± 0.01</td>
<td>93 ± 4</td>
</tr>
<tr>
<td>FeNi₃ – fs – annealed</td>
<td>3.544 ± 0.006</td>
<td>44.51 ± 0.07</td>
<td>90 ± 5</td>
</tr>
<tr>
<td>FeNi₃ – ws – annealed</td>
<td>3.541 ± 0.007</td>
<td>44.39 ± 0.09</td>
<td>85 ± 2</td>
</tr>
<tr>
<td>Leech – furnace-cooled [9]</td>
<td>3.5441 ± 0.0003</td>
<td>44.52 ± 0.01</td>
<td>-------</td>
</tr>
<tr>
<td>Wakelin – furnace-cooled [1]</td>
<td>3.5522 ± 0.0007</td>
<td>44.82 ± 0.03</td>
<td>-------</td>
</tr>
<tr>
<td>Lutts – furnace-cooled [65]</td>
<td>3.5550</td>
<td>44.928</td>
<td>-------</td>
</tr>
</tbody>
</table>

Figure 17: Change in the (a) unit cell volume and (b) crystallite size of ingot and ribbons of FeNi₃ with isothermal annealing compared to those reported by Leech [9], Wakelin [1], and Lutts [65] for quenched and furnace-cooled specimens of FeNi₃.

5.1.3 Thermal analysis of ingot and ribbons comprised of pure FeNi₃

Differential scanning calorimetry (DSC) measurements have been performed to study the chemical order-disorder transformation in ingot and ribbon samples of FeNi₃.
and to evaluate the effect of using different fabrication techniques on the formation of L12 phase in FeNi3 before and after annealing.

5.1.3.1 Calorimetric data from as-arc-melted ingot and as-spun ribbon samples

Calorimetry measurements obtained upon heating show an endothermic peak followed by an endothermic shoulder at $T = 592 \pm 10 \, ^\circ\text{C}$ for both the as-made ingot and the ribbon samples, as seen in Fig. 18(a). As described in Chapter 4, the area enclosed by the endothermic peak is associated with the enthalpy of a phase transition in the FeNi3 compound upon heating. Furthermore, the endothermic shoulders found at the higher temperature edge of the DSC traces are associated with the Curie transition temperature of the samples [9,36]. Similar values of Curie temperature for the as-made ingot and ribbon samples have been obtained through DSC measurements of these samples; $T_C$ values are included with the magnetic properties of these samples in Table 6 of the following section. The degree of chemical ordering formed in the as-made ingot and ribbon samples as well as those reported by Kaya [29] and Takahashi [36] have been estimated based on the enthalpy of the endothermic peak for a completely ordered FeNi3 sample (reported by Leech [9]) and plotted in Fig. 18(b). Based on this calculation, the as-arc-melted ingot sample of pure FeNi3 fabricated in this study is 35% chemically ordered and the as-spun ribbon sample is 19% chemically-ordered.
Figure 18: a) DSC heating scans of the as-made ingot and ribbon samples of pure FeNi₃. b) Estimated degree of chemical ordering formed in the as-made ingot and ribbon samples fabricated in this study based on the enthalpy of endothermic peak for a completely ordered FeNi₃ sample reported by Leech [9]. The degree of chemical ordering reported by Kaya [29] and Takahashi [36] as included for reference. The measurement errors are smaller than the symbols.

5.1.3.2 Changes in calorimetric data after annealing

After isothermal annealing at $T = 470 \degree C$ for two weeks, the DSC heating scans of the FeNi₃ samples show an endothermic peak for both of the annealed ingot and ribbon samples, Fig. 19(a). The endothermic peak of the annealed ingot developed a high-temperature shoulder in the DSC data that occurs at $T = 630 \degree C$. Upon isothermal annealing, the degree of chemical ordering in the ingot sample of FeNi₃ increases from 35% to 100% while that of the ribbon sample increases from 19% to 86%, Fig. 19(b).
Figure 19: a) DSC heating scans of the as-made and annealed ingot and ribbon samples of FeNi3. b) Estimated degree of chemical ordering formed in as-made and annealed samples of pure FeNi3 fabricated in this study as well as those reported by Kaya [29] and Takahashi [36] based on the enthalpy of endothermic peak for a completely ordered FeNi3 reported by Leech [9]. The measurement errors are smaller than the symbols.

5.1.4 Magnetic characterization of pure ingot and ribbon samples of FeNi3

The magnetic character of FeNi3 ingot and ribbon samples was examined in the as-made and annealed states at room temperature. The magnetic properties were determined by both magnetic measurement and by thermal analysis, as described in Chapter 3.

5.1.4.1 Magnetic properties of as-arc-melted ingot and as-spun ribbon samples

The room-temperature magnetic hysteresis loops of the FeNi3 ingot and ribbon samples in their as-made states possess a high saturation magnetization and a coercivity that is close to zero, Fig. 20. The magnetic properties of the as-made ingot and ribbon samples as well as the corresponding literature values have been summarized in Table 5. The saturation magnetization of the as-spun ribbons ($M_s = 108.0 \pm 0.6$ emu/g) is 5%
higher than that of the as-arc-melted ingot \((M_S = 103.00 \pm 0.08 \text{ emu/g})\). Furthermore, as shown in the magnified plot of the first quadrant of the hysteresis loops of these samples, the initial susceptibility (the slope of the magnetization curve) of the as-arc-melted ingot \((\chi = 0.28 \text{ emu/gOe})\) is greater than that of the as-spun ribbon \((\chi = 0.22 \text{ emu/gOe})\). It is also noted that the field required to reach magnetic saturation (anisotropy field) is larger for as-spun ribbon \((H = 3720 \text{ Oe})\) than for the as-arc-melted ingot sample \((H = 1680 \text{ Oe})\) of FeNi\(_3\).

![Field-dependent magnetization behavior of as-arc-melted ingot and as-spun ribbons of FeNi\(_3\) at room temperature. The first quadrant of the hysteresis loops are shown in greater detail.](image-url)

**Figure 20:** Field-dependent magnetization behavior of as-arc-melted ingot and as-spun ribbons of FeNi\(_3\) at room temperature. The first quadrant of the hysteresis loops are shown in greater detail.
Table 5: Magnetic properties of as-made ingot and ribbon samples of pure FeNi$_3$ as well as the values for quenched/cold-worked FeNi$_3$ samples reported by Leech [9] and Wakelin [1] respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Saturation Magnetization (emu/g)</th>
<th>Susceptibility (emu/Oe.g)</th>
<th>Anisotropy field (Oe)</th>
<th>Curie Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi$_3$ (as-arc-melted ingot)</td>
<td>103.30 ± 0.08</td>
<td>0.28 ± 0.02</td>
<td>1680 ± 50</td>
<td>592 ± 5</td>
</tr>
<tr>
<td>FeNi$_3$ (as-spun ribbon)</td>
<td>108.0 ± 0.6</td>
<td>0.22 ± 0.02</td>
<td>3720 ± 50</td>
<td>592 ± 5</td>
</tr>
<tr>
<td>Leech [9] (quenched ingot)</td>
<td>110</td>
<td>-----</td>
<td>-----</td>
<td>590 ± 5</td>
</tr>
<tr>
<td>Wakelin [1] (cold-worked ingot)</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>598 ± 5</td>
</tr>
</tbody>
</table>

5.1.4.3 Change in magnetic properties with annealing

The room-temperature hysteresis curves of the ingot and ribbon samples in the as-made and annealed states are displayed in Fig. 21(a,b). The magnetic properties obtained from magnetic and DSC measurements of these samples as well as the literature values are summarized in Table 6. The as-arc-melted ingot sample possesses a saturation magnetization of $M_S = 103.30 \pm 0.08$ emu/g which increases by 9% to $M_S = 113.60 \pm 0.08$ emu/g upon annealing. Furthermore, the as-arc-melted ingot sample has higher anisotropy field ($H_K = 1680$ Oe) and higher susceptibility ($\chi = 0.28$ emu/gOe) values than does the annealed ingot sample ($\chi = 0.14$ emu/gOe and $H_K = 2250$ Oe), which means that the anisotropy field and susceptibility of the ingot sample decreases with annealing. The as-spun FeNi$_3$ ribbon possesses $M_S = 108.0 \pm 0.6$ emu/g which increases by 3% to $M_S = 111.0 \pm 0.6$ emu/g after annealing. The same trend after annealing appears for susceptibility and anisotropy field of this sample; the susceptibility of pure FeNi$_3$ ribbons
increases from $\chi = 0.22 \text{ emu/Oe.g}$ to $\chi = 0.28 \text{ emu/Oe.g}$ and the anisotropy field for this sample increases from $H_K = 1680 \text{ Oe}$ to $H_K = 2250 \text{ Oe}$ upon annealing, Fig. 21(c-e).

Figure 21: Field-dependent magnetization behavior of as-made and annealed a) ingot and b) ribbon samples of FeNi$_3$. The change in c) saturation magnetization, d) anisotropy field, and e) susceptibility of the ingot and ribbon samples of pure FeNi$_3$ with isothermal annealing. Measurement errors are smaller than the markers.
Table 6: Magnetic properties of as-made and annealed ingot and ribbon samples of pure FeNi$_3$ as well as the values for quenched/cold-worked and furnace-cooled FeNi$_3$ samples reported by Leech [9] and Wakelin [1].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Saturation Magnetization (emu/g)</th>
<th>Susceptibility (emu/gOe)</th>
<th>Anisotropy field (Oe)</th>
<th>Curie Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi$_3$ (as-arc-melted ingot)</td>
<td>103.30 ± 0.08</td>
<td>0.28 ± 0.02</td>
<td>1680 ± 50</td>
<td>592 ± 5</td>
</tr>
<tr>
<td>FeNi$_3$ (annealed ingot)</td>
<td>113.60 ± 0.08</td>
<td>0.14 ± 0.02</td>
<td>2250 ± 50</td>
<td>-----</td>
</tr>
<tr>
<td>FeNi$_3$ (as-spun ribbon)</td>
<td>108.0 ± 0.6</td>
<td>0.22 ± 0.02</td>
<td>3720 ± 50</td>
<td>592 ± 5</td>
</tr>
<tr>
<td>FeNi$_3$ (annealed ribbon)</td>
<td>111.0 ± 0.6</td>
<td>0.28 ± 0.02</td>
<td>3760 ± 50</td>
<td>-----</td>
</tr>
<tr>
<td>Leech [9] (quenched ingot)</td>
<td>110</td>
<td>-----</td>
<td>-----</td>
<td>590 ± 5</td>
</tr>
<tr>
<td>Leech [9] (furnace-cooled ingot)</td>
<td>116</td>
<td>-----</td>
<td>-----</td>
<td>590 ± 5</td>
</tr>
<tr>
<td>Wakelin [1] (cold-worked ingot)</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>598 ± 5</td>
</tr>
<tr>
<td>Wakelin [1] (furnace-cooled ingot)</td>
<td>115</td>
<td>-----</td>
<td>-----</td>
<td>681 ± 5</td>
</tr>
</tbody>
</table>
5.2 Understanding the effects of alloying additions on the L12 phase formation in FeNi3

The principle objective of this section of the thesis is to study the effect of Cu and Mn as ternary alloying additions on the progression of chemical ordering and formation of L12 phase in the FeNi3 compound through structural, magnetic, and calorimetric analyses. To fulfill this objective, 2 at.% Cu and 2 at.% Mn were separately added to FeNi3 during the arc-melting process in order to make ingot samples of pure, Cu-substituted and Mn-substituted FeNi3.

5.2.1 Compositional Characterization of as-arc-melted pure and substituted FeNi3

As-arc-melted ingot samples of pure and substituted FeNi3 are homogeneous in composition, shiny, and without any sign of surface oxidation. The chemical composition and homogeneity of as-arc-melted ingots were verified by scanning electron microscopy energy-dispersive spectroscopy (EDS) analysis. Three measurements were taken on each sample and the average compositions are presented in Table 7.

<table>
<thead>
<tr>
<th>Compound</th>
<th>at.% Ni</th>
<th>at.% Fe</th>
<th>at.% Cu</th>
<th>at.% Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi3 – as-arc-melted ingot</td>
<td>74 ± 1</td>
<td>26.1 ± 0.5</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>(FeNi3)0.98Cu0.02 – as-arc-melted ingot</td>
<td>73 ± 1</td>
<td>24.6 ± 0.5</td>
<td>2.3 ± 0.1</td>
<td>------</td>
</tr>
<tr>
<td>(FeNi3)0.98Mn0.02 – as-arc-melted ingot</td>
<td>73 ± 1</td>
<td>24.8 ± 0.5</td>
<td>------</td>
<td>2.5 ± 0.1</td>
</tr>
</tbody>
</table>

5.2.2 Structural characterization of pure and substituted FeNi3

Structural results shown in this section have been achieved by X-ray diffraction (XRD) measurements performed at room temperature. Laboratory-based XRD
measurements utilizing Cu-Kα radiation were carried out on as-arc-melted and annealed ingot samples.

5.2.2.1 Structural properties of as-arc-melted ingot samples

The XRD patterns of all as-arc-melted ingot samples (pure and substituted FeNi₃), as presented in Fig. 22(a), reveal a face-centered cubic (fcc) phase with no additional phase. Figure 22(b) shows an enlargement of the (111) Bragg peak to emphasize the differences in peak position and intensity produced by elemental substitution of FeNi₃ with Cu and Mn. The Bragg peaks of the phases formed in the as-arc-melted ingots of pure and substituted FeNi₃ are broad and show only slight changes in positions and intensities with the addition of 2 at.% Cu or Mn.

![Figure 22: (a) X-ray diffraction patterns of pure, Cu-substituted, and Mn-substituted FeNi₃ using Cu-Kα radiation. (b) An enlargement of (111) peak.](image)

Figure 22: (a) X-ray diffraction patterns of pure, Cu-substituted, and Mn-substituted FeNi₃ using Cu-Kα radiation. (b) An enlargement of (111) peak.
Table 8 summarizes the calculated lattice parameters, unit cell volumes, and crystallite sizes of pure and substituted FeNi$_3$ as-arc-melted ingots as well as those reported for quenched/cold-worked samples of FeNi$_3$ by Leech [9], Wakelin [1], Lutts [65], and Swartzendruber [25]; these results have been also plotted in Fig. 23(a). Structural results reveal a 0.2% and 0.4% expansion in the unit cell of FeNi$_3$ with the addition of 2 at.% Cu and 2 at.% Mn, respectively. At the same time there is no significant difference in the crystallite sizes of these alloys, Fig. 23(b).

Table 8: Calculated Lattice parameters and unit cell volumes of as-arc-melted pure and substituted FeNi$_3$ as well as the values for quenched/cold-worked samples of FeNi$_3$ reported by Leech [9], Wakelin [1], Lutts [65], and Swartzendruber [25].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice Parameter (Å)</th>
<th>Unit Cell Volume (Å$^3$)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi$_3$ (as-arc-melted ingot)</td>
<td>3.555 ± 0.002</td>
<td>44.93 ± 0.03</td>
<td>45 ± 1</td>
</tr>
<tr>
<td>(FeNi$<em>3$)$</em>{0.98}$Cu$_{0.02}$</td>
<td>3.557 ± 0.003</td>
<td>45.01 ± 0.04</td>
<td>43 ± 2</td>
</tr>
<tr>
<td>(FeNi$<em>3$)$</em>{0.98}$Mn$_{0.02}$</td>
<td>3.560 ± 0.003</td>
<td>45.12 ± 0.04</td>
<td>48 ± 1</td>
</tr>
<tr>
<td>Leech – as quenched [9]</td>
<td>3.5470 ± 0.0003</td>
<td>44.63 ± 0.01</td>
<td>-----</td>
</tr>
<tr>
<td>Wakelin – cold-worked [1]</td>
<td>3.5544 ± 0.0002</td>
<td>44.91 ± 0.01</td>
<td>-----</td>
</tr>
<tr>
<td>Lutts – as quenched [65]</td>
<td>3.5556</td>
<td>44.950</td>
<td>-----</td>
</tr>
<tr>
<td>Swartzendruber – as quenched [25]</td>
<td>3.554</td>
<td>44.890</td>
<td>-----</td>
</tr>
</tbody>
</table>
5.2.2.2 Change in structural properties with annealing

The change in the crystal structure of the pure and substituted FeNi$_3$ ingots with annealing have been studied by X-ray diffraction. Figure 24 compares the XRD patterns of each ingot sample before and after the annealing process. No evidence of a superstructure peak associated with the L1$_2$ phase was observed in the XRD patterns of annealed ingot samples. X-ray diffraction patterns of the annealed pure and substituted FeNi$_3$ ingots show the same patterns as those of the arc-melted ones (containing a fcc phase). Furthermore, upon annealing the Bragg peaks of all ingot samples shift to larger 2θ values and become narrower; these changes are the greatest for the Cu-substituted FeNi$_3$ and the smallest for the Mn-substituted ingot sample.

Figure 23: Change in (a) unit cell volume and (b) crystallite size of FeNi$_3$ with substitution of 2 at.% Cu or Mn as ternary alloying elements. Unit cell volume of the phases formed in the ingot sample in this study have been compared to those reported by Leech [9], Wakelin [1], and Lutts [65] for quenched/cold worked and furnace-cooled specimens of FeNi$_3$. 

---

**Figure 23:** Change in (a) unit cell volume and (b) crystallite size of FeNi$_3$ with substitution of 2 at.% Cu or Mn as ternary alloying elements. Unit cell volume of the phases formed in the ingot sample in this study have been compared to those reported by Leech [9], Wakelin [1], and Lutts [65] for quenched/cold worked and furnace-cooled specimens of FeNi$_3$. 

5.2.2.2 Change in structural properties with annealing

The change in the crystal structure of the pure and substituted FeNi$_3$ ingots with annealing have been studied by X-ray diffraction. Figure 24 compares the XRD patterns of each ingot sample before and after the annealing process. No evidence of a superstructure peak associated with the L1$_2$ phase was observed in the XRD patterns of annealed ingot samples. X-ray diffraction patterns of the annealed pure and substituted FeNi$_3$ ingots show the same patterns as those of the arc-melted ones (containing a fcc phase). Furthermore, upon annealing the Bragg peaks of all ingot samples shift to larger 2θ values and become narrower; these changes are the greatest for the Cu-substituted FeNi$_3$ and the smallest for the Mn-substituted ingot sample.
The lattice parameters, unit cell volumes, and crystallite sizes of all the annealed ingot samples as well as those reported for furnace-cooled samples of FeNi$_3$ by Leech [9], Wakelin [1], and Lutts [65] have been summarized in Table 9 and plotted in Fig. 22. The unit cell volumes of the phases formed in all (pure, Cu-substituted, and Mn-substituted) ingot samples in this study are found to decrease with annealing with the largest change for Cu-substituted and the smallest change for Mn-substituted FeNi$_3$ ingot sample. The crystallite sizes of all the ingot samples increase upon isothermal annealing, as presented in Fig. 25(b); this enlargement is greatest for the Cu-substituted ingot and the least for the Mn-substituted ingot sample.
Table 9: calculated Lattice parameters and unit cell volumes of annealed ingots of pure and substituted FeNi$_3$ as well as the values for furnace-cooled FeNi$_3$ samples reported by Leech [9], Wakelin [1], and Lutts [65].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Parameter (Å)</th>
<th>Unit Cell Volume (Å$^3$)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi$_3$ – annealed ingot</td>
<td>3.552 ± 0.001</td>
<td>44.81 ± 0.01</td>
<td>93 ± 4</td>
</tr>
<tr>
<td>(FeNi$<em>3$)$</em>{0.98}$Cu$_{0.02}$ – annealed ingot</td>
<td>3.549 ± 0.004</td>
<td>44.70 ± 0.05</td>
<td>115 ± 5</td>
</tr>
<tr>
<td>(FeNi$<em>3$)$</em>{0.98}$Mn$_{0.02}$ – annealed ingot</td>
<td>3.557 ± 0.002</td>
<td>45.01 ± 0.03</td>
<td>85 ± 2</td>
</tr>
<tr>
<td>Leech – furnace-cooled [9]</td>
<td>3.5441 ± 0.0003</td>
<td>44.52 ± 0.01</td>
<td>-----</td>
</tr>
<tr>
<td>Wakelin – furnace-cooled [1]</td>
<td>3.5522 ± 0.0007</td>
<td>44.82 ± 0.03</td>
<td>-----</td>
</tr>
<tr>
<td>Lutts – furnace-cooled [65]</td>
<td>3.5550</td>
<td>44.928</td>
<td>-----</td>
</tr>
</tbody>
</table>

Figure 25: Change in (a) unit cell volume and (b) crystallite size of as-arc-melted pure and substituted FeNi$_3$ with isothermal annealing compared to those reported by Leech [9], Wakelin [1], and Lutts [65] for quenched and furnace-cooled specimens of FeNi$_3$.

5.2.3 Thermal analysis of pure and substituted FeNi$_3$

Calorimetry measurements have been performed to study the chemical order-disorder transformation in pure and substituted FeNi$_3$ ingot samples and to assess the
effects of each alloying element on the formation of L1₂ phase in FeNi₃ before and after annealing.

5.2.3.1 Calorimetric data from as-arc-melted ingot samples

The DSC signals of the as-arc-melted ingots of pure, Cu-substituted, and Mn-substituted FeNi₃ all show endothermic peaks in the temperature range of \( T = 450 \, ^{\circ}\text{C} \) to \( T = 600 \, ^{\circ}\text{C} \) (Fig. 26). As described in Chapter 3, the area enclosed by the endothermic peak is associated with the enthalpy of chemical disordering phase transition in FeNi₃ compound upon heating. The measured enthalpy of the endothermic peak seen in the DSC heating scan of the pure FeNi₃ ingot sample is 20 ± 2 J/g which decreases to 13 ± 2 J/g for the Cu-substituted FeNi₃ ingot sample and to 8 ± 2 J/g for Mn-substituted FeNi₃ ingot sample, Fig. 26(a). As shown in Fig. 26(b) the degree of chemical ordering formed during fabrication process (calculated based on Leech’s results for a completely ordered sample of FeNi₃ [9]) is 35% for the pure FeNi₃ ingot, 22% for Cu-substituted, and 14% for Mn-substituted as-arc-melted ingot samples.
Figure 26: a) DSC heating scans of the as-arc-melted pure and substituted FeNi$_3$ ingot samples. b) Degree of chemical ordering formed in as-arc-melted ingots of pure and substituted FeNi$_3$ fabricated in this study as well as those reported by Kaya [29] and Takahashi [36] based on the enthalpy of endothermic peak for a completely ordered FeNi$_3$ reported by Leech [9]. The measurement errors are smaller than the symbols.

The endothermic peak in the DSC trace of the pure FeNi$_3$ ingot sample has a sharp shoulder at $T = 592$ °C which disappears with alloying additions. As presented in section 5.5.3, this shoulder is associated with the Curie transition temperature (magnetic order-disorder transition) in this compound [9,36] and disappears with adding alloying elements as shown in Fig. 26(a). However, comparing the heating and cooling scans of pure FeNi$_3$ ingot reveals that the Curie temperature in the heating scan happens at the exact same temperature as the onset in the cooling scan of this compound [66]. Considering the onset in the DSC cooling scans as the Curie temperature, it can be said that adding ternary elements results in a reduction in the Curie transition temperature of FeNi$_3$, Fig. 27(b).
These results are also included with the magnetic properties of these samples in Table 12 of the following section.

Figure 27: a) Observed Curie temperature features on heating and cooling scans of DSC results for the as-arc-melted pure and substituted FeNi3 ingot samples. b) Change in Curie temperature with elemental substitution of FeNi3 ingot sample.

5.2.3.2 Change in calorimetric data with annealing

Differential scanning calorimetry (DSC) has been performed on annealed ingot samples under the same conditions as those of the as-arc-melted ones. The DSC heating trace of the annealed ingot sample for each composition has a significantly larger endothermic peak magnitude as compared to that of the as-arc-melted sample with the same composition, as seen in Fig. 28(a). The estimated degree of chemical ordering (based on Leech’s report [9]) formed in each sample in as-arc-melted and annealed states has presented in Fig. 28(b). The degree of chemical ordering obtained from the DSC
results of the Cu-substituted sample has increased from 22% to 78% (56% increase) with annealing, from 35% to 100% (65% increase) for the pure FeNi$_3$, and from 14% to 112% (98% increase) for the Mn-substituted ingot samples. The degree of chemical ordering estimated for the annealed Mn-substituted ingot sample (112%) is relative to that reported for a completely chemically ordered FeNi$_3$ sample and means that more L1$_2$ phase has formed in the annealed Mn-substituted ingot sample in fabricated this study than did in the pure ingot sample fabricated by Leech [9].

**Figure 28:** a) DSC signal of chemical disordering transformation in annealed pure and substituted FeNi$_3$. b) Degree of chemical ordering formed in as-arc-melted and annealed ingots of pure and substituted FeNi$_3$ ingots fabricated in this study as well as those reported by Kaya [29] and Takahashi [36] based on the enthalpy of endothermic peak for a completely ordered FeNi$_3$ (reported by Leech [9]). The measurement errors are smaller than the symbols.
The DSC heating and cooling scans of the annealed ingot samples as well as their first derivatives have been shown in Fig. 29. Even though the onset temperature in the cooling scans of the as-arc-melted matches the endothermic shoulder appearing in the heating scan, this is not the case for annealed ingots. The value of $T_C$ for the annealed pure FeNi$_3$ ingot is obtained from the endothermic shoulder appearing in the heating scan of DSC results for this sample [9] and it matches with the second discontinuity in the first derivative of the same scan. However, this value does not match with the onset temperature in the cooling scan of the same sample ($T_C = 590$ °C), Fig. 29(a). The same features have been seen for the annealed Cu-substituted FeNi$_3$ ingot sample. The DSC results of the annealed Mn-substituted FeNi$_3$ ingot sample contains no endothermic shoulder (neither there is any feature during the heating scan nor any discontinuity in the first derivative of this scan). The values of $T_C$ for the as-arc-melted and annealed ingot samples have been summarized in Table 10 and plotted in Fig. 29(d).
Figure 29: Heating and cooling scans as well as their first derivatives in the DSC results of a) pure, b) Cu-substituted, and c) Mn-substituted FeNi₃, (d) change in Curie temperature of pure and substituted FeNi₃ ingot samples in as-arc-melted and annealed states.
Table 10: Curie temperature of the chemically ordered and chemically disordered pure and substituted FeNi₃ ingot samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Curie Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi₃ – annealed ingot</td>
<td>628 ± 5</td>
</tr>
<tr>
<td>FeNi₃ – as-arc-melted ingot</td>
<td>590 ± 5</td>
</tr>
<tr>
<td>(FeNi₃)₀.₉₈Cu₀.₀₂ – annealed ingot</td>
<td>623 ± 5</td>
</tr>
<tr>
<td>(FeNi₃)₀.₉₈Cu₀.₀₂ – as-arc-melted ingot</td>
<td>570 ± 5</td>
</tr>
<tr>
<td>(FeNi₃)₀.₉₈Mn₀.₀₂ – annealed ingot</td>
<td>------</td>
</tr>
<tr>
<td>(FeNi₃)₀.₉₈Mn₀.₀₂ – as-arc-melted ingot</td>
<td>562 ± 5</td>
</tr>
</tbody>
</table>

5.2.4 Magnetic characterization of pure and substituted FeNi₃

Room-temperature magnetic measurement has been performed to study the effect of alloying additions on the magnetic properties of pure and substituted FeNi₃ ingot samples in both as-arc-melted and annealed states.

5.2.4.1 Magnetic Character of as-arc-melted ingot samples

The change in the hysteresis loop of as-arc-melted FeNi₃ with the addition of 2 at.% Cu or Mn is shown in Fig. 30. The as-arc-melted Cu-substituted and Mn-substituted FeNi₃ samples have about the same saturation magnetization ($M_S = 103.00 ± 0.08$ emu/g) and coercivity ($H_C = 3$ Oe) as those of the pure as-arc-melted FeNi₃. However, adding 2 at.% Cu or Mn increases the field required to reach magnetic saturation (anisotropy field) of the pure FeNi₃ ingot sample from $H_K = 1680$ Oe to $H_K = 2880$ Oe for Cu-substituted FeNi₃ ingot sample and to $H_K = 2180$ Oe for Mn-substituted FeNi₃ ingot sample. Furthermore, the susceptibility of the pure FeNi₃ ($\chi = 0.28$ emu/gOe) decreases to $\chi = \ldots$
0.16 emu/gOe with adding 2 at.% Cu and to $\chi = 0.2$ emu/gOe with adding 2 at.% Mn to this compound. These results are summarized in Table 11.

![Figure 30: $M(H)$ plots measured at room temperature for pure and substituted as-arc-melted FeNi$_3$ samples at different zooms.]

Table 11: Magnetic properties of as-arc-melted pure, Cu-substituted and Mn-substituted FeNi$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Saturation Magnetization (emu/g)</th>
<th>Susceptibility (emu/gOe)</th>
<th>Coercivity (Oe)</th>
<th>Anisotropy field (Oe)</th>
<th>Curie Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi$_3$ (as-arc-melted ingot)</td>
<td>103.60 ± 0.08</td>
<td>0.28 ± 0.02</td>
<td>3 ± 0.1</td>
<td>1680 ± 50</td>
<td>590 ± 5</td>
</tr>
<tr>
<td>(FeNi$<em>3$)$</em>{0.98}$Cu$_{0.02}$</td>
<td>103.00 ± 0.08</td>
<td>0.16 ± 0.02</td>
<td>3 ± 0.1</td>
<td>2880 ± 50</td>
<td>566 ± 5</td>
</tr>
<tr>
<td>(FeNi$<em>3$)$</em>{0.98}$Mn$_{0.02}$</td>
<td>105.00 ± 0.08</td>
<td>0.20 ± 0.02</td>
<td>3 ± 0.1</td>
<td>2180 ± 50</td>
<td>565 ± 5</td>
</tr>
</tbody>
</table>

5.2.4.2 Change in magnetic properties of ingot samples with annealing

Magnetic loops of the as-arc-melted and annealed ingot samples of pure and substituted FeNi$_3$ at room temperature are shown in Fig. 31. The magnetic properties obtained from the $M(H)$ measurements of these samples as well as literature values are
summarized in Table 12 and are plotted in Fig. 31. A 6% increase in saturation magnetization of Cu-substituted FeNi$_3$ (from $M_S = 103$ emu/g to $M_S = 110.3$ emu/g), a 9% increase for the pure FeNi$_3$ ingot (from $M_S = 103.6$ emu/g to $M_S = 113.6$ emu/g), and a 10% increase for the Mn-substituted ingot sample (from $M_S = 105$ emu/g to $M_S = 117.2$ emu/g) upon annealing has been measured. Furthermore, as the saturation magnetization of the samples increases with annealing, the magnitude of the applied field required to reach saturation (anisotropy field) also increases. A 11% increase in anisotropy field of the Cu-substituted ingot sample (from $H_K = 2870$ Oe to $H_K = 3200$ Oe), 34% for the pure ingot (from $H_K = 1680$ Oe to $H_K = 2250$ Oe), and 36% increase for the Mn-substituted ingot (from $H_K = 2170$ Oe to $H_K = 3010$ Oe) upon isothermal annealing have been measured. Decrease in the susceptibility of the ingot samples with isothermal annealing was also detected through magnetic measurements of these samples. A 12% reduction in the susceptibility of the Cu-substituted ingot (from $\chi = 0.16$ emu/gOe to $\chi = 0.14$ emu/gOe), a 50% reduction for the pure ingot (from $\chi = 0.28$ emu/gOe to $\chi = 0.14$ emu/gOe), and 75% decrease for the Mn-substituted ingot (from $\chi = 0.2$ emu/gOe to $\chi = 0.05$ emu/gOe) were measured upon isothermal annealing.
Table 12: Magnetic properties of as-arc-melted and annealed ingot samples of pure and substituted FeNi$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Saturation Magnetization (emu/g)</th>
<th>Susceptibility (emu/gOe)</th>
<th>Magnetization Field (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeNi$_3$ – as-arc-melted ingot</td>
<td>103.30 ± 0.08</td>
<td>0.28 ± 0.02</td>
<td>1680 ± 50</td>
</tr>
<tr>
<td>FeNi$_3$ – annealed ingot</td>
<td>113.60 ± 0.08</td>
<td>0.14 ± 0.02</td>
<td>2250 ± 50</td>
</tr>
<tr>
<td>(FeNi$<em>3$)$</em>{0.98}$Cu$_{0.02}$ – as-arc-melted ingot</td>
<td>103.00 ± 0.08</td>
<td>0.16 ± 0.02</td>
<td>2870 ± 50</td>
</tr>
<tr>
<td>(FeNi$<em>3$)$</em>{0.98}$Cu$_{0.02}$ – annealed ingot</td>
<td>110.30 ± 0.08</td>
<td>0.14 ± 0.02</td>
<td>3200 ± 50</td>
</tr>
<tr>
<td>(FeNi$<em>3$)$</em>{0.98}$Mn$_{0.02}$ – as-arc-melted ingot</td>
<td>105.00 ± 0.08</td>
<td>0.20 ± 0.02</td>
<td>2170 ± 50</td>
</tr>
<tr>
<td>(FeNi$<em>3$)$</em>{0.98}$Mn$_{0.02}$ – annealed ingot</td>
<td>117.20 ± 0.08</td>
<td>0.05 ± 0.02</td>
<td>3010 ± 50</td>
</tr>
</tbody>
</table>
Figure 31: $M(H_{\text{app}})$ plots measured at room temperature for as-arc-melted and annealed ingot samples of a) (FeNi$_3$)$_{0.98}$Cu$_{0.02}$, b) FeNi$_3$ and c) (FeNi$_3$)$_{0.98}$Mn$_{0.02}$. Change in d) saturation magnetization, e) anisotropy field, and f) susceptibility with isothermal annealing at $T = 470 \, ^\circ\text{C}$ for two weeks.
6. DISCUSSION & CONCLUSIONS

This thesis is focused on understanding the factors affecting the chemical order-disorder transformation in FeNi$_3$ (Fe-75 at.% Ni). FeNi$_3$ is employed as a model system to study the chemical ordering transformation in different compositions of iron-nickel alloys which undergo this type of phase transformation.

This chapter provides discussion and interpretation of the results presented in Chapter 5, within two major sections. Section 6.1 is dedicated to the discussion of the results obtained regarding understanding the role of rapid solidification prior to isothermal annealing on the formation of L1$_2$ phase in this compound, which fulfills the first aim of this thesis. Section 6.2 discusses the results obtained on the fulfillment of second aim of this project which is to evaluate the effect of ternary alloying additions on L1$_2$ phase formation in FeNi$_3$.

6.1 Understanding the effects of rapid solidification on the L1$_2$ phase formation in pure FeNi$_3$

Analyses of the structural, magnetic, and calorimetry results of the as-made and annealed pure FeNi$_3$ alloy are presented in Sections 6.1.1, 6.1.2, and 6.1.3, respectively. Section 6.1.4 discusses the progression of chemical ordering transformation in bulk and ribbons of pure FeNi$_3$ during isothermal annealing.

6.1.1 Analysis of structural results

The evolution of the crystal structure in the pure FeNi$_3$ ingot and in ribbon samples before and after isothermal annealing is analyzed in this section. The XRD patterns of all the as-made samples (ingot and ribbons) are in agreement with the standard XRD pattern of FeNi$_3$ published by Ahmed [6], Fig. 14(a). The unit cell volumes of the phases formed
in the as-arc-melted ingot sample of FeNi$_3$ are in agreement with the values reported by Wakelin [1], Lutts [65], and Swartzendruber [25] for quenched/cold-worked ingots of FeNi$_3$. The value of unit cell volume reported by Leech [9] for the phases formed in the quenched FeNi$_3$ ingot is ~ 0.6% smaller than that of the as-arc-melted ingot and is closer to the values calculated for the phases produced on the free and wheel sides of the rapidly solidified ribbon samples in this thesis, Fig. 15(a). Therefore, the phases formed in the as-spun ribbon samples of FeNi$_3$ during melt-spinning in this thesis are confirmed to have the same structural properties as those formed in the quenched FeNi$_3$ sample in Leech’s report.

The calculated unit cell volumes of the phases formed in all samples (formed in the ingot and on both sides of ribbons) reduce upon isothermal annealing at $T = 470$ °C for two weeks, as seen in Fig. 17(a). Wakelin [1], Leech [9], and Lutts [65] have reported similar trends, and attributed this decrease to an increase in the degree of chemical ordering (formation of L1$_2$ phase) in this compound as the ordered phase has a smaller unit cell volume than the disordered phase. The results reported here agree with this analysis and it is concluded that the isothermal annealing has been effective in increasing the degree of chemical ordering in the ingot and ribbon samples of pure FeNi$_3$.

The peak broadening in the XRD results of the as-arc-melted ingot sample is larger than those of the both sides of the melt-spun ribbons. This result is attributed to the smaller crystallite size formed in the ingot sample compared to that of the ribbon sample. At this time, it is not clear why the crystallites formed in the as-spun ribbon sample of pure FeNi$_3$ are larger than those formed in the pure as-arc-melted ingot sample. The crystallite sizes of the phases formed in the ingot sample increase during annealing. This
increase is attributed to the tendency to reduce the energy of system with eliminating the grain boundaries (grain coarsening). However, the crystallite sizes of the phases formed on the both sides of the as-spun ribbons, which are larger than that of the as-arc-melted ingot sample, do not change during annealing, Fig. 17(b). As rapid solidification can produce defects such as vacancies and dislocations in the lattice, it is hypothesized that the effect of annealing has been dedicated to defect recovery and not to grain growth for the ribbon samples.

6.1.2 Analysis of calorimetry results

As described in Chapter 2, the area enclosed by the endothermic/exothermic peak that appears during the heating/cooling scans in the calorimetry results of alloys which undergo a chemical order-disorder transformation is a measure of the energy associated with the rearrangement of atoms in the lattice [4]. Upon heating a chemically ordered sample, atomic rearrangement takes the crystal structure from a chemically ordered state to a chemically disordered state. Therefore, the endothermic peaks measured during heating scans of the DSC results of the samples in this study are associated with the chemical disordering phase transformation [9,36].

As mentioned in Chapter 2, the values for the measured enthalpy determined during calorimetric studies of FeNi$_3$ have been used to estimate the degree of chemical ordering in alloys which undergo this type of phase transformation [9,36]. The estimated degree of chemical ordering for the as-spun ribbon sample (19%) is significantly lower than that of the as-arc-melted ingot (35%), Fig. 18(b). These results are consistent with the dependence of the degree of chemical ordering on the cooling rate with which the FeNi$_3$ sample was cooled from a temperature greater than the critical temperature of
chemical order-disorder transformation ($T_{OD}$). The estimated cooling rate and degree of chemical ordering ranges for the ingot and ribbon samples are plotted in Fig. 32 and all compared with a curve extracted from Bozorth’s results on the correlation between magnetocrystalline anisotropy and cooling rate (see Chapter 2 for details) [35]. The cooling rate is inversely related to the degree of chemical ordering formed in FeNi$_3$ during cooling process. Furthermore, the cooling rate during the melt-spinning process is higher than that of the arc-melting process, which is much slower. Thus, the difference in cooling rates is concluded to be the cause of the lower degree of chemical ordering in the as-spun ribbons compared to that of the as-arc-melted ingot sample.

![Figure 32: Dependence of degree of chemical ordering on the cooling rate with which the sample cools from $T_{OD}$. This graph has been achieved based on the anisotropy constants for FeNi$_3$ reported by Bozorth [35].](image)

The endothermic peaks in the DSC signals of the as-arc-melted ingot and of as-spun ribbon samples are followed by higher-temperature shoulders at $T = 590$ °C, Fig. 18(a).
Leech [9] and Takahashi [36] reported the same feature appearing at the same temperature and associated it with the magnetic disordering transformation (the Curie transition) for FeNi$_3$. The Curie temperature for pure FeNi$_3$ obtained from DSC measurements in this thesis is also in agreement with the value of $T_C$ detected during magnetic measurements of quenched FeNi$_3$ by Wakelin [1].

The measured enthalpy values determined from the DSC results of the annealed ingot and ribbon samples is the sum of the heat absorbed during both the chemical and magnetic disordering transformations. As the heat absorbed during the magnetic disordering transition is trivial compared to that absorbed during the chemical disordering transition [36], the difference in the measured enthalpy values between the ingot and ribbon samples (both in as-made and annealed states) is most likely due to difference in the heat absorbed during the chemical disordering transformation in these samples. The enthalpy of chemical disordering and the estimated degree of chemical ordering is higher for the annealed ingot sample than for the annealed ribbon. Thus, it can be concluded that the annealed ingot sample of FeNi$_3$ in this study has higher degree of chemical ordering than that of the annealed ribbon sample. Based on comparisons made to Leech’s report [9], the degree of chemical ordering in annealed ingot sample of FeNi$_3$ is 100% and this sample is completely chemically ordered while the annealed ribbons are 87% chemically ordered. It should be noted that estimating about the same change in the degree of chemical ordering in the pure annealed ingot and ribbon samples shows that melt-spinning prior to annealing does not prevent the progression of chemical ordering in FeNi$_3$ during isothermal annealing. Since the as-spun ribbon sample contains less degree of chemical ordering than the as-arc-melted ingot sample, undergoing the same change in
the degree of chemical ordering for these samples leads the ribbon sample to contain less degree of chemical ordering than the ingot sample after isothermal annealing.

The second endothermic peak observed in the DSC heating scan (which occurs at $T = 630 \, ^\circ C$) of the annealed ingot sample with 100% chemical ordering in this study is similar in shape and amplitude to the peak associated with the Curie temperature reported by Leech which occurs at $T = 590 \, ^\circ C$ as determined during calorimetry study of a furnace-cooled FeNi$_3$ sample [9]. The endothermic peak observed in this study is tentatively assigned to the Curie transition of chemically ordered FeNi$_3$. If this is true, there is a 40 °C increase in the Curie temperature of the FeNi$_3$ ingot sample upon chemical ordering, which is consistent with the experimental results obtained by Wakelin [1] and with theoretical results reported by Dang [67]. However, increase in $T_C$ with chemical ordering is not in agreement with Leech’s report on equal values for the $T_C$ of the chemically ordered phase and disordered phase of FeNi$_3$ [9]. Furthermore, as seen in Fig. 16, there is no feature indicating magnetic disordering in the DSC heating signal of the annealed ribbons, which shows that the magnetic and the chemical disordering transformations happen at the same temperature range for this sample.

6.1.3 Analysis of magnetic results

As mentioned in Chapter 2, an increase in the degree of chemical ordering or of the L1$_2$ phase formation in FeNi$_3$ alters the magnetic properties of this compound [1,10,34]. The variations in the magnetic properties of FeNi$_3$ (as another indirect technique to estimate the degree of chemical ordering in this compound) have been used to confirm the results obtained during the calorimetry studies of the FeNi$_3$ samples in this thesis.
The values of the saturation magnetization for the as-spun ribbons and for the as-arc-melted ingot sample are in agreement with the values reported for quenched samples of this compound by Leech [9] and Wakelin [1]. As the shapes of ribbon and ingot samples used for magnetic measurement are different, it is hard to compare the extrinsic magnetic properties of these samples.

Comparing the room-temperature magnetic measurements of the as-arc-melted and the annealed ingot samples of pure FeNi$_3$ shows a 9% increase in saturation magnetization, a 34% increase in anisotropy field, and a 50% decrease in initial susceptibility for this sample after annealing, Fig. 21. On the other hand, the $M(H)$ measurements of the as-spun and annealed ribbon samples show only a 3% increase in saturation magnetization, no change in anisotropy field, and a 21% increase in susceptibility upon annealing. Considering the reports by Leech [7], Grabbe [8], Pan [20], and Bozorth [25] on the enhancement in the saturation magnetization and magnetocrystalline anisotropy as well as reduction in susceptibility of FeNi$_3$ with increase in the degree of chemical ordering (increase in L1$_2$ phase formation) in this compound, the magnetic results are consistent with the DSC results that show a higher degree of chemical order in the ingot samples than in the ribbon samples of pure FeNi$_3$. It is confirmed in this study that the chemically ordered phase in FeNi$_3$ (L1$_2$) has higher saturation magnetization and anisotropy field as well as lower initial susceptibility than the chemically disordered phase in this compound (A1).
6.1.4 Conclusions on understanding the effect of rapid solidification on the L1$_2$ phase formation in FeNi$_3$

The effect of rapid solidification (herein, melt-spinning) conducted prior to annealing on the progression of the chemical ordering transformation in FeNi$_3$ during isothermal annealing is quantified by coupled calorimetry and magnetic measurements. Structural, calorimetry and magnetic results for as-made and annealed ingot and ribbon samples of pure FeNi$_3$ have been presented in Chapter 5 and interpreted here.

Higher values of enthalpy of chemical disordering (observed in the DSC results), larger values of saturation magnetization and greater values of anisotropy field (achieved through magnetic characterization results) imply that the annealed FeNi$_3$ ingot sample has a higher degree of chemical ordering (greater content of the L1$_2$ phase) than does the ribbon sample. These results lead to the conclusion that rapid solidification carried out prior to isothermal annealing at $T = 470 \, ^\circ$C, has not improved the progression of chemical ordering and formation of L1$_2$ phase in FeNi$_3$ during annealing.

Even though quenching (rapid solidification) has been introduced as a technique to increase the vacancy concentration in lattice and improve the short-range diffusion rate during annealing [44,68], melt-spinning (as a rapid solidification technique) prior to isothermal annealing at $T = 470 \, ^\circ$C did not enhance the formation of the L1$_2$ phase in the FeNi$_3$ ribbon samples. The lower degree of chemical ordering in the ribbon sample as compared to that of the ingot after isothermal annealing can be attributed to two main effects. First, since the fabricated ribbons in this study are on the micro-scale in thickness, it is possible that any vacancies which have been produced through rapid solidification could easily reach the surface during isothermal annealing and leave the
lattice before being used as diffusion pathways. To prevent this occurrence, thicker ribbon samples are required.

The second explanation for greater degree of chemical ordering formed in the annealed ingot than the annealed ribbon may be a suboptimal temperature was chosen for isothermal annealing. Studies on the effect of quenching prior to isothermal annealing on enhancement of the degree of chemical ordering in CuAu$_3$ [44] and FeNi$_3$ [42] show that quenching can help to increase the rate of diffusion only if the quenched samples were annealed at temperatures much lower than $T_{OD}$ for these compounds. Thus, a lower isothermal annealing temperature may be needed for the samples subjected to rapid solidification prior to annealing in order to prevent the elimination of the processing-induced vacancies.
6.2 Understanding the role of alloying additions on the L12 phase formation in FeNi3

This section is focused on understanding the effects of ternary alloying additions on the L12 phase formation (degree of chemical ordering) in the FeNi3 compound through structural, magnetic and calorimetry studies of as-arc-melted and annealed ingot samples of pure, Cu-, and Mn-substituted FeNi3. Details of these characterization results are provided in Section 5.2 and the following sections are dedicated to the analyses and discussion of the obtained results.

Analyses of the structural, magnetic, and calorimetry results are presented in Sections 6.2.1, 6.2.2, and 6.2.3, respectively. Section 6.2.4 discusses the effect of each alloying addition on the progression of chemical ordering transformation in FeNi3 compound during isothermal annealing.

6.2.1 Analysis of structural results

X-ray diffraction results presented in Fig. 22 show no change in peak position and peak broadening of Bragg peaks of pure FeNi3 ingot sample after adding 2 at.% Cu or Mn to this compound. Furthermore, the concentration of the alloying elements added to the parent compound is sufficiently low that any effects on the unit cell volume and crystallite size of FeNi3 in the as-arc-melted state are minor. Thus, it can be said that adding 2 at.% Cu or Mn to FeNi3 does not significantly change the microstructural properties of this compound in its as-arc-melted state.

Although no superstructure peak is visible in the XRD patterns of the annealed pure and substituted ingot samples, an observation which is attributed to use of Cu-Kα as the XRD radiation source, the unit cell volumes of these samples decreased after annealing. This result is in agreement with the data reported by Wakelin [1], Leech [9], and Lutts [7]
which has been attributed by these authors to an increase in the degree of chemical ordering (formation of L1\textsubscript{2} phase). Thus, based on the structural results, the degree of chemical ordering has been increased in the pure, Cu-substituted and Mn-substituted FeNi\textsubscript{3} ingot sample during isothermal annealing at $T = 470 \, ^\circ\text{C}$ for two weeks.

6.2.2 Analysis of calorimetry results

As discussed in Section 6.1.2, the endothermic peaks observed during the DSC heating scans of the FeNi\textsubscript{3} samples are attributed to the chemical disordered transformation that occurs upon heating. As can be seen in Fig. 23, there is a decrease in the enthalpy, and therefore in the estimated degree of chemical ordering of the as-arc-melted FeNi\textsubscript{3} upon substituting 2 at.% Cu or Mn. These results lead to two conclusions: (a) Cu and Mn are incorporated in the lattice structure of FeNi\textsubscript{3}, and (b) these ternary alloying elements impede the formation of the L1\textsubscript{2} phase in FeNi\textsubscript{3} during the fabrication process (arc-melting).

Since the onset temperature values in the DSC cooling peaks of the as-arc-melted ingots in this study are considered to be the Curie temperatures for these samples \cite{9,36}, the effect of ternary alloying additions on the Curie temperature of FeNi\textsubscript{3} compound can be studied via DSC measurements. The Curie temperature of the as-arc-melted FeNi\textsubscript{3} ingot decreases after adding 2 at.% Cu or Mn to this compound; this effect is attributed to a change in the electronic structure of FeNi\textsubscript{3} with ternary alloying addition to this alloy system.

Calorimetric analysis of the annealed ingots can help to understand the role of each alloying element in prevention/promotion of the L1\textsubscript{2} phase formation in FeNi\textsubscript{3} during isothermal annealing. The measured value of the enthalpy of chemical disordering
transformation and the estimated degree of chemical ordering increases upon annealing for each ingot sample. Thus, isothermal annealing at $T = 470 \, ^\circ\text{C}$ for two weeks has been effective to promote the formation of $\text{L}_1^2$ phase in these samples. The increase in the estimated degree of chemical ordering for the Cu-substituted FeNi$_3$ ingot sample upon annealing is less than that of the pure ingot sample. Therefore, adding 2 at.% Cu to FeNi$_3$ has prevented the progression of $\text{A}_1$-to-$\text{L}_1^2$ phase transformation in this compound, Fig 28(b). Furthermore, a larger increase in the estimated degree of chemical ordering formed upon isothermal annealing in the Mn-substituted ingot has been detected relative to that of the pure FeNi$_3$. This results indicates that adding 2 at.% Mn to FeNi$_3$ improves the progression of chemical ordering transformation during isothermal annealing, Fig. 28(b).

Since the annealed FeNi$_3$ sample in this study is considered to be 100% chemically ordered (as described in Section 6.1.2), the second endothermic peak in the DSC results obtained for this sample is attributed to the Curie temperature for the $\text{L}_1^2$ phase formed during isothermal annealing in this sample ($T_{C,\text{L}_1^2} = 630 \, ^\circ\text{C}$). Upon heating in the DSC, the chemically ordered FeNi$_3$ sample (annealed ingot) undergoes a chemical disordering transformation and the crystal structure of this sample changes from $\text{L}_1^2$ to $\text{A}_1$. Therefore, the discontinuity in the first derivative of the cooling scan is attributed to the Curie temperature for the $\text{A}_1$ ($T_{C,\text{A}_1} = 590 \, ^\circ\text{C}$) phase formed after heating this sample, Fig. 29. As reported by Wakelin [1] and Dang [67], the $T_C$ of the $\text{L}_1^2$-FeNi$_3$ phase is higher than that of the $\text{A}_1$-FeNi$_3$ phase; therefore, the difference in the values of $T_C$ for the chemically ordered and chemically disordered FeNi$_3$ samples in this thesis is due to the difference in the degree of chemical ordering formed in these samples.
Estimating the Curie temperature of the Cu-substituted FeNi₃ ingot sample can help to understand the role of Cu in the prevention or promotion of chemical ordering in FeNi₃. As mentioned before, the noted decrease in the Curie temperature of the as-arc-melted FeNi₃ sample with Cu addition (from $T_C = 590 \, ^\circ C$ to $T_C = 570 \, ^\circ C$) indicates that this ternary element has been incorporated in the lattice structure of FeNi₃ during arc-melting. The Curie temperature of this sample has increased from $T_{C,A1} = 570 \, ^\circ C$ to $T_{C,L12} = 623 \, ^\circ C$ ($53 \, ^\circ C$ increase) after annealing which is a larger change relative to that of the pure FeNi₃ (40 \, ^\circ C increase), Fig. 29. As the change in the estimated degree of chemical ordering in the Cu-substituted FeNi₃ sample upon annealing is less than that of the pure FeNi₃ ingot sample, the increase in the Curie temperature of the Cu-substituted ingot sample upon annealing is not related to increase in the degree of chemical ordering in this compound. From the Fe-Cu equilibrium phase diagram, it can be found that Fe and Cu have only an extremely limited solid solubility being less than 5 at% below 810 °C, and do not form any intermetallic compound, even though their atomic radii are quite similar. This is in accordance with the fact that the Fe-Cu binary system has a large positive heat of mixing (13kJ/mol) [69]. Therefore, it is hypothesized that the increase in the Curie temperature of Cu-substituted FeNi₃ ingot sample after annealing is due to Cu atoms gaining enough thermal energy and leaving the lattice structure of FeNi₃ during isothermal annealing. This analysis of the DSC results obtained from the Cu-substituted FeNi₃ ingot sample clarifies the influence of Cu addition in progression of chemical ordering in FeNi₃.

The DSC results obtained from the chemically ordered Mn-substituted FeNi₃ ingot sample contain no feature in either data from the heating scan or its first derivative.
Therefore, Mn addition to FeNi$_3$ has affected the nature of chemically ordered sample of this compound in such a way that the chemical and magnetic disordered transformations take place in the same temperature range for this compound.

6.2.3 Analysis of magnetic results

The magnetic properties of FeNi$_3$ change upon substitution of 2 at.% Cu or Mn to this compound, as seen in Fig. 30 and Table 12. However, these changes are not significant and the as-arc-melted substituted ingot samples have similar magnetic properties to the as-arc-melted pure FeNi$_3$ ingot sample. Upon annealing at $T = 470 \, ^\circ C$ for two weeks, the saturation magnetization, anisotropy field, and susceptibility of the ingot samples all changed significantly, as seen Fig. 31. An increase in the saturation magnetization and the anisotropy field as well as a decrease in the initial susceptibility values of the pure FeNi$_3$ ingot after annealing have been detected which are consistent with the results reported by Leech [9], Grabbe [10], Pan [70], and Bozorth [34]. These changes in the magnetic properties of FeNi$_3$ upon annealing are associated with an increase in the degree of chemical ordering (L$_{12}$ phase formation) in this compound achieved during isothermal annealing at $T = 470 \, ^\circ C$. Similar changes have been detected in the magnetic properties of the Cu- and Mn-substituted FeNi$_3$ ingot samples after annealing. The measured increase in the values for saturation magnetization and anisotropy field as well as the decrease in the initial susceptibility values of the Mn-substituted ingot sample after annealing are more than those measured for the pure FeNi$_3$ ingot sample, as seen in Fig. 31. Therefore, it is deduced that Mn promotes the A1-to-L$_{12}$ transformation in FeNi$_3$ during isothermal annealing. On the other hand, the increase in the saturation magnetization and anisotropy field as well as decrease in susceptibility
values of the Cu-substituted ingot sample after annealing is less than those of the pure FeNi$_3$ ingot sample, Fig. 31. Thus, Cu addition to FeNi$_3$ inhibits the A1-to-L1$_2$ transformation in this compound. These results show that the ternary alloying elements can change the magnetic properties of FeNi$_3$ depending on their role in advancement or suppression of chemical ordering transformation during isothermal annealing.

6.2.4 Conclusions on understanding the effect of alloying additions on the L1$_2$ phase formation in FeNi$_3$

This section provides conclusions from the results presented in Section 5.2 of this thesis on understanding the role of Cu or Mn as ternary alloying elements on the degree of chemical ordering (L1$_2$ phase formation) in FeNi$_3$.

The difference in the estimated degree of chemical disordering as well as the trend of change in magnetic properties for each ingot sample before and after annealing represents the performance of each alloying element in improving/preventing the formation of the L1$_2$ phase in FeNi$_3$ during isothermal annealing.

Analyses of the calorimetry and magnetic results shows a 98% increase in the degree of chemical ordering, a 10% increase in saturation magnetization, and a 36% increase in anisotropy field, as well as a 75% decrease in the susceptibility values of the Mn-substituted FeNi$_3$ ingot sample upon annealing. On the other hand, the same analysis reveals a 76% increase in the degree of chemical ordering, a 9% increase in saturation magnetization, and 34% increase in anisotropy field, as well as a 50% decrease in the susceptibility values for the pure FeNi$_3$ ingot sample after annealing. Coupled calorimetry and magnetic results of the as-arc-melted and annealed Mn-substituted FeNi$_3$ ingot samples compared to those of the pure FeNi$_3$ ingot samples indicates that even though
Mn disrupts formation of the L1₂ phase during arc-melting (as discussed in Section 6.2.2), it has the most efficient role on the advancement of this transformation during isothermal annealing (as discussed in Section 6.2.2 and 6.2.3). The phase diagram of the Mn-Ni system [71] shows the same chemical ordering transformation (A1→L1₂) at the MnNi₃ region as that of the Fe-Ni system [25] at the FeNi₃ region. Furthermore, comparing the standard XRD patterns of both of these compounds shows the signature L1₂ phase for both compositions of FeNi₃ and MnNi₃, Fig 33. Therefore, it is hypothesized that the reason for increase in the rate of A1→L1₂ phase transformation in FeNi₃ with Mn addition is replacement of Fe with Mn and the tendency of Mn and Ni to form L1₂-MnNi₃ during the annealing process.

![Figure 33: Standard X-ray diffraction patterns of L1₂ phase in FeNi₃ and MnNi₃ [71].](image-url)
Upon annealing the Cu-substituted FeNi₃ ingot sample, a 56% increase in the degree of chemical ordering, a 3% increase in the saturation magnetization, and an 11% increase in the anisotropy field, as well as a 12% decrease in susceptibility values of this sample have been measured. Comparing these results with those measured for pure FeNi₃ before and after isothermal annealing indicates that Cu disrupts the formation of L₁₂ phase in FeNi₃ through leaving the lattice structure of this compound during isothermal annealing.
7. RECOMMENDATIONS FOR FUTURE WORK

This section serves to provide recommendations for future experiments which may be useful to address the questions raised in this thesis. It is expected that results obtained from experiments and guidance recommended in this section provides more insights on the A1 → L12 phase transformation in FeNi3 compound.

Results obtained in this thesis are used to investigate the factors affecting the chemical order-disorder phase transformation in iron-nickel alloys through coupled calorimetric and magnetic analyses of FeNi3-based samples. The effect of rapid solidification conducted prior to isothermal annealing and addition of a third element on the progression of A1-to-L12 phase transformation was studied through fabrication of ingot and ribbons of pure FeNi3 samples and performing isothermal annealing at T = 470 °C. However, there are still some questions to be addressed, specifically:

1) Does the thickness of the fabricated FeNi3 ribbons affect the L12 phase formation in this compound during isothermal annealing?

**Recommendation:** Ribbon samples of pure FeNi3 can be fabricated by manipulating the orifice dimension of the crucible during the melt-spinning process; this can change the thickness of ribbon samples. Performing isothermal annealing at T = 470 °C for two weeks on the ribbons with larger thickness, and conducting direct (X-ray diffraction using Co-Kα radiation) or indirect (coupled calorimetry and magnetic characterization) measurements method in order to evaluate the degree of chemical ordering in the samples. This set of experiments can help in investigating the role of samples’ thickness on the L12 phase formation in the fabricated ribbons during the isothermal annealing.
2) What is the suitable annealing temperature for the ribbon samples of pure FeNi$_3$ which have been subjected to rapid solidification?

**Recommendation:** Future work regarding this question will be focused on the isothermal annealing of the fabricated ribbon and ingot samples (under the same fabrication conditions as the ones in this study) at lower temperature ranges. Performing the direct or indirect characterization methods suggested in literature to evaluate the degree of chemical ordering in the annealed ribbons will result in choosing a suitable annealing temperature for samples which have been subjected to rapid solidification prior to isothermal annealing.

3) To what extend does the Mn addition to FeNi$_3$ enhances the A1-to-L1$_2$ phase transformation in the compound? Is there any optimum point for this addition?

**Recommendation:** Future works aimed at addition of greater amounts of Mn to the ingot sample of FeNi$_3$ will be useful in investigating the role of this ternary alloying element in progression of chemical ordering in FeNi$_3$. 
8.0 NOMENCLATURE

Letters

a  Lattice parameter, Å
A  Area, \( m^2 \)
A1 fcc chemically disordered phase
Cp specific heat capacity, J/K
d  interplanar spacing in a lattice, Å
DSC  differential scanning calorimetry
EDS energy-dispersive X-ray spectroscopy
E_K  anisotropy energy, erg/cc
f  atomic scattering factor
fcc face-centered cubic center
F  structure factor
FWHM full width at half maximum, B
H, k, l  miller indices
H_{app} applied magnetic field, Oe
H_C coercivity, Oe
H_K anisotropy field, Oe
K  anisotropy constant, \( \text{erg/cc} \)
k  scherrer constant, taken as 0.9
K_{\alpha} emission lines
K\textsubscript{\beta} emission lines
L\textsubscript{\alpha} emission lines
L\textsubscript{10} fct chemically ordered phase
L\textsubscript{12} fcc chemically ordered phase
n order of reflection
M magnetization, emu/g
M\textsubscript{S} saturation magnetization, emu/g
P pressure, atm
SEM scanning electron microscopy
t time, sec
T temperature, °C
T\textsubscript{C} Curie temperature, °C
T\textsubscript{OD} chemical order-disorder temperature, °C
V Volume, (Å\textsuperscript{3})
VSM vibrating sample Magnetometry
XRD X-ray diffraction

Greek
\alpha-, \beta-site denotes a particular lattice site in a unit cell
\alpha directional cosine
\gamma chemically disordered phase
$\Sigma$  summation operator

$\theta$  angle, °

$\lambda$  wavelength of radiation, Å

$\mu$  linear absorption coefficient

$\pi$  ratio of a circle's circumference to its diameter, 3.14159
9.0 REFERENCES


[63] Loving, M., Understanding the magnetostructural transformation in FeRh thin film, 2014.


