Defect structures, phase characterization, and microstructure complexity of rare-earth GdNi1–xCox alloys

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Defect structures, phase characterization, and microstructure complexity of rare-earth GdNi$_{1-x}$Co$_x$ alloys

by

Timothy Edward Prost

A thesis submitted to the graduate faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

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2017

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DEDICATION

To my wonderful wife, Sarah, who has been a constant source of confidence, love, and support throughout my academic career.
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ABSTRACT

Rare-earth transition metal alloys and compounds exhibit extraordinary magnetic behavior and properties, but are typically difficult to fully homogenize. The presence and persistence of linear features in giant magnetocaloric ($\text{Gd}_5\text{Si}_2\text{Ge}_2$) materials is well known and their effect on the paramagnetic to ferromagnetic transition has been documented. Similarly, other Gd compounds have been studied for their magnetic properties but their microstructure has not been thoroughly explored. In this work, giant magnetoelastic effect compounds $\text{GdNi}_{1-x}\text{Co}_x$ are investigated using electron microscopy techniques in order to determine changes to microstructure as a result of the substitution of Co for Ni.

Initial investigations of the as-cast and annealed microstructures reveal a persistent $\text{Gd(Ni,Co)}_2$-type phase as a minor phase (roughly 5 vol.%) from $x=0.00$ to $0.30$, while both $x=0.50$ and $1.00$ contain a significant (roughly 38 and 21 vol.%, respectively) amount of a secondary phases. The secondary phase in $x=0.50$ is determined via energy dispersive x-ray spectroscopy (EDS) to be approximately $\text{Gd}_4(\text{Ni,Co})_3$, while the phases in $x=1.00$ are $\text{GdCo}_2$ and $\text{Gd}_4\text{Co}_3$. Electron backscattered diffraction analysis of the $x=0.30$ specimen indicates an extreme directionality to the grain structure with columnar grains 30-50 $\mu$m wide by upwards of 1000 $\mu$m long when viewed parallel to the growth axis. Upon sectioning perpendicular to the growth axis, several new microstructural features are discovered including distinct lines which are surrounded by dendritic arms radiating outward. These distinct linear features are determined through TEM investigations to be mirror twins on the (110) plane and appear to be several tens of $\mu$m long. Further, the dendrites are identified as being deficient in Co (compared to the matrix) while the boundary between the light and dark regions exhibits characteristics of an anti-phase boundary. When annealed, the dendrites grow to encompass the entire grain, and the boundaries between these regions straighten out and become more regular. Similar microstructures are noted for the other members between $x=0.00$ and $0.30$ while variations in the Ni:Co ratio for the matrix
and 1:2 phases are noted. Other microstructural features noticed include stacking faults and
the persistence of wide linear features with a composition different than that of the matrix. The
composition of these wide features is determined via EDS to be between the Gd$_4$(Ni,Co)$_3$ and
Gd$_3$(Ni,Co)$_2$-type phases. Atom probe tomography data correlates well with this and indicates
the composition of the wide linear features in $x=0.30$ to be Gd$_3$(Ni,Co)$_2$.

The $x=0.50$ specimen contains Gd(Ni,Co), Gd(Ni,Co)$_2$, Gd$_4$(Ni,Co)$_3$, and Gd$_{12}$(Ni,Co)$_7$-
type phases. Diffraction analysis of the 1:1 phase is in good agreement with literature values
for this composition. The 12:7 phase is fitted to the Ho$_{12}$Co$_7$ P12$_1$/c1 crystal structure with
lattice parameters $a=7.56\,\text{Å}$, $b=12.51\,\text{Å}$, $c=11.46\,\text{Å}$, $\beta=108.8^\circ$ compared to literature values of
$a=8.41\,\text{Å}$, $b=11.39\,\text{Å}$, $c=11.16\,\text{Å}$, $\beta=124.2^\circ$ differing significantly from literature likely due to the
presence of Ni. However, the 4:3 phase has not been indexed for this composition before and
when fitted to the Gd$_4$Co$_3$ P6$_3$/m crystal structure lattice parameters of $a=b=11.81\,\text{Å}$, $c=4.20\,\text{Å}$
were calculated compared to literature $a=b=11.81\,\text{Å}$, $c=4.05\,\text{Å}$. The GdCo sample contained a
eutectic region containing both the 4:3 phase and regions ranging in composition from 12:7 to
Gd metal (including regions near the Gd$_3$Co composition).

The instability of Co in the GdNi-type crystal structure seeds the breakdown of the solid
solution and may be the cause for the numerous microstructural features seen here. Annealing
for long periods has a significant effect, but does not fully remove these features. Effects of
these features on the magnetic properties has not been performed and is required to determine
if they play a significant role. In the case where they impact the bulk properties, steps should
be taken in synthesis of specimen to ensure the bulk properties measured are not in any way
due to microstructural inhomogenities such as those seen here.
CHAPTER 1. INTRODUCTION

To provide a clean and sustainable future issues such as production, storage, and use of energy in all forms must be addressed. In order to conform with the current supply of and demand for energy, great advancements in any one, or simultaneous systematic increases in all, are necessary. Amazing improvements have been made in solar panel photovoltaics (PV) technology, and wind turbine farms have sprouted up across the United States.[1] Flowing water has been a power source for centuries, and recently measures have been taken to harness the power of the ocean’s waves and tides to generate electricity.[1] Despite all of this, technologies centering around both the transmission and storage of this energy still lag behind. The use of long transmission lines is inefficient and incurs unnecessary losses in transmitted power.[1] Though the de-localization of power generation, through widespread adoption of wind turbines and solar panels, can help compensate for some of these losses, the physical limitations of transporting electricity cannot be overcome easily. And, unfortunately, once the electricity reaches the user the methods by which it is consumed are in some instances exceedingly inefficient. More advanced designs are needed at every level of the energy cycle to ensure the continued, safe, clean production, storage/transportation, and use of electricity.

The need for safer, cleaner energy has become increasingly important in the past few years due to studies linking burning of fossil fuels to climate change.[2] There are already renewable sources being exploited for energy production (e.g. hydro-electric, solar collectors, and wind turbines), but means for efficient storage and usage remain problematic. Transmission line and unaccounted-for losses totaled up to 7.3% of all electricity generated in 2007 and has averaged around 6.7% from 2002 to 2012 according to the U.S. Energy Information Administration.[3] That totals up to 264 million Megawatt-hours for 2012, equal to 9.511x10^{17} Joules or roughly equivalent to 20 million tons of coal\(^1\) lost.[3]

\(^1\)This value was calculated based upon the data for 2012 only; averages of coal burned for electricity generation, total electricity generation, and electricity losses for the 2002 to 2012 time period yield a figure closer to 30 million
However, one of the most wasteful uses of energy is in the cooling of spaces and goods. When heating a room, there are many “clean” options including solar energy or geothermal heating which may not be the most efficient means, but come from renewable sources and have little impact on the environment. Even “clean” burning fossil fuels like natural gas can be used with little impact; however, cooling remains a difficult task. While the vapor-compression cycle has been a testament to humanity’s ingenuity, it remains one of the least efficient uses of energy today, and a change in the methods used to cool must be found.

Impetus for this change comes from the need to increase efficiency, and reduce harmful chemicals produced and circulated within the consumer market. Current vapor-compression cycle A/C units, refrigerators and freezers are notoriously inefficient (i.e. 40% of the Idealized Carnot cycle [4]) wasting electricity and thereby causing excess pollution from energy sources such as fossil fuel burning power plants. The use of such refrigerants containing chlorofluorocarbons (CFC’s) also has been linked to Ozone depletion and climate change according to the European Directive 2006/40/EC. Though many CFC containing refrigerants have been banned, or phased out, other, newer ones continue to be replaced due to potential environmental hazards. Magnetic refrigeration cycles have been proven to be capable of achieving 60% Carnot efficiency,[4] while simultaneously removing the need for toxic refrigerants. Instead, magnetic refrigeration uses solid “refrigerants” and the heat transfer fluid, while variable, is often water.

Materials capable of increasing efficiency at every link in the chain of the energy cycle will always be important. Magneto-caloric materials (MCM’s) have a huge potential to help reduce waste, but efficiency shouldn’t be pushed only on the areas where it is needed most, it should become a cultural obligation to think about efficiency in every aspect. Energy recovery can be attained by materials which convert excess heat or deformation into magnetic or electrical signals. The main thrust of this research is to improve the state of the art materials for energy storage and usage, focusing on magnetism-structure coupled rare-earth alloys which can fill some niches of energy recovery and production. The work done here will be on forming structure-property relationships and performing thermodynamic and kinetic analyses of each of these materials to better understand the mechanisms which make them worthwhile and

\[ \text{tons of coal wasted per year for the 10 year time period.}[3] \]
to improve their performance by adjusting synthesis and processing parameters based upon what is discovered. This will be achieved by the combination of electron microscopy and other characterization techniques to confirm results. The author of this work would like to make it clear that this work is done as part of a larger group working on these materials and the characterization performed by the other members will help paint a more complete picture of the overall focus of the funding project.

Extraordinary Responses

The way in which materials react to any given stimulus is sometimes taken for granted, though the landscape of functional materials is far from static. Take for instance heat; most materials begin to expand with increasing temperature, this is denoted by assigning a positive thermal expansion coefficient $\alpha [\text{K}^{-1}]$.

$$\alpha_V = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \quad \text{(1)}$$

where $V$ is the volume of the specimen and the subscript $p$ indicates a pressure-constant process. This relation can be interpolated to a single dimension instead in which case the length change can be measured:

$$\alpha_l = \frac{1}{l} \left( \frac{\partial l}{\partial T} \right)_p \quad \text{(2)}$$

Most materials have a positive coefficient of thermal expansion meaning that a temperature increase will cause the specimen to expand. Some materials, under extreme conditions, can exhibit a negative thermal expansion coefficient, as is the case with ice ($\text{H}_2\text{O}(s)$) below 73 K.[5] However, a few materials have been engineered to have a negative thermal expansion, but the effect is usually owing to a deliberately structured configuration which is highly anisotropic having a positive thermal expansion in the other directions.[6] Outside of this phenomenon, there are many others which can be exploited for use in a number of applications. One of the more interesting categories is that of magnetic phenomena in which a magnetic field induces a change in a number of different properties of the material. A few examples include magnetism
linked with: physical dimensions of the material (magnetostriction (MS)), electrical resistance (magnetoresistance (MR)), and temperature of the material (magnetocaloric effect (MCE)). Each of these have interested the scientific community for decades, but magnetocaloric materials (MCM’s) have found renewed interest.

The long history of the MCE starts with its discovery and first appearance in literature in 1881 by Emil Warburg, a German physicist. At the time it was only a novelty and was not seen in literature until years later, when almost simultaneously William Giaque and Peter Debye separately developed theoretical models which could employ MCM’s as solid state refrigerants. The techniques developed by the two were used for years to study matter at very low temperatures (below 1 K), and in 1949 Giaque won the Nobel Prize in Chemistry for his contribution. Since then, the focus of MCM applications has shifted toward magnetic refrigeration to replace commercial and consumer refrigerators operating near room-temperature (RT). Initially disregarded due to lack of materials capable of operating at these temperatures, the advent of some impressive refinement of rare earth materials led to behavior seen for the first time in high-purity Gadolinium-alloys which could potentially fill this position.

Magnetism and Magnetic Materials

Magnetic materials have been a curiosity of the human race since the first lodestones (Fe(II,III) Oxide) were picked up by our ancestors. Since then a great deal of work has been done to measure, label and categorize a plethora of different types of magnetic materials. We now have paramagnets (PM), ferromagnets (FM), ferri-magnets (FiM), diamagnets (DM), and anti-ferromagnets (AfM). The first “magnets” known were actually ferrimagnets, which act similarly to ferromagnets in many cases.

To adequately explain magnetism and magnetic materials would exceed the scope of this document, thus only a brief overview will be entertained. It is important to first investigate how a magnetic material reacts to an externally created magnetic field (i.e. from a current passed through a circular wire). All materials react to magnetic fields in different ways. The field external to the material is denoted $H$, and the continuation of that field within the material is typically referred to as magnetic induction $B$. $B$ is a combination of the external applied field
and the materials own magnetization $M$,

$$B = \mu(H + M), \mu = \mu_0\mu_r^2$$  

(3)

where, $\mu_0$ is the permeability of free space, and $\mu_r$ is the relative permeability of the material. A typical measurement of magnetic materials is done by subjecting them to an external field ($H$) and measuring the induction ($B$) then increasing or decreasing the field ($H$) and remeasuring. This can be achieved by a number of devices all having their benefits and drawbacks. For simplicity’s sake, assume that a material can be probed in such a way as to measure, but not disturb, the induction ($B$) present inside the material all while being subjected to an external, varied field ($H$). Ferromagnetic materials (such as Iron) will react to an external field ($H$) by first increasing their internal magnetization ($M$) linearly, followed by an exponential increase, and eventual asymptotic approach to what is called saturation ($M_s$ or $B_s$) as can be seen in Figure 1 (origin to $B_s$). Since $B$ is proportional to $H$ plus $M$, it will continue to increase linearly after the saturation point. Upon lowering $H$ the internal magnetization remains near $M_s$ until approaching $H = 0$ where it begins to fall. The value of $B$ at $H = 0$ is called the remanence or remanent magnetism ($B_r$), and represents the magnetic induction present within the material when the applied field is zero. This is one measure of the “strength” of a magnet. The next metric comes from the amount of applied field in the opposite direction necessary to

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2There are variations of this same equation which depend on the system of units being used; therefore for clarity only SI units will be used in this document.
“demagnetize” the material (or make $B = 0$). At this point in the curve the corresponding field is called the coercive field ($H_c$) or just the coercivity of the material. After this point the materials follows a similar curve to saturation in the other direction and to complete the loop the field is reversed and the material is returned to the initial saturation in the primary direction. This behavior is referred to as hysteresis, since the material reacts to a stimulus based upon its history. If the loop is reversed before reaching saturation, a smaller version of the full loop is created. This and any loop not reaching saturation in both directions are referred to as minor loops.

The magnetization of a ferromagnet takes place by the growth (and reduction) of regions of uniform magnetic alignment called domains. These domains are similar to the granular structure of many metals, in the sense that each grain contains atoms configured similarly and of a common orientation, and each domain is composed of similarly aligned magnetic moments. The exact partitioning of the domains depends on many factors including the grain size and relative crystallographic orientation (i.e. texture) among all grains, and the history of magnetization. When these domains grow, shrink, or move in response to external fields they can change the overall magnetization of the sample from zero net magnetization, when all domains are randomly oriented, to the saturation magnetization which occurs when all domains are similarly oriented. However, if the applied field is not parallel with the preferred crystallographic direction of magnetization, called the easy axis, then the domain orientation rotates reversibly to the direction of a sufficiently high applied field (called technical saturation, Figure 2 d).

The magnetization of a ferromagnet can be destroyed by heating it to its Curie temperature ($T_c$) at which point it undergoes a magnetic transition and becomes paramagnetic, where it loses its hysteretic behavior and the induction reacts to an applied field linearly with slope $\mu$ and no hysteretic behavior.

$$\frac{B}{H} = \mu$$ (4)

When the temperature is lowered back to the ferromagnetic range ($< T_c$), the spontaneous creation of domains has an interesting effect on the material. It causes a change in dimensions called magnetostriction ($\lambda$), and is present in most ferromagnetic materials to varying degrees.
Figure 2  Behavior of a ferromagnetic material with (a) zero applied field and (b-d) applied field (H) of varied strength.
(a) multiple randomly oriented domains within the material, zero (or near-zero) net magnetization. (b) domains oriented close to the direction of the applied field begin to grow while those perpendicular or anti-parallel shrink. (c) all domains oriented parallel and (d) moments are reversibly turned within the existing domains to the direction of H. Image courtesy of [12]
Magnetostriction is defined as the change in length divided by the initial length.

\[ \lambda = \frac{dL}{L} \]  

(5)

When an isotropic ferromagnet is brought to saturation the strain is equal to \( e \) whereas the strain associated with the spontaneous magnetization just below \( T_c \) is equal to \( \frac{e}{3} \). This spontaneous magnetostriction is labeled \( \lambda_0 \) and for isotropic materials it is calculated as follows:

\[ \lambda_0 = \int_{-\pi/2}^{\pi/2} e \cos^2 \theta \sin \theta d\theta = e/3 \]  

(6)

The saturation magnetostriction (\( \lambda_s \)) can be calculated easily since all domains will be oriented in a single direction.

\[ \lambda_s = e - \lambda_0 = \frac{2}{3} e \]  

(7)

However, many materials are not isotropic and in fact experience different saturation magnetostriction in different crystallographic directions. These can be measured and used to calculate a range of magnetostriction values in a given direction for any orientation of applied magnetic field. These values can be used to determine the overall \( \lambda \) for a given polycrystalline material to mitigate the effect, or used to orient a single crystal for practical applications. Magnetostrictive materials currently are used as actuators where high load/pressure is needed and some are used as transducers or magnetic sensors.[13] One of the most commonly known and one of the only commercially available magnetostrictive material is Terfenol-D an alloy composed of Terbium, Dysprosium and Iron (\( \text{Tb}_x \text{Dy}_{(1-x)} \text{Fe}_{1.95} \) with \( x \) varying from \( 0.27 \leq x \leq 0.32 \).[13] First developed for the navy as a more sensitive sonar transducer, it has found applications in many different sensors and actuators and could find use in energy recuperation from mechanical systems.

Similar to magnetostriction in ferromagnets, magnetocaloric materials respond to alignment of magnetic moments by a change in temperature. When an MCM is magnetized the magnetic moments align reducing the magnetic entropy which must be compensated by an increase in temperature. This phenomenon can be described thermodynamically through the manipulation of the following Maxwell relation:

\[ \frac{\partial M}{\partial T} \bigg|_B = \frac{\partial S}{\partial B} \bigg|_T, \]  

(8)
where, $M$ is the magnetization of the material, $T$ is the temperature, $S$ is the entropy, and $B$ is the magnetic induction within the material. (8) when rewriting and integrating becomes:

$$
\Delta S_M(T, \Delta H)\Delta H = \mu_0 \int_{H_i}^{H_f} \left( \frac{\partial M(T, H)}{\partial T} \right)_H \, dH
$$

(9)

where $H_i$ and $H_f$ are the initial and final values for the applied field during the cycle and $\Delta S_M$ is the magnetic entropy change (i.e. the change in entropy due to a change in magnetic field at a given temperature). The relation (8) can also be manipulated to yield a temperature change for a given start temperature and change in applied field:

$$
\Delta T_{ad}(T, \Delta H)\Delta H = -\mu_0 \int_{H_i}^{H_f} \left( \frac{T}{c(T, H)} \times \frac{\partial M(T, H)}{\partial T} \right)_H \, dH
$$

(10)

The subscript “ad” refers to an adiabatic process (no heat or mass transfer between the system and its surroundings), and $c(T, H)$ is the specific heat for a given temperature ($T$) and applied field ($H$). A further simplification of this relationship includes assuming that the $c_p$ (the constant pressure specific heat) does not change with applied field (i.e. $c_p = c(T) \neq c(T, H)$). Then, substituting (9) into (10) and applying the aforementioned assumption gives:

$$
\Delta T_{ad}(T, \Delta H)\Delta H \approx -\frac{T \Delta S_M(T, \Delta H)}{c_p}
$$

(11)

With this relationship it is possible to rank potential magnetocaloric effect materials based upon the target temperature range, the magnetic entropy change across that temperature range and applied field at any given temperature, and the specific heat of the material. All of these variables can be readily measured. The MCE has been used to achieve very low temperatures, the process by which was explained by William F. Giaque in his 1949 Nobel Prize Lecture [9], and can follow a number of thermodynamic paths to achieve these low temperatures. The first and simplest method outlined by Giaque is called adiabatic demagnetization (Figure 3). A magnetocaloric material (MCM) is first brought into contact with a thermal reservoir and a magnetic field is applied. Upon application of the field the MCM begins to heat up as a result of a reduction in the magnetic entropy ($-\Delta S_M$ in Eq 11) but since it is in thermal contact with the reservoir, it releases that excess heat to the surroundings. Once the system is in
equilibrium the thermal contact between MCM and surroundings is broken thus creating an adiabatic situation and the magnetic field can be removed. The removal of the field allows the magnetic moments to relax back to a random orientation causing $S_M$ to increase and the temperature of the MCM is reduced by $\Delta T_{ad}$.

A magnetocaloric material could find use in a number of applications to varying degrees. Though the focus of this work on MCM’s is for replacement of vapor compression cycle refrigeration devices, it was first described and initially gained notoriety as a method for studying very low temperature physics.[8] The use of MCM’s allowed scientists to achieve record low temperatures and to use the same technologies to study other materials cooled by these systems near the same very low temperatures. While this behavior can be found in many ferromagnets both $\Delta S_M$ and $\Delta T_{ad}$ are typically very small at temperatures far from $T_c$ (Figure 4). Therefore, for practical use as a refrigerant, MCE materials should be selected with a $T_c$ near the intended operating temperature of the device. The ferromagnetic$\leftrightarrow$paramagnetic transition is described thermodynamically as a discontinuity in the second derivative of the free energy curve (e.g. discontinuity in $c_p$). This second-order phase transformation is denoted by a change in magnetic entropy which normally manifests as excess heat. However, if a simultaneous crystallographic (first-order) phase transition occurs (as is the case with Gd$_5$Si$_2$Ge$_2$) the effect can be increased dramatically.[11] This so-called Giant Magnetocaloric Effect (GMCE) is accompanied by values of $|\Delta S_M|$ almost three times as high (Figure 5) as that of pure Gd.
Figure 4  Calculated magnetic entropy vs $T/T_c$ curve for zero field ($b_0 = 0$) and applied field ($b_0 = 6.7 \times 10^{-5}$). Image courtesy of [14].

Figure 5  Mangetic entropy change as a function of temperature for different magnetic field cycles. Comparison with pure Gd for reference. Image courtesy of [11].
The underlying principles of this process are different than that of normal MCM’s in that a simultaneous structural and magnetic transformation occurs augmenting the change in entropy.

**Literature review**

Another interesting system for high-tech applications is the rare-earth nickel alloys, first studied by Abrahams[15] and Walline[16]. Both investigated the crystallography and the magnetic properties of various Lanthanide-Nickel compounds and both noted the atypical behavior of Gadolinium based compounds. GdNi, like CeNi, PrNi, NdNi, SmNi, and TbNi is monoclinic and forms in the CrB-type ordered structure (space group Cmcm)[16, 17, 18, 19], however its magnetic properties vary greatly from the rest of the prepared alloys. While both GdNi$_2$ and GdCo$_2$ exhibit magnetocaloric behavior [20], the GdNi (1:1) compound has also been found to exhibit magnetoelastic coupling.[21] When a material exhibits large magnetostriction and high sensitivity ($dB/d\sigma_H$) due to the elastic coupling of magnetism and crystal structure it can find applications as so-called magneto-elastic stress sensors and are thus coined magnetoelastic materials.[22, 23] Previous work has determined the intriguing relationship between the magnetoelastic effect in GdNi, and the effects of a change in composition following the formula GdNi$_{1-x}$Co$_x$[24]. XRD patterns from the composition range indicates a shift in lattice parameters until a second phase is formed in $x=0.50$ and then a completely different crystal structure at $x=1.00$.[24] The similarities between the trend in lattice parameters with varying composition, and the magnetostriction of GdNi at 60 K are stark and suggest the change in magnetic interaction between Gd-Ni and Gd-Co as the impetus for the structure change (Figure 6). This link between composition and magnetostriction can be potentially useful to enhance the effect, or to specially tailor the effect for particular applications as sensors, actuators, or transducers. Gadolinium-transition metal alloys exhibit a strong link between small scale changes and large scale phenomena; in fact, the slight change in alloying element can cause extreme changes in bulk properties. Also, as has been seen before, the use of high purity rare earth metals can cause tremendous unforeseen changes in magnetic properties.[10] Further study of this and other high-purity Gd alloys is a promising avenue to solve current problems with efficient use and production of energy. Though typical bulk sample measurements are
necessary to determine a material’s capabilities, it is often imperative to investigate on a much smaller scale. Electron microscopy is the tool of choice for those investigating phase purity and physical phenomena arising from atomic structure. It has been shown recently that the ability of typical XRD analysis to identify phases smaller than 5 vol% is very poor\cite{25} and secondary phases in a highly linked specimen like Gd$_5$(Si,Ge)$_4$ can have significant effects on the large scale behavior, actually seeding the FM$\leftrightarrow$PM transition (Figure 7).\cite{26} Upon applying a magnetic field (#1) the first regions in the scan to light up (high induction) are the platelets. The smooth curve in c.) represents the Hall signal as a function of field for a single platelet while the other curves therein represent the surrounding regions. Upon applying a field the platelet is definitively the first phase to respond, though the signal from all three points drop at the same time upon removing the field. The presence of these plates highly influences the magnetic behavior at a bulk scale. Gd-Co compounds have been heavily studied for both their magnetocaloric and magnetostrictive properties dating back to the initial crystallographic study by Buschow et. al.\cite{27} Where seven different compounds were identified and an eighth was suggested near Gd$_2$Co with $x\approx\frac{7}{4}$ though a single phase specimen was not created or indexed. The Gd$_3$Co compound was noted for its large forced magnetostriction\cite{28}, though it wasn’t until after single crystals of the material were made\cite{29} that the true properties could be studied. Many trends in rare-earth transition metal compounds were evaluated through observation
of crystal structure and thermodynamic stability. It was noted that the interatomic distance between Lu-Co and Y-Co compounds have a larger impact on the structure and formation of these compounds than the same interatomic distances in Lu-Fe and Y-Fe compounds.\[30\]. This trend was also noted in the review by Kirchmayr and Poldy on magnetism in compounds of rare earth and specifically 3d transition metals.\[31\] Further, Kirchmayr alluded to many relationships including that between the exchange energy vs. the ratio (R/r) of atomic center distance (R) to radius of 3d shell (r); the so-called Bethe-Slater curve. Also distinct relationships between many crystal structures which form in these alloys was depicted schematically (Figure 8).

Across the GdNi$_{1-x}$Co$_x$ range the similarities between Ni and Co would seem to outweigh the amount of change seen here. Electronic coordination differences between Ni and Co have been suggested as reason for the dissolution of the solid solution\[24\], but a previous study\[32\] has answered some questions about the nature of the magnetism and its effect on the structure in GdNi. However, shifting the composition toward GdCo raises many other questions. The main focus of this work will be on determining how the microstructure of GdNi changes across the GdNi$_{1-x}$Co$_x$ composition range from $x=0.00$ to $1.00$. The following chapters will report the work which was carried out to determine how the addition of Co destabilizes the GdNi-type
phase and finally results in a two-phase sample at \( x = 0.50 \) (as determined in \([24]\)). Further, identification of the phases seen in the \( x = 0.50 \) will be performed via electron diffraction techniques as well as energy dispersive x-ray spectroscopy. Also, the nature of common features found in samples between \( x = 0.00 \) and 0.30 will be discussed and identified. Finally, a general discussion of microscopy observations will be given and the results of which will be correlated to thermodynamic data collected for all specimens in the family, followed by general conclusions.

This dissertation will be organized as a series of journal articles centered around the \( \text{GdNi}_{1-x}\text{Co}_x \) family of alloys and the work described above presented in the following three chapters (2-4). After which a general discussion will be presented in Chapter 5 and general conclusions will be made in Chapter 6. References for each chapter will immediate follow the text.

**Bibliography**


L. White (eds.), Climate change 2014: Impacts, adaptation, and vulnerability.


CHAPTER 2. CRYSTALLOGRAPHIC AND COMPOSITIONAL CONTRIBUTIONS TO THE BREAKDOWN OF THE GdNi$_{1-x}$Co$_x$ SOLID SOLUTION

A paper published in Journal of Alloys and Compounds

T. E. Prost, L. S. Chumbley, Y. Mudryk, V. K. Pecharsky

Abstract

The GdNi-GdCo pseudo-binary system, GdNi$_{1-x}$Co$_x$, has been investigated by scanning electron microscopy (SEM). While x-ray powder diffraction analysis indicates the existence of the GdNi-type phase in samples up to $x=0.50$, SEM investigation of the $x=0.50$ sample reveals a two-phase microstructure consisting of the GdNi (1:1) phase and a new Gd$_3$(Ni,Co)$_2$ (3:2) phase. Energy dispersive x-ray spectroscopy (EDS) of the 1:1 phase in the $x=0.50$ sample indicates a composition near GdNi$_{0.60}$Co$_{0.40}$ which is assumed to be the upper limit of the solid solution. The persistence of $\sim$5 vol.% of a Gd(Ni,Co)$_2$-type (1:2) secondary phase, fine features penetrating entire grains, and slight Ni,Co composition changes are observed in samples from $x=0.00$ to 0.30. EDS analyses of these 1:2 regions indicate a sharp increase in Co with increasing $x$, while the matrix remains at the nominal composition despite variations suggested from backscattered electron (BSE) imaging. Electron backscattered diffraction analysis points to significant texturing with large similarly oriented grains; the coupons have an overwhelming tendency to grow in the [010] direction in columnar grains roughly 50$\mu$m wide and hundreds of microns long. BSE images of $x=0.30$ sectioned along the long direction $(yz)$ of the grains exhibit contrast variations reminiscent of “tiger stripes” while those of surfaces cut perpendicular to the long direction $(xy)$ exhibit long thin features (“stitches”) surrounded by darker dendritic regions. Orientation Imaging Microscopy (OIM) of the stitches reveals small rotations of roughly 40°.
from one side of the stitch to the other, fitting with a mirror twin on the (110) plane. The formation of these twins is assumed to relieve stress caused by the incompatibility of Co in the GdNi matrix and the directional solidification during arc melting.

Introduction

Lanthanide-transition metal alloys continue to attract a great deal of attention by the scientific community as many of these alloys exhibit physical behaviors that are interesting to both basic and applied science. For example, the magnetocaloric effect which is observed as a reversible entropy or temperature change in response to a varying magnetic field was documented as early as 1918.[1, 2] Following the work of Brown[3], who demonstrated the feasibility of magnetic cooling near room temperature, the discovery of the "giant" magnetocaloric effect (GMCE) in Gd$_5$Si$_2$Ge$_2$ [4] using high purity Gd[5] accelerated the prototyping of magnetic refrigeration systems containing these and related materials.[6] The renewed interest in calorics has also encouraged the discovery of other material systems which exhibit this phenomenon.[7, 8] Other materials in this family which couple large magnetostriction and high sensitivity can find applications as so-called magneto-elastic stress sensors and are generally referred to as magnetoelastic materials.[9] Indeed, a number of systems have been studied including the lanthanide-nickel (R-Ni) alloys, first examined independently by Abrahams[10], Walline[11], and Dwight.[12] GdNi, like many other light lanthanide R-Ni alloys, is orthorhombic and orders in the CrB-type structure (space group Cmcm)[11, 13, 14, 15] depicted in Figure 9; its Curie temperature ($T_C$) is the highest among R-Ni alloys, and it exhibits a large spin-only magnetic moment[10]. GdNi, along with GdCu$_2$, has also been shown to exhibit an anomalous thermal expansion below its $T_C$.[16] While both GdNi$_2$ and GdCo$_2$ exhibit substantial magnetocaloric effect [17], the GdNi (1:1) compound has both appreciable magnetocaloric effect and has been found to display non-trivial magnetoelastic coupling and a large anisotropic magnetostriction.[18]

Interestingly, there exists a relationship between the effects of magnetoelastic behavior in GdNi and the effects of Ni-Co substitution in the GdNi$_{1-x}$Co$_x$ system ($x\leq0.30$).[20] This correlation was noted in lattice parameters calculated from Rietveld analysis of X-ray powder
diffraction (XRD) and magnetic measurements of selected compositions in this alloy system. The XRD patterns of the samples indicate systematic changes in lattice parameters between \( x=0.00 \) and \( x=0.30 \) compositions (corresponding to the shifts in Bragg peaks visible in Figure 10). Further, comparison between the as-cast and annealed samples reveals a distinct sharpening in many of the Bragg peaks attributable to improved chemical homogeneity upon annealing. The appearance of additional Bragg peaks in the XRD pattern of \( x=0.50 \) suggests a secondary phase formation and an end to the solid solution. The \( x=1.00 \) sample exhibits a completely different diffraction pattern. As the solid solution was the main focus of the previous investigation[20] these additional peaks in \( x=0.50 \) and \( x=1.00 \) XRD patterns were not identified but will be investigated here. Similarities between the trend in lattice parameters with varying composition and the magnetostriction of GdNi at 60 K suggest a difference in magnetic Gd-Ni and Gd-Co interactions as an impetus for the anomalous lattice parameters change and, ultimately, structural instability. Namely, the influence of Co on the GdNi structure is similar to the influence of the applied magnetic field.[21] This link between composition and magnetostriction can be potentially useful to enhance, or to specially tailor the effect for application in magnetoelastic sensors, actuators, or transducers.

It is well known that the sensitivity of XRD analyses to detect impurity phases is limited to a few volume percent, but for Gd-based systems investigated by Cu K\( _\alpha \) radiation, whose

Figure 9  Crystal structure of Gd(Ni,Co), the blue box is the unit cell, Gd–Gd and (Ni,Co)–(Ni,Co) bonds are present to show the layered nature of the material.[19]
Figure 10  X-ray Diffraction Patterns for the range of compositions and heat treatments (AC: as-cast; AN: annealed 800°C 7 days; AL: annealed 700°C 18 days). Significant peak sharpening for $x=0.05$ through $x=0.30$ occurred during annealing. Notice the peak shift with composition is most apparent in the AN or AL samples. Peaks in $x=0.00$ to $x=0.30$ all belong to the 1:1-type phase. Extra peaks begin to appear in $x=0.50$ suggesting a second phase and neither phases are present in $x=1.00$. Selective reproduction of patterns marked with * from Ref. [20].

Energy is near the L-absorption edge of Gd, the limits of detection can be much worse.[22] Further, secondary phases in an extraordinarily responsive specimen like Gd$_5$(Si,Ge)$_4$ can have significant effects on bulk magnetic behavior; small inclusions of Gd$_5$(Si,Ge)$_3$ actually seed the paramagnetic to ferromagnetic transition in the Gd$_5$(Si,Ge)$_4$ matrix, promoting the formation of the low-volume ferromagnetic phase in the bulk due to stress concentrated in a narrow interfacial region between the platelet-like inclusions and the matrix.[23]

For the GdNi$_{1-x}$Co$_x$ system, differences observed in the density of states near the Fermi level when Ni is replaced by Co have been suggested as the main reason for the termination of the solid solution [20], and previous studies [21] have answered some questions about the
nature of the magnetism and its effect on the crystal structure of GdNi. However, the behavior observed when shifting the composition toward GdCo raises many other questions including but not limited to: how the Co concentration affects the microstructure and local crystal structure; what impact, if any, does annealing have on the microstructure and phase purity; and exactly how much Co can be accommodated in the parent GdNi lattice. In this study these questions have been answered using electron microscopy, associated spectroscopy techniques, and closer inspection of the previously available data.

Experimental

High purity Gadolinium was prepared by the Materials Preparation Center of Ames Laboratory. Major impurities include: O (342 ppm wt.), C (153 ppm wt.), N (370 ppm wt.), Fe (20 ppm wt.), Cu (9.3 ppm wt.), La (1.9 ppm wt.), Ce (49 ppm wt.), Pr (3.9 ppm wt.), Tb (3.6 ppm wt.), Yb (<20 ppm wt.), and W (1.6 ppm wt.) for an overall purity of (99.86 at.% with respect to all elements). Nickel and Cobalt were both purchased commercially (>99.9 at.% with respect to all elements). In total, eight compositions were prepared and investigated (x=0.00, 0.05, 0.10, 0.15, 0.20, 0.30, 0.50, and 1.00) in the rather sparsely populated composition space of the Gd-Ni-Co ternary phase diagram available (Figure 11).

Each alloy was arc melted in ≤10-g buttons, flipped and re-melted multiple times to ensure homogeneity. Typical weight loss during melting was less than 0.1 wt%. The samples were sealed in quartz tubes, filled with He at roughly 0.3 bar and heat treated at various temperatures and lengths to reach equilibrium. Analyses were performed for each of these three states: as-cast (AC), annealed at 800°C for 7 days (AN), and annealed at 700°C for 18 days (AL). Powder X-ray Diffraction (XRD) was carried out using a PANalytical X’Pert diffractometer employing Cu Kα radiation. Samples of each composition were prepared for microscopy analysis via traditional methods (i.e. grinding and polishing) with a final step employing a 0.25 µm diamond suspension. Electron microscopy characterization was performed using a JEOL 5910 scanning electron microscope (SEM) with a Noran Vantage energy dispersive x-ray spectroscopy (EDS) system and solid-state backscattered electron (BSE) detector. Orientation imaging microscopy (OIM) was performed using an Amray 1845 Field Emission SEM equipped with
an EDAX electron backscattered diffraction (EBSD) detector and TSL OIM analysis software. Wavelength dispersive x-ray spectroscopy (WDS) spectra were measured using a JEOL JXA-8200 microprobe at 15kV 25nA probe diameter of 8µm. The Nickel $K_{\alpha}$ (measured at 115.4 nm), Cobalt $K_{\alpha}$ (124.6 nm), and Gadolinium L (142.4 nm) were all measured on LIF crystal for diffraction. Peaks were measured for 15 seconds while high and low backgrounds were measured for 5 seconds approximately 5mm above and below the peak positions. For clarity of further analyses both carbon and oxygen signals ($\leq$7at.% combined) were removed from EDS and WDS measured compositions as surface oxidation and contamination occurs rapidly.
Results and Discussion

SEM images of as-cast samples ($x=0.00, 0.30, 0.50,$ and $1.00$) can be seen in Figure 12. A two-phase system appears at $x=0.50$ indicating the definite cessation of the solid solution of the GdNi based CrB crystal structure (“1:1”). The microstructures of $x=0.00$ and $0.30$ samples both exhibit large matrix grains with small amounts of secondary phase regions (dark spots in Figure 12(a and b)) determined by EDS to match compositionally to the MgCu$_2$-prototype cubic Laves phase Gd(Ni,Co)$_2$ (“1:2”). Though the 1:2-type phase is present in the SEM images (Figure 12) the small volume concentration ($< 5 \text{ vol.}\%$) prevented detection via XRD (absence in Figure 10), which appeared to be single phase. More interesting however, are the more subtle contrast variations present in BSE images of both $x=0.00$ and $x=0.30$. These features permeate entire matrix grains and appear to encompass a large fraction of the structure. The XRD results indicate that the observed contrast is not due to the presence of two different crystal structures, suggesting a chemical segregation in the same CrB-prototype structure (e.g. spinodal decomposition). Slight variations in EDS and WDS analysis across these features showed no consistent change in composition from one feature to another, likely due to their small size and homogeneous distribution. The $x=0.50$ sample exhibits a two-phase microstructure consisting of the 1:1-type (the darker phase) and a phase fitting compositionally between Gd$_3$(Ni,Co)$_2$ and Gd$_4$(NiCo)$_3$ (the lighter phase). WDS analysis of these phases can be seen in Table 1. This is consistent with the rejection of Co from the 1:1 phase discussed previously and indeed the composition of the 1:1 phase in $x=0.50$ is roughly 23 at.% Co and 27 at.% Ni. This segregation may indicate an upper limit to the solid solution of Co in the 1:1 phase at $x=0.45$. The $x=1.00$ (GdCo) sample has a dendritic microstructure where the dendrites match the 1:2 phase and the matrix phase is near Gd$_4$Co$_3$, both of which have been reported in the Gd-Co system. Also of note is a light phase in Figure 12(d) with a composition near Gd$_2$Co; this phase is not present in any of the Gd-Co phase diagrams reported in literature.

Upon annealing, “tiger stripes” of lighter and darker regions were observed for $x=0.00$, 0.15 and 0.30 (Figure 13). This is likely due to the coarsening of the features observed in
Figure 12  SEM images captured in backscattered electron detector mode for as-cast samples (a) \(x=0.00\), (b) \(x=0.30\), (c) \(x=0.50\) (d) \(x=1.00\). (a and b) gray spots are Gd(Ni,Co)\(_2\)-type secondary phases, while the other features are of unknown origin with no discernible composition difference from the matrix. (c and d) breakdown of the solid solution is evident and a completely different microstructure is observed. (c) light regions are Gd\(_3\)(Ni,Co)\(_2\)-type or Gd\(_4\)(Ni,Co)\(_3\)-type phase, dark regions Gd(Ni,Co)-type phase. (d) light phase is Gd\(_2\)Co, matrix phase is approximately Gd\(_4\)Co\(_3\) while the dark dendrites are Gd(Co)\(_2\)

the as-cast samples. Further, it is noted that the 1:2 phase regions become both larger and more homogeneous (in the case of \(x=0.00\)) after annealing due to uptake of Ni/Co. Both the \(x=0.50\) and 1.00 samples melted upon annealing, which is consistent with the presence of low-temperature eutectics in both Gd-Ni and Gd-Co binary phase diagrams; therefore only the data from as-cast samples were considered for these compositions.

The microstructures of most interest are of those samples near a composition of \(x=0.30\) as this is the region where samples begin to show an anomalous magnetic behavior wherein \(T_C\) decreases with increasing \(x(\text{Co})\).\(^{[20]}\) As-cast and annealed \(x=0.30\) samples exhibit contrasting
regions in BSE images indicating slight fluctuations in composition (Figures 12, 13, 14). Notably, the degree of variations in BSE mode images increases with annealing for long periods, and the 1:2-type phase regions appear to grow in size (Figure 14). EDS analysis of the 1:2-type regions indicate an increase in Co composition with annealing (Figure 15).

Despite the presence of the 1:2 phase in all samples up to $x=0.3$ the composition of the matrix phase was relatively consistent and very near to the nominal composition (Table 1). The variations noted in Nickel and Cobalt may be a result of sampling the fine features rather than actual variations, while the Gadolinium composition remained relatively steady.

Since SEM/EDS and WDS were inconclusive in determining whether the nature of the tiger stripes is related to compositional variation, OIM was used to determine whether local
crystallographic variations existed which could account for the observed contrast (Figure 16). The grains present are very large and elongated, with grains 30-60 μm wide and 100’s of microns long. The out of plane orientation for each pixel in Figure 16(a) corresponds to the legend in Figure 16(c) and was compiled and presented as a surface plot of texture in Figure 16(b). The long direction of the grains was found to be the [010] suggesting a preferential solidification direction. Relatively small misalignments are observed between these grains; in the image shown only a single small grain at the top exhibits a large rotation from the neighboring grains (>60°).

The long dimension of the grains aligned with the vertical direction of the arc melted button, typically the dominant thermal gradient during solidification, similar to what was observed in Gd₁₁Ni₄In₉.[25] All initial samples (i.e. those containing tiger stripes) were cut parallel to that
Table 1  WDS data for samples $x=0.00$, 0.15, 0.30, 0.50 and 1.00 averaged for all available heat treatments. Note the composition of the second phase ($\text{Gd}_3\text{Ni}_2\text{Co}_4$ in $x=0.15$). Rows marked with * indicates data presented in [20], † denotes new data.

<table>
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<th>$x(\text{Co})_{\text{nom.}}$</th>
<th>Phase</th>
<th>Averaged Composition (at.%, O-corrected)</th>
<th>$x(\text{Co})_{\text{meas.}}$</th>
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<td>Ni</td>
<td>Co</td>
<td>Gd</td>
</tr>
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<td>0.00 ± 0.00</td>
<td>50.38 ± 0.26</td>
</tr>
<tr>
<td>0.00 (1:2)</td>
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<td>0.00 ± 0.00</td>
<td>32.77 ± 0.24</td>
</tr>
<tr>
<td>0.15 (1:1)</td>
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<td>7.22 ± 0.44</td>
<td>50.29 ± 0.47</td>
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<tr>
<td>0.15 (1:2)</td>
<td>22.13 ± 0.19</td>
<td>44.08 ± 0.03</td>
<td>33.79 ± 0.19</td>
</tr>
<tr>
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<td>14.73 ± 0.83</td>
<td>50.02 ± 0.22</td>
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<tr>
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<tr>
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<td>22.69 ± 1.56</td>
<td>49.34 ± 0.23</td>
</tr>
<tr>
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<td>45.79 ± 0.21</td>
<td>54.21 ± 0.21</td>
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<tr>
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<td>0.00 ± 0.00</td>
<td>67.25 ± 0.19</td>
<td>32.75 ± 0.19</td>
</tr>
</tbody>
</table>

direction (called the “$yz$” direction). One sample in the as cast state was sectioned on a face perpendicular to the previous samples (denoted “$xy$”) revealing a completely different pattern of light and dark regions. In this case the matrix appeared light with darker dendrite-like regions with very fine, straight lines in the middle which are not continuous but instead broken up like stitches. These “stitches” are present along the axis of the dendrites and can be seen in Figure 17a. The BSE images indicate a slight but noticeable difference in composition from matrix to “dendrite” to 1:2 phase.

The EDS results (Figure 18) indicate a slight but noticeable shift in composition between these areas. EDS point analyses of the stitches indicates a lower Co concentration while the dendrites directly surrounding them contain more Co than the matrix area, which remains near the nominal composition. Even considering the large variations in the data there is still clear separation in composition between the stitches and the dendrites suggesting that the stitch is a favorable state, either compositionally or structurally. If these stitches are as thin as they appear (~200nm) a large majority of the x-rays considered as coming from the stitch are actually produced by the region immediately surrounding the stitch. However, an EDS line scan across a stitch reveals a reduction in Co and a simultaneous increase in Ni while the Gd signal remains the same; the EDS profile can be seen in Figure 19 next to an image of the
Figure 16  (a) OIM generated Inverse Pole Figure showing grain orientation (legend present in (c)), large, namely very long grains oriented near the [001] direction out of the plane of the image. While slight rotations are observed from one grain to the next, most are oriented with the [010] near the long direction indicating a highly textured microstructure.(b) Surface plot of individual pixel orientations showing texturing out of the plane of the page.

...region of interest. This scan was performed across a stitch in the region identified as being the matrix between darker contrast dendrites. The results corroborate what was seen in the point analyses, namely, the stitch appears to reject Co to the surrounding areas with the intensity profile suggesting a kinetic process (e.g. diffusion) responsible.

OIM was performed to determine grain structure and orientation on the as cast $x=0.30$ “$xy$” sample. The difference in microstructure from the previous “$yz$” to this orientation is notable. Small needle-like grains are intermixed with larger ones, which would seem to extend through the material (Figure 20). Again, the out of plane orientation for each pixel in Figure 20(a) corresponds to the legend in Figure 20(c) and was compiled and presented as a surface plot of texture in Figure 20(b). The majority of the grains are oriented within a few
degrees of the [010] direction out of plane which is in excellent agreement with OIM of the “yz” orientation. The small needle-like grains (indicated by black lines in Figure 20) have an angular relationship of approximately $37^\circ$ with only one of their neighbors each, indicating a crystallographic relationship. This technique is not exact enough to determine any epitaxy, but a mirror twin along the [110] directions does have an angular relationship of roughly $37.15^\circ$. No indication of the dendrites was noted in the OIM inverse pole figures suggesting a compositional transition only, although small crystallographic fluctuations would be too minor for this technique to notice.

The annealing process has a much greater effect on the microstructure as viewed from the “xy” direction. The dendrites coarsen upon annealing becoming regions of nearly homogeneous contrast surrounding the stitches, likely ending at grain boundaries. SEM images of both as-cast, and annealed $x=0.30$ can be seen in Figure 17. While the variations among WDS spectra in the $x=0.00$ and $x=0.15$ matrix regions are relatively low (deviation in Table 1), the values for the $x=0.30$ have a large range with most variation coming from the AC sample. Further analysis of the AL sample of $x=0.30$ is needed, but the persistence of the stitches, changes in dendrites, and coarsening of 1:2 phases are noted.
Figure 18  Averaged EDS point analyses, notice Ni-Co tradeoff between stitch and dendrites while matrix remains near nominal. Error bars are one standard deviation of data set.

Conclusions

The results of this investigation using SEM, EDS/WDS, and OIM in conjunction with the XRD analyses show that in GdNi\(_{1-x}\)Co\(_x\) alloys the solid solution with the CrB-type crystal structure is indeed terminated at approximately \(x=0.45\) (22.5 at.% Co). Excess Nickel and Cobalt are rejected from the matrix and form the Gd(Ni,Co)\(_2\) compound in all compositions up to \(x=0.3\). Annealing has a distinct effect on the feature size and shape and on the overall homogeneity of the samples. Microscopy confirms the \(x=0.50\) composition to be past the solid solution forming a second major (\(\approx 50\) vol%) phase alongside the 1:1-type phase in a eutectic microstructure. GdCo (\(x=1.00\)) exhibits a dendritic microstructure with two main, expected phases, and a third unexpected phase not present in the literature. The expected phases are the 1:2 and 4:3 phases; the third was identified as nearly Gd\(_2\)Co by WDS though further analysis
Figure 19  EDS linescan across a linear feature in GdNi$_{0.7}$Co$_{0.3}$. There appears to be a tradeoff of Cobalt(red) for Nickel(green) near the feature while the Gadolinium content (blue) remains relatively uniform.

is needed.

The substitution of Co into the GdNi crystal structure produces interesting microstructural features, particularly in the $x=0.30$ samples, termed “tiger stripes” and “stitches,” depending upon the direction of viewing. When viewed from the $yz$ direction large elongated grains with tiger stripes are seen. These stripes are either too fine, or vary too little in composition to be characterized quantitatively through EDS. Upon viewing the $xy$ direction, the microstructure appears quite different with dendritic regions emanating from the stitches. EDS point analyses suggest a higher concentration of Co in the dendrites than in the matrix, and less Co at the stitches while a linescan both agrees with this and indicates a diffusional segregation of Co during solidification. These unforeseen variations in the microstructure may have a significant effect on the anisotropic magnetic properties of GdNi-based alloys that are generally not expected to be noticeable in polycrystalline materials, and are likely responsible for the very broad Bragg peaks present in the as-cast sample XRD patterns. Upon annealing the Bragg peaks sharpen as expected, and the dendrites coarsen significantly and in some cases disappear.
Figure 20  (a) OIM generated Inverse Pole Figure showing grain orientation for grains belonging to the GdNi-type crystal structure (Cmcm). Black lines indicate boundaries fitting a mirror twin on the [110] plane. (b) Texture of individual pixels confirming preferential orientation near [010] out of the plane of the page. (c) Legend for colors in (a).

Acknowledgments

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Bibliography


CHAPTER 3. TEM ANALYSIS OF COMPLEX SEGREGATION AND SOLIDIFICATION FEATURES IN GdNi\textsubscript{0.7}Co\textsubscript{0.3}

A paper submitted to Acta Materialia

T. E. Prost, L. S. Chumbley

Abstract

Giant magnetoelastic effect compounds GdNi\textsubscript{1-x}Co\textsubscript{x} are investigated using transmission electron microscopy (TEM). Compounds with x=0.3 were previously identified as transitional in this solid solution and found to contain many previously unknown microstructural features which proved difficult to identify via scanning electron microscopy (SEM) techniques. Focused ion beam (FIB) lift-out technique was used to prepare TEM samples of these regions, and high resolution TEM (HRTEM), selected area electron diffraction (SAED) and scanning TEM (STEM) techniques were used in this study to identify the features. The previously seen stitches correspond to mirror twins at least as long as the lift-out specimen (approximately 15$\mu$m), and the dendrites radiating from these twins were found to be anti-phase boundary (APB)-like features with very slight variations in lattice parameters. When annealed at 700 °C for 18 days the microstructure was shown to change, eliminating the irregular APBs and forming instead straight regions emanating from the twin in a chevron pattern. This new form of APB was determined to be similar to those found in the as-cast sample only much smaller.

Introduction

Since the discovery of the giant magnetocaloric effect (GMCE) in Gd\textsubscript{5}(Si\textsubscript{0.5}Ge\textsubscript{0.5})\textsubscript{4} (GdSiGe “5:4”) in 1997 [1] there has been a renewed effort to discover more revolutionary rare-earth compounds. Indeed, a number of studies on the 5:4 family have been performed and significant
inroads have been made through careful inspection of the resulting microstructure of these compositions. Persistent Widmanstätten-like plates in the 5:4-type matrix were discovered by electron microscopy [2] and determined to actually seed the paramagnetic (PM) to ferromagnetic (FM) transition [3] in these materials. The plates were observed in other compounds following the formula R₅(SiₓGe₁₋ₓ)₄ (where R = Gd, Tb, Dy, Er) and determined to be of the 5:3-type (R₅(SiₓGe₁₋ₓ)₃) by transmission electron microscopy (TEM) [4, 5, 6]. It is worth noting that before electron microscopy analysis of these materials the Widmanstätten-like plates were unknown since their volume percentage was below the limit for observation by X-ray diffraction (XRD) analysis [7]. All of these lessons learned must be applied to future studies in order to use the materials and resources efficiently and effectively.

With the renewed interest in gadolinium-based compounds afforded by the discovery of the GMCE many new systems have been investigated including the Gd-Ni compound. The orthorhombic crystal structure, in which the 1:1 GdNi compound forms, follows the CrB prototype (Cmcm) and was first reported separately by Abrahams and Walline in 1964 while summarizing magnetic properties and crystal structure of numerous rare earth-transition metal alloys [8, 9]. Many other rare earth-transition metal (RT) binary and ternary alloys form the same crystallographic units, which stack variably forming a number of similar structures between the CrB and the FeB stacking variants [10, 11, 12]. And indeed, many of these exhibit interesting magnetic anomalies, including Gd₁₋ₓYₓNi where the heat capacity (C)-temperature (T) response varies with composition (x) [13]. Both GdNi and GdCu₂ have been shown to exhibit an anomalous thermal expansion below their Curie and Néel temperatures (Tc and TN), respectively [14]. The substitution of Co for Ni in the GdNi2-GdCo2 pseudo-binary system allows the Tc to be tuned and increases the magnetocaloric effect (MCE) [15]. The particularly "giant" magnetoelastic coupling found in GdNi by Gratz et. al. was suggested to be due to coupling of Gd moments and work by Uhlříková et. al. [16] indicates a saturation magnetization of μₛ = 7.2µB/f.u., which was attributed to conduction band electron contributions by Mallik et al [13, 17]. Successful tailoring of the giant magnetoelastic effect (GMEE) in GdNi via substitutions in the rare earth and transition metal sites could directly impact transducer technology. So far, work has been done to understand effects of substitution of Y for Gd, which
significantly reduces the $4f$ electron contribution to the magnetic moment and reduces the $T_C$ [13]. Substitutions of Cu for Ni similarly reduce the $T_C$ and the magnetic moment [18].

The substitution of Co into the Gd-Ni compound following the GdNi$_{1-x}$Co$_x$ formula has been shown to affect the parent CrB lattice in a way reminiscent of the giant magnetoelastic response in Gd-Ni below its $T_C$ [19]. The density of states calculations performed by Paudyal, et al. [20] indicate an unfavorable electronic state for the formation of the Gd-Co compound, thus the lack of this phase in literature [21] and on the reported phase diagram [22]. As such, when substituting Co into the GdNi parent compound it is not surprising that the microstructure which forms appears to reject Co, forming a secondary phase (Gd(Ni,Co)$_2$-type) at a concentration of around 5 vol.% [19]. What is surprising is that this rejection also occurs in the arc-melted ingots of the parent Gd-Ni ($x=0$) compound at nominal 1:1 composition. This suggests that either the Gd(Ni,Co)$_2$ phase is more stable than the matrix or that the arc melting environment promotes the formation of this secondary phase. The relatively rapid solidification of the arc melting process has been shown to influence the texture of these materials [23]; however, the presence of other microstructural features and the difficulty in identifying them warrants closer inspection. As was the case with the 5:3 platelets in the 5:4 matrix, the use of TEM has uncovered two major microstructural features, which may form due to the inherent properties of the alloy or to the arc melting process and have an unknown effect on the magnetic properties.

This paper will go into detailed characterization of these features and propose alternative synthesis and processing avenues necessary for single phase samples to be created, which may impact the bulk magnetic properties of these alloys and facilitate adoption into industrial usage. TEM analysis is performed on samples of GdNi$_{0.7}$Co$_{0.3}$ in as-cast (AC) and annealed (AL) states revealing the nature of these features and allowing the influence of Co on the parent lattice to be directly observed.

**Experimental Procedures**

High purity gadolinium, prepared by the Materials Preparation Center at Ames Laboratory (98 at.% with respect to all elements), was combined with nickel and cobalt, purchased at
commercial purities (>99 at.% with respect to all elements), in the correct proportions and arc-melted multiple times (∼7x) for homogeneity, flipping the ingot between each melting. Portions of the ingot were annealed following two profiles: 800 °C for 7 days (designated AN) and 700 °C for 18 days (designated AL). Scanning electron microscopy (SEM) samples were taken from the ingot, mounted, and mechanically polished with a final 0.25 µm lapping step using diamond suspension. Samples for transmission electron microscopy (TEM) inspection were first sectioned by a core-drill, mechanically polished, dimpled, and ion milled to perforation. Since the ion-milling method produced poor yield, an electro-polishing set-up was used for subsequent samples. The polishing was performed on a modified twin-jet electropolisher using an electrolyte of Methanol - 8vol.% Perchloric Acid - 2vol.% 2-Butoxyethanol.

Scanning electron microscope (SEM)/focused ion beam (FIB) investigations were performed on polished samples using a FEI Helios NanoLab 660 (Ga⁺ ion source). TEM characterization was completed on both a Phillips CM30 TEM operating at 200kV with a LaB6 source and a FEI Tecnai G² F20 TEM operating at 200kV with a field emission gun (FEG) source. High angle annular dark field (HAADF) images and energy dispersive x-ray spectroscopy (EDS) information was collected on the Tecnai using scanning TEM (STEM) mode. SEM/FIB Lift-out technique was used to prepare TEM samples from specific locations.

Selected area electron diffraction (SAED) patterns were collected using diffraction mode in the TEMs and measurements were taken in ImageJ and verified using CaRIne Crystallography software. Best fit for lattice parameters was calculated using linear regression of all fitted and identified patterns for each specimen and location. Simulation of electron beam material interaction substantiated the information seen in high resolution TEM (HRTEM) images captured in the Tecnai G² F20. These simulations, using QSTEM software, replicated all parameters (accelerating voltage, aberrations, etc.) corresponding to the Tecnai G² F20 instrument.

**Results and Discussion**

TEM analysis including bright-field (BF) imaging and SAED was performed on multiple samples of GdNi₀.₇Co₀.₃ in as-cast (AC) and annealed (AL) heat treatment state. Preparation of these samples was carried out via the dimple and polish method on sections of the arc-melted
Table 2  Lattice parameters determined by XRD and TEM for the CrB prototype GdNi crystal of compositions in the GdNi$_{1-x}$Co$_x$ alloy system. SAED determined parameters of the $x=0.30$ composition vary from sample to sample and from those determined by XRD Reitveld analysis. SAED of the TEM/FIB sample is in the AC state. Rows marked with $\dagger$ indicates data presented in [19], * denotes new data.

<table>
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<th>$a$(Å)</th>
<th>$b$(Å)</th>
<th>$c$(Å)</th>
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button in two orientations (vertical and horizontal). The typical microstructure observed via scanning electron microscopy (SEM) of each of these two orientations was observed previously [23] and in this study, TEM investigations of the same two specimen orientations resulted in different measured lattice parameter values.

An apparent discrepancy exists between lattice parameters determined through XRD refinement [19] and SAED in the TEM. Lattice parameters for two TEM samples are compared to those determined by XRD in Table 2. The $a$ parameter was calculated from a very distant zone axis due to the nature of the sample preparation and the ingot from which it was created. Difficulties in proper SAED characterization procedures arise for samples that are formed through this traditional dimple and perforate method and are attributable to the area and orientation selection of this preparation technique.

Moreover, the lattice parameters change not only between samples, but also from one location to another within the sample, suggesting fluctuations attributable to several different phenomena including local strain, spinodal decomposition and the presence of anti-phase boundaries (APB). Previous studies have noted a strong correlation between bulk lattice parameters and composition [19] and, separately, variations in composition across the different regions of the $x=0.30$ sample [23] corroborating the variation seen in lattice parameters. It is
well known that XRD Reitveld analysis is more accurate than SAED analysis; however, the extreme variation seen here is not characteristic of the technique itself and is likely due to fluctuations in the crystalline lattice.

TEM samples prepared traditionally produce an observable region (∼200nm²) which cannot be directly chosen, but when a focused ion beam (FIB) is used to prepare TEM samples the features seen in [23] can be directly investigated. The area selected via FIB Lift-Out technique is indicated by the white rectangle in Figure 21(a). A low magnification STEM/HAADF image of this sample is presented in Figure 21(b). From this sample, it can be determined that there are many microstructural features present including the irregular boundaries demarcating lighter and darker regions. The imaging parameters for these images create a situation where both atomic number and diffraction contrast occur. This is most noticeable where both finer features and the lighter and darker regions are present (as in the lower right corner of Figure 21(b). The boundary between these light and darker regions is highlighted in Figure 21(c) in which a feathered appearance to the boundary is pointed out by outlined arrows (solid black arrows indicate the location of the twin boundary). Solidification of this specimen (progressing from bottom to top in the image) appears to have caused a pinning of these lighter and darker regions at the twin boundary and as the solidification front passes, the “phase” with higher surface energy pulls the region inward creating these feathered, interleaving regions.

After investigation of the FIB prepared TEM samples, the large linear feature was verified as being a twin boundary; this is more clearly represented in Figure 22. The contrast in these HAADF images is due primarily to diffraction, highlighting defects and crystallographic features such as the boundaries between the lighter and darker regions. The inserts in Figure 22 (a and b) highlight the changes to the contrast mechanisms as the sample is tilted roughly 12 degrees. In Figure 22 (a), the side above the twin boundary is in focus while the side below it is not, while the reverse is true in (b). This shift in contrast and apparent focus while tilting allows for a quick assessment of the nature of these features. Since this is the case we can move forward with the argument that this is a twin boundary, though direct observation is needed to prove its existence. Diffraction analysis as well as high resolution TEM is used here to confirm the identity of the feature previously termed a “stitch.”
Figure 21  a.) SEM image of $x=0.3$ AC. b.) STEM/HAADF image of lift-out sample prepared by FIB lift out with APB’s present (bright irregular lines through sample) and twin boundary (indicated by white arrows) passing through the entire sample. c.) Close-up of white square in b showing APB and twin (filled arrows) near edge; notice feathered appearance of APB (outlined arrows). Insert is a closeup of the boundary.
SAED analysis of the boundary presents a typical pattern indicative of twins with a common 110 reflection (Figure 23 a). Selection of one reflection from each twin can be used to create a dark field image where the light regions represent just one of the twins (Figure 23 b and c) from this analysis it is clear that this large long boundary is indeed a twin. High resolution TEM (HRTEM) images of the boundary near the edge of the sample give even more proof that this is a twin and depict the nature of the boundary as rather linear (Figure 24 a). A simulation of the HRTEM image for the prototype crystal structure is shown in Figure 24 e and has excellent correlation with the image in a. Note that the insert in Figure 24 a, an FFT of the HRTEM image, represents what the SAED pattern should look like for that area and that it corresponds very well to the pattern seen in Figure 23 a.

The unknown features permeating both sides of the twin boundary were investigated in a similar manner starting with SAED analysis. The SAED pattern contains a second set of reflections (points connected by dashed lines in Figure 25a) indicating a slight shift in lattice parameters across the boundary. DF imaging of individual primary reflections was not possible.
Figure 23  SAED analysis of the boundary indicating its true nature as a mirror twin on the [110] plane. a.) SAED pattern formed with 100 µm Selected Area Aperture (SAA) across the twin, with reflections present from each side of the boundary (solid lines connect the reflections of one side, and dashed the other). Reflection labels correspond to nearby spots pointed out by solid arrows. b.) Dark-field (DF) image created by selecting the (020) reflection indicated by a solid arrow. c.) DF image created by selecting the corresponding (020) reflection from the twin, indicated by an outlined arrow in the SADP to the left.
Figure 24  a.) HRTEM image of the twin boundary near the edge (insert is a FFT of the image with good correlation to the SAED image in Figure 23 a). b.) Simulated HRTEM image of a perfect [110] mirror twin in the GdNi$_{0.7}$Co$_{0.3}$CrB prototype crystal structure.

Figure 25  TEM investigation of the boundaries present throughout the crystal. a.) SAED pattern of the boundary showing two sets of reflections with slight variations in lattice parameters. b.) TEM bright field image of the APB. The white circle indicates from where the pattern was collected, white arrows denote the twin boundary, and black arrows highlight a stacking fault which passes through the APB with minimal deflection.
due to their close proximity making it difficult to separate, and the DF images for those created with higher order reflections were too faint to gain reliable information. As such, HRTEM images (Figure 26 a) at the boundary were collected and show not only coherence between the two sides but also a slight (roughly 4°) shift in the [100] direction across this boundary (corresponding nicely to the shift observed in the SAED pattern). An FFT of the HRTEM image in Figure 26 a is presented in the insert, and corresponds directly with the SAED pattern in Figure 25 a. A simulation of this boundary using the lattice parameters and angles determined from the SAED pattern and the HRTEM image is shown in Figure 26 b and shows good correlation with the experimental HRTEM image. The nature of this feature is difficult to observe directly, and multiple possible explanations exist, one being an anti-phase boundary (APB) where areas of varying Ni:Co ratio exist driving the lattice parameter mismatch. In this scenario changes in $a$ and $b$ noted via SAED from light to dark regions are attributed to very slight shifts in the Ni:Co ratio. Another explanation would be a highly strained lattice, though the irregular arrangement of these regions would suggest otherwise.
Figure 27  a.) STEM/HAADF image containing a light and dark region with a 1:2-type spherical particle in the lower left region of the image. The line indicates the linescan location with the origin at the cross; the square is used by the software to determine and correct for specimen drift. b.) A plot of the composition variation across the APB. The slope of the Gd points was determined to be horizontal within one standard deviation of the linear regression while the atomic percentage of Ni increases and Co decreases across this boundary. Error bars are equal to the size of the markers.
STEM/EDS analysis was performed across these boundaries and point analyses produced data with little statistical significance, though some linescans did show a slight shift in the Ni:Co ratio across the boundary (Figure 27). A secondary phase was noted occasionally in the TEM samples (as in Figure 27 a, lower left); the composition of which was determined by EDS to be 1:2-type with approximate composition Gd$_2$NiCo$_3$. The contrast seen in this image is due to a combination of average atomic number (Z) and diffraction; the light appearance of the 1:2 particle is due to diffraction effects more so than composition. Before FIB sections, the dispersion of these particles was unknown, but was determined to be located far (roughly 5µm) from the twin boundaries. The approximate composition of the bulk (outside these particles) remains near nominal ($x=0.30$).

As expected from the previous study, the change in microstructure from as-cast to annealed samples is stark, although the large-scale twin boundaries appear to stay intact (Figure 28). The regions of light and dark noticed in the as-cast lift-out sample grow and shrink competitively and form bands extending from the twin boundary in a chevron pattern. These bands were investigated and shown to correlate with the APB seen in the as-cast sample (Figure 25), though the bands themselves are the source of disturbance, as determined by SAED of the respective regions.

Diffraction analysis of the different areas (marked 1, 2 and 3 in Figures 28 and 29) confirms the crystallographic differences in each area. SAED patterns for each of these three regions do not indicate any difference in measured lattice parameters, although area two does expose an extra set of reflections at larger $\mathbf{g}$ indicative of a region with slightly different lattice parameters present in the selected area. This split is similar to what was observed in the APB diffraction patterns of the AC sample, though it is a minimal shift in lattice parameters reflecting 0.41% and 0.65% changes in $a$ and $b$, respectively. As was previously noted, the shift in $a$ and $b$ in these regions could be due to very localized Ni:Co ratio fluctuations or residual stress from the sample synthesis or preparation. During annealing however, there should be sufficient energy and time for any stress relaxation to occur, though chemical fluctuations are more difficult to alleviate in rare earth compounds and may persist even after extensive annealing/homogenizing.
Figure 28  a.) SEM of x=0.3 Annealed, white rectangle indicates the FIB lift-out area.  b.) STEM/HAADF image with solidification Morphology of specimen, again long twin throughout depth of the lift-out sample with radiating boundaries. Notice differences in these boundaries between as-cast and annealed samples.  c.) Close up near original surface, circles indicate regions where SADP’s were taken.
Conclusions

In this study we investigate the odd microstructural features seen in GdNi$_{0.70}$Co$_{0.30}$ via transmission electron microscopy techniques with a view toward determining the underlying causes for their formation. The majority of the features are hypothesized to be due to local fluctuations in the Ni:Co ratio. Lattice parameters determined by SAED differ largely from those determined by XRD analysis and are attributed to these local compositional fluctuations. The use of the lift-out technique for sample preparation was required due to the inhomogeneity and localization of these extremely large microstructural features which made it difficult to identify in traditionally prepared TEM samples. The size of these [110] mirror-twin boundaries and the relative lack of kinks or other defects indicates the extreme stability of these features and may be the driving force for other compositional variations. Due to the large sensitivity of lattice parameters to composition in the GdNi$_{1-x}$Co$_x$ system the lack of variation in EDS signal across the lighter and darker regions seen in the STEM images of the AC sample is attributed to a shift in composition smaller than the detection limits of EDS. The formation of the 1:2-type phase allows the matrix phase to remain in the Cr-B-type (1:1) parent crystal.
structure while rectifying local variations in composition. Annealing of this alloy results in the coalescence of the light/dark regions into small bands where very minute fluctuations in the lattice parameters are present. Diffraction patterns from the resulting bands indicate the presence of a slightly shifted lattice similar to the APBs seen in the as-cast samples and are therefore thought to be semi-coherent regions. The presence of these features suggests an unsettled thermodynamic landscape which can be exploited through processing techniques including annealing and solidification focusing on cooling rates in the $1 \times 10^{-2}$ °C/min range in order to create highly sensitive transducers and actuators made out of these compounds.

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CHAPTER 4. IDENTIFICATION OF UNKNOWN PHASES IN GdNi$_{1-x}$Co$_x$ AT LOW AND HIGH Co CONTENT

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Abstract

Transmission electron microscopy techniques are used to characterize alloys created in the GdNi$_{1-x}$Co$_x$ family with $x=0.00$, 0.10, 0.15, 0.20, 0.50, and 1.00. Energy dispersive x-ray spectroscopy is performed and results in determining a trend of nano-scale features across the composition range $x=0.00$ to $x=0.20$. Within this range, the presence of the Gd(Ni,Co)$_2$-type phase, variations in the Ni:Co ratio in the Gd(Ni,Co)-type matrix phase and the existence of Gd metal particles are most noteworthy. The presence of linear features, similar to those seen in the $x=0.30$ specimen previously, is noted for $x=0.00$ to $x=0.20$. The $x=0.50$ specimen contains the following: Gd(Ni,Co), Gd(Ni,Co)$_2$, Gd$_4$(Ni,Co)$_3$ and the rarely discussed Gd$_{12}$(Ni,Co)$_7$ phase. Diffraction analysis of the 1:1 phase is in good agreement with literature values for this composition. The 12:7 phase is fitted to the Ho$_{12}$Co$_7$ P12$_1$/c1 crystal structure with lattice parameters $a=7.56\text{Å}$, $b=12.51\text{Å}$, $c=11.46\text{Å}$, $\beta=108.8^\circ$ compared to literature values of $a=8.41\text{Å}$, $b=11.39\text{Å}$, $c=11.16\text{Å}$, $\beta=124.2^\circ$ which differs significantly from literature likely due to the presence of Ni. However, the 4:3 phase has not been indexed for this composition before. When fitted to the Gd$_4$Co$_3$ P6$_3$/m crystal structure, lattice parameters of $a=b=11.81\text{Å}$, $c=4.20\text{Å}$ are calculated, as compared to literature values of $a=b=11.59\text{Å}$, $c=4.05\text{Å}$. The GdCo sample contains a eutectic structure containing both the 4:3 phase and regions ranging in composition from 12:7 to Gd metal (including regions near the 3:1 composition).
Introduction

Several studies have been performed on the rare-earth transition metal compounds and alloys, typically focusing on their magnetic and electrical properties. These studies often hinge on X-ray diffraction (XRD) analysis to determine the phase purity of the specimen, though XRD has been shown to miss important phases in other rare-earth compounds.[1] The $R_x T_y$ compounds (where $R$ is a lanthanide rare-earth element and $T$ is a d-block transition metal) have found sustained interest from the scientific community. A thorough review of the magnetic properties of rare earth-3d intermetallics is given in [2] and highlights many commonalities between structures and magnetism of different compositions in this family. Most notable in that study was the interplay of exchange energy and the ratio of the atomic radius to the radius of the 3d shell ($R/r$) and the subsequent impact of alloying rare earths with $T=\text{Ni, Co, and Fe}$.[2] Indeed, Givord et. al. had previously noted the formation of certain $R_x T_y$ compounds depended upon the relative atomic radii of the rare-earth species and that the effect of the interatomic distances in LuCo and YCo compounds are secondary to the magnetic ordering, while they directly determine the magnetic ordering in analogous LuFe and YFe compounds.[3] A simple model for the rare-earth contributions to the magnetic anisotropy based on the single ion model was shown to have good agreement with literature values and a relation drawn between $R\text{Co}_5$ and $R_2\text{Co}_{17}$ compounds based on rare earth nearest neighbor interatomic distances.[4] All of these observations point to a strong link between electronic structure and the formation and stability of these $R_x T_y$ compounds. Those materials with $R=\text{Gd}$ have been noted to have some of the highest Curie temperatures and most uncommon magnetic properties and transitions.

The lanthanide-nickel (R-Ni) equiatomic alloys were first examined and documented independently by Abrahams[5], Walline[6], and Dwight[7]. In these studies it was noted that GdNi crystallizes in an orthorhombic structure following the CrB-prototype (space group Cmcm)[6, 8, 9, 10]. Its Curie temperature ($T_C$) is the highest among R-Ni alloys, and it exhibits a large spin-only magnetic moment.[5] GdNi, along with GdCu$_2$, has been shown to exhibit an anomalous thermal expansion below its $T_C$.[11] While both GdNi$_2$ and GdCo$_2$ ex-
hibit a substantial magnetocaloric effect [12], the GdNi (1:1) compound has both an appreciable
magnetocaloric effect and has been found to display non-trivial magnetoelastic coupling and
a large anisotropic magnetostriction.[13] There is an unusually large forced magnetostriction
in the Gd\textsubscript{x}Co\textsubscript{y} compounds near \(x=y=0.50\), the maximum of which corresponds to different
composition for different temperatures.[14] The magnetocaloric effect in the rarely studied
Gd\textsubscript{12}Co\textsubscript{7} compound is a second order transition with a high magnetic entropy change of 2.96
J kg\textsuperscript{-1} K\textsuperscript{-1} and 4.60 J kg\textsuperscript{-1} K\textsuperscript{-1} for transitions of 0-1T and 0-2T, respectively.[15] GdNiC\textsubscript{2}
and GdCoC\textsubscript{2} both are anti-ferromagnetic at low temperatures (20.0K and 15.6K respectively)
and their magnetic structures differ greatly[16] while their crystal structures are nearly identi-
cal, solidifying in the CeNiC\textsubscript{2}-prototype structure (space group Amm2) with slight variations
in lattice parameters.[17] RNi\textsubscript{3} crystallizes in the PuNi\textsubscript{3}-prototype (space group R\textsuperscript{3}) crystal
structure predominantly, though CeNi\textsubscript{3} is its own prototype (space group P6\textsubscript{3}/mmc); the
R\textsubscript{2}Ni\textsubscript{7} set form in the Gd\textsubscript{2}Ni\textsubscript{7}-type rhombohedral (space group R\textsuperscript{3}m), Ce\textsubscript{2}Ni\textsubscript{7} (space group
P6\textsubscript{3}/mmc), and Nd\textsubscript{2}Ni\textsubscript{7} (disputed depending on processing, but similar to both R\textsuperscript{3}m and
P6\textsubscript{3}/mmc) structures.[18] The crystal structure and lattice parameters determined in [18] de-
pend heavily on the annealing profile, requiring temperatures between 600 and 1200 °C for
durations between 14 hours and 15 days to achieve a single phase specimen. However, even
after annealing for long periods, these alloys tend to contain significant inhomogeneities and
secondary phases stemming from the difficulty in purification of rare-earth elements and their
affinity for carbon and oxygen.[19] To mitigate these problems, efforts have been made to create
high purity and single phase specimens through single-crystal synthesis methods. A single crys-
tal grown by the Czochralski method exhibits the first observed magnetic moment attributed
to Co in the Gd-rich Gd\textsubscript{3}Co antiferromagnetic phase (though f-d hybridization effects were not
taken into account).[20] Single crystal growth of RCo\textsubscript{5} compounds only works for rare-earth
elements with low vapor pressure such as Y, Nd, and Gd while Sm is more difficult to keep
stoichiometric throughout the process.[21] Other methods for processing include powder pro-
duction, compaction and sintering, which can all be done in controlled atmospheres. However,
as was the case in compacted and sintered powders of SmCo\textsubscript{5} and GdCo\textsubscript{5}, decomposition at low
temperatures into the R\textsubscript{2}Co\textsubscript{7} and R\textsubscript{2}Co\textsubscript{17} was inevitable.[22] Despite the great lengths taken
to keep oxygen and carbon out of the powder and the subsequent sintered specimen, they were present in the resulting sample.

To truly give full weight to the magnetic and electrical properties determined for these alloys and compounds, the specimen being tested must be phase pure, or at the very least considerations must be taken to adjust for the plethora of phases and crystal structures which can form in these complex systems. One of the most reliable and direct methods for determining such information lies in electron microscopy techniques. This study aims to fully explore the phase purity and microstructural effects of the synthesis and processing of the alloys in the GdNi$_{1-x}$Co$_x$ family. It has already been determined that the solid solution for the GdNi-prototype phase ends near $x=0.30$[23, 24] and that this composition contains a multitude of crystallographic anomalies and nano-scale fluctuations in composition.[25] This paper aims to take a more detailed look at the other compositions in the GdNi$_{1-x}$Co$_x$ near $x=0.00$ and 1.00 in order to better understand the effects Co has on the GdNi-prototype structure and what hybrid Gd(Ni-Co) phases form as a result. A combination of electron diffraction analysis and energy dispersive x-ray spectroscopy is be used to shed some light on this interesting family of compounds.

**Experimental Procedures**

High purity gadolinium, prepared by the Materials Preparation Center of Ames Laboratory (98 at.% with respect to all elements), was combined with nickel and cobalt, purchased at commercial purities (>99 at.% with respect to all elements). Samples with cobalt were annealed at 700 °C for 18 days (designated AL); however samples $x=0.50$ and 1.00 melted upon annealing and were investigated in the as-cast state. Transmission Electron Microscopy (TEM) foils were prepared traditionally from the bulk and individual TEM lift-out samples were formed via Focused Ion Beam (FIB) lift-out technique. Those prepared traditionally were reduced to 3mm diameter discs roughly 100µm think and electropolished to perforation on a modified twin-jet electropolisher using an electrolyte of Methanol - 8vol.% Perchloric Acid - 2vol.% 2-Butoxyethanol.

Scanning Electron Microscopy (SEM)/Focused Ion Beam (FIB) investigations were per-
formed on polished samples using a FEI Helios NanoLab 660 (Ga⁺ ion source). Backscattered Electron (BSE) images were used to locate regions for lift-out. TEM characterization was completed using a FEI Tecnai G² F20 TEM operating at 200kV with a Field Emission Gun (FEG) source. High angle annular dark field (HAADF) images and energy dispersive x-ray spectroscopy (EDS) information was collected on the Tecnai using scanning TEM (STEM) mode. EDS spectra contain data requiring computational treatment, comparing what is observed to what is expected. Many factors including average density of the specimen, interaction volume, and particular x-ray interactions may obfuscate these results. Further, characteristic x-rays produced from inside the specimen may be absorbed and re-emitted by another element causing shifts in composition from what is expected. Absolute values for compositions may change depending on these factors up to 5%, but relative compositions for areas in the same, or similarly prepared specimens should be considered real. The authors of this work have made every effort to prepare specimens of equal size and shape, though slight deviations are possible. The EDS spectra fitting software reports uncertainty for each point, and in the cases reported herein, all uncertainty values for individual points were ≤2% and are left off of composition graphs for clarity.

Selected area electron diffraction (SAED) patterns were collected using diffraction mode in the TEMs and measurements were taken in ImageJ and verified using CaRIne Crystallography software. The lattice parameters were calculated using linear regression of all fitted and identified patterns for each specimen and location.

**Results**

The members of the GdNi₁₋ₓCoₓ family investigated herein include those with x=0.00, 0.10, 0.15, 0.20, 0.50, and 1.00 since x=0.30 has been previously characterized in depth [24]. Starting with GdNi, the prototype alloy, a series of tests was performed for each of the six compositions remaining.
Figure 30  BF images of GdNi with 100µm SAA at zone axes a.) B=[1 2 0], b.) B=[1 1 0], and c.) B=[0 1 1].

Figure 31  Super lattice reflections seen near the edge of specimen. a.) SAED pattern 400µm SAA, B=[0 1 1], with superlattice reflections indicated by triangle outlines. g=\frac{1}{2}(1 1 1), \frac{1}{2}(1 1 1), \frac{1}{2}(1 1 1), \frac{1}{2}(1 1 1), (1 0 0), and (1 0 0). Filled triangles point out extra reflections due to fluctuations in lattice parameters and linear features. b.) HRTEM image of thin area with linear features (black square in Figure 30). Insert shows FFT of the HRTEM image with corresponding superlattice reflections.
GdNi

GdNi has been studied previously, and there is much literature concerning its magnetic properties and crystal structure; however, in this case an arc melted sample of GdNi was investigated to determine any and all microstructural defects present. The first thing noticed was a set of very small linear features that disappear for certain tilting angles (Figure 30); particularly when the zone axis is B=[1 1 0]. Selected area diffraction patterns (SADPs) of these areas showed superlattice reflections (Figure 31a) as well as spot splitting of the higher order reflections. The splitting is due to collection of diffraction information from regions with different lattice parameters. An HRTEM image of the region indicated by the black squares in Figure 30 is presented in Figure 31 and includes two of the linear features indicating how little their presence appear to impact the crystal structure. When viewed edge on, there was no contrast fluctuations across these features indicating a very thin geometry. It is possible that these were simply stacking faults, which were also discovered in the GdNi$_{0.7}$Co$_{0.3}$ specimen [25]. The insert in Figure 31b is an FFT of the HRTEM image, which should approximate the SADP shown in Figure 31a with very good correlation and does, indeed, replicate the superlattice spots. Aside from these linear features, the GdNi sample exhibited a eutectic structure [24] which, when examined in samples removed via FIB lift-out, turns out to be GdNi and GdNi$_2$ phases as determined by EDS mapping and subsequent quantification (Figure 32). The presence of Pt and C at the surface are due to the lift-out process where a protective layer is deposited before using the Ga$^+$ ion source to mill out the sample (thus the Ga implantation and subsequent signal). As was discovered in the x=0.30 composition, it takes a significant amount of time and heat to homogenize these alloys and slight variations in the composition cannot easily be avoided through synthesis and processing.

GdNi$_{0.90}$Co$_{0.10}$

Upon introduction of Co into the lattice, an immediate change is noticed in the lattice parameters as well as the microstructure. There appears to be a hesitance for Co to substitute into GdNi (as was noted in [26, 23, 24]) and so the presence of both the 1:2-type phase and
Figure 32  Top: Left: STEM/HAADF image of an eutectic region in the GdNi specimen. The cross marks the same location for all x-ray intensity maps with a composition corresponding to GdNi$_2$. Middle: Gd intensity map. Right: Ni intensity map. Bottom: Left: Carbon intensity map. Middle: Pt intensity map. Right: Gallium intensity map.
Figure 33  Above: SEM/FIB image of the region from which the lift-out was taken (white rectangle). Below: STEM/HAADF image of the resulting lift-out sample with a large number of long linear features reminiscent of those found in other specimens
Gd metal is noted from $x=0.10$ to $x=0.30$. Figure 33 contains an image of the surface from which the lift-out was taken as well as the resulting lift-out sample. In this case the features present at the surface (namely, the phases which appear lighter and darker, respectively in the BSE image) do not extend more than a few microns into the sample. The majority of the specimen fits the nominal composition, but the extra phases were probed more closely to identify their composition. Figure 34 contains an image of a small thin region on the FIB lift-out of GdNi$_{0.90}$Co$_{0.10}$ with arrows demarcating the areas where EDS point evaluations were taken. The EDS determined compositions of these regions contained a significant amount of oxygen and carbon and were subsequently treated with the signals included and after subtracting their contribution. The consistent presence of small amounts (roughly 5 at.%) of carbon in EDS signals is normal for surface sensitive analysis techniques which have not been preserved in controlled atmospheres. Spots 1-3 are undissolved Gd metal while 4-7 are approximately the nominal 1:1 phase, spot 8 fits the 1:1-type but contains a significant amount of Co. However, the composition at spots 9-12 are that of the Gd(Ni,Co)$_2$ phase with small amounts of Ni compared to Co. While the presence of long linear features was discovered in this specimen (Figure 33), diffraction analysis was not performed and the specimen did not contain a significant amount of thin region free of defects for HRTEM analysis.

GdNi$_{0.85}$Co$_{0.15}$

The composition GdNi$_{0.85}$Co$_{0.15}$ was noted to be the turning point for the magnetic properties of these alloys; however, when investigated via SEM there were significant amounts of the 1:2-type phase present, and some regions with very different BSE contrast (presumably due to composition or crystallographic orientation). A FIB Lift-out was taken from the region indicated by a rectangle in Figure 35 across this boundary of light and darker material. The STEM/HAADF image of the lift-out sample, shown in Figure 35, reveals the interesting microstructure of the region. There is a long interpenetrating grain stretching from the top left of the image through the center and to the lower right (denoted by points 4-6), but it appears that the surrounding area is unaffected by the growth of this grain. There are white streaks permeating from one side to the other of this grain indicating a similar crystallographic ori-
Figure 34  Above: STEM/HAADF image of GdNi0.9Co0.1 with EDS points called out. Below: Left: EDS determined compositions, O and C included. Right: O and C subtracted. Error for each point is \( \leq 2\% \), approximately the size of the markers.
Figure 35  Above: SEM BSE image showing location of FIB Lift-out across contrast segregation in GdNi$_{0.85}$Co$_{0.15}$. Below: STEM/HAADF image of GdNi$_{0.85}$Co$_{0.15}$ with points indicating locations for EDS spot analyses.
Figure 36  
EDS compositions in GdNi$_{0.85}$Co$_{0.15}$ for points in Figure 35. Left: EDS determined compositions, O and C included. Right: O and C subtracted. Error for each point is $\leq 2\%$, approximately the size of the markers.

The SADPs of different regions within the GdNi$_{0.85}$Co$_{0.15}$ specimen indicate lattice parame-
Figure 37  SAED patterns of different regions in the GdNi\textsubscript{0.85}Co\textsubscript{0.15} lift-out sample, B=[011].

a.) normal pattern with extra reflections (indicated by filled triangles). b.) roughly the same pattern of a neighboring area showing superlattice reflections (outlined triangles). c.) another nearby area exhibiting both phenomena.

meter inconsistencies and chemical ordering as seen in Figure 37 a and b, respectively, while the pattern in c shows an area where the two features are seen simultaneously. The presence of split reflections could indicate a trend in crystallographic features similar to what was seen in the $x=0.30$ sample. The lack of superlattice reflections in Figure 37b may indicate a relationship between an area where there are lattice parameter fluctuations (split reflections) and a randomization of Ni and Co locations in the lattice.

\textbf{GdNi\textsubscript{0.80}Co\textsubscript{0.20}}

The microstructure for the $x=0.2$ specimen exhibits many of the same features seen in the other compositions in this family. STEM/HAADF images show a plethora of long linear features extending across entire grains, as well as a small precipitate phase near the surface, and small elongated regions of a slightly different composition (Figure 38). EDS point analyses of the matrix vs precipitate show a relatively nominal composition outside of a Gd(Ni,Co)\textsubscript{2}-type precipitate similar to the other alloys in this family. When oxygen and carbon signals are removed from the compositions the result is near nominal in all but one case (point 10) where the Co content spikes up to 14 at.% (equivalent to $x=0.3$). The darker, elongated regions mentioned previously were probed in greater detail and reveal near nominal (GdNi\textsubscript{0.80}Co\textsubscript{0.20}) composition suggesting either a topographic or crystallographic nature (Figure 39). Point analyses indicate
Figure 38 Above: STEM/HAADF image of GdNi$_{0.80}$Co$_{0.20}$ with points showing EDS composition analyses. Below: Left: EDS determined compositions, O and C included. Right: O and C subtracted. Error for each point is $\leq 2\%$, approximately the size of the markers.
Figure 39  Above: STEM/HAADF of GdNi$_{0.80}$Co$_{0.20}$ AL close-up of edge in previous figure. Below: Left: EDS determined compositions, O and C included. Right: O and C subtracted. Error for each point is $\leq 2\%$, approximately the size of the markers.
Figure 40  EDS linescan composition across feature in GdNi$_{0.80}$Co$_{0.20}$ lift-out sample (black line in Figure 39 origin is at the cross). Left: EDS determined compositions, O and C included. Right: O and C subtracted. Error for each point is $\leq2\%$, approximately the size of the markers.

The composition of the dark streaks as very close to nominal with points 1-4 containing around 10 at.\% oxygen and points 8-10 containing roughly 10 at.\% carbon. The oxygen and carbon signals are relatively small, indicating surface contamination rather than distribution in the lattice. When subtracted out, the compositions match very closely with the Gd(Ni,Co)$_2$ phase for 1-4, and the GdNi$_{0.80}$Co$_{0.20}$ 1:1-type phase for points 5-10. A linescan across one of the fine linear features was performed (black line starting at the cross in the STEM/HAADF image in Figure 39). There was no significant change in composition across this feature (plotted in Figure 40), and it can be seen in the HAADF image that this linear feature pierces and seems to have separated the darker elongated region near point 1 (indicated by an outlined arrow in Figure 39). This type of separation and shift along with the composition data would indicate a crystallographic nature to these features similar to what was seen in GdNi$_{0.7}$Co$_{0.3}$.

GdNi$_{0.70}$Co$_{0.30}$

This system was studied in detail in the previous chapters and will not be repeated here; however it is important to note that this is the last composition in which a nearly single-phase sample was created. For $x=0.5$ additional peaks in the XRD pattern are observed, and the
Upon investigation of $x=0.5$ samples prepared by traditional methods, a mixture of Gd(Ni,Co) and Gd(Ni,Co)$_2$ was discovered as expected from previous studies. Diffraction analysis (Figure 41) fit one region with the Gd(Ni,Co) 1:1 prototype with lattice parameters $a=3.43\,\text{Å}$, $b=10.81\,\text{Å}$, $c=4.00\,\text{Å}$ which is in good agreement with literature, while the EDS determined composition was near nominal $54.8$ at.% Gd, $24.1$ at.% Ni and $21.1$ at.% Co. A FIB lift-out sample was prepared near the boundary of two of these regions to index and identify their respective crystal structures. Composition analysis was performed to help determine which regions belonged to which phase. An STEM/HAADF image of the lift-out sample is present in Figure 42 with many points indicating the location of EDS spot analyses. Points marked with squares belong to a high Gd phase, likely the Gd$_{12}$Co$_7$-type with roughly $10$ at.% Ni substituted for Co. It should be noted here that this phase has not been in the published phase diagrams for Gd-Co since 1992[27] though this composition was found to exist in the $x=1.00$ samples and was confirmed via SAED analysis herein. The rest belong to Gd$_4$Co$_3$ with varying amounts of Ni. Those marked with a triangle have almost equal amounts of Ni and Co ($21$ at.% each) while those marked with circles contain much more Co than Ni. GdNi$_{0.50}$Co$_{0.50}$
Figure 42  STEM/HAADF image of GdNi$_{0.50}$Co$_{0.50}$ FIB lift-out) with EDS points from different regions of the specimen.
EDS results for the previous figure are averaged for each set of points: squares, triangles, and circles. Square points belong to the Gd$_{12}$(Ni,Co)$_7$-type phase with a significant amount of Ni substituted for Co whereas the circle points correspond to grains of the same phase with less Ni. Notice the lack of the GdNi-type phase in this lift-out sample. XRD has previously proved the existence of this phase in a large majority. Averaged results of the EDS composition analysis are present next to the STEM/HAADF image in Figure 42 and indicate a composition of Gd$_{12}$(Ni,Co)$_7$ for the points designated by squares and a composition of Gd$_4$(Ni,Co)$_3$ for the circles and triangles. The latter phase is separated into two categories. An equal amount of nickel and cobalt is present for those marked with triangles, whereas the regions marked with circles retain the 4:3 composition but are deficient in Ni. SAED pattern analysis was carried out on the 12:7 and 4:3-type phases independently. The first set of patterns from the area marked with points 1 and 2 can be seen in Figure 43, while those from a region near point 6 can be seen in Figure 44. Identification of the phase matches the Gd$_{12}$Co$_7$-type phase with space group P12$_1$/c1 with the following zone axes for each pattern: a.) B=[0 1 2], b.) B=[0 0 1] and c.) B=[1 0 2] with signs of double diffraction occurring due to separate regions with similar crystal structure, but slight variation in lattice parameters. The lattice parameters fitted for these patterns is slightly different than what is in the literature for Gd$_{12}$Co$_7$, likely due to the presence of Ni. Lattice parameters were determined from these patterns to be the following a=7.56Å, b=12.51Å, c=11.46Å, $\beta=108.8^\circ$ compared to literature values of a=8.41Å, b=11.39Å, c=11.16Å, $\beta=124.2^\circ$. The patterns are consistent with the crystal structure for the
Gd\(_4\)(Ni,Co)\(_3\)-type phase with space group P6\(_3\)/m and the following zone axes: a.) B=[7 5 2 12], b.) B=[20 22 2 3] and c.) B=[4 5 1 9]. Lattice parameters fit to these patterns resulted in a=b=11.81Å, c=4.20Å compared to literature a=b=11.59Å, c=4.05Å. Diffraction pattern analysis of each 12:7 and 4:3-type phases are in good agreement with literature values; however, the angle for the monoclinic 12:7-type phase was significantly different for this composition. This is thought to be due to the profound effect that the Ni-Co ratio plays on the crystal structure as noted in previous studies. There were extra spots noticed in Figure 43 c (black triangles) where B=[102] indicating a nearby grain with a 2° rotation. No such spots were noticed in the 4:3-type phase.

**GdCo**

A sample prepared with the global composition of 50 at.% Gd and 50 at.% Co should solidify in the following succession: GdCo\(_2\), Gd\(_4\)Co\(_3\), and finally Gd\(_3\)Co according to published phase diagrams. The resulting microstructure has been studied previously [24]; however, the crystal structure and nano-scale distribution of these phases has not been previously studied. As such, a FIB lift-out was taken from a region with a number of phases present in an attempt to identify each of the resulting phases. A STEM/HAADF image of the resulting lift-out sample is presented in Figure 45 with multiple points outlining the areas of EDS point analyses. It can be seen that there is significant local segregation of the phases. Points 3-9 and 16 correspond to the Gd\(_4\)Co\(_3\) phase, while points 1 and 2 fit more closely to the Gd\(_{12}\)Co\(_7\) phase. Points 10-13...
and 15 have been identified as Gd$_3$Co though there may be some overlap with phases which are richer in Gd or Gd metal. Meanwhile, the composition of spot 14 indicated only Gd metal and is likely undissolved in the arc melting process.

SAED was not performed on the regions containing multiple phases due to difficulty in separation and identification of phases that have similar structures and diffraction patterns. However, crystal structure analysis was carried out on the area around point 16 (Figure 46) and resulted in the identification of the P6$_3$/m hexagonal Gd$_4$Co$_3$-type phase with very good agreement with the published literature values for the lattice parameters: $a=b=11.58\,\text{Å}$, $c=4.10\,\text{Å}$. The two overlapping patterns in Figure 46b are likely a result of double diffraction since those two zone axes are separated by only 0.96° while the appearance of the patterns in c appears to be from a different, neighboring grain.

Discussion

The GdNi compound contains long linear features of a crystallographic nature and has been compared to what was seen in $x=0.30$ in the previous study. A eutectic region is formed between the GdNi and GdNi$_2$ phases, and EDS mapping has confirmed the relative compositions of the neighboring regions. Once Co is substituted for Ni a third phase appears in the SEM images and the remainder of the compositions in the series appear to contain this phase. When investigated with EDS, this third phase is consistently Gd metal with small percentages of carbon and/or oxygen. Samples with $x=0.00$ through 0.30 have been shown to contain long linear features which are absent in the $x=0.50$ and 1.00 specimen. These long linear features are thereby further linked to the CrB-prototype Gd(Ni,Co) phase. Diffraction analysis of GdNi$_{0.85}$Co$_{0.15}$ indicated the presence of coherent lattice parameter fluctuations that are similar to the APBs seen in GdNi$_{0.70}$Co$_{0.30}$ previously. Closer inspection of the GdNi$_{0.20}$Co$_{0.20}$ specimen revealed the presence of another phase, though EDS probes did not reveal any significant changes in composition around these areas, possibly due to the small volume of the phase sampled. Traditionally prepared samples of GdNi$_{0.50}$Co$_{0.50}$ were investigated and found to contain the GdNi 1:1 prototype phase as well as a 1:2 Gd(Ni,Co)$_2$ phase. The lattice parameters were determined by SAED analysis and fit relatively closely to those previously determined via
Figure 45 Above: STEM/HAADF image of a FIB lift-out sample of GdCo with points indicating EDS locations from an eutectic region (image rotated for clarity). Below: Left: EDS determined compositions, O subtracted. Right: O included. Error for each point is ≤2%, approximately the size of the markers.
XRD refinement. However, the lift-out specimen contained neither the 1:1 or 1:2-type phases. It contained two different phases: Gd₁₂Co₇ and Gd₄Co₃ determined through composition analysis; however, the lattice parameters determined from the diffraction patterns differed greatly from what is found in the literature and is likely attributable to the presence of Ni. Meanwhile, the microstructure of the \( x=1.00 \) sample was that of a typical eutectoid including the Gd₄Co₃ and Gd₁₂Co₇ phases though the latter was only determined via EDS.

**Conclusions**

STEM/HAADF imaging, energy dispersive x-ray spectroscopy, and selected area electron diffraction analysis of the alloys in the GdNi\(_{1-x}\)Co\(_x\) family with \( x=0.00, 0.10, 0.15, 0.20, 0.50, \) and 1.00 was performed and sheds light on the nano-scale distribution of Co throughout the substitution. Though the literature is full of potential compounds which could form in this pseudo-binary system, the introduction of Co into the GdNi lattice causes the immediate segregation into Gd(Ni,Co)\(_2\) and Gd metal. Long linear features and electron diffraction spot splitting were noted for all specimen between \( x=0.00 \) and 0.20, but not for either \( x=0.50 \) or 1.00. GdNi\(_{0.50}\)Co\(_{0.50}\) samples contained many phases (Gd₁₂(Ni,Co)₇, Gd₄(Ni,Co)₃, Gd(Ni,Co)₂ and Gd(Ni,Co)) suggesting the instability at higher Co concentrations. Samples prepared at \( x=0.50 \) were the only ones to contain all four of these phases. For \( x=0.50 \), lattice parameter
measurements for the Gd$_{12}$(Ni,Co)$_7$ and Gd$_4$(Ni,Co)$_3$ phases were significantly different from literature values for Gd$_{12}$Co$_7$ and Gd$_4$Co$_3$, respectively and are attributed to the presence of Ni. GdCo samples exhibited a typical eutectoid microstructure as expected for the composition region on the phase diagram, though, again the presence of the Gd$_{12}$Co$_7$ phase and Gd metal is noteworthy.

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CHAPTER 5. GENERAL DISCUSSION

A general review and discussion of the results from chapters 2-4 will tie together some of the trends and nuances which were not conveyed in the individual chapters. First, results that were omitted from the papers for brevity will be exhibited and discussed. Then alloys from $x=0.00$ to $0.30$ will be reviewed and their commonalities discussed, after which the alloys with high Co composition ($x=0.50$ and 1.00) will be treated similarly.

Recent progress in GdNi$_{0.70}$Co$_{0.30}$

When the first stitches were noticed in the annealed $x=0.30$ specimen, attempts were made to directly identify their origin. However, these techniques proved inadequate to this end and as such atom probe tomography (APT) was performed on samples removed through a similar lift-out technique as described previously. Unfortunately, sample oxidation and contamination with Ga$^+$ ions caused multiple samples to be unusable as APT needle samples. The only needle that ran successfully had significant Ga$^+$ damage and the information gained from the experiment did not seem to correlate well with the stitches or other features seen up to that point. This lack of undeniably stitch-like features present in the APT samples frustrated the attempt, preventing any clear conclusions from being drawn at the time of the experiment. Subsequently, the work presented in chapter 3 identified these features as twins, though multiple other crystallographic features were discovered in the process. Several specimens for each as-cast and annealed $x=0.30$ samples were prepared via lift-out, though only the first two were presented previously.

Starting again with the as-cast sample a somewhat different microstructure is observed where instead of a stand-alone twin boundary, a very thin twinned grain is present (Figure 47). The width of this twinned grain is roughly 200nm and it appears to span the entire length of the lift-out specimen, though the thickness of the lift-out sample makes this difficult to directly observe. Figure 48 contains HRTEM images of either side of this region that identify this feature
Figure 47  STEM/HAADF image of the second as-cast $x=0.30$ specimen. Black square indicates region for subsequent image.

Figure 48  HRTEM images of either side of a 200nm wide twinned region. Inserts are FFTs of the respective images.
as a long, thin grain with twin boundaries on either side. The inserts in Figure 48 are FFTs of each image. These FFTs simulate what a diffraction pattern would look like and correspond to what would be seen for a mirror twin on the (1 1 0) plane.

Multiple other linear features are present in this lift-out sample (Figures 49 and 50). The larger of these features form a 75° angle with the twin boundary, while there are smaller streaks running parallel to this twin boundary. A high magnification STEM/HAADF image of the area outlined by the square in Figure 49 is presented in Figure 50 and shows the location of EDS point (circles) and linescan (line starting from the cross) data collection. EDS analysis of this specimen resulted in a consistently large amount of carbon while the oxygen composition was often below 20 at.% (Figure 51). Fitting of EDS spectra indicates that the material between the twin boundaries is approximately the same composition as that of the area surrounding the linear features. Meanwhile, a linescan through the twin boundary indicates no appreciable difference between the two areas (Figure 52). Figure 53 contains an STEM/HAADF image of the
Figure 50  STEM/HAADF image with EDS point and linescan locations. Linescan starts at the cross.

Figure 51  STEM/EDS point analysis of call-outs in Figure 50. Left: EDS determined compositions, O and C subtracted. Right: O and C included. Error bars are equal to the size of the markers.
Figure 52  STEM/EDS linescan for line in Figure 50. Left: EDS determined compositions, O and C subtracted. Right: O and C included. Error bars are equal to the size of the markers.

Figure 53  STEM/HAADF image with EDS point and linescan locations. Linescan starts at the cross.
edge of the lift-out sample with multiple linear features and a black line indicating the location of the EDS linescan (starting from the cross). Carbon content for this line was determined to be around 50 at.% which can be either considered as contamination, or could indicate the presence of the Gd(Ni,Co)C$_2$-type phase (Figure 54). Results of the linescan (black line in Figure 50) across the twin boundary and into one of the linear features were not consistent with those of a linescan (black line in Figure 53) through one of the linear features alone (Figure 52 vs. 54, respectively). These results point to a large amount of carbon in the twinned grain, and very low Co content throughout (roughly 10 at.% when corrected for C and O). Irregularities in both linescans are likely due to sample drift and the points in Figure 54 after the 30nm mark are thought to be that of the matrix composition. HRTEM images of these features are present in Figure 55 and 56.

The thicker features are pierced by the thinner ones and exhibit phase contrast when compared to the matrix phase. This difference can be due to many factors, and positive identification of the phase is needed to determine these mechanisms. The EDS data indicates a secondary phase with two possibilities: one, neglecting the carbon signal as surface contamination, the composition fits closely with Gd$_3$Ni$_2$ and two, including the carbon signal the composition data points to Gd(Ni,Co)C$_2$. Either option would be able to form coherently with the matrix. These
Figure 55  HRTEM images of the intersection of wider linear features and thinner features that appear to be stacking faults.

Figure 56  HRTEM images of wider linear features showing coherence of the feature. Inserts are FFTs of the corresponding image.
features were also present in the other specimens \((x=0.00 \text{ to } 0.30)\). The thinner features are found to be stacking faults, which have been seen in the previous two chapters and seem to be very common in the Cmcm GdNi-type crystal structure.

An STEM/EDS linescan of the larger linear features (in as-cast \(x=0.30\)) did not elucidate their nature nor that they possessed any correlation with the matrix phase; however, when the same type of features were scanned perpendicular to their direction (Figure 57) a trend was noticed in which Gd increased and Ni decreased in these areas. One such large linear feature from \(x=0.30\) as-cast is shown in Figure 57 with a black line indicating the location of the scan (starting at the cross). The composition values appear relatively noisy, but a trend can be seen where the linear feature appears to be roughly 60 at.% Gd, 30 at.% Ni and 10 at.% Co (Figure 58). As it turns out, this corresponds well with what was seen in one of the APT scans of the same as-cast GdNi\(_{0.70}\)Co\(_{0.30}\) sample previously thought to be unimportant because it was not consistent with a stitch.
Figure 58  STEM/EDS linescan data of the third as-cast $x=0.30$ specimen across a wide linear features. Black line indicates location of EDS linescan, starting at the cross. Error bars are equal to the size of the markers.

Figure 59  APT reconstruction of as-cast specimen showing initial positions of Gd-Ni ions. a.) projection along the “x”-axis. b.) oriented to view the feature edge-on. Black line represents a plane projected into the plane of the page used for the concentration profile in the direction of the arrows.
A reconstruction of the concentration of Gd-Ni ion locations from the atom probe needle is presented in Figure 59a and the same data from a different orientation is shown in 59b. When viewed edge-on (59b) a concentration of Gd-Ni ions with an irregular shape can be seen just left of the middle. The black line in Figure 59 represents a plane (projected into the paper) that is stepped from left to right (following the arrows) in increments of 1 Å. A one dimensional concentration is calculated from averaging all atoms in the reconstruction which touch the plane at a given step. A portion of the resulting concentration profile is presented in Figure 60. The change in composition in this case corresponds very closely with what was seen in the STEM/EDS scan in Figure 57, although the values for the maximum (in Gd) and minimum (in Ni) concentrations are somewhat different from those determined by EDS. Compared to the atom probe the number of counts collected in the EDS scan is quite low, causing noise to be of great concern and leading to possible errors in spectral analysis. In addition, the EDS results can be obfuscated by the effects of sample drift. In this case, the added data from the APT scan tends to support that the EDS analysis is giving reliable data in this instance.

The similarities between this scan and the previous EDS scan (Figure 58) point to the conclusion that these larger linear features are actually a secondary phase with a composition
Figure 61  STEM/HAADF image of the second annealed $x=0.30$ specimen highlighting the double band of twins.

around 55-60 at.% Gd, 30-35 at.% Ni and roughly 10 at.% Co. Looking at the phase diagrams for Gd-Ni and Gd-Co there are two options for the composition of this phase, $\text{Gd}_3\text{Ni}_2$ with substitutions of Co, or $\text{Gd}_4\text{Co}_3$ with Ni substituted for Co. Those two phases have been studied, though the atomic positions for only the $\text{Gd}_4\text{Co}_3$-phase have been identified in literature. This lack of information makes it difficult to positively identify this phase, and additional work involving and diffraction analysis and pattern and image simulation is needed. Further, these features have an approximate width of 3nm (according to the HRTEM images), and may contain a significant amount of carbon in some cases.

When another sample of the annealed $x=0.30$ material was investigated using TEM, a similar microstructure was observed, although a major difference was noted. In this second case there were micro/nano twins present in a double banded region (between the lines pointed out by arrows in Figure 61). The TEM BF image is presented in Figure 62a with a higher magnification and HRTEM image in b and c, respectively. FFT analysis of the HRTEM image in Figure 62c (see insert) supports the micro/nano-twinned structure in this region.
Figure 62 TEM/BF and HRTEM images of annealed $x=0.30$ specimen. a.) Bright field TEM image of twins. b.) Higher resolution image showing micro/nano-twin structure. c.) HRTEM image of micro/nano-twins. Insert is an FFT of the HRTEM image.

and corresponds well with SAED patterns collected elsewhere in this specimen (Figure 63c). Another region on this sample, indicated by the arrow in Figure 64 was noted to have a composition near Gd$_3$O$_2$.

Overall the specimens with compositions between $x=0.00$ and $x=0.30$ contain secondary and tertiary phases, crystallographic features including dislocations, stacking faults, and twins in a surprising quantity. These specimens are prone to mechanical defect formation and many of the specimen examined showed an extreme concentration of dislocations and stacking faults near the mechanically polished surface. The lessons learned from the microstructure analysis are that for many of these $R_xT_y$ compounds extreme care must be taken in the synthesis and processing techniques and parameters used to form them. Otherwise, physical properties measured from these specimen which are thought to be single phase may be misleading to the researcher.

DSC analysis

Differential scanning calorimetry (DSC) had been performed on the full set of compositions in this family; however, the true impact of the results could not be easily interpreted until the microstructure of these specimens was well known. Now, having detailed information to aid in deciphering the form and location of the DSC peaks it is worth returning to a consideration
Figure 63  HRTEM and SADP images of annealed $x=0.30$ specimen. a.) HRTEM image of twins b.) Higher resolution HRTEM image showing micro/nano-twin structure. c.) SADP of the region showing streaking characteristic of micro/nano-twins. Insert is FFT of image in b.

Figure 64  STEM/HAADF image of the second annealed $x=0.30$ specimen. Arrow indicates region of Gd metal.
of these results. DSC scans for each composition were performed from 500-1300-500 °C at 20K/min three times in succession as a check for repeatability. Events resulting in heat flow peaks were tallied for heating and cooling in each cycle. Figure 65 contains the collected peak temperatures for DSC events as a function of composition \(x\) in GdNi\(_{1-x}\)Co\(_x\) (open circles). Literature values for transitions that should occur for each end-member composition (equiatomic GdCo and GdNi respectively) are also presented on this figure as are the phase diagrams for the end members (Gd-Ni and Gd-Co) for reference.

The thermal events seen for the equiatomic GdCo specimen correspond well to literature values while those for the GdNi composition differ only slightly from literature (likely due to scan parameters). There were no peaks that indicated the presence of Gd\(_3\)Ni\(_2\), in direct contradiction with what was seen using electron microscopy techniques, where Gd\(_3\)Ni\(_2\) was identified. This could be due to the relative low volume concentration of these features resulting in a very small, diffuse peak in the DSC data. It is also possible that there is an unexpected stability of these features in the GdNi matrix and melt simultaneously. According to electron microscopy investigations and XRD analysis, the GdNi-prototype phase should exist in all compositions, up to and including \(x=0.50\) composition. While the DSC data appears to agree with this, both the Gd(Ni,Co)-Gd(Ni,Co)\(_2\) eutectic and liquidus temperatures continuously decrease for increasing Co concentrations. For \(x=0.00\) to 0.50 there are unexpected transitions between 900 and 1200 °C. One explanation for these peaks is the presence of Gd(Ni,Co)\(_2\) which when heated follows the reactions GdNi\(_2\)→GdNi\(_3\) (1010 °C), GdNi\(_3\)→Gd\(_2\)Ni\(_7\) (1110 °C), Gd\(_2\)Ni\(_7\)→GdNi\(_4\) (1200 °C), and GdNi\(_4\)→GdNi\(_5\) (1270 °C) indicating a large volume percentage of the GdNi\(_2\)-type phase. However, Co cannot be blamed entirely for the formation of the Gd(Ni,Co)\(_2\)-type phase since it and the previously mentioned peaks were present in the \(x=0.00\) sample as well. The liquidus temperature for this pseudo-binary increases relatively smoothly from equiatomic GdCo (approximately 1040 °C) to the contiguous melting temperature of the GdNi compound (1280 °C). Extra peaks for the \(x=0.50\) composition correspond well to the Gd\(_4\)Co\(_3\)-GdCo\(_2\) peritectic transition (670 °C) as well as to the GdNi-Gd\(_3\)Ni\(_2\) peritectic transition (690 °C). The crystal structure for Gd\(_3\)Ni\(_2\) is noted in literature as tetragonal but the lattice parameters and atomic locations are not known and as such this structure was not
Figure 65 Above: Pseudo-binary for GdCo-GdNi comprised of peak positions determined from DSC scans (500-1300-500 °C 3-times) plotted as a function of composition \((x)\). Below: binary phase diagrams for Left: Co-Gd, line and label for Gd\textsubscript{12}Co\textsubscript{7} adapted from [1], filled arrow denotes the equiatomic composition, outlined arrow indicates the temperature of the liquidus at 50 at.%Gd; and Right: Gd-Ni. Both diagrams adapted from [2].
Figure 66  Schematic diagram of the relationship between $xy$ and $yz$ microstructures in as-cast (above) and annealed (below) states. Red lines indicate twin boundaries, blue lines indicate APBs between light and dark regions. Green spots indicate 1:2 phase.

used as a candidate for diffraction analysis procedures. Further studies in the Co rich region are needed to fill in some of the blanks on this diagram, but the observations of this thesis are a start to understanding the thermodynamic impact Co plays in the GdNi equiatomic system.

**General comments**

As a line compound, the 1:1 phase forms at very high temperature ($1280\,^\circ\text{C}$) and it has been shown that temperature and magnetic field have a profound influence on the lattice parameters of GdNi. The arc melting process is likely the cause for a number of the interesting microstructures seen herein. Twinning at the stitches could act as pinning sites for dislocations and for changes in ordering or variations in composition or structure. As Co is substituted for Ni, the GdNi-type (Cmcm) structure is destabilized and can easily revert to the 1:2 Fd$\bar{3}$m structure. But this requires great deal of Co/Ni, so pathways of composition variations are formed and 1:2 regions nucleate and emerge. For the $x=0.30$ AC $xy$ sample it appears that the 1:2 inclusions are found primarily in the darker regions emanating from the stitches. Indeed, in the $yz$ samples the 1:2 grains form at the grain boundaries and within the grains, negating
this relation, but closer investigation reveals that those within the grains are inside regions of
dark stripes. The relation between $xy$ and $yz$ directions is schematically depicted in Figure 66
where the red lines are the twins (stitches) the blue lines are the anti-phase boundaries between
the lighter matrix and darker (dendrites) regions and the green circles show the approximate
location of the 1:2-type phase precipitates.

The GdNi solid solution is indeed terminated between $x=0.30$ and $x=0.50$ (15 and 25 at.%
Co, respectively) and while much work is to be done, the microstructures shown here have shed
some light onto the nature of the solid solution. Excess nickel and cobalt are rejected from the
matrix and forms the Gd(Ni,Co)$_2$ compound in all compositions up to $x=0.3$. Annealing has
a profound effect on the distribution of phases and homogeneity of the samples.

Both DSC and microscopy confirm the $x=0.5$ composition (25 at.\%Co) to be past the
solid solution, forming both Gd$_2$(Ni,Co)$_7$-type and Gd$_4$(Ni,Co)$_3$-type phases alongside the
Gd(Ni,Co)-type and Gd(Ni,Co)$_2$-type phases. The GdCo sample exhibits a dendritic mi-
crostructure typical of a peritectic solidification, fitting with thermodynamic information for
Gd:Co compounds in the equiatomic range.

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CHAPTER 5. CONCLUSIONS

The results of this investigation using SEM, EDS/WDS, and OIM in conjunction with the XRD analyses show that in GdNi$_{1-x}$Co$_x$ alloys the solid solution with the CrB-type crystal structure is indeed terminated at approximately $x=0.45$ (22.5 at.% Co). Excess nickel and cobalt are rejected from the matrix and form the Gd(Ni,Co)$_2$ compound in all compositions up to $x=0.3$. The overall arrangement of grains in these samples is a set of columnar, spanning hundreds of microns and potentially the entire height of the arc-melted buttons (roughly 10mm). The grains have an effective diameter near 100 µm as determined by EBSD orientation imaging microscopy. Lattice parameters determined by SAED differ largely from those determined by XRD analysis and are attributed to local compositional fluctuations. Linear features called stitches were determined to be the result of (1 1 0) mirror twins surrounded by regions of fluctuating Ni:Co. The size of these twin boundaries and the relative lack of kinks or other defects indicate the extreme stability of these features, and both their existence and the strain they cause may be the driving forces for other compositional variations. Due to the large sensitivity of lattice parameters to composition in the GdNi$_{1-x}$Co$_x$ system, even the small fluctuation in Ni:Co composition which was noticed in STEM/EDS is attributed to the production of anti-phase boundaries and regions of dark and light material. Annealing of this alloy results in the coalescence of the light/dark regions into small bands where minute fluctuations in the lattice parameters are still present. Long linear features and electron diffraction spot splitting, which are indicative of APB-like regions, were noted for all specimen compositions between $x=0.00$ and 0.20. The presence of Gd$_{12}$(Ni,Co)$_7$, Gd$_4$(Ni,Co)$_3$, Gd(Ni,Co)$_2$ and Gd(Ni,Co)-type phases was observed throughout this family of compositions and all four were present in GdNi$_{0.50}$Co$_{0.50}$ samples. In the $x=0.50$ sample lattice parameter measurements for the Gd$_{12}$(Ni,Co)$_7$-type phase fitted to the Ho$_{12}$Co$_7$ P12$_1$/c1 crystal structure resulted in lattice parameters of $a=7.56\text{Å}$, $b=12.51\text{Å}$, $c=11.46\text{Å}$, $\beta=108.8^\circ$ compared to literature values of
a=8.41Å, b=11.39Å, c=11.16Å, β=124.2°. Those for the Gd$_4$(Ni,Co)$_3$-type phase fitted to the Gd$_4$Co$_3$ P6$_3$/m crystal structure resulted in lattice parameters of a=b=11.81Å, c=4.20Å, as compared to literature values of a=b=11.59Å, c=4.05Å. GdCo samples exhibited a typical eutectoid microstructure as expected for the composition region on the phase diagram; however, the presence of the Gd$_{12}$Co$_7$ phase is noteworthy since it has been removed from the phase diagram.

Next, some potential avenues for future work on these compounds will be explored. Many Gd-Ni and Gd-Co compounds studied in the literature exhibit important magnetic properties, many others require further study. In the case of the GdNi$_{1-x}$Co$_x$ family, crystallographic analysis of the larger linear features (Gd$_3$(Ni,Co)$_2$ in $x=0.00-0.30$) is required to ensure correct identification. Also, as was the case with Gd$_5$(Si,Ge)$_3$ platelets in Gd$_5$(Si,Ge)$_4$ samples, their role in bulk magnetic behavior and their thermodynamic stability should be investigated in the even that the presence or absence of them is needed for a particular application. The exact location of the solid solution termination and the rest of the Co-rich side of the pseudo-binary phase diagram should also be investigated to look more closely at the 12:7-type phase with a significant amount of Ni. Further, the Gd$_{12}$(Ni$_{1-x}$Co$_x$)$_7$ family of alloys is strongly suggested as an interesting new direction to take with this project.