ABSTRACT

FAN, MIN. On the Formation and Evolution of Cu-Ni-rich Bridges of Alnico Alloys with Thermomagnetic Treatment and Tempering. (Under the direction of Dr. Carl C. Koch and Dr. Justin Schwartz).

Despite decades of research and development of Alnico alloys, significant uncertainties in the underlying structure-property relationships remain. Here we report the observation of Cu-bridges during the thermomagnetic treatment and tempering. First, the results of the thermomagnetic treatment research show the effect of Ti on the Alnico microstructure and nanostructure, and the corresponding influence on magnetic properties. We show that Ti fosters the conditions resulting in the formation of Cu-Ni-rich bridges in the $\alpha_2$ phases between the $\alpha_1$ phases. For Alnico containing Ti, a typical chessboard-like morphology with Cu-Ni-rich bridges is observed, whereas in the absence of Ti, the $\alpha_1$ phases connect to each other readily, especially with a high Co concentration, and a maze-like morphology with Cu-rich white plate precipitates rather than Cu-rich bridges is observed. Furthermore, in Alnico containing Ti, an inhomogeneous distribution of Ni is found in the $\alpha_2$ phases, including loops with high Ni concentration surrounding the $\alpha_1$ phase, and high concentrations in the bridges as well. An increase in the Cu concentration is also observed in the loops around the $\alpha_1$ phases (Ni-Cu loops), and direct contact between the Cu-Ni-rich bridges and Ni-Cu loops is observed in lieu of direct contact between the bridges and the $\alpha_1$ phases. We also observe that the bridges are not perfectly round but ellipsoidal, with the long axis along the connection of two adjacent $\alpha_1$ phases. Energy-dispersive X-ray spectroscopy line scans of the bridges shows that two types of Cu-Ni-rich bridges exist: those with more Cu than Ni, and those with more Ni than Cu. A three-dimensional model is presented that explains the conditions and process of bridge formation, consistent with the observed composition distributions. Second, the results of the tempering research show that the effect of
tempering on the microstructure evolution of Cu-Ni bridges of Alnico alloys. Energy-dispersive X-ray spectroscopy (EDS) maps and line scans show that tempering can change the elemental distribution in the Cu-Ni bridges, but not the morphology and distribution of Cu-bridges. Cu concentration in the Cu-Ni bridges increases after the tempering while other elements concentrations decrease, especially for Ni and Al. The boundary of Cu bridges becomes sharper with tempering. The possible reason for these features is the largest ratio of $2C_{44}/(C_{11}-C_{12})$ of Cu. Besides, Ni-Cu loop around $\alpha_1$ phase becomes inconspicuous with the tempering. The diffusion of Fe & Co to $\alpha_1$ phase during the tempering, which increases the difference of saturation magnetization between $\alpha_1$ and $\alpha_2$ phases, is also observed by EDS. In a word, $\alpha_1$, $\alpha_2$ and Cu-bridges are concentrated with its major elements during the tempering respectively, which leads to the improvement of magnetic properties of sample after tempering. The manners how these features formed through the elemental diffusion were discussed with the energy theories.
On the Formation and Evolution of Cu-Ni-rich Bridges of Alnico Alloys with Thermomagnetic Treatment and Tempering

by
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DEDICATION

To my dear wife, Haiyan Xiang

To my dear parents, Chunsheng Fan and Guilan Du

To my dear brother, Zhen Fan
BIOGRAPHY

Min Fan was born in Hongtong, Shanxi, China to parents Chunsheng and Guilan on June 25th, 1986. He attended Beijing University of Technology (China) from 2004 as undergraduate, majoring Materials Science and Engineering. He completed the undergraduate thesis under the supervision of Prof. Dongtao Zhang on magnetic refrigeration and earned the Bachelor degree in 2008. After that, he joined Prof. Tounan Jin group in 2008 to start his master study on Multiferroics. In 2009, Min was selected to continue his research in Peking University, supervised by Prof. Guobao Li and Prof. Jianhua Lin (President). He completed the master thesis under the supervision of Prof. Tounan Jin, Prof. Guobao Li and Prof. Jianhua Lin in 2011. In 2013, Min came to US to pursue his Ph.D degree at North Carolina State University. There, he was co-advised by Prof. Carl C. Koch (Member, National Academy of Engineering) and Prof. Justin Schwartz (Head, Department of Materials Science and Engineering) and worked on the microstructure and permanent magnetic property of Alnico alloys.
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Chapter 1 Introduction

The research of Alnico alloys is drawing more and more attentions in this decade, after about 30 years suspension due to the discovery of the rare-earth magnets. Figure 1.1 is the history of the development of permanent magnetic materials. The revival of Alnico is due to the rapid development of the markets of permanent magnetic materials based electric machines in the hybrid vehicles and wind turbines, and the increment in the price of the rare-earth elements as well. Alnico alloys do not contain the rare-earth elements, and the kind of the elements is more than six, which result in the lack of understanding of the magnetic mechanism until now. Current understanding about magnetic mechanism is the magnetic property of Alnico is due to magnetic shape anisotropy induced by spinodal decomposition during the thermomagnetic treatment, which is different from the magnetocrystalline anisotropy. The shape anisotropy is from the needle like ferromagnetic $\alpha_1$ phase (Fe and Co rich) in the non-ferromagnetic or less ferromagnetic $\alpha_2$ matrix (Ni, Al and Ti rich). The spinodal decomposition takes place at the temperature right below the Curie temperature, within the controlled magnetic field, which is different from the traditional nucleation and growth. The key to research Alnico is to vary the concentration of each element as well as the temperature and time of thermomagnetic treatment to achieve the optimized microstructure with good magnetic properties, attributed to the optimized spinodal decomposition. Because the microstructure of Alnico is in nano-scale so advanced microscopic technology is required. Figure 1.2 is the comparison of TEM image[1] taken in 1974 and STEM image [2] taken in 2014 of Alnico 8. It is apparent that a new feature, Cu-bridge, was observed by advanced TEM recently, which supplies important information to researchers to figure out the mechanism of Alnico and improve its magnetic properties. Inspired by this, we use an aberration-corrected STEM FEI Titan 80-300 with extra high resolution (TEM
Mode: point-to-point: 0.20 nm, information limit: 0.10 nm; STEM Mode: 0.07 nm (sub-Angstrom)) to research the microstructure, magnetic properties and mechanism of Alnico related to the formation and evolution of Cu-bridges during the thermomagnetic treatment and tempering.

Figure 1.1 History of the commercially produced permanent magnets with increasing maximum energy product [3]

This work begins with an overview of the literatures relevant to Alnico alloys. Most of important topics about Alnico researches were reviewed, including the spinodal decomposition in general conditions and specifically in Alnico, and comparison of two theory about spinodal decomposition in Alnico; magnetization reversal mechanism about the shape anisotropy of the two phases; alloying design according to the thermodynamic and magnetic theory; recent excellent research results about typical Alnico 5, 8 and 9 magnets.
Next, a detailed description of the procedures and relevant theories of the experimental methods used in synthesis and material characterization were given. The following chapters describing the results also contain the specific descriptions of the experimental methods, designed for each research.

![Figure 1.2 TEM image[1] taken in 1974 and STEM image[2] taken in 2014 of Alnico 8](image)

Chapter 4 focuses on the formation and evolution of Cu-Ni-rich bridges during the thermomagnetic treatment. Two Alnico alloys, one contains Ti while the other does not, have been compared to assess the role of Ti on the formation of Cu-rich bridges and the effect of Cu-rich bridges on the microstructure and magnetic properties of Alnico. Two types of Cu bridges were observed in the sample with Ti showing typical chessboard microstructure and maze-like morphology with connected $\alpha_1$ phases was observed in the sample without Ti. The formation of chess board morphology was discussed based on the Cahn’s theory and Neel-Ziljtra theory and
new features of Cu-bridges observed. Besides, pin effect of Cu-bridges to restrict the coalescence of $\alpha_1$ phases was discussed.

Chapter 5 focuses on the evolution of Cu-Ni-rich bridges during the tempering. Tempering cannot change the morphology but the elemental distribution of the Cu-rich bridges. Cu concentration in the Cu-Ni bridges increases after the tempering while other elements concentrations decrease, especially for Ni and Al. The boundary of Cu bridges becomes sharper with tempering. The possible reason for these features is the largest ratio of $2C_{44}/(C_{11}-C_{12})$ of Cu. Besides, Ni-Cu loop around $\alpha_1$ phase becomes inconspicuous with the tempering. The diffusion of Fe & Co to $\alpha_1$ phase during the tempering, which increases the difference of saturation magnetization between $\alpha_1$ and $\alpha_2$ phases, is also observed by EDS. Although the composition changes are not large, they are distinguishable and can be the evidence for the effects of tempering on the improvement of the magnetic properties.

Chapter 6 is based on three co-authored published papers. First work describes a combined computational-experimental approach to design Alnico alloys. Sobol’s algorithm was used to randomly generate alloy composition and 5 optimized alloys in 80 alloys were got after extensive experiments. This work proves the effect of response surface methodology on optimizing the magnetic properties while minimizing the time and cost in synthesizing the alloys by random experimentation. The second is the further work to prove the efficacy of the combined meta-modeling and experimental approach in design optimization of the alloys. The last work is the research on the magnetic properties of NiFeCrCoMnZn high entropy alloy. The relationship of microstructure and magnetic properties were discussed based on the x-ray diffraction and electron microscopy results.
Finally, Chapter 7 summarizes this work and makes some suggestions about the future work, including the microstructure of Cu-bridge, the effect of Cu content on the morphology and distribution of Cu-bridges, the distribution of Hf, in-situ TEM research on spinodal decomposition, the interconnectivity or fully isolation of $\alpha_1$, and the relationship between cross-section of $\alpha_1$ and magnetic property.

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Chapter 2 Literature Review

2.1 Alnico magnets

With the demand for clean energy and transportation increasing, there is a strong interest to develop high-flux density permanent magnetic materials. Because permanent magnetic materials based electric machines have some irreplaceable advantages compared with traditional motors with gear, such as lighter weight, quieter, requiring less maintenance, etc. However, current excellent permanent magnets mainly based on rare earth elements, such as neodymium (Nd) or samarium (Sm), which are relatively rare and quite expensive, although they show exceptionally strong magnetic properties in Figure 2.1[1]. Researchers expect to find alternative magnet alloys, based on more abundant and less strategically important elements, for the future application in permanent magnet based electric machines [2]. In this situation, high-energy product Alnico magnets are drawn extensive attention [1, 3-14].

Alnico magnets contain mainly iron (Fe), aluminum (Al), nickel (Ni), and cobalt (Co) based on the Al-Ni-Fe system, with minor addition of copper (Cu) and titanium (Ti). Some grades of Alnico may contain tiny niobium (Nb), hafnium (Hf), silicon (Si) or sulfur (S) to increase the remanence, working temperature or oxidation resistance. Now there are 29 grades of Alnicos (17 cast grades, 10 sintered grades, 2 bonded grades) and widely used in the industry for their high Curie temperature (850 ~ 950 °C), wide range of working temperatures, excellent corrosion resistance, good magnetic stability and acceptable magnetic properties[15, 16]. Alnico has many trade names such as Columax, Alcomax 3SC, Alni, Hycomax, Ticonal, etc. China named Alnico with the letters LNG followed by a number for clarification, but not widely used. Mostly Alnico is known under its more common grade names, such as Alnico 5, Alnico 8, Alnico 9, Alnico5-7,
Alnico8HC, Alnico 6, Alnico 2, Alnico3, etc[16]. Alnico alloys come in both isotropic and anisotropic grades. Alnico 2, 3 and 4 are isotropic grades and have coercivities of 480-550 Oe, remanence of 7000-7100 G, and maximum energy products of 1.35-1.5 MGOe. The most commonly used Alnico alloys are anisotropic Alnico 5, 8 and 9, which have coercivities of 630-2170 Oe, remanence of 6700-13500 G, and maximum energy products of 2.9-10.0 MGOe [17]. The compositions and magnetic properties of isotropic and anisotropic thermomagnetically treated Alnicos are listed in Table 2.1[18].

Figure 2.1 Maximum energy product of various commercial permanent magnets versus costs [1]

Alnico alloys have been discovered around 80 years ago. The first grade of Alnico magnets, composed of 55~63% Fe, 25~30% Ni, 12~15% Al, was first discovered by Mishima in 1932 and known as the Mishima alloys or Fe$_2$NiAl, which actually does not contain Co[18]. In 1939, Snoek first speculated that the optimized magnetic properties were reached when the alloy is
heterogeneous and there were two ferromagnetic phases, $\alpha_1$ and $\alpha_2$ phase. At the same year, Betteridge first found the addition of Cu can increase the energy product. However, the addition of Cu will increase the rate of precipitation so the alloys must be cooled or quenched more rapidly. Co was firstly discovered to increase the coercivity through increase the difference of saturation magnetization of $\alpha_1$ and $\alpha_2$ phase, as well as the Curie temperature, by Betteridge in 1939 and Zumbusch in 1942. The addition of 4~5% Ti can significantly improve the coercivity, discovered by Betteridge in 1939[18].

Thermomagnetic treatment is the most critical step in the synthesis of Alnico magnets, discovered by Olive and Shedden in 1938[18]. Extensive researches focuses on the improvements of thermomagnetically treated Alnico 5. Some important conclusions are got: the effect of tempering on magnetic properties cannot be improved with the application of magnetic field; good magnetic properties only can be obtained within a narrow range of Al concentration, 8-9%; high concentration of Al (above 6%) will result in the absence of the detrimental $\gamma$ phase (details in following paragraph)[18]; Cu will increase the homogenization temperature and lower the Curie temperature, and prevent the formation of $\gamma$ phase by decreasing the rate of cooling through the $\gamma$ FCC phase[19]. A typical heat treatment of Alnico 5 is: first, solutionizing treatment at 1250 °C to obtain $\alpha$ phase; second, fast cooling down to about 900 °C to prevent the detrimental $\gamma$ phase; third, cooling down to 600 °C in a magnetic field, which $\alpha$ will decompose to $\alpha_1$ and $\alpha_2$ phases via spinodal decomposition; last, tempering at 650 °C for 6h followed by 550 °C for 24h. Next great advance in Alnico history is researchers found if the contents of Co and Ti increase to 32-36 % and 4-5 %, respectively, much higher coercivity will be obtained in the new Alnico alloy. This new Alnico is the Alnico 8 alloy. In 1959, Koch et al. [18] discovered that isothermal magnetic treatment is required to get the sufficient decomposition for the Alnico 8
since it contains Ti with large radius and low rate of diffusion. Besides, Wright and Bronner revealed that a small addition of Nb is beneficial to the magnetic properties. Alnico 9 is Alnico 8 with well aligned columnar grains. Ti increases the difficulty to form the columnar grains by decreasing the grains size. S, Se or Te was used to promote the formation of columnar grains as the compensation of Ti. Of course, the best magnetic properties are obtained for single crystal Alnico but it is not practical.

![Figure 2.2 A schematic diagram of mold for columnar grains [20]](image)

The two main processing methods for Alnico magnets are sintering and casting. Both types can be isotropic or anisotropic. Sintering is carried out using powders, e.g. ball milling, due to the low melting temperature of aluminum. The powers are mixed, pressed, and sintered. Sintered
Alnicos generally show lower remanence than cast Alnicos, but sintering is more economical for small parts compared with casting, since they are easy to be shaped and require less finishing. Cast alloys can have equiaxed, semi-columnar, or columnar grains. The equiaxed magnets, e.g. Alnico 8, are usually sand cast without water-cooling plate or heated molds. Columnar cast magnets, e.g. Alnico 9, have oriented grains along the [001] direction parallel to the growth direction, which is also the growth direction of α₁ phase. The increase in orientation leads to an increase in coercivity. The columnar castings mold is typically composed of a heated sand sidewall and a water-cooling plate at the bottom. The huge temperature gradient drives the grains elongating to columnar grains in Figure 2.2. The semi-columnar castings use a water-cooling plate as well but do not use heated molds. Alnico alloys also can be milled to powder and then bonded to required magnet shape. However, the magnetic properties of bonded magnets are not as good as those cast or sintered[18].

Alnico magnets cannot be conventionally drilled or machined due to their high hardness and brittleness, so Alnico parts are not normally used as structural members. The principle of application is to select the simplest shape according to the requirements. In most conditions, slots are preferred over holes, and parts with cross sections of less than 0.125" (3.18 mm) should be avoided[16]. If necessary, the finished surface may be produced by grinding, although it would highly increase the cost. Paint can be applied for improved appearance. Aluminum jacket can be used to facilitate the mounting of the magnet in the motor assemblies.
Table 2.1 Compositions and magnetic properties of isotropic and anisotropic thermomagnetically treated Alnicos[18]

<table>
<thead>
<tr>
<th>Alnico grades</th>
<th>Character istics</th>
<th>Composition (Fe balanced)</th>
<th>Br</th>
<th>Hc</th>
<th>(BH)(_{max})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Co</td>
<td>Ni</td>
<td>Al</td>
<td>Cu</td>
</tr>
<tr>
<td>1, 4</td>
<td>Low Co</td>
<td>3-5</td>
<td>21-28</td>
<td>11-13</td>
<td>2-4</td>
</tr>
<tr>
<td>2</td>
<td>Medium Co</td>
<td>12-14</td>
<td>16-20</td>
<td>9-11</td>
<td>3-6</td>
</tr>
<tr>
<td>3</td>
<td>Extra high Hc</td>
<td>17-20</td>
<td>18-21</td>
<td>8-10</td>
<td>2-4</td>
</tr>
<tr>
<td>5</td>
<td>Co free</td>
<td>0</td>
<td>24-30</td>
<td>12-14</td>
<td>0-3</td>
</tr>
<tr>
<td>6</td>
<td>Random grain</td>
<td>23-25</td>
<td>12-15</td>
<td>7.8-8.5</td>
<td>2-4</td>
</tr>
<tr>
<td>5DG, 7, (5-7)</td>
<td>Random grain, higher Hc of 5</td>
<td>23-25</td>
<td>13-16</td>
<td>7.8-8.5</td>
<td>2-4</td>
</tr>
<tr>
<td>8</td>
<td>Directed grain of 5</td>
<td>24-25</td>
<td>13-15</td>
<td>7.8-8.5</td>
<td>2-4</td>
</tr>
<tr>
<td>8HC</td>
<td>Random grain, high Hc</td>
<td>32-36</td>
<td>14-16</td>
<td>7-8</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>Random grain, extra-high Hc</td>
<td>37-40</td>
<td>14-15</td>
<td>7-8</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Directed grain of 8</td>
<td>32-36</td>
<td>14-16</td>
<td>7-8</td>
<td>4</td>
</tr>
</tbody>
</table>
2.2 Spinodal decomposition

Although Alnico magnets have been widely used for around 80 years, the mechanism is still unclear, which results in slow improvements for Alnico magnets. The following descriptions about the mechanism are attributed to the current understanding about the Alnico alloys. Magnetic properties of Alnico are from the spinodal decomposition of the alloy with a Fe-Co rich strongly ferromagnetic phase (α₁) in a Ni-Al rich non-ferromagnetic matrix phase (α₂). The α₁ phase has B2 or BCC crystal structure while the α₂ phase has BCC crystal structure [15]. The high coercivity is from the separation of the ferromagnetic particles, which makes domain walls difficult to pass from one α₁ particle to another. Figure 2.3 is a scheme of microstructure of Alnico resulting from the spinodal decomposition in a magnetic field.

![Microstructure of Alnico](image)

Figure 2.3 A scheme of microstructure of Alnico resulting from the spinodal decomposition in a magnetic field[21]

2.2.1 Conception of spinodal decomposition

Spinodal decomposition is a mechanism that a solution of multiple components separates into distinct phases with different chemical compositions and physical properties, which is different
from the classical nucleation. The phase separation occurs uniformly throughout the material during spinodal decomposition, not just at the discrete nucleation sites. The decomposition is determined solely by diffusion, because no thermodynamic barriers need to be overcome inside the spinodal region. Therefore, general diffusion equation can be used to analyze the features of the decomposition.

Figure 2.4 (a) Temperature versus compositions and (b) Gibbs energy of mixing versus the compositions at \( T_2 \)[22]

There are some important terms involved with spinodal decompositions. *Binodal Curve* (or *Coexistence Curve*)[22] is a bell-like curve defining the region in a phase diagram for a binary
mixture, which a transition occurs from miscible components to metastable or unstable single-phase mixtures. The points of Binodal curve are extracted from the compositions that have common tangents in the Gibbs energy of mixing vs composition, which have equal chemical potentials of two components in two phases. *Miscibility gap* is the region within the coexistence curve of a phase diagram. *Spinodal Curve* is the curve represents the transition from a metastable region from an unstable region in the coexistence region of a binary mixture, determined by where the curvature of the free-energy curve is negative. The nucleation happens above the spinodal curve while spinodal decomposition happens below the spinodal curve.

In Figure 2.4(a), the composition of one alloy is $X_0$, inside the spinodal curve. When it is solutionizing treated at a high temperature $T_1$, and then quenched to a low temperature $T_2$, the composition will be uniform and its free energy will be $G_0$ on the G curve in the phase diagram. Figure 2.4(b) is the free energy curve as a function of composition for the low temperature $T_2$, in which the equilibrium phase compositions are those points with the minimum of free energy. Spinodes, marked as $S_1$ and $S_2$ in Figure 2.4(a), are corresponding to the inflection points of the curve b, which have $d^2G/dc^2 = 0$. The regions between two spinodes are under the relationship of $d^2G/dc^2 < 0$. In this situation, the alloy will become unstable instantly, because any tiny fluctuation in composition ($d^2G/dc^2 < 0$) will result in A-rich and B-rich regions, which will cause the decreasing of the total free energy. Therefore, “up-hill” diffusion takes place until the equilibrium compositions $X_1$ and $X_2$ are reached. For the alloy with the composition of $X_0'$, outside the spinodal curve, if it is solutionizing treated at the same high temperature $T_1$, and then quenched to same low temperature $T_2$, the alloy will be metastable because the small variations in composition ($d^2G/dc^2 > 0$) lead to an increase in free energy. In this case, nuclei must be
formed with a composition different from the matrix to decrease the free energy. Therefore the transformation outside the spinodal curve must proceed by a process of nucleation and growth.

The main difference between spinodal decomposition and nucleation and growth are: first, during spinodal decomposition, fluctuations of chemical composition are developed with small amplitude at the beginning and grow with time until discernible precipitates of equilibrium composition are formed; during nucleation and growth, the equilibrium precipitates have required equilibrium composition at all stages and have a sharp interface between them and their parents in Figure 2.5; second, spinodal decomposition involves uphill diffusion while nucleation and growth develop following the concentration gradient from high concentration to lower one.

Figure 2.5 Evolution of phase separation in spinodal decomposition and during nucleation and growth[23]
2.2.2 Spinodal Decomposition in Alnico

Specifically for Alnico alloy, the spinodal decomposition is developed as the following description (Figure 2.6). The samples are first heated to 1300 °C (solutionizing treatment) to get one homogeneous phases followed by quenching into water. Then the samples are mounted along magnetic direction during the thermomagnetic treatment at 800 °C, which spinodal decomposition takes place. To optimize the magnetic property, multiple tempering will be chosen to further increase the difference of two phases. The procedures of heating treatments including the temperature and time at each step are described in the Figure 2.7.

Figure 2.6 A schematic phase diagram of Alnico [21]
There are two types of solutionizing treatment for Alnico alloys, one is high temperature treatment at 1250 °C, and the other is low temperature treatment at 900 °C. The typical time for treatment are 20~60 minutes. During solutionizing treatment, the existence of magnetic field is not so important if the following thermo-magnetic treatment is working at an optimum temperature\[3\]. Researchers mainly use high temperature treatment method in the laboratories. The alloys are solution treated in vacuum or argon at 1250°C for 20~60 min and quench into water. The aim of quenching is to keep the homogenous phase and avoid spinodal decomposition without controlling the direction by magnetic field. The only attention required is to avoid the formation of $\gamma$ phase. The $\gamma$ phase is a disordered solid solution based on $\gamma$Fe (FCC) and transforms to $\alpha_{\gamma}$ (BCC) phase at lower temperature. These two phases are detrimental to the magnetic properties of the Alnico. The $\gamma$ phase is usually formed in the range of 850~1100 °C in Figure 2.8. Below 850 °C, the phase will transform into $\alpha_{\gamma}$. As mentioned, the structure with $\alpha_1$ and $\alpha_2$ is desired for high performance Alnico. Therefore, in most situations, if cooling happens at the temperature range forming $\alpha+\gamma_1$ phases, the undesired structure of $\alpha_1+\alpha_2+\gamma_1$ will be formed at room temperature and magnetic property will be highly deteriorated. The solutionizing only
can be done at 900°C if there is no γ phase present[24]. The low-temperature treatment is still an important heat treatment method for the Alnico manufacturing industry, because oxidation loss and the brittleness can be avoided with this method.

Thermomagnetic treatment is the most critical step to obtain the permanent magnetic property for Alnico alloys. The temperature and time varies depending on the compositions. There are two typical thermomagnetic treatments, one is continuous cooling magnetic treatment for Alnico 5-type alloys and the other is isothermal magnetic treatment for Alnico 8-type alloys. For continuous cooling, the part is brought to 900°C from the solutionizing temperature, and cooled

Figure 2.8 A scheme of equilibrium phase diagram for Alnico magnets [3]
in a magnetic field to around 600°C. The cooling rates in the literature range from 0.1°C/s to 1.8°C/s [17, 24]. The best properties are achieved through an isothermal thermo-magnetic treatment in Alnico 8-type alloys. For this treatment method, the quenched samples are heated to the temperature (~800°C) and held in a magnetic field (>3000 Oe) for approximately 10 minutes [17, 25].

Tempering is the last step of the heat treatment of Alnico. Both magnetic and mechanical properties will be enhanced after tempering. The time and temperature during the tempering are not specified although the range of temperature is always 650-500 °C. It has been proved that multi-step tempering is better than one temperature tempering [26] and the application of magnetic field during the tempering [3] cannot make virtual improvement on the magnetic properties.

2.2.3 Comparison of Neel-Zijlstra theory and Cahn theory

Neel-Zijlstra theory and Cahn theory are two most important theories for explaining the mechanism of spinodal decomposition of Alnico. According to Neel-Zijlstra theory[27], the procedures of spinodal decomposition is that initially very small spherical particles (α₁) are formed at the high temperatures and then the elongation of the particles will take place until the formation is complete; if the decomposition takes place in a magnetic field, the spherical particles will elongate into ellipsoids with their long axes parallel to the applied field. There are two energies related with this process: interfacial energy (Fs) and magnetostatic energy (Fm), that Fs is defined as the product of the interface tension and the amount of interface per unit volume. The elongation is thermodynamically favorable since there is an increase in Fs and a larger reduction in Fm of the particles. That is to say, the elongation is favorable when Fm/Fs is
large. According to Neel-Zijlstra theory, the axes of elongated particles are parallel to the applied magnetic field, irrespective of crystallographic directions of the alloy. Cahn theory [28] demonstrated that the elastic energy plays an important role as well as the magnetic energy and which one dominates the direction of $\alpha_1$ depends on the magnitude of the energies. The magnetic field suppresses the spinodal decomposition wave along the magnetic field direction, which is due to the difference of magnetic energy $F_m$ of spinodal wave parallel and perpendicular to the field. The elastic energy is related to elastic modulus, which is anisotropic in most cases of crystalline materials. The magnetic energy is parallel to the field direction while the elastic energy is parallel to the crystallography. Besides, he figured out that waves parallel to the $<100>$ directions in the $\{100\}$ in cubic crystals are favorable when $2C_{44}-C_{11}+C_{12}>0$ [28] and magnetic energy is larger than elastic energy only when temperature is near the Curie temperature. Both of them have their own limitations: the observation of initial spherical particles at the beginning stage of spinodal decomposition is the evidence of Neel-Zijlstra theory; electron micrographs show that the spindal decomposition waves are same in three $<100>$ direction, which is different from the description from Cahn theory about the suppression from spinodal decomposition. However, Neel-Zijlstra theory is only supported by the longer thermomagnetic treatment experiments, which is much longer than actual heat treatment of Alnico alloys, whereas Cahn theory is supported by a part of shorter thermomagnetic treatment experiments.
2.3 Magnetic mechanism of Alnico

2.3.1 Conversion of CGS and SI unit[29]

Unit system should be a basic knowledge for any discipline, but it is exceptionally complex in magnetics for historical reason. The conversions of important terms and relations in magnetics are listed in the Table 2.2.

<table>
<thead>
<tr>
<th>Variables</th>
<th>cgs units</th>
<th>Conversion</th>
<th>SI units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic energy</td>
<td>E</td>
<td>1 erg = 10^{-7} J</td>
<td>J(joule)</td>
</tr>
<tr>
<td>Magnetic field strength, magnetizing force</td>
<td>H</td>
<td>1 Oe= 10^{3}/4\pi \text{ Am}^{-1}=79.58 \text{ Am}^{-1}</td>
<td>\text{ Am}^{-1}</td>
</tr>
<tr>
<td>Magnetic flux</td>
<td>\Phi</td>
<td>1 Mx = 10^{-8} Wb</td>
<td>Wb(weber)</td>
</tr>
<tr>
<td>Magnetic induction, Magnetic flux density</td>
<td>B</td>
<td>1G=10^{-4} T</td>
<td>T(tesla)</td>
</tr>
<tr>
<td>Magnetic moment</td>
<td>m</td>
<td>1 \text{ emu} \cdot 10^{-10} \text{ Am}^{-1}</td>
<td>\text{ Am}^{-1}, joule per tesla (J/T)</td>
</tr>
<tr>
<td>(Volume) magnetization</td>
<td>M</td>
<td>1 \text{ emu} \cdot \text{ cm}^{-3}=10^{3} \text{ A/m}</td>
<td>\text{ Am}^{-1}</td>
</tr>
<tr>
<td>(Volume) magnetization</td>
<td>4\pi M</td>
<td>1G=10^{3}/4\pi \text{ A/m}</td>
<td>\text{ Am}^{-1}</td>
</tr>
<tr>
<td>(Mass) magnetization</td>
<td>\sigma, M</td>
<td>1 \text{ emu/g}= 1 \text{ Am}^{2}/\text{kg}</td>
<td>\text{ Am}^{2}/\text{kg}</td>
</tr>
<tr>
<td>Demagnetization factor</td>
<td>D, N</td>
<td>cgs =1/4\pi SI</td>
<td>dimensionless</td>
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Table 2.2 Conversions of important terms and relations in magnetics[29](continued)

<table>
<thead>
<tr>
<th>Relations</th>
<th>cgs units</th>
<th>SI units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic energy</td>
<td>E= -m·H</td>
<td>erg</td>
</tr>
<tr>
<td>Magnetic induction, Magnetic flux density</td>
<td>B =H +4(\pi)M</td>
<td>G</td>
</tr>
<tr>
<td>Magnetic susceptibility</td>
<td>(\chi=\frac{M}{H})</td>
<td>emu·cm(^3) Oe(^{-1})</td>
</tr>
<tr>
<td>Magnetic permeability</td>
<td>(\mu=\frac{B}{H}=1+4\chi)</td>
<td>G Oe(^{-1})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SI symbol</th>
<th>SI unit</th>
<th>Fundamental constituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>newton</td>
<td>kg m s(^{-2})</td>
</tr>
<tr>
<td>J</td>
<td>Joule</td>
<td>kg m(^2) s(^{-2})</td>
</tr>
<tr>
<td>T</td>
<td>tesla</td>
<td>kg m(^2) A(^{-1})</td>
</tr>
<tr>
<td>Wb</td>
<td>weber</td>
<td>kg m(^2) s(^{-2}) A(^{-1})</td>
</tr>
<tr>
<td>H</td>
<td>henry</td>
<td>kg m(^2) s(^{-2}) A(^{-2})</td>
</tr>
</tbody>
</table>

Notes: 1. \(\mu_r=\frac{\mu}{\mu_0}=1+\chi\), all in SI; 2. \(\mu_0=4\pi \times 10^{-7}\) H/m
2.3.2 Shape anisotropy

The typical structure of Alnico alloys is the well-aligned array of the single domain particles ($\alpha_1$) embedded in non-ferromagnetic matrix ($\alpha_2$), which leads to the shape anisotropy.

2.3.2.1 Demagnetizing factor of a single particle

The prerequisite to understand how shape anisotropy controls magnetic property is the concept of the internal demagnetizing field of a magnet. If a body is initially magnetized by an applied field to A, the magnetization cannot maintain but will decrease to C under the action of the demagnetizing field $H_d$, once the applied field is removed. O-C is the demagnetizing-field line, with a slope of $-1/\text{Nd}$, where Nd is the demagnetizing coefficient or demagnetizing factor in Figure 2.9[29]. This energy is that associated with the demagnetizing field of the specimen, and is variously called the magnetostatic energy, which equal to the area of the shaded triangle OCD.

$$E_{ms} = -\frac{1}{2} H_d M$$

The demagnetizing field ($H_d$) is proportional to the magnetization and sensitive to the shape, given by:

$$H_d = -N_d M$$

where Nd is the demagnetizing factor. The value of Nd depends on the shape of the body.

The $\alpha_1$ phase can be considered as prolate ellipsoid, the shape-anisotropy constants $K_s$ for prolate ellipsoid or rod (Figure 2.10) is given by

$$K_s = 0.5(N_a - N_c)M^2 \text{ erg/cm}^3 \ (CGS).$$
where $N_c$ and $N_a$ are demagnetizing coefficients along $c$ (half-length in the long axis) and $a$ (the radius in the short axis).

![Diagram of magnetostatic energy of a magnetized body in zero applied field](image1)

**Figure 2.9** Magnetostatic energy of a magnetized body in zero applied field[29].

![Diagram of prolate ellipsoid](image2)

**Figure 2.10** Prolate ellipsoid[29]

Put $c/a=m$. Then

$$N_c = \frac{4\pi}{(m^2 - 1)} \left[ \frac{m}{\sqrt{m^2 - 1}} \ln \left( m + \sqrt{m^2 - 1} \right) - 1 \right] (CGS)$$

$$N_a = \frac{4\pi}{2} - N_c (CGS)$$

When $m=c/a$ is large (representing a long, thin rod), then

$$N_c = \frac{4\pi (\ln(2m) - 1)}{m^2} (CGS), [29]$$

$$N_a = 2\pi (CGS), [29]$$
Therefore $N_c$ approaches zero as $m$ become large. The strength of shape anisotropy then depends on both the axial ratio $c/a$ and the magnetization $M$; the larger the $c/a$ ratio and $M$, the larger the shape anisotropy.

### 2.3.2.2 Magnetization reversal mechanism of an array of particles

The hysteretic behavior is determined by the magnetization reversal mechanism, which has the lowest $H_c$. Two basic mechanisms related to magnetization reversal of an array of particles are uniform rotation and magnetization curling. The uniform rotation mode changes to the curling mode for a system when $R$ is larger than one critical size in Figure 2.9. Average diameters of $\alpha_1$ in Alnico have seen in the literature range from 5-50 nm [30-32], which is under the relationship of curling mode. When the magnetization reversal is entirely controlled by curling, the coercivity is independent of the packing fraction ($p$), because there are no particle interaction effects. However, magnetostatic interaction domain can be observed during demagnetization, which indicates that some inter-particle interaction does occur [1]. The process is that $\alpha_1$ phases already reversed will tend to assist the reversal of adjacent $\alpha_1$ phase and result in lower coercivity compared to those entirely controlled by curling mode. Therefore, for alnico, curling and magnetostatic interaction domains are the mechanism of magnetization reversal, so all of the size, shape, isolation and packing fraction of the $\alpha_1$ phases are critical to the magnetic properties of Alnico[18], which are determined by the isothermal annealing time.
The $\alpha_1$ phases are required to be elongated single domains and must be separate sufficient to avoid coalescence, so the volume fraction $p$ (i.e. packing fraction) is one critical restriction. The development to understand the coercivity in Alnico mainly underwent three stages. First, Stoner-Wohlfarth theory[18], discovered in 1948, show that $H_c$ of an aligned assembly of identical non-interacting (i.e. infinitely dilute) single domain particles with uniaxial shape anisotropy is

$$H_c = (N_c - N_a) M_s$$

where $(N_c - N_a) = 0.5$, when length/diameter = 16

However, researchers found $H_c$ calculated from this theory, is considerably larger than the observed value of 60 kAm$^{-1}$, the particle interaction can’t be neglected. Then the equation was
adjusted with the speculation by Neel 1947, Zijlstra 1962. The effects of particle interactions on the coercivity can be described with

\[ H_c(p) = H_c(0)(1 - p), \]

where \( H_c(p) \) is the Hc for a particle packing fraction \( p \) and \( H_c(0) \) is the Hc for a particle packing fraction of zero. If take the effects of particle interactions into account, the coercivity of a fully aligned array of single domain particles with uniaxial shape anisotropy is

\[ H_c = (1 - p)(N_c - N_a)M_s \]

where \( p \) is usually in the range 0.6 ~ 0.7 and \((N_c - N_a) =0.5 \) when length/diameter = 16. In this situation, the theoretical value of Hc=300kAm\(^{-1}\), so there is still a very significant difference between the theoretical and observed Hc (60kAm\(^{-1}\)). One more factor, ferromagnetic matrix, was in consideration of Baran in 1959. A general expression derived by Baran for the coercivity of well-aligned ferromagnetic rods[18], accounting for the reduction in Hc due to particle interactions and the possibility that the matrix is also ferromagnetic,

\[ H_c = p(1 - p)(N_c - N_a)(M_1 - M_2)^2/M_s' \]

where \( p \) is the volume fraction of the ferromagnetic phase \( \alpha_1 \), \( M_1 \), \( M_2 \) and \( M_s' \) are the saturation magnetizations of \( \alpha_1 \), \( \alpha_2 \) and the alloy, and \( N_c \) and \( N_a \) are demagnetizing coefficients along the long and short axes, respectively. This equation shows that three factors are important to improve the coercivity: the difference of \( M_1 \) and \( M_2 \) would be as large as possible, the volume fraction \( p \) would be as near half as possible, and the \( \alpha_1 \) phase would be isolated and as long and narrow as possible, so that the difference of \( N_c \) and \( N_a \) is large. Alloy design of Alnico develops according to these principles.
2.4 Alloy design

Phase diagram cannot be referred during the alloy design of Alnico since it contains at least six elements. All the researches are empirical, and coercivity and energy product oriented.

2.4.1 Co

Alnico magnets containing above 24% Co are the only group of Alnico that can be heat-treated in external magnetic field. Co increases Curie temperature to ~850 °C, when spinodal decomposition happens at 700~850 °C. Therefore, the addition of Co will increase the sensitivity of Alnico to the magnetic field. More than half of Co atoms are in α₁ to increase M₁-M₂, raise the Curie temperature of α₁ phase, control the orientation of α₁ particles by applying a magnetic field during the thermomagnetic treatment, to obtain the elongated and aligned particles of α₁ phases [33]. Additional cobalt can be added to increase coercivity but lower the remanence. High cobalt content favors the precipitation of the deleterious γ phases.

2.4.2 Ti

1 ~ 9% Ti additions are the range of concentration for high coercivity Alnico alloys. Most of Ti distributes into the α₂ phase, increasing M₁-M₂ [31]. Ti increases coercivity by raising the Curie temperature and promoting the elongation of the α₁ phases as Co. It increases the elastic and surface energy. Besides, Ti is most active metallic elements in the alloys and tends to react with the impurity elements such as N, S, or O during solidification. This process will purify the main phases and reduces the adverse effects of the impurity elements on magnetic properties. Ti can increase the time required to form the deleterious γ phases. It lowers the remanence by decreasing the grain size and the possibility of columnar grains.
2.4.3 Al

High concentration of Al (above 6%) will result in the absence of the γ phase [18].

2.4.4 Cu

Cu mainly distributes into the α₂ phase, increasing M₁-M₂, and promotes the thermomagnetic treatment process by enhancing the diffusion rate of α₂ [31]. Cu bridges may play a critical role in the magnetic property of Alnico 8-type alloys.

2.4.5 Nb

Nb is often used to promote the growth of columnar grains during directional solidification by restricting the formation of equiaxed grains [20]. 1% is the optimized concentration for Nb to reach the peak of the coercivity. Besides, Nb probably can diminish the γ phase and getter the carbon and nitrogen.

2.5 Typical Alnico 5, 8 & 9

Table 2.3 Nominal composition of Alnico 5-7, 8 & 9 in wt. % [10]

<table>
<thead>
<tr>
<th>Alnico</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Al</th>
<th>Cu</th>
<th>Ti</th>
<th>Nb</th>
<th>S</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-7</td>
<td>49.9</td>
<td>24.3</td>
<td>14.0</td>
<td>8.2</td>
<td>2.3</td>
<td>0</td>
<td>0.99</td>
<td>&lt;0.01</td>
<td>0.16</td>
</tr>
<tr>
<td>8</td>
<td>30.0</td>
<td>40.1</td>
<td>13.0</td>
<td>7.1</td>
<td>3.0</td>
<td>6.5</td>
<td>0</td>
<td>&lt;0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>9</td>
<td>35.5</td>
<td>35.4</td>
<td>13.1</td>
<td>7.0</td>
<td>3.2</td>
<td>5.0</td>
<td>0.51</td>
<td>0.18</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Alnico 5, 8 and 9 are most famous magnets in Alnico family because of their excellent magnetic performance. Alnico 5-7 alloys is the name for one specific type of Alnico 5, which have grains oriented along the magnetic field and are commonly used in Alnico 5 series. The commercial compositions and the magnetic properties of Alnico 5-7, 8 & 9 are listed in Table 2.3 in Figure 2.12, respectively. Magnetic hysteresis loops demonstrates that Alnico 5-7 has highest magnetic
remanence (Br), Alnico 8 has highest coercivity (Hc) and Alnico 9 has highest maximum energy product ((BH)\text{max}) at the expense of Br and Hc. The higher Br for the alnico 5-7 and 9 are consistent with their high grain alignment parallel to the applied field direction while Alnico 8 contains randomly oriented grains\cite{18}. Nb in Alnico 5-7 and 9 is added to promote the formation of columnar grains which facilitate the grain alignment and increase the Br. Alnico 5-7 alloy has lower Co: Fe ratio and no Ti, compared with Alnico 8 and 9, which results in the lowest Hc. Alnico 8 has higher concentration of Co and Ti than those in Alnico 9.

Figure 2.12 Magnetic hysteresis loops of Alnico 5 (black), Alnico 8 (red) and Alnico 9 (blue)\cite{5}.

HAADF STEM images of three types of Alnico with high magnification are shown in Figure 2.13. Alnico 5-7 show a “brick and mortar”\cite{10} like microstructure in transverse direction ([001]) and irregular elongated blocks in longitudinal direction ([011]). The edges of bricks in [001] direction are round and the blocks in [011] direction are branching in some extent. The $\alpha_1$ phase is 40~60 nm in cross-section (transverse) and 100 ~ 300 nm in length (longitudinal), while the width of the $\alpha_2$ phase is 5~15 nm. HAADF STEM images of Alnico 8 along the transverse
direction show a “mosaic” structure composed of nearly 35 nm sized “tiles” in nano-scale, which are linked with Cu-rich precipitates (3~5 nm in diameter). These precipitates are set at the corner of two [24] $\alpha_1$ phase facets and in the $\alpha_2$ phase. The needle-like $\alpha_1$ are perpendicular to each other observed in longitudinal direction. Alnico 9 shows similar “mosaic” structure in transverse direction as Alnico 8 but well aligned parallel needle-like $\alpha_1$ phases in longitudinal direction, which are much longer (>400 nm) than those in Alnico 5-7 along this direction. The length of $\alpha_1$ phase depends on the magnitude of the projected applied magnetic field on the $<100>$ directions. That is to say, $\alpha_1$ phases will be elongated to one of three possible variants of $<100>$ directions preferred by the applied field while Alnico 8 have random oriented grains and Alnico 9 have oriented grains. This is the reason of the difference of microstructure of Alnico 8 and 9 in longitudinal direction. HAADF STEM imaging in higher magnification and corresponding energy dispersive X-ray spectroscopy (EDS) mapping of Alnico 5–7 and 9 in Figure 2.14 confirmed that the brighter region in HAADF STEM images is the $\alpha_1$ phase (red) and the darker region is the $\alpha_2$ matrix (green). For alnico 9, Cu-bridges (light blue) at the corner of the $\alpha_1$ correspond to the brightest region in HAADF STEM imaging. High resolution images show that $\alpha_1$ in both Alnico 5-7 and Alnico 9 is BCC structure while $\alpha_2$ in Alnico 5-7 is $B_2$ structure and $L2_1$ structure. The models of these three crystal structures are shown in Figure 2.15.
Figure 2.13 HAADF STEM images of $\alpha_1$ of Alnico 5(a, b), 8(c, d) and 9 (e, f) alloys [10] in [001] & [010] directions
Figure 2.14 HAADF STEM image (a), corresponding EDS mapping (b) and high-resolution HAADF image (c) of Anico 5–7 close to the [100] zone axis; HAADF STEM image (d), corresponding EDS mapping (e) and high-resolution HAADF image (f) of Anico 9 close to the [100] zone axis[10].

Figure 2.15 Models of three crystal structures[34]: (i) BCC; (ii) B\(_2\) and (iii) L\(_{21}\)
<table>
<thead>
<tr>
<th>Table 2.4 Comparison of Alnico 5-7 and Alnico 8 &amp; 9 in all respects</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Microstructure</strong></td>
</tr>
<tr>
<td>$\alpha_1$ phases</td>
</tr>
<tr>
<td>$\alpha_2$ phases</td>
</tr>
<tr>
<td>No Cu-bridges exist</td>
</tr>
<tr>
<td><strong>Composition</strong></td>
</tr>
<tr>
<td>Ratio of Co to Fe</td>
</tr>
<tr>
<td><strong>Processing</strong></td>
</tr>
<tr>
<td><strong>Magnetic properties</strong></td>
</tr>
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<td></td>
</tr>
</tbody>
</table>

The differences of Alnico 5 and Alnico 8 (&9) in all aspects, microstructure, composition, processing and magnetic properties, are summarized in Table 2.4. It is obvious that the biggest difference between Alnico 5 and 8(& 9) is Cu-bridges in Alnico 8 and 9, which is also the inspiration of my thesis research. Details will be discussed in Chapter 4 and 5.

Although there are extensive technical challenges due to the small interatomic distances and similar atomic numbers of Alnico alloys, atomic-scale EDS maps were applied by Ping[34] to show the atomic-scale chemical composition at individual lattice sites for the two phases. Figure 2.16 shows Fe and Co atoms occupy the A-sites or B-sites, respectively, in $\alpha_1$ phase along [001] direction, and Figure 2.17 indicates Co and Ni atoms are at A-sites and Al, Ti and Fe are at B-sites (B$_1$ or B$_{II}$), in $\alpha_2$ phase along [001] direction. Figure 2.18 reveals the atomic occupation along [110] direction, because B$_1$ and B$_{II}$ sites of the L2$_1$ structure overlap in the [001] direction, but not in [110] direction (shown in Figure 2. 14(iii)). In the [110] direction, it is obvious that Al and Ti atoms occupy the B$_1$ and B$_{II}$ sites, respectively. Fe atoms occupy B$_{II}$ sites although it is not very clear due to the relatively small concentration in $\alpha_2$ phase.

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Figure 2.16 Atomic scale EDS map of Fe (a), Co (b), combination (c) of Fe (red) and Co (green) along [001] direction in $\alpha_1$ phases[34]

Figure 2.17 Atomic scale EDS map of combination of Co and Ni (a), Al, Ti and Fe (b), and line scans (c) of Co, Ni, Al, Ti and Fe along [001] direction in $\alpha_2$ phases[34]
Figure 2.18 Atomic scale EDS map of $\alpha_2$ in [110] direction Co/Ni (a); Al (b); Ti (c) and Fe (d).

High-resolution HAADF image of $\alpha_2$ phase (e) [34]
2.5 References cited


Chapter 3 Experimental Techniques

3.1 Alloy synthesis

3.1.1 Weighing

All raw materials are from Alfa Aesar®

Table 3.1 Specifications of the elements for preparation of Alnico alloys

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>Iron granules, 1-2 mm (0.04-0.08 in), 99.98% (metals basis)</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>Cobalt pieces, 99.94% (metals basis)</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>Aluminum slug, 1.98 mm (0.078 in) dia x 8.0 mm (0.315 in) length, 99.99% (metals basis)</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>Nickel slug, 3.175 mm (0.125in) dia x 3.175 mm (0.125in) length, 99.98% (metals basis) + 50 mm x 50 mm, Nickel foil, 0.1 mm (0.004 in) thick, 99.5% (metals basis)</td>
</tr>
<tr>
<td>Titanium</td>
<td>Ti</td>
<td>Titanium granules, -15 mesh, 99.9% (metals basis excluding Na and K), 10g</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>Copper shot, 0.8-2 mm (0.03-0.08 in), 99.5% (metals basis), 100 g</td>
</tr>
<tr>
<td>Hafnium</td>
<td>Hf</td>
<td>Hafnium wire, 0.5 mm (0.02 in) dia, 99.95% (metals basis excluding Zr), Zr nominal 3%, 100 cm</td>
</tr>
<tr>
<td>Niobium</td>
<td>Nb</td>
<td>Niobium wire, 0.5 mm (0.02 in) dia, 99.96% (metals basis excluding Ta), 100 cm</td>
</tr>
</tbody>
</table>

According to the weight percent of each element, the mass of each element was calculated while the total mass for each sample is 5 grams. Each element was well stored and weighed out to within 0.001 grams in a glove box filled with high purity argon (< 1 ppm oxygen). Each
weighed-out sample was put into glass vials within an argon atmosphere, so the samples were well conserved before casting.

3.1.2 Arc melting/casting

Bulk samples were prepared in a partial pressure of argon by non-consumable electrode arc melting using equipment and a process similar to that described in [1]. An electric arc is generated from 98% tungsten (W) + 2% lanthanum oxide (La₂O₃) electrode with a gas tungsten arc welding (GTAW) power supply to heat and melt the materials. The casting takes place inside of a sealed chamber that is evacuated to < 50 mTorr and refilled with high purity argon at least 3 times before operation. A negative pressure around -10 psi is the operational pressure. A Ti button was melted before each sample to getter any residual oxygen. Bulk elements (purity > 99%) were melted on a water-cooled copper hearth and then flipped and remelted at least thrice to ensure the elements were well mixed. The melting time was around 5~7 seconds. Overlong melting will result in the detrimental evaporation of low melting temperature elements, such as aluminum, and change the elemental compositions. If actual mass deviates from the designed during the post-weighing, which indicates some elements have missed or evaporated, then the weighing and melting/casting process will be repeated. Samples were drop cast into a water-cooled 3-mm-diameter cylindrical copper mold in Figure 3.1 (a) and cut into 3 mm diameter by 3 mm long cylinders using a low-speed diamond wafering saw. This specific mold designed with 7mm top half and 3mm bottom half is to promote the formation of 3 mm part and facilitate the magnetic test by a superconducting quantum interference device (SQUID) with a 3mm-diameter brass sample holder in Figure 3.1(b). Magnetic properties are very sensitive to the shape of the sample[2], so all the samples should be a perfect cylinder with the same dimensions and any unintended factors should be avoided. The sample solidifies before it reaches the bottom of the
mold, causing the end of the cylinder to be rounded. This rounded section should be cut off and/or grounded to flat. The upper and lower surface of the cylinder should be parallel to each other and perpendicular to the side surface.

Figure 3.1 Water-cooled 3-mm-diameter cylindrical copper mold (a) and 3mm-diameter SQUID sample holder (b).

3.2 Thermal and magnetic treatments

3.2.1 Solutionizing treatment and quenching

The elemental distribution in as-cast Alnico alloy is not uniform due to the different cooling rate in different position during casting. To get the homogenization, the solutionizing treatment was conducted in a horizontal Lindberg tube furnace with a quartz tube and a type K (chromel/alumel) thermocouple for accurate temperature measurements. Samples were placed separately on an alumina (Al₂O₃) boat to avoid mutual contaction. The boat was located in a 10-centimeter wide uniform hot zone in the middle of the furnace, monitored by the thermocouple. The annealing temperature varies depending on the composition, generally from 1200 °C to 1300 °C. For this thesis, samples were annealed for 30 minutes at 1250 °C in this hot zone with
forming gas (98 % argon + 2 % hydrogen) flowing to avoid oxidation. One end of the tube was open during the annealing process to facilitate the quenching work. Once annealing was done, the boat with samples was pulled out with a metal bar through the open end and quenched into cold water in Figure 3.2. The water level should be high enough for the instant cooling of the samples. The time from pulling out to quenching was less than 5 seconds to maintain the homogenized single phase and avoid the detrimental γ phase formed[3]. Samples were dried and cleaned before the next step.

Figure 3.2 Assembly for the solutionizing treatment and quenching

3.2.2 Thermomagnetic treatment

As the most critical step for Alnico preparation, thermomagnetic treatment must be optimized. Two typical ways are continuous cooling magnetic treatment for Alnico 5-type alloys and isothermal magnetic treatment for Alnico 8-type alloys. Here since our research focuses on the
Alnico 8-type alloys, so all the thermomagnetic treatments mentioned would be isothermal magnetic treatment.

The thermomagnetic treatment takes place in a vertical tube furnace, which was installed in the center of a ring-shaped superconducting magnet in Figure 3.3. Three thermocouples, $T_1$, $T_2$, and $T_3$, were set to monitor the temperature during the treatment. $T_1$ and $T_2$ are fixed 3 millimeters away from the samples while $T_1$ is used to gather data for the computer in Figure 3.3 and $T_2$ is to automatically control the furnace to reach the temperature we set; $T_3$ was fixed between the metal shell and the ceramic core of the furnace for safety. The samples were mounted in the center of the magnet, with their axial directions parallel to the magnetic field as shown in Figure 3.4. The uniform zone of the magnetic field is 36 cm below the upper surface of the magnet, so the samples were mounted in that zone. Alnico magnetic properties are more sensitive to temperature than time during thermomagnetic treatment[4], so temperature fluctuation was controlled in the acceptable range of $\pm 2$ °C. The process of thermomagnetic treatment was designed into 6 steps: firstly, ramp up the magnet to 3 T in 2 hours; secondly, heat up the furnace to 800 °C in around 35 minutes; thirdly, anneal the samples for 10 minutes at 800 °C with 3 T magnetic fields; fourthly, cool down the furnace to lower than 200 °C in around 4 hours; fifthly, ramp down the magnet to 0 T in 2 hours; lastly, remove the samples for the next step.
3.2.3 Tempering

Tempering was conducted in the same quartz tube furnace as the solutionizing treatment, but with two ends closed. The tube was fixed in position and the furnace was installed on a track so that it could be moved over the tube. The tube was evacuated to < 50 mTorr and refilled with 98 % argon + 2 % hydrogen mixed gas at least three times before being moved into the furnace. The furnace tube was filled with the gas with positive pressure up to 2-5 psi during the whole annealing process. Multi-step tempering is most efficient to optimize the magnetic properties,
and the temperature and time also depend on the compositions. For this work, the tempering time and temperature is at 650 °C for 4 hours, then 600 °C for 6 hours and finally 550 °C for 16 hours. Temperature fluctuation observed at each step was in the acceptable range of ±5 °C. Samples were cooled by removing the tube from the furnace immediately after the time was up. This allowed for fast cooling in ambient temperature but maintained the controlled atmosphere. The cooling rate is around 3-5 °C/s.

3.3 Magnetic testing

Magnetic measurements were made using a Quantum Design MPMS superconducting quantum interference device vibrating sample magnetometer (SQUID-VSM). The MPMS uses a superconducting helium-cooled magnet to apply a magnetic field up to ± 7T at temperatures from 1.8 to 400 K. Typical measurements are magnetic moment versus applied field at constant temperature and magnetic moment versus temperature at constant applied field. Here we only research the magnetic property of Alnico at room temperature, so magnetic hysteresis measurements were performed sweeping the magnetic field from -3 T to 3 T at room temperature. Coercivity, remanence, saturation magnetization, and energy product were extracted from the hysteresis loops and calculated by using Origin 10. Typical sample holders are quartz flat-surface holder and brass groove holder. Because Alnico is a hard magnet, such that the magnetic deviation induced by the holder cannot affect the test results, so the endurable brass groove holder was chosen. GE7031 varnish was used to mount the samples into the groove of the holders. The varnish was dried with the heater (around 45 minutes) before test, so it is strong enough to resist the shift of the sample in the magnetic field up to 3T. The varnish was removed with acetone when the test was done, and the sample was uninstalled and cleaned for microstructure research.
3.4 Electron Microscopy

3.4.1 FIB “Lift-Out” Technique

Jet polishing is a common and efficient way to prepare good metallic TEM samples, but even after demagnetization, a 3 mm jet polished Alnico sample will still induce strong electronic beam deviation, which would affect the TEM analysis detrimentally. Therefore, focused ion beam (FIB) in-situ “lift-out” technique was chosen and conducted in a FEI Quanta 3D FEG Dual Beam instrument used for TEM/HRTEM sample preparation.

The specific procedures of FIB described as following: A 2 um x 10 um Pt rectangle was deposited over the area of interest as a protection layer with a thickness of ~2 μm. Stair-step FIB trenches were cut on each side of the area of interest with 3 - 7 nA beam currents of Ga⁺ ions accelerated to 30 keV. A thin (<1 μm) rectangular (~15 x 10 μm) machined-out membrane was then lifted out of the bulk sample by an OmniProbe micromanipulator and positioned onto a molybdenum (Mo) grid. Copper grid is more common used than molybdenum grid for its better finish, but molybdenum grid has to be chosen here, because the copper grid would interfere with the EDS results of copper in Alnico. The membrane was thinned to electron transparency through the applications of 1 nA to 300 pA, 30keV Ga⁺ ions with the milling angle of 52 ± 2° followed by a final polishing using 48 pA, 5 keV Ga⁺ ions with milling angle of 52 ± 5°.

Many extra challenges were confronted during the FIB preparation of Alnico, because of its magnetic anisotropy, strong magnetic field and highly complex microstructure. The specific features of spinodal decomposition are along [001] direction from the magnetic shape-anisotropy. If the final polished membrane is not perfect along the direction of magnetization direction, [001], in most situation (S)TEM can’t reach this direction by tilting and then the EDS results will
be incorrect in Figure 3.5. Therefore, directional control must be run through the whole process.

The attentions in each step are listed as follows:

1. **Cast** - The sample must be machined into perfect cylinder with two parallel top and bottom surfaces, which are perpendicular to the wall. Sample with round or tilt tip is unacceptable. Too thin sample will result in the difficulty in attention #4, so it is not good, either. Random shapes may result in failure of observation of spinodal decomposition morphology. See Figure 3.6 (a)

2. **Thermomagnetic treatment** - The cylindrical sample should be mounted perfectly with axis parallel to the magnetic field during thermomagnetic treatment. See Figure 3.6 (b)

3. **Mechanical polishing** - The round profile must be polished into two parallel surfaces for FIB operation. The new surfaces should be perpendicular to the top and bottom surface. Small errors here may result in huge problem in FIB lift-out work. See Figure 3.6 (c)

4. **Demagnetization** - Demagnetization is necessary since electronic beams will drift away by the interference of the magnetic field induced by the magnetic samples. After demagnetization, the image is still bent to some extent, but not as serious as before. See Figure 3.6 (d)

5. **Hog out during FIB** - The membrane must be hogged out parallel to the cross section (i.e. perpendicular to the magnetic field), so the observation in this sample is conducted along [001]. See Figure 3.6 (e).

![Figure 3.5 A scheme of EDS map of $\alpha_1$ phases along and not along [001] direction](image)

- Perfect [001]
- \begin{tabular}{|c|c|}
  \hline
  $\alpha_1$ & $\alpha_1$ \\
  \hline
  $\alpha_1$ & $\alpha_1$ \\
  \hline
\end{tabular}
- NOT Perfect [001]
- \begin{tabular}{|c|c|}
  \hline
  $\alpha_1$ & $\alpha_1$ \\
  \hline
  $\alpha_1$ & $\alpha_1$ \\
  \hline
\end{tabular}
Figure 3.6 Schematic images describing the attentions required during FIB-milling of Alnico alloys
6. **Thinning during FIB** - The membrane must be thinned along the surface of hoggéd-out, or else [001] direction is difficult to reach by tilting. See Figure 3.6 (f)

7. **Thinning during FIB** – Although thinner TEM sample will be better for observation, Pt area must be left so that the film is not bent. Window-like sample with thick frames in four fringes would be the best choice. See Figure 3.6 (g)

8. **Final polishing during FIB** - Use small current 48 pA to polish, large current may bring in too many scratches and ruin the morphology of spinodal decomposition.

**3.4.2 Scanning/Transmission Electron Microscopy (S/TEM)**

Structural and compositional properties were performed in an aberration-corrected FEI Titan G2 microscope with an X-FEG source and ChemiSTEM technology operated in the scanning transmission electron microscopy (STEM) mode at 200 keV. The electron beam probe size is 0.1 nm in a convergent angle of 21 mrad. The energy-dispersive x-ray spectroscopy (EDS) maps of regions of interest were acquired for 900 s. An annular dark-field detector with 100 mm camera length, corresponding to a collection angle of 77-300 mrad, was used to obtain STEM high-angle annular dark-field (HAADF) images. The image contrast in HAADF is proportional to the atomic number (Z), the material density or the sample thickness, enabling us to detect different phases in the microstructure[5]. As mentioned before, direction controlling is very critical to get the correct microstructure information and EDS images for Alnico research. One challenge is how to reach the expected axis zones by tilting within the limited angles. [001] is the most important direction since it is the sole direction that morphology of Cu-bridges information can be shown. Its Kikuchi lines are quite similar to those of [111] direction. The simulated Kikuchi lines of [001] and [111] directions are supplied here for comparisons.
Figure 3.7 Simulated Kikuchi lines of [001] and [111] directions
Figure 3.7 Simulated Kikuchi lines of [001] and [111] directions (Continued)
3.3 References cited


Chapter 4 On the Formation and Evolution of Cu-Ni-rich Bridges of Alnico Alloys with Thermomagnetic Treatment

Min Fan, Y. Liu, R. Jha, G.S. Dulikravich, J. Schwartz, C.C. Koch, accepted by IEEE Transactions on Magnetics in April, 2016. M. Fan prepared the samples, conducted magnetic and microstructure tests, and the analysis of the experimental data.

4.1 Abstract

Despite decades of research and development of Alnico alloys, significant uncertainties in the underlying structure-property relationships remain. Here we report on the effects of Ti on the Alnico microstructure and nanostructure, and the corresponding influence on magnetic properties. We show that Ti fosters the conditions resulting in the formation of Cu-Ni-rich bridges in the $\alpha_2$ phases between the $\alpha_1$ phases. For Alnico containing Ti, a typical chessboard-like morphology with Cu-Ni-rich bridges is observed, whereas in the absence of Ti, the $\alpha_1$ phases connect to each other readily, especially with a high Co concentration, and a maze-like morphology with Cu-rich white plate precipitates rather than Cu-rich bridges is observed. Furthermore, in Alnico containing Ti, an inhomogeneous distribution of Ni is found in the $\alpha_2$ phases, including loops with high Ni concentration surrounding the $\alpha_1$ phase, and high concentrations in the bridges as well. An increase in the Cu concentration is also observed in the loops around the $\alpha_1$ phases (Ni-Cu loops), and direct contact between the Cu-Ni-rich bridges and Ni-Cu loops is observed in lieu of direct contact between the bridges and the $\alpha_1$ phases. We also observe that the bridges are not perfectly round but ellipsoidal, with the long axis along the connection of two adjacent $\alpha_1$ phases. Energy-dispersive X-ray spectroscopy line scans of the bridges shows that two types of Cu-Ni-rich bridges exist: those with more Cu than Ni, and those with more Ni than Cu. A three-
dimensional model is presented that explains the conditions and process of bridge formation, consistent with the observed composition distributions.

4.2 Introduction

The family of Fe-Al-Ni-Co (Alnico) magnetic alloys have been available commercially for decades and are used in many applications, including motors, generators, loudspeakers, sensors, headphones, etc. Although other systems, such as Nd-Fe-B, have higher magnetic properties, Alnico alloys remain of interest due to their low cost, sufficient permanent magnetic properties, especially for high temperature applications (~400 °C), and established acceptance in the commercial market [1].

The permanent magnetic properties of Alnico alloys, typically Fe, Co, Ni, Al, Ti with a small addition of Cu and Nb, is attributed to shape anisotropy. This shape anisotropy is obtained through spinodal decomposition [2] during thermomagnetic treatment at 800~850 °C [3], resulting in a periodic distribution of rod-like ferromagnetic $\alpha_1$ phases (mainly Fe and Co) in the non-ferromagnetic $\alpha_2$ matrix (mainly Ni, Al and Ti). The $\alpha_1$ rods are formed with their axes of elongation parallel to the <100> direction, the magnetic easy-axis direction. The temperature and time of the thermomagnetic treatment have been studied to optimize the size and shape of the $\alpha_1$ phase formed in this step. Important conclusions from these studies include that Alnico magnetic properties are more sensitive to temperature than time during thermomagnetic treatment [4], and that the preferred direction of magnetization is determined more by the direction of the thermomagnetic field and less by the crystallographic anisotropy [5]. Additionally, high Co content (>24%) increases the sensitivity of Alnico to the thermomagnetic treatment, increasing the coercivity ($H_c$) and remanence ($B_r$), but favors the precipitation of the detrimental face-centered cubic (fcc) $\gamma$ phase. Furthermore, these studies conclude that Ti can
prevent the formation of the γ phase and increase $H_c$, but decreases $B_r$ [6]. With increasing Co and Ti, the thermomagnetic temperature ($T_s$) increases while thermal stability deteriorates [7].

The focus of recent work is primarily on the crystallography and magnetic structural characterization [3, 8-12] and computational optimization [13-18] of commercial Alnico. Studies have concentrated on the two main phases, $\alpha_1$ and $\alpha_2$, and only a few papers refer to a particular precipitate between two adjacent $\alpha_1$ phases (but actually in the $\alpha_2$) in Alnico alloys containing Ti, such as Alnico 8 and Alnico 9 [4, 19], due to the lack of advanced characterization technologies at the time. Of the recent studies, Xing et al. and Zhou et al. [9, 11] reported this area is Cu-rich and may play an important role in the final magnetic properties as spacers between adjacent $\alpha_1$ phases. This paper investigates in detail the Cu-rich bridges using high-resolution transmission electron microscopy techniques. The formation of the bridges, as well as their evolution and their effects on the $\alpha_1$ phase during further coarsening, are discussed. The composition distributions of the bridges are also shown and discussed.

### 4.3 Experimental procedure

Alnico samples with two stoichiometries, sample A containing Ti and sample B without Ti, were formed via identical processes. Table 1 summarizes the compositions of each sample; note that the only difference between the two samples is the presence of Ti, with a corresponding decrease in Fe, in sample A. The Co, Ni, Al, Cu, Hf and Nb contents are identical.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>A</td>
<td>32.3</td>
</tr>
<tr>
<td>B</td>
<td>36.5</td>
</tr>
</tbody>
</table>
Bulk samples were prepared in a partial pressure of argon by non-consumable electrode arc melting. A Ti button was melted before each sample to getter any residual oxygen. Bulk elements (purity > 99%) were melted on a water-cooled copper hearth and then flipped and remelted at least thrice to ensure the elements were well mixed. Samples were drop cast into a water-cooled 3-mm-diameter cylindrical copper mold and cut into 3 mm diameter by 3 mm long cylinders. The as-cast samples were heat treated with typical procedures for Alnico. First, the samples were solutionized at 1250 °C followed by water quenching. Then the samples were thermomagnetically treated at 800 °C for 10 minutes with a 3 T magnetic field along the cylindrical axis. The aim of this work is to research the growth of bridges during spinodal decomposition so the samples were not tempered; a subsequent publication will focus on the evolution of bridges during tempering [20].

Magnetic hysteresis measurements were performed with a Quantum Design superconducting quantum interference device (SQUID) magnetometer to sweep the magnetic field from -3 T to 3 T at room temperature. $H_c$, $B_r$ and the maximum of energy product $(BH)_{max}$ are extracted from the hysteresis loops.

Structural and compositional properties were analyzed via transmission electron microscopy (TEM). The TEM foil (rectangular, length ~ 20 μm x width ~ 10 μm) was prepared using a focused ion beam (FIB) lift-out technique in a FEI Quanta 3D FEG dual-beam instrument in the transverse orientation. $\alpha_1$ phases form along the direction of magnetic field during thermomagnetic treatment, the [001] direction, so the samples are observed along the magnetic field direction, i.e. the transverse orientation. The FIB cut specimens were first thinned by Ga+ ions at 30 keV, followed by 5 keV for final thinning. Energy-dispersive x-ray spectroscopy
(EDS) analysis was performed in an aberration-corrected FEI Titan G2 microscope with an X-FEG source and ChemiSTEM technology, operated in the scanning transmission electron microscopy (STEM) mode at 200 keV. The electron beam probe size is 0.1 nm in a convergent angle of 21 mrad. The EDS maps of regions of interest were acquired for 900 s. An annular dark-field detector with 100 mm camera length, corresponding to a collection angle of 77-300 mrad, was used to obtain STEM high-angle annular dark-field (HAADF) images. The image contrast in HAADF is proportional to the atomic number (Z), the material density or the sample thickness, enabling us to detect different phases in the microstructure [13].

4.4 Results

4.4.1 Magnetic properties

Table 2 summarizes the magnetic behavior of the two samples, A and B, in terms of $H_c$, $B_r$ and $(BH)_{\text{max}}$. As mentioned, the aim of this work is to research the growth of bridges during spinodal decomposition so the samples were not tempered. Due to the lack of tempering, the magnetic properties were not optimized. With tempering, $H_c$ of sample A increases to 1300 Oe. If directionally solidified, $B_r$ increases as well. With these changes, $(BH)_{\text{max}}$ becomes similar to Alnico 9.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$H_c$ (Oe)</th>
<th>$B_r$ (T)</th>
<th>$(BH)_{\text{max}}$ (kJ/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1100</td>
<td>0.53</td>
<td>12</td>
</tr>
<tr>
<td>B</td>
<td>40</td>
<td>0.2</td>
<td>0.39</td>
</tr>
</tbody>
</table>

4.4.2 Microstructure

Figure 1 shows HAADF images and EDS maps of samples A and B observed along the [001] direction, parallel to the magnetic field during thermomagnetic treatment (see Appendix A for
the uniformity of spinodal phases in the low magnification images). Three distinguishable areas are observed in sample A: the \( \alpha_1 \) phase, the hard magnetic phase, is seen as bright areas of primarily Fe and Co, the \( \alpha_2 \) phase, the soft magnetic phase, is seen as a dark matrix of primarily Ni and Al, and Cu-rich areas, which are small, bright circles, and appear to be precipitates bridging adjacent \( \alpha_1 \) phases. The EDS maps show compositional variations corresponding to HAADF STEM images. The average size of the \( \alpha_1 \) phase in sample A is about 26 +/- 4 nm. The main element of \( \alpha_1 \), Fe, has a larger contrast difference between \( \alpha_1 \) and \( \alpha_2 \) than Co. Similarly, the main element of \( \alpha_2 \), Ni, has a larger contrast difference between \( \alpha_1 \) and \( \alpha_2 \) than Al and Ti. The Cu-rich bridges occupy the sites between adjacent \( \alpha_1 \) phases. The distribution of the Cu-rich bridges is not uniform and depends on the edges and shape of \( \alpha_1 \) phases. In Figure 1(a), where the edges of the \( \alpha_1 \) phases are round, only one bridge forms, whereas when the \( \alpha_1 \) phases are more square-shaped with rounded corners, there tends to be two bridges. When the gap between two \( \alpha_1 \) phases is sufficiently narrow to favor coalescence, Cu-rich bridges are absent and the concentration of Fe increases in the gap. Nb behaves similarly to Ni, Al and Ti, which are concentrated in the \( \alpha_2 \) phase. The distribution of Hf is not considered because the major peaks of Hf and Cu overlap in the EDS spectrum. Electron energy loss spectroscopy (EELS) is also ineffective for verifying the Hf distribution because the Hf composition is too low.

In the HAADF image of sample B in Figure 1(b), obscured and connected \( \alpha_1 \) phases are observed in the dark \( \alpha_2 \) matrix, although with less contrast between the two phases than in sample A. No Cu-rich bridges are observed, but mutually perpendicular bright precipitates are seen. In the EDS maps of sample B, both \( \alpha_1 \) and \( \alpha_2 \) phases structurally appear like mazes. The average width of the \( \alpha_1 \) phases in sample B is about 20 nm. The black areas in the Fe and Co (\( \alpha_2 \) phases) are much smaller than the \( \alpha_2 \) areas containing Ni and Al, so the \( \alpha_1 \) and \( \alpha_2 \) phases partially
overlap with less clear phase boundaries. Thus, quantitative measurement of the $\alpha_1$ phase size is unreliable. Furthermore, in sample B, Cu does not form Cu-rich bridges but is dispersed in the $\alpha_2$ phase like the other $\alpha_2$ elements, Ni and Al. Although the composition of the white stripe precipitates is not considered, Hf does show specific concentration in those regions.

Figure 2(a) shows a higher magnification HAADF image and the corresponding EDS maps of sample A, focusing on the $\alpha_1$ phase. One special feature is that a loop with a high Ni concentration surrounds the $\alpha_1$ phase, concentrating near the Cu-rich bridges. In addition, a loop with increased Cu concentration is observed around the $\alpha_1$ phase. The Ni and Cu peaks in the line scans (Figure 2(b, c)) confirm the existence of Ni and Cu loops and shows them to be ~2 nm wide. Although the compositions of different elements cannot be compared through the intensity curves of line scans, the change of concentration of one specific element among different areas can be revealed by the change of the intensities in those areas. In Figure 2(a), the Cu-rich bridges are not perfectly round but have a preferred direction, as the long axis is along the connection between adjacent $\alpha_1$ phases. Co and Ti are distributed away from the bridges while Fe and Al are not. Figure 2(b, c) also confirm the differences in contrast observed in Figure 1, i.e., that Fe has a higher contrast between $\alpha_1$ and $\alpha_2$ than Co and that Ni has higher contrast between $\alpha_1$ and $\alpha_2$ than Al and Ti.

Figures 3 and 4 show high magnification EDS maps and line scans along the [001] direction to study the composition of the bridges in sample A. The thickness of TEM foils ensures only one layer of each phase exists along the [001] direction. HAADF images and corresponding line scans show the change of concentration of one specific element among different areas via the change of intensities, and EDS maps with quantitative analysis (Table 3) reveal the compositions of bridges. We refer to these bridges as Cu-Ni-rich bridges, and to differentiate between two
types, we refer to those in which the Cu content is highest as Cu>Ni bridges (seen in Figure 3) and those in which the Ni content is highest as Ni>Cu bridges (seen in Figure 4). Note that the existence of Ni-rich loops and Ni>Cu bridges was recently reported by Zhou et al. [22].

Table 4.3 Compositions (at. %) of two types of Cu-Ni bridges

<table>
<thead>
<tr>
<th>Types of Bridges</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Al</th>
<th>Ti</th>
<th>Cu</th>
<th>Hf</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu&gt;Ni (Figure 3)</td>
<td>11.03</td>
<td>16.57</td>
<td>21.75</td>
<td>16.99</td>
<td>3.05</td>
<td>29.55</td>
<td>0.89</td>
<td>0.17</td>
</tr>
<tr>
<td>Ni&gt;Cu (Figure 4)</td>
<td>10.14</td>
<td>16.12</td>
<td>28.24</td>
<td>18.27</td>
<td>2.76</td>
<td>23.21</td>
<td>1.27</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 3(a) shows a HAADF image centered on a Cu>Ni bridge between α₁ phases (top and bottom) and the dark α₂ matrix (left and right). The ellipsoid bridge has a preferred direction with the long axis along the connection of two α₁ phases. Note, however, that the bridge does not contact the adjacent α₁ phases but instead contacts the high concentration Ni-Cu loop, which is not be observed at lower magnification. This is confirmed by the two Ni peaks on the two sides of the Cu peaks in the vertical line scan in Figure 3(b). The Cu peak in the horizontal line scan in Figure 3(c) shows that the bridge has a much higher Cu concentration than the α₂ phases. As listed in Table 3, the Cu concentration is higher than Ni in the bridge area shown in Figure 3(d).

Figure 4(a) shows a HAADF image centered on a Ni>Cu bridge between α₁ phases (top and bottom) and the dark α₂ matrix (left and right). This bridge has a similar shape and distribution as the Cu>Ni bridge, but the line scans are quite different. A large Ni plateau I seen at the center of the vertical line scan in Figure 4(b) and a Ni peak at the center in the horizontal direction in Figure 4(c). The Ni plateau is wider than the Cu peak in vertical direction in Figure 4(b), which is evidence that the bridges contact the Ni-Cu loops but not the α₁ phase. In both types of bridges, Co and Ti have large compositional change in the bridge area, consistent with the observation that Co and Ti form away from Cu-Ni-rich bridges. Similarly, as shown in Table 3, the Ni concentration is higher than Cu in the bridge area shown in Figure 4(d).
4.5 Discussion

Figure 1 shows that the addition of Ti results in significant changes in the morphology after spinodal decomposition. For sample A, which contains Ti, the $\alpha_1$ phase has sharp, well-defined boundaries, Ni-Cu loops and Cu-Ni-rich bridges. Sample B, without Ti, shows connected $\alpha_1$ phases with obscured, ill-defined boundaries. Furthermore, the $\alpha_1$ and $\alpha_2$ phases partially overlap, with Cu dispersed in $\alpha_2$ as well as in plate-like precipitates, and with no Cu-Ni-rich bridges. The Ni-Cu loop observed in Figure 2 indicates an inhomogeneous distribution of Ni in the $\alpha_2$ phase of sample A. The high Ni concentration is not only in the loops around the $\alpha_1$ phases, but also in the connections between adjacent $\alpha_1$ particles where Cu-Ni-rich bridges are formed (Figures 3 and 4). Therefore, Cu-Ni-rich bridges actually form in the environment of the Ni-Cu loops and the number of the bridges depends on the distance between adjacent $\alpha_1$ phases. These features imply the existence of an interrelationship between the Ni-Cu loops, Cu-Ni-rich bridges and Ti. Previous research [5, 23] on the mechanisms of spinodal decomposition in Alnico was unaware of the Cu-Ni-rich bridges due to the lack of high resolution analysis at the time. The results here imply that the existence of bridges is important for understanding the morphology and magnetic properties of Alnico alloys.

4.5.1 Conditions for the formation of Cu-Ni-rich bridges

Ti ions have a large radius and a low diffusion rate [24] and can increase the elastic energy of an alloy [25]. Therefore the $\alpha_1$ phases in sample A form sharp edges with high elastic energy and do not readily diffuse into the $\alpha_2$ phases during spinodal decomposition. These conditions facilitate the formation of Cu-Ni-rich bridges, whose formation decreases the high elastic energy. For sample B without Ti, elements in different phases mutually diffuse more readily, so the $\alpha_1$ and $\alpha_2$ phases partially overlap and the phase boundaries are broad and poorly-defined. The bridges do
not precipitate for the same reason, the high diffusion rate. The larger positive enthalpy of mixing, $\Delta H^{\text{mix}}$, of two elements means these two elements have a stronger repulsive interaction and are more difficult to mix, while a larger negative $\Delta H^{\text{mix}}$ means the two elements are easier to mix [26]. So $\Delta H^{\text{mix}}$ of the binary liquid in an A–B system [27] is indirect evidence explaining the formation of the Cu bridges in the sample with Ti. Cu is the hardest element to be mixed with other elements, so it precipitates readily. Fe and Co are the second and third most difficult to mix and are ferromagnetic at high temperature, so they form the $\alpha_1$ phase during the thermomagnetic treatment by spinodal decomposition. In sample A, Ti is the easiest element to mix and Ni and Al are the two easiest elements to mix with Ti; therefore, Ni, Al and Ti form the $\alpha_2$ phase whereas Cu is repelled by the $\alpha_2$ phase, encouraging the precipitation of bridges. In the absence of Ti, Al is the easiest to be mixed in sample B. The negative enthalpy of Al-Ni is smaller than that of Ti-Al-Ni in the $\alpha_2$ phase, so the $\Delta H^{\text{mix}}$ differences between $\alpha_2$ and Cu decrease and Cu is more readily accommodated in the $\alpha_2$ phase. Oversaturated Cu in the $\alpha_2$ phase forms the plate-like precipitates.

### 4.5.2 Bridge formation process

Figure 5 illustrates a three-dimensional (3D) model and a corresponding two-dimensional (2D) transverse view of the Cu-Ni-rich bridge formation process. At the initial stage of spinodal decomposition, the spherical $\alpha_1$ phases form as seen in Figure 5(a, a’). The elongation of $\alpha_1$ into ellipsoids is thermodynamically favorable since there is an increase in interfacial energy and a larger reduction in the magnetostatic energy of the particles. Coarsening reduces the magnetostatic energy and interfacial area of the initial single $\alpha_1$ particle, so it is favorable as well [23, 28]. During $\alpha_1$ phase elongation and coarsening, the elements in $\alpha_2$ concentrate on the outer surface of the $\alpha_1$ phase because of the low diffusion rate due to addition of Ti (Figure 5(b, b’)).
The $\alpha_2$ phase has much higher Ti content than $\alpha_1$, so the diffusion rate in $\alpha_2$ is smaller than that in $\alpha_1$. During spinodal decomposition, the $\alpha_2$ phase distributing near the $\alpha_1$ boundaries is “squeezed out” by the coarsening $\alpha_1$. The squeezed elements cannot diffuse to the matrix because of the low diffusion rate, so there an abnormally high concentration of $\alpha_2$ results around the $\alpha_1$. Cu enrichment around the outside $\alpha_1$ surface is thermodynamically favorable because Cu accelerates decomposition by promoting diffusion in the $\alpha_2$ phase [29], and more Cu is required around $\alpha_1$ to maintain the decomposition rate. Cu is repelled by both the $\alpha_1$ and $\alpha_2$ phases as discussed previously, so Cu concentrates on $\alpha_1$-$\alpha_2$ interfaces. Cu has high solubility in Ni and low solubility in Co and Ti [30], so a loop with high Ni concentration forms around the Cu. When the distance between two adjacent Cu-Ni loops around $\alpha_1$ phases is sufficiently short due to elongation and coarsening, the initial spherical Cu-Ni-rich bridges form as seen in Figure 5(c, c’), reducing the total elastic energy, because the edges of the $\alpha_1$ phase have the largest elastic strain [23].

Once the spherical Cu-Ni-rich bridges nucleate between two Ni-Cu loops around $\alpha_1$ phases, the reduction of the elastic strain allows the bridges to grow and leads to the formation of a Cu-Ni cylinder between two Ni-Cu loops; this illustrated in Figure 5(d). At this time, the elastic energy dominates rather than the magnetic energy because of the reduction of Fe and Co in the $\alpha_2$ phase during decomposition.

Table 4.4 Elastic constants of the main bcc elements in Alnico alloys [23, 31]

<table>
<thead>
<tr>
<th></th>
<th>C11</th>
<th>C12</th>
<th>C44</th>
<th>2C44/(C11-C12)</th>
<th>Y(100)</th>
<th>Y(110)</th>
<th>Y(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>2.37</td>
<td>1.41</td>
<td>1.16</td>
<td>2.42</td>
<td>2.10</td>
<td>3.38</td>
<td>3.67</td>
</tr>
<tr>
<td>Al</td>
<td>1.08</td>
<td>0.622</td>
<td>0.284</td>
<td>1.24</td>
<td>0.99</td>
<td>1.12</td>
<td>1.14</td>
</tr>
<tr>
<td>Cu</td>
<td>1.7</td>
<td>1.23</td>
<td>0.75</td>
<td>3.19</td>
<td>1.15</td>
<td>2.33</td>
<td>2.61</td>
</tr>
<tr>
<td>Ni</td>
<td>2.5</td>
<td>1.6</td>
<td>1.185</td>
<td>2.63</td>
<td>2.05</td>
<td>-</td>
<td>3.88</td>
</tr>
</tbody>
</table>
The elastic energy is related to the elastic modulus, which is anisotropic in most crystalline materials. Table 4 shows the elastic constants of the main Alnico bcc elements. If \(2C_{44} - C_{11} + C_{12} > 0\), the waves parallel to the \(<100>\) directions in the \([29]\) planes in cubic crystals are favored because the elastic coefficient \(Y\) is smallest \([23, 31]\). For both Cu and Ni, \(2C_{44}/(C_{11} - C_{12}) > 1\), which is even larger than Fe, so Cu and Ni have the lowest elastic energy in \(<100>\) and decompose most rapidly with this orientation with the smallest wavelength. Because the two adjacent \(\alpha_1\) phases are already formed along the \(<100>\) direction, the Cu-Ni-rich bridges grow along the chosen \(<100>\) direction. Interestingly, Cu has the largest anisotropy \((2C_{44}/(C_{11} - C_{12}))\), and Ni has the second largest, of all cubic elements in Alnico, which, in addition to the repulsive interaction by \(\alpha_1\) and \(\alpha_2\) phases, is likely the reason Cu and Ni are the two main elements in both types of the bridges. In the 3D view in Figure 5(d), the length of Cu-Ni cylinder is always shorter than the \(\alpha_1\) phase. Cu and Ni from nearby areas feed the cylinder continuously, decreasing the elastic energy, which is another reason for the high concentration of Cu and Ni in the bridges. The oval shape of the Cu-Ni-rich bridges is probably due to the different repulsive interactions from different phases as mentioned before. The larger repulsive interaction with \(\alpha_1\) phases results in the larger radial portion of the Cu-Ni-rich bridges being near the \(\alpha_1\) phases, so the long axis is parallel to the connection and the short axis is perpendicular to the connection.

### 4.5.3 Evolution of the bridges and effects on \(\alpha_1\) phases

Figure 6 shows a schematic model illustrating the evolution of Cu-Ni-rich bridges and their “pinning” effect on the \(\alpha_1\) phases. In the presence of bridges, the \(\alpha_1\) phase coarsening rate is non-uniform with a slower coarsening rate near the bridges due to the lack of Fe and Co; this is illustrated in Figure 6(a). Therefore, the \(\alpha_1\) phase edges straighten with coarsening and the shape changes from round to a rounded square as seen in Figure 6(b). In this situation, a larger portion
of the edges reach the critical distance for the formation of Cu-Ni-rich bridges, and a single bridge separates into two bridges in the narrower \( \alpha_2 \) phase gap between adjacent \( \alpha_1 \) phases. This two-bridge structure further slows \( \alpha_1 \) phase coarsening. The abnormally high concentration of Fe in the narrow \( \alpha_2 \) phase area (as observed in Figure 1(a)) shows that Fe diffuses from the \( \alpha_1 \) phase to the \( \alpha_2 \) phase during thermomagnetic treatment. This is opposite of the normal diffusion direction of Fe from the \( \alpha_2 \) phase to the \( \alpha_1 \) phase during spinodal decomposition. This phenomenon is likely due to the attraction of two nearby \( \alpha_1 \) phases when they are sufficiently close; this is shown in Figure 6(c). With increasing thermomagnetic treatment time, this increment of Fe in the \( \alpha_2 \) phase results in the coalescence of two adjacent \( \alpha_1 \) phases, shown in Figure 6(d). Elements in the Cu-Ni-rich bridges between the original adjacent \( \alpha_1 \) phases diffuse to the outside of the new, larger \( \alpha_1 \) phases during coalescence. Therefore, when the new and larger \( \alpha_1 \) phases form, at least four highly concentrated Cu-bridges remain and pin the \( \alpha_1 \) phases, preventing them from connecting to adjacent \( \alpha_1 \) phases. As a result, Alnico with Ti has larger spaces between the \( \alpha_1 \) phases.

For sample B without bridges, the \( \alpha_1 \) phases coarsen uniformly as in Figure 6(e). In Figure 6(f), two adjacent \( \alpha_1 \) phases have connected, although the diameter of the \( \alpha_1 \) phases is \( D_2 \), equal to that in Figure 6(b). Finally, the connected adjacent \( \alpha_1 \) phases overlap as in Figure 6(g), although the diameter of the \( \alpha_1 \) phases is only \( D_3 \), the same as in Figure 6(c). Lastly, the plate-like precipitates partially separate \( \alpha_1 \) phases but do not prevent the adjacent \( \alpha_1 \) phases from connecting in the direction along the magnetic field. Therefore, the morphology of an arbitrary cut in the [001] direction resembles a maze-like structure.
4.5.4 Comparison to commercial Alnico 5, 8 and 9 alloys

Alnico 5, 8 and 9 are common commercial alloys. Alnico 5 and Alnico 8 (and 9) have very different compositions [11] as well as magnetic treatments [28]; that is, continuous cooling for Alnico 5 and isothermal for Alnico 8 and 9. As a result a clear discussion is difficult. Here we prepared two samples with only one difference, the presence of Ti. Sample A has similar composition, microstructure, processing and magnetic properties as Alnico 9, and is representative of Alnico 8 and 9-series alloys. Sample B is considered as a transitional sample, since it was prepared with the same processing as A and Alnico 8 (and 9), and does not contain Ti as Alnico 5. Neither sample B nor Alnico 5 contain Ti, but they have large differences in Co concentration, processing, microstructure and magnetic properties. The $\alpha_1$ phase connections in sample B do not exist in Alnico 5, most likely due to the higher Co concentration in sample B. Therefore, sample B is more sensitive to magnetic field than Alnico 5 [6] and the $\alpha_1$ phases in sample B elongate from a smaller size than those in Alnico 5. Alnico 5 contains less Co and was exposed to a continuous cooling magnetic treatment, so $\alpha_1$ phases in Alnico 5 are not sufficiently long to connect in the direction along the magnetic field during the short annealing time. Although sample A and Alnico 8 and 9 have longer $\alpha_1$ phases, they also have Cu-Ni-rich bridges, so their $\alpha_1$ phases are isolated as compared to those in Alnico 5. The low diffusion rate due to Ti, and the restriction due to the Cu-Ni-rich bridges, result in slower coarsening and the finer $\alpha_1$ phases in Alnico 8 and 9 than Alnico 5.

4.5.5 Relationship between $\alpha_1$ phases morphology and magnetic properties

Baran derived a general expression for the coercivity of well-aligned ferromagnetic rods [32], accounting for the reduction in $H_c$ due to particle interactions and the possibility that the matrix is also ferromagnetic,
\[ H_c = p(1-p)(D_z-D_x)(M_1-M_2)^2/M_s' \]

where \( p \) is the volume fraction of the ferromagnetic phase \( \alpha_1 \), \( M_1, M_2 \) and \( M_s' \) are the saturation magnetizations of \( \alpha_1, \alpha_2 \) and the alloy, and \( D_z \) and \( D_x \) are demagnetizing coefficients along the long and short axes, respectively. As the \( \alpha_1 \) phases become smaller, \( D_z \) increases, and as the distance between the \( \alpha_1 \) phases increases, the magnetostatic interactions decrease. Alnico without Ti forms wider \( \alpha_1 \) phases that are closer to each other, as in Alnico 5, or poorly connected \( \alpha_1 \) phases as in sample B, because of the lack of Cu-Ni-rich bridges. Therefore, the presence or absence of bridges, which is influenced by Ti, plays an important role in the coercivity.

**4.5.6 Composition distribution in the Cu-Ni-rich bridges**

Table 5 illustrates the distributions of the main elements in the Cu-Ni-rich bridges according to the line scans in Figures 3 and 4. Note that the Cu, Co, Fe and Ti distributions are the same in both bridge types. The Cu concentration has a maximum at the center and decreases radially outward, whereas Co, Fe and Ti have the opposite distribution. In the Cu>Ni bridges, the Ni distribution is the same as Co, Fe and Ti, and the opposite of Cu, whereas in the Ni>Cu bridges, the Ni is relatively constant as compared to the other constituents. The Al distribution is affected by Ni and is opposite of Cu in the Cu>Ni bridges and fairly uniform in Ni>Cu bridges. It is possible that Cu is repelled from the Fe and Co in \( \alpha_1 \), and that Ti mixes more readily with Ni and Al, but not Cu, based on \( \Delta H^{mix} \). Another explanation for the maximum Cu concentration at the bridge center is that Cu and Ni are fcc, so they tend to form an fcc phase at the center of the bridges to be separated from the bcc matrix.
4.6 Summary

The micro- and nanostructures of Alnico alloys with and without Ti, samples A and B, respectively, have been compared to assess the role of Ti on the formation of Cu-rich bridges and the effect of Cu-rich bridges on the microstructure and magnetic properties of Alnico. For sample A with Ti, a typical chessboard-like morphology with detached $\alpha_1$ phases, separated by the Cu-rich bridges, was observed. For sample B, a maze-like morphology with connected $\alpha_1$ phases was observed. EDS studies of sample A showed the presence of a Ni-Cu loop and two types of bridges, Cu>Ni and Ni>Cu. The elemental distribution of the bridges was interpreted based on the enthalpy of mixing, $\Delta H_{\text{mix}}$. Ti facilitates the formation of the Cu-Ni bridges primarily by inhibiting diffusion.

The formation of the chess-board morphology was explained via two classical theories. Cu-bridges are formed to decrease the elastic energy, and the bridge orientation is determined consistent with Cahn’s theory [15, 23], since less ferromagnetic elements remain after spinodal decomposition, even though the initial stage of spinodal decomposition is more consistent with the Neel-Ziljtra theory [5]. Furthermore, in sample A, the coarsening and thus the shape and size of $\alpha_1$ phases is strongly influenced by a pinning effect due to the presence of the bridges, whereas the absence of bridges in sample B in a more disordered, maze-like distribution of the $\alpha_1$ and $\alpha_2$ phases. Based on similarities between the compositions of sample A and Alnico 8 and 9, and sample B and Alnico 5-7, these results can be extended to these commercial alloys.

4.7 Acknowledgements

This work was supported by the Air Force Office of Scientific Research under Contract No. FA9550-12-1-0440. The authors acknowledge the use of the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and
the National Science Foundation.

4.8 List of Figures

Figure 4.1 HAADF images along [001], and corresponding EDS maps of Fe (red), Co (green), Ni (dark blue), Al (light blue), Ti (purple), Cu (yellow), Hf (Orange) and Nb (Green), for (a) sample A and (b) sample B. The concentration of Fe increases along the arrow in (a) with the decreasing distance between adjacent $\alpha_1$. For the specific $\alpha_1$ phase, $s$, there is only one bridge on the left, right and bottom sides with round edges while two bridges on the top side with the square edge.
Figure 4.2 Higher resolution analysis of the α1 phases in Sample A along [001]. (a) HAADF image and EDS map, with Fe (red), Co (green), Ni (dark blue), Al (light blue), Ti (purple), Cu (yellow), Hf (Orange), and Nb (Green), (b) EDS line scans from the α1 to α2 phase, and (c) EDS line scan at higher resolution.
Figure 4.3 High resolution analysis of a Cu>Ni bridge. (a) HAADF image, (b) line scans along vertical direction, (c) line scans along horizontal direction and (d) corresponding EDS maps of Fe (red), Co (green), Ni (dark blue), Al (light blue), Ti (purple), Cu (yellow), Hf (Orange) and Nb (Green) for the Cu bridge. The area inside the red circle is the region for quantitative analysis.
Figure 4.4 High resolution analysis of a Ni>Cu bridge. (a) HAADF image, (b) line scans along vertical direction, (c) line scans along horizontal direction and (d) corresponding EDS maps of Fe (red), Co (green), Ni (dark blue), Al (light blue), Ti (purple), Cu (yellow), Hf (Orange) and Nb (Green) for the Cu bridge. The area inside the red circle is the region for quantitative analysis.
Figure 4.5 Schematic illustration of the three-dimensional model (and corresponding two-dimensional transverse projection) showing the process of Cu-Ni-rich bridge formation. (a, a’) initial spherical $\alpha_1$ phases having just nucleated, (b, b’) the Ni-Cu loops form when the initial spherical $\alpha_1$ phases are elongating and coarsening, (c, c’) when the distance between the adjacent Ni-Cu loops is sufficiently small, Cu-Ni-rich bridges form (the yellow arrows represent the diffusion directions), and (d) the final morphology of spinodal decomposition.
Figure 4.6 Schematic illustration comparing the coarsening processes of Alnico with bridges (a, b, c and d) and without bridges (e, f and g). Note that the lengths of the black arrows represent the coarsening rates. In (a) and (e), the minimum distance between adjacent $\alpha_1$ phases just reaches the critical size ($s$) and the bridges nucleate in (a) but not in (e). In this situation, the diameter of $\alpha_1$ phases is $D_1$. (b) and (f) show that the size of $\alpha_1$ phases enlarge from $D_1$ to $D_2$. (b) shows that $\alpha_1$ phases coarsen from round to square-shaped with rounded corners because of the restrictions from the bridges, whereas in (f) $\alpha_1$ phases connect because of the absence of any restrictions. (c) and (g) show further coarsening of $\alpha_1$ phases to $D_3$. In (c) a two-bridge structure further restricts the coarsening of $\alpha_1$ phases when the distance between adjacent $\alpha_1$ phases just reaches the critical size ($s'$), whereas in (g) the $\alpha_1$ phases overlap. Lastly, in (d), the coalescence of the $\alpha_1$ phases occurs even with the bridges, but this requires much longer thermomagnetic treatment.
Table 4.5 Distributions of the main elements in the Cu-Ni-rich bridges

<table>
<thead>
<tr>
<th>Table. 5</th>
<th>Cu</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
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</table>
4.9 References cited


Appendix A

Figure 4.7 HAADF images of sample A(a) and B(b) along [001] direction
Appendix B

Figure 4.8 HR HAADF images and ball-and-stick model of $\alpha_1$ and $\alpha_2$ phases and Cu bridge in Alnico along [001] direction
Figure 4.8 HR HAADF images and ball-and-stick model of $\alpha_1$ and $\alpha_2$ phases and Cu bridge in Alnico along [001] direction (Continued)
Figure 4.9 HR HAADF images and ball-and-stick model of $\alpha_1$ and $\alpha_2$ phases in Alnico along [011].
Figure 4.10 HR HAADF images and ball-and-stick model of $\alpha_1$ and $\alpha_2$ phases in Alnico along [111].
Figure 4.11 EDS maps of Alnico along [011] direction
Figure 4.12 EDS maps of Alnico along [111] direction
Chapter 5 On the Evolution of Cu-Ni-rich Bridges of Alnico Alloys with Tempering


5.1 Abstract:
Tempering is a critical step in Alnico alloy processing, yet the effects of tempering on microstructure have not been well studied. Here we report these effects, and in particular the effects on the Cu-Ni bridges. Energy-dispersive X-ray spectroscopy (EDS) maps and line scans show that tempering changes the elemental distribution in the Cu-Ni bridges, but not the morphology and distribution of Cu-bridges. The Cu concentration in the Cu-Ni bridges increases after tempering while other element concentrations decrease, especially Ni and Al. Furthermore, tempering sharpens the Cu bridge boundaries. These effects are primarily related to the large \(2C_{44}/(C_{11}-C_{12})\) ratio for Cu, largest of all elements in Alnico. In addition, the Ni-Cu loops around the \(\alpha_1\) phases become inconspicuous with tempering. The diffusion of Fe and Co to the \(\alpha_1\) phase during tempering, which increases the difference of saturation magnetization between the \(\alpha_1\) and \(\alpha_2\) phases, is observed by EDS. In summary, \(\alpha_1\), \(\alpha_2\) and Cu-bridges are concentrated with their major elements during tempering which improves the magnetic properties. The formation of these features formed through elemental diffusion is discussed via energy theories.

5.2 Introduction
Alnico alloys draw intensive attention because of their low cost, acceptable permanent magnetic properties and applicability to high temperature applications (~400 °C) [1]. Alnico alloys are composed mainly of Fe, Co, Ni, Al, Ti, Cu and Nb, and are prepared by sintering powders or
casting. The permanent magnetic properties of Alnico alloys are attributed to shape anisotropy; the rod-like ferromagnetic $\alpha_1$ phases, comprised mainly of Fe and Co, are distributed periodically in the non-ferromagnetic $\alpha_2$ matrix, comprised mainly of Ni, Al and Ti. This essential composite structure is achieved through spinodal decomposition. The $\alpha_1$ rods are formed with their axes of elongation parallel to the <100> direction, the easy magnetization direction. The final magnetic properties are obtained through two critical steps, thermomagnetic treatment at 800-850 °C for 10-20 minutes and low temperature tempering at 550-650 °C for 10-20 hours [2].

Spinodal decomposition occurs during thermomagnetic treatment, and the temperature and time of this step have been studied to optimize the size and shape of the $\alpha_1$ phase formed [1, 3-15]. Additionally, the contents of critical elements, such as Co and Ti, were varied to improve the permanent magnetic properties and thermal stability of Alnico alloys [13]. Of the recent studies, Zhou et al. [16] reported the Cu-rich bridges might play an important role in the final magnetic properties as spacers between adjacent $\alpha_1$ phases. Subsequently, we reported recently the formation and evolution of Cu-rich bridges during thermomagnetic treatment[17]. We showed that Ti fosters the conditions resulting in the formation of Cu-Ni-rich bridges, which are precipitated to decrease the elastic energy. The coarsening and thus the shape and size of $\alpha_1$ phases are influenced strongly by a pinning effect due to the presence of the bridges. The Cu-Ni bridges are distributed non-uniformly and the distribution depends on the edges and shape of $\alpha_1$ phases. Furthermore, Ni-Cu loops are observed around the $\alpha_1$ phases, and direct contact between the Cu-Ni-rich bridges and Ni-Cu loops is observed rather than direct contact between the bridges and the $\alpha_1$ phases. Two types of Cu-Ni-rich bridges are observed, those with more Cu than Ni, and those with more Ni than Cu.
Tempering is the other critical step for final shape anisotropy, yet it has drawn much less attention. This is partly because the shape and size of the $\alpha_1$ phase in Alnico is well developed during the thermomagnetic treatment, and no microstructural changes were observed during low temperature tempering with the microscopy available at the time of the earlier studies. Therefore, the underlying mechanism of the effects of temperature on Alnico magnetic properties remains unclear. Especially, when the Cu-Ni bridges were observed [16, 17], it was not clear whether the Cu-Ni bridges change during tempering, affecting the final magnetic properties. In this paper, high magnification energy-dispersive X-ray spectroscopy (EDS) is used to observe microstructural changes during tempering, including the evolution of Cu-Ni bridges and the subtle but important changes in the distribution of atoms between the phases and bridges.

5.3 Experimental procedure

Bulk samples (wt%: Fe32.3-Co36.9-Ni13.5-Al7.2-Ti4.1-Hf2.1-Cu3.0-Nb0.9) were prepared in a partial pressure of argon by non-consumable electrode arc melting. A Ti button was melted before each sample to getter any residual oxygen. Bulk elements (purity>99%) were melted on a water-cooled copper hearth and then flipped and remelted at least thrice to ensure the elements were well mixed. Samples were drop cast into a water-cooled 3-mm-diameter cylindrical copper mold and cut into 3 mm diameter by 3 mm long cylinders. The as-cast samples were heat treated with typical procedures for Alnico. First, the samples were solutionized at 1250 °C followed by water quenching. Then the samples were thermomagnetically treated at 800 °C for 10 minutes in a 3 T magnetic field along the cylindrical axis. The aim of this work is to compare the difference in microstructures and magnetic properties of samples before and after tempering, so sample A is untempered and sample B is tempered at 650 °C for 4 hours, 600 °C for 6 hours, and finally 550
°C for 10 hours. Note that multi-step tempering improves the magnetic properties more effectively than one step tempering [18].

Magnetization hysteresis measurements were performed in a Quantum Design superconducting quantum interference device (SQUID) magnetometer by sweeping the magnetic field from -3 T to 3 T at room temperature. The coercive magnetic field ($H_c$), remanent field ($B_r$) and the maximum of energy product ($BH_{max}$) are extracted from the magnetization hysteresis.

Structural and compositional properties were analyzed via transmission electron microscopy (TEM). The TEM foil (rectangular, length ~ 20 μm x width ~ 10 μm) was prepared using a focused ion beam (FIB) lift-out technique in a FEI Quanta 3D FEG dual-beam instrument in the transverse orientation. $α_1$ phases form along the magnetic field direction during thermomagnetic treatment, the [001] direction, so the samples are observed along the magnetic field direction, i.e. the transverse orientation. The FIB cut specimens were first thinned by Ga+ ions at 30 keV, followed by 5 keV for final thinning. EDS analysis was performed in an aberration-corrected FEI Titan G2 microscope with an X-FEG source and ChemiSTEM technology, operated in the scanning transmission electron microscopy (STEM) mode at 200 keV. The electron beam probe size is 0.1 nm in a convergent angle of 21 mrad. EDS maps of regions of interest were acquired for 900 s. An annular dark-field detector with 100 mm camera length, corresponding to a collection angle of 77-300 mrad, was used to obtain STEM high-angle annular dark-field (HAADF) images. The image contrast in HAADF is proportional to the atomic number (Z), the material density or the sample thickness, enabling us to detect different phases in the microstructure[19].
5.4 Results

5.4.1 Magnetic properties

Table 1 summarizes the magnetic behavior of the two samples, A before tempering and B after tempering, including $H_c$, $B_r$ and $(BH)_{max}$. With tempering, $H_c$ increases from 1100 Oe (A) to 1300 Oe (B). $B_r$ is relatively low, due to the random grain orientations. If directionally solidified, $B_r$ increases. With this change, $(BH)_{max}$ becomes similar to Alnico 9 [16].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$H_c$ (Oe)</th>
<th>$B_r$ (T)</th>
<th>$(BH)_{max}$ (kJ/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1100</td>
<td>0.53</td>
<td>12</td>
</tr>
<tr>
<td>B</td>
<td>1300</td>
<td>0.58</td>
<td>16</td>
</tr>
</tbody>
</table>

5.4.2 Microstructure

Figure 1 shows HAADF images of samples A and B observed along the [001] direction, parallel to the magnetic field during thermomagnetic treatment. Three distinguishable areas are observed in each sample: the hard magnetic $\alpha_1$ phase appears as bright areas of primarily Fe and Co, the soft magnetic $\alpha_2$ phase is seen as a dark matrix of primarily Ni and Al, and the Cu-rich areas, which are small, bright circles appearing as precipitates bridging adjacent $\alpha_1$ phases. The average size of the $\alpha_1$ phase in samples A and B are same, about 26 +/- 4 nm. The distribution of the Cu-rich bridges is non-uniform and depends on the edges and shape of the $\alpha_1$ phases[17]. No obvious microstructural changes due to tempering are observed at this magnification.

Figure 2 shows high magnification HAADF images and the corresponding EDS compositional maps of samples A and B, focusing on the $\alpha_1$ phase. Samples A and B have some common features. The main element of $\alpha_1$, Fe, has a larger contrast difference between $\alpha_1$ and $\alpha_2$ than Co; similarly, the main element of $\alpha_2$, Ni, has a larger contrast difference between $\alpha_1$ and $\alpha_2$ than Al.
and Ti. Significant differences between samples A and B are also observed. There are no obvious Ni-Cu loops around the \( \alpha_1 \) phases in B, whereas they are present in A. The Cu contrast between \( \alpha_1 \) and \( \alpha_2 \) in B is smaller than in A, and for the bridge areas, Cu has a larger contrast between the bridges and \( \alpha_2 \) in B than in A. Co and Ti form sharper bridges boundaries in B than in A, and Ni and Al are rare in the bridges in B but are the same as in \( \alpha_2 \) in A. Note that the Hf distributions are not considered because the major peaks of Hf and Cu overlap in the EDS spectrum. Electron energy loss spectroscopy (EELS) is also ineffective for verifying the Hf distribution because the composition is too low.

Figure 3 shows EDS line scans from the \( \alpha_1 \) to the \( \alpha_2 \) phases. Although the compositions of different elements cannot be compared through the line scan intensities, spatial variations of the concentration of a specific element is revealed. The line scans shows that Fe has a larger intensity difference between \( \alpha_1 \) and \( \alpha_2 \) than Co, and Ni has a larger intensity difference between \( \alpha_1 \) and \( \alpha_2 \) than Al and Ti in both A and B. This is the evidence for the common features, but it does not reveal the possible changes of elemental distributions in \( \alpha_1 \) and \( \alpha_2 \) due to tempering. Therefore, quantitative EDS in Table 2 summarizes elemental compositions in \( \alpha_1 \) and \( \alpha_2 \) phases before and after tempering. For the different features, the small bumps in the Ni and Cu curves in the line scans in B (Figure 3(c,d)), compared to the peaks of Ni and Cu in A (Figure 3(a,b)), is the evidence that the Ni-Cu loops disappear due to tempering. The contrast in Cu between \( \alpha_1 \) and \( \alpha_2 \) before and after tempering cannot be differentiated in the line scans due to the low intensity difference.
Table 5.2 Compositions of $\alpha_1$ and $\alpha_2$ in untempered (A) and tempered (B) samples

<table>
<thead>
<tr>
<th>Elements</th>
<th>Wt %</th>
<th>Untempered A</th>
<th>Tempered B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\alpha_1$</td>
<td>$\alpha_2$</td>
</tr>
<tr>
<td>Fe</td>
<td>32.3</td>
<td>46.6</td>
<td>12.6</td>
</tr>
<tr>
<td>Co</td>
<td>36.9</td>
<td>41.8</td>
<td>37.2</td>
</tr>
<tr>
<td>Ni</td>
<td>13.5</td>
<td>6.1</td>
<td>22.2</td>
</tr>
<tr>
<td>Al</td>
<td>7.2</td>
<td>2.8</td>
<td>9.5</td>
</tr>
<tr>
<td>Ti</td>
<td>4.1</td>
<td>0.9</td>
<td>9.2</td>
</tr>
<tr>
<td>Cu</td>
<td>3.0</td>
<td>1.4</td>
<td>3.5</td>
</tr>
<tr>
<td>Hf</td>
<td>2.1</td>
<td>0.1</td>
<td>2.6</td>
</tr>
<tr>
<td>Nb</td>
<td>0.9</td>
<td>0.3</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Quantitative EDS in Table 2 summarizes the compositions of each element before and after tempering. Shown are the average values with identically sized areas in each phase along the [001] direction. The TEM foil thickness ensures only one layer of each phase exists along the [001] direction. Table 2 shows that tempering increases the Fe and Co in the $\alpha_1$ phase and the Al, Ni and Ti in the $\alpha_2$ phase, so the diffusion direction is from $\alpha_2$ to $\alpha_1$ for Fe and Co and from $\alpha_1$ to $\alpha_2$, for Ni, Al and Ti.

Figure 4 the HAADF images and the corresponding EDS line scans at higher magnification to study changes in the Cu-Ni bridges due to tempering. Figure 5 shows the corresponding EDS elemental maps. Again, some features are similar; both samples have similar bridge size and the bridges in both have one preferred direction, as the long axis lies along the connection of two $\alpha_1$ phases in Figure 4(a, b). Furthermore, the bridges do not contact with two adjacent $\alpha_1$ phases, but exhibit gaps with a high concentration of Ni between $\alpha_1$ and the bridges, Figure 4(c,d). There are also some clear differences between samples A and B shown in the line scans along the [100] direction. In the horizontal direction, Ni has two very small peaks along the bridge boundary in B (Figure 4f) whereas there are no obvious Ni peaks in that area of sample A (Figure 4e). In both
directions, the Cu concentrations increased significantly with tempering (Figure 4(c-f)). The EDS maps of Cu-Ni bridges shown in Figure 5 also show changes due to tempering. In B, relative to A, the Cu contrast between bridges and $\alpha_2$ is large and the bridge boundaries are sharper in Co and Ti, and the Ni and Al distributions are smaller.

5.5 Discussion

The similarity of HAADF images of A and B in Figure 1 indicates that the size and distribution of Cu bridges, formed during the thermomagnetic treatment, and the $\alpha_1$ and $\alpha_2$ phases, did not change with tempering. Therefore, the improvement of magnetic properties is due to changes in the morphology or elemental distributions observable only at higher magnification. These were shown in Figures 2-5 via the EDS maps and line scans. The disappearance of the Ni-Cu loops, smaller Cu contrast between $\alpha_1$ and $\alpha_2$, and larger Cu contrast between bridges and $\alpha_2$ in B indicate that Cu diffuses from $\alpha_2$ to the bridges during tempering. The larger intensity difference between Cu and other elements in the bridge area, the well-defined Ni peaks around the bridge in sample B (Figure 4), compared with the smaller intensity difference between Cu and other elements and the undefined Ni peaks in sample A, indicate that tempering facilitates the growth of Cu bridges and the diffusion of Ni from bridges to the bridge boundaries. The small distributions of Ni and Al in the bridges in B (Figure 5) compared to the almost uniform distributions of those in A also provide evidence for these features.

The evolution of Cu-Ni-rich bridges during the tempering needs to be discussed based on these new features in the context of the recent results on the formation and evolution of Cu-Ni-rich bridges during the thermomagnetic treatment[17]. At the stage of the thermomagnetic treatment, Cu-Ni loops form because it is thermodynamically favorable to concentrate Cu in $\alpha_2$ at the $\alpha_1$ boundary and because Ni has high solubility in Cu. This also promotes the coarsening of $\alpha_1$ and
spinodal decomposition. When the samples are tempered at 550 °C - 650 °C, the temperature is not sufficiently high to activate the spinodal decomposition, so the α₁ phases cannot elongate, coarsen or coalesce, and the formation of Cu loops is not thermodynamically favored. Thus, the Cu and Ni loops disappear via diffusion from the loops to α₂ during tempering. During the thermomagnetic treatment, when the distance between adjacent α₁ phases is small enough with the coarsening of α₁, Cu and Ni in α₂ diffuse to the bridges to decrease the elastic energy[17] and Cu-Ni bridges form. According to Cahn’s theory, if \(2C_{44}-C_{11}+C_{12}>0\), the waves parallel to the \(<100>\) directions in the \([20]\) planes in cubic crystals are favored because the elastic coefficient \(Y\) is smallest \([17, 21, 22]\). For both Cu and Ni, \(2C_{44}/(C_{11}-C_{12})>1\), which is even larger than Fe, so Cu and Ni have the lowest elastic energy in \(<100>\) and decompose most rapidly with this orientation with the smallest wavelength. During tempering, although no magnetic field is applied, the intermediate temperature promotes Cu diffusion from α₂ to the bridges to decrease the elastic energy, because the growth of Cu-Ni bridges is dominated by elastic energy rather than magnetic energy[17]. The sizes of α₁, α₂ and bridges are fixed during thermomagnetic treatment as shown in Figure 1, so the Cu concentration in the bridges increases, as shown in Figure 4, with decreasing Cu concentration in Ni-Cu loops and α₂ (Figures 2-3). One special feature is the high ratio of the Cu concentration to the Ni concentration after tempering (Figure 4), as compared to their relatively low ratio after thermomagnetic treatment. One possible reason is the ratio of \(2C_{44}/(C_{11}-C_{12})\) for Cu (3.19) is larger than for Ni (2.63)[17], so Cu is more favorable than Ni and dominates in the bridges after the lengthy tempering. The Cu atoms concentrating in the bridges “squeeze” other elements out, resulting in the smaller distribution of Ni and Al in the bridges, and the sharper bridge boundaries in Co and Ti in the EDS maps in Figure 5. The very small Ni peaks in Figure 4(d,f) are due to its thermodynamically
favorable concentration in the bridges, even though Cu atoms are squeezing them out. In previous work on thermomagnetic treatment, we found two types of Cu-Ni bridges, those with more Cu than Ni and those with more Ni than Cu. Here we found only one type of bridge, with very high Cu concentration, after tempering, which may be attributed to this predomination of Cu atoms. These bridges with very high Cu concentration and sharp boundaries may be one reason for the better magnetic properties after tempering, because the bridges contain less magnetic elements (Ni and Co) and increase the difference of saturation magnetization between bridges and the other two main phases. This interpretation, however, remains speculative.

5.6 Conclusion
In this paper, the microstructures of Alnico alloys before and after tempering were compared. Tempering changes the elemental distribution in Cu-rich bridges rather than the morphology and size of these bridges. The tremendous increment of Cu concentration in the bridges indicates that tempering facilitates the growth of the Cu bridges and supplies us the information to discuss the effect of tempering on the Cu-Ni bridges. The predominance of Cu in the bridges is attributed to the largest ratio of $2C_{4d}/(C_{11}-C_{12})$ of all elements present. The loops around $\alpha_1$ become obscure with diffusion during tempering. Furthermore, both the $\alpha_1$ and $\alpha_2$ phases reach their final equilibrium compositions with a maximum saturation magnetic polarization by diffusion during tempering. Although the compositional changes are not large, they are distinguishable and provide evidence for the underlying mechanisms by which tempering improves the magnetic properties of Alnico.

5.7 Acknowledgements
This work was supported by the Air Force Office of Scientific Research under Contract No. FA9550-12-1-0440. The authors acknowledge the use of the Analytical Instrumentation Facility
(AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation.

5.8 List of Figures

![Figure 5.1](image)

Figure 5.1: HAADF images along [001] for (a) untempered sample A and (b) tempered sample B.
Figure 5.2: High-resolution HAADF images and EDS maps of the α₁ phases in (a) sample A and (b) sample B along [001]. Note: Fe (red), Co (green), Ni (dark blue), Al (light blue), Ti (purple), Cu (yellow), Hf (Orange), and Nb (Green). Note that (a,b) are from[17]
Figure 5.3: Low and high resolution EDS line scans from the $\alpha_1$ to $\alpha_2$ phase for (a,b) sample A and (c,d) sample B. Note that (a,b) are from[17]
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Figure 5.5: EDS maps of Cu bridges, with Fe (red), Co (green), Ni (dark blue), Al (light blue), Ti (purple), Cu (yellow), Hf (Orange), and Nb (Green) for (a) sample A and (b) sample B.

References cited

Chapter 6 Co-Authoried Publications

Full papers are not included in the thesis

6.1 A Combined Computational-experimental Approach to Design of High-Intensity Permanent Magnetic Alloys

Rajesh Jha, George S Dulikravich, Min Fan, Justin Schwartz, Carl Koch, Igor N Egorov, Carlo Poloni


6.1.1 Abstract

AlNiCo magnets are permanent magnetic alloys based on the Al-Ni-Co-Fe system. In the present work, Sobol’s algorithm was used to randomly generate alloy compositions so that they are properly distributed in the variable space. The final 80 candidate alloys were selected after examining the phase equilibria and magnetic property predicted by thermodynamic database Factsage™ in the desired temperature of exposure. The magnets were synthesized and tested for desired properties of interest. The various properties were fitted by response surfaces generated by Radial Basis Function module available in commercial optimizer, “modeFRONTIER”. It was followed by optimization for predicting alloy composition for improved properties. This task was simultaneously performed by another commercial optimizer, IOSO. The 5 Pareto optimized candidate alloys were synthesized and tested. One of the optimized candidate alloys dominated the initial 80 candidate alloys in most of the properties. This proves the efficacy of response surface methodology in optimizing the desired properties while minimizing the time and cost in synthesizing the alloys by random experimentation.


Accepted by Journal of Alloys and Compounds, 2016

6.2.1 Abstract

A multi-dimensional random number generation algorithm was used to distribute chemical concentrations of each of the alloying elements in the candidate alloys as uniformly as possible while maintaining the prescribed bounds on the minimum and maximum allowable values for the concentration of each of the alloying elements. The generated candidate alloy compositions were then examined for phase equilibria and associated magnetic properties using a thermodynamic database in the desired temperature range. These initial candidate alloys were manufactured, synthesized and tested for desired properties. Then, the experimentally obtained values of the properties were fitted with a multi-dimensional response surface. The desired properties were treated as objectives and were extremized simultaneously by utilizing a multi-objective optimization algorithm that optimized the concentrations of each of the alloying elements. This task was also performed by another conceptually different response surface and optimization algorithm for double-checking the results. A few of the best predicted Pareto optimal alloy compositions were then manufactured, synthesized and tested to evaluate their macroscopic properties. Several of these Pareto optimized alloys outperformed most of the candidate alloys on most of the objectives. This proves the efficacy of the combined meta-modeling and experimental approach in design optimization of the alloys. A sensitivity analysis of each of the alloying elements was also performed to determine which of the alloying elements contributes
the least to the desired macroscopic properties of the alloy. These elements can then be replaced with other candidate alloying elements such as not-so-rare earth elements.
6.3 Structure and Magnetic Properties of a Multi-principal Element Ni-Fe-Cr-Co-Zn-Mn Alloy

AJ Zaddach, C Niu, AA Oni, M Fan, James Michael LeBeau, Douglas Lee Irving, Carl C Koch


6.3.1 Abstract

A nanocrystalline alloy with a nominal composition of Ni$_{20}$Fe$_{20}$Cr$_{20}$Co$_{20}$Zn$_{15}$Mn$_{5}$ was produced by mechanical alloying and processed using annealing treatments between 450 and 600 °C for lengths from 0.5 to 4 h. Analysis was conducted using x-ray diffraction, transmission electron microscopy, magnetometry, and first-principles calculations. Despite designing the alloy using empirical high-entropy alloy guidelines, it was found to precipitate numerous phases after annealing. These precipitates included a magnetic phase, α-FeCo, which, after the optimal heat treatment conditions of 1 h at 500 °C, resulted in an alloy with reasonably good hard magnetic properties. The effect of annealing temperature and time on the microstructure and magnetic properties are discussed, as well as the likely mechanisms that cause the microstructure development.
Chapter 7 Summary and Suggestions for Future Works

7.1 Summary
This thesis research focuses on the formation and evolution of the Cu-rich bridges in the Alnico alloys during the thermomagnetic treatment and tempering. Cu-rich bridges, discovered in 2013, may be the main reason for the special microstructure of Alnico 8-type alloys with superior magnetic properties. The discussion about the mechanism of the formation and evolution of Cu-rich bridges could be a pioneering work to improve the researchers’ understanding about the Alnico alloys and provide some help to future optimization of Alnico alloys containing Cu-bridges.

Chapter 4 focuses on the thermomagnetic treatment. We report on the effects of Ti on the Alnico microstructure and nanostructure, and the corresponding influence on magnetic properties. We show that Ti fosters the conditions resulting in the formation of Cu-Ni-rich bridges in the $\alpha_2$ phases between the $\alpha_1$ phases. For Alnico containing Ti, a typical chessboard-like morphology with Cu-Ni-rich bridges is observed, whereas in the absence of Ti, the $\alpha_1$ phases connect to each other readily, especially with a high Co concentration, and a maze-like morphology with Cu-rich plate precipitates rather than Cu-rich bridges is observed. Furthermore, in Alnico containing Ti, an inhomogeneous distribution of Ni is found in the $\alpha_2$ phases, including loops with high Ni concentration surrounding the $\alpha_1$ phase, and high concentrations in the bridges as well. An increase in the Cu concentration is also observed in the loops around the $\alpha_1$ phases (Ni-Cu loops), and direct contact between the Cu-Ni-rich bridges and Ni-Cu loops is observed in lieu of direct contact between the bridges and the $\alpha_1$ phases. We also find that the bridges are not perfectly round but ellipsoidal, with the long axis along the connection of two adjacent $\alpha_1$ phases. Energy-dispersive X-ray spectroscopy line scans of the bridges shows that two types of Cu-Ni-rich
bridges exist: those with more Cu than Ni, and those with more Ni than Cu. A three-dimensional model is presented that explains the conditions and process of bridge formation, consistent with the observed composition distributions.

Chapter 5 focuses on the tempering. Tempering is a significant procedure for Alnico alloy preparation. Here we report the effect of tempering on the microstructure evolution of Cu-Ni bridges of Alnico alloys. Energy-dispersive X-ray spectroscopy (EDS) maps and line scans show that tempering can change the elemental distribution in the Cu-Ni bridges, but not the morphology and distribution of Cu-bridges. Cu concentration in the Cu-Ni bridges increases after the tempering while the other elements concentrations decrease, especially for Ni and Al. The boundary of Cu bridges becomes sharper with tempering. The possible reason for these features is the largest ratio of $2C_{4d}/(C_{11}-C_{12})$ of Cu. Besides, Ni-Cu loop around $\alpha_1$ phase becomes inconspicuous with the tempering. The diffusion of Fe & Co to $\alpha_1$ phase during the tempering, which increases the difference of saturation magnetization between $\alpha_1$ and $\alpha_2$ phases, is also observed by EDS. In a word, $\alpha_1$, $\alpha_2$ and Cu-bridges are concentrated with its major elements during the tempering respectively, which leads to the improvement of magnetic properties of sample after tempering. The manners how these features formed through the elemental diffusion were discussed with the energy theories.

### 7.2 Suggestions for Future Works

According to the results obtained in this work, further studies are suggested as following:

1. The microstructure of Cu-rich bridges should be revealed to better understanding of these special precipitates. It cannot be completely exhibited due to the limitation of present TEM sample preparation technology. HR HAADF images in two directions of the sample are
necessary to explain the microstructure. Cu-rich bridges are needle-like with 100 nm in length and 5nm in diameter. We have already got the HR HAADF image along the long axis (i.e. [100] direction) of the Cu-bridge but we cannot prepare sample along the short axis (i.e. [010] direction), since the preparation of TEM sample with 5nm thickness is impossible with current technology. If the thickness is larger than 5nm, the sample examined with TEM will be overlap of the Cu-rich bridges and $\alpha_1$ phases. Of course, even though the sample with 5 nm thickness can be prepared in future, another challenge is how to locate the position of the Cu-rich bridges during the sample preparation in FIB.

(2) The effect of Cu content on the morphology and distribution of Cu-bridges should be researched. Comparison of the microstructures in a series of samples with varied Cu content is important to better understand the Cu-bridges. Optimized Cu-bridge with optimized Cu content may result in better magnetic properties. Besides, as mentioned in this thesis, Ti promotes the formation of the Cu-bridge, so the relationship between Cu and Ti is another interesting topic to be studied.

(3) Hf was not distinguished in this thesis due to the overlap of the peaks of Hf and Cu in EDS maps, and the low intensity in EELS with such small amount of Hf. Samples with higher Hf contents should be examined in EELS to check the actual distribution of Hf in Alnico alloys. If Hf has same distribution as Cu (as we observed in EDS), samples with Cu partially replaced by Hf should be conducted. Cu-Hf bridges may improve the performance of Alnico in high temperature application.

(4) In-situ TEM research will supply direct observation of spinodal decomposition, so it is very meaningful. Heating stage is available for most current TEM facilities but the magnetic field is difficult to be conducted without disturbing the beam. If the magnetic field can be conducted
with good beam, the experiment can be designed as following: First, TEM film of as-cast sample is solutionized at 1250 °C for 30 min and quenched in vacuum. The sample should be cut into film before solutionizing treatment to avoid any microstructure change or internal stress induced by the TEM sample preparation. Second, the sample is thermomagnetically treated at 800°C with magnetic field higher than 3000 Oe. The direction of magnetic field must be perpendicular to the film so the spinodal decomposition can be observed directly. The whole procedure of thermomagnetic treatment should be recorded as video. Some significant points of observations are: the formation of spherical $\alpha_1$ phase in the early stage, the time that Cu-bridges forms, the evolution of $\alpha_1$ phase and Cu-bridges. Third, the sample is tempered with designed temperatures and times to obtain the optimized magnetic properties. One concern about this experiment is that the film is so thin that the diffusion in the film may be different from that in the bulk sample and spinodal decomposition observed is not representative.

(5) The interconnectivity or fully isolation of $\alpha_1$ is very important to discuss the magnetic mechanism. This has not been observed yet because of the small volume of APT sample and the relatively low resolution of FIB 3D-rebuild compared with the size of $\alpha_1$ phase. Of course, it will be more challenge for Cu-bridges, because of the smaller size of Cu-bridge than $\alpha_1$. If the $\alpha_1$ has high percent interconnection, the magnetic reversal mechanism will not be single domain reversal mechanism.

(6) The cross-section shape of $\alpha_1$ phase can be round, oval or diamond. I have one speculation based on paper reviews, that is the samples containing $\alpha_1$ phase with sharp corners (diamond-like) have better coercivity. In this situation, the Cu-bridges site on the corner of the diamond $\alpha_1$ phase. Such $\alpha_1$ phase with diamond-like cross-section may have larger elastic energy in the corner, so Cu-bridges form earlier than $\alpha_1$ with round-like cross-section, and then the packing
fraction (volume fraction of $\alpha_1$) is optimized. As mentioned in Chapter 2, $H_c = p(1 - p)(N_c - N_a)(M_1 - M_2)^2/M_s$, the coercivity is maximum when both of the volume fraction of $\alpha_1$ and $\alpha_2$ are 0.5 in Figure 7.1. Or the diamond cross-section induces special magnetic reversal mechanism. The challenge is how to design the experiments so that the samples containing $\alpha_1$ phase with gradual changing cross-section can be prepared with gradual changing compostion.

![Diagram showing volume fraction of $\alpha_1$](image)

**Volume fraction of $\alpha_1$>0.5**  **Volume fraction of $\alpha_1$=0.5**

Figure 7.1 A schematic image of the microstructure of Alnico with different types of $\alpha_1$

All in all, there are still so many unclear mechanisms, and most of commercial Alnico alloys were discovered by the arbitrary experiments, so current commercial Alnico alloys only reach half of the theoretical magnetic properties. Fortunately, more and more research groups pay attention to the Alnico alloy and the mystery of Alnico will be revealed soon.