2014

Effects of heat treatment and processing modifications on microstructure in alnico 8H permanent magnet alloys for high temperature applications

Haley Marie Dillon
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/etd

Part of the Electromagnetics and Photonics Commons, and the Mechanics of Materials Commons

Recommended Citation
Dillon, Haley Marie, "Effects of heat treatment and processing modifications on microstructure in alnico 8H permanent magnet alloys for high temperature applications" (2014). Graduate Theses and Dissertations. 13867.
https://lib.dr.iastate.edu/etd/13867

This Thesis is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Effects of heat treatment and processing modifications on microstructure in alnico 8H permanent magnet alloys for high temperature applications

by

Haley M. Dillon

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

Major: Materials Science and Engineering

Program of Study Committee:
Iver Anderson, Major Professor
R. William McCallum
Kai-Ming Ho

Iowa State University
Ames, Iowa
2014
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF FIGURES</th>
<th>iv</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>viii</td>
</tr>
<tr>
<td>NOMENCLATURE</td>
<td>ix</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>x</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xi</td>
</tr>
</tbody>
</table>

## CHAPTER 1. INTRODUCTION
1.1 Purpose of Study
1.2 Objectives

## CHAPTER 2. LITERATURE REVIEW
2.1 Background to Magnet Terminology 4
2.2 History of Alnico Magnet Development 6
2.3 Alnico Phase Diagram
   2.3.1 Gamma Phase 9
2.4 Alnico Alloy Additions
   2.4.1 Co and Ni 10
   2.4.2 Al and Cu 10
   2.4.3 Gamma Stabilizers 11
   2.4.4 Alpha Stabilizers 11
   2.4.5 Ti, Nb, Si, S, Te, C, and Columnar Growth 12
2.5 Heat Treatment Effects on Microstructure 12
   2.5.1 Solutionizing Treatment 13
   2.5.2 Magnetic Anneal 14
      2.5.2.1 Other Field Effects 18
      2.5.2.2 Spinodal Refinement 18
   2.5.3 Draw 20
2.6 Processing Methods of Alnico Material 21

## CHAPTER 3. RELEVANT CHARACTERIZATION TECHNIQUES
3.1 Field Emission Scanning Electron Microscopy 23
3.2 Transmission Electron Microscopy 24
3.3 Energy Dispersive X-Ray Spectroscopy 25
3.4 X-Ray Diffraction 25
3.5 Hysteresis Graph 25

## CHAPTER 4. HEAT TREATMENT EFFECTS ON COMMERCIAL ALNICO
4.1 Spinodal Refinement 26
<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Experimental Methods</td>
<td>27</td>
</tr>
<tr>
<td>4.1.2 Results and Discussion</td>
<td>28</td>
</tr>
<tr>
<td>4.2 Commercial Microstructure of Alnico 8H</td>
<td>30</td>
</tr>
<tr>
<td>4.2.1 Experimental Methods</td>
<td>30</td>
</tr>
<tr>
<td>4.2.2 Results and Discussion</td>
<td>31</td>
</tr>
<tr>
<td>4.3 Modified Heat Treatments on Commercial Alnico 8H</td>
<td>36</td>
</tr>
<tr>
<td>4.3.1 Experimental Methods</td>
<td>36</td>
</tr>
<tr>
<td>4.3.2 Results and Discussion</td>
<td>37</td>
</tr>
<tr>
<td>4.4 Conclusions</td>
<td>46</td>
</tr>
<tr>
<td>CHAPTER 5. GAS ATOMIZED ALNICO</td>
<td>48</td>
</tr>
<tr>
<td>5.1 Hot Consolidation Methods</td>
<td>48</td>
</tr>
<tr>
<td>5.1.1 Experimental Methods</td>
<td>49</td>
</tr>
<tr>
<td>5.1.1.1 Hot Isostatic Pressing</td>
<td>49</td>
</tr>
<tr>
<td>5.1.1.2 Spark Plasma Sintering</td>
<td>49</td>
</tr>
<tr>
<td>5.1.2 Results and Discussion</td>
<td>50</td>
</tr>
<tr>
<td>5.1.2.1 Hot Isostatic Pressing</td>
<td>50</td>
</tr>
<tr>
<td>5.1.2.2 Spark Plasma Sintering</td>
<td>52</td>
</tr>
<tr>
<td>5.2 Modified Commercial Heat Treatments on HIP Samples</td>
<td>59</td>
</tr>
<tr>
<td>5.2.1 Experimental Methods</td>
<td>59</td>
</tr>
<tr>
<td>5.2.2 Results and Discussion</td>
<td>61</td>
</tr>
<tr>
<td>5.3 Conclusions</td>
<td>64</td>
</tr>
<tr>
<td>CHAPTER 6. GAMMA PHASE AVOIDANCE</td>
<td>66</td>
</tr>
<tr>
<td>6.1 Short Duration High Temperature Solutionization</td>
<td>66</td>
</tr>
<tr>
<td>6.1.1 Experimental Methods</td>
<td>66</td>
</tr>
<tr>
<td>6.1.2 Results and Discussion</td>
<td>67</td>
</tr>
<tr>
<td>6.2 Low Temperature Gamma Suppression</td>
<td>68</td>
</tr>
<tr>
<td>6.2.1 Experimental Methods</td>
<td>69</td>
</tr>
<tr>
<td>6.2.2 Results and Discussion</td>
<td>69</td>
</tr>
<tr>
<td>6.3 Conclusions</td>
<td>74</td>
</tr>
<tr>
<td>CHAPTER 7. CONCLUSIONS</td>
<td>75</td>
</tr>
<tr>
<td>7.1 Recommendations for Future Work</td>
<td>77</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>78</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

| Figure 2.1 | Example hysteresis graph with coercivity, remanence, saturation, and maximum energy product points labeled. | 5 |
| Figure 2.2 | “Calculated isopleth from the NiAl side to the Fe corner of the Fe-Ni-Al phase diagram”. | 8 |
| Figure 2.3 | Schematic of phase diagram for alnico magnets with magnet composition labeled. | 9 |
| Figure 2.4 | Electron micrographs of alnico 8 magnetically annealed for 10 minutes at a) 750°C, b) 780°C, c) 810°C, d) 830°C. The top row shows samples parallel to the magnetic field direction, the bottom row is perpendicular to the magnetic field. | 17 |
| Figure 2.5 | Chu and Fei TEM micrographs of 1.5, 3, 5, and 10 min magnetic anneals after 1250°C solutionizing and vacuum cool. Average size of particles in bottom left corner. | 19 |
| Figure 2.6 | Schematic of typical alnico 8 solutionization, magnetic anneal, and draw. | 21 |
| Figure 3.1 | Quanta FEI 250 field emission SEM equipped with an Oxford X-Max 85 mm² EDS detector that was used for microstructure analysis. | 23 |
| Figure 4.1 | Schematic of magnetic annealing setup with sliding tube furnace inside magnetic pole pieces. | 27 |
| Figure 4.2 | HAADF STEM images of a) 1250°C solutionized as-quenched sample, b) 1.5 minute 800°C magnetically annealed sample, c) 10 minute 800°C magnetically annealed sample. | 28 |
| Figure 4.3 | STEM images of a) Chu 10 minute 800°C magnetically annealed sample, and b) 1250°C solutionized as-quenched sample. Average particle size of 6 nm and 8 nm, respectively. | 29 |
| Figure 4.4 | FE-SEM images of (a)(b) as-cast alnico 8H, and (c)(d) cast and drawn (fully heat treated) alnico 8H. | 31 |
| Figure 4.5 | FE-SEM image of cast and drawn alnico 8H showing a) the spinodal structure near a grain boundary with γ phase, and b) the spinodal structure in an interior grain area, representative of the bulk spinodal | 32 |
Figure 4.6  FE-SEM image of as-sintered alnico 8H showing many large impurity phases and grain boundary γ phase.

Figure 4.7  FE-SEM image of sintered and drawn alnico 8H showing large oxides and large porous impurities and grain boundary γ phase. The “A” corresponds to an EDS point analysis of the medium gray particle.

Figure 4.8  EDS map of elements for Figure 4.7 showing Al₂O₃ and Ti particles, Fe-rich γ phase, and O, C, and Si enrichment of the porous impurity area.

Figure 4.9  FE-SEM images of a) as-sintered alnico 8H, and (b)(c)(d) sintered and drawn alnico 8H.

Figure 4.10  FE-SEM images of a) Sample 1, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 810°C for 1 hr, b) Sample 4, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 750°C for 1 hr, (c)(d) Sample 2, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 810°C for 1 hr, followed by 2 hr draw at 650°C. (e)(f) Sample 3, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 810°C for 1 hr, followed by 4 hr draw at 650°C.

Figure 4.11  FE-SEM images of (a)(b) Sample 6, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 750°C for 1 hr, followed by 4 hr draw at 650°C, c) Sample 7, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 700°C for 8 hr, d) Sample 8, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 650°C for 8 hr.

Figure 4.12  Hysteresis graph measurements of a) Samples 1, 2, and 3, 810°C MA series, b) Samples 4 and 6, 750°C MA series and c) Samples 9, 7, and 8, extended MA series.

Figure 4.13  Microstructure of a quaternary L₂₁ Heusler alloy containing increasing amounts of Co with γ phase precipitates (white phase). Images obtained by Ma, Yang, and Liu.

Figure 4.14  Compositions of spinodal decomposition phases α₁ (commercial BCC) and α₂ (commercial L₂₁) are compared to the composition of the γ and σ phases. γ composition displayed is measured after σ appears, which differs only slightly from composition before σ presence. Composition data was acquired by EDS from TEM analysis (Figure 4.16), γ and σ compositions are obtained from gas-atomized HIP consolidated alnico.
8H material, while $\alpha_1$ and $\alpha_2$ phase information was obtained from commercial material of the same type.

Figure 4.15 Composition of $\gamma$ before and after splitting into the lamellar morphology of $\gamma + \sigma$, along with composition of $\sigma$. All composition data was acquired by EDS from TEM analysis of gas-atomized HIP consolidated alnico 8H material.  

Figure 4.16 TEM EDS areas used for composition of $\gamma$ and $\sigma$ phases in Figures 4.14 and 4.15. Images courtesy of Lin Zhou.

Figure 5.1 FE-SEM image of <20 μm gas-atomized alnico 8H powders used for the HIP process at 1250°C.

Figure 5.2 FE-SEM image of 1250°C HIP consolidated sample using < 20 μm gas-atomized alnico 8H powders showing grain boundary $\gamma$ phase and grain size.

Figure 5.3 FE-SEM image of 1250°C HIP consolidated sample using < 20 μm gas-atomized alnico 8H powders showing $\gamma$ phase size and spinodal structure.

Figure 5.4 OIM of 1250°C HIP sample showing grain size and grain orientation. Colors correlate to grain alignment with a crystallographic axis, color legend on the left.

Figure 5.5 FE-SEM images of gas-atomized alnico 8H powders consolidated by 770°C SPS showing sample density and intercellular $\gamma$ and $\sigma$ phases.

Figure 5.6 FE-SEM images of gas-atomized alnico 8H powders consolidated by 740°C SPS showing sample density and intercellular $\gamma$ and $\sigma$ phases.

Figure 5.7 EDS linescan (in yellow) from a cross section of a 70 μm gas-atomized powder particle in the as-atomized state. Linescan data for Al (in red) corresponds to the position on the FE-SEM image below it.

Figure 5.8 EDS linescan data for other elements showing little to no change across cell boundaries. FE-SEM image of 770°C 5 min SPS sample showing $\gamma + \sigma$ growth at cell boundaries. ADZ spacing from EDS is roughly 7 μm, matching cell boundary spacing from SPS samples. ADZ width, ~2 μm, also corresponds to $\gamma + \sigma$ phase width in SPS samples. Images have been sized to match scale bars.

Figure 5.9 FE-SEM images of a) Sample 11, (etched), b) Sample 14, c) Sample 16, and d) Sample 17.
Figure 5.10  FE-SEM images of a) Sample 20, b) Sample 18, c) Sample 19, d) Sample 11, (etched), e) Sample 14, and f) Sample 16.

Figure 5.11  Hysteresis graph measurements of a) Samples 14 and 16, showing increased coercivity with a long draw and shorter MA time, b) Samples 11 and 14, showing significantly increase remanence and saturation after solutionization, c) Samples 10 and 15, showing benefits of solutionization and short MA time, d) Samples 16 and 17, difference between a one-step and two-step MA.

Figure 6.1  FE-SEM images of (a)(b) 5 minute 1250°C solutionized SPS sample, (c)(d) as-received 770°C SPS.

Figure 6.2  HAADF STEM image of sample 22, magnetically annealed at 650°C for 8 hr showing spinodal splitting with an average spacing of 5-7 nm. Images courtesy of Lin Zhou.

Figure 6.3  XRD powder data from a) Samples 21-25 and 28, and b) Samples 23, 26, and 27 showing very limited spinodal splitting at 650°C, but suppression of γ upon annealing at 810°C.

Figure 6.4  FE-SEM image of sample 23, 20 μm powder particle with a) largest contrast settings available in FE-SEM, and b) contrast greatly enhanced using ImageJ software. Beginnings of local composition fluctuations seem to be occurring at 810°C in some of the larger powders.

Figure 6.5  EDS linescan (in yellow) from a cross section of an 11 μm gas-atomized powder particle in the as-atomized state, sample 21. Powders were cold isostatic pressed in Al for cross sectioning purposes, so the particle edge effects in the linescan are not accurate.

Figure 6.6  FE-SEM of sample 17, MA 1 hr 650°C, MA 10 min 810°C, drawn 4 hr 650°C, 10 hr 590°C, showing very small γ+σ growth off an oxide particle.
LIST OF TABLES

Table 2.1  Summary of MMPA Standard 0100-00 compositions and magnetic properties for current cast alnico grades (remaining composition Fe, <2% other additions). ........................................... 7

Table 4.1  Summary of MMPA Standard 0100-00 compositions and magnetic properties for alnico grades used within the study (remaining composition Fe, <2% Si, Nb, and S). ........................................... 31

Table 4.2  Heat treatment history of each commercial alnico 8H sample once it was received. Samples were received in a fully heat treated state. ........................................... 37

Table 5.1  Heat treatment history of each gas-atomized alnico 8H sample after the 1250°C HIP process. ........................................... 60

Table 5.2  FE-SEM of sample 17, MA 1 hr 650°C, MA 10 min 810°C, drawn 4 hr 650°C, 10 hr 590°C, showing very small γ+σ growth off an oxide particle ........................................... 61

Table 6.1  Heat treatment history of each gas-atomized alnico 8H 3-12 μm powder sample. ........................................... 69
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>High temperature B2 single phase</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>Fe-Co rich phase spinodally decomposed from $\alpha$, B2 structure</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>Ni-Al rich phase spinodally decomposed from $\alpha$, L2$_1$ structure</td>
</tr>
<tr>
<td>$\alpha_r$</td>
<td>Low temperature allotropic transformation of $\gamma$ phase to bcc structure</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Harmful Fe rich grain boundary phase, fcc structure</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Fe$_2$Ti Laves-type phase, hcp structure</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Harmful Co-Ti-Al rich grain boundary phase, possible L2$_1$ structure</td>
</tr>
<tr>
<td>ADZ</td>
<td>Aluminum depleted zones</td>
</tr>
<tr>
<td>Draw</td>
<td>Long time (4-48 hrs) low temperature anneal</td>
</tr>
<tr>
<td>HIP</td>
<td>Hot isostatic pressing</td>
</tr>
<tr>
<td>MA</td>
<td>Magnetic anneal</td>
</tr>
<tr>
<td>RE</td>
<td>Rare earth</td>
</tr>
<tr>
<td>SPS</td>
<td>Spark plasma sintering</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

I would like to thank my graduate advisor and committee chair, Iver Anderson, and my committee members, Bill McCallum, and Kai-Ming Ho for their guidance throughout my research.

I would also like to express my sincere appreciation to my colleagues and collaborators Andriy Palasyuk, Lin Zhou, Ramya Chandrasakar, Kevin Dennis, and Wei Tang for their support and assistance over the course of this project, as well as Steve Constantinides and Arnold Magnetic Technologies for providing magnet material and helpful advice.

In addition, I would like to thank my friends, family, and loved ones for their endless encouragement and love during my college career.

This work was supported by DOE-EERE-VT, PEEM and Propulsion Materials Programs, at the Ames Laboratory, which is operated by Iowa State University under contract DE-AC02-07CH11358.
ABSTRACT

Alnico is a commercially available series of permanent magnet alloys, which form a nanoscale bcc-intermetallic spinodally decomposed structure. The major mechanism of coercivity in these alloys is shape anisotropy produced by the spinodal morphology. A series of heat treatments, with and without external magnetic field, is crucial to developing optimal magnetic properties. Alnico 8H has a coercivity of 1900 Oe, the highest of all commercial alnico grades, and was used to investigate heat treatment effects on microstructure and magnetic properties.

Conventional alnico 8H permanent magnets are manufactured by casting or sintered blended elemental powder techniques. Oxides, especially in sintered varieties, can make up as much as 4% of the magnet, reducing total magnetization. Detrimental grain boundary γ phase, and a newly observed σ phase are present in finished commercial magnets, reducing coercivity. Intragranular γ was also found in sintered varieties. Growth of γ occurred as much as 200°C below its reported thermodynamically stable temperature, as shown in recent phase diagrams.

Pre-alloyed alnico 8H (without minor Si, S, or Nb additions) was gas atomized into fine single-phase spherical powders to investigate alternative consolidation methods and processing routes. Hot isostatic pressing at 1250°C produces a fully dense compact with small amounts of γ phase and very a low oxide content. Heat-treating in a similar manner to commercial alnico yields a maximum energy product slightly exceeding standard commercial values. Spark plasma sintering (SPS) at lower temperatures generates compacts 80-92% dense, with a large intercellular network of γ and σ phases.
Two methods of reducing $\gamma+\sigma$ were explored using gas-atomized material. Rapid solutionization at 1250°C followed by water quenching can eliminate the $\gamma+\sigma$ network caused by SPS. Low temperature magnetic annealing can suppress $\gamma$ growth in later high temperature heat treatments. Reducing $\gamma$ using either of the two approaches increases saturation magnetization and remanence by 10-30% of commercial values. By further optimizing the heat treatment process, gas-atomized alnico 8H material should exceed the maximum energy product for all alnico grades.
CHAPTER 1. INTRODUCTION

In recent years there has been a marked shift towards environmental awareness in the areas of energy and transportation. In 2012, the Environmental Protection Agency passed new legislation tightening emissions standards in progressive steps from 2012 to 2025 [1]. Cars and light trucks model year 2025 and after will have a required fuel economy at or greater than 54.5 miles per gallon (mpg).

In order for the “2025 Challenge” to be realized, considerable steps will have to be made in alternative energies and vehicle technologies. Alternative fuels such as biofuels or hydrogen could lower greenhouse gas emissions while still using traditional or modified internal combustion engines. All-electric motors would be nearly emission-free, and therefore even more advantageous. Of the types of electric motors, permanent magnet (PM) based synchronous motors have several advantages; they are typically more compact, lighter in weight, quieter, and require less maintenance [2]. This only holds true if the permanent magnets are sufficiently energy dense, such as neodymium iron boron or samarium cobalt magnets.

Rare-earth (RE) magnets and rare-earth materials have increasingly been used in technological devices. High demand for critical RE elements such as dysprosium and neodymium have caused the major source country, China, to enact strict export limits. Limited global supply has caused large price fluctuations, which are undesirable if PM motors are to stay competitive and maintain a reasonable price/performance ratio. A permanent magnet that maintains a high maximum energy product while using abundant, relatively inexpensive elements would be attractive. Alnico magnets, which are already an
industrially produced magnet type, are an Fe-Co based alloy with significant Al, Ni, Cu, and Ti additions. Grades with the highest energy product, alnico 5-7, 8, and 9 are noteworthy due to their high Curie temperature (~850°C), and low temperature dependence of energy product (~0.2%/°C).

Alnico magnets have not seen any significant advancement in composition or processing since the mid-1970s due to the rise in popularity of the rare-earth based magnet. At the time, research and alloy design were done empirically, making small variations in composition and observing the change in magnetic properties [3]. In the last decade, advances in computational modeling and characterization have made it possible to re-examine alnico. Computations by R. Skomski et al. show that in an optimally segregated spinodal system, theoretical energy product of alnico is in excess of current values (5-9 MGOe for later grades), with a maximum of \( \mu_0 M_r^2/12 \) when the volume fraction of the magnetic phase is 2/3 total volume [4]. A target maximum energy product of 20 MGOe at 180°C is a performance/price point that would allow alnico to compete with RE permanent magnets, and is achievable according to the theoretical calculations.

1.1 Purpose of Study

Recent studies have shown that alnico forms a nanoscale bcc-intermetallic spinodally decomposed structure [5], [6]. The major mechanism of coercivity in alnico is shape anisotropy, which is developed through a complex series of heat treatments that were empirically established pre-1970 [3]. If the heat treatment effects on microstructure of the alnico system could be understood, then alloy processing could be improved to achieve the 20 MGOe target energy product target for PM motors.

Alnico 8H grade was primarily used for this study due to its already high coercivity
(1900 Oe) and equiaxed grain structure. Using this alloy grade, the goal was to investigate current heat treatment processes and their effect on microstructure and magnetic properties, and how the performance of the alloy could be improved using different processing methods. Each step of the conventional heat treatment process was examined for changes to microstructure and magnetic properties. Cast, sintered blended powder, and homogenous gas-atomized powder techniques were also studied for effects on magnetic properties and microstructure development.

1.2 Objectives

One of the primary objectives of this study is to determine the microstructural changes caused by conventional heat treatment steps, and how these changes affect the magnetic properties. Significant research has been done to link alloying additions, heat treatments, and magnetic properties, but few studies are able to compare the changes to microstructural phenomena. Gas-atomized alnico 8H powder was used to investigate different consolidation and heat treatment techniques that are not possible with commercially produced magnet material. Given the findings of Skomski that an optimally segregated spinodal structure needs a spinodal spacing on the order of 10 nm, an additional objective of this study is to establish processing approaches which limit the spinodal spacing to this range while reducing the deleterious γ phase. Another principal objective of the study focuses on investigations of the grain boundary γ phase and methods of γ reduction. The aim of all experiments was to help progress towards the goal of a cost-effective, high energy product permanent magnet that can be used as an alternative to RE permanent magnets in electric motor applications.
CHAPTER 2. LITERATURE REVIEW

2.1 Background to Magnet Terminology

All classes of material will respond to an applied magnetic field in one of three ways. Ferromagnetic (and ferrimagnetic) materials are strongly attracted to a magnetic field. This attraction is caused by a net magnetic moment within the material, which induces a force to align the magnetic moment with the applied magnetic field. The net magnetic moment is caused by the spin and orbital moments of unpaired individual electrons. Paramagnets are also attracted to an applied magnetic field due to unpaired electron dipoles; however, the attraction is many times weaker than that of a ferromagnet [7]. Thermal energy at room temperature is enough to randomize the dipole moments in a paramagnet when the applied field is removed. In ferromagnets, the temperature at which thermal energy is enough to randomize the dipole moments is known as the Curie temperature; after this temperature, the ferromagnet behaves as a paramagnet [7].

The third type of magnetism, diamagnetism, is a much weaker effect than ferromagnetism or paramagnetism. It is caused by the tiny current loops created by electron orbitals, or curved trajectory of electrons in the case of metals, and causes the material to be repelled from applied magnetic fields. This occurs in all materials, but the effect is overshadowed in the case of paramagnetic and ferromagnetic materials [7].

Ferromagnetic materials are typically categorized into two groups, soft or hard magnets. Soft magnets lose their magnetization as soon as an applied magnetic field is removed, and are characterized by their lack of coercivity ($H_C$) and remanence ($B_r$). Remanence is the magnetization left behind in a material after the applied field is removed,
and is measured in gauss. Coercivity is the amount of magnetic field required to reduce the magnetization to zero after the material has been magnetized, and is in units of oersteds. Magnetization is a measure of the density of induced magnetic dipole moments, with units of gauss or tesla. Soft magnets are very useful for functions where control of magnetization and demagnetization or fast switching of magnetic pole directions is required. Examples of soft magnet applications are hard drives, transformers, and inductors.

Hard magnets, or permanent magnets, are used in generators, electric motors, and speakers, among other uses. Remanence and coercivity are important aspects of these magnets. They are typically compared by the metric of maximum energy product ($BH_{\text{max}}$). Maximum energy product is a measure of the available magnetic energy stored in a permanent magnet and has units of gauss-oersteds. The higher the energy product, the less magnetic material will be required for a given application [7]. As is the case in most magnet materials, raising the coercivity comes at the expense of magnetization, so a balance must be found to optimize the maximum energy product. A hysteresis graph showing coercivity, remanence, and maximum energy product is shown in Figure 2.1.

![Hysteresis Graph](image)

Figure 2.1 Example hysteresis graph with coercivity, remanence, saturation, and maximum energy product points labeled [8].
2.2 History of Alnico Magnet Development

The first alni-type magnets were discovered in 1931 by Mishima in Japan [9]. These magnets were an Fe-Ni-Al based system that exhibited twice the coercivity (500 Oe) of the magnetic cobalt steels that were available at the time. Cobalt and copper were added in the several years following the discovery to form alnicos. It was found that controlled cooling from a temperature above 1100°C and a several hour heat treatment at 550-700°C improved the magnetic properties [10]. Annealing treatments under an applied magnetic field were also found to improve magnetic properties of certain alnicos [11].

In 1939 it was shown that alnico magnetic properties could be attributed to a two phase system of bcc $\alpha_1$ and $\alpha_2$. $\alpha_1$ being an Fe-Co rich ferromagnetic phase, and $\alpha_2$ a Ni-Al rich phase. An fcc $\gamma$ phase was also observed in certain compositions, which negatively affects magnetic properties [12], [13]. In 1952, the $\alpha_1$ phase was found to align in rods along the <100> direction, and anisotropic alnico 5 grades were developed [14]. Additions of 3-8% Ti were added in the 1950s to greatly increase the coercivity of alnicos while sacrificing some of the remanence, resulting in the anisotropic alnico 8 grade [10], [15], [16].

It was not until 1958 that the $\alpha_1$ and $\alpha_2$ phases were recognized as a spinodal decomposition [16]–[18]. The length of $\alpha_1$ aligned rods in alnico 8 were found to be longer than those in alnico 5s, suggesting that shape anisotropy played an important role in determining coercivity [16], [19]. After 1962, research was focused on alloying additions and heat treatment methods which would improve the length and alignment of spinodal decomposition and columnar grain growth, and eliminate or reduce $\gamma$ phase formation. These developments will be discussed in greater depth in sections 2.4-2.5.
After 1980, research on bulk alnico had largely stopped due to the discovery of the ultra-high coercivity samarium cobalt and neodymium iron boron RE magnets. Demand for critical RE materials such as Dy reached an all-time high in 2011, and has caused a renewed interest in alnico, particularly in high-temperature applications such as electric vehicle motors [20], [21]. Today research continues in areas of microstructure, processing, and composition modification to improve magnetic properties.

A table of current manufacturing standards for alnico names, compositions, and properties is shown in Table 2.1. Alnico grades 1, 2, and 3 are magnetically isotropic. Grades 5, 5DG, 5-7, 6, 8, 8HC, and 9 are magnetically anisotropic. Magnetic anisotropy does not indicate anisotropy of grain structure, except in grades 5-7 and 9, which are chill-cast to produce columnar grain growth. Sintered powder versions of grades 2, 5, 6, 8, and 8HC are also manufactured. Sintered grades have a moderate decrease in magnetic properties compared to their cast counterparts, except in the case of alnico 6, which has slightly superior properties in the sintered form.

Table 2.1 Summary of MMPA Standard 0100-00 compositions and magnetic properties for current cast alnico grades (remaining composition Fe, <2 wt.% other additions) [22].

<table>
<thead>
<tr>
<th>Class</th>
<th>Al wt%</th>
<th>Ni wt%</th>
<th>Co wt%</th>
<th>Cu wt%</th>
<th>Ti wt%</th>
<th>BH_{max} MGOe</th>
<th>Br Gauss</th>
<th>H_c Oersted</th>
<th>H_i Oersted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast Alnico 1</td>
<td>12</td>
<td>21</td>
<td>5</td>
<td>3</td>
<td>-</td>
<td>1.4</td>
<td>7200</td>
<td>470</td>
<td>480</td>
</tr>
<tr>
<td>Cast Alnico 2</td>
<td>10</td>
<td>19</td>
<td>13</td>
<td>3</td>
<td>-</td>
<td>1.7</td>
<td>7500</td>
<td>560</td>
<td>580</td>
</tr>
<tr>
<td>Cast Alnico 3</td>
<td>12</td>
<td>25</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>1.35</td>
<td>7000</td>
<td>480</td>
<td>500</td>
</tr>
<tr>
<td>Cast Alnico 5</td>
<td>8</td>
<td>14</td>
<td>24</td>
<td>3</td>
<td>-</td>
<td>5.5</td>
<td>12800</td>
<td>640</td>
<td>640</td>
</tr>
<tr>
<td>Cast Alnico 5DG</td>
<td>8</td>
<td>14</td>
<td>24</td>
<td>3</td>
<td>-</td>
<td>6.5</td>
<td>13300</td>
<td>670</td>
<td>670</td>
</tr>
<tr>
<td>Cast Alnico 5-7</td>
<td>8</td>
<td>14</td>
<td>24</td>
<td>3</td>
<td>-</td>
<td>7.5</td>
<td>13500</td>
<td>740</td>
<td>740</td>
</tr>
<tr>
<td>Cast Alnico 6</td>
<td>8</td>
<td>16</td>
<td>24</td>
<td>3</td>
<td>1</td>
<td>3.9</td>
<td>10500</td>
<td>780</td>
<td>800</td>
</tr>
<tr>
<td>Cast Alnico 8</td>
<td>7</td>
<td>15</td>
<td>35</td>
<td>4</td>
<td>5</td>
<td>5.3</td>
<td>8200</td>
<td>1650</td>
<td>1860</td>
</tr>
<tr>
<td>Cast Alnico 8HC</td>
<td>8</td>
<td>14</td>
<td>38</td>
<td>3</td>
<td>8</td>
<td>5.0</td>
<td>7200</td>
<td>1900</td>
<td>2170</td>
</tr>
<tr>
<td>Cast Alnico 9</td>
<td>7</td>
<td>15</td>
<td>35</td>
<td>4</td>
<td>5</td>
<td>9.0</td>
<td>10600</td>
<td>1500</td>
<td>1500</td>
</tr>
</tbody>
</table>
2.3 Alnico Phase Diagram

Current alnico alloys do not have a theoretically or experimentally determined phase diagram due to their 8+ element system (Al, Ni, Co, Fe, Cu, Ti, Si, S, Nb…). The early alloys of Fe-Ni-Al have been modeled as a binary phase diagram of NiAl+Fe, but have been debated about the shape of the miscibility gap (spinodal decomposition) and the γ and γ+α phase fields. The most recent diagram from Eleno is shown in Figure 2.2.

![Alnico Phase Diagram](image)

Figure 2.2 “Calculated isopleth from the NiAl side to the Fe corner of the Fe-Ni-Al phase diagram” [23].

As stated in section 2.2, final microstructure is very important to the magnetic properties of alnico. Various alloying elements affect the shape of the phase diagram, particularly, the size of the α (B2) field, the γ field, and the spinodal temperature. Investigations in alloying additions are discussed in section 2.4.

A phase diagram schematic for current alnico compositions was proposed by Stanek in 2010 and is shown in Figure 2.3. A three phase region obscures the top of the spinodal in
the diagram, but it suggests a spinodal splitting temperature around 850°C, near the Curie
temperature of 860°C. For magnet compositions, it indicates an fcc $\gamma$ stable region from
1175°C to 850°C, with an allotropic transformation of $\gamma$ to bcc $\alpha$ at 850°C.

![Figure 2.3](image)

Figure 2.3 Schematic of phase diagram for alnico magnets with magnet composition labeled [24].

### 2.3.1 Gamma Phase

The Fe rich fcc $\gamma$ phase is very harmful to the magnetic properties of alnico. It tends
to nucleate and grow on the grain boundaries over its stable range of 1175-850°C; this
drastically lowers the coercivity [3], [10], [25]. Reasons for exactly why coercivity is
lowered is not well studied; it is suspected that the Fe-Co rich grain boundaries act as soft
magnetic “shorts” for domain wall movement [10]. Quick quenching from temperatures
above 1200°C is required to bypass growth of $\gamma$ [3], [10], [16]. Time-temperature-
transformation (TTT) curves have been developed for the $\alpha \rightarrow \gamma$ transition by Clegg and Planchard. They indicate that between 1000 and 1100°C $\gamma$ transformation occurs fastest, at less than 5 minutes [26], [27]. Transformation time is affected by alloying additions as discussed in section 2.4, with $\alpha$ stabilizers increasing transformation time, and $\gamma$ stabilizers decreasing transformation time.

The TTT curves show that at 800°C the $\alpha \rightarrow \gamma$ transition should occur after 100 minutes, long past the time of any heat treatments at that temperature [26], [27]. However, other researchers have shown the existence of $\gamma$ or a $\gamma$-like phase well before 100 minutes, and at lower temperatures (~700°C) [10], [28]–[31]. This is problematic for alnico heat treatments, which are in this temperature range to achieve maximal spinodal decomposition and magnetic properties (as discussed in section 2.5).

2.4 Alnico Alloy Additions

2.4.1 Co and Ni

Co and Ni are both $\gamma$ stabilizers and require higher temperatures to homogenize to single phase $\alpha$ (called a solutionization treatment) [10], [31] Both have been shown to increase coercivity; Ni to a lesser extent than Co [10]. Ni also reduces the remanence, balancing its increase in coercivity. Co also increases the Curie temperature significantly, allowing for a spinodal decomposition heat treatment under applied magnetic field (known as a magnetic anneal).

2.4.2 Al and Cu

Al and Cu are both fcc in structure, but are $\alpha$ phase stabilizers, and lower the required solutionization temperature. Cu also decreases the cooling rate necessary to suppress $\gamma$ growth after solutionizing [10]. This is contrary to the effects of Cu in steels and other
systems, where it is a mild γ stabilizer [32]. Both Al and Cu positively influence coercivity, but small additions of Cu also slightly increase remanence [10]. Hetherington and Xing found that during spinodal decomposition in alnico 8 and 9, Cu precipitates out of the α₂ phase into particles that increase the magnetic separation between α₁ phases, and therefore increase coercivity [33], [34]. In earlier alnicos it was observed that Cu stayed in the α₂ and lowered its Curie temperature, also increasing coercivity [33].

2.4.3 Gamma Stabilizers

Many of the attempted alloy additions in alnico became γ phase stabilizers. γ phase stabilizers either increase the required solutionization temperature to the point that it reaches the liquidus, or increase the cooling rate necessary to bypass γ growth on the way down from the solutionization, or both. Reported γ stabilizers include the already mentioned Co and Ni, as well as C, N, Mn, Ru, Rh, Pd, Re, Os, Ir, Pt, and Au [35].

2.4.4 Alpha Stabilizers

Counterpart to γ stabilizers, α stabilizers tend to lower the temperature required for solutionization, or decrease the cooling rate necessary to avoid γ growth. All of the reported α stabilizers also increase coercivity to some degree. These elements include Cu, Al, Si, Ti, Nb, Zr, Ta, and Mo [10], [27], [29], [36]–[40]. Clegg claimed Nb to be a γ stabilizer, however this was opposite of what was found by others [26]. Nb is also a moderate α stabilizer in steels [41]. Ti, Nb, Zr, and V are also thought to stabilize an additional ε phase, with an Fe₂X-type composition [26], [29], [42]. Not much is known about the effects of this phase.
2.4.5 Ti, Nb, Si, S, Te, C, and Columnar Growth

Ti and Nb are α stabilizers. They also neutralize any C in the alloy melt by forming carbides [42]. C is a very strong γ stabilizer and even small amounts (0.14%C) are extremely detrimental to the magnetic properties [10]. Both Ti and Nb increase coercivity, but Ti decreases remanence more than Nb. Ti and Nb also getter oxygen in the melt to form oxides, which refine the grain structure [43]. For chill-cast alnicos such as alnico 9, the refined grain structure produced by Ti and Nb completely inhibits columnar grain growth. Columnar grain growth causes the majority of grains to align perpendicular to the chill plate, and large shape anisotropy can be gained when spinodal decomposition occurs along this direction (facilitated by the magnetic anneal). S or Te can be added along with Ti or Nb to regain columnar growth capabilities [30], [44].

In another approach, C and S are added to recover columnar growth from Ti additions [45]. Palmer states that grain refinement is caused by titanium oxides and nitrides. With the addition of C, titanium oxides become titanium carbides, and with the addition of S, titanium nitrides become titanium sulfides, neither of which refine the grain structure. However, this cannot be done in a nitrogen rich environment, or the titanium carbides instead become titanium carbo-nitrides, which are detrimental to magnetic properties [43]. Precise C additions need to be made to prevent detrimental effects caused by free carbon in the alloy. Due to the drawbacks of the C control method, typically S or S + Te are used to promote columnar growth [46].

2.5 Heat Treatment Effects on Microstructure

Two years after the Mishima patent, separate work by Köster, Messkin, and Steinhaus developed the theory that the magnetic properties were achieved through precipitation
hardening [10]. This called for the usual processing to develop precipitation hardening effects: high temperature 1100°C solutionization and a lower temperature (500-700°C) precipitation heat treatment. In 1938 it was found that significantly better magnetic properties could be attained if the precipitation heat treatment was done under an applied magnetic field (a magnetic anneal) [11]. After it was discovered that $\alpha_1$ and $\alpha_2$ precipitates were actually spinodally decomposed, the magnetic annealing treatment was found to be most beneficial near the spinodal splitting temperature [18]. A low temperature annealing treatment (or draw), like the sort performed on the early alni alloys was found to be helpful for increasing coercivity, and was thought to increase the amplitude of the spinodal splitting compositions [28].

2.5.1 Solutionizing Treatment

The temperature for solutionization varies depending on the type of alnico and its composition. As discussed in section 2.4, certain elements change the single phase $\alpha$ temperature range. Solutionization must occur in this region between the $\alpha + \gamma$ phase field and the solidus (see Figures 2.3 and 2.3) [38]. Alnicos with a smaller amount of Co and a larger amount of Fe, including alnico 1, 2, 3, 5, 5-7, and 6 can have a solutionization temperature ranging from 1350°C to as low as 950°C. These alnicos are heat treated differently from the 8 and 9 grades [16].

In the case of the low Co/high Fe alnicos (0-24%Co, 48-60%Fe), it was found that continuous cooling at a specified rate, varying from 0.5 to 6.8°C/s by increasing Fe content, was more favorable than quenching and isothermal annealing [27], [28]. De Vos proposed that asymmetry of the miscibility gap causes the phase fraction of $\alpha_1$ and $\alpha_2$ to differ with temperature. At lower temperature isothermal anneals, high Fe content alnico has a
continuous $\alpha_1$ Fe-Co rich phase and discontinuous $\alpha_2$ Ni-Al rich phase, which is not advantageous for coercivity. When continuously cooled from high temperature, the phase fraction of $\alpha_1$ is lowered so that it is discontinuous. When cooled in the presence of a magnetic field these discontinuous particles grow into rods, causing shape anisotropy and additional coercivity [28]. A typical alnico 5 with a composition of 8Al-14Ni-24Co-51Fe-3Cu (wt.%) is solutionized at 1350°C, and cooled to 900°C at a rate of 4°C/s to prevent $\gamma$ growth. Controlled cooling from 900°C to 600°C is done under a magnetic field before drawing at 650-550°C [3].

Low Fe content alnico grades 8, 8H, and 9 were found to benefit from quenching from the solutionization temperature and then isothermal magnetic annealing rather than continuous cooling. As explained by De Vos, this is due to the low Fe content and the asymmetrical shape of the miscibility gap. Alnico 8H, with a typical composition of 8Al-14Ni-38Co-29Fe-3Cu-8Ti (wt.%) is solutionized at 1250°C and quenched by moving air [22]. This temperature is also effective for alnicos 8 and 9.

A study on the spinodal decomposition of alnico 8 by Pashkov noted that even with water quenching from the solutionizing temperature, fine spinodal splitting occurred [47]. He proposed that this was due to the volume change (0.05Å) and influence of elastic energy on the decomposition. Zhou et al. have shown through 3D atom probe that the spinodal structure after solutionizing and oil quenching is a continuous network, and has not formed discrete particles [48]. Due to the continuous nature of the spinodal decomposition after solutionizing, the magnetic properties of a solutionized magnet are very poor. Saturation magnetization is high, but there is no coercivity, as shape anisotropy has not been developed [3], [28], [48]–[50].
2.5.2 Magnetic Anneal

A magnetic anneal (MA), or an isothermal heat treatment under an applied magnetic field, is not performed on earlier isotropic grade alnicos. Anisotropic grades are cooled from around 900°C to 600°C under a magnetic field to align the spinodal decomposition in the field direction [3].

Grades 8, 8H, and 9 are magnetically annealed for 10-30 minutes at a temperature ranging from 800-850°C depending on composition. As stated by De Vos, a lower temperature isothermal magnetic anneal after quenching from the solutionizing temperature allows the fraction of $\alpha_1$ phase to be larger while remaining discontinuous [28]. Studies by Iwama suggest that the phase fraction of $\alpha_1$ and $\alpha_2$ are tunable and significantly change with as little as 10°C difference in temperature [51]. Theoretical calculations indicate that an ideal $\alpha_1$ phase fraction is 66%, however, current alnico 8 and 9 have 50% or less $\alpha_1$ after heat treatment [4], [34].

Many studies have been done on the optimum magnetic annealing temperature. For typical 8, 8H, and 9 compositions, it was experimentally found that 810°C for 10 minutes or less was ideal [24], [27], [51]. Calculations by Cahn support this temperature choice. He reasons that the energies responsible for the early stages of spinodal decomposition under an applied magnetic field are chemical free energy, magnetostatic, magnetostrictive, elastic, exchange, and surface energy. Of these, only two contribute to anisotropy—elastic and magnetostatic energy, while the remaining energy contributions are isotropic [18]. The elastic energy density due to the compositional waves (initial spinodal decomposition) is:

$$f_{elastic}^\parallel = A_\parallel^2 \eta_\parallel^2 Y$$

$$f_{elastic}^\perp = A_\perp^2 \eta_\perp^2 Y$$
Where $A$ is amplitude, and $\eta = d\ln a/dc$ where $a$ is the strain free lattice parameter. $Y$ is a directional dependence term, which causes $\{100\}$ plane waves to be favored for spinodal decomposition. The magnetostatic energy change due to the rearrangement of magnetization is:

$$\delta F_{mag} = - \int (H \cdot \delta M) \, dV$$

$$\delta F_{mag}^\parallel = 0$$

$$\delta F_{mag}^\perp = \frac{\pi A^2_\perp \left( \frac{\partial M}{\partial c} \right)^2}{V}$$

Where $H$ is magnetic field, $M$ is magnetization, $V$ is volume, and $c$ is composition. Assuming that $H$ slowly varies over lengths much greater than the wavelength of spinodal decomposition, the parallel component becomes zero. The perpendicular magnetostatic component will be greatest for composition waves parallel to the internal magnetic field, and lowest for perpendicular waves [18].

Since magnetostatic and elastic energy anisotropy favor different decomposition directions, the dominant energy will be responsible for the final structure. Magnetostatic anisotropy favors the magnetic field direction and elastic energy favors $\{100\}$ planes. If both of these are aligned, such as in columnar grained alnico, the result is very well defined rods along $[100]$ with high shape anisotropy and coercivity. However, if both energies are approximately equal but unaligned, a combination of both will result, and a crosshatching of spinodal rods is observed [48], [51]. If the magnetostatic energy is considerably larger than the elastic energy, the spinodal will ignore crystallographic preferences and will decompose into rods parallel to the magnetic field. This only becomes the case when the material is near
its Curie temperature. The magnetostatic energy is dependent on the \((\partial M/\partial c)^2\) term, which is relatively small except near the Curie temperature.

The Curie temperature of single phase \(\alpha\) has been shown to be around 810°C in alnico 8 grades, explaining why this was found as the optimum magnetic annealing temperature [18], [51], [52]. Figure 2.4 from Iwama illustrates the spinodal decomposition alignment and size with temperature for alnico 8. It has also been found that the applied magnetic field is only necessary at the start of spinodal decomposition when composition waves begin to appear and establish their structure. The anisotropy effects will remain, and continue to improve, when further heat treated without a field [3], [18], [28], [51].

![Figure 2.4 Electron micrographs of alnico 8 magnetically annealed for 10 minutes at a) 750°C, b) 780°C, c) 810°C, d) 830°C. The top row shows samples parallel to the magnetic field direction, the bottom row is perpendicular to the magnetic field.](image)

Magnetic property measurements of solutionized and magnetically annealed samples return poor results. Coercivity is very low. It is believed that the composition of the \(\alpha_2\) phase...
produced from an 810°C anneal is still too rich in Fe-Co and is ferromagnetic at room temperature [3], [24], [28]. Figures 2.2 and 2.3 show that the Fe-Co content of the $\alpha_2$ phase is larger at higher temperatures due to the curve of the miscibility gap. By following the magnetic anneal with a low temperature anneal, or draw, the advantages of the magnetic anneal on the magnetic properties is observed.

2.5.2.1 Other Field Effects

The effects of magnetic annealing at angles to the preferred crystallographic direction were studied in alnico 5. Iwama found that the shape anisotropy constant, and the shape anisotropy, sharply declined (70% decrease) past 15° off-axis from the field direction [53]. Therefore, it is preferable for shape anisotropy to align in [100] directions with the magnetic field as much as possible.

Sun investigated the effects of high strength magnetic field on magnetic annealing of alnico 8. Using a magnetic field strength of 10T and a magnetic annealing temperature of 830°C, he found that the phase fraction of $\alpha_1$ increased, and the rod length parallel to the field increased to hundreds of nanometers. However, the connectivity of the rods also increased, showing many dumbbell type shapes rather than spherical rods. He concluded that the strong magnetic field enhanced the atomic diffusion rate parallel to the applied field more so than perpendicular to the field [54].

2.5.2.2 Spinodal Refinement

Chu and Fei studied the morphology of spinodal decomposition in the early stages of magnetic annealing. They used an alnico 8 with a composition of 36.1Fe-33.2Co-16.3Ni-5.3Al-3.6Ti-3.0Cu-1.5Si-1.0Nb (wt.%). This is 1-3% lower in Co, Al, Ti, and Cu content compared to the standard alnico 8 composition, and 1% higher in Ni [22]. After solutionizing
bulk material at 1250°C and vacuum cooling, they magnetically annealed small samples for 1.5, 3, 5, and 10 minutes at 800°C in a 0.34 T applied field. Transmission electron microscope (TEM) results were compared for the solutionized and magnetically annealed (MA) samples, showing an initial coarsening of the spinodal structure, followed by a refinement of the large coarsened particles into two or more smaller particles. Average sizes of these particles were found to be 6.7 nm, 24.0 nm, 10.7 nm, 16.6 nm, and 5.7 nm for the solutionized sample, 1.5, 3, 5, and 10 minute MA, respectively [55]. TEM images of these results are shown in Figure 2.5.

Figure 2.5 Chu and Fei TEM micrographs of 1.5, 3, 5, and 10 min magnetic anneals after 1250°C solutionizing and vacuum cool [55]. Average size of particles in bottom left corner.

From the sizes of the spinodal particles they concluded that two refinements had occurred after 10 minutes of annealing, yielding the smallest average particle size. They concluded after initial spinodal splitting from single phase α, spinodal particles coarsened due to interfacial energy. High interfacial energy caused particles to grow, lowering total energy until particles reached a critical size (between 0 and 1.5 minutes MA). At this point, the elastic strain energy caused by the coherent particles became too large, and particles split to reduce elastic strain energy (between 1.5 and 3 minutes MA). Between the 3 and 10 minute magnetic anneal the coarsening and splitting process repeated, showing a coarsened
structure at 5 min MA, and the most refined, 6 nm particles after 10 min magnetic annealing [55].

Chu and Fei also studied these effects at temperatures ranging from 800-865°C. They found that reaction time was much faster at 800°C. Particles coarsened and split faster than at 850°C or 865°C. Two refinements occurred in the 800°C sample over 10 minutes, while only one refinement occurred in the 850 and 865°C samples. They reasoned that this was due to increased elastic strain energy at 800°C compared to the higher temperatures. This increased elastic strain energy was caused by the increased elastic modulus at lower temperatures [56].

2.5.3 Draw

The draw, sometimes called the temper or low temperature annealing treatment, is done in the range of 650 to 550°C, and is performed on both continuously cooled and magnetically annealed alnico types. Typically, the draw starts at 650°C and ramps down in temperature, spending longer time at lower temperatures. Figure 2.6 shows a schematic of a typical alnico 8 heat treatment with a ramped draw. Due to the shape of the miscibility gap (Figures 2.2 and 2.3), Fe-Co content of the α₂ phase decreases with decreasing temperature, while Fe-Co content of the α₁ phase increases with decreasing temperature. In other words, the amplitude of the spinodal decomposition increases with lower temperature without increasing in wavelength.

Drawing starts at temperatures in the 630-650°C range due to increased diffusion at those temperatures. Drawing at 650°C alone will yield an α₂ phase with a Curie temperature around 300K, or room temperature. Further drawing for 6-40 hours at 590°C and 550°C will lower the α₂ Curie temperature to below room temperature [16], [26], [28], [50], [52], [57]. Drawing for very long times (500+ hours) will begin to coarsen the spinodal wavelength and
is detrimental to magnetic properties [28]. Forster studied the long term high temperature operation of alnicos 5 and 8, finding that 550°C and 590°C were stable operating temperatures for each, respectively [58]. This suggests diffusion and coarsening are very limited at these temperatures.

![Figure 2.6 Schematic of typical alnico 8 solutionization, magnetic anneal, and draw [24].](image)

Magnetic properties after the draw treatment are considered optimal. Coercivity is greatly enhanced when \( \alpha_2 \) is paramagnetic surrounding a ferromagnetic \( \alpha_1 \), while remanence and saturation are only slightly decreased. Typical magnetic property values for different alnico grades after the draw are shown in Table 2.1.

### 2.6 Processing Methods of Alnico Material

The majority of commercial alnico magnets produced today are cast using traditional methods. Alnico is hard, brittle and is not easily machinable, with a Rockwell C hardness of 45-55 [22]. It is cast into small ingots so only minimal surface grinding may be necessary for a finished product. Small or complex magnet shapes are made from sintered elemental and master alloy powders that are blended before die pressing. Elemental Ni, Co, Fe, Cu, FeAl, and FeTi, along with recycled alnico powders are compacted and sintered around 1300°C.
Both sintered and cast magnets require the heat treatments examined in section 2.5 for optimal properties.

Due to the sharp cooling rate required from 1200 to 700°C to avoid forming γ phase, other methods of producing alnico material have been studied. Alnico 5 was produced by extractive melt spinning for rapid solidification to avoid γ. Sieving was used to separate fragmented (melt spun) flake to < 250 μm diameter powders. A wheel speed of 8.5-33 m/s yielded average grain sizes of 2.5-25.6 μm. The powders solidified into the high temperature single phase α and were compacted, sintered, and heat treated similar to the commercial process. Magnetic properties of the fully treated sintered melt spun power magnet slightly exceeded the properties of cast alnico 5 with a maximum energy product of 5-6 MGOe compared to 5.5 MGOe. Energy product was significantly higher than traditional sintered alnico 5, at only 3.9 MGOe [22], [59].

Water and gas atomization have also been attempted on alnico powders. Both offer rapid solidification of single phase α without nucleation of γ phase. Water atomization generates jagged, irregular powders which do not compact easily [60]. Powders of 37Fe-8.2Al-17.6Ni-26.6Co-3.3Cu-7.2Ti (wt.%) composition were gas atomized by Song. This does not correlate to any standard grade of alnico, but is roughly an alnico 6 with several percent more Ni and Co, and 6% more Ti. The powders produced were oval in shape and averaged 119 μm in size [60]. Magnetic properties of the powders were unexceptional, however they did not receive a traditional heat treatment and are not of standard composition. Despite melt spinning and gas atomization being economical powder production methods, neither of these techniques have been put into commercial practice.
CHAPTER 3. RELEVANT CHARACTERIZATION TECHNIQUES

Many techniques were used to analyze the alnico commercial samples and gas-atomized powders for microstructure, composition, and magnetic properties. The analysis methods primarily used and presented in this study are reviewed in the following sections. These include field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD), and hysteresis graph.

3.1 Field Emission Scanning Electron Microscopy

Figure 3.1 Quanta FEI 250 field emission SEM equipped with an Oxford X-Max 85 mm² EDS detector that was used for microstructure analysis.

FE-SEM was utilized in this study to examine microstructure between the resolution capabilities of traditional SEMs and TEMs. Three different types of samples were primarily observed: commercial or gas-atomized consolidated samples, TEM foils, and gas-atomized
powder cross sections. Consolidated samples and powder cross sections were prepared in a similar manner. Powder samples were mounted into epoxy and allowed to set. Consolidated samples were glued to a metal puck using Crystalbond. SiC papers from 320-1200 grit were used to achieve a flat sample before polishing with a diamond/oil or diamond/water suspension of 3 μm and 1 μm particle size using a low-nap microfiber or nylon polishing wheel. Epoxy mounted samples were sputter coated in 5 nm of iridium. TEM foils were prepared using a wedge polisher to polish one edge of a 1 x 1.5 x 2 mm sample, followed by ion milling.

A Quanta FEI 250 field emission SEM equipped with an Oxford X-Max 85 mm² EDS detector was used to examine the samples. For large samples, a typical accelerating voltage of 10 kV was used with a spot size of 3.0 as the optimal compromise between resolution of spinodal spacing and compositional differences, with modifications depending on the particular sample. TEM foils were sometimes imaged with a higher accelerating voltage (15-20 kV) and smaller spot sizes. All images were captured in backscattered mode, except in the case that the sample was etched with sulfuric and nitric acid.

### 3.2 Transmission Electron Microscopy

A Tecnai G2 F20 (200kV, FEG) TEM was used to observe spinodal spacing and other nanostructuring. TEM foils were prepared on consolidated samples by cutting a 1 x 1.5 x 2 mm sample using electrical discharge machining. The long edge of the sample was cut to correspond to the applied magnetic field direction in samples that were magnetically annealed. Samples were typically viewed perpendicular to the applied magnetic field (transverse), but were also examined parallel to the applied magnetic field (longitudinal). A
long edge was thinned for observation using a mechanical wedge polisher, followed by low voltage ion-milling with Ar for short times, using a liquid nitrogen stage.

3.3 Energy Dispersive X-ray Spectroscopy

EDS was used to analyze the composition of phases using both TEM and FE-SEM. For FE-SEM, EDS maps and linescan quantifications were allowed to collect for 10 minutes. Small area quantifications were collected for 5 minutes. An Oxford X-Max 85 mm² EDS detector with an Aztec software system were used on FE-SEM samples.

3.4 X-ray Diffraction

X-ray diffraction was used to evaluate the relative composition of samples, determine the crystal structure information, and detect γ phase. All samples evaluated were gas-atomized powder, with an off-axis cut Si disc placed under the powders. A Co x-ray source tube with a wavelength of 1.7902 Å was used on a PANalytical XRD system. A two-theta range of 20° to 110° with a step size of 0.15° and a count time of 0.5 seconds were used as typical parameters.

3.5 Hysteresis Graph

The magnetic properties were measured using a Laboratorio Elettrofisico Engineering Walker LDJ Scientific AMH-5 Hysteresis graph with a 5 mm coil and a maximum applied field of 5.0 kOe. Measurements were done at room temperature in a closed-loop setup. A standard size of 3 mm diameter by 8 mm cylinders was used for all measurements. Samples were inserted into 3 mm inner diameter, 5 mm outer diameter, 8 mm long aluminum sleeves to assure they remained centered and straight inside the coil during measurements.
CHAPTER 4. HEAT TREATMENT EFFECTS ON COMMERCIAL ALNICO

4.1 Spinodal Refinement

The first step of this study was to repeat the recent (2000) experiment of Chu, Fei, Li, and Yang on spinodal refinement of alnico 8 during heat treatment at 800°C [55]. A splitting mechanism of this type had not been reported before, and did not follow the established theory on magnetic annealing effects. By conventional thermodynamics one would expect a coarsening of the spinodal wavelength with time at elevated temperatures, rather than splitting. “Splitting” in this sense refers to an additional refinement of the spinodal structure, and not the initial spinodal decomposition. Chu proposes that while particles initially coarsen due to reduction in the interfacial energy, a coarsened particle has increased elastic strain energy, which is responsible for refinement.

A 2010 paper on nanostructured magnetic materials suggests that a very high energy product can be achieved with fine wires on the order of 10 nm. Alnico spinodal decomposition and directionally aligned rods can be approximated by these thin wires. The maximum energy product given by the theory is:

\[ BH_{MAX} = \frac{1}{12} \mu_0 M_r^2 \]

Where \( \mu_0 \) is the permeability of free space, and \( M_r = fM_s \), with \( f \) as the volume fraction of wires [4]. If \( f \) is the optimal 2/3, this yields a maximum energy product of nearly 50 MGOe for alnicos, an order of magnitude greater than their current optimal properties.

If secondary splitting occurs in the early stages of magnetic annealing as suggested by Chu, a very fine spinodal structure could be produced that would be at or below the 10 nm
size range required by Skomski’s calculations. Given the potential importance of Chu’s initial results, a repeat study was conducted on commercial alnico 8H material to confirm the observation of spinodal refinement with magnetic annealing.

4.1.1 Experimental Methods

Commercial cast alnico grade 8H was obtained from Arnold Magnetic Technologies in its finished, demagnetized form. Center sections of the commercial magnet ingots were cut into 3 mm diameter by 8 mm cylinders using electrical discharge machining (EDM). All previous microstructure was destroyed by solutionizing the samples at 1250°C in vacuum (10^{-6} torr) for 1 hour and quenching into silicone oil using an Oxy-Gon high temperature quenching furnace. An 800°C magnetic anneal (MA) was done in a 1 Tesla magnetic field applied along the axis of the cylinder. Figure 4.1 shows a schematic of the magnetic annealing furnace setup.

![Figure 4.1 Schematic of magnetic annealing setup with sliding tube furnace inside magnetic pole pieces.](image)
Following Chu’s work, solutionized samples were magnetically annealed for 1.5, 3, 5, and 10 minutes. The furnace was heated to 800°C while still below the sample (see Figure 4.1). Once the furnace was at temperature, it was moved up into the magnetic field, over the sample. Samples reached 800°C in less than 5 minutes. Timing for the magnetic anneal started once the sample thermocouple reached 795°C. The furnace was dropped below the sample after the prescribed annealing time and samples were allowed to air cool. Samples were characterized by TEM and 3DAP with the help of L. Zhou and M. Miller of Ames Lab and Oak Ridge National Lab [48].

4.1.2 Results and Discussion

Figure 4.2 HAADF STEM images of a) 1250°C solutionized as-quenched sample, b) 1.5 minute 800°C magnetically annealed sample, c) 10 minute 800°C magnetically annealed sample [48].

TEM micrographs of the solutionized, 1.5 min MA, and 10 min MA clearly show a coarsening of the spinodal structure. Average size of $\alpha_1$ particles are 8 nm, 12 nm, and 20 nm for as-solutionized, 1.5 min MA, and 10 min MA, respectively. In comparison, Chu finds an average size of 24 nm and 5.7 nm for 1.5 min MA and 10 min MA. A side by side comparison of the as-solutionized sample and Chu’s 10 min MA are shown in Figure 4.3.
Additionally, Figure 4.1(a) shows that spinodal decomposition has not formed into discrete particles in the solutionized sample, and thus has no coercivity.

![STEM images of a) Chu 10 minute 800°C magnetically annealed sample and b) 1250°C solutionized as-quenched sample. Average particle size of 6 nm and 8 nm, respectively.](image)

Figure 4.3 STEM images of a) Chu 10 minute 800°C magnetically annealed sample [55], and b) 1250°C solutionized as-quenched sample. Average particle size of 6 nm and 8 nm, respectively.

Our study finds that alnico 8 follows conventional thermodynamics of spinodal decomposition, and does not undergo secondary splitting as suggested by Chu. There were several differences between the two studies, however. The alnico 8H composition used for this study was 30.0Fe-40.1Co-13.0Ni-7.1Al-6.5Ti-3.0Cu-0.04Si-1.0Nb (wt.%, determined by chemical analysis from NSL Analytical), while the alnico 8 used by Chu’s group was reported as 36.1Fe-33.2Co-16.3Ni-5.3Al-3.6Ti-3.0Cu-1.5Si-1.0Nb (wt.%) composition. Several percent more Co and Ti are present in our samples, which could affect the elastic strain or interfacial energy between the $\alpha_1$ and $\alpha_2$ phases. McCurrie suggests that Co decreases the interfacial energy between the two phases, but based on our results it is still favorable for interfacial energy to coarsen the spinodal structure [3].
The quenching method from solutionization temperature was considerably different between the two studies. Solutionized samples in this study were quenched in oil. Chu describes their samples as vacuum quenched. Vacuum quenching is a substantially slower cooling rate, which would have left a larger and more defined spinodal structure. Chu does not report average particle size for the solutionized material. It is possible our samples had not reached the point of refinement in the same time frame as Chu’s; however, magnetic anneals ranging from 15-30 minutes have been performed on the same material and do not show any evidence of refinement. Other considerations are the difference in applied field strength of 1 T compared to 0.34 T, though it has been shown that this difference in field strength has relatively little effect on microstructure [3], [54].

4.2 Commercial Microstructure of Alnico 8H

Commercial alnico 8H exhibits the highest coercivity of any alnico magnet. It made sense to examine the microstructure for potential coercivity mechanisms not explained by the spinodal structure theory. Analysis of the spinodal structure and nanostructure observations of alnico 8H are published elsewhere [34], [48].

4.2.1 Experimental Methods

Commercial alnico grade 8H was obtained from Arnold Magnetic Technologies in cast and sintered varieties, in two stages of processing. Both sintered and cast varieties were observed in an un-heat treated state after casting (or sintering) and in a fully heat treated form. These states are referred to as “as-cast” or “as-sintered,” and drawn. Magnetic properties of these varieties follow the Magnetic Materials Producers Association (MMPA) Standard 0100-00 and are provided in Table 4.1.
Table 4.1 Summary of MMPA Standard 0100-00 compositions and magnetic properties for alnico grades used within the study (remaining composition Fe, <2% Si, Nb, and S) [22].

<table>
<thead>
<tr>
<th>Class</th>
<th>Al wt%</th>
<th>Ni wt%</th>
<th>Co wt%</th>
<th>Cu wt%</th>
<th>Ti wt%</th>
<th>BH\text{max} MGOe</th>
<th>B_r Gauss</th>
<th>H_c Oersted</th>
<th>H_i Oersted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast Alnico 8H</td>
<td>8</td>
<td>14</td>
<td>38</td>
<td>3</td>
<td>8</td>
<td>5.00</td>
<td>7200</td>
<td>1900</td>
<td>2170</td>
</tr>
<tr>
<td>Sintered Alnico 8H</td>
<td>7</td>
<td>14</td>
<td>38</td>
<td>3</td>
<td>8</td>
<td>4.5</td>
<td>6700</td>
<td>1800</td>
<td>2020</td>
</tr>
</tbody>
</table>

Center sections of the commercial magnet ingots were cut into discs using electrical discharge machining. The discs were prepared by standard metallography grinding and polishing practices using a diamond in oil suspension.

4.2.2 Results and Discussion

![FE-SEM images](image)

Figure 4.4 FE-SEM images of (a)(b) as-cast alnico 8H, and (c)(d) cast and drawn (fully heat treated) alnico 8H.
Figure 4.5 FE-SEM image of cast and drawn alnico 8H showing a) the spinodal structure near a grain boundary with γ phase, and b) the spinodal structure in an interior grain area, representative of the bulk spinodal structure.

Several observations can be made from these micrographs. As-cast alnico 8H has already spinodally decomposed. In the absence of an applied magnetic field the particles split along all three \{100\}. The drawn sample has a much more regular and directionally aligned spinodal (Figure 4.4(d)). Very small 10-100 nm aluminum oxide particles are observed in the interior grain in the as-cast sample (Figure 4.4(b)). In the drawn sample, these oxides have coalesced into larger 1-5 μm oxides that can sit interior to the grain or on the boundaries.

Grain boundary γ phase (light gray) can be seen throughout the sample in both as-cast and drawn cases. A dark gray Ti-Al-Co rich phase is also observed, always attached to the γ phase. The spinodal decomposition wavelength is noticeably enlarged near the grain boundary γ phases, as shown in Figures 4.4(a)(c) and 4.5. Neither the spinodal enlargement nor the Ti-Al-Co rich phase has been reported. These features are discussed in section 4.3.
Figure 4.6 FE-SEM image of as-sintered alnico 8H showing many large impurity phases and grain boundary $\gamma$ phase.

Figure 4.7 FE-SEM image of sintered and drawn alnico 8H showing large oxides and large porous impurities and grain boundary $\gamma$ phase. The “A” corresponds to an EDS point analysis of the medium gray particle.
Figure 4.8 EDS map of elements for Figure 4.7 showing Al₂O₃ and Ti particles, Fe-rich γ phase, and O, C, and Si enrichment of the porous impurity area.
The most evident features of the sintered alnico 8H are the large patches of impurity phases, which are present in both as-sintered and drawn samples. These include $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{Nb}_2\text{O}_5$, $\text{TiC}$, $\text{TiS}_2$, and what seem to be faceted Ti particles. EDS point analysis shows a composition of 93Ti-3Al-4C (wt.%) for the Ti particles (Figure 4.7 “A”). The porous areas of the impurities, such as the upper right of Figure 4.7, are nonhomogeneous bulk composition rich in Si, O, and C (Figure 4.8). It is notable that in the as-sintered case, only $\gamma$ phase is present, while in the drawn sample, the Ti-Al-Co rich phase is interspersed with $\gamma$ in
a lamellar type morphology. In both the as-sintered and drawn sintered samples, intragranular γ is observed. These γ particles are most visible in Figure 4.9(a)(c)

Spinodal decomposition wavelength and the fraction and size of the γ phase (plus the Ti-Al-Co rich phase) between cast and sintered varieties is similar. Spinodal decomposition wavelength, or spinodal spacing, is 40 nm from the center of α₁ and α₂. The major difference is the larger fraction of oxides and impurities (3.5%) in the sintered variety, compared to < 1% in the cast variety. This decrease in the total magnetic material could be the cause of the reduced magnetization and remanence, which is more largely affected by sintering than the coercivity (see Table 4.1). Small intragranular γ, not present in cast microstructure, could be responsible for the dip in coercivity.

### 4.3 Modified Heat Treatments on Commercial Alnico 8H

Cast commercial alnico 8H was solutionized and re-processed to observe the microstructure and magnetic properties during each stage of heat treatment. One of the primary objectives of this study is to determine the microstructural changes caused by conventional heat treatment steps, and how these changes affect the magnetic properties. Some modifications were made to the heat treatments to better suit laboratory facilities.

#### 4.3.1 Experimental Methods

Commercial alnico grade 8H magnets were obtained from Arnold Magnetic Technologies in their finished form. Center sections of the ingots were cut into 3 mm diameter by 8 mm cylinders. In order to study the effects of heat treatment on microstructure, the thermal history of the magnet sample was erased using a solutionizing heat treatment. The samples were solutionized at 1250°C in vacuum (10⁻⁶ torr) for 1 hour and quenched into silicone oil using an Oxy-Gon high temperature quenching furnace. A magnetic anneal (MA)
was done for 1 hour in a 1 Tesla magnetic field applied along the axis of the cylinder. Figure 4.1 shows a schematic of the magnetic annealing furnace setup. The furnace was moved over the samples after it had reached proper temperature, and time started once the sample was at temperature (~5 minutes). The furnace was removed and samples were allowed to air cool.

A following annealing treatment (draw) was done in a box furnace in air. Table 4.2 shows the processing temperatures and times for each cylinder. Magnetic measurements were taken in a closed-loop setup using a hysteresis graph with a 5 mm coil. Discs were prepared by standard metallography practices and were demagnetized prior to viewing. EDS mapping was used to determine composition. A Quanta FEI 250 field emission SEM equipped with an Oxford X-Max 85 mm² EDS detector was used for characterization.

Table 4.2 Heat treatment history of each commercial alnico 8H sample once it was received. Samples were received in a fully heat treated state.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solutionizing treatment</th>
<th>Thermo-magnetic anneal</th>
<th>Draw</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ºC</td>
<td>Hr</td>
<td>ºC</td>
</tr>
<tr>
<td>1</td>
<td>1250</td>
<td>1</td>
<td>810</td>
</tr>
<tr>
<td>2</td>
<td>1250</td>
<td>1</td>
<td>810</td>
</tr>
<tr>
<td>3</td>
<td>1250</td>
<td>1</td>
<td>810</td>
</tr>
<tr>
<td>4</td>
<td>1250</td>
<td>1</td>
<td>750</td>
</tr>
<tr>
<td>5</td>
<td>1250</td>
<td>1</td>
<td>750</td>
</tr>
<tr>
<td>6</td>
<td>1250</td>
<td>1</td>
<td>750</td>
</tr>
<tr>
<td>7</td>
<td>1250</td>
<td>1</td>
<td>700</td>
</tr>
<tr>
<td>8</td>
<td>1250</td>
<td>1</td>
<td>650</td>
</tr>
<tr>
<td>9</td>
<td>1250</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

4.3.2 Results and Discussion

Solutionizing and quenching the alloy destroyed previous microstructure and fixed the spinodal structure into a small spacing that is not visible on the FE-SEM scale. Three-dimensional atom probe (3DAP) shows that the spinodal decomposition still exists, but forms a continuous matrix with an average spacing of less than 10 nm, rather than the discrete rods
found in the fully heat treated structure [48]. Figure 4.12(c) shows that the magnet is almost completely soft at this first stage. As discussed in section 2.5, this is caused by the continuous matrix of α₁ that acts as a single magnetic domain. As expected from the commercial microstructure, large particles of Al₂O₃ and Fe₂O₃ were present (Figure 4.10(a)). The large black rods in Figure 4.10(c)(f) and 4.11(c) are TiS₂.

After 1 hour of magnetic annealing (Figure 4.10(b)), γ phase is present on most grain boundaries and the spinodal spacing has coarsened to 30-40 nm. The magnet is still completely soft at this stage (Figure 4.12(a)). There is some evidence that this is due by the high levels of Fe and Co left in the α₂, causing it to be ferromagnetic at room temperature [3], [24], [28], [48]. After extended periods of heat treatment (3+ hours), a portion of the grain boundary phase segregated to a lamellar structure with a Co-Ti-Al enriched dark phase, and γ phase. Slight presence of Si and P were also observed in the dark phase.

During magnetic annealing, this structure remained distinct at the grain boundaries, as seen in Figure 4.10(b) and Figure 4.11(c)(d). Upon drawing at 650°C, however, both phases grew out from the grain boundaries, shown in Figure 4.10(c)(d)(e)(f) and 4.11(f)(a)(b). Since this only occurred in heat treatments without an applied magnetic field, this indicates that applied field is affecting the diffusion characteristics of the grain boundary phases. For sample 2, drawn for 2 hours, γ particles spread an average of 3 µm from the grain boundary. In sample 3, drawn 4 hours, the particles spread an average of 5 µm from the boundary. Previous magnetic annealing temperature appears to affect the size of these particles, with larger particles (1-3 µm) formed in samples treated at 810°C and smaller (< 1 µm) particles formed in 750°C MA samples.
Figure 4.10 FE-SEM images of a) Sample 1, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 810°C for 1 hr, b) Sample 4, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 750°C for 1 hr, (c)(d) Sample 2, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 810°C for 1 hr, followed by 2 hr draw at 650°C. (e)(f) Sample 3, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 810°C for 1 hr, followed by 4 hr draw at 650°C.
Figure 4.11 FE-SEM images of (a)(b) Sample 6, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 750°C for 1 hr, followed by 4 hr draw at 650°C, c) Sample 7, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 700°C for 8 hr, d) Sample 8, solutionized at 1250°C for 1 hr, thermo-magnetically annealed at 650°C for 8 hr.

Figure 4.12 Hysteresis graph measurements of a) Samples 1, 2, and 3, 810°C MA series, b) Samples 4 and 6, 750°C MA series and c) Samples 9, 7, and 8, extended MA series.
Enlarged spinodal spacing is also observed near the grain boundary phases (Figure 4.10(d) and 4.11(b)) with an average size of 120 nm compared to 30-40 nm for interior grain spinodal spacing. Since the grain boundary phases grow with continued drawing time, it is possible this spinodal enlargement effect could be caused by diffusion of elements to the grain boundaries. Recalling the phase diagrams in section 2.3, γ phase should not be stable at temperatures below 850°C. However, XRD shows that grain boundaries are fcc γ, and not the allotropic bcc αγ, indicating that γ is stable over a larger range than previously thought. Compared to the α1 phase, γ has additional Ni and Cu, both fcc elemental structures, which could be stabilizing the high temperature fcc and preventing transformation to bcc (Figure 4.14).

Interestingly, the dark grain boundary phase does not have any distinguishable XRD peaks. No mention of this phase is found in literature. De Vos mentions that after two months of annealing time, another fcc γ2 phase is present, but does not elaborate on its composition or morphology [16]. Higuchi studies an ε phase by adding Ti to an alnico 5 grade. This ε phase was an Fe2Ti Laves-type intermetallic with an hcp structure [29], [61]. The ε phase co-precipitated with the α1 rods, and increased in stable temperature range with increasing Ti. Since the composition, structure, and morphology are not what is observed in alnico 8H, the dark phase is not ε.

The composition of the dark phase is reminiscent of a Heusler alloy of the Co2TiAl type. Dark phase composition varies across the sample area and contains significant amounts of Fe and Ni along with the enriched Co, Ti, and Al, so it cannot be a stoichiometric Co2TiAl. However, Heusler alloys have many different compositions along with quaternary varieties and alloy substitutions are commonly made with Fe, Ni, and other elements. In an
alloy of M₂XY, M is commonly Co, Ni, and Fe, X is often Ti or Fe, and Y is a group III, IV, or V element (such as Al or P) [62]–[65]. Atomic composition of the dark phase suggests (Co+Ni)₂(Ti+Fe)(Al+P) as the possible ordering. All of these alloy variations have an L₂₁ structure [62], [63], [65]. This could explain why the dark grain boundary phase is not observed in XRD measurements, as the α₂ peaks are very strong in comparison. Additionally, Heusler alloys containing Co often contain an fcc γ phase precipitate in comparable morphologies to what is seen in alnico 8H (Figure 4.13) [64], [66], [67]. Heusler alloys are characteristically ferromagnetic, with Curie temperatures ranging from 128K to 1100K depending on composition [62].

If the dark grain boundary phase is similar to a Heusler type alloy and is ferromagnetic, then, like γ, it is also detrimental to the magnetic properties of alnico. Hereafter the Co-Ti-Al rich dark grain boundary phase will be referred to as σ to avoid confusion with the α₁ phase.

The lamellar morphology of the γ and σ phases are suggestive of a larger scale spinodal decomposition. Compositions are not the same as α₁ and α₂, but show similar trends (Figure 4.14). Several problems exist with this theory, however, if σ is a Heusler type phase. Room temperature XRD still shows γ as fcc in structure, and spinodal decomposition cannot occur from fcc → fcc + L₂₁. Additionally, the σ phase only appears after significant heat treatment time, indicating there is a barrier to its nucleation. From Figure 4.15, the small changes in γ phase composition cannot account for the appearance of so much σ phase, nearly a 1:1 ratio in certain areas. Substantial diffusion of elements to and from the α₂ and α₁ phases is required to explain the compositions of γ + σ. Therefore it is more likely that
lamellar $\gamma + \sigma$ is not a spinodal decomposition but proceeds by a nucleation and growth mechanism similar to $\gamma$ growth in other Heusler alloys [64], [66], [67].

Figure 4.13 Microstructure of a quaternary L2$_1$ Heusler alloy containing increasing amounts of Co with $\gamma$ phase precipitates (white phase). Images obtained from Ma, Yang, and Liu [67].
Figure 4.14 Compositions of spinodal decomposition phases $\alpha_1$ (commercial BCC) and $\alpha_2$ (commercial L21) are compared to the composition of the $\gamma$ and $\sigma$ phases. $\gamma$ composition displayed is measured after $\sigma$ appears, which differs only slightly from composition before $\sigma$ presence. Composition data was acquired by EDS from TEM analysis (Figure 4.16), $\gamma$ and $\sigma$ compositions are obtained from gas-atomized HIP consolidated alnico 8H material, while $\alpha_1$ and $\alpha_2$ phase information was obtained from commercial material of the same type.
Figure 4.15 Composition of $\gamma$ before and after splitting into the lamellar morphology of $\gamma + \sigma$, along with composition of $\sigma$. All composition data was acquired by EDS from TEM analysis of gas-atomized HIP consolidated alnico 8H material.
It is difficult to differentiate the effects of $\gamma$ and $\sigma$ on the magnetic properties from the effects of spinodal decomposition. While it may appear from Figure 4.12 that with the growth of the grain boundary phases, there is a significant jump in coercivity, simultaneously shape anisotropy from the spinodal phases is increasing. Optimal commercial magnetic properties were not achieved in these heat treated samples, probably because of the simplified heat treatment and shortened time and higher temperature of the draw.

4.4 Conclusions

What is clear from the experiments on commercial alnico 8H is that conventional processing of alnico is not fully optimized. Oxides, especially in sintered varieties, can make up as much as 4% of the magnet, reducing total magnetization and remanence. Detrimental grain boundary $\gamma$, and the newly observed $\sigma$ phase are present in finished commercial magnets, possibly creating weak points for domain walls to pass through. Intragranular $\gamma$ was found in sintered varieties, further harming coercivity. Additionally, spinodal decomposition
wavelength in the finished magnets is 40 nm, which is too large for optimal magnetic properties according to theoretical calculations [4], [48].

A solution to the processing problems may come in the form of powder metallurgy. Gas atomization of alnico would provide very clean, homogenous powder, reducing the oxide content. Furthermore, the cooling rate of gas atomization can be upwards of $10^4$-$10^6\degree$C/s, avoiding nucleation of $\gamma$ and avoiding spinodal decomposition [68]. Without spinodal decomposition or gamma nucleation in the starting material, a new approach can be taken with heat treatments. Initial investigations into gas-atomized alnico processing are examined in the following chapter.
CHAPTER 5. GAS ATOMIZED ALNICO

Alnico 8H powder of 7.3Al-13.0Ni-38.0Co-32.3Fe-3.0Cu-6.4Ti (wt.%) composition was close-coupled gas-atomized using Ames Laboratory facilities. This is without the slight amounts (< 2 wt.%) of Nb, Si, or S additions found in commercial magnets. High purity (99.99%) starting materials and strict atmosphere control in the gas atomization process were used to reduce oxides and impurities like those found in commercial sintered powder. Starting materials were melted and heated to 1625°C before gas atomizing with 425 psi Ar gas. The resulting powders were spherical and averaged 30 μm in diameter. Chemical analysis by NSL Analytical shows the powders are very close to the starting composition: 32.4Fe-38.1Co-12.9Ni-7.3Al-6.4Ti-3.0Cu. XRD and TEM results (not shown) also determined that the powders solidified in the high temperature single phase α, completely avoiding spinodal composition. The powders were sorted into size ranges by sieving and air classification. Powders in the <20 μm, and 63-75 μm were used as the starting materials for experiments.

5.1 Hot Consolidation Methods

Two methods of powder consolidation were explored in this study. A high temperature 1250°C hot isostatic pressing, or HIP, sample was used to measure magnetic properties of gas-atomized alnico that could be compared to commercial cast and sintered varieties. A lower temperature 740-770°C spark plasma sintering (SPS) technique was used to test the feasibility of low temperature consolidation to avoid the harmful γ and σ phases.
5.1.1 Experimental Methods

5.1.1.1 Hot Isostatic Pressing

Gas-atomized alnico 8H powders < 20 μm in size were loaded into a stainless steel HIP can (FE-SEM of the powder is shown in Figure 5.1). Before sealing, the powders were outgassed at 425°C for 2 hours under high vacuum (10⁻⁵ torr). The can was sealed under vacuum by electron beam welding. The HIP process was done under pressure of 60 MPa for 4 hours, at 1250°C. Center sections of the HIP consolidated alnico were cut into 3 mm diameter by 8 mm cylinders using electrical discharge machining (EDM). Discs were prepared by standard metallography practices and were demagnetized prior to viewing. EDS mapping was used to determine composition. Orientation imaging microscopy (OIM) was used to determine grain size and orientation.

![FE-SEM image of <20 μm gas-atomized alnico 8H powders used for the HIP process at 1250°C. The scale bar is 50 μm.](image)

5.1.1.2 Spark Plasma Sintering

Spark plasma sintering was done by Quad City Manufacturing Laboratory at temperatures of 680, 740, and 770°C. This method was used to take advantage of the accelerated densification due to Joule heating effects at the particle contact points so that
lower temperature consolidation could be achieved [69]. A powder size range of 63-75 μm was used to better observe the densification mechanisms at particle contact points. SPS was done at 60 MPa with a 5 minute hold for the 770°C sample. For the 680 and 740°C samples, SPS parameters were 70 MPa with a 15 minute hold. Ramp rates for all samples were 100°C/min and 30 MPa/min. A 20 mm diameter graphite die was used to produce roughly 15 mm tall cylinders. For the 680 and 740°C samples, the graphite die and end caps were lined with Ta foil. Center sections of the SPS consolidated alnico were cut into 3 mm diameter by 8 mm cylinders using electrical discharge machining (EDM). Discs were prepared by standard metallography practices and were demagnetized prior to viewing. EDS mapping was used to determine composition. A Quanta FEI 250 field emission SEM equipped with an Oxford X-Max 85 mm² EDS detector was used for characterization.

5.1.2 Results and Discussion

5.1.2.1 Hot Isostatic Pressing

![FE-SEM image of 1250°C HIP consolidated sample using < 20 μm gas-atomized alnico 8H powders showing grain boundary γ phase and grain size.](image)
Figure 5.3 FE-SEM image of 1250°C HIP consolidated sample using < 20 μm gas-atomized alnico 8H powders showing γ phase size and spinodal structure.

Figure 5.4 OIM of 1250°C HIP sample showing grain size and grain orientation. Colors correlate to grain alignment with a crystallographic axis, color legend on the left.
As observed in Figures 5.2 and 5.3, the HIP process achieved full density of the gas-atomized powders. Additionally, oxides and impurities are << 1%, much improved compared to the sintered commercial powders (3-4% oxides and impurities). Unfortunately, slow cooling from HIP temperature due to the bulk of the sample and the surrounding gas caused some γ phase to form. The percentage and size of γ phase is comparable to commercial 8H, about 0.5-1% of the sample, averaging 0.6 μm in width. As in commercial cast 8H (before heat treatment), there is no presence of σ phase.

It is obvious from Figure 5.3 that spinodal decomposition has already occurred. It has an average spacing of 30 nm, nearly as large as fully heat treated material. This is to be expected due to the slow cool and presence of γ phase, as spinodal decomposition occurs on a much quicker time scale.

OIM results show the random orientation of grains in the HIP sample, as anticipated for an alnico 8 grade. Average size of grains is 30 μm, but with a large size distribution, which is apparent in Figure 5.4. The starting powder size was < 20 μm with grain sizes of 10 μm or smaller, indicating a substantial amount of grain growth occurred during the 4 hour HIP process. Future HIP processing should be done for a shorter amount of time, with a quicker cooling method to prevent grain overgrowth and avoid γ formation.

5.1.2.2 Spark Plasma Sintering

The SPS sample consolidated at 680°C held together as a compact, but was too fragile to be cut or polished for analysis. Density was approximately 65%, essentially tap density of the powders. This temperature is not viable for consolidation at 70 MPa.
Figure 5.5 FE-SEM images of gas-atomized alnico 8H powders consolidated by 770°C SPS showing sample density and intercellular γ and σ phases. Scale bars are (a) 500 μm, (b) 100 μm, (c) 20 μm, and (d) 5 μm.
The 770°C SPS sample was 91.5% dense, calculated by image analysis using ImageJ software. Figure 5.5(b) and 5.5(c) show that the particles did not deform with 60MPa pressure. Instead, densification was mostly caused by fractured material filling in voids. Additionally, most particles do not show evidence of necking, indicating that 5 minutes at 770°C is not enough time for diffusion to take place. Without necking, the strength of the magnet compact is considerably lowered.
The most significant and troubling observation is the extent of $\gamma$ and $\sigma$ phase growth within the sample, shown in Figure 5.5(c) and 5.5(d). Within 5 minutes at 770°C, large growth of $\gamma$ and $\sigma$ occurs between the cellular solidification structures of the gas-atomized powders. These phases can make up as much as 10-20% of the magnet material, with average intercellular growth spacing of 7 μm. According to literature, $\gamma$ phase should not be stable at this temperature, and should not grow (see Figure 2.3).

There are several possible explanations as to why this effect is observed. The Joule heating at particle contact points could be much higher than the bulk temperature of the sample, causing nucleation and growth of the phases at the contact points. Both phases are observed to cross over particle boundaries frequently, so it is possible that the particle contacts serve as nucleation points. A graphite die is used for the SPS process, and carbon is a well-known $\gamma$ stabilizer [35]. Additional carbon content within the sample was not observed with EDS, but it is possible that carbon amounts lower than what is detectable played a role in $\gamma/\sigma$ formation. The $\gamma$ and $\sigma$ phase fraction and size stayed relatively constant across the width of the magnet compact. One would expect that if C was stabilizing $\gamma$, the percentage would be greater towards the edges. Another possibility is that the missing Si or Nb from the gas-atomized powder composition is lowering the range where $\gamma$ is stable. Both of these elements are known $\alpha$ stabilizers [27], [29]. Typically, $\alpha$ stabilizers have the most effect on the upper temperature of the $\gamma$ phase field, so the missing alloy additions cannot account for all of the excessive $\gamma/\sigma$ growth.

To avoid any $\gamma$ stabilizing effects of C, the 740°C SPS sample die was furnished with Ta foil liners for the die body and end caps. Ta has the further benefit of being an $\alpha$ stabilizer [16]. Despite this, and the lower temperature, intercellular $\gamma$ and $\sigma$ growth still occurred.
(Figure 5.6(c)(d)). For the 740°C sample, σ and γ phases made up 5-8% of the magnet material (not including porosity). This is still much higher than the 0.5-1% found in commercial or HIP consolidated magnets. The density only reached 79.5% in the 740°C sample.

With reduced temperature and neutralized carbon effects, continued intercellular growth of γ and σ indicate those areas are particularly favorable for γ growth. EDS linescans on the 63-75 μm as-atomized powders used for SPS show Al depleted regions of the same average spacing as cell boundaries (Figure 5.7). Local compositions of other elements near cell boundaries did not show obvious enrichment or depletion. From Figure 4.15, γ phase is low in Al. An aluminum depletion could cause the driving force towards γ to be higher in those areas. Additionally, Al is a strong α stabilizer and a low Al area would be more likely to form γ [32], [41]. Al depleted zones (ADZ) in as-atomized powders are 1-3 μm in width, which corresponds well to the width of γ+σ regions in SPS samples.

The coupled growth of σ with γ is likely caused by the rejection of Al and Ti upon γ nucleation and growth. σ is enriched in both Al and Ti, and Ti is also a strong α stabilizer [32], [41]. Coupled formation of γ and σ upon local depletion or enrichment of Al and Ti would explain the eutectoid-like lamellar morphology.

Local composition gradients could also account for nucleation of γ often observed coming from Al₂O₃, TiO₂, TiS₂, and other particles. A very small depletion zone of Al or Ti in the adjacent material could be causing nucleation of γ. Most of these impurity particles lie on the grain boundaries, where γ growth could be thermodynamically favored. Interior grain oxides are also often observed with small γ precipitates. Examples of γ nucleation from Al and Ti rich particles are shown in Figures 4.4, 4.6, 4.7, 4.9, 4.10, and 4.11.
Figure 5.7 EDS linescan (in yellow) from a cross section of a 70 μm gas-atomized powder particle in the as-atomized state. Linescan data for Al (in red) corresponds to the position on the FE-SEM image below it.
Figure 5.8 EDS linescan data for other elements showing little to no change across cell boundaries. FE-SEM image of 770°C 5 min SPS sample showing $\gamma + \sigma$ growth at cell boundaries. ADZ spacing from EDS is roughly 7 μm, matching cell boundary spacing from SPS samples. ADZ width, ~2 μm, also corresponds to $\gamma + \sigma$ phase width in SPS samples. Images have been sized to match scale bars.
Given the high percentage of the detrimental \( \gamma \) and \( \sigma \) phases, and the low density of the compacts, it is evident that low temperature SPS is not an effective means of consolidation by itself. In chapter 6, two methods of \( \gamma/\sigma \) reduction are discussed which could be used in conjunction with SPS to produce a more useful magnet.

5.2 Modified Commercial Heat Treatments on HIP Samples

Heat treatments similar to commercial processes, like those done in section 4.3, were done on the HIP samples to compare the magnetic properties with commercial values.

5.2.1 Experimental Methods

Center sections of the HIP consolidated alnico were cut into 3 mm diameter by 8 mm cylinders using electrical discharge machining (EDM). Samples were not solutionized, with the belief that HIP at 1250°C would have the same effect. Later samples were solutionized for 10 minutes at 1250°C and water quenched to eliminate the 0.5-1% \( \gamma \) present after slow cooling from HIP. Magnetic annealing (MA) was done for 1 hour at two temperatures, 810°C and 750°C, in a 1 Tesla magnetic field applied along the axis of the cylinder. Figure 4.1 shows a schematic of the magnetic annealing furnace setup. The furnace was heated to temperature while still below the sample. Once the furnace was at temperature, it was moved up into the magnetic field, over the sample. Both furnace temperature and sample temperature were monitored with new, matching K-type nickel-chrome sheathed thermocouples and matching extension wire and connectors. These were calibrated such that the sample temperature was \( \pm 5 \)°C from the furnace program at all times. The furnace was dropped below the sample after the prescribed annealing time and samples were allowed to air cool. The magnetic field was removed once the samples fell below 300°C.
A subsequent annealing treatment (draw) was done in a box furnace in air at 650°C for 8 hours. Some samples received a stepped draw of 650°C for 4 hours and 590°C for 10 hours. Table 5.1 shows the processing temperatures and times for each cylinder. Magnetic measurements were taken in a closed-loop setup using a hysteresis graph with a 5 mm coil. Discs were prepared by standard metallography practices and were demagnetized prior to viewing. In some cases, an etchant of 25% HNO₃ and 25% H₂SO₄ was used to bring out the spinodal structure. It also preferentially etches γ. The etchant was applied with a cotton swab and was immediately rinsed away with deionized water.

Table 5.1 Heat treatment history of each gas-atomized alnico 8H sample after the 1250°C HIP process.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solutionizing treatment</th>
<th>Thermo-magnetic anneal</th>
<th>Draw</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C Min</td>
<td>°C min</td>
<td>°C hr</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>810 60</td>
<td>650 8</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>810 60</td>
<td>650 8</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>750 60</td>
<td>650 8</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>750 60</td>
<td>650 8</td>
</tr>
<tr>
<td>14</td>
<td>1250 10</td>
<td>810 60</td>
<td>650 8</td>
</tr>
<tr>
<td>15</td>
<td>1250 10</td>
<td>810 10</td>
<td>650 4</td>
</tr>
<tr>
<td>16</td>
<td>1250 10</td>
<td>810 10</td>
<td>590 10</td>
</tr>
<tr>
<td>17</td>
<td>1250 10</td>
<td>650 60</td>
<td>650 4</td>
</tr>
<tr>
<td>18</td>
<td>1250 10</td>
<td>810 10</td>
<td>590 10</td>
</tr>
<tr>
<td>19</td>
<td>1200 5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>as</td>
<td></td>
<td>hipped</td>
</tr>
</tbody>
</table>
5.2.2 Results and Discussion

Table 5.2 Closed-loop hysteresis graph magnetic property measurements of gas-atomized HIP consolidated heat treated samples compared to standard commercial properties set by the MMPA [22].

<table>
<thead>
<tr>
<th>Type</th>
<th>$B_{Hmax}$ (MGOe)</th>
<th>$B_r$ (T)</th>
<th>$B_s$ (T)</th>
<th>$H_c$ (Oe)</th>
<th>$H_{ci}$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast 8H</td>
<td>5.0</td>
<td>0.72</td>
<td></td>
<td>1900</td>
<td>2170</td>
</tr>
<tr>
<td>Sintered 8H</td>
<td>4.5</td>
<td>0.67</td>
<td></td>
<td>1800</td>
<td>2020</td>
</tr>
<tr>
<td>Sample 11</td>
<td>2.32</td>
<td>0.64</td>
<td>0.91</td>
<td>1168</td>
<td>1321</td>
</tr>
<tr>
<td>Sample 14</td>
<td>3.62</td>
<td>0.87</td>
<td>1.17</td>
<td>1090</td>
<td>1145</td>
</tr>
<tr>
<td>Sample 16</td>
<td>5.15</td>
<td>0.92</td>
<td>1.17</td>
<td>1377</td>
<td>1450</td>
</tr>
</tbody>
</table>

Figure 5.9 FE-SEM images of a) Sample 11, (etched), b) Sample 14, c) Sample 16, and d) Sample 17.
Figure 5.10 FE-SEM images of a) Sample 20, b) Sample 18, c) Sample 19, d) Sample 11, (etched), e) Sample 14, and f) Sample 16.

It is clear from the micrographs and magnetic property data that solutionizing HIP samples has several positive effects. From Figure 5.10(b), there is no remaining $\gamma$ phase after solutionizing. However, solutionization temperature is critical, as shown in Figure 5.10(c) of a 5 minute 1200°C anneal with 17% $\gamma$ phase. Solutionizating the HIP samples limited $\gamma$ nucleation and growth so that only very minimal amounts were detected after short MA times. After 1 hour, $\gamma+\sigma$ width in solutionized samples was 0.25 $\mu$m or less, compared to 1 $\mu$m or more in non-solutionized samples (Figure 5.10(d)(e)).
Figure 5.11 Hysteresis graph measurements of a) Samples 14 and 16, showing increased coercivity with a long draw and shorter MA time, b) Samples 11 and 14, showing significantly increase remanence and saturation after solutionization, c) Samples 10 and 15, showing benefits of solutionization and short MA time, d) Samples 16 and 17, difference between a one-step and two-step MA.

The final spinodal spacing in sample 11, which was cooled from HIP and magnetic annealed for 1 hour, averaged 90 nm. Solutionizing at 1250°C followed by a water quench
and MA for 1 hr at 810°C (sample 14) results in a final spinodal spacing of 60 nm. However, if the solutionized sample is magnetically annealed at 810°C for a shorter amount of time, as in sample 16 and 17, the spinodal spacing is 30-40 nm, which is the same spacing found in commercial samples. The smaller spinodal spacing and reduced γ and σ provided by the solutionization and quench increase maximum energy product by 56% in sample 14 compared to sample 11.

A shorter MA time, as well as a longer draw, increases maximum energy product by an additional 42% in sample 16. Sample 16, solutionized and magnetically annealed at 810°C for 10 minutes, with a stepped draw of 4 hrs at 650°C and 10 hrs at 590°C, had a maximum energy product of 5.15 MGOe. This value slightly exceeds standard commercial values for cast alnico 8H, and significantly exceeds the sintered 8H value of 4.5 MGOe. Magnetic properties in Table 5.2 show that the increased BH_{max} is caused by increased remanence to 0.92 T. Coercivity values for sample 16 were fair, not quite reaching commercial values. It would be reasonable to expect that with advanced optimization of the HIP, magnetic annealing, and drawing processes, additional improvements to coercivity and maximum energy product can be made.

### 5.3 Conclusions

What is clear from the experiments on gas-atomized alnico 8H is that both microstructure and nanostructure control are required for optimum magnetic properties in alnico. Spark plasma sintering of gas-atomized powders is perhaps not a viable consolidation method when performed on larger as-atomized powders due to their cellular solidification structure and aluminum depletion on cell boundaries. However, it did highlight that local
inhomogeneity of Al and Ti is likely an important nucleation mechanism for γ phase and γ+σ coupled growth.

Hot isostatic pressing of gas-atomized alnico is analogous to cast commercial 8H, but has the added benefit of a much lower content of oxides and other impurities, reducing γ nucleation sites. With a shorter HIP procedure, faster cooling, and an optimized heat treatment, gas-atomized HIP alnico 8H has promise as a high energy product alnico. Our current experimental energy product values match or exceed commercial 8H.

Methods to control local compositional fluctuation outside the range of γ nucleation temperatures should be considered to limit nucleation of γ during the magnetic annealing step. Chapter 6 examines two approaches for homogenization to suppress γ, which can be used on gas-atomized powders or consolidated material.
CHAPTER 6. GAMMA PHASE AVOIDANCE

6.1 Short Duration High Temperature Solutionization

The solutionization step of heat treatments is a type of γ phase avoidance already used in commercial alnico processing. Slow cooling from casting or sintering can allow 1-2% of γ to form, which would continue to grow during the following heat treatments. Solutionizing at 1250°C will remove the initially formed γ. Slow cooling through the critical range of 1200 to 800°C allows γ to re-nucleate on the numerous Al and Ti oxides, sulfides, and carbides, and grow during the MA and drawing steps.

The high temperature required to solutionize alnico into single phase α has the added benefit of very fast diffusion and long diffusion distances over short time. Rapid solutionization for 5 minutes should homogenize composition fluctuations, including α₁ and α₂ splitting, as well as remove γ, while maintaining grain size. Rapid cooling by quenching will ensure γ does not have time to nucleate, and will refine the spinodal structure to less than 10 nm.

6.1.1 Experimental Methods

Center sections of the 770°C SPS sample containing 10-20% γ phase were cut into 3 mm diameter by 8 mm cylinders using electrical discharge machining (EDM). Cylinders were sealed in a quartz tube with 1/3 atm argon before solutionizing in a Lindberg 59545-E1 box furnace at 1250°C for 5 minutes. The samples were water quenched and the quartz tube was broken to expedite cooling. Discs were prepared by standard metallography practices and were polished with a diamond water suspension.
6.1.2 Results and Discussion

Figure 6.1 FE-SEM images of (a)(b) 5 minute 1250°C solutionized SPS sample, (c)(d) as-received 770°C SPS.

Figure 6.1 is clear evidence that a 5 minute solutionizing time is sufficient to remove $\gamma + \sigma$ at 1250°C. Section 5.2 samples 14-18 show that 5-10 minutes of solutionization with a water quench will slow $\gamma$ nucleation and growth so that it is nearly non-existent after a 10 minute magnetic anneal, and minimal compared to commercial alnico when magnetically annealed for an hour.
6.2 Low Temperature Gamma Suppression

While rapid solutionization is an improvement over commercial methods, and significantly reduces γ and σ phases in the final microstructure, it is not the only method to remove composition fluctuations. A temperature low enough to be outside the range of γ nucleation, but high enough for diffusion to take place could be used to anneal gas-atomized powders and remove the aluminum depleted zones (ADZ) from the cell boundaries that were shown in section 5.1. As-atomized powders have very minimal oxides, with only a thin Al₂O₃ layer on the particle surface; the main contributor to γ nucleation are the ADZ on the cell boundaries.

From the diffusion distance approximation \( x \approx (Dt)^{1/2} \) where \( D \) is the Arrhenius relation \( D = D_0 e^{-Q/RT} \) it can be shown that Al will homogenize at a temperature of 650°C in slightly over 1 hour. Using values of \( D_0 = 30 \text{ cm}^2/\text{s} \) and \( Q = 234 \text{ kJ/mol} \) for diffusion of Al in α-iron, a diffusion distance of 0.8 μm is found for 1 hour at 650°C [70]. The ADZ areas average 2 μm in width, so 1 hour is just shy of homogenization according to the approximation. Any possible Ti depleted zones would also be homogenized, with a diffusion distance of approximately 15 μm in this time (\( D_0 = 2.1 \times 10^3 \text{ cm}^2/\text{s} \) and \( Q = 293 \text{ kJ/mol} \) in α-Fe) [71].

A low temperature 650°C magnetic anneal should also set the spinodal to a very fine spacing in the applied field direction. It is suspected that spinodal splitting occurs at this temperature due to the coercivity developed in the extended 650°C MA in sample 8 from section 4.3.
6.2.1 Experimental Methods

Gas-atomized powders in the 3-12 μm size range were wrapped in Ta foil and sealed in quartz in 1/3 atm argon. The quartz tube was loaded into the magnetic annealing furnace and heated up to 650°C with a heating rate of 50°C/min. A magnetic field of 1 T was applied at the start of heating. Furnace setup is shown in Figure 4.1. Samples were cooled in air.

Some samples received another magnetic anneal, conducted in the same way at 810°C for various times. Table 6.1 shows the processing times and temperatures for the powders.

Table 6.1 Heat treatment history of each gas-atomized alnico 8H 3-12 μm powder sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Low temp. magnetic anneal</th>
<th>Thermo-magnetic anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>hr</td>
</tr>
<tr>
<td>21</td>
<td>as atomized</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>650</td>
<td>8</td>
</tr>
<tr>
<td>23</td>
<td>650</td>
<td>8</td>
</tr>
<tr>
<td>24</td>
<td>650</td>
<td>8</td>
</tr>
<tr>
<td>25</td>
<td>650</td>
<td>1</td>
</tr>
<tr>
<td>26</td>
<td>650</td>
<td>3</td>
</tr>
<tr>
<td>27</td>
<td>*no applied field</td>
<td>790*</td>
</tr>
<tr>
<td>28</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.2.2 Results and Discussion

Figure 6.2 HAADF STEM image of sample 22, magnetically annealed at 650°C for 8 hr showing spinodal splitting with an average spacing of 5-7 nm. Images courtesy of Lin Zhou.
Figure 6.3 XRD powder data from a) Samples 21-25 and 28, and b) Samples 23, 26, and 27 showing very limited spinodal splitting at 650°C, but suppression of γ upon annealing at 810°C.
Figure 6.4 FE-SEM image of sample 23, 20 μm powder particle with a) largest contrast settings available in FE-SEM, and b) contrast greatly enhanced using ImageJ software. Beginnings of local composition fluctuations seem to be occurring at 810°C in some of the larger powders.

Figure 6.5 EDS linescan (in yellow) from a cross section of an 11 μm gas-atomized powder particle in the as-atomized state, sample 21. Powders were cold isostatic pressed in Al for cross sectioning purposes, so the particle edge effects in the linescan are not accurate.
Figure 6.3(a) shows very limited spinodal splitting at 650°C. TEM results from Figure 6.2 show that splitting exists and is 5-7 nm wide, but is not sharp and discrete. However, this indicates that considerable diffusion is taking place. This result is expected given that draw temperatures as low as 550°C are found beneficial to magnetic properties. After magnetic annealing at 810°C, none of the powders showed any γ peaks, even after 30 minutes. Field-emission SEM show no obvious γ in any of the powder samples. In some larger powders treated at 810°C, slight compositional differences appear on grain boundaries, shown in the enhanced contrast Figure 6.4(b).

Time at 650°C effects the degree of spinodal splitting that occurs at 810°C, with more time providing greater splitting into α₁ and α₂. Even sample 26, with only 1 hour at 650°C, shows greater separation than sample 28, treated at 790°C for 45 minutes. Sample 28 also has significant γ growth shown in Figure 6.3(a). Figure 6.3 indicates that by spinodally decomposing at low temperature, it is less likely for γ to form. Compositions of α₁ and α₂ are similar to γ and σ, as shown in Figure 4.14. Since α₁ and α₂ are the stable phases at low temperature, it is unlikely that they would transform to a less stable phase of similar composition. However, high-temperature α is not stable, and a region depleted in α stabilizers (such as near an Al or Ti oxide or a cell boundary) could transform to fcc γ. This could be especially sensitive around 800°C, where γ is more stable but α is not. While spinodal splitting has occurred in samples that have been 1250°C solutionized and cooled, they have not split completely, and large amounts of single phase α still exist. Relatively quick heating to 810°C without decomposing the remaining single phase α would then allow faster γ
Figure 6.6 FE-SEM of sample 17, MA 1 hr 650°C, MA 10 min 810°C, drawn 4 hr 650°C, 10 hr 590°C, showing very small γ+σ growth off an oxide particle.

nucleation. Solutionizing still has a beneficial effect on later heat treatments, since γ nucleation is slower than γ growth from previously nucleated particles. A low temperature 650°C heat treatment on consolidated material was performed on sample 17 from chapter 5 for 1 hr. One hour is not sufficient for complete spinodal splitting (Figure 6.3(b)), and very fine growth of γ+σ was observed from an Al₂O₃ particle (Figure 6.6). A longer low temperature treatment to fully spinodally decompose α phase may completely suppress γ nucleation.

The size range of powders used for the low temperature magnetic annealing study was 3-12 μm. Solidification microstructure for gas-atomized particles in this size range differs significantly from those of 63-75 μm as shown in section 5.1. Cellular solidification did not occur 3-12 μm powders, and no cell boundaries with ADZ were found in EDS
linescans (Figure 6.5), so it cannot be stated with certainty that ADZ and other local composition fluctuations are removed with a low temperature MA. However, if spinodal splitting takes place and suppresses γ nucleation as XRD suggests, a similar effect could occur in larger powder sizes.

### 6.3 Conclusions

Rapid solutionization is an effective method for removing compositional fluctuations in α, which seems to be a significant factor in γ nucleation and γ+σ coupled growth. Complete solutionization can occur in less than 5 minutes. Using the same diffusion approximations as in section 6.2, 1250°C for 5 minutes has a diffusion distance of 92 μm for Al. This is many times what is necessary to homogenize the material.

Low temperature 650°C magnetic anneal will suppress γ growth for even longer amounts of time, up to 30 minutes when held at 810°C. This seems to be the effect of more complete spinodal splitting at 810°C, which is assisted by a long (3+ hr) 650°C MA.

A combination of these methods could be explored in consolidated material and larger powder sizes. A rapid solutionization treatment can be incorporated to destroy any ADZ or previously nucleated γ, followed by quenching, which leaves a small spinodal spacing and a significant amount of single phase α. Long 650°C annealing could then develop the spinodal splitting, while remaining finely spaced, before a high temperature 810°C MA to completely split and improve magnetic properties.
CHAPTER 7. CONCLUSIONS

The preceding chapters have discussed processing methods for use in alnico 8H material to control microstructure and ultimately improve magnetic properties. Commercial alnico 8H were found to have as much as 4% volume of oxides and other impurities. Approximately 1% volume of the detrimental γ phase was found, as well as a previously unreported phase, likely L2₁ in structure, which has been named σ. Nucleation of γ and σ was often observed on oxides, sulfides, and carbides.

Gas atomization of pre-alloyed alnico powders is advantageous due to the very low oxide content, and rapid cooling rates to solidify without nucleation of γ or spinodal splitting. Full density consolidation by HIP was successful, and the resulting heat-treated samples were significantly higher in remanence and saturation compared to commercial alnico 8H, but did not achieve the same coercivity. Maximum energy product matched or slightly exceeded commercial values.

Spark plasma sintering of gas-atomized powders caused excessive coupled growth of γ and σ phases along the cell boundaries of the powders, even at temperatures of 740°C. This highlighted a possible mechanism for γ nucleation in the α phase at sites with a local composition fluctuation, e.g., aluminum depletion. This was confirmed by EDS linescans of 63-75 μm powders showing aluminum depleted zones (ADZ) at the cell boundaries. A similar phenomenon could be occurring near Al and Ti oxides, sulfides, and carbides, explaining the frequent nucleation of γ at these sites. The coupled growth of σ with γ is probably caused by the rejection of Al and Ti from γ phase; σ is rich in both Al and Ti and both are strong α stabilizers.
The detrimental effects of even small amounts of $\gamma$ from hot isostatic pressing was observed from magnetic property measurements of heat treated samples, resulting in a drastic decrease in maximum energy product. Increased spinodal decomposition spacing also decreased energy product. It is clear from magnetic property data that both spinodal nanostructure and microstructure must be controlled for optimum magnetic properties in the finished magnet.

Microstructure control should include methods of reducing oxides and impurities, as well as other areas of compositional variation in $\alpha$, and eliminating any $\gamma$ product phases that have formed during casting/sintering/other processing methods. Rapid high temperature solutionization and water quenching were effective at removing all $\gamma+\sigma$ growth at grain and cell boundaries. Low temperature magnetic annealing at 650°C was found to suppress $\gamma$ growth at the usual magnetic annealing temperature of 810°C for up to 30 minutes. XRD data shows that a very fine scale spinodal decomposition is promoted by a 650°C MA. Longer annealing times at 650°C assist with a more complete spinodal splitting at 810°C due to the higher diffusional mobility. Samples without this low temperature (650°C) treatment still have a significant portion of single phase $\alpha$ after short 810°C anneals. These samples also have a higher percentage of $\gamma$ nucleation and growth. This observation suggests that $\gamma$ nucleates in areas of single phase $\alpha$, but not in areas of spinodally decomposed $\alpha_1$ and $\alpha_2$. Rapid solutionization of a HIP consolidated gas-atomized alnico 8H sample, followed by low temperature magnetic annealing for greater than 3 hours, along with a subsequent heat treatment process to promote optimized spinodal nanostructure could be expected to have improved magnetic properties over the 5.15 BH$_{\text{max}}$ achieved to date.
7.1 Recommendations for Future Work

Several of the hypotheses presented here could be more thoroughly investigated to develop a better understanding of the thermodynamics and kinetics of the alnico system, particularly in regards to the γ and σ phases. A time-temperature-transformation study of the γ phase should be completed. Effects of oxides and impurities, cooling and heating rates, grain size, decomposition of α, and local homogeneity of the starting material will need to be considered.

Further analysis of the gas-atomized powders should be pursued to determine what size ranges of powders exhibit cell boundaries with ADZ, and if any other composition fluctuations exist. Low temperature annealing effects on powders with ADZ should be conducted to see if the fluctuations are removed.

Additional XRD analysis on heat-treated powders should be performed to confirm initial results that low temperature annealing enhances spinodal composition, and that γ phase is nucleated primarily in single phase α regions.

Finally, optimization of the spinodal nanostructure, i.e., spinodal decomposition spacing of 15nm or less, along with considerations of complete suppression of the micron-scale (solidification-related) γ nucleation and growth mechanisms should be studied and achieved for ultimate magnetic property improvements.
REFERENCES


