Prospects for Improving alnico

Matthew J. Kramer

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Acknowledgements

- Qingfeng ‘Sam’ Xing and Lin Zhou
  - TEM
- Ping Lu, Sandia National Laboratory
  - Aberration corrected STEM/EDS mapping
- Kevin Dennis and Haley Dillon
  - Sample preparation
- Fran Laabs
  - OIM
- Warren Straszheim
  - SEM/ EPMA
- Steve Constantinides, Arnold Magnetic Technologies
  - Supplied samples and invaluable insights
- Mike Miller, Oak Ridge National Laboratory
  - 3D atom probe
- Iver Anderson and Bill McCallum
Energy Density

- RE permanent magnets clearly best all older technologies
  - BUT!
Variety of Synthesis Routes

- Casting or Sintering
- Isotropic alloys containing up to 12% Co are called **Alnico**
- Orientation of the spinodal can be biased with the application of a magnetic field
  - Alcomax - 20-25% Co with $H_{ci} \ 45-60 \ \text{kA/m}$
- Directional growth using heated molds or Bridgemann methods
  - Arkomax 800 and Alnico 9
Alloying Challenges

• Various other transition metals are added to improve various properties such as $H_{ci}$
  – Ti, Cu and Nb are most common
    • Empirically developed in the 50’s and 60’s
  – Why are some additions more effective?

• Control Al loss during processing

• Improve castabilty without degrading magnetic properties.

Uncertain how to improve the coercivity ($H_{ci}$) while maintaining Remanent Flux Density ($B_r$)!
Microstructure

- Fe-Co rich precipitates in Ni-Al rich matrix
  - Decomposes along \{001\} planes
  - Proceeds in the \langle001\rangle directions
- Preferential growth of precipitates parallel to a magnetic field
  - Spinodal decomposition range lies below $T_{(c)}$, allowing alignment
- Aligned precipitates enhance coercivity through shape anisotropy
Isotropic vs Grain Aligned

- Random grain orientation results in low magnetization
  - Projection of the applied field to the prismatic directions
- Grain alignment increases $B_r$.
  - Need defects to pin flux
    - Columnar vs equiaxed
Volume Fraction

• Role of Ni-Al rich phase
  – Maintains shape anisotropy by separating needles
  – Average spacing ~7.4nm (grain aligned 5-7)
• Volume fraction of Fe-Co rich particles
  – 62% for 5-7
• Theoretical maximum in energy product occurs at f=2/3
  – Assumes a pure NiAl matrix and pure FeCo rods

STEM micrograph of columnar Arnold Alnico 5-7 looking along the growth axis.

Alnico samples investigated

- Extensive characterization of alnico samples from Arnold
  - High Fe, directionally cast 5-7
  - High Co, isotropic 8
    - Performed quenching experiments on samples from Arnold
  - Directionally grown 9
- Role chemistry and nanostructure on $B_r$ and $H_{ci}$.

<table>
<thead>
<tr>
<th>sample</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Al</th>
<th>Cu</th>
<th>Nb</th>
<th>Ti</th>
<th>$B_r$ (kG)</th>
<th>$H_{ci}$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-7</td>
<td>49.9</td>
<td>24.3</td>
<td>14.0</td>
<td>8.2</td>
<td>2.3</td>
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<td>13.5</td>
<td>740</td>
</tr>
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<td>8</td>
<td>30.0</td>
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<td>10.6</td>
<td>1500</td>
</tr>
</tbody>
</table>
5-7 in more detail

- What are the structures of the two phases?
- How coherent are the interfaces?
- Partitioning of the elements?
- Where does the domain wall pinning occur?
HRTEM VS STEM Imaging

- **HRTEM**
  - Planer illumination
  - Multi-beam scattering
  - Image contrast
    - Thickness
    - defocus
- **Z-contrast**
  - Scans a fine probe
  - Electrons are scattered to an annular detector
  - Strength of the scattering $\sim Z$

From Eiji Abe and An Pang Tsai
Structure and Chemistry

- Only TEM/STEM provides both the sensitivity and spatial resolution.

Energy Dispersive Detector

- Incident converged beam

- Specimen

- ADF detector 10-50 mrad

- HAADF detector > 50 mrad off-axis

- BF detector < 10 mrad

Probe corrected STEM images taken at Sandia with a FEI Titian
Interface

- EDS mapping of the Fe-Co rich regions (red) and the Al-Ni rich regions (green)

- HR STEM imaging of the coherent interface
Atom Probe Tomography

- Greater spatial resolution and lower limit sensitivity
  - Define a small volume and count atoms along the axis orthogonal to the interface
  - Confirmed STEM/EDS

Chemical distribution along a volume within the larger data set
Precise Atomic Distributions

• What is the composition of the Fe-Co and Al-Ni rich regions?
• How sharp is the interface
  – Define unique surfaces and count atoms in an area at a fixed distance from that surface
    • Higher counts
    • Interface maybe less sharp

Chemical distribution as a distance from a iso-surface
Summary 5-7

- Well defined ‘prismatic blocks’ of well faceted –(001) - bcc (Fe,Co) ~ 40-60 nm in diameter but of uncertain length (> 100 nm).
- Thin, ~ 5 nm, B2 (Ni,Al,Co,Fe), with minor Cu
- Fully coherent interfaces
- Volume fraction bcc:B2 ~ 61:39

Composition of the Spinodal Phases

<table>
<thead>
<tr>
<th></th>
<th>bcc</th>
<th>B2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at.%</td>
<td>(error)</td>
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<tr>
<td>Fe</td>
<td>68.1</td>
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<tr>
<td>Co</td>
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<td>0.06</td>
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<tr>
<td>Si</td>
<td>0.5</td>
<td>0.11</td>
</tr>
<tr>
<td>Ga</td>
<td>0.4</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Effect of Changing Chemistry

- Add a bit more Co, Cu and Ti
  - $B_r \downarrow$
  - $H_{ci} \uparrow$
- Doubles energy density
Alnico 8

- Cast alloy
  - Random grain orientation
  - But heat treated in a magnetic field
- Higher Co and Ti

<table>
<thead>
<tr>
<th>sample</th>
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<th>Al</th>
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<th>Ti</th>
<th>Br</th>
<th>Hci</th>
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</table>
**Alnico 8**

- Significant change in chemistry and morphology for alnico 8 (and 9)

**EBSD pole figure showing a grain well aligned to the applied field during cooling**

**STEM HAADF image showing Fe-Co (bright regions) interspersed with intermetallic**
Electron diffraction shows that the intermetallic phase is no longer the B2 but is an ordered fcc (DO$_3$ or L1$_2$).

TEM and APT both show clear segregation of the Cu to the regions in-between the bcc and L1$_2$. 
Alnico 8

• Summary
  – ‘NiAl’ L$_{21}$ appears more continuous
  – Cu precipitates at boundary between the ‘AlNi’
  – FeCo more blocky rather than prismatic?
    • Need to get a clearer picture of the 3D morphology
  – bcc : L$_{21}$ as low as 29:71

<table>
<thead>
<tr>
<th>Element</th>
<th>bcc at.% (error)</th>
<th>L$_{21}$ at.% (error)</th>
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<tr>
<td>Fe</td>
<td>52.3 0.60</td>
<td>18.8 0.79</td>
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<tr>
<td>Co</td>
<td>37.6 0.58</td>
<td>32.3 0.95</td>
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<tr>
<td>Ni</td>
<td>3.2 0.21</td>
<td>15.8 0.74</td>
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<tr>
<td>Al</td>
<td>4.3 0.24</td>
<td>14.6 0.71</td>
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<tr>
<td>Cu</td>
<td>0.7 0.10</td>
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<td>Ti</td>
<td>1.4 0.14</td>
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<tr>
<td>Si</td>
<td>0.2 0.05</td>
<td>0.4 0.12</td>
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<tr>
<td>Ga</td>
<td>0.3 0.07</td>
<td>0.3 0.11</td>
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</table>

Most data sets show a high Fe and Co in the L$_{21}$ phase.
Alnico 9

- Cast alloy
  - Aligned grain orientation
  - and heat treated in a magnetic field
- Less Co and Ti than 8

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<tr>
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<th>Ni</th>
<th>Al</th>
<th>Cu</th>
<th>Nb</th>
<th>Ti</th>
<th>Br</th>
<th>Hci</th>
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<td>0.5</td>
<td>5.0</td>
<td>10.6</td>
<td>1500</td>
</tr>
</tbody>
</table>
• Morphology very similar to the alnico 8
  – $L2_1$ as the matrix phase
  – Cu between bcc and $L2_1$

Dark field image confirming the $L2_1$ structure of the intermetallic

HRTEM showing the coherent interfaces and the different ordering of the intermetallic
STEM EDS mapping reveals some subtleties in the Al-Ni-Ti distributions
Longitudinal section

HAADF STEM image taken under [100] zone axis.
Composition Profiles
alnico 9

- Al and Ni enrichment at the GB
- High Fe and Co content to matrix

Chemical distribution as a distance from the Fe-Co and Al-Ni phases
Alnico 9

• Summary
  – Very high aspect ratio
    • Ends more tappered
  – 3DAP though shows similar chemical distributions
  – bcc:L2₁ 53:47
    • Higher ratio may explain the slightly higher Bᵣ

<table>
<thead>
<tr>
<th></th>
<th>bcc at.%</th>
<th>L2₁ at.%</th>
<th>bcc (error)</th>
<th>L2₁ (error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>54.4</td>
<td>10.8</td>
<td>1.26</td>
<td>0.65</td>
</tr>
<tr>
<td>Co</td>
<td>36.5</td>
<td>28.7</td>
<td>1.22</td>
<td>0.94</td>
</tr>
<tr>
<td>Ni</td>
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<td>20.6</td>
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</tr>
<tr>
<td>Al</td>
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<td>0.89</td>
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<tr>
<td>Cu</td>
<td>0.4</td>
<td>1.5</td>
<td>0.16</td>
<td>0.25</td>
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<tr>
<td>Ti</td>
<td>0.5</td>
<td>12.9</td>
<td>0.18</td>
<td>0.70</td>
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<tr>
<td>Cr</td>
<td>0.1</td>
<td>0.9</td>
<td>0.08</td>
<td>0.19</td>
</tr>
<tr>
<td>O</td>
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<td>0.1</td>
<td>0.13</td>
<td>0.07</td>
</tr>
<tr>
<td>N</td>
<td>0.0</td>
<td>0.1</td>
<td>0.03</td>
<td>0.04</td>
</tr>
<tr>
<td>Ga</td>
<td>0.2</td>
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<td>0.10</td>
<td>0.06</td>
</tr>
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# Spinodal Phases

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<thead>
<tr>
<th></th>
<th>Fe-Co</th>
<th>'Al-Ni'</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>bcc phase (at. %)</td>
<td>intermetallic phase (at. %)</td>
</tr>
<tr>
<td>5-7</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Fe</td>
<td>68.1</td>
<td>52.3 54.4</td>
</tr>
<tr>
<td>Co</td>
<td>24.2</td>
<td>37.6 36.5</td>
</tr>
<tr>
<td>Ni</td>
<td>2.6</td>
<td>3.2   3.5</td>
</tr>
<tr>
<td>Al</td>
<td>3.6</td>
<td>4.3   4.0</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5</td>
<td>0.7   0.4</td>
</tr>
<tr>
<td>Nb</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>Ti</td>
<td>1.4</td>
<td>0.5   0.3</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Si</td>
<td>0.5</td>
<td>0.2   0.4</td>
</tr>
</tbody>
</table>
Estimate Limits

- $B_r \approx f*M_s$
- $H_{c_i} \approx (1-f)(N_b-N_a)4\pi*M_s$
- $H_{c_i} \approx 1/2(1-f)B_r + H_a$
- $BH_{\text{max}}$ occurs where $f \approx 2/3$
- $BH_{\text{max}} < \mu_0 M_s^2/12 \approx 1/2 H_{c_i}B_r$

## Theoretical Limits

<table>
<thead>
<tr>
<th></th>
<th>Alnico 5-7</th>
<th>Alnico 8</th>
<th>Alnico 9</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>aspect ratio</strong></td>
<td>~ 5:1</td>
<td>~ 10:1</td>
<td>&gt; 10:1</td>
</tr>
<tr>
<td><strong>fraction bcc phase (f)</strong></td>
<td>0.62</td>
<td>0.4</td>
<td>0.53</td>
</tr>
<tr>
<td><strong>Fe:Co in bcc phase</strong></td>
<td>0.74</td>
<td>0.58</td>
<td>0.60</td>
</tr>
<tr>
<td><strong>mole % Fe+Co in bcc</strong></td>
<td>0.92</td>
<td>0.90</td>
<td>0.91</td>
</tr>
<tr>
<td><strong>$\sim M_s$ (KG) for bcc based on Fe:Co</strong></td>
<td>23.8</td>
<td>23.9</td>
<td>23.9</td>
</tr>
<tr>
<td><strong>Fe:Co in intermetallic</strong></td>
<td>0.44</td>
<td>0.37</td>
<td>0.27</td>
</tr>
<tr>
<td><strong>mole % Fe+Co in bcc</strong></td>
<td><strong>0.31</strong></td>
<td><strong>0.51</strong></td>
<td><strong>0.40</strong></td>
</tr>
<tr>
<td><strong>$B_r$ (KG)</strong></td>
<td>measured: 13.5</td>
<td>calculated: 13.6</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>measured: 8.2</td>
<td>calculated: 8.6</td>
<td>11.5</td>
</tr>
<tr>
<td><strong>$H_{ci}$ (Oe)</strong></td>
<td>measured: 740</td>
<td>calculated: 3105</td>
<td>1500</td>
</tr>
<tr>
<td></td>
<td>measured: 1860</td>
<td>calculated: 4365</td>
<td>3715</td>
</tr>
<tr>
<td><strong>$BH_{max}$ (MGOe)</strong></td>
<td>measured: 7.5</td>
<td>calculated: 21.1</td>
<td>21.4</td>
</tr>
<tr>
<td></td>
<td>measured: 5.3</td>
<td>calculated: 18.8</td>
<td>9.0</td>
</tr>
</tbody>
</table>
Summary

- The 5-7 has both a different nanoscaling of the spinodal and the non-magnetic phase which forms with the bcc phase.
  - The bcc in 5-7 has higher Fe:Co, consistent with the bulk
  - Has a higher phase fraction of the bcc
  - The Cu is uniform in the B2 phase
  - Uniform long prismatic bcc grains aligned to the applied field
    - \{001\} type facets coherent with the B2
Summary

- The 8 and 9 alloys have faceted bcc grains separated from the L2₁ by Cu.
- Is L2₁ is too high in elements with moments?
  - Also see small FeCo nodules in the L2₁ phase.
- Is the high Co and Fe needed to form the L2₁ phase?
- Pathway to finer FeCo phase is unclear
  - Simply quenching faster won’t work.
  - Need to develop the isolated grains
  - What role does Cu and Ti play?
Summary

• The 5-7 with low Co and no Ti has higher proportion of the bcc and narrower separation of the non-magnetic phase.
  – Consistent with the higher Br and lower $H_{ci}$
• The 8 and 9 have higher Co and Cu and added Ti resulting in less bcc but with larger separation.
  – The non-magnetic phase is $L2_1$ with $\{110\}$ faceting with bcc
  – Consistent with the higher $H_{ci}$ and lower Br
Challenges to improving alnico

- Alnico 5-7 has acceptable $B_r$
  - How to improve $H_{ci}$?
    - Is the spacing too small
- Alnico 8 and 9 have acceptable $H_{ci}$
  - Is the high Co needed to form the coherent L2$_1$?
    - At least reduce cost!
  - How to increase fraction of the bcc?
- Hinges on knowing what controls coercivity.
Observations

• Cu appears as a rod to sheet like precipitates only a few nm in thickness between the ‘Al-Ni’ and ‘Fe-Co’ phases in the alnico 8 and 9 and is uniform in the ‘Al-Ni’ in the 5-7.
• Ti partitions to the ‘Al-Ni’ phase.
• The Fe:Co ratio is considerably higher in the ‘Fe-Co’ phase in the 5-7.
• Volume fraction of the ‘Fe-Co’ lower in the alnico 8 and 9.
• The 8 has the highest Co studied
  – Responsible for the lower $B_r$?
    • Note Fe:Co is $\sim$ 58:42
    • Volume fraction bcc $\sim$ 50%
  – Responsible for forming $L2_1$
  – Change in bcc morphology
    • Role in $H_{ci}$?
• Where is the pinning?

Data is consistent with AlNi$_2$Ti SG225,
$\alpha$=5.74 (~2x bcc Fe)
Al 0,0,0
Ni $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$
Ti $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$
size of Al-Ni rich phase. 10-20nm long, ~several nanometer wide

size 30-50nm long, ~12nm wide

size ~20nm along diagonal direction of those patches

All images are taken along [110] zone axis at the same magnification. The bright region is the FeCo-rich phase, while the dark region is the AlNi-rich phase. The AlNi-rich phase showed D03 ordering. The as quenched sample has similar morphology as the 5min annealed one, but with smaller grain size. Their phase boundaries are bounded by \{110\} and \{100\} planes. However, the 10min annealed one shows a distinctive change in morphology. Its phase boundaries are \{001\}, \{100\}, or \{110\} planes.
Alnico 8, 1250°C quenched

- Images waiting for MM but consistent w/ TEM.
  - Unable to suppress spinodal
- BUT only 1 interface over 87M counts.
- ~ 1 nm sized Cu clusters
90s hold at 850°C
10 min hold at 850°C
The spatial distribution of the spinodal is coarser, but in many respects the general elemental distributions don’t change much.

- But are differences in the details

The other TM are more uniform in concentration in the optimal alloy (except Co) while Ni, Al and Ti

But the finer spinodal is interconnected!