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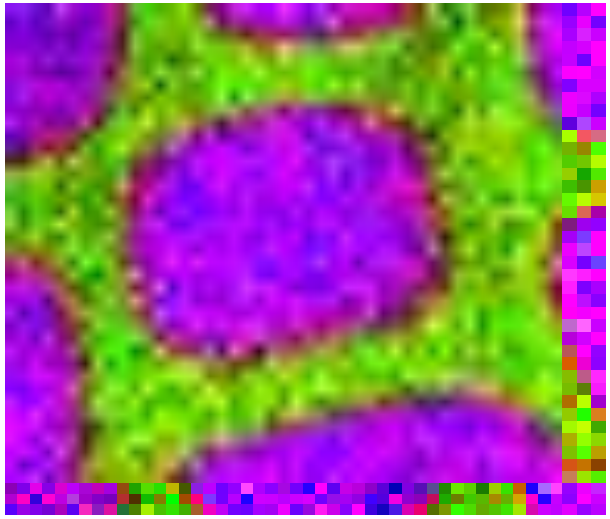

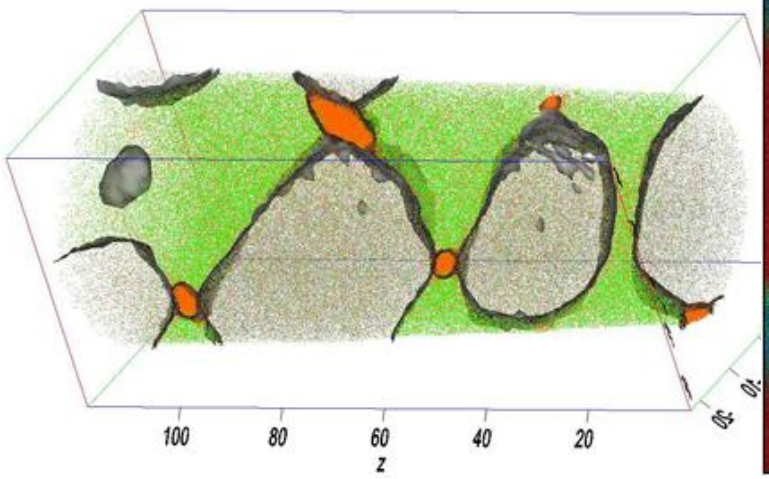

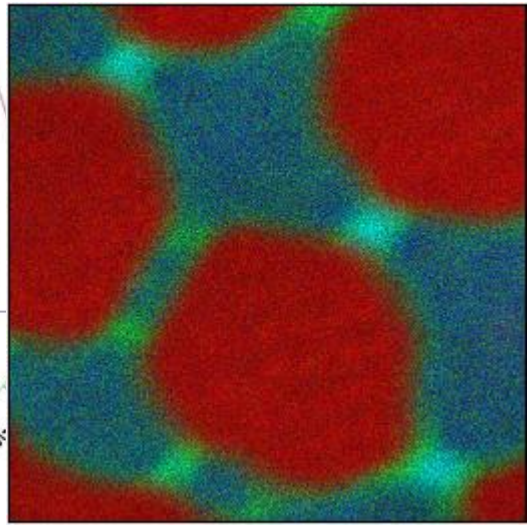

Prospects for Improving alnico

Matthew J. Kramer

2013 TMS Spring Meeting

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Acknowledgements

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  - Aberration corrected STEM/EDS mapping
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    - 3D atom probe
- Iver Anderson and Bill McCallum

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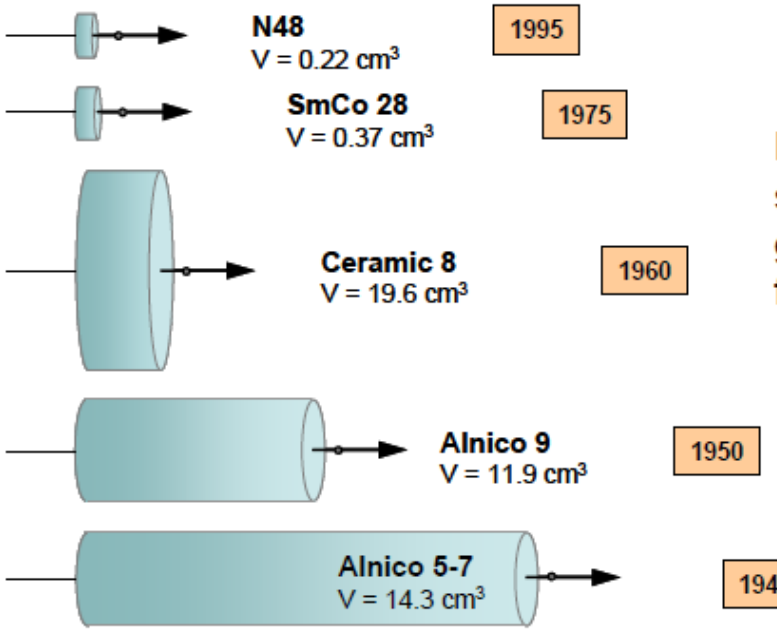
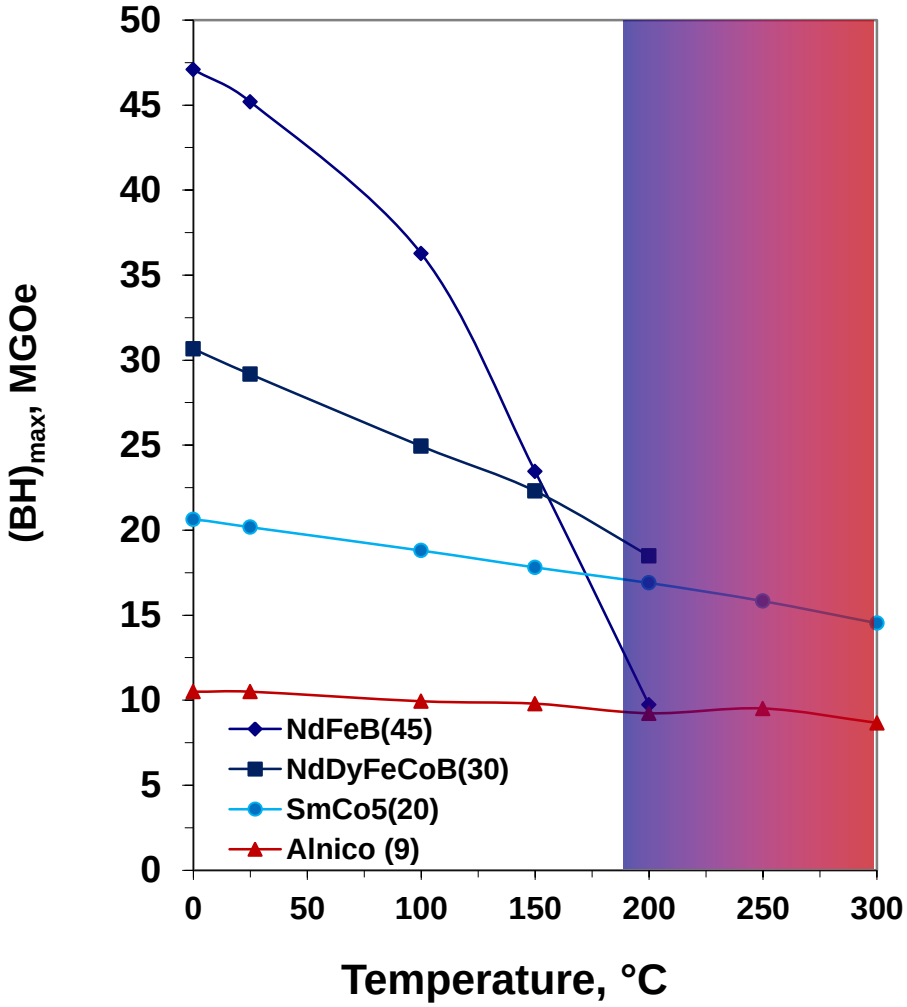
Energy Density

- 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 kA/m
- Directional growth using heated molds or Bridgemann methods
  - Arkomax 800 and Alnico 9

Alloying Challenges

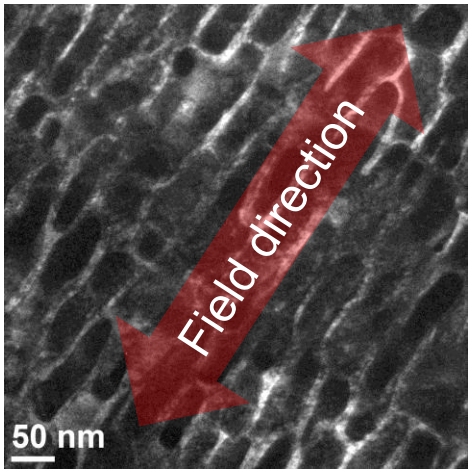
- Various other transition metals are added to improve various properties such as H_{ci}
  - Ti, Cu and Nb are most common
    - Empirically developed in the 50's and 60's
  - *Why are some additions more effective?*
- Control Al loss during processing
- Improve castabilty without degrading magnetic properties.

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

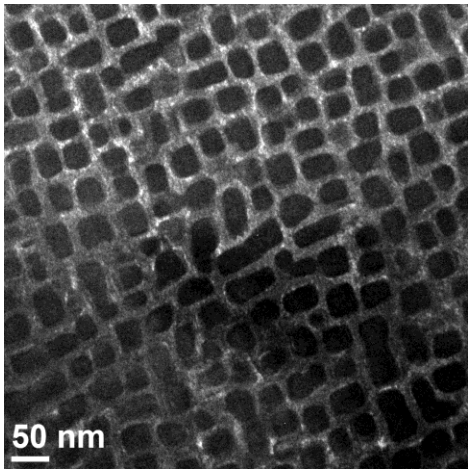
Microstructure

- Fe-Co rich precipitates in Ni-Al rich matrix
  - Decomposes along {001} planes
  - Proceeds in the <001> 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

Longitudinal



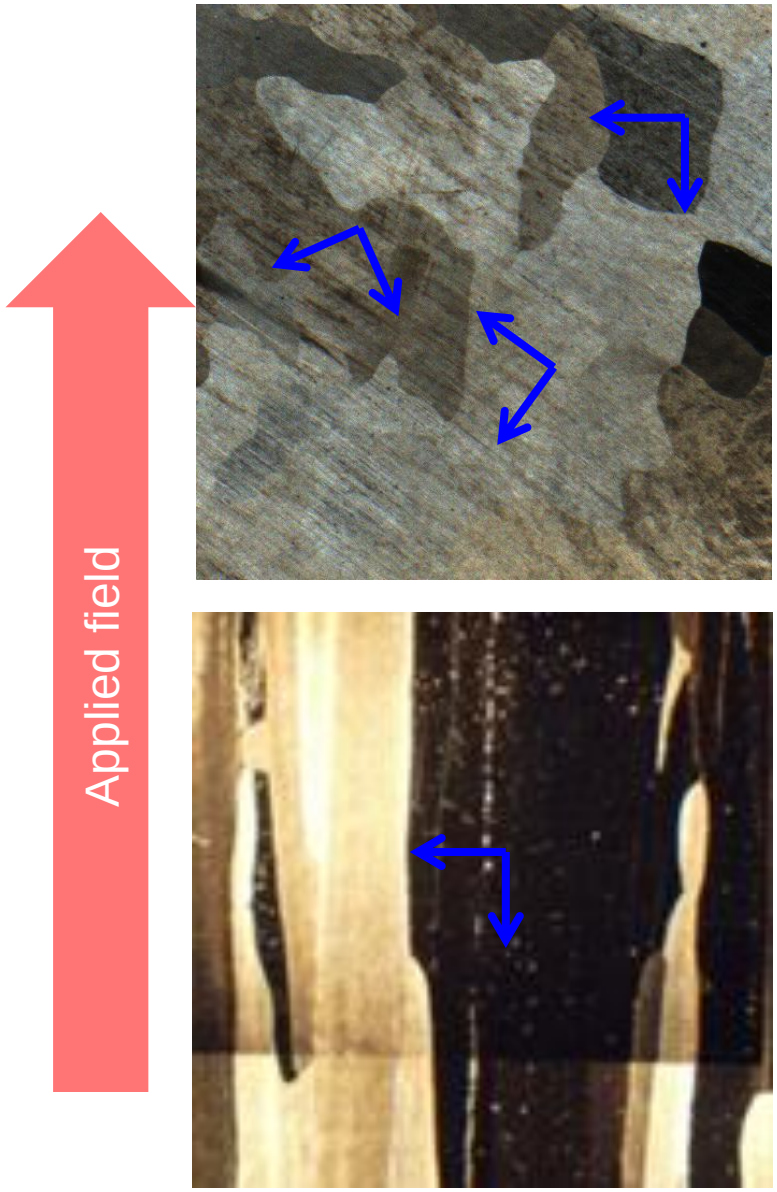
Transverse



TEM DF images of Arnold Alnico 5-7

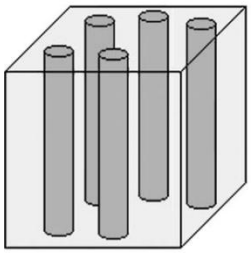
Isotropic vs Grain Aligned

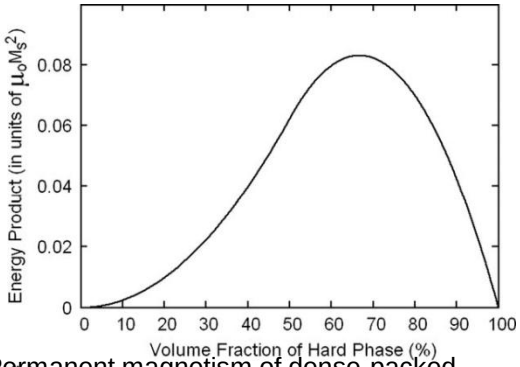
- Random grain orientation results in low magnetization
  - Projection of the applied field to the prismatic directions
- Grain alignment increases B_r.
  - Need defects to pin flux
    - Columnar vs equiaxed



Volume Fraction

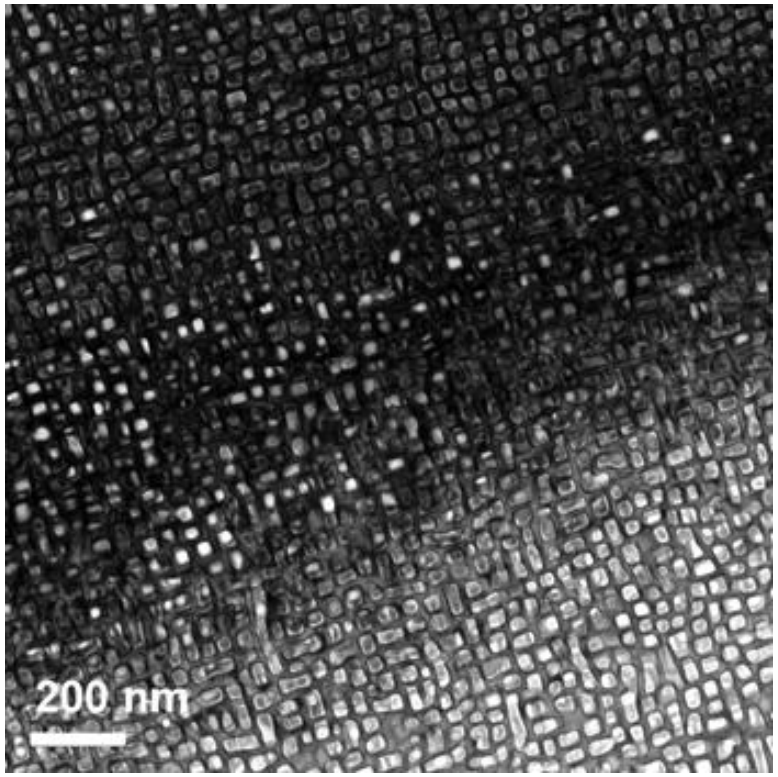
- Role of Ni-Al rich phase
  - Maintains shape anisotropy by separating needles
  - Average spacing ~7.4nm (grain aligned 5-7)
- Volume fraction of Fe-Co rich particles
  - 62% for 5-7
- Theoretical maximum in energy product occurs at f=2/3
  - Assumes a pure NiAl matrix and pure FeCo rods





(a) (b)

Skomski, R. et al.(2010). Permanent magnetism of dense-packed nanostructures. *Journal of Applied Physics*, *107*(9)



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

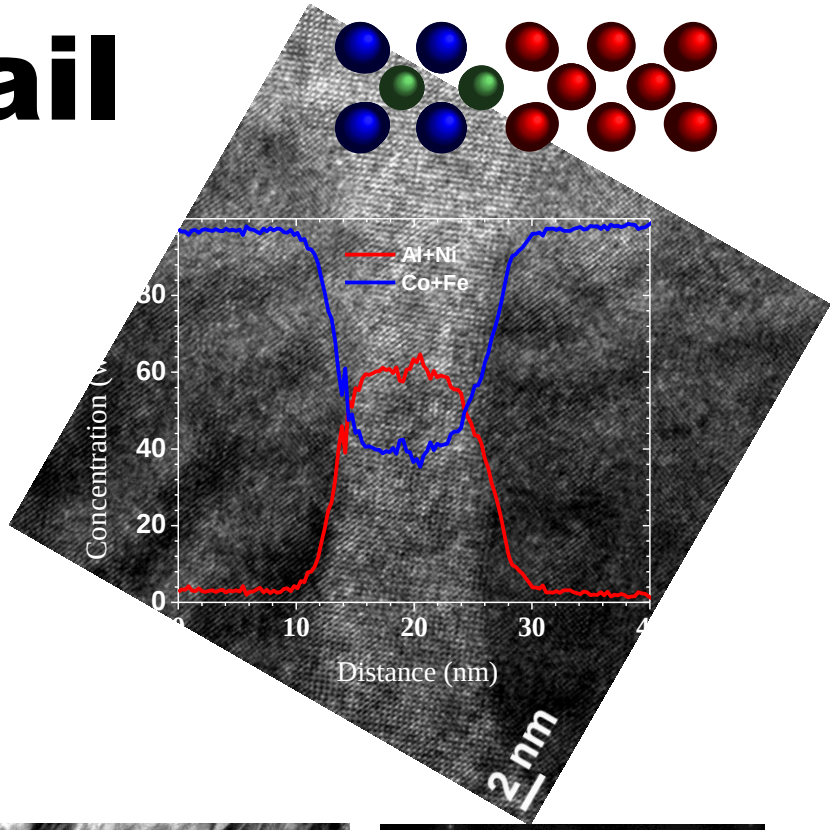
Alnico samples investigated

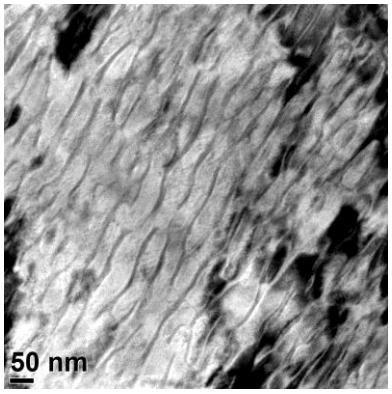
- Extensive characterization of alnico samples from Arnold
  - High Fe, directionally cast 5-7
  - High Co, isotropic 8
    - Performed quenching experiments on samples from Arnold
  - Directionally grown 9
- Role chemistry and nanostructure on B_r and H_{ci}.

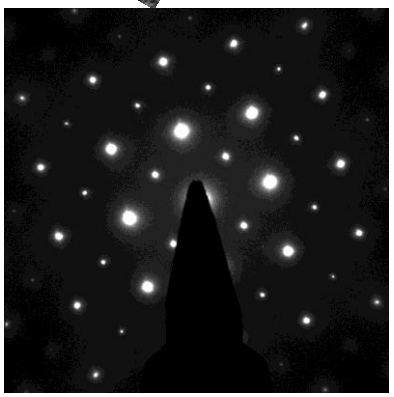
	composition in wt. %							Br	Hci
sample	Fe	Co	Ni	Al	Cu	Nb	Ti	(kG)	(Oe)
5-7	49.9	24.3	14.0	8.2	2.3	1.0	0.0	13.5	740
8	30.0	40.1	13.0	7.1	3.0	0.0	6.5	8.2	1860
9	35.5	35.4	13.1	7.0	3.2	0.5	5.0	10.6	1500

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?

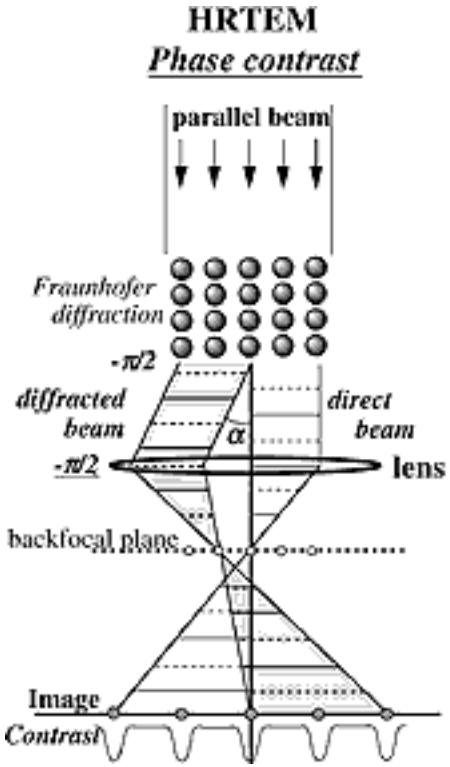


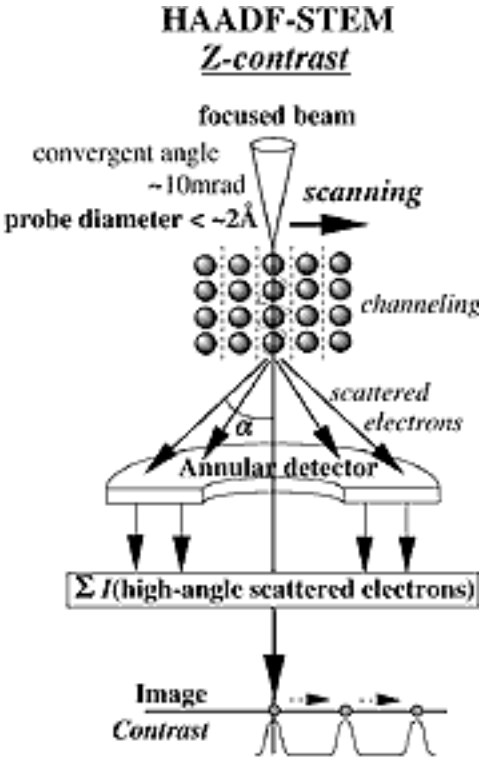




HRTEM VS STEM Imaging

- 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 ~ Z

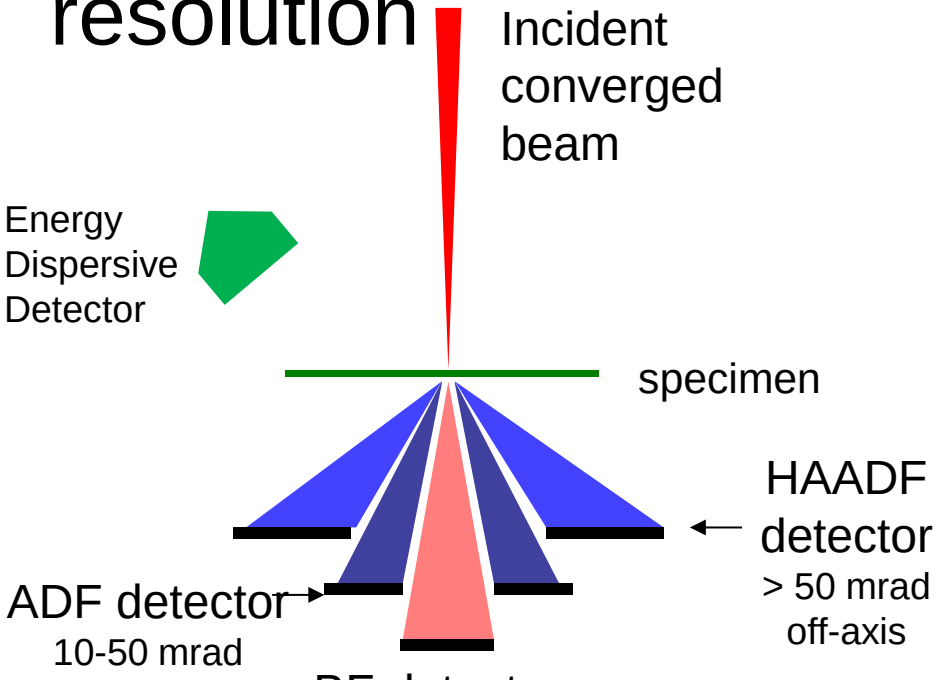


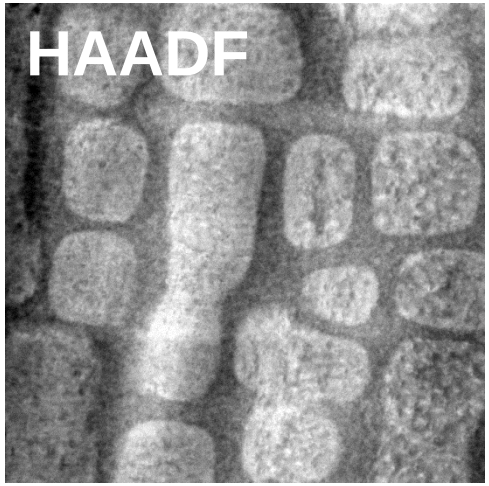


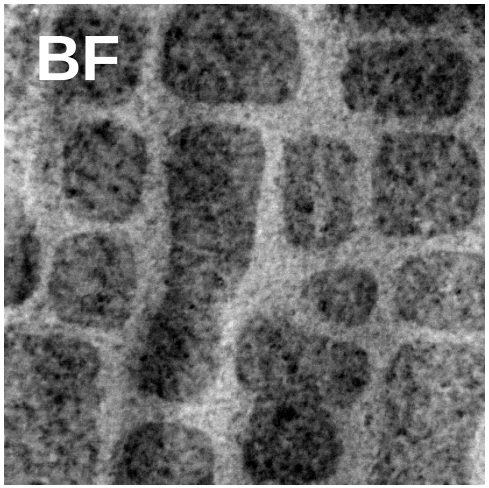
From Eiji Abe and An Pang Tsai

Structure and Chemistry

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



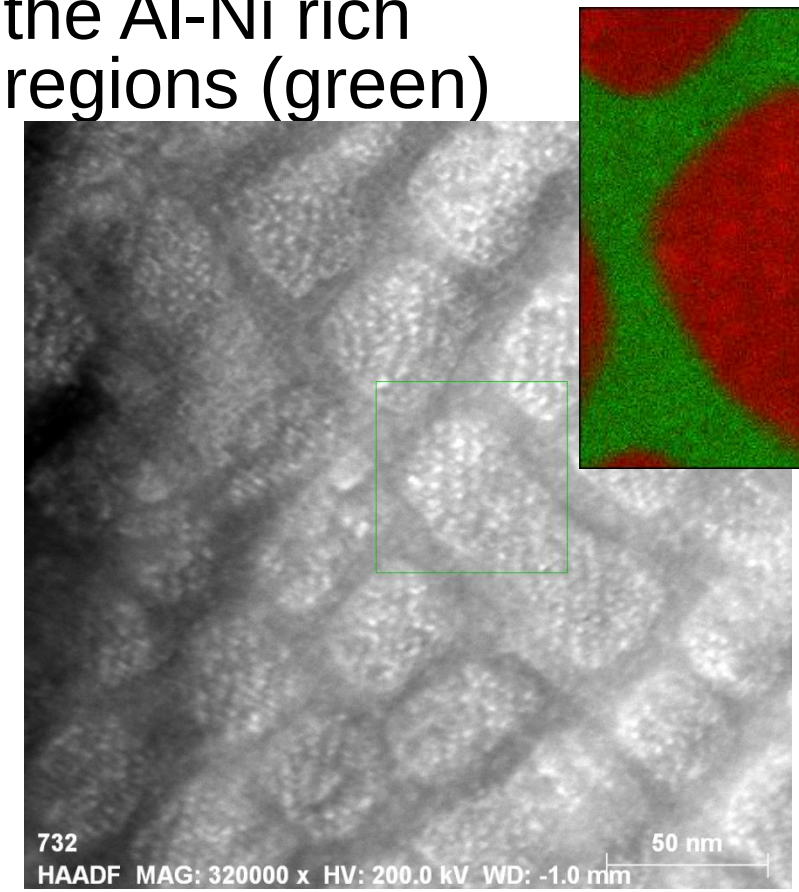


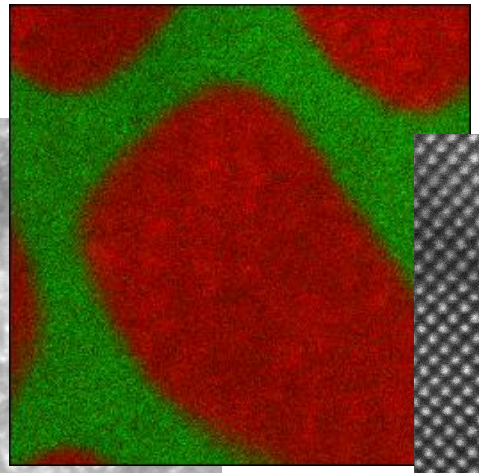


Probe corrected STEM images taken at Sandia with a FEI Titian

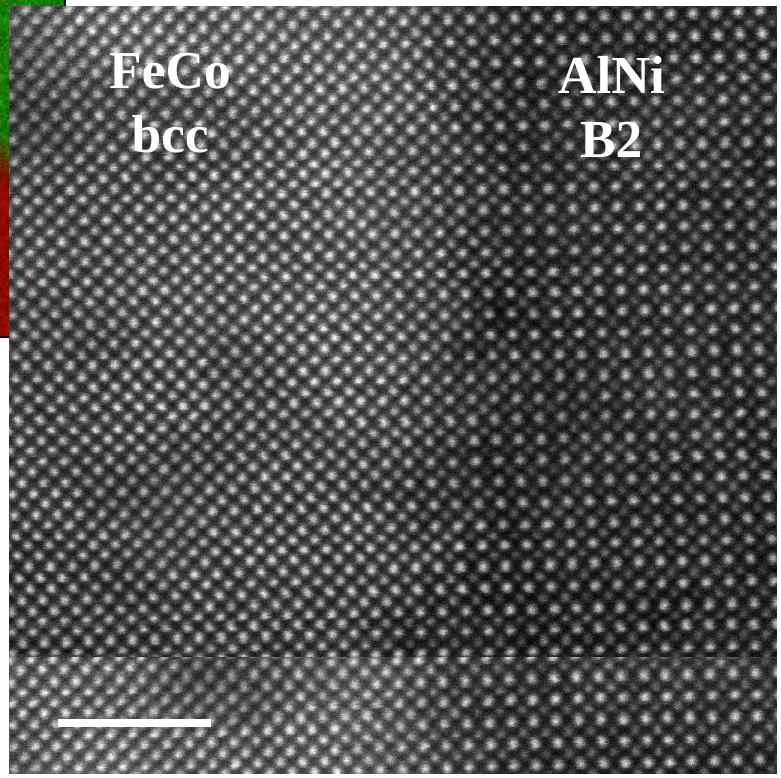
Interface

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



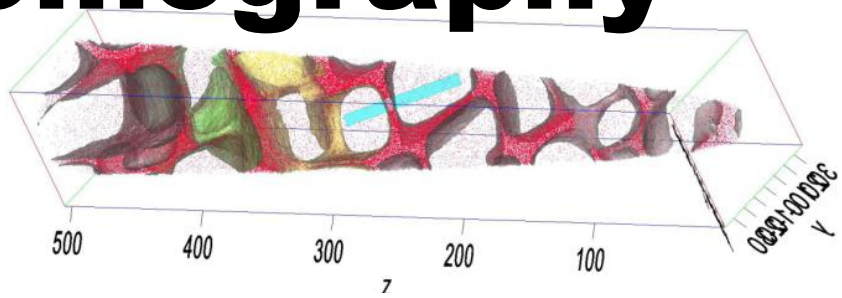


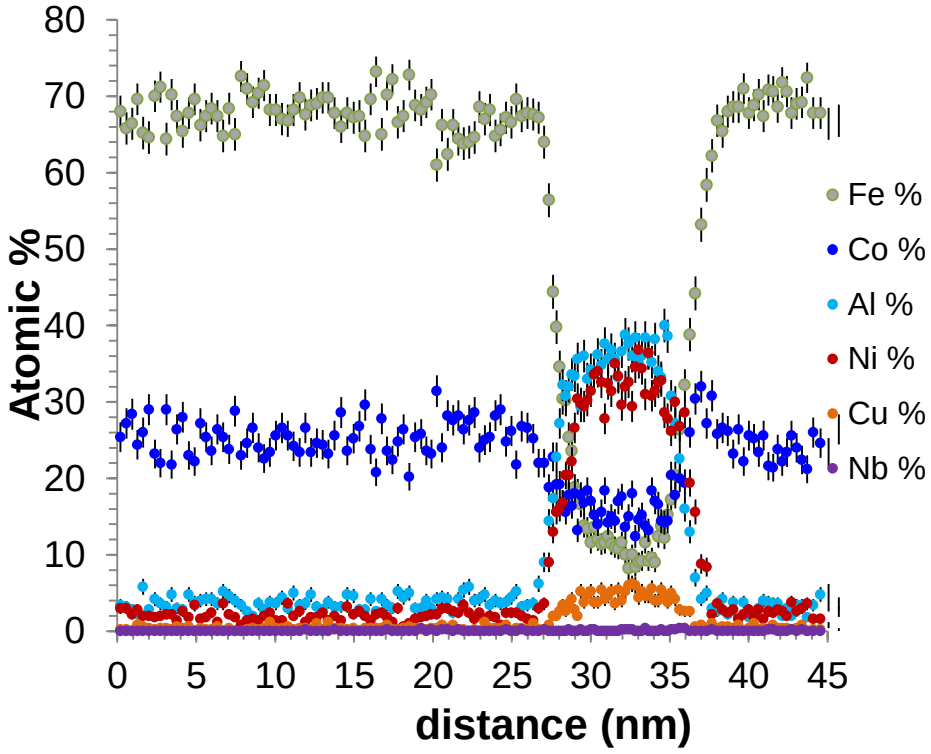
- HR STEM imaging of the coherent interface



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

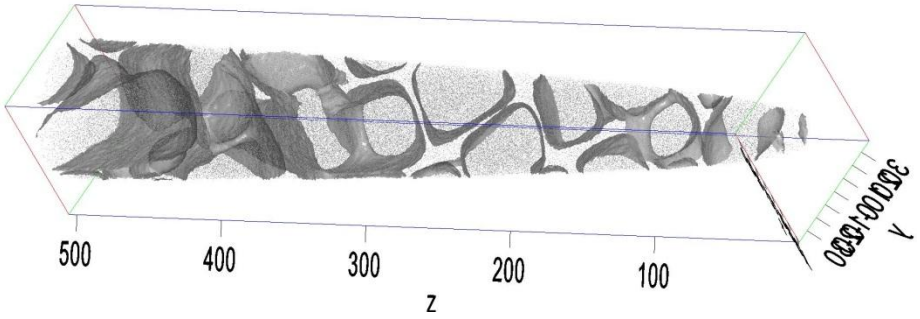


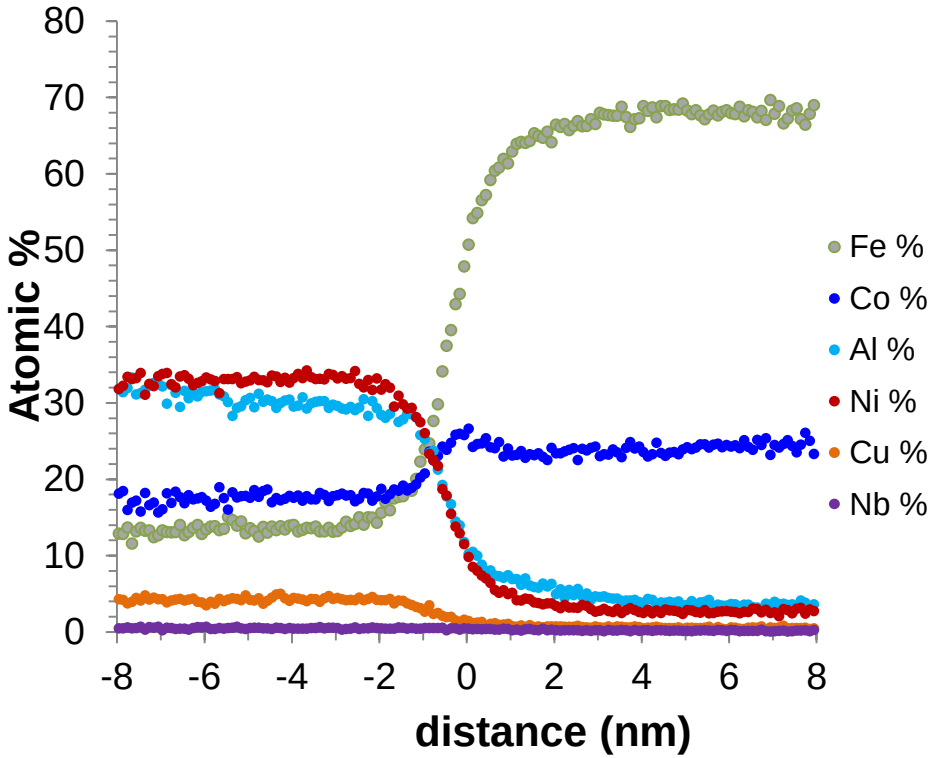


Chemical distribution along a volume within the larger data set

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

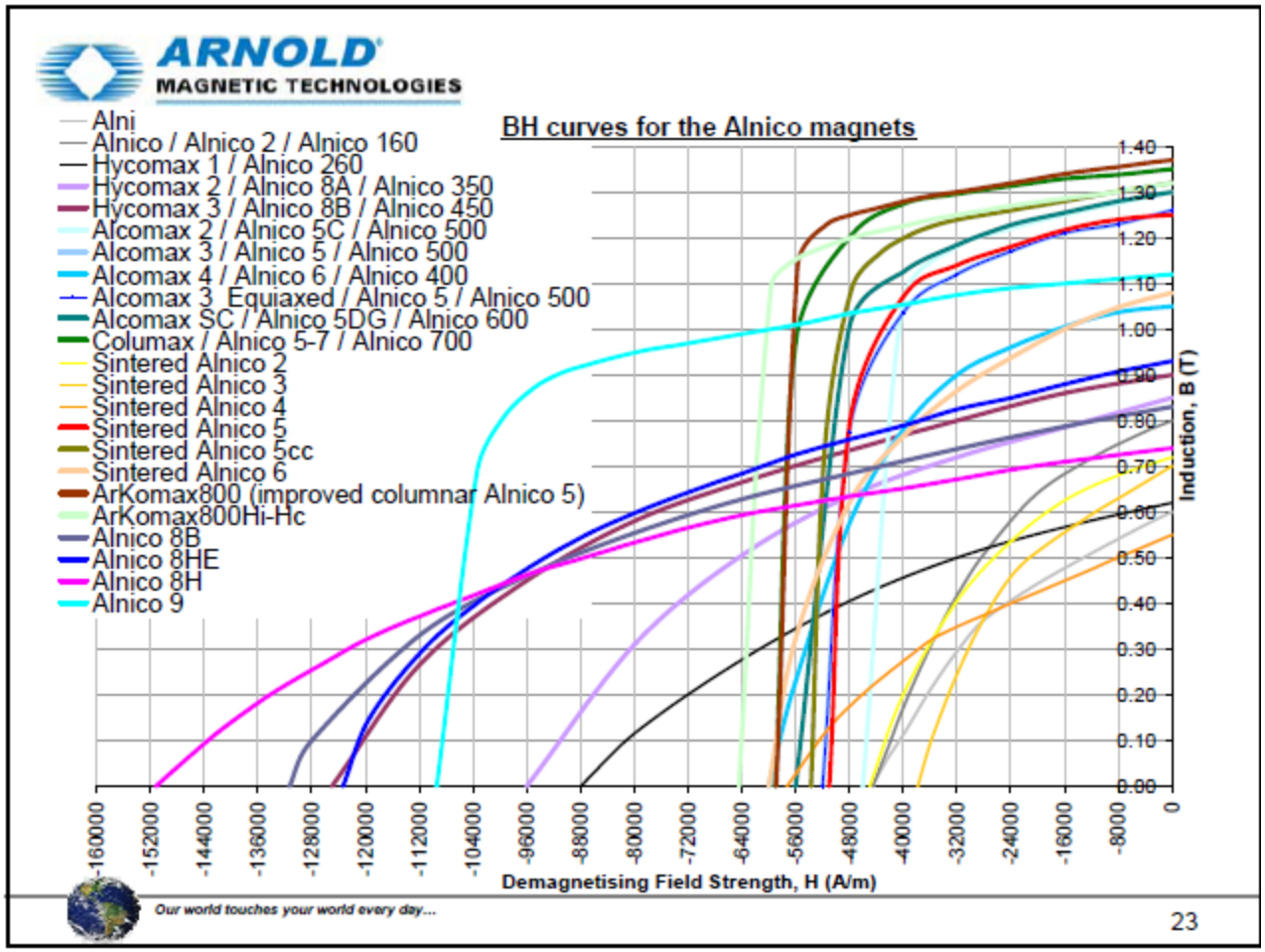
- Well defined ‘prismatic blocks’ of well faceted –(001) - bcc (Fe,Co) ~ 40-60 nm in diameter but of uncertain length (> 100 nm).
- Thin, ~ 5 nm, B2 (Ni,Al,Co,Fe), with minor Cu
- Fully coherent interfaces
- Volume fraction bcc:B2 ~ 61:39

Composition of the Spinodal Phases

	bcc		B2	
	at.%	(error)	at.%	(error)
Fe	68.1	0.78	13.4	0.46
Co	24.2	0.72	17.4	0.51
Ni	2.6	0.27	33.0	0.63
Al	3.6	0.31	30.6	0.62
Cu	0.5	0.11	4.2	0.27
Nb	0.1	0.06	0.5	0.09
Si	0.5	0.11	0.3	0.08
Ga	0.4	0.11	0.6	0.10

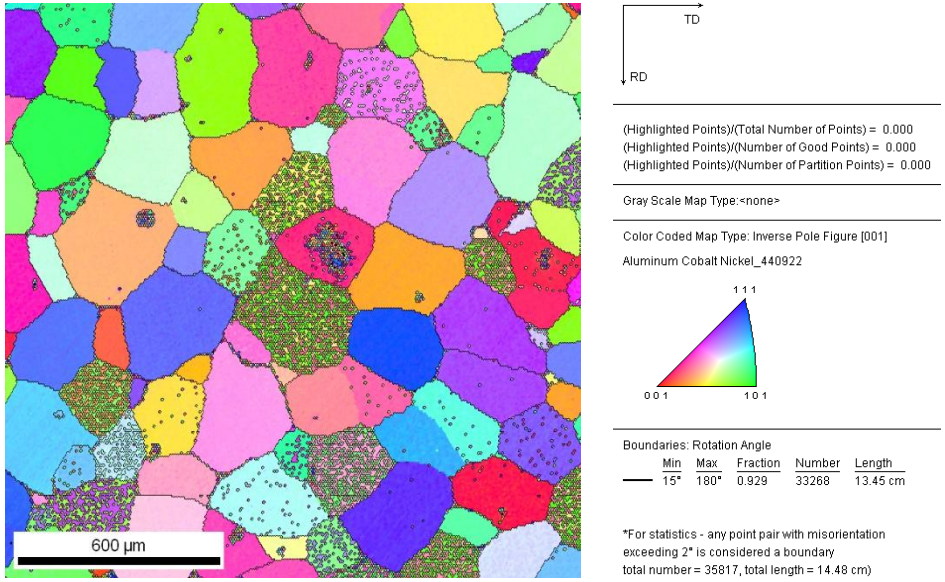
Effect of Changing Chemistry

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



Alnico 8

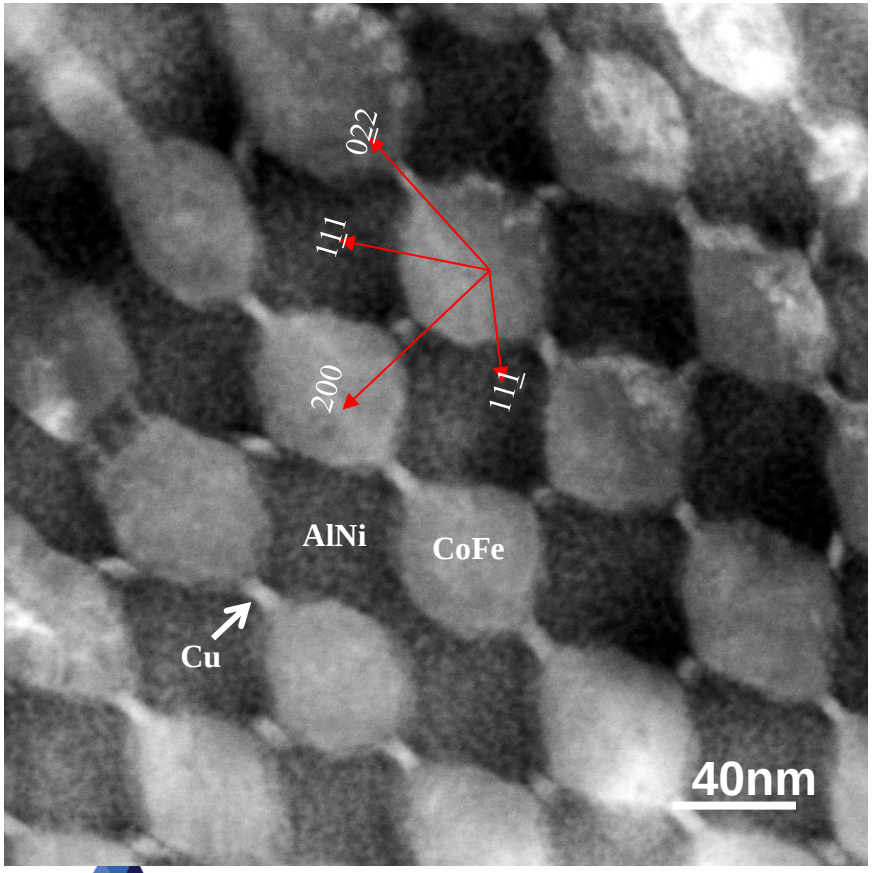
- Cast alloy
  - Random grain orientation
  - But heat treated in a magnetic field
- Higher Co and Ti



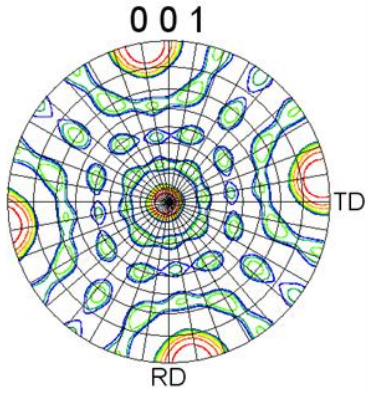
	composition in wt. %							Br	Hci
sample	Fe	Co	Ni	Al	Cu	Nb	Ti	(kG)	(Oe)
5-7	49.9	24.3	14.0	8.2	2.3	1.0	0.0	13.5	740
8	30.0	40.1	13.0	7.1	3.0	0.0	6.5	8.2	1860
9	35.5	35.4	13.1	7.0	3.2	0.5	5.0	10.6	1500

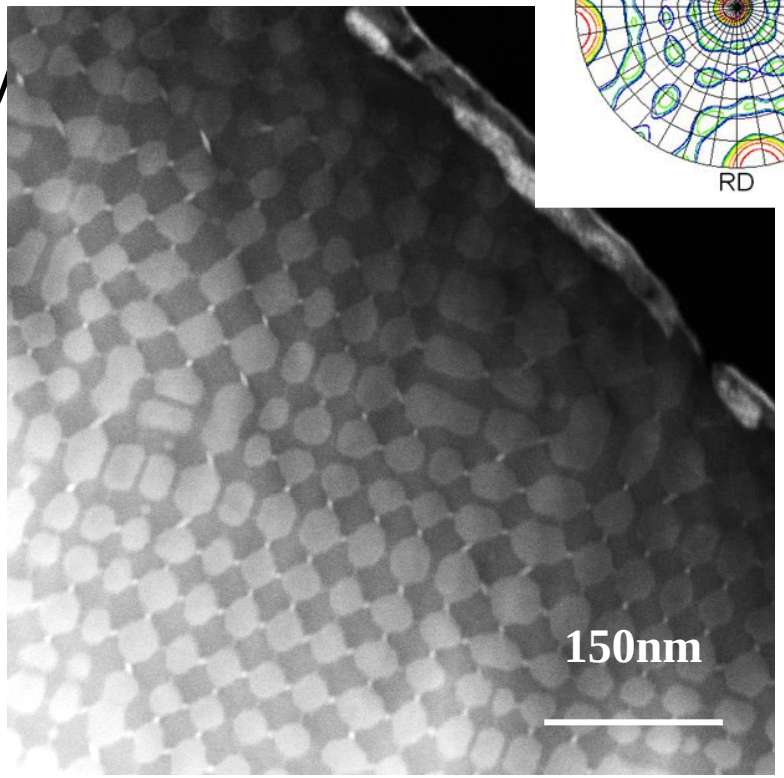
Alnico 8

- 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

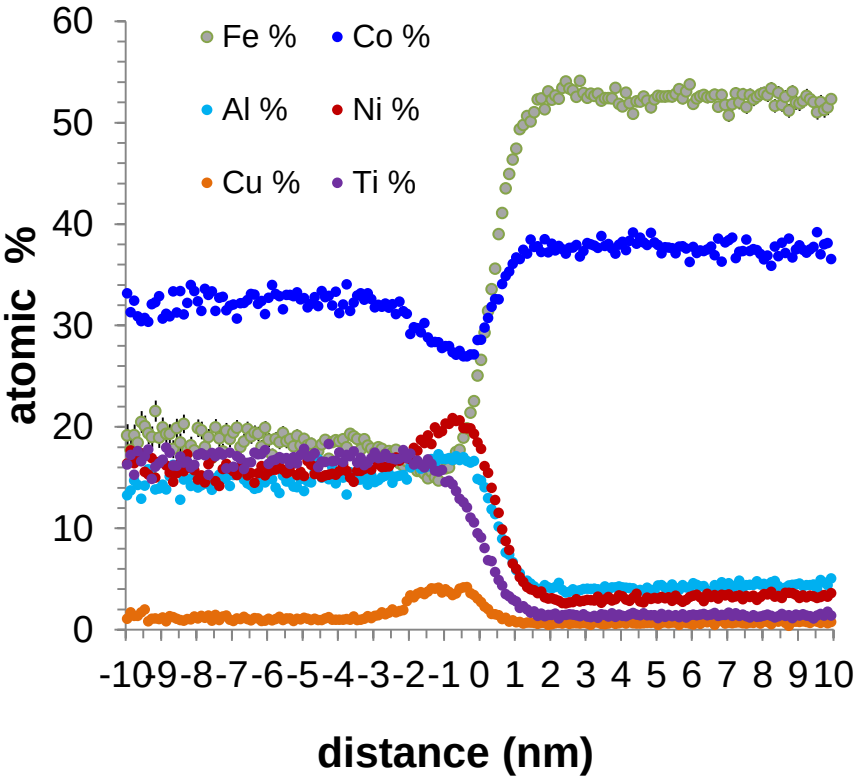


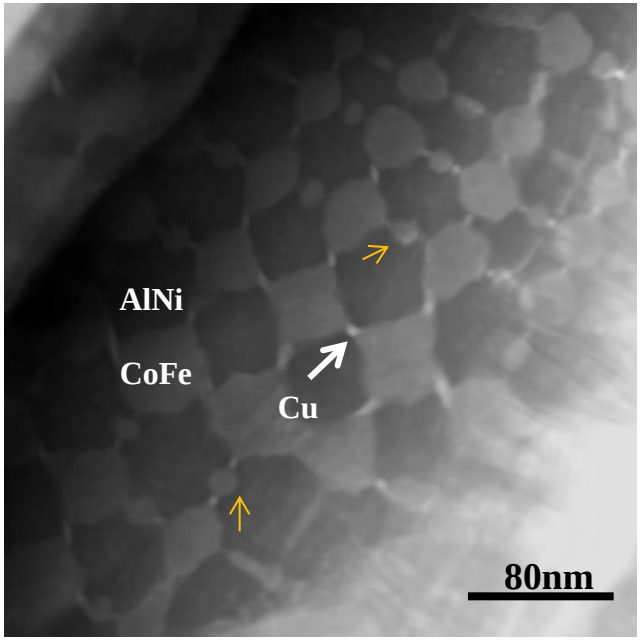


STEM HAADF image showing Fe-Co (bright regions) interspersed with intermetallic

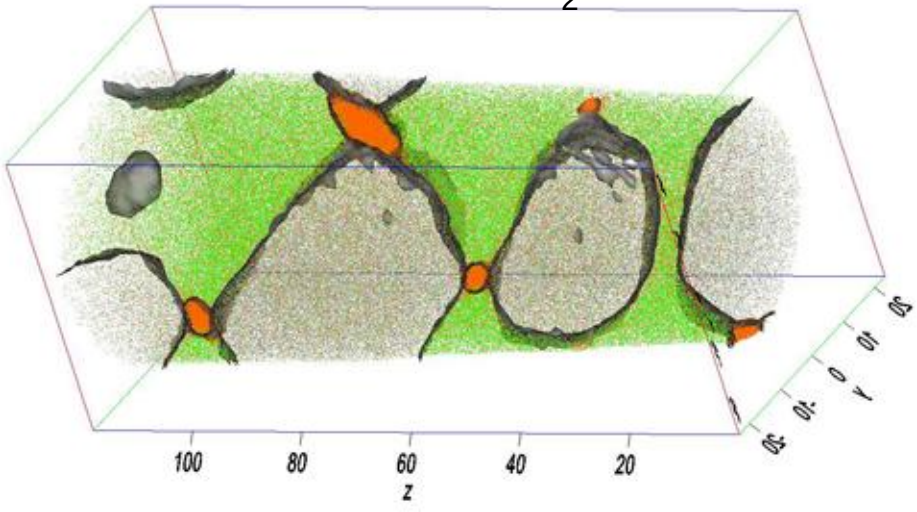
Alnico 8

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

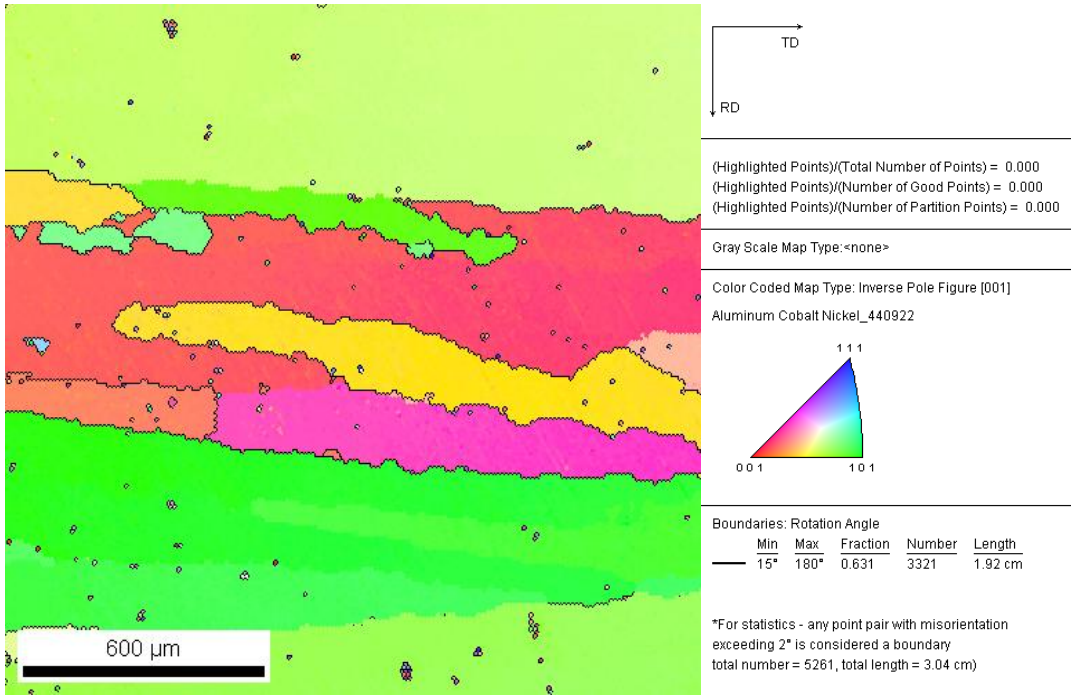
- Summary
  - 'NiAl' $L2_1$ appears more continuous
  - Cu precipitates at boundary between the 'AlNi'
  - FeCo more blocky rather than prismatic?
    - Need to get a clearer picture of the 3D morphology
  - bcc : $L2_1$ as low as 29:71

	bcc		$L2_1$	
	at.%	(error)	at.%	(error)
Fe	52.3	0.60	18.8	0.79
Co	37.6	0.58	32.3	0.95
Ni	3.2	0.21	15.8	0.74
Al	4.3	0.24	14.6	0.71
Cu	0.7	0.10	1.1	0.21
Ti	1.4	0.14	16.8	0.76
Si	0.2	0.05	0.4	0.12
Ga	0.3	0.07	0.3	0.11

Most data sets show a high Fe and Co in the $L2_1$ phase.

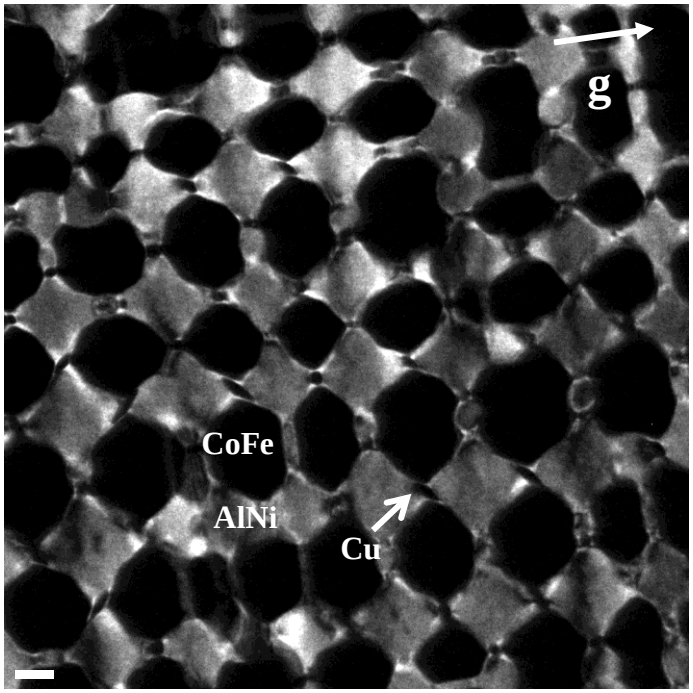
Alnico 9

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

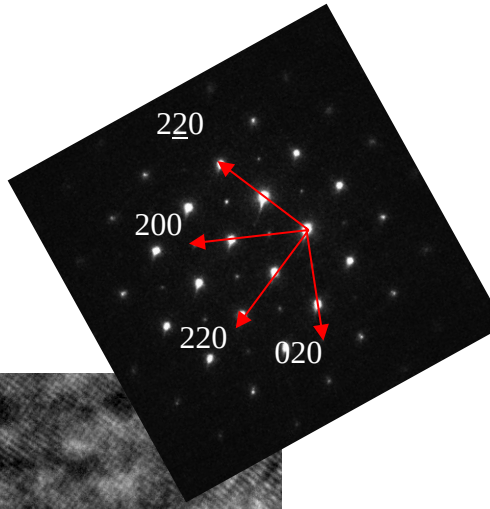


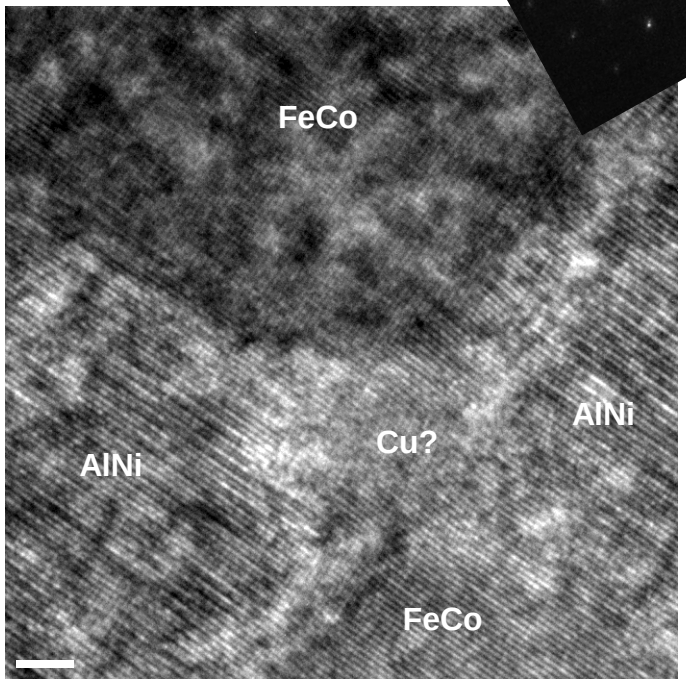
	composition in wt. %							Br	Hci
sample	Fe	Co	Ni	Al	Cu	Nb	Ti	(kG)	(Oe)
5-7	49.9	24.3	14.0	8.2	2.3	1.0	0.0	13.5	740
8	30.0	40.1	13.0	7.1	3.0	0.0	6.5	8.2	1860
9	35.5	35.4	13.1	7.0	3.2	0.5	5.0	10.6	1500

- Morphology very similar to the alnico 8
  - $L2_1$ as the matrix phase
  - Cu between bcc and $L2_1$

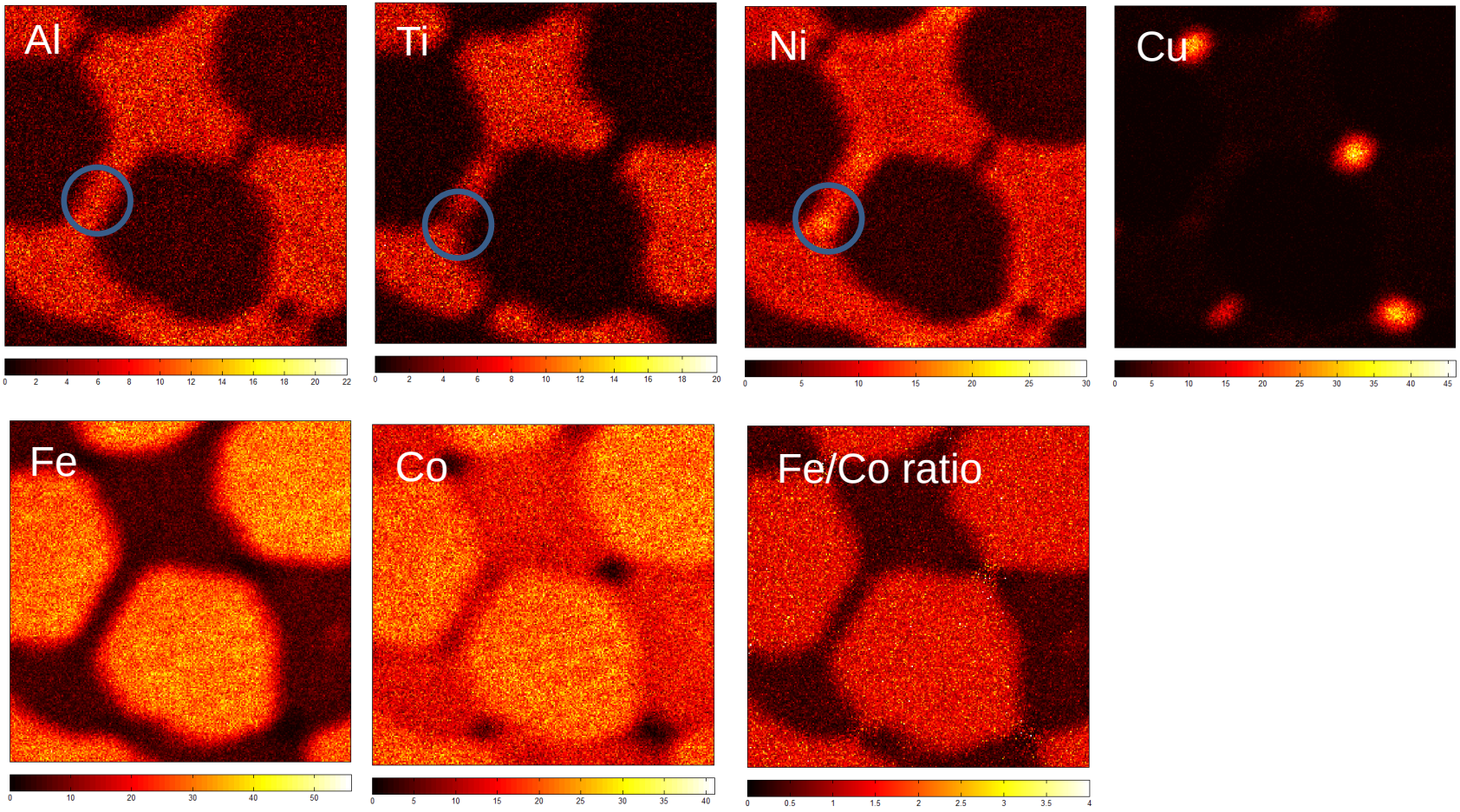


Dark field image confirming the $L2_1$ structure of the intermetallic



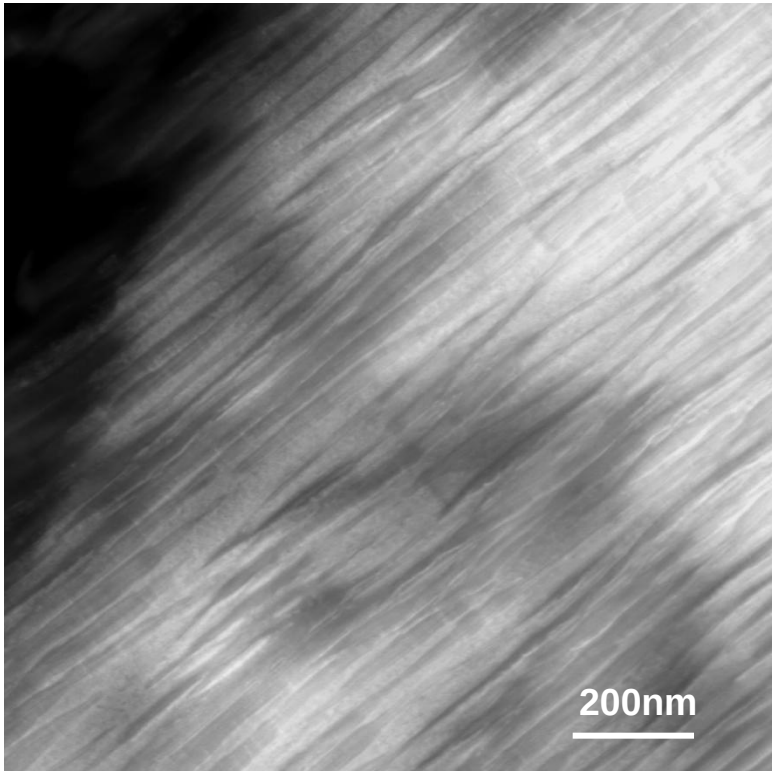


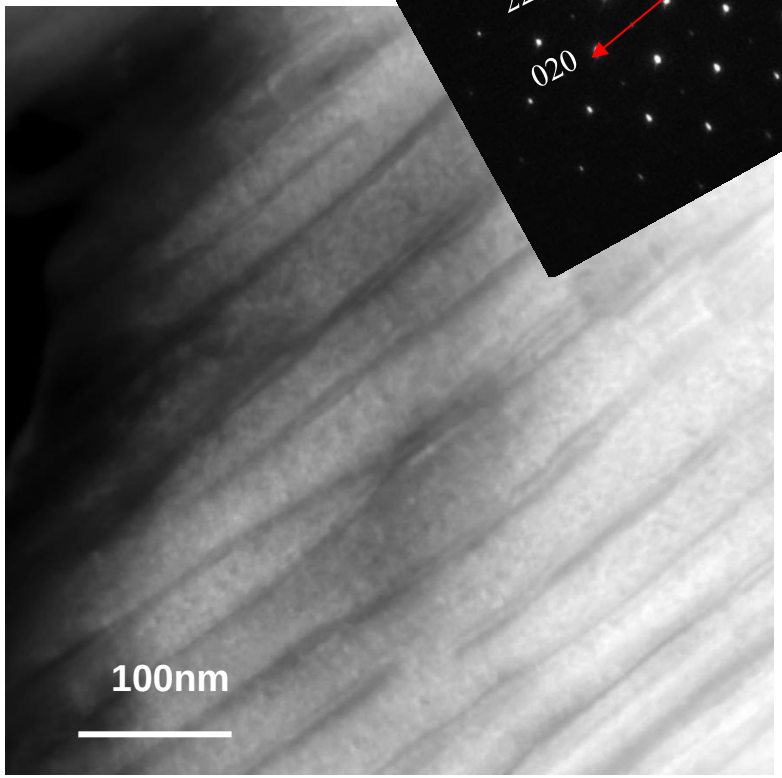
HRTEM showing the coherent interfaces and the different ordering of the intermetallic

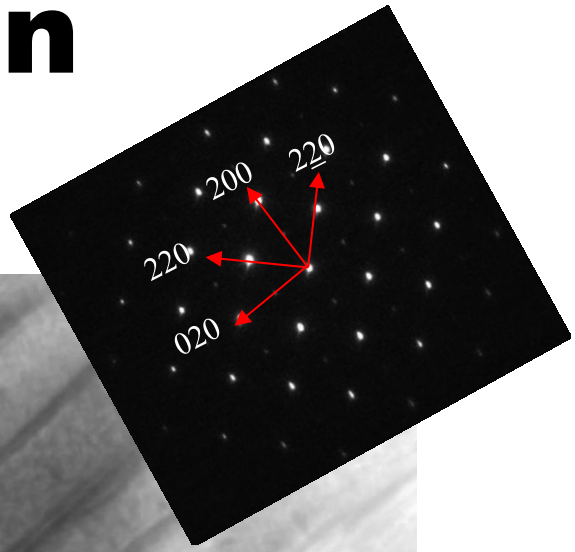


- STEM EDS mapping reveals some subtleties in the Al-Ni-Ti distributions

Longitudinal section



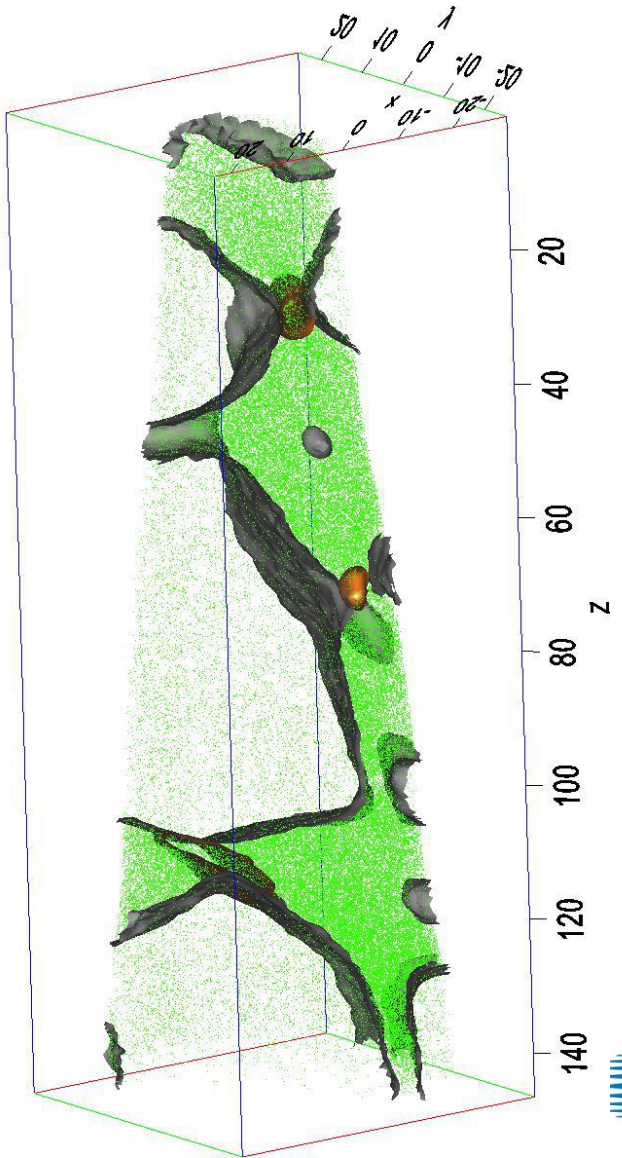


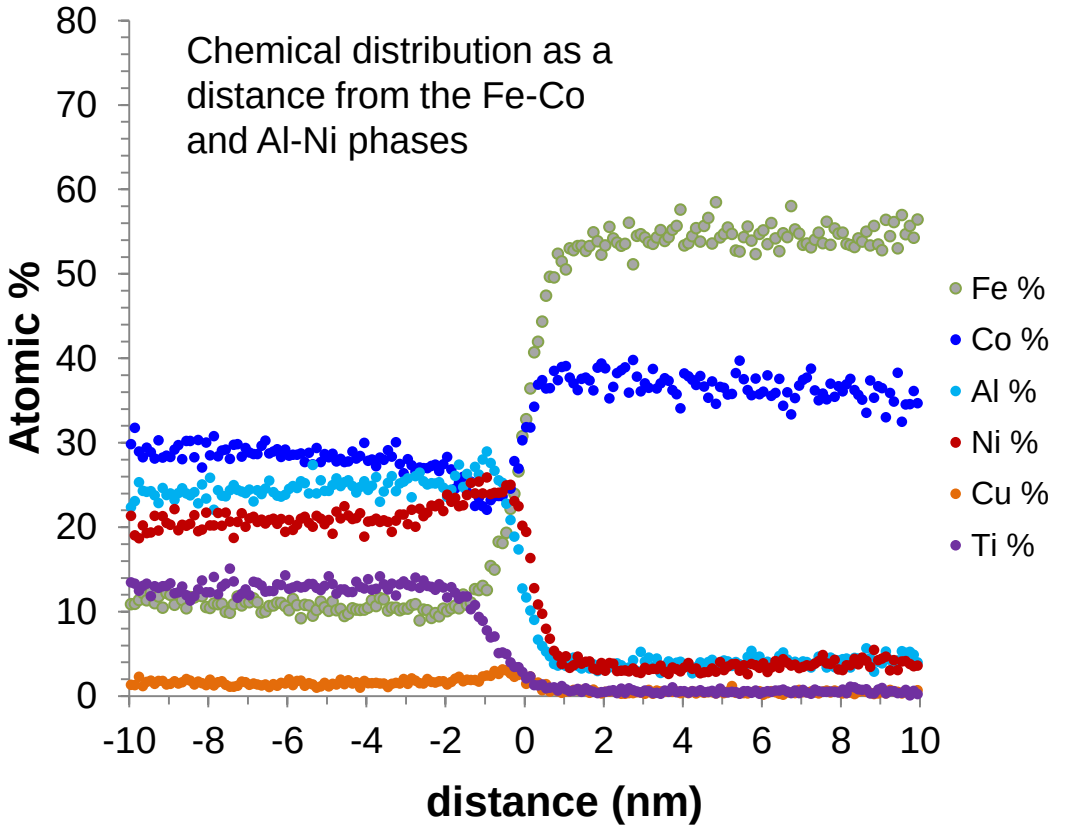


HAADF STEM image taken under [100] zone axis.

Composition Profiles alnico 9

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





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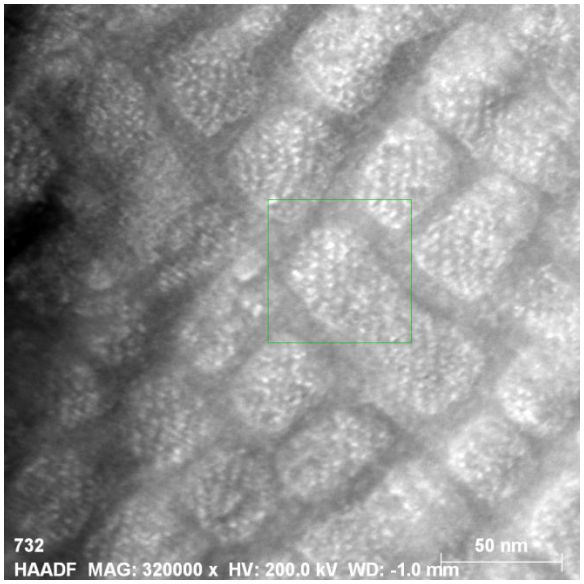
Alnico 9

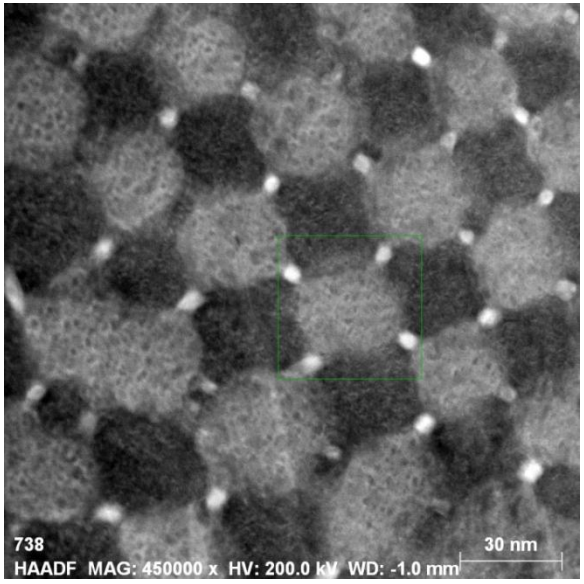
- Summary
  - Very high aspect ratio
    - Ends more tappered
  - 3DAP though shows similar chemical distributions
  - bcc:$L2_1$ 53:47
    - Higher ratio may explain the slightly higher B_r

	bcc		$L2_1$	
	at.%	(error)	at.%	(error)
Fe	54.4	1.26	10.8	0.65
Co	36.5	1.22	28.7	0.94
Ni	3.5	0.46	20.6	0.84
Al	4.0	0.49	24.4	0.89
Cu	0.4	0.16	1.5	0.25
Ti	0.5	0.18	12.9	0.70
Cr	0.1	0.08	0.9	0.19
O	0.3	0.13	0.1	0.07
N	0.0	0.03	0.1	0.04
Ga	0.2	0.10	0.1	0.06

Spinodal Phases

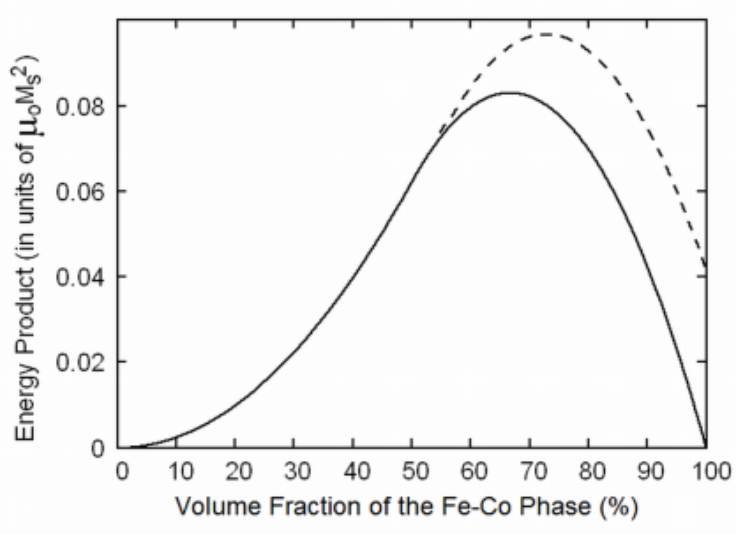
	Fe-Co			'Al-Ni'		
	bcc phase (at. %)			intermetallic phase (at. %)		
	5-7	8	9	5-7 B2	8 – $L2_1$	9 - $L2_1$
Fe	68.1	52.3	54.4	13.4	18.8	10.8
Co	24.2	37.6	36.5	17.4	32.3	28.7
Ni	2.6	3.2	3.5	33.0	15.8	20.6
Al	3.6	4.3	4.0	30.6	14.6	24.4
Cu	0.5	0.7	0.4	4.2	1.1	1.5
Nb	0.1			0.5		
Ti		1.4	0.5	0.3	16.8	12.9
Cr			0.1			0.9
Si	0.5	0.2			0.4	

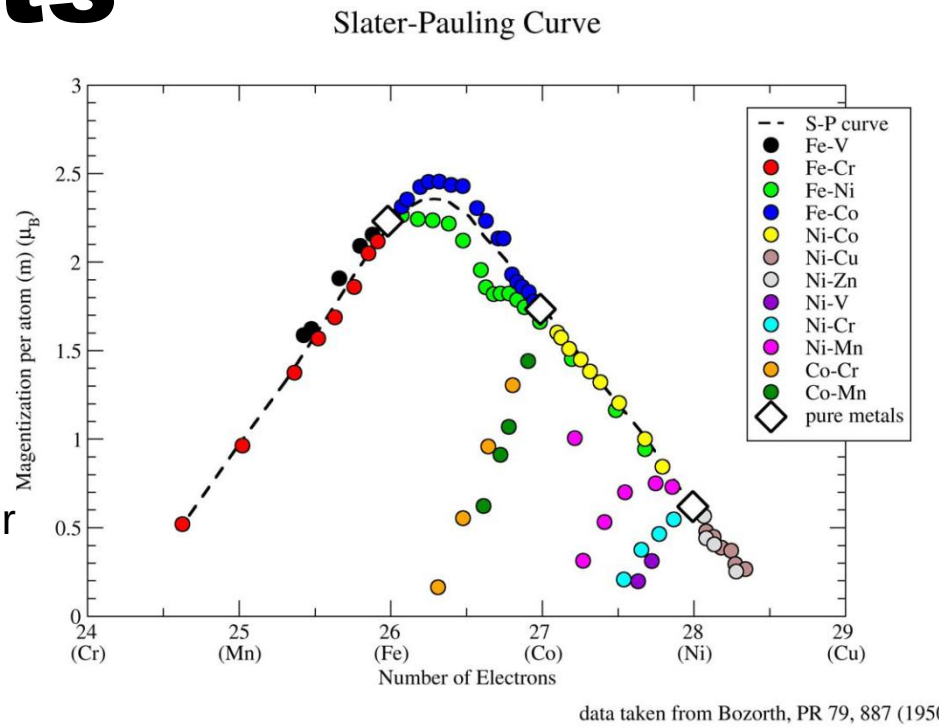




Estimate Limits

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





Luborsky, F. E., et. al., J Appl Phys 28 (1957), 344.
Skomski, R., et. al. J Appl Phys 107, Doi 10.1063
Skomski, R., et. al. IEEE Trans. Magn, in press

Theoretical Limits

		Alnico 5-7	Alnico 8	Alnico 9
aspect ratio		~ 5:1	~ 10:1	> 10:1
fraction bcc phase (f)		0.62	0.4	0.53
Fe:Co in bcc phase		0.74	0.58	0.60
mole % Fe+Co in bcc		0.92	0.90	0.91
~M_s (KG) for bcc based on Fe:Co		23.8	23.9	23.9
Fe:Co in intermetallic		0.44	0.37	0.27
mole % Fe+Co in bcc		0.31	0.51	0.40
B_r (KG)	measured	13.5	8.2	10.6
	calculated	13.6	8.6	11.5
Hc_i (Oe)	measured	740	1860	1500
	calculated	3105	4365	3715
BH_{max} (MGOe)	measured	7.5	5.3	9.0
	calculated	21.1	18.8	21.4

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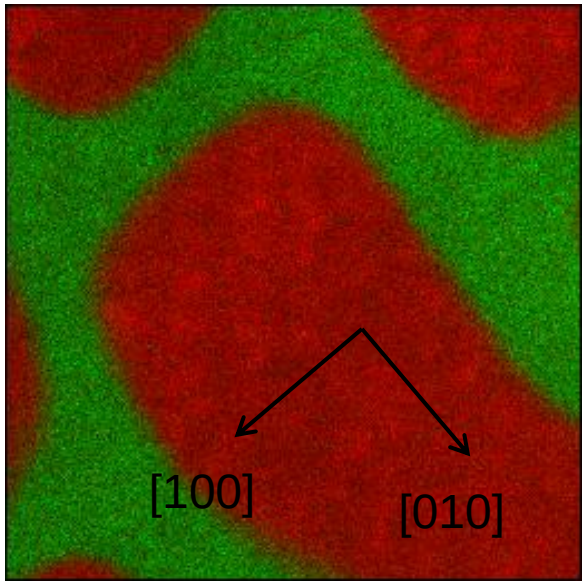
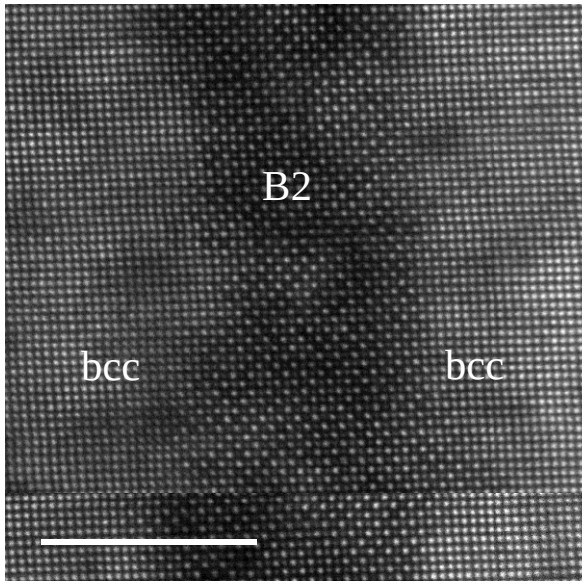
Summary

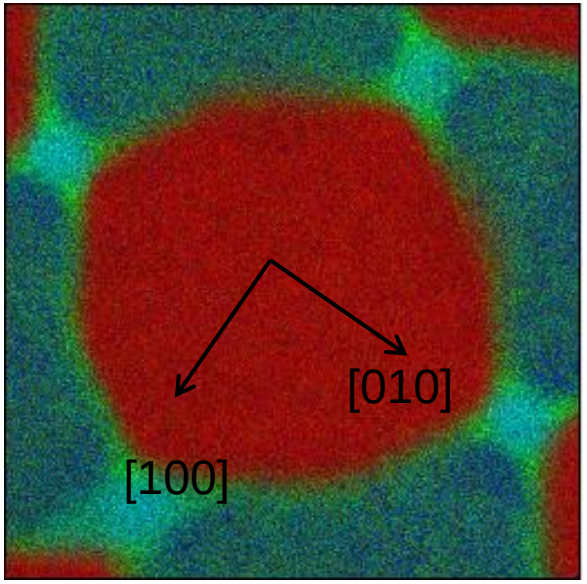
- The 5-7 has both a different nanoscaling of the spinodal and the non-magnetic phase which forms with the bcc phase.
  - The bcc in 5-7 has higher Fe:Co, consistent with the bulk
  - Has a higher phase fraction of the bcc
  - The Cu is uniform in the B2 phase
  - Uniform long prismatic bcc grains aligned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

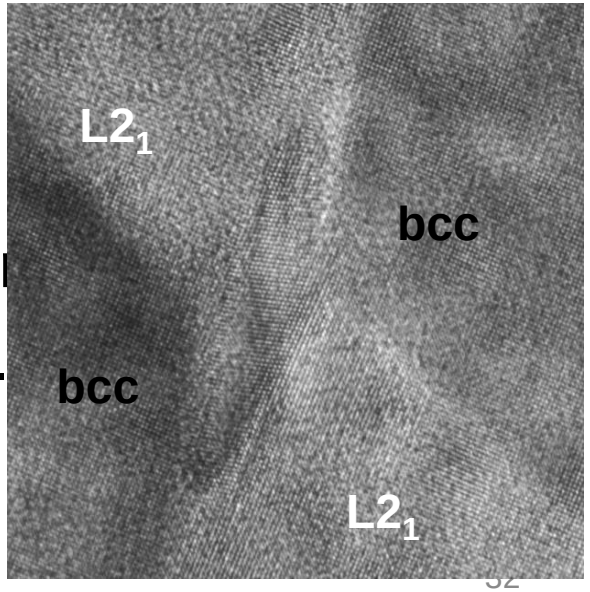




Summary

- The 8 and 9 alloys have faceted bcc grains separated from the $L2_1$ by Cu.
- Is $L2_1$ is too high in elements with moments?
  - Also see small FeCo nodules in the $L2_1$ phase.
- Is the high Co and Fe needed to form the $L2_1$ 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

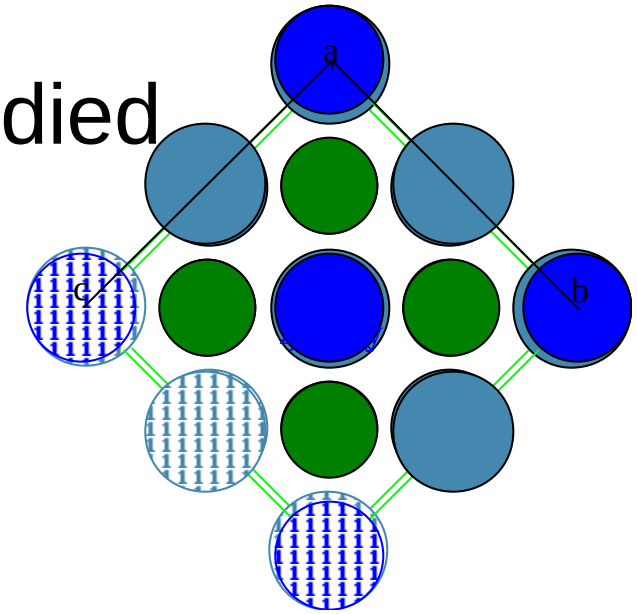
- Alnico 5-7 has acceptable B_r
  - How to improve H_{ci}?
    - Is the spacing too small
- Alnico 8 and 9 have acceptable H_{ci}
  - Is the high Co needed to form the coherent $L2_1$?
    - At least reduce cost!
  - How to increase fraction of the bcc?
- Hinges on knowing what controls coercivity.

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.

Summary Continued

- The 8 has the highest Co studied
  - Responsible for the lower B_r?
    - Note Fe:Co is ~ 58:42
    - Volume fraction bcc ~ 50%
  - Responsible for forming $L2_1$
  - Change in bcc morphology
    - Role in H_{ci}?
- Where is the pinning?

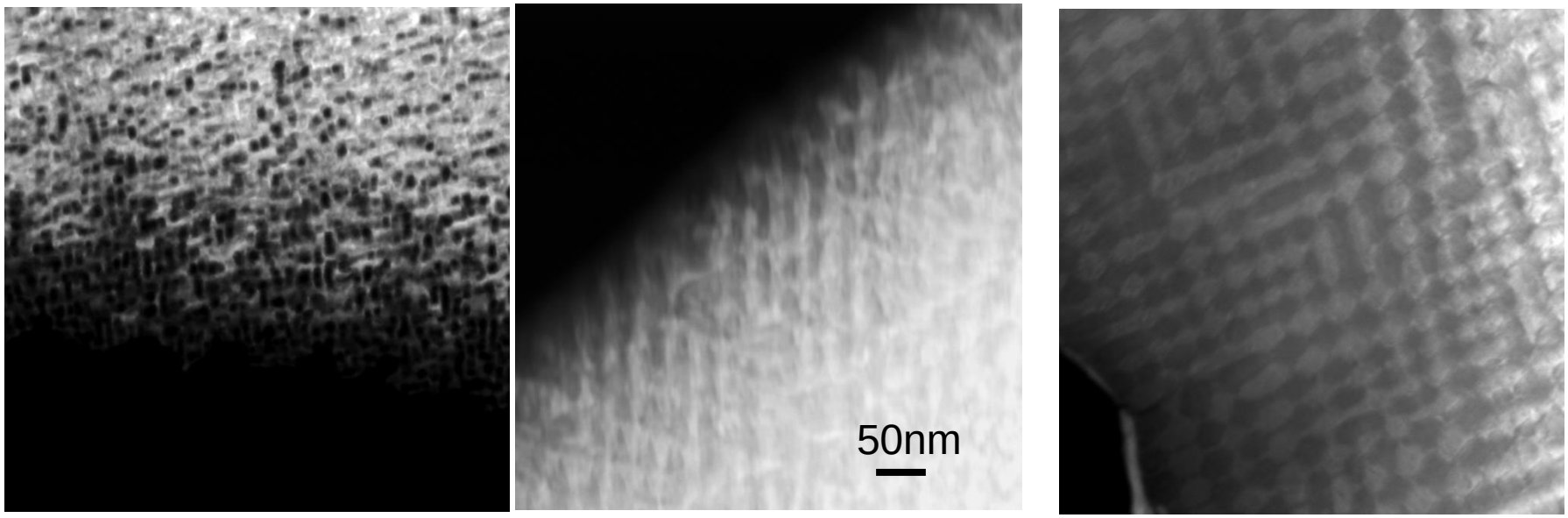


Data is consistent with $AlNi_2Ti$ SG225,
a=5.74 (~2x bcc Fe)
Al 0,0,0
Ni ¼, ¼, ¼
Ti ½, ½, ½

1250°C as quenched

800°C 5 min annealed

800°C 10 min annealed



size of Al-Ni rich phase.

10-20nm long, ~several nanometer wide

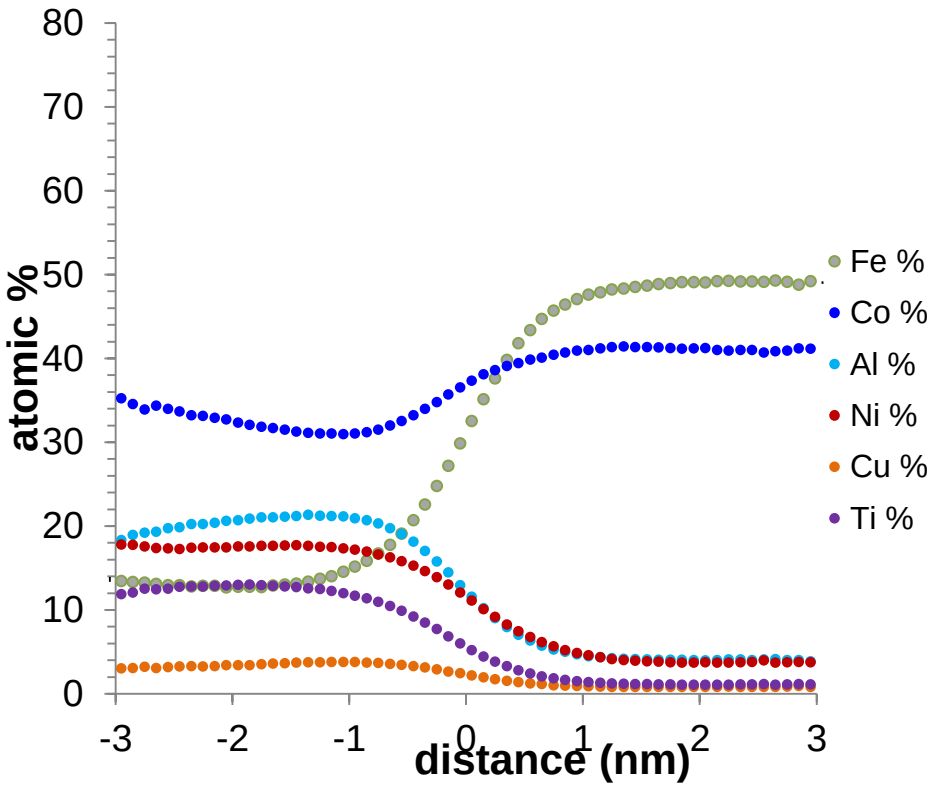
size 30-50nm long, ~12nm wide

size ~20nm along diagonal direction of those patches

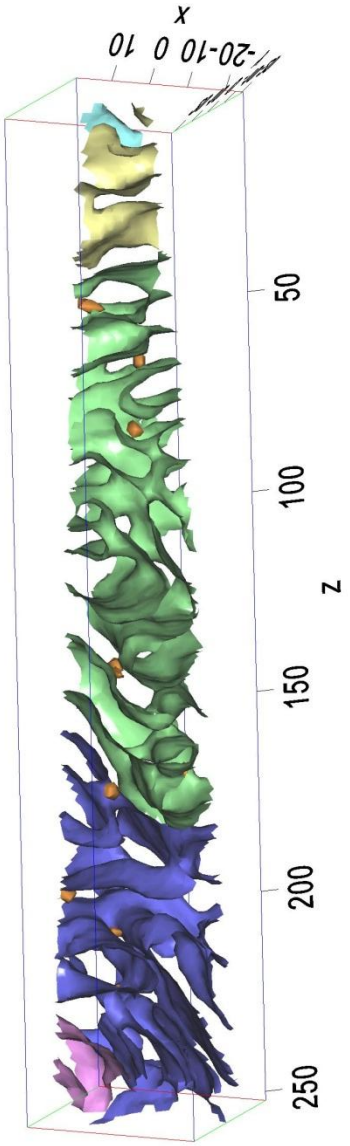
All images are taken along [110] zone axis at the same magnification. The bright region is the FeCo-rich phase, while the dark region is the AlNi-rich phase. The AlNi-rich phase showed $D0_3$ ordering. The as quenched sample has similar morphology as the 5min annealed one, but with smaller grain size. 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 {111}, {001} or {110} planes.

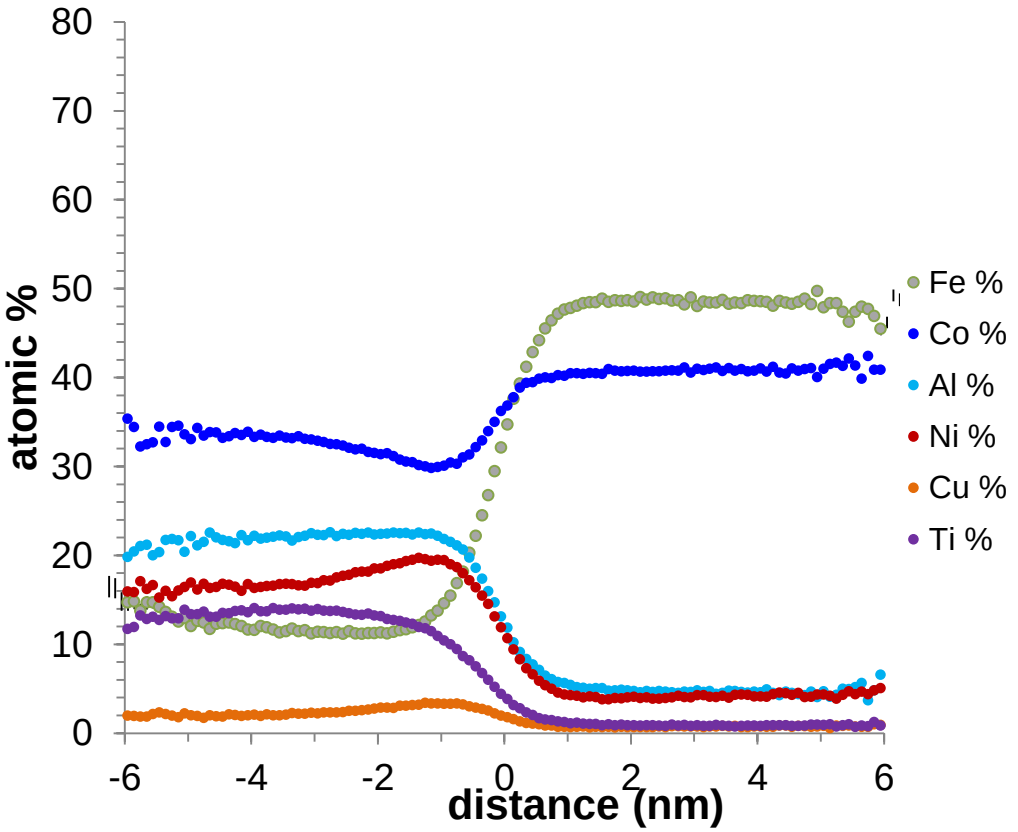
Alnico 8, 1250°C quenched

- Images waiting for MM but consistent w/ TEM.
  - Unable to suppress spinodal
- **BUT only 1 interface over 87M counts.**
- ~ 1 nm sized Cu clusters

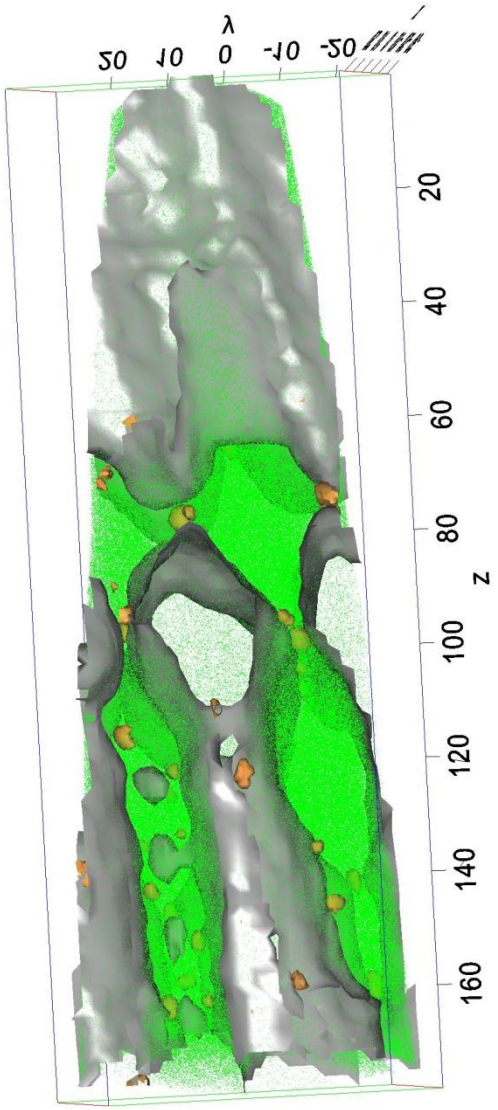


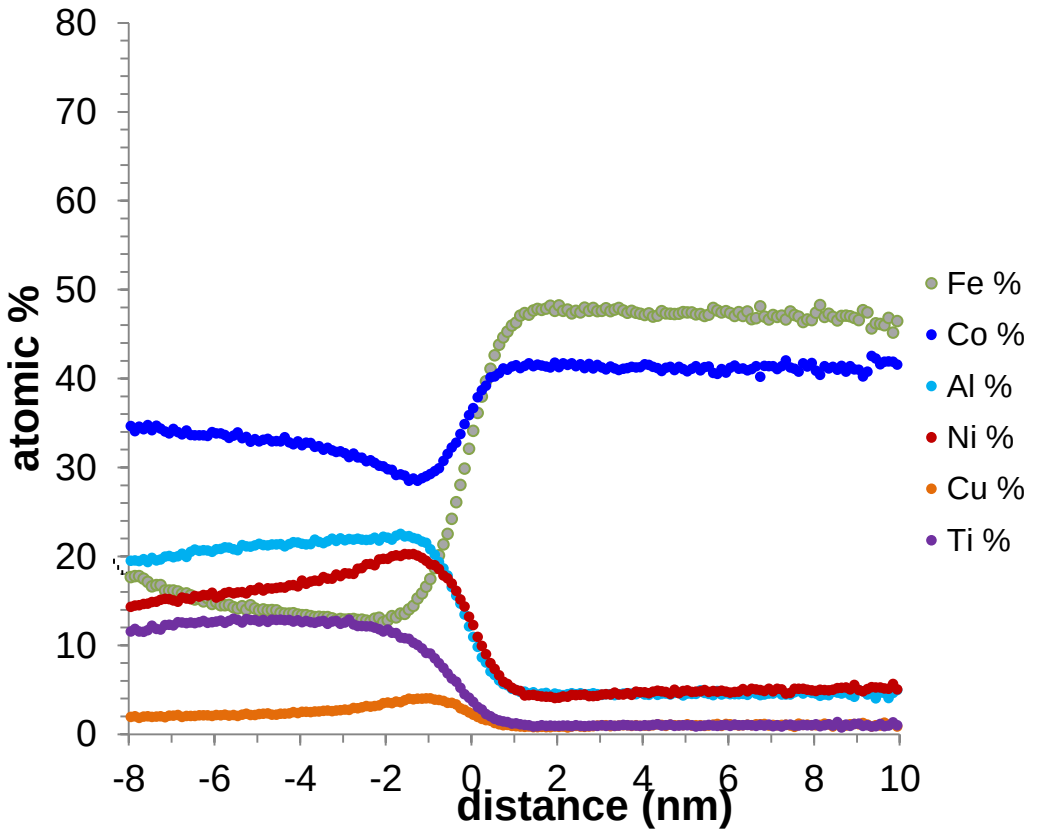
90s hold at 850°C





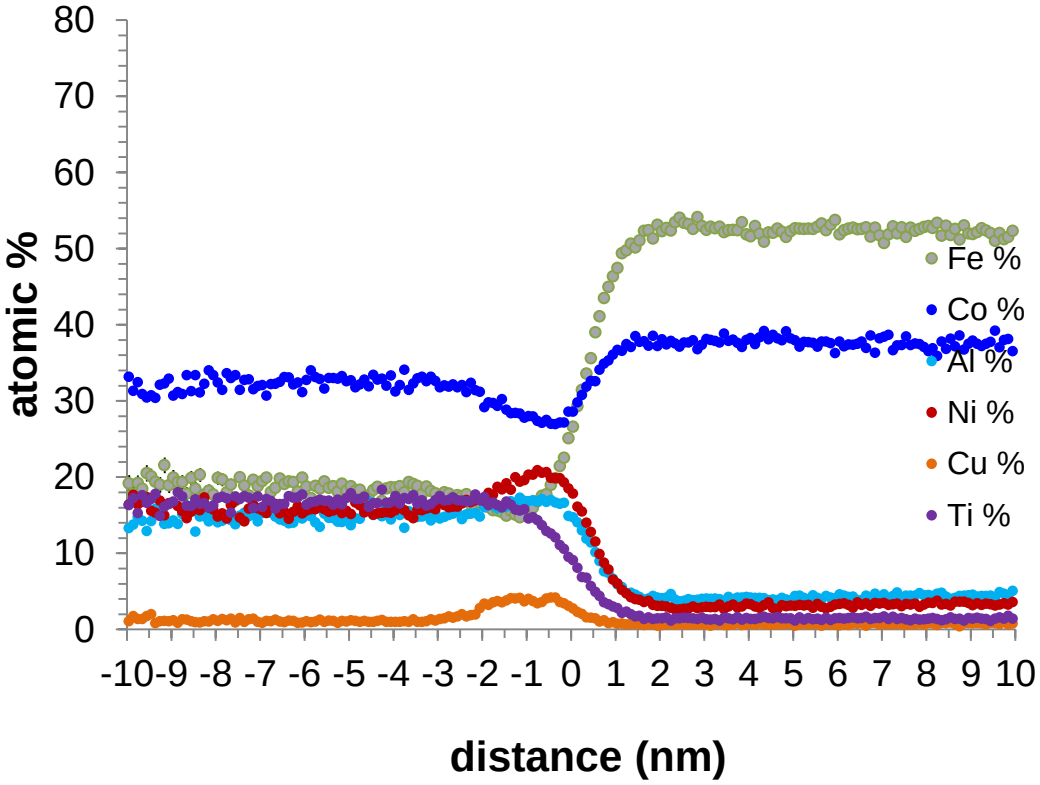
10 min hold at 850°C





Optimal alnico 8

- 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!