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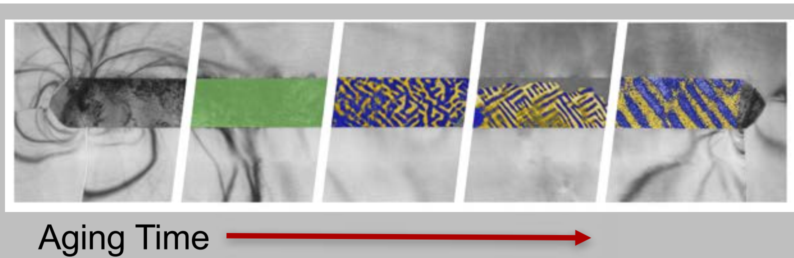

M&M 2016
MICROSCOPY & MICROANALYSIS
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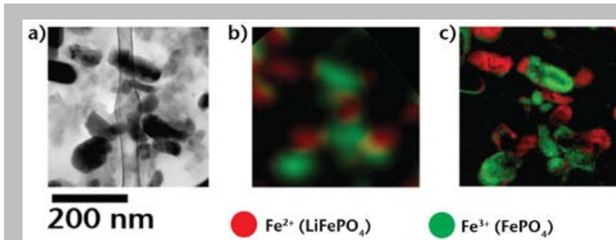

Using Energy-Filtered TEM to Solve Practical Materials Problems with Inspirations from Gareth Thomas

Joshua D. Sugar, Farid El Gabaly, William Chueh, Kyle Fenton, Paul G. Kotula, Velimir Radmilovic, Norman C. Bartelt, Joseph T. McKeown, Andreas M. Glaeser, and Ron Gronsky

U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

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Prof. Thomas' Legacy Influenced and Inspired My Education Greatly

- I was a graduate student of Andy Glaeser and Ron Gronsky from between 2001 and 2007
  - I would occasionally pass Prof. Thomas in halls when he was around and exchange friendly head nods
    - Students could be heard whispering "G.T. is here today" or "That's G.T."
- Ron Gronsky was an original Prof. Thomas student
- The capabilities and expertise that Prof. Thomas built for UC Berkeley materials science and at LBNL NCEM inspired the topic of my PhD dissertation work and continue to influence the research portfolio that I pursue today
  - Electron Microscopy
  - Metallurgy
  - Phase transformations

Prof. Thomas' 1970's Work Nucleated My PhD Dissertation Topic

- Work from the 1970's incubated a number of my interests in materials science capabilities and problems
  - E.P. Butler and G. Thomas, *Structure and properties of spinodally decomposed Cu-Ni-Fe alloys,* Acta Met **18**, 1970.
  - R.J. Livak and G. Thomas, *Spinodally decomposed Cu-Ni-Fe alloys of asymmetrical compositions,* Acta Met **19**, 1971.
  - R.J. Livak and G. Thomas, *Loss of Coherency in spinodally decomposed Cu-Ni-Fe alloys*, Acta Met **22**, 1974.
  - R. Gronsky and G. Thomas, *Discontinuous coarsening of spinodally decomposed Cu-Ni-Fe alloys*, Acta Met **23**, 1975.
- This work inspired me to learn analytical TEM and continue to use this knowledge to solve materials problems

What was the next step for this work?

Can Decomposition of Cu-Ni-Fe Be Directed and Controlled Through Dimensional Confinement?

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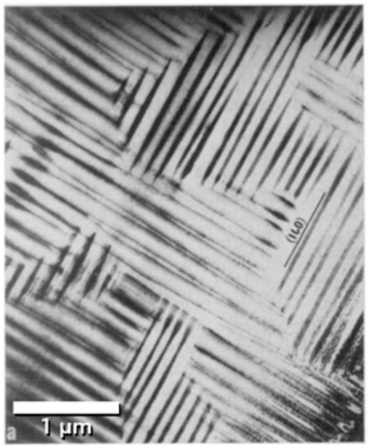

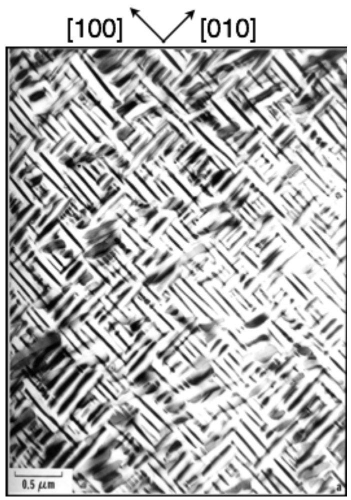

R.J. Livak and G. Thomas, *Spinodally decomposed Cu-Ni-Fe alloys of asymmetrical compositions,* Acta Met **19**, 1971.
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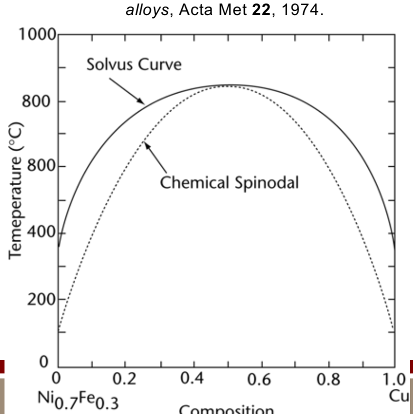
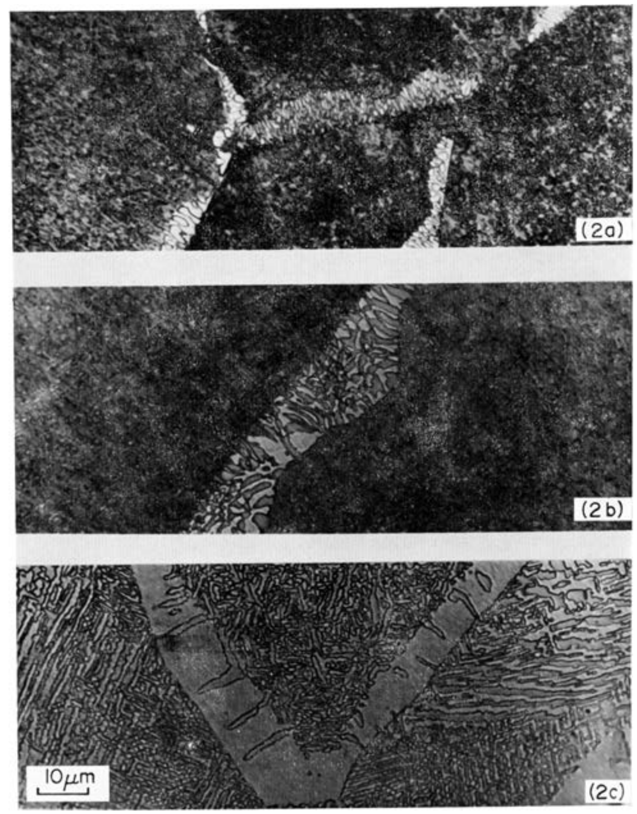


Clear development of modulated structure domains in bulk parallel to {100}



500 hr 654°C

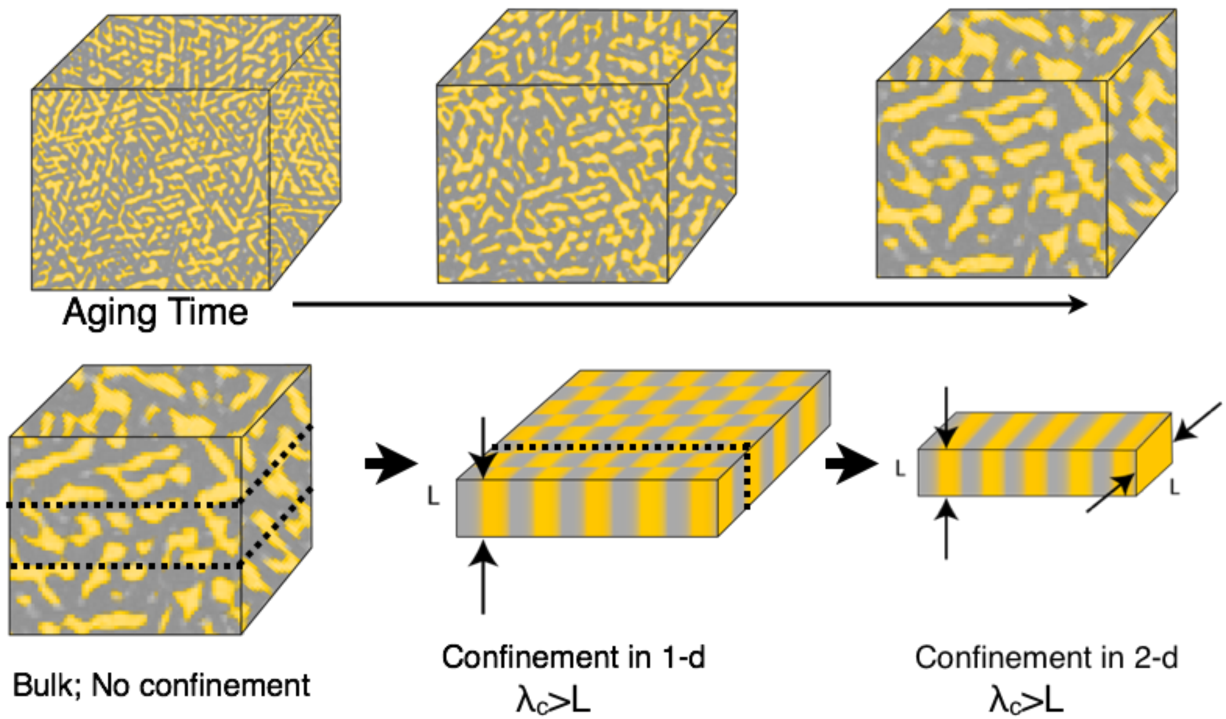
500 hr 748°C

500 hr 838°C

R. Gronsky and G. Thomas, *Discontinuous coarsening of spinodally decomposed Cu-Ni-Fe alloys*, Acta Met **23**, 1975.

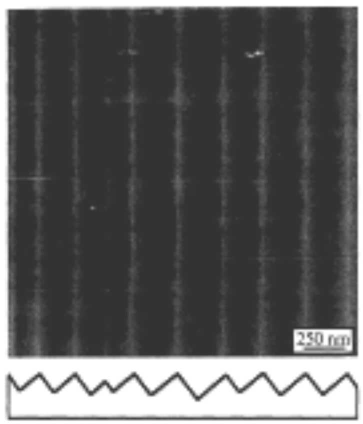
Coarse structure near brain boundaries suggests a single domain is possible in an extended volume

Can Decomposition of Cu-Ni-Fe Be Directed and Controlled Through Dimensional Confinement?



When spatial dimensions are smaller than preferred modulation wavelength, can wavelengths be frustrated such that modulation is directed in a specific direction?

Directing Confinement With Surface Faceting on $\{10\bar{1}0\}$-Al_2O_3

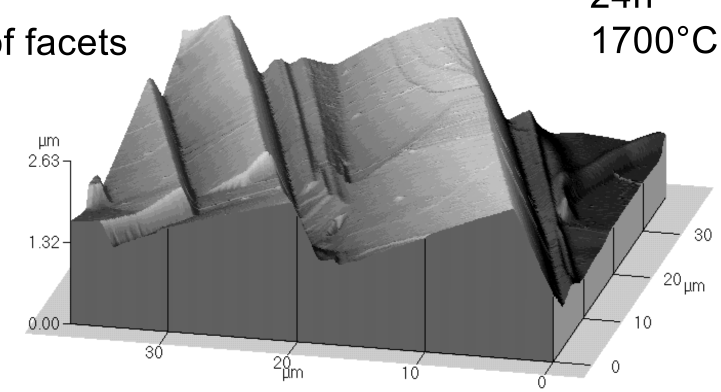


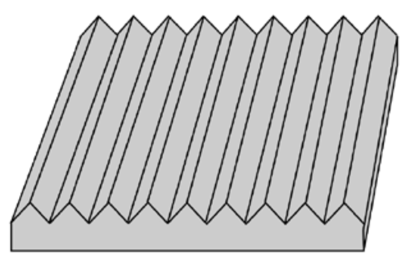
Heffelfinger, J.R., M.W. Bench, and C.B. Carter, *On the Faceting of Ceramic Surfaces.* Surface Science, 1995. **343**(1-2): p. L1161-L1166.

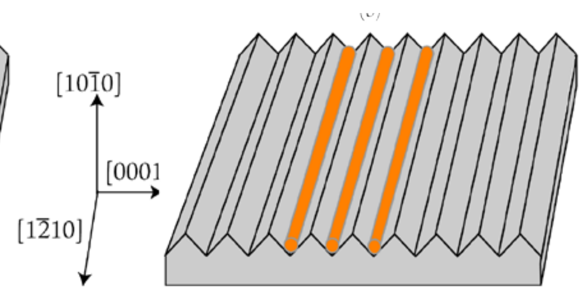
Can we direct film growth or dewetting to form long wires with a modulated structure?

AFM of facets

24h
1700°C



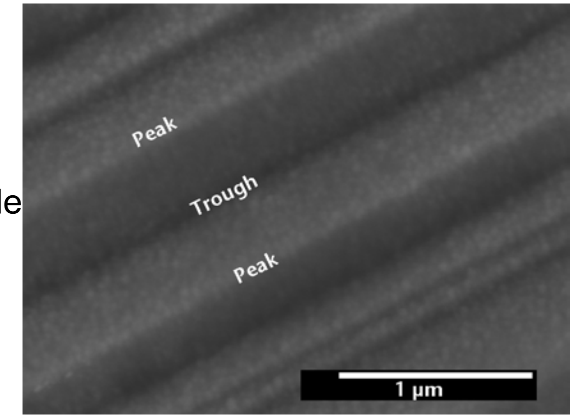


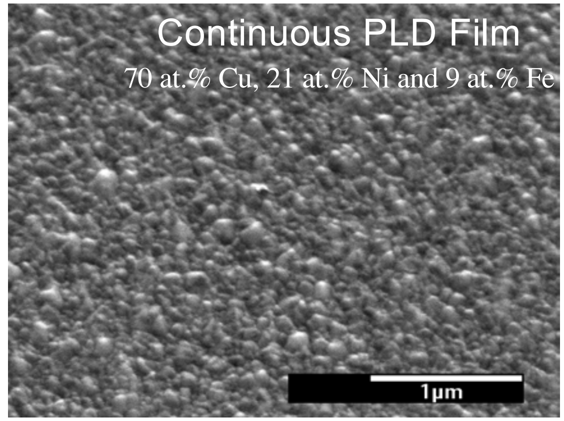


Directing Confinement With Surface Faceting on $\{10\bar{1}0\}$-Al_2O_3

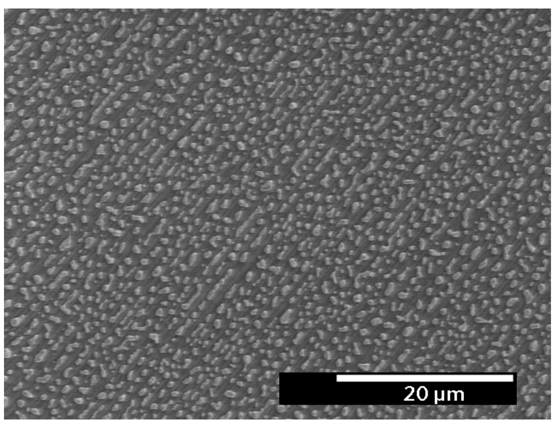
1600°C
12 h

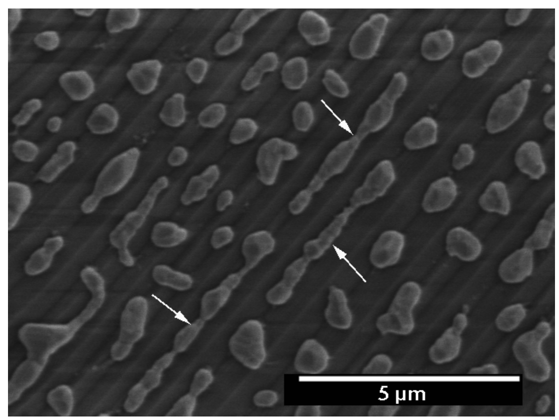
~100 nm tall
~300 nm wide





700°C
8 h





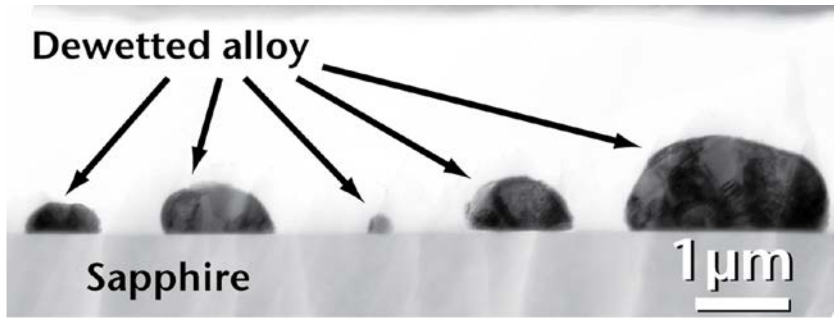
Dewetting Mechanisms

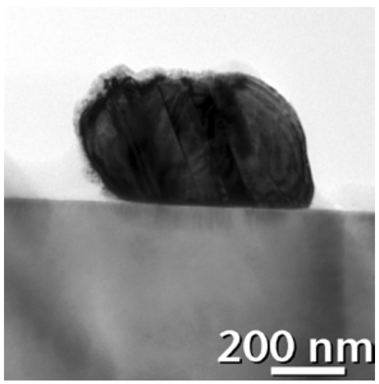
1. Lattice parameter difference between Cu and Ni-Fe rich phases causes thickness variation
    1. ”spinodal dewetting”
    2. Bischof, J., et al., *Dewetting Modes of Thin Metallic Films: Nucleation of Holes and Spinodal Dewetting.* Physical Review Letters, 1996. **77**(Copyright (C) 2010 The American Physical Society): p. 1536.
2. Film surface curvature on a faceted surface leads to chemical potential-driven flow to troughs
    1. Basu, J., et al., *Nanopatterning by solid-state dewetting on reconstructed ceramic surfaces.* Applied Physics Letters, 2009. **94**(17).
3. Grain boundaries in polycrystalline film act as nucleation sites
    1. Genin, F.Y., W.W. Mullins, and P. Wynblatt, *Capillary instabilities in polycrstalline metallic foils – experimental obeservations of thermal pitting in nickel.* Acta Metallurgica Et Materialia, 1994. **42**(4): p. 1489-1492.

Sugar, J.D., et al., *Encapsulation-induced stabilization of dimensionally restricted metallic alloy wires.* Acta Materialia, 2010. **58**(16): p. 5332-5341.

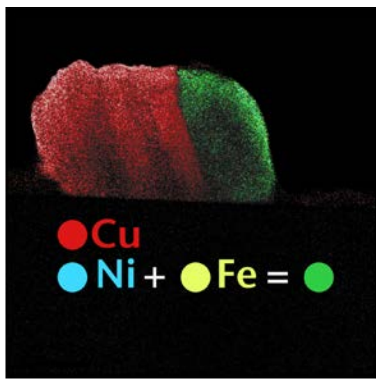
Directing Confinement With Surface Faceting on $\{10\bar{1}0\}$-Al_2O_3

BF Image
20 h 700°C

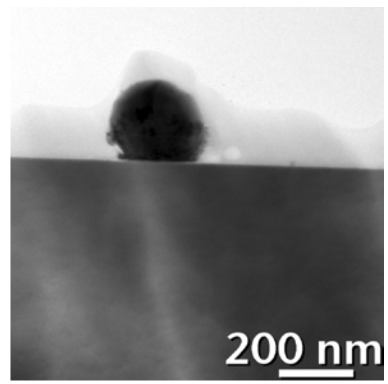




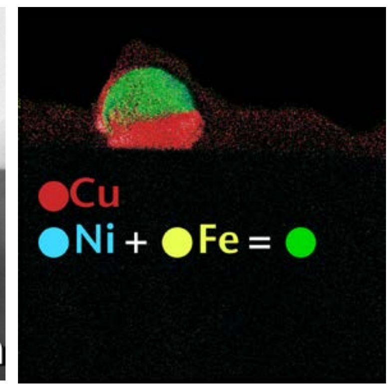
Zero loss Image



Composite ETEM map



Zero loss Image



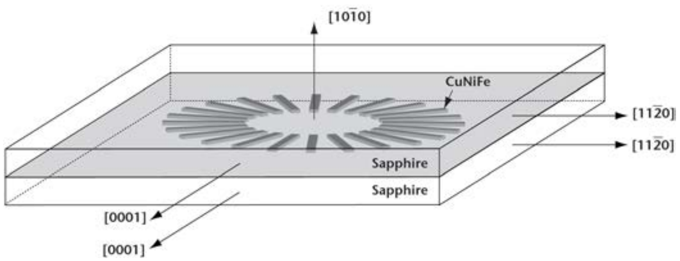
Composite EFTEM map

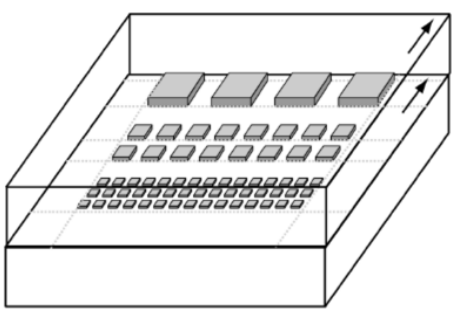
Alloy wires dewet into single bi-phase particles. What about full confinement to prevent dewetting?

Sugar, J.D., et al., *Encapsulation-induced stabilization of dimensionally restricted metallic alloy wires.* Acta Materialia, 2010. **58**(16): p. 5332-5341.

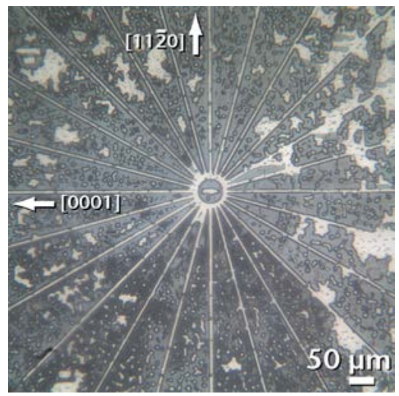
Complete Encapsulation Induced Stabilization

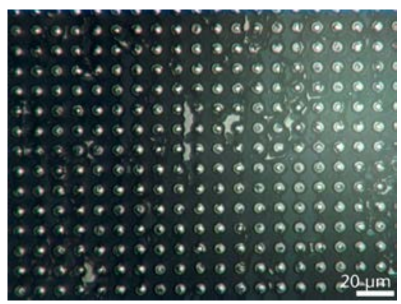
1. Pattern definition with UV lithography
2. PLD of metallic alloy film
3. Diffusion bonding of sapphire crystals

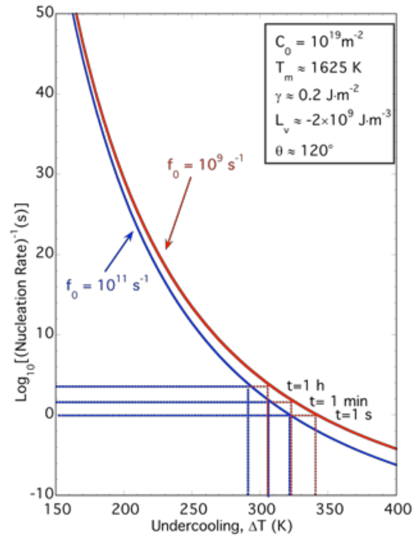




Remelt and solidify metal to form single crystals



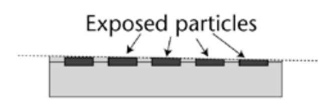




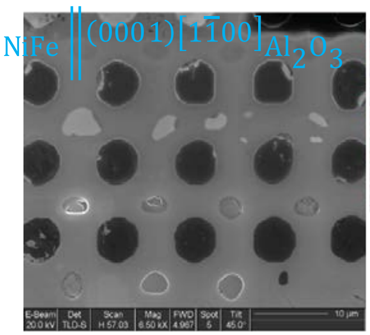
Nucleation-Controlled Liquid Phase Epitaxy

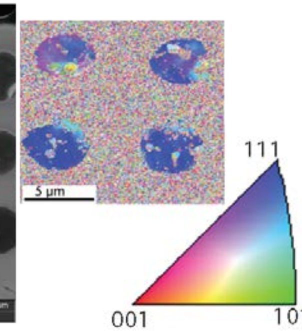
- Cooled at a sufficiently slow cooling rate so that one nucleation even happen in each particle

$$N = f_0 C_0 \exp\left(-\frac{16\pi\gamma_{sl}T_m^2}{3L_v kT(\Delta T)^2}S(\theta)\right)$$



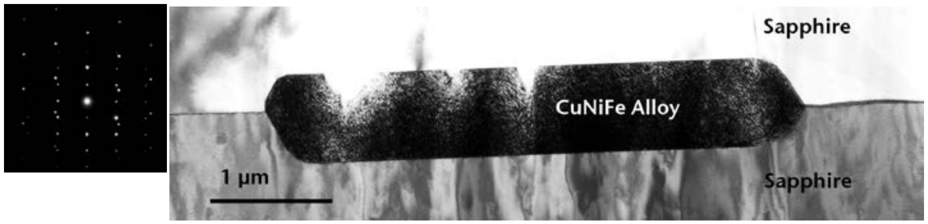
$(111)[1\bar{1}0]_{CuNiFe} \,||\, (0001)[1\bar{1}00]_{Al_2O_3}$



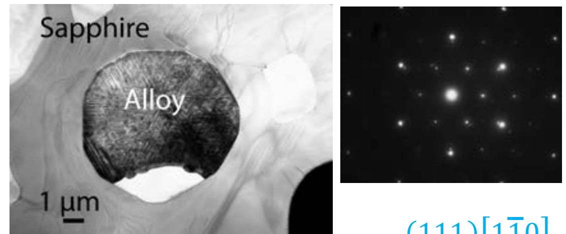


Sugar, J.D., et al., *Spatially confined alloy single crystals for model studies of volumetrically constrained phase transformations.* Applied Physics Letters, 2006. **89**(17).

Formation of Regular Pattern After Coarsening

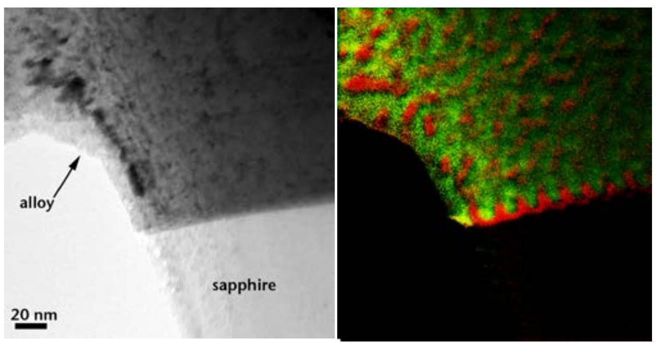


Cross sectional BF image

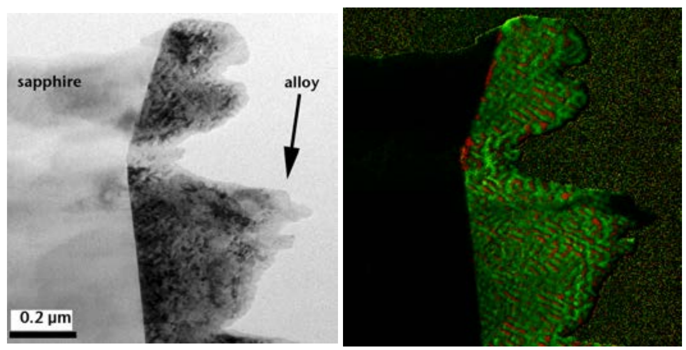


Top Down BF image

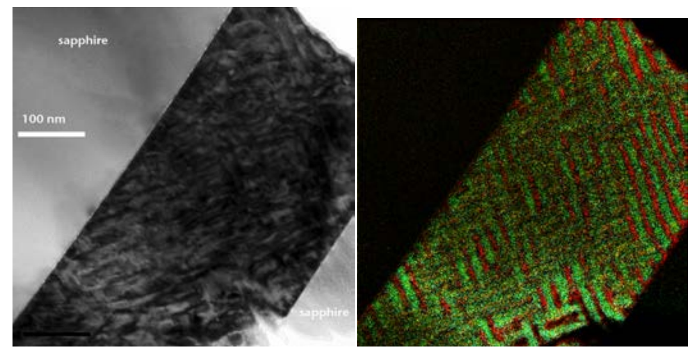
$(111)[1\bar{1}0]_{CuNiFe} \| (0001)[1\bar{1}00]_{Al_2O_3}$



900°C Quench
λ~15 nm



700°C 30 min
λ~21 nm



700°C 90 min
λ~23 nm

Cu Ni Fe Ni and Fe Overlay

Formation of Regular Pattern After Coarsening

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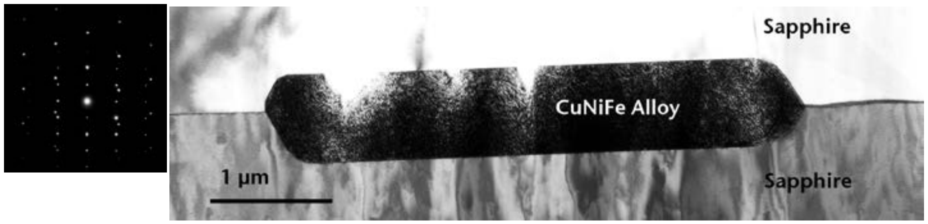
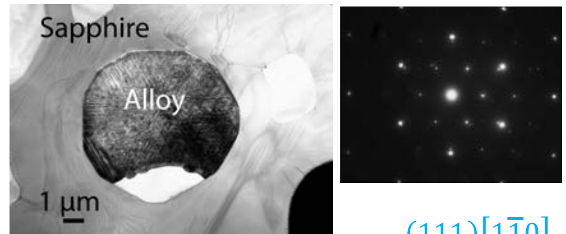
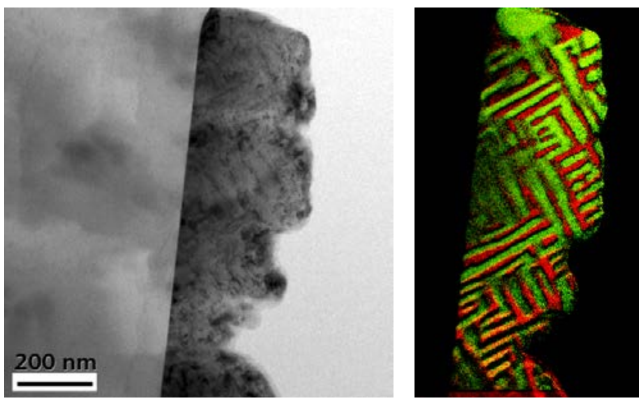


Cross sectional BF image

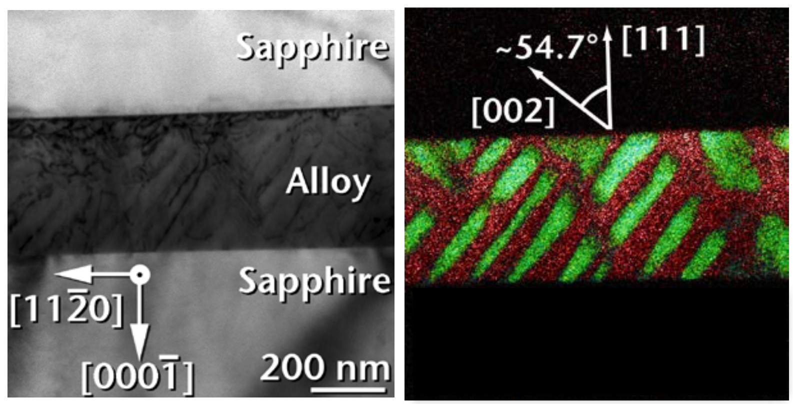


Top Down BF image

$$(111)[1\bar{1}0]_{CuNiFe} \parallel (0001)[1\bar{1}00]_{Al_2O_3}$$



700°C 300 min
λ ~40 nm



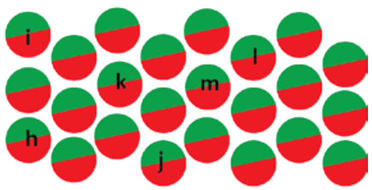
700°C 11280 min
λ ~100 nm

- Start to see one domain of modulated structure fill a cavity
- Orientation relationship does not allow for 90° patterning
- Initial stages of “directed decomposition” are visible at long aging times
- Probably a smaller cavity would aid in seeing this phenomena at earlier aging times

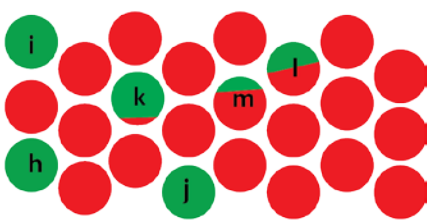
Cu Ni Fe Ni and Fe Overlay

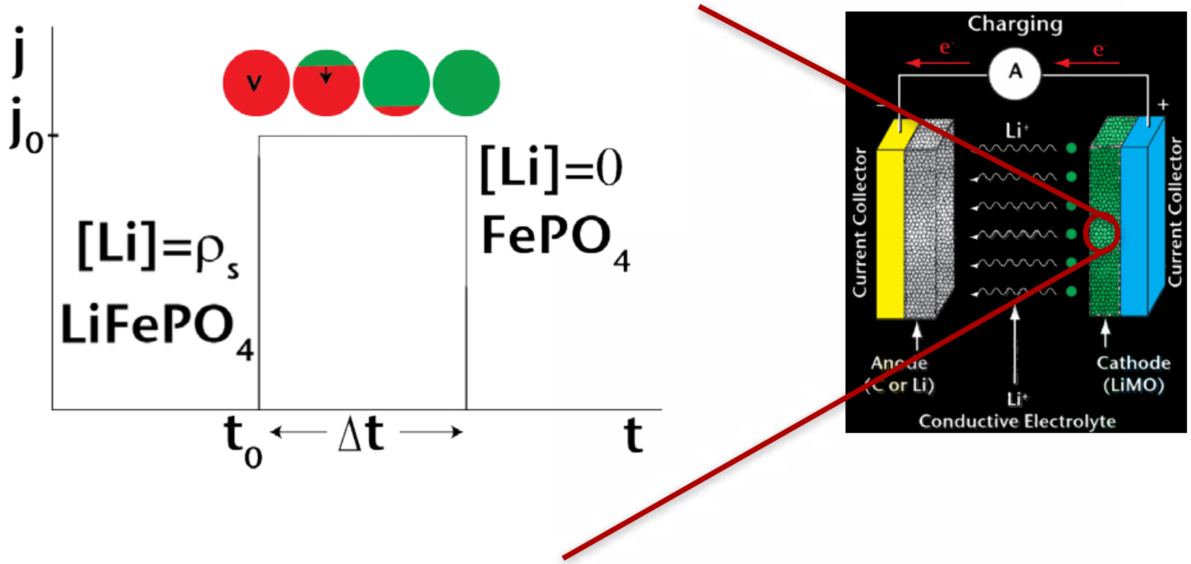
EFTEM Knowledge and Capability Inspired New Measurement for Li-ion Batteries

- Consider 2 Rate Limiting Cases for Charge/Discharge Transformation
  - Phase boundary migration rate limits

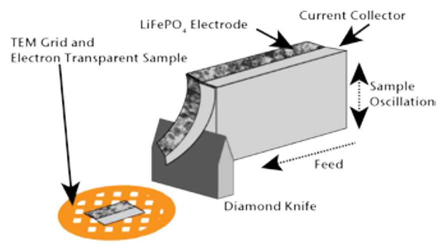


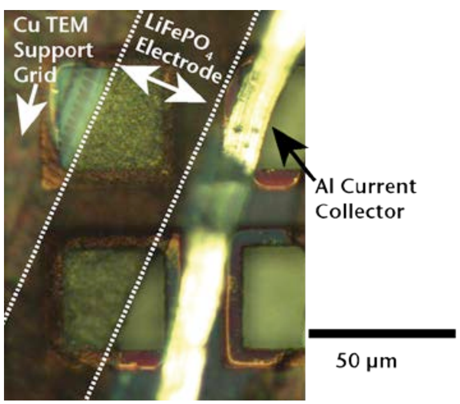
  - Probability of new phase nucleating (nucleation rate) limits



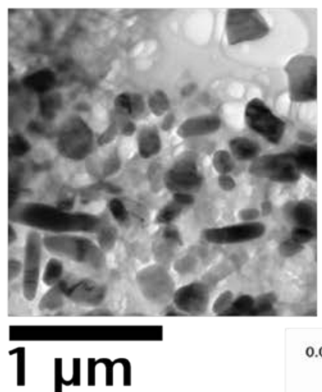


EFTEM Enabled Measurement of Li Without Beam Damage Effects

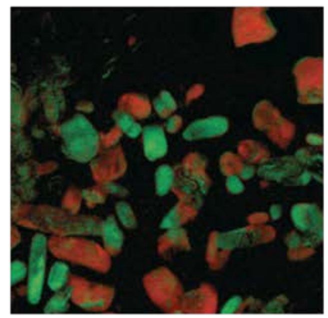




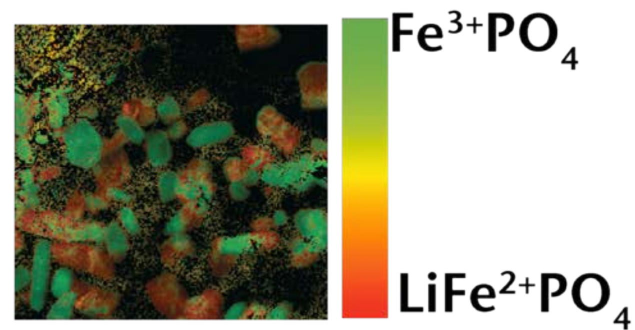
BF TEM image

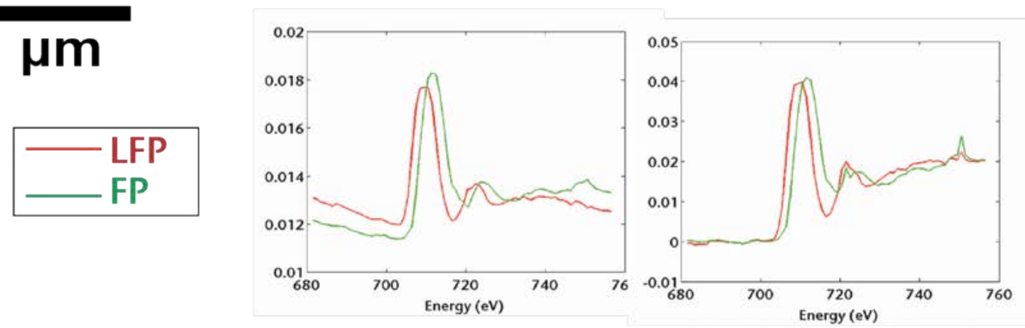


EFTEM Map of Fe state from MSA pure components



EFTEM Map Of Fe State Calculated from MLLS

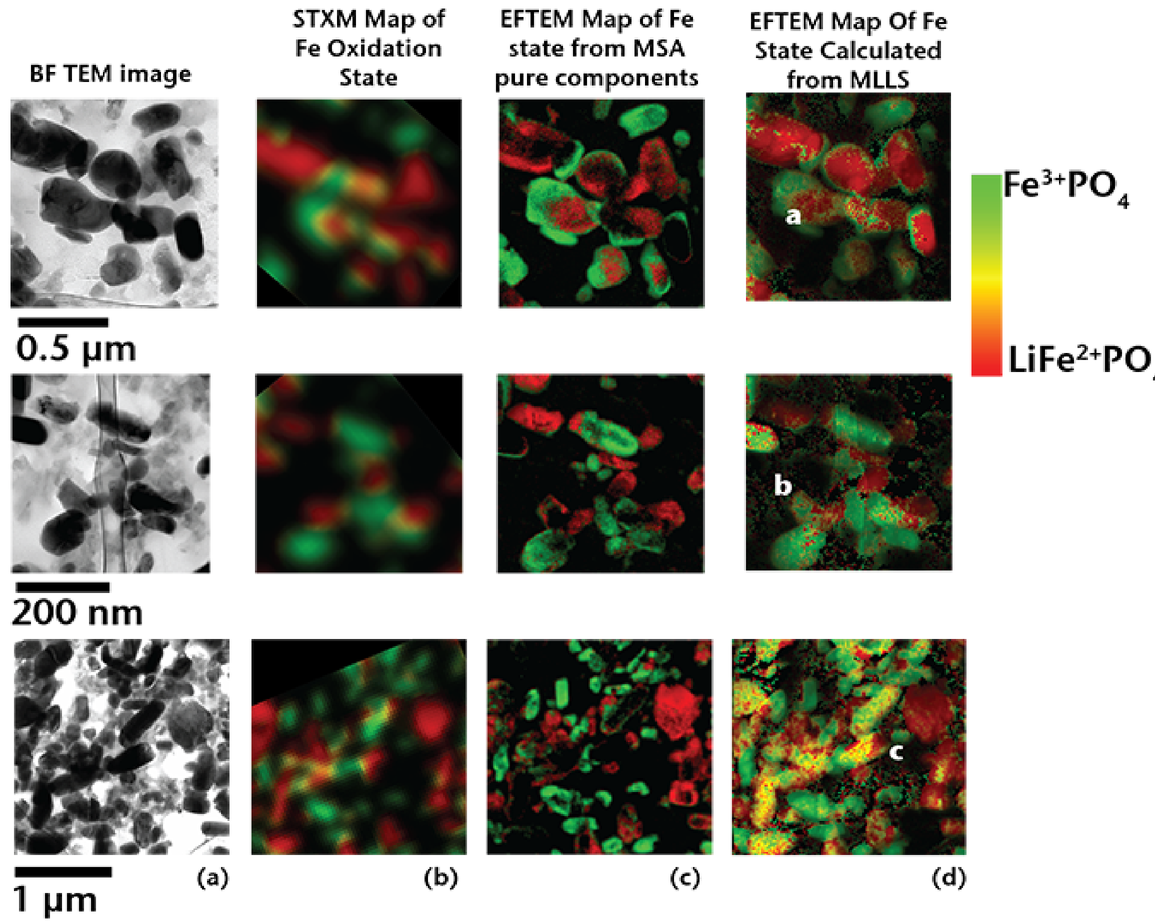




LFP Cathode at 50% State of Charge

Confirm a Particle-By-Particle Transformation Reaction And Validate with STXM

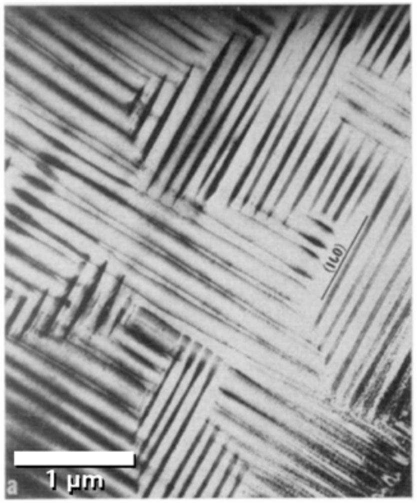
- Most of the time particles are either completely $LiFePO_4$ or $FePO_4$
- A small fraction of particles appear mixed
  - Most of the time this is because particles overlapping in the projection view
  - Sometimes this is the result of non-linear thickness effects
    - Intensity is redistributed from the core edge energy as a result of plural scattering
    - Convolution of core-edge spectra with low-loss or plasmon spectrum
- Rarely do we find a single particle that exhibits both Fe^{2+} and Fe^{3+}
- Charging time is independent of time for individual particle and depends on nucleation rate for forming the new phase



Chueh, W.C., et al., *Intercalation Pathway in Many-Particle LiFePO4 Electrode Revealed by Nanoscale State-of-Charge Mapping.* Nano Lett, 2013. **13**(3): p. 866-72.

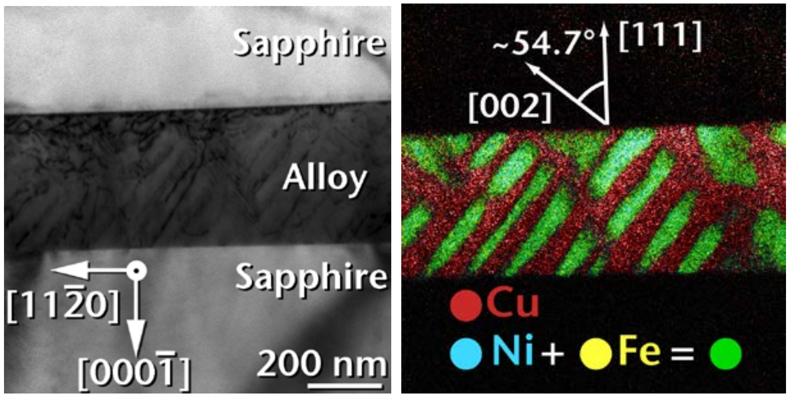
Summary and Conclusions

- Prof. Thomas work from the 1970’s inspired the work that was the basis for my PhD dissertation work



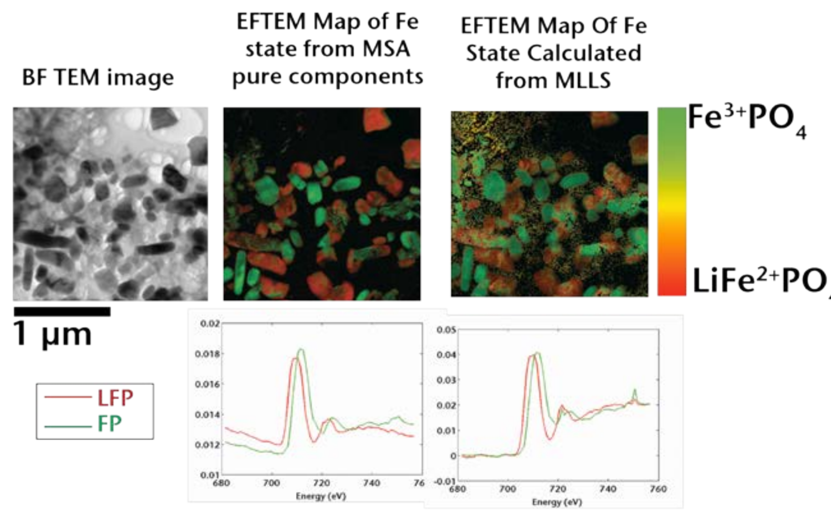
Summary and Conclusions

- Prof. Thomas work from the 1970's inspired the work that was the basis for my PhD dissertation work
- Ultimately my interest in understanding volumetric confinement in CuNiFe alloys required me to learn EFTEM, which began my interest and journey in analytical electron microscopy



Summary and Conclusions

- Prof. Thomas work from the 1970's inspired the work that was the basis for my PhD dissertation work
- Ultimately my interest in understanding volumetric confinement in CuNiFe alloys required me to learn EFTEM, which began my interest and journey in analytical electron microscopy
- I continue to use and develop the capabilities and knowledge that were inspired by Prof. Thomas to solve relevant materials problems today (Li-ion batteries)



Summary and Conclusions

- I spoke here today to share with you my personal experience of how I was inspired by Prof. Thomas and how his career impacted me even as a second generation student
- Prof. Thomas left a legacy that continues to impact and inspire microscopy and materials science professionals to solve hard problems and develop new capabilities
- I thank Prof. Thomas for the work he did at UC Berkeley and LBNL and am happy that I had the pleasure to benefit from it