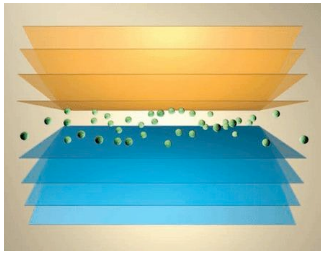


Complexions for Informed Design

CHARACTERIZATION AND MODELING OF COMPLEXION ENGINEERED MICROSTRUCTURES

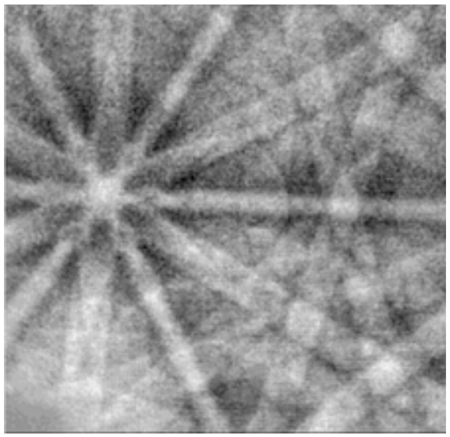
GREG ROHRER AND TONY ROLLETT

Outline

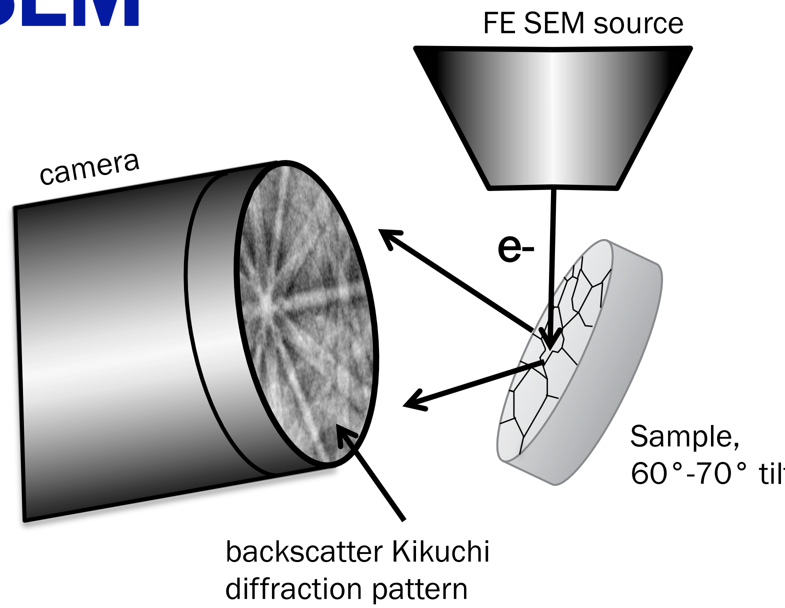
1. Mesoscale characterization and Modeling of complexion engineered microstructures

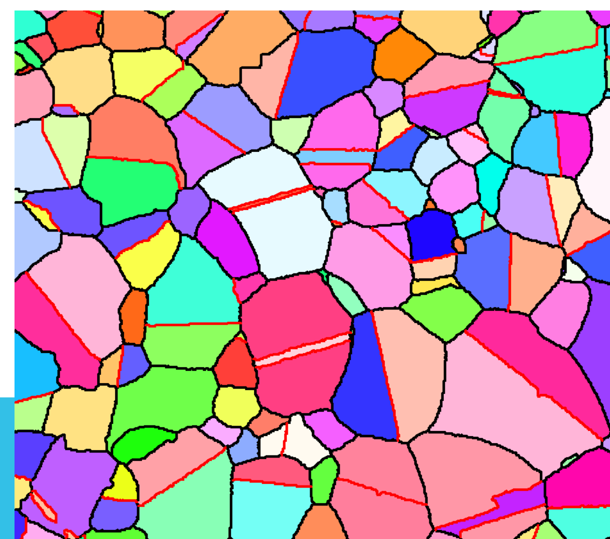
2. Characterizing and modeling Interface distributions in nanoscale materials

All Measurements Based on Orientation Mapping in the SEM



Electron backscattered diffraction pattern, indexed by computer





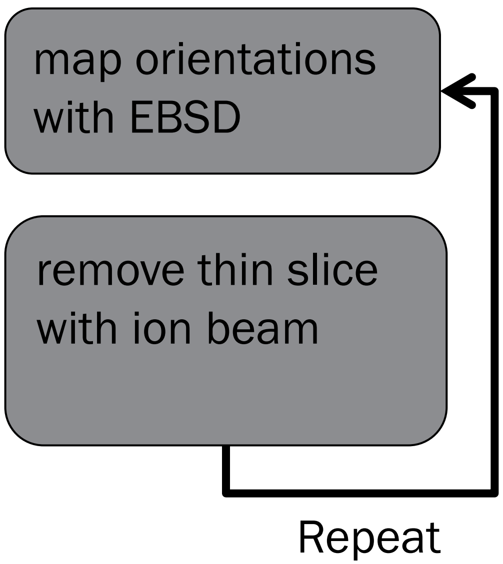
(110)
(001) (100)

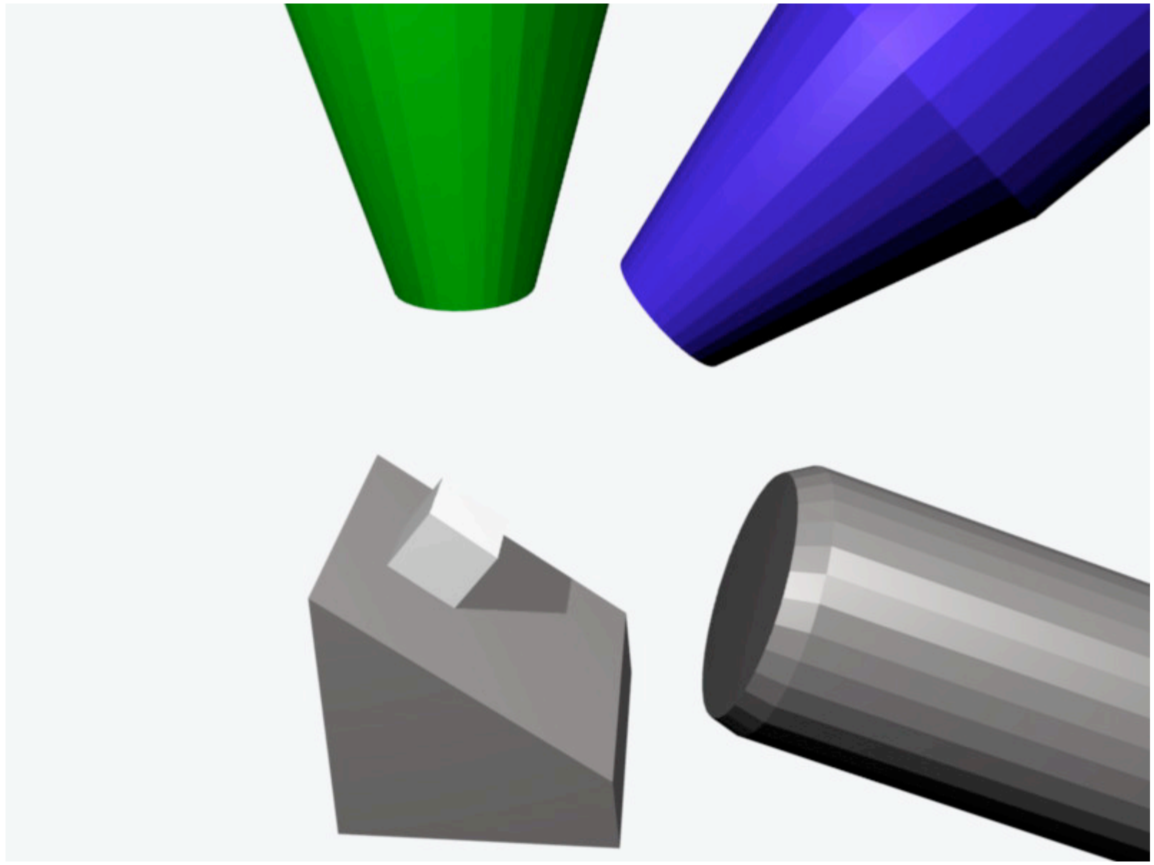
Inverse pole figure map (TiO_2) displays accumulated orientations.

100μm

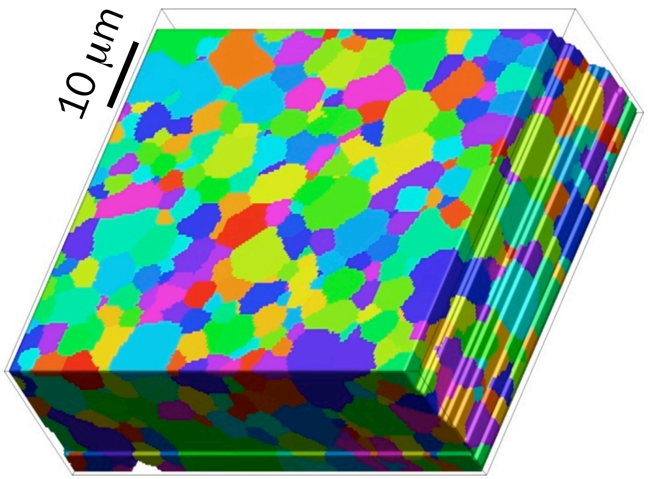
Automated Serial Sectioning in the FIB

Nova 600 NovaLab
DB-FIB SEM

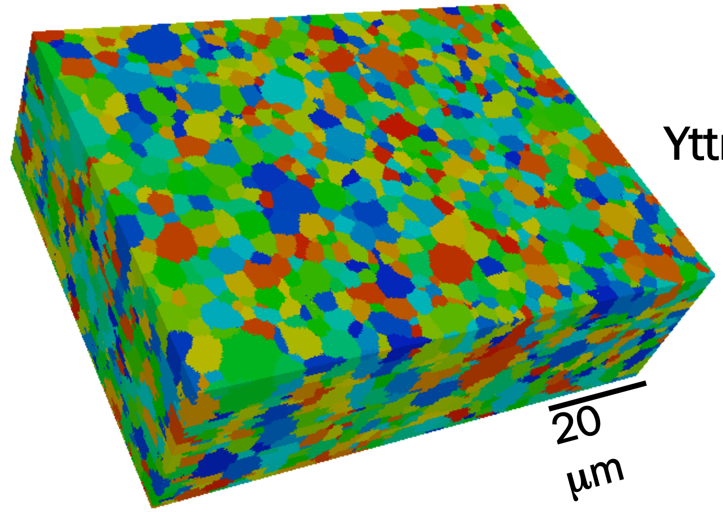




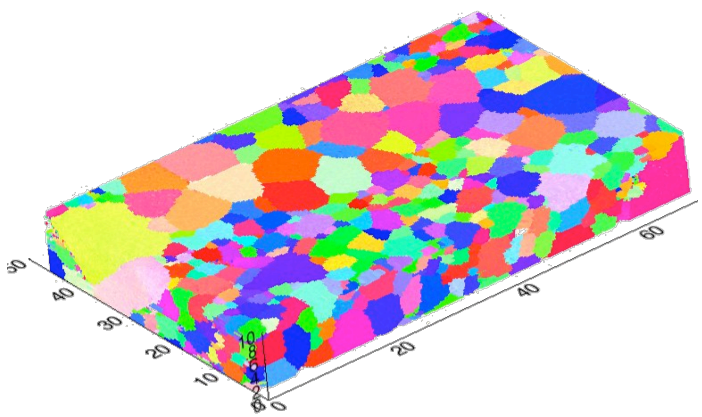
Some of the Materials Studied



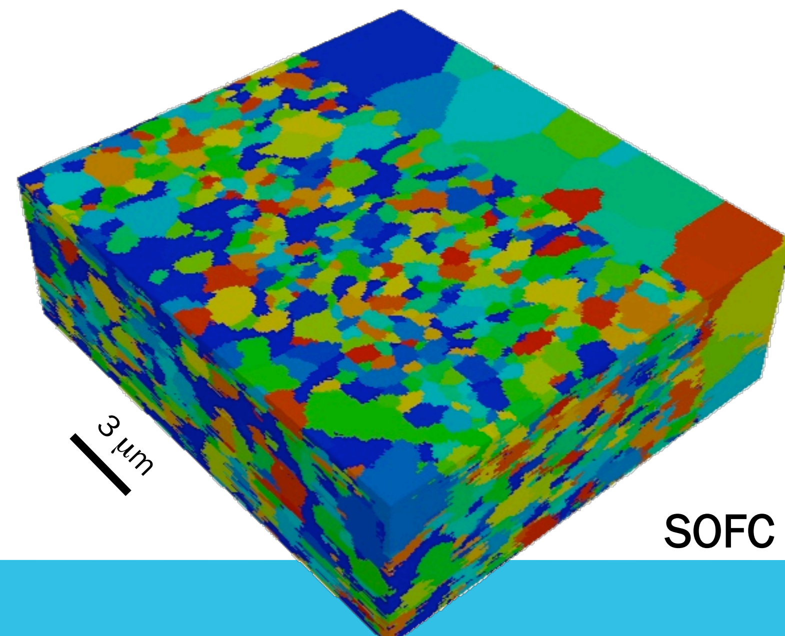
Yttria-Stabilized Zirconia



Yttria



Strontium Titanate

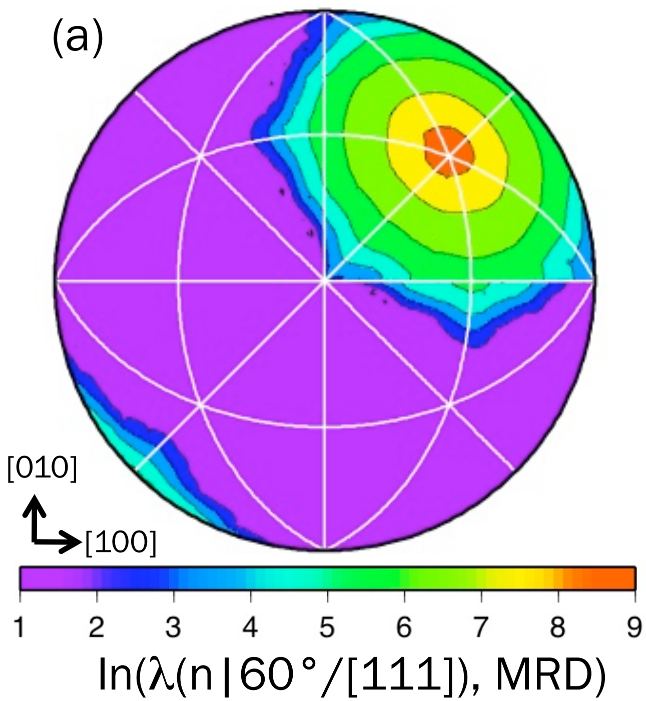


SOFC

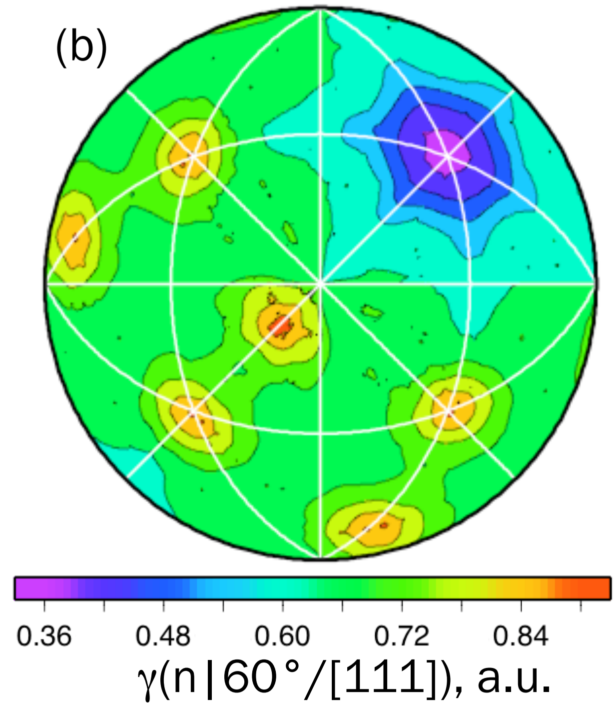
Distribution of GB planes and energies in the bicrystal reference frame - Ni

Σ3 – Grain Boundary

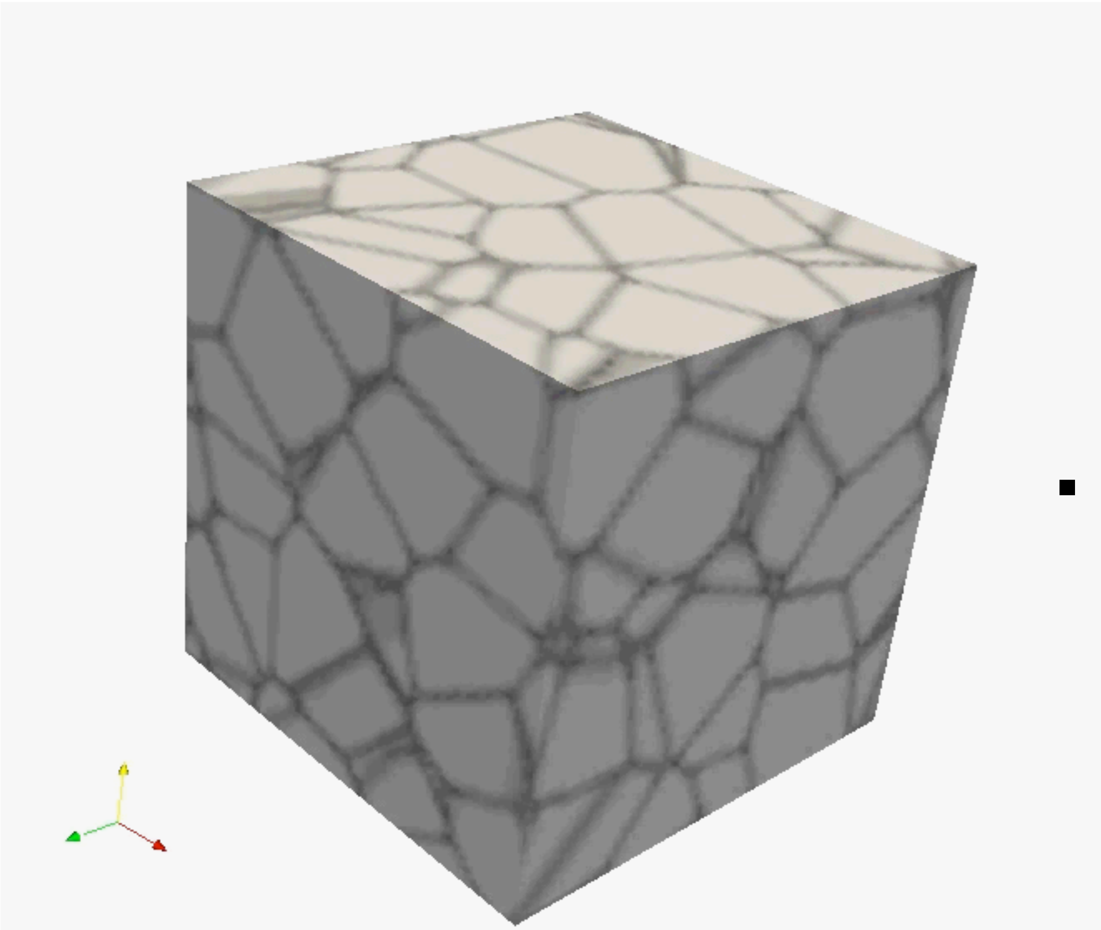
Grain Boundary Plane Distribution



Grain Boundary Energy Distribution



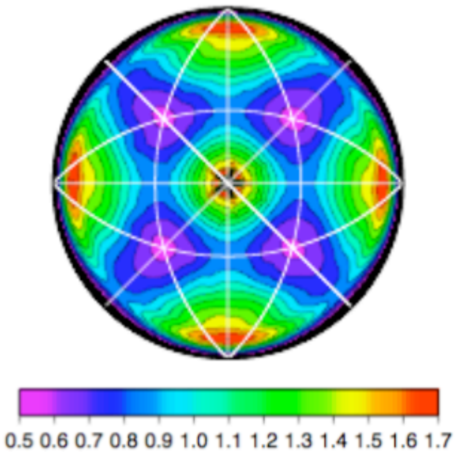
Accurate simulations of microstructure evolution



- Test models for transition from normal to complexion state.
  - Detailed modeling of solute-boundary interaction for isolated grains, and polyxtal networks.
  - Models use information about solute-GB interaction from atomistic scale simulations & theory.
- Test ideas about how mixtures of normal and complexion state boundaries influence grain growth.
  - Larger scale models with constitutive descriptions of normal↔complexion transitions based on atomistic and detailed mesoscale modeling

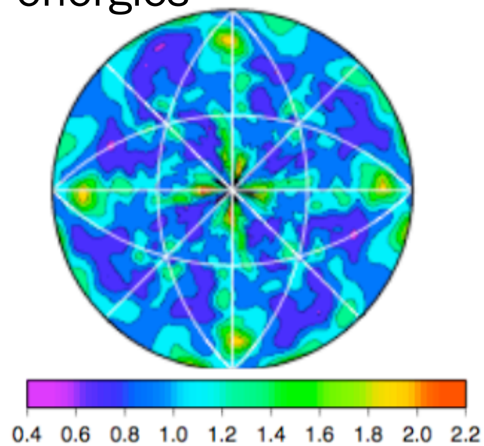
Results of Simulations of Ni

Assumed Energy Distribution



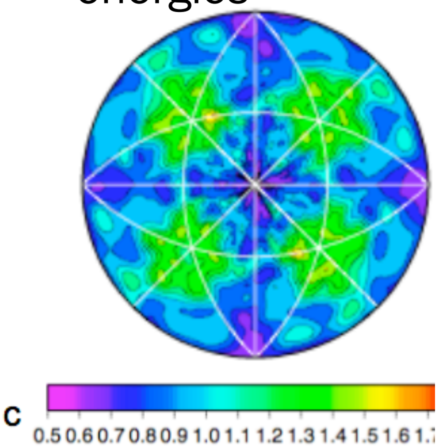
b

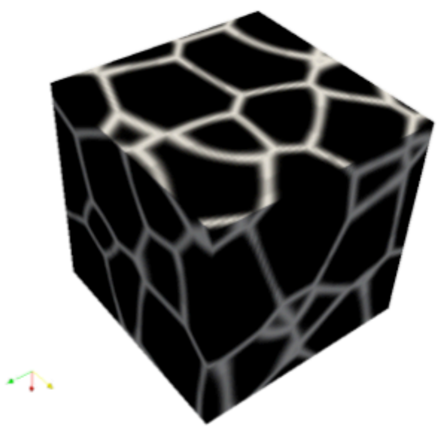
Interface distribution assuming isotropic energies



c

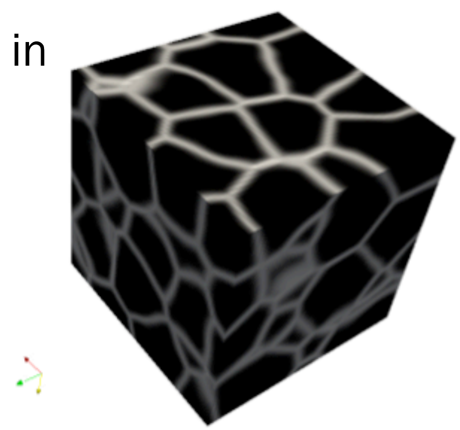
Interface distribution assuming anisotropic energies





Note differences in dihedral angles

e



Systems To Study in MURI

Initial work:

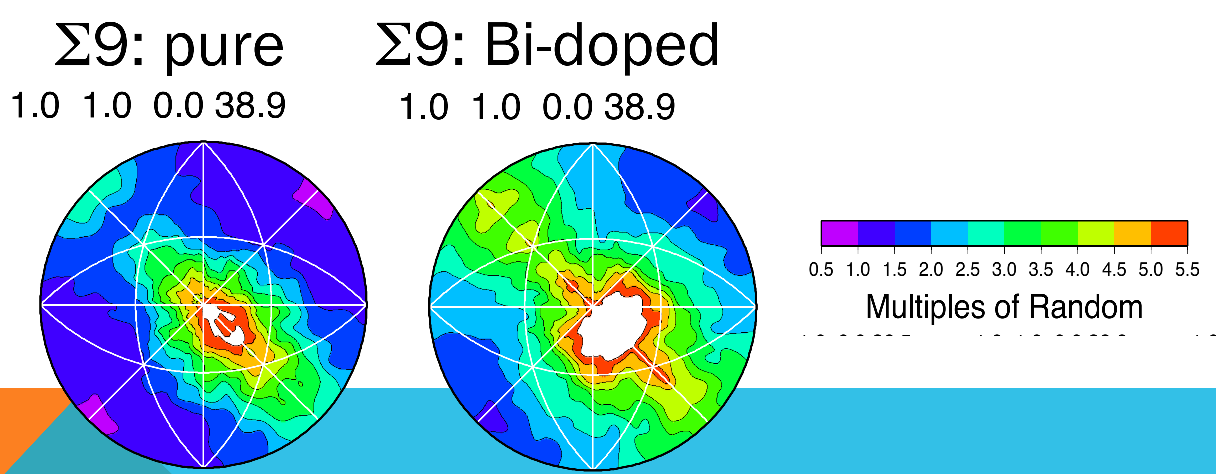
Ni-Bi (this will connect with ongoing research at Lehigh and Clemson)

Next Priority:

Metal Complexionized Ceramics (This will start after successful synthesis by Lehigh)

Exploratory systems:

WC-Co (Model metal-ceramic system that has evidence of complexions)
Sn and Sb-doped ZnO (exploratory system that has evidence for complexions)
YSZ (collaborating with the Clemson and Illinois groups)



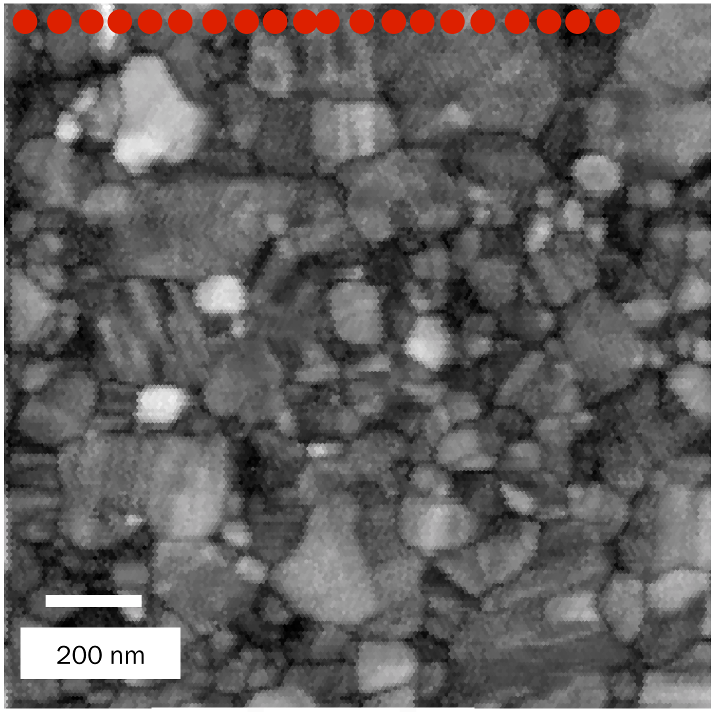
Outline

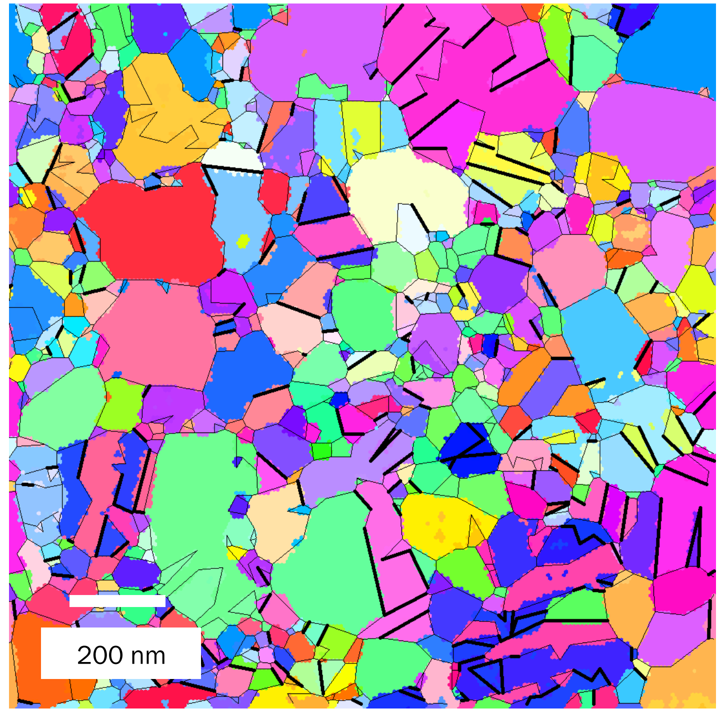
1. Mesoscale characterization and Modeling of complexion engineered microstructures

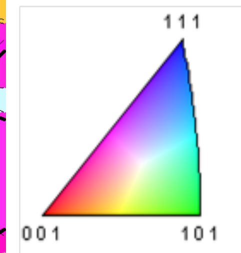
2. Characterizing and modeling Interface distributions in nanoscale materials

Orientation Mapping at the Nanoscale

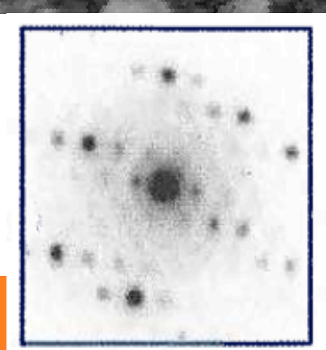
Accurate orientation mapping of a Cu thin Film with a man grain size of 86 nm!







Inverse pole figure map with reconstructed boundaries.

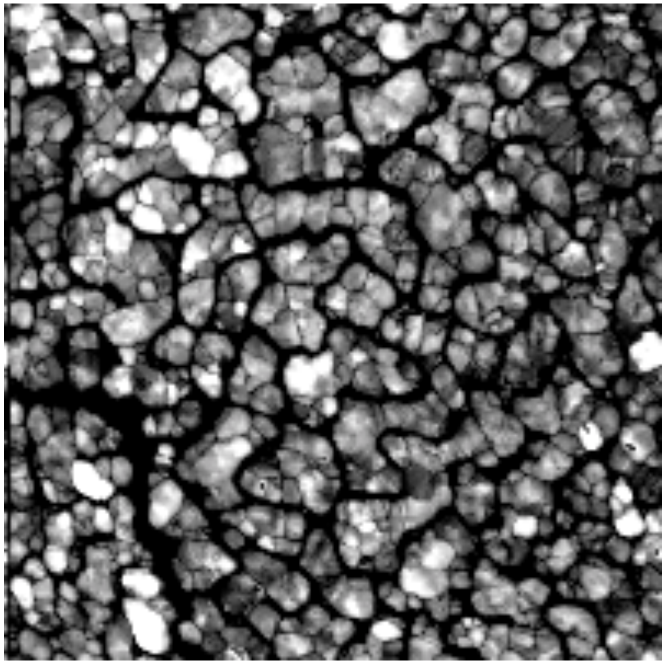


NanoMegas has developed a commercial package known as ASTAR that combines nanoprobe with precession diffraction.

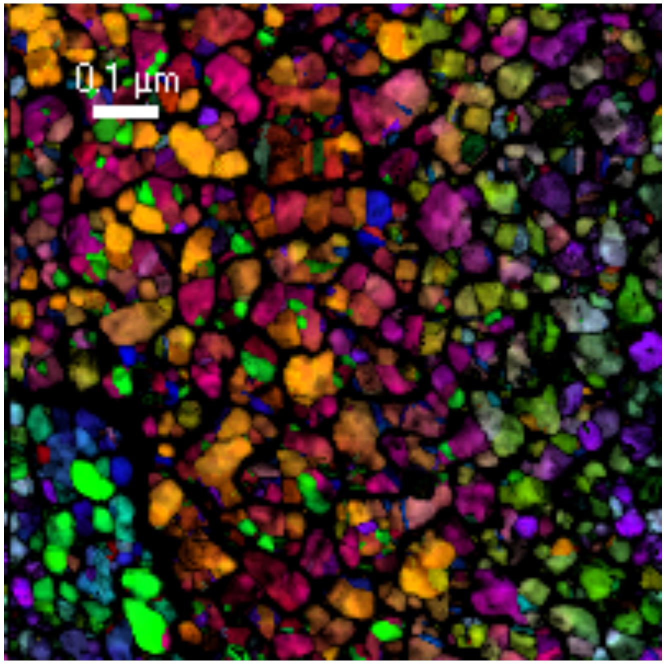
Courtesy of: A. Darbal and K. Barmak

Orientation Mapping at the Nanoscale

Confidence Map



Orientation Map



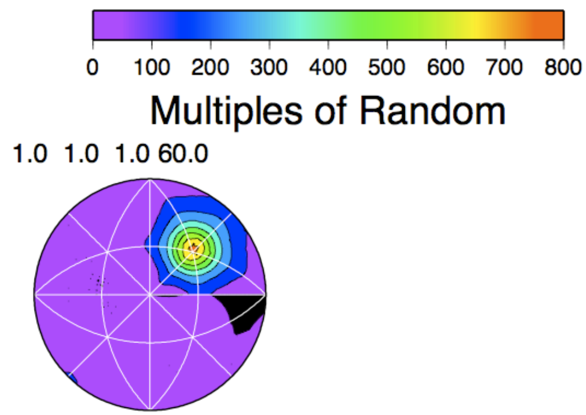
Fe:Pt thin file hard disc drive material

Courtesy of: S. Granz, M. Kryder

Nanoscale Interface Data

- Compute Interface distributions
- Compute grain boundary energies
- Use as input for Phase Field Models

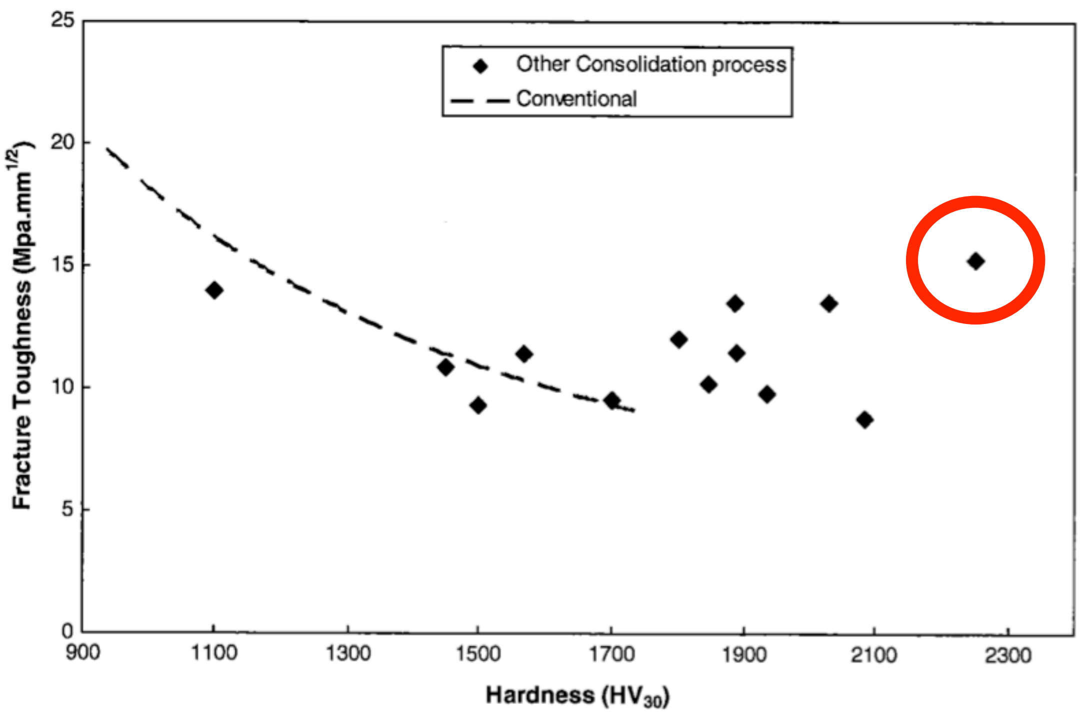
$\Sigma 3$ boundaries in a thin Cu film



Computed based data from Darbal and Barmak

Systems of interest

Nanosized WC/Co



Z. Z. Fang, X. Wang, T. Ryu, K. S. Hwang, and H. Y. Sohn, "Synthesis, sintering, and mechanical properties of nanocrystalline cemented tungsten carbide - a review," *International Journal of Refractory Metals & Hard Materials,* **27** [2] 288-99 (2009).

- Extend to other systems produced by SPS

Y_2O_3-doped aluminas

SiO_2-doped aluminas

Metal complexionized ceramics

Summary

1. Characterization and Modeling of complexion engineered microstructures

- Techniques
  - 3D mesoscale interface structure studies (GBCD measurements)
  - Grain Boundary Energy Measurements (towards complexion selection rules)
  - Modeling Microstructure evolution (phase field method)
- Systems (possible)
  - Ni-Bi, Metal Complexionized Ceramics, WC-Co, ZnO-Sn,Sb, YSZ

2. Characterizing Interface Distributions in nanoscale materials

- Techniques
  - Use emerging TEM-based orientation mapping (nanomegas system)
  - 3D structural studies of the GBCD and GBED
  - Modeling Microstructure evolution (phase field method)
- Systems
  - WC-Co, Ytrria and silica doped aluminas

3. Work accomplished by two MSE graduate students integrating characterization and modeling.

Extras

PHASE FIELD MODEL FORMULATION

$$\{\phi\} = \{\phi_1, \phi_2, \ldots\ldots\ldots, \phi_N\}$$

$$F(\{\phi\}) = \int_\Omega \left(f^{pot}(\phi) + f^{kin}(\phi)\right) dV$$

$$\sum_{i=1}^{N} \phi_i(x,t) = 1$$

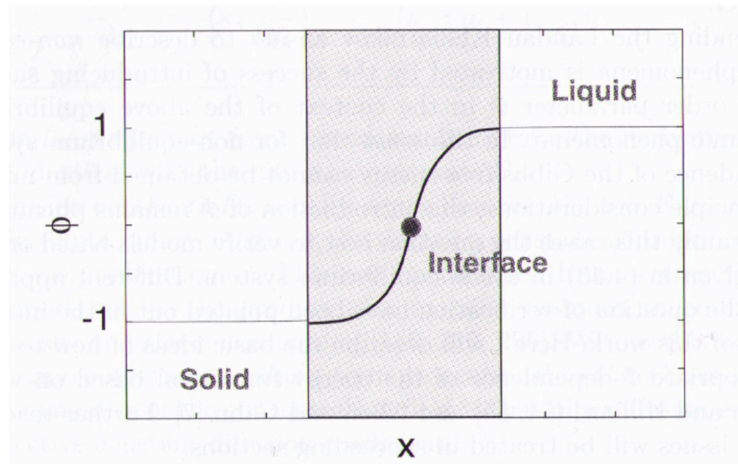
For grain *i*,

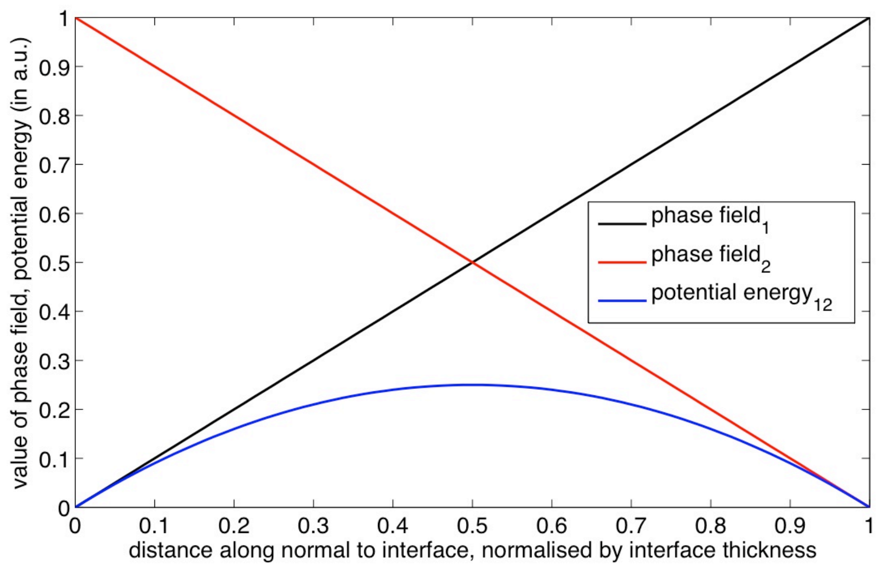
$$\phi_k = \delta_{ik}, 1 \le k \le N$$

$f^{pot}(\phi)$ defined such that it is at a minima within each grain interior

$$f^{pot} = \sum_{\alpha=1}^{N} \sum_{\beta=\alpha+1}^{N} w_{\alpha\beta} |\phi_\alpha| |\phi_\beta|$$

$$f^{kin} = \sum_{\alpha=1}^{N} \sum_{\beta=\alpha+1}^{N} \frac{\varepsilon_{\alpha\beta}}{2} \nabla\phi_\alpha \nabla\phi_\beta$$





Steinbach, *Physica D* **134** (1999) 385–393.

Diffuse interface approach in materials science, ed. Emmerich, p40

SOLUTE DRAG

What is the equilibrium segregation C_B^{eq} as a function of boundary velocity?

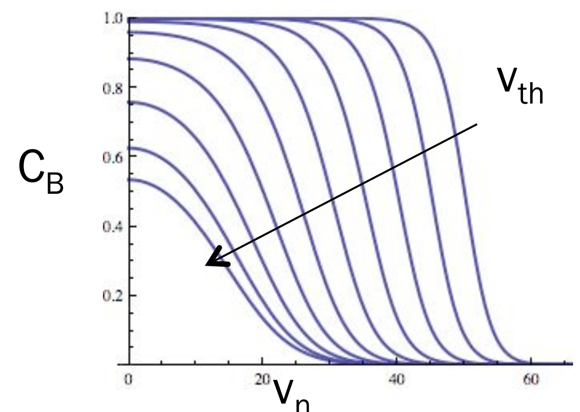
$$\mathbf{j}^{\pm} = \pm C_V^{\pm} \mu K \left(C_B - C_B^{eq}\right) \mathbf{n}$$

Approximate the boundary as a two-state system

	Energy
Bound state	$-E_0 + mv_n^2/2$
Unbound state	$mv_{th}^2/2$

The canonical distribution from statistical mechanics then implies

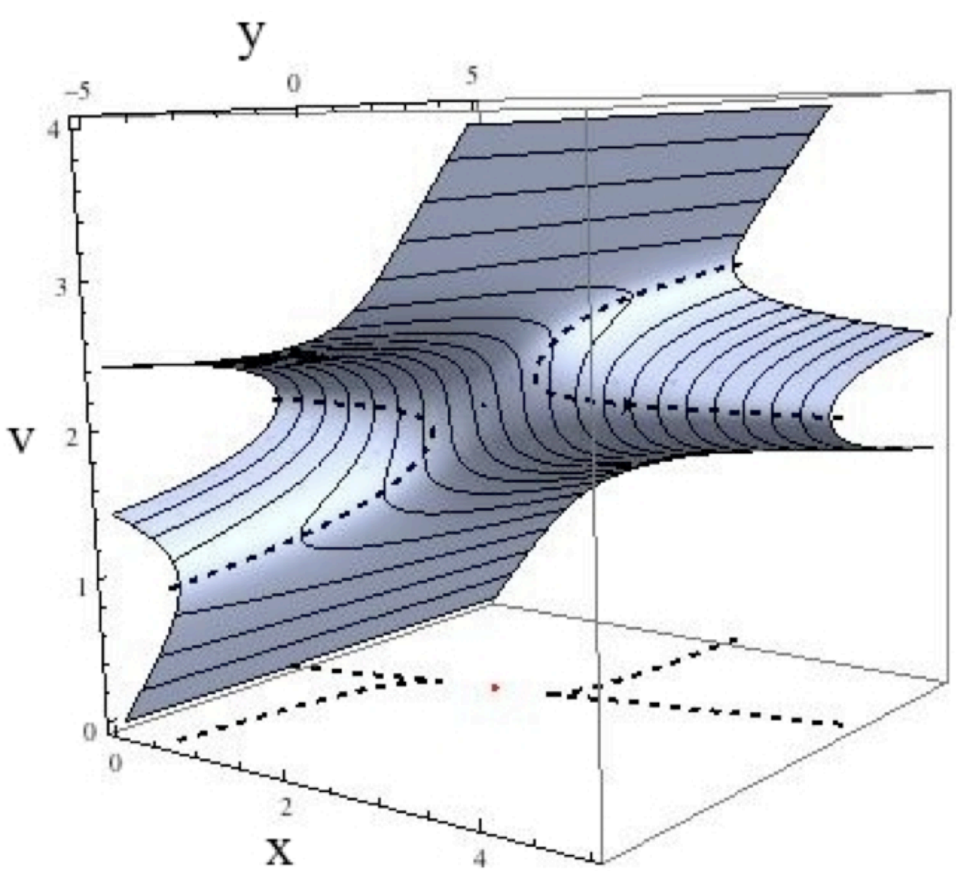
$$\Gamma_2^{eq} = (\Gamma - \Delta\Gamma) \frac{e^{-\beta\epsilon_2}}{e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}}$$



SOLUTE DRAG

Rate of change of boundary velocity, *v*, with respect to driving force, τ.

$$\frac{\partial v}{\partial \tau} = -v - yv\,\mathrm{sech}^2\left[\delta + \omega\left(1 - v^2\right)\right] + x$$



$$\frac{\partial v_n}{\partial t} = -L\frac{\delta}{\delta v_n}\frac{dG}{dt}$$