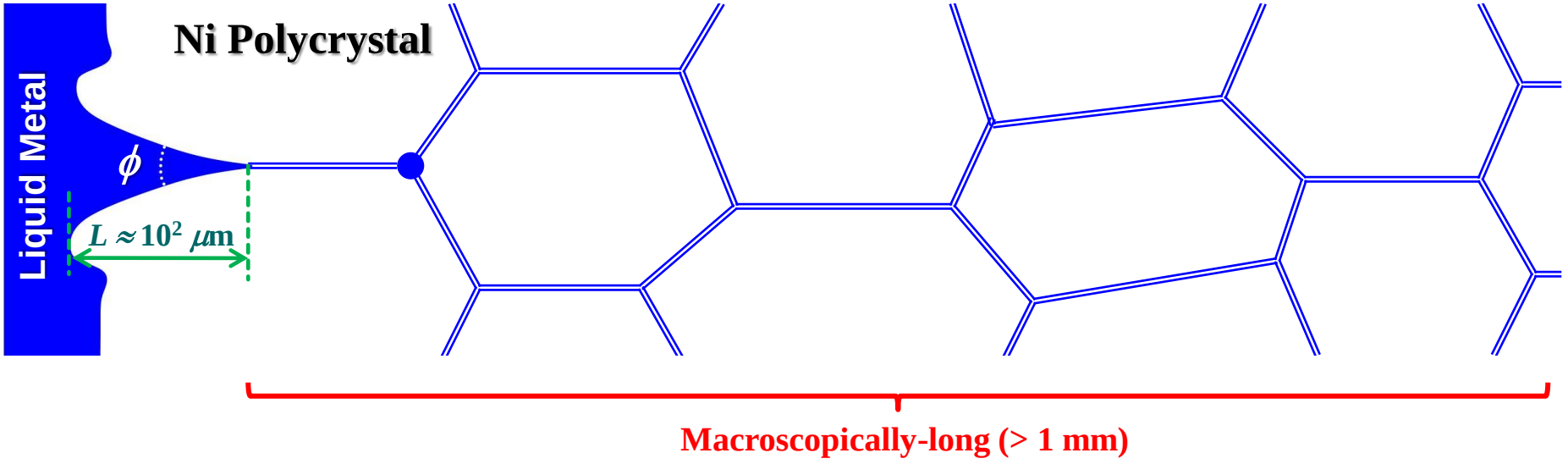
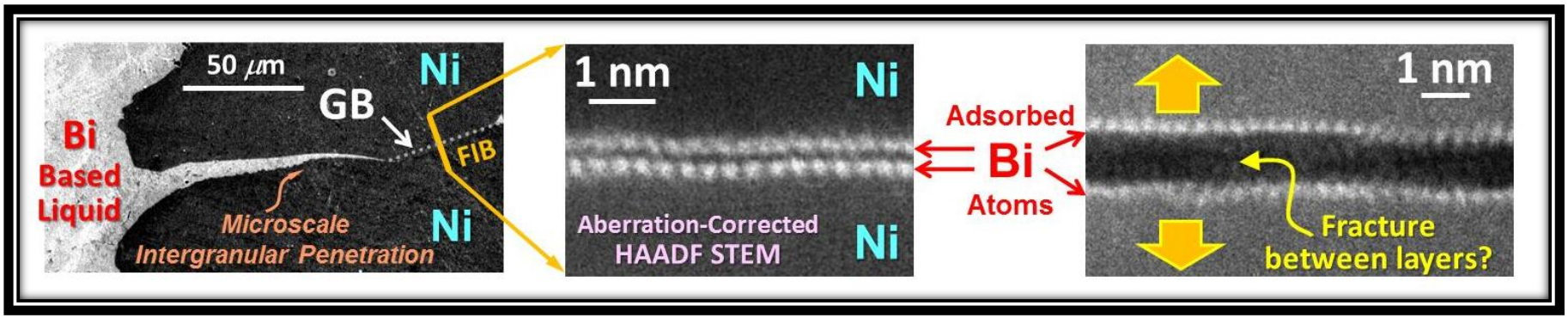
Updates on Ni-Bi & Cu-Bi Experiments…

Prior Results [*Science* 331:1730 (2011)]

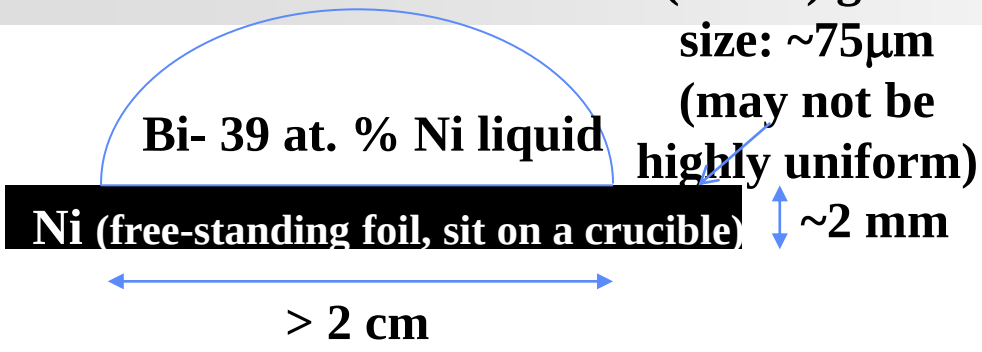
Ni foil annealed in contact with a Bi-Ni liquid at 1100 °C for 5 hrs



Q: Do these bilayers promote or inhibit grain growth?



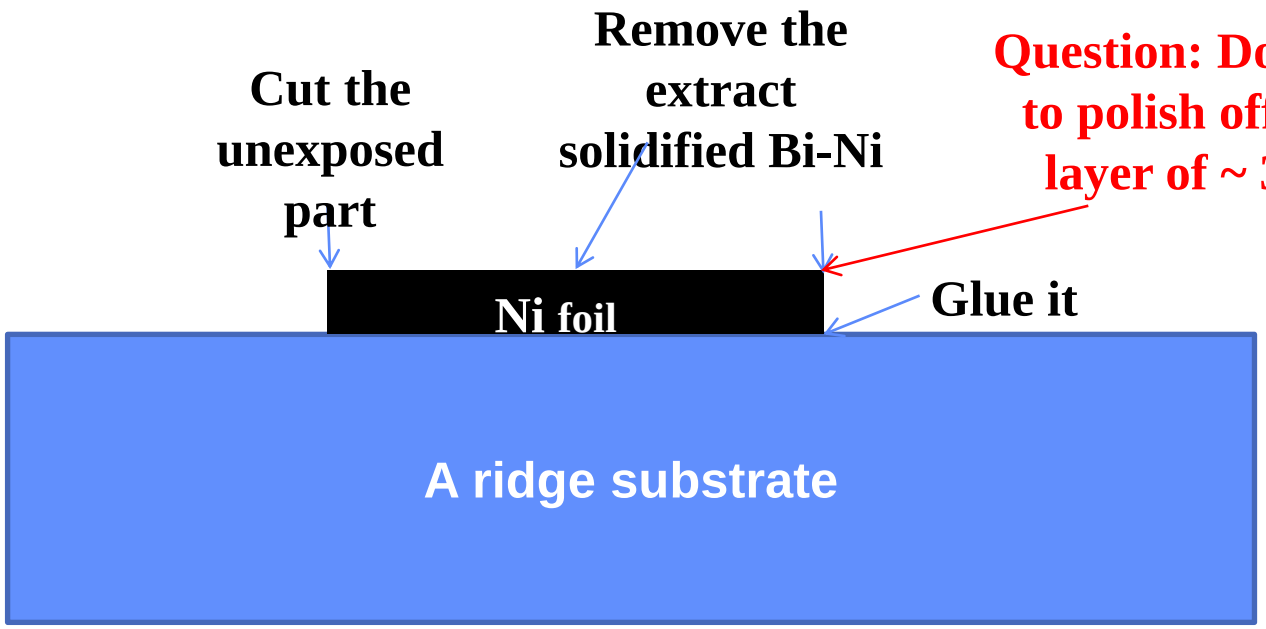
Proposed Specimen:



Annealed at 1100 °C, for 5 hrs
in 5 % H2 balanced by Ar

We will try to water quench – hope it will survive – if not, furnace cooling instead?

Then…



Clemson is current preparing such specimens – if and once successful, we will specimens to CMU for EBSD and GB character mesaurements

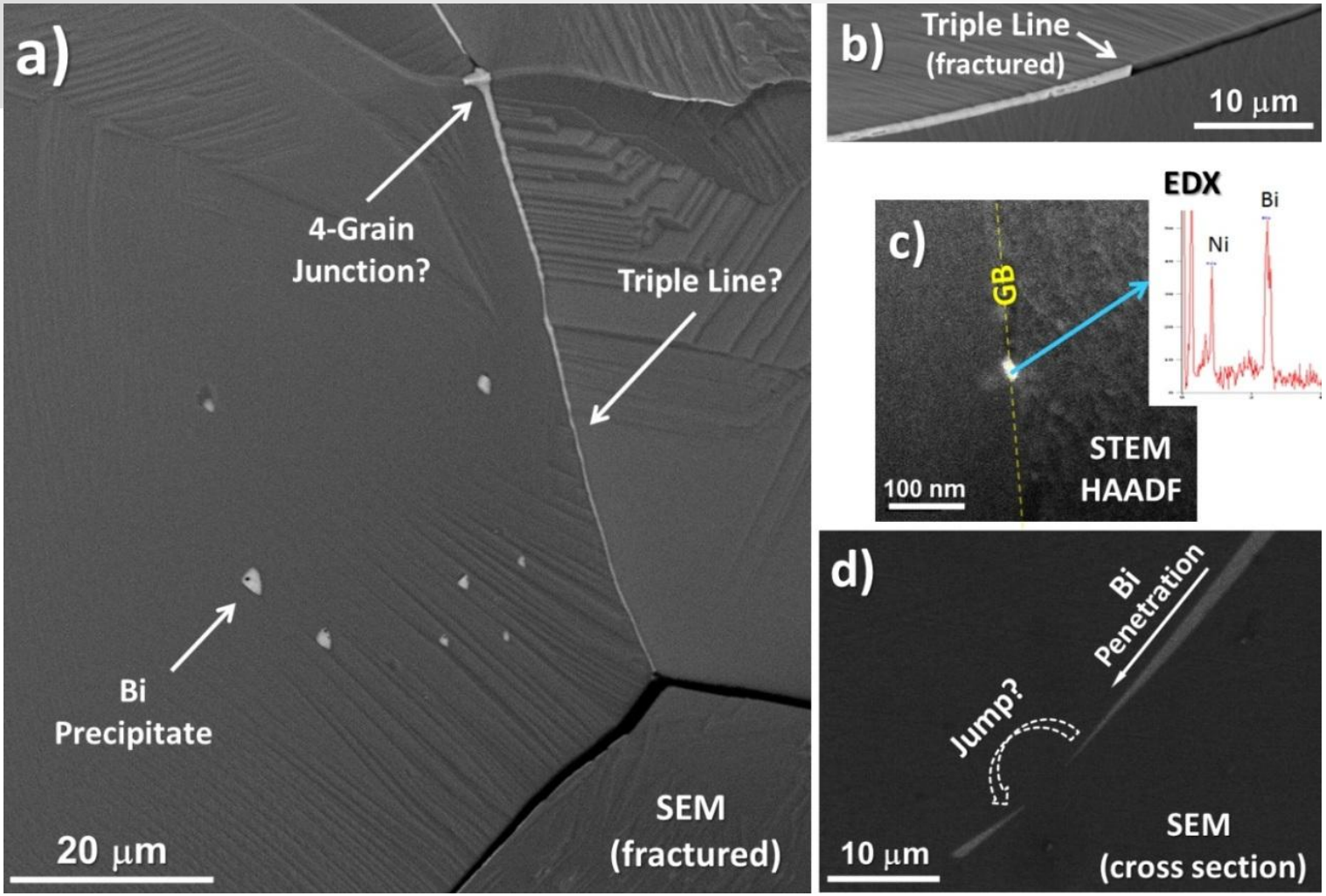
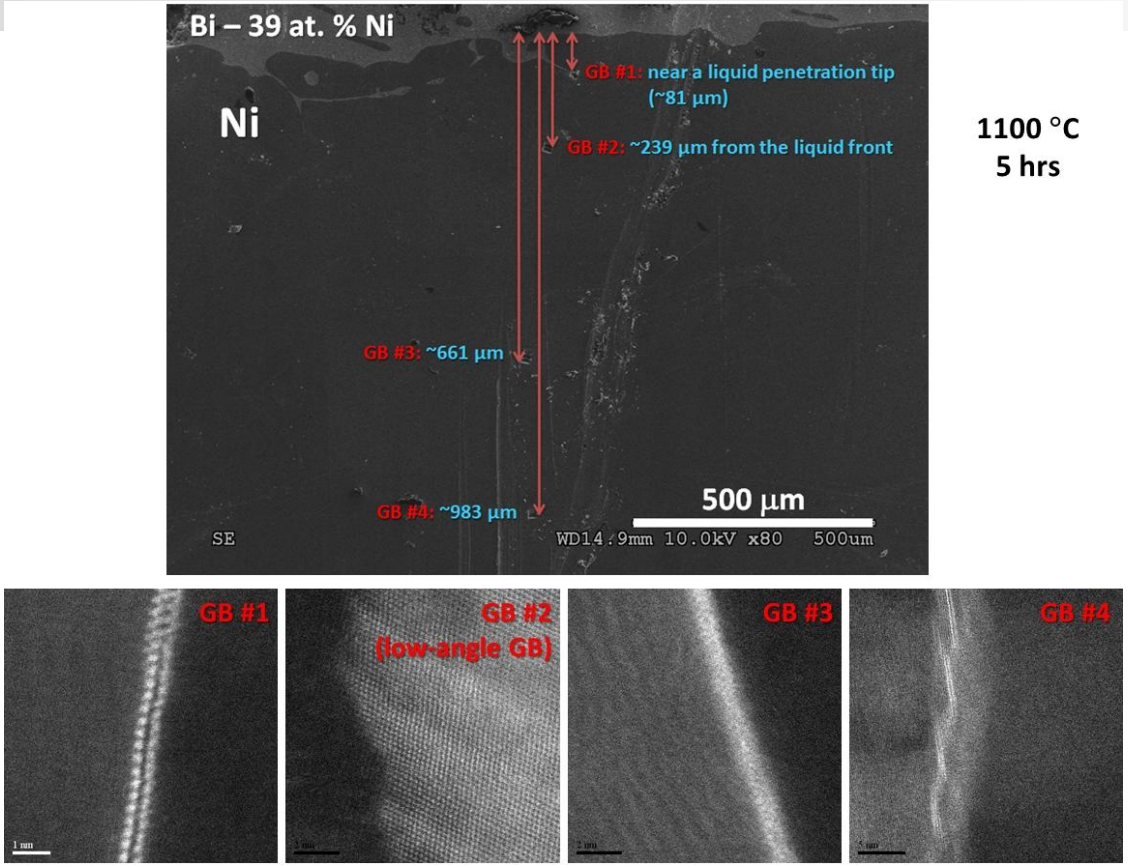


Fig. S10. a) and b) SEM micrographs of fractured surfaces indicating the precipitation of isolated small Bi particles and the occurrence of triple line wetting. c) STEM HAADF micrograph of a nanoscale Bi precipitate at a GB. d) Cross-sectional SEM micrograph showing a gap in the penetrating liquid Bi film along a Ni GB.

An Actual Example (Cross Section)…

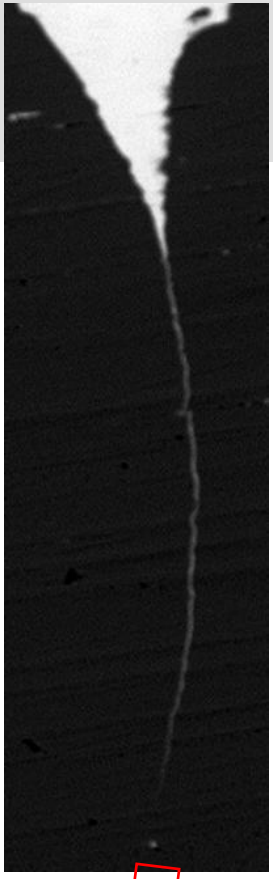
Q: Do these bilayers promote or inhibit GB diffusion?

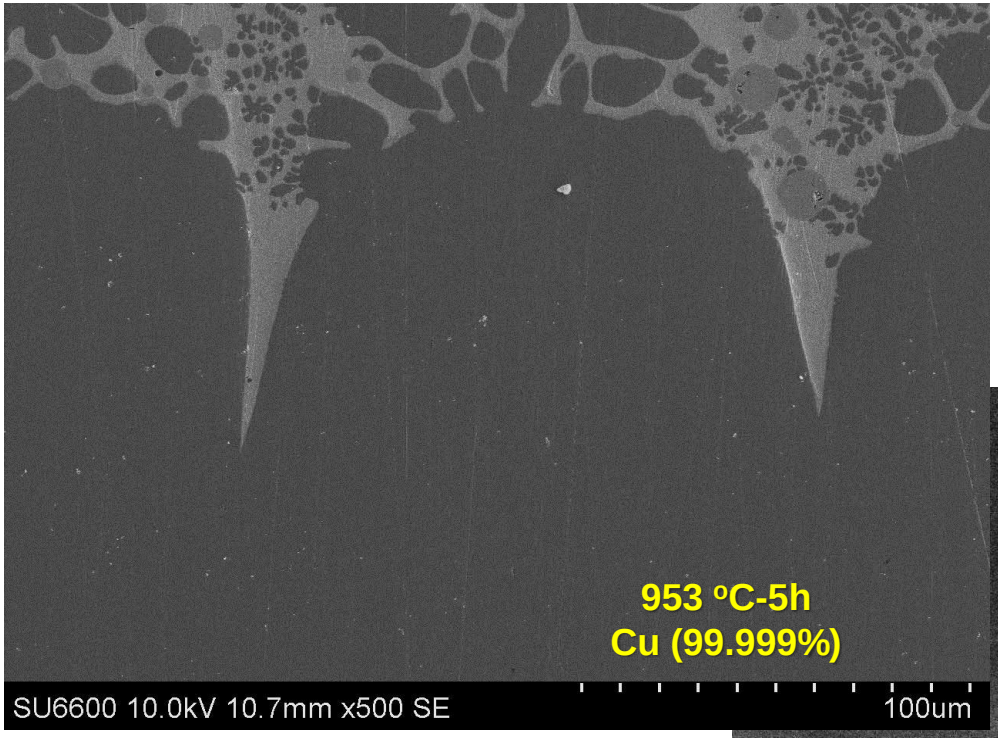


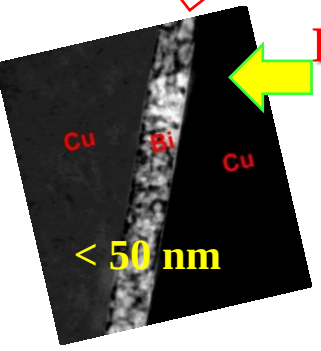
Lehigh sent specimens to UIUC to measure diffusivities of the exact GBs that were examined by HAADF-STEM…

Fig. S6. SEM micrograph of four GBs at different distances from the liquid front and the corresponding STEM HAADF micrographs of these GBs. Locations where TEM specimens were lifted using a FIB (the trenches) can be seen in the SEM micrograph, and the approximate distances to the liquid front are labeled. GB #2, which is virtually free of Bi adsorption, was found to be a low-angle GB by EBSD characterization (Fig. S7). GB #4 was faceted; yet bilayers were observed at all six (6) facets that can be clearly imaged. These observations are schematically illustrated in Fig. 3(A) in the Report.

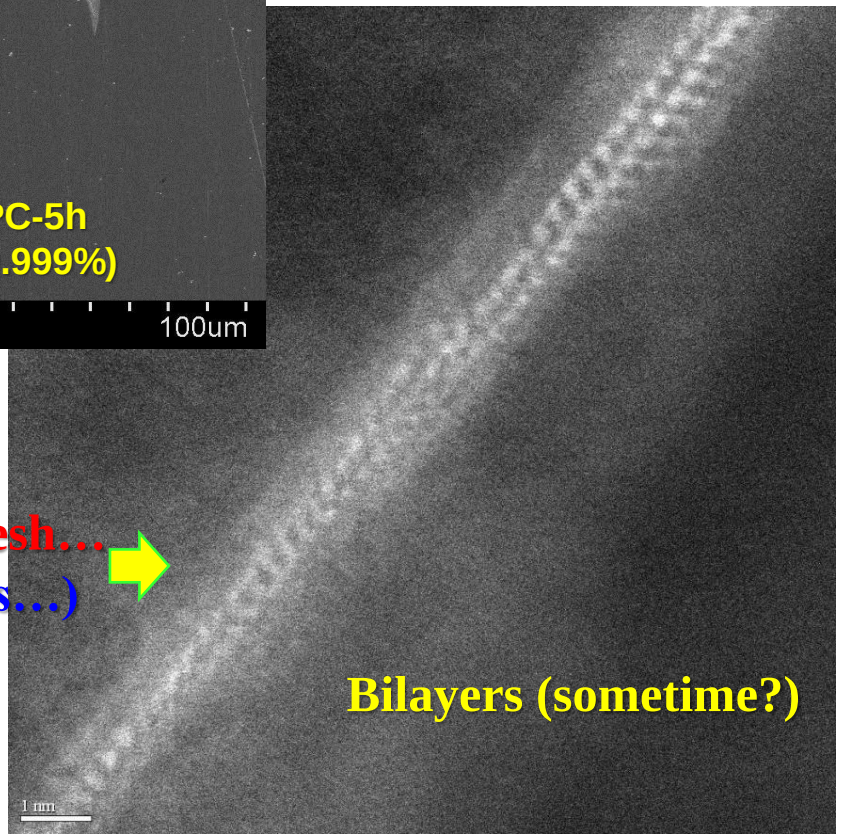
Cu-Bi







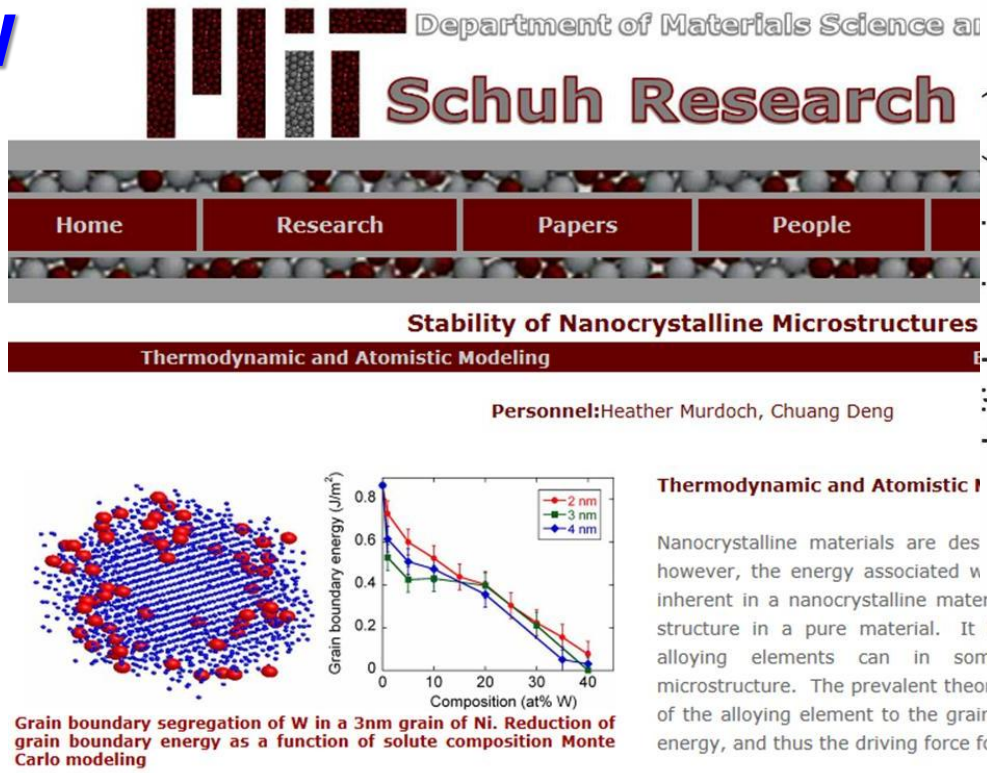
HAADF-STEM images from Animesh…
(Animesh will present more details…)

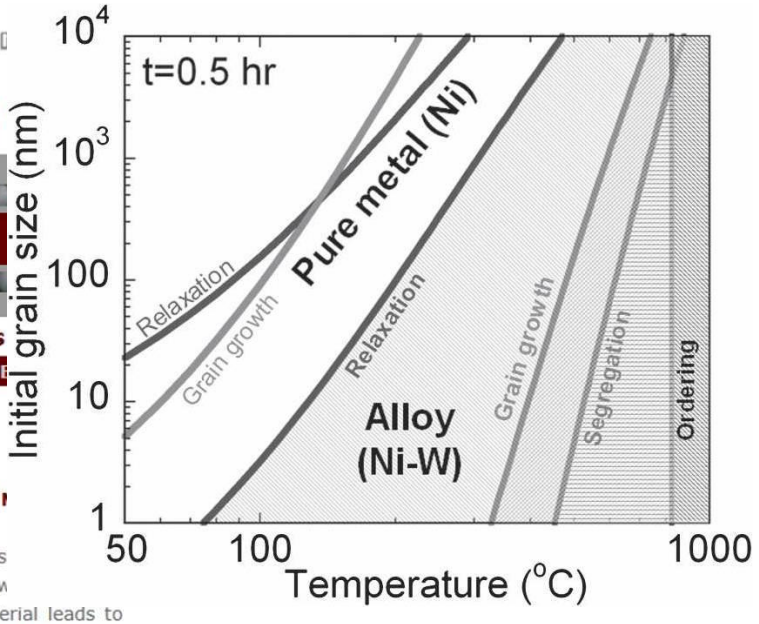


Bilayers (sometime?)

Bilayers: Promote or Inhibit Grain Growth?
Some Background & Motivations…

Ni-W



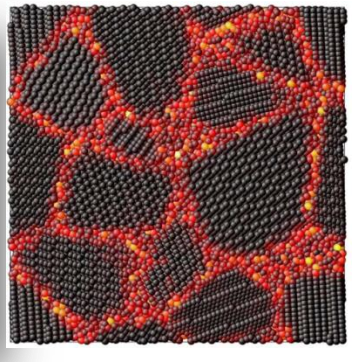


Cu-Bi

PHYSICAL REVIEW B **76**, 024111 (2007)

Stabilization of Cu nanostructures by grain boundary doping with Bi: Experiment versus molecular dynamics simulation

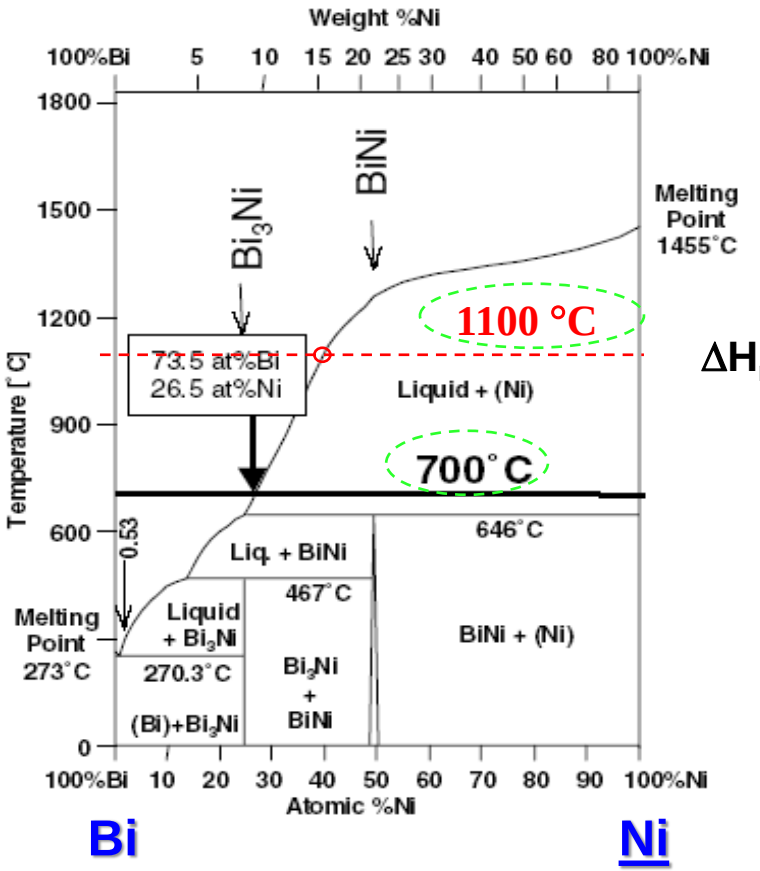
S. G. Mayr* and D. Bedorf
I. Physikalisches Institut, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany
(Received 22 October 2006; revised manuscript received 22 March 2007; published 20 July 2007)



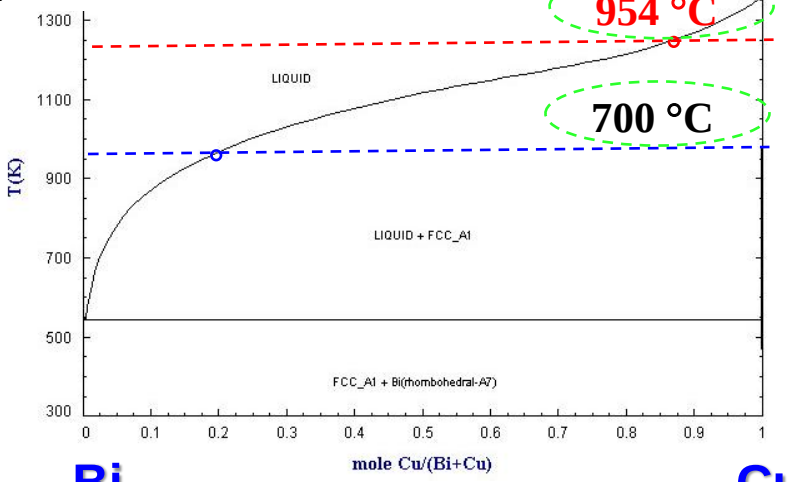
Comparison of 3 Model Systems

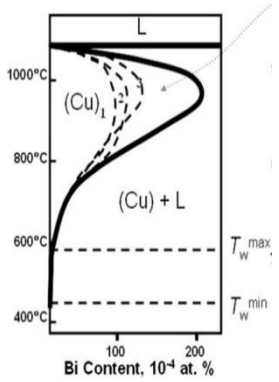
Miedema Model:

$\Delta H_{mix}^{(50\%Ni\text{-}50\%Bi)}$ = **-3.7 kJ/mol**



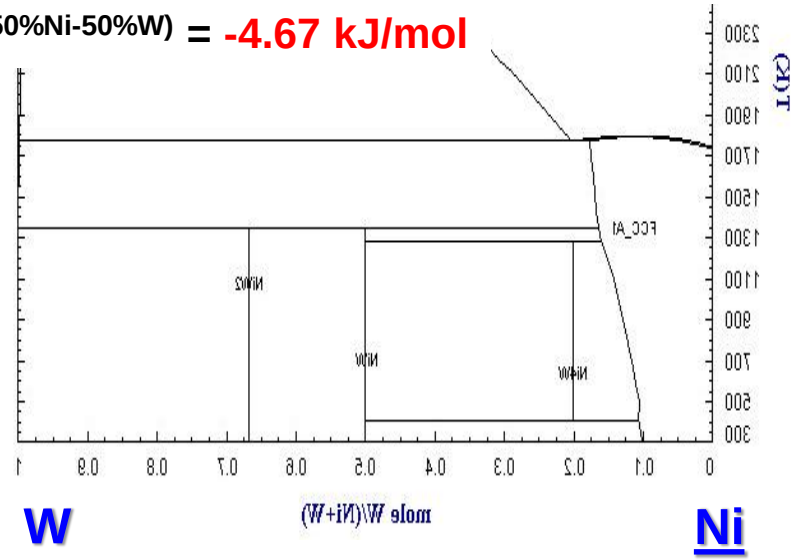
$\Delta H_{mix}^{(50\%Cu\text{-}50\%Bi)}$ = **+3.56 kJ/mol**





Straumal et al.

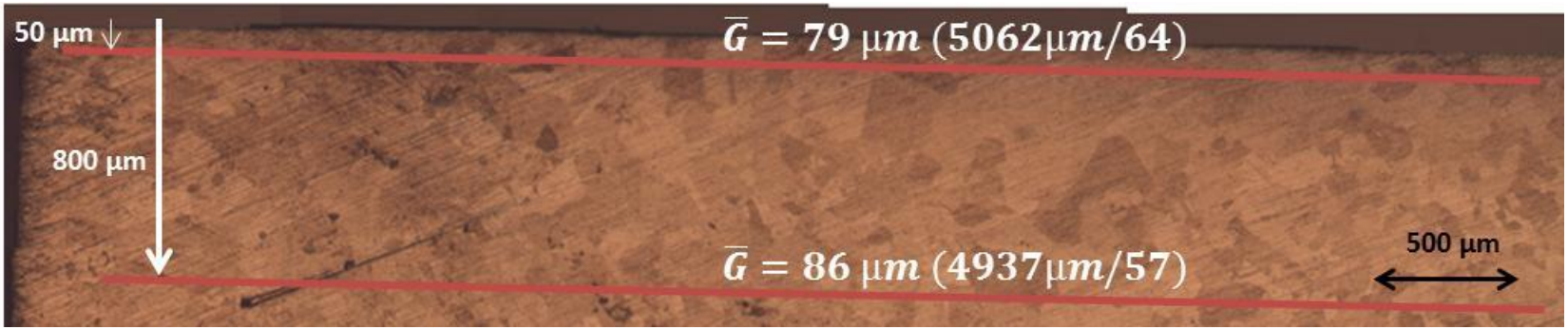
$\Delta H_{mix}^{(50\%Ni\text{-}50\%W)}$ = **-4.67 kJ/mol**



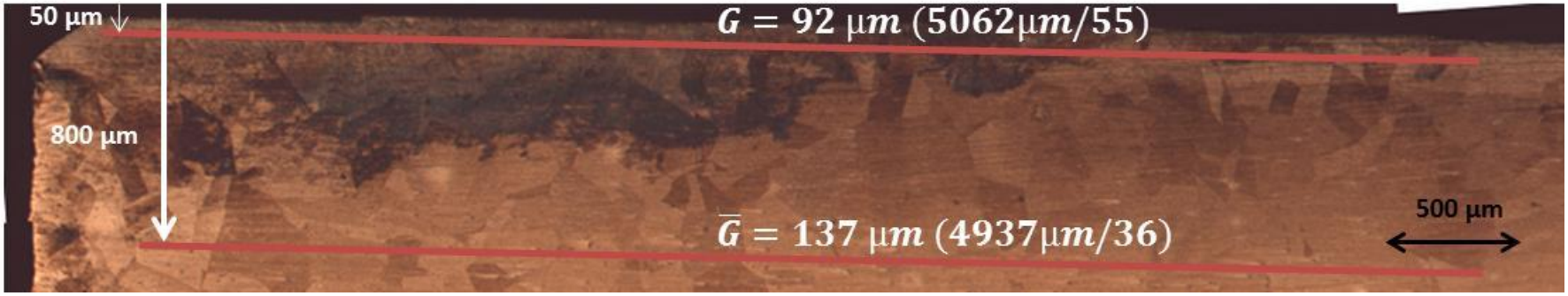
A Preliminary Study (a better experiment w/ smaller/uniform grain size?)

Grain Growth of Ni: The Effect of Bi-based Bilayers

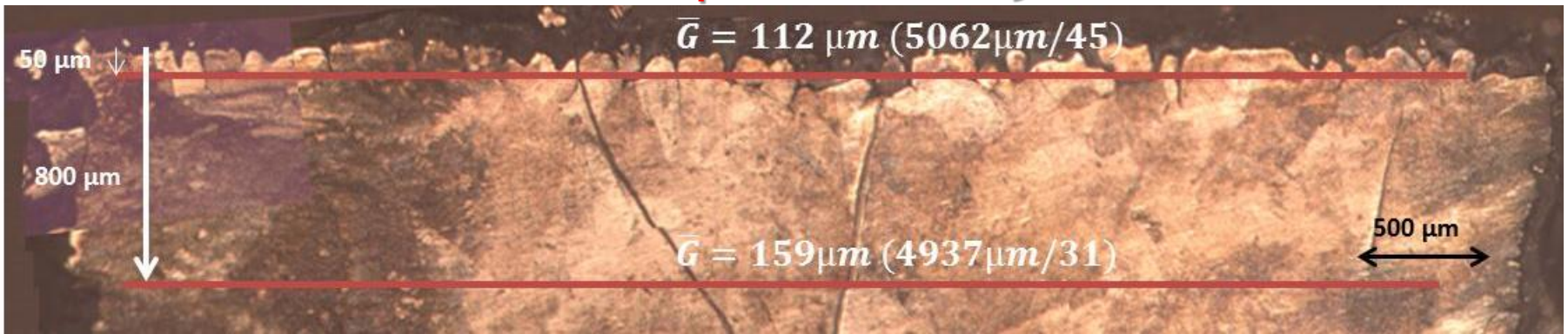
Ni foil – as-received



Ni foil annealed without Bi at 1100 °C for 5 hrs



Ni foil annealed in contact with a Bi-Ni liquid at 1100 °C for 5 hrs

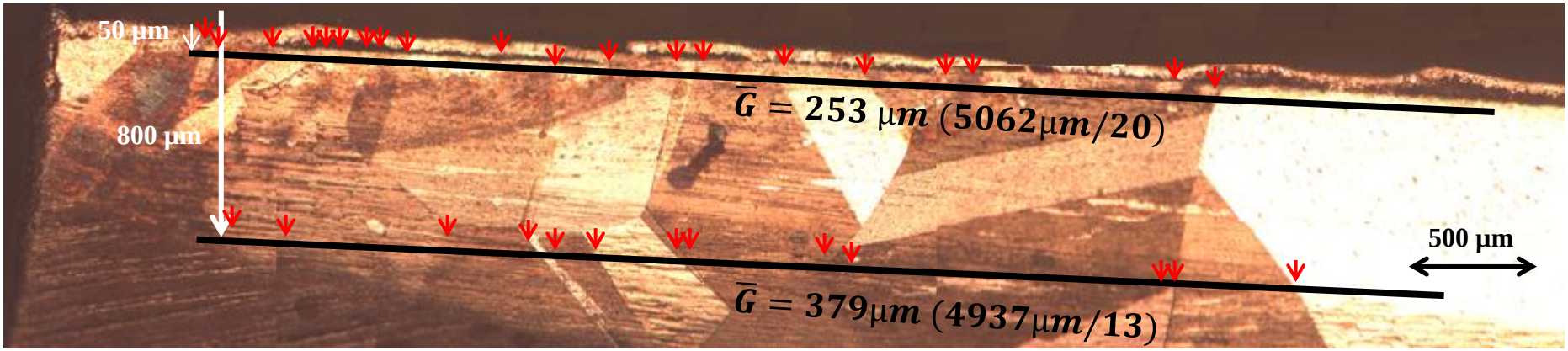


A Preliminary Study (a better experiment w/ smaller/uniform grain size?)

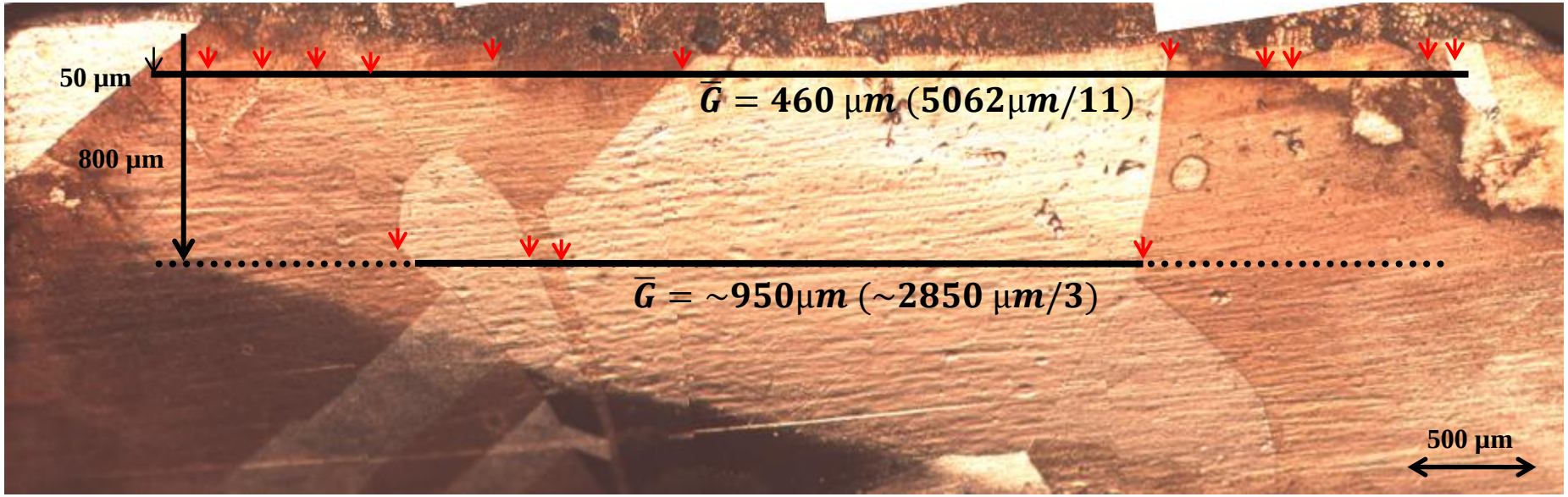
Grain Growth of Cu: The Effect of Bi

Cu foil annealed without Bi at 954 °C for 5 hrs

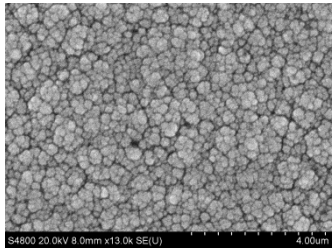
Initial Grain Size 80-100 μm (need to be checked)

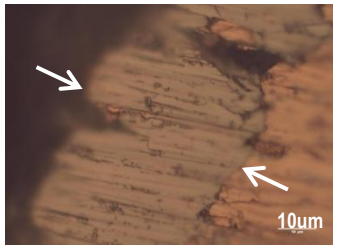


Cu foil annealed in contact with a Bi-Ni liquid at 954 °C for 5 hrs → Bi actually promotes GG?



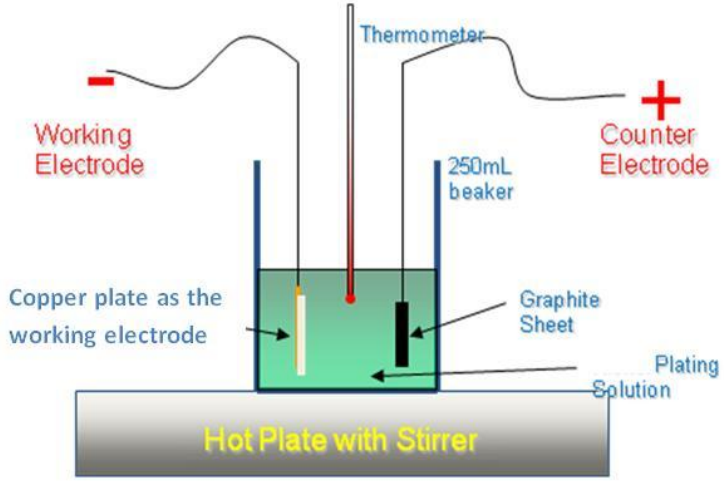
Ni-W: A Quick Screening by HAADF STEM?





Thickness : 45 μm

From the Master Thesis (May 2009) of
HanSeung Park, Clemson University



H_2O 500mL
$NiSO_4 \cdot 6H_2O$ 7.89g (0.06M)
$Na_3C_6H_5O_7 \cdot 2H_2O$ 44g (0.3M)
NaBr 7.725g (0.15M)
$Na_2WO_4 \cdot 2H_2O$ 23.25g (0.14M)
NH_4Cl 13.25g (0.5M)

	at.% W	FWHM	2-theta	XRD Grain Size
Pure Ni film	0%	1.1138	44.68	7.7nm
0.07M $Na_2WO_4 \cdot 2H_2O$	15.6%	2.2640	43.70	3.7nm
0.14M $Na_2WO_4 \cdot 2H_2O$	22.47%	3.3043	44.36	2.5nm
0.21M $Na_2WO_4 \cdot 2H_2O$	20.3%	3.3820	44.00	2.5nm

	FWHM	2-theta	XRD Grain Size
As-deposited	3.3043	44.36	2.5nm
400 °C annealing	1.4329	43.76	5.9nm
600 °C annealing	0.4330	43.62	19.7nm

A bit thinking on thermodynamic models of bilayers in Ni-Bi (and Cu-Bi?)

"Wetting & Adsorption"

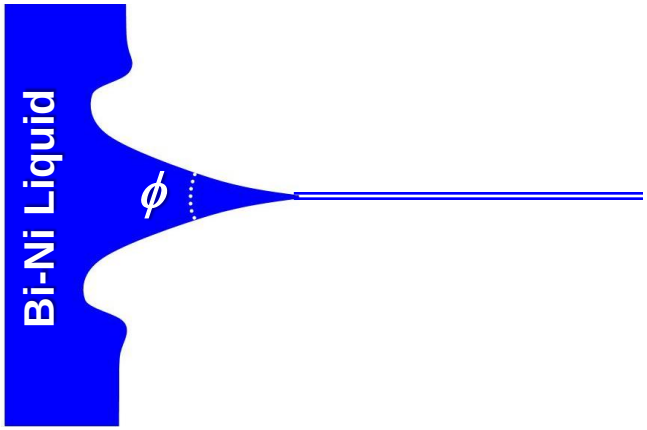
Miedema-type models

Average general Ni ("clean") $\gamma_{GB}^{(Ni,0)} \approx \frac{1}{3}\cdot\gamma_{Ni}^{surface} = \frac{1}{3}\cdot\frac{H_{Ni}^{vap}}{C_0 V_{Ni}^{2/3}} = 0.82 J/m^2$

Experimental: 0.92 J/m² (700 °C, 99.999 wt. % Ni)

Interfacial energy (Ni & Bi-Ni liquid) $\gamma_{SL} \approx \underbrace{\frac{H_{\mathrm{Ni}}^{\mathrm{fuse}}}{C_0 V_{Ni}^{2/3}}}_{\text{(Enthalpic)}} + \underbrace{\frac{\Delta H_{Ni\,in\,Bi}^{\mathrm{interface}}(F_{Bi}^{Ni})^2}{C_0 V_{Ni}^{2/3}}}_{\text{(Interaction)}} + \underbrace{\frac{1.9RT}{C_0 V_{Ni/Bi}^{2/3}}}_{\text{(Entropic)}} = 0.12 J/m^2$ **(700 °C)**

$\gamma_{GB}^{(Ni,0)} > 2\cdot\gamma_{SL}$ **But NOT complete wetting because** $\gamma_{GB}^{(Ni-Bi,eq.)} < \gamma_{GB}^{(Ni,0)} = 0.82 J/m^2$



Measured average dihedral angle 44.7° (at 700 °C)

Decrease due to bilayer adsorption of Bi

$$\gamma_{GB}^{(Ni-Bi,eq.)} = 2\cdot\gamma_{SL}\cdot\cos\left(\frac{\phi}{2}\right) \approx 0.22 J/m^2$$

To estimate adsorption energy to compare with models?

$$\gamma_{GB}^{(Ni-Bi,eq.)} \approx \gamma_{GB}^{(Ni,0)} - \Gamma_{X\to 0}(H_{ads} + kT\ln X)$$

Why Bilayer?

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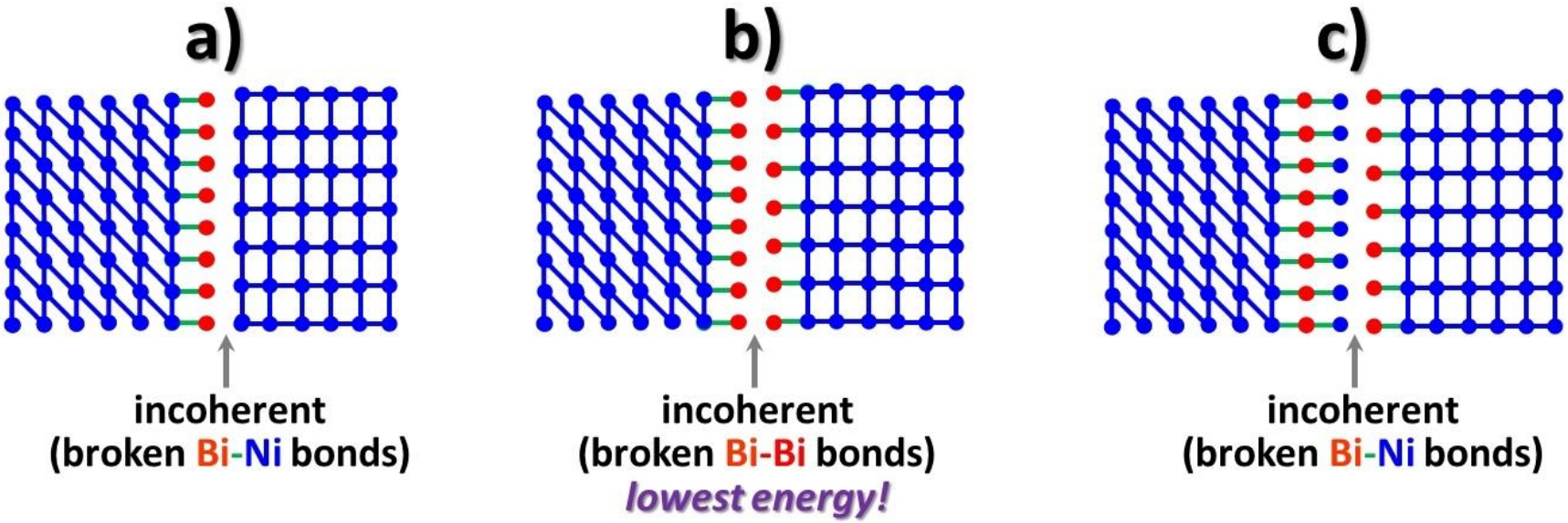
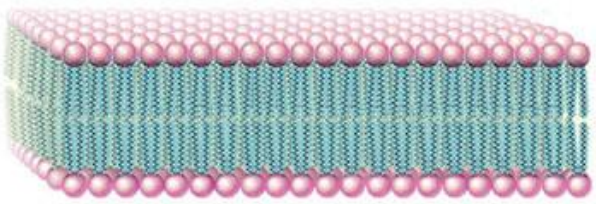
The Miedema Model: Formation enthalpy for a $Bi_{0.5}Ni_{0.5}$ alloy = -3.7 kJ/mol

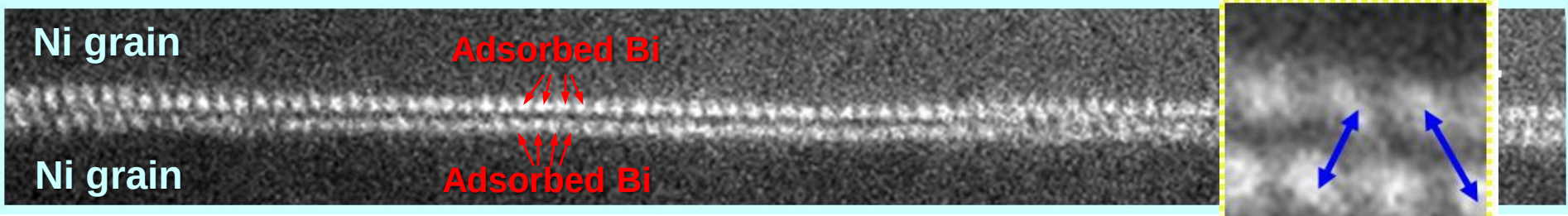
Strong Ni-Bi: $\frac{1}{2}|E_{Ni\text{-}Ni}| + \frac{1}{2}|E_{Bi\text{-}Bi}| < |E_{Ni\text{-}Bi}|$

Weak Bi-Bi: $|E_{Bi\text{-}Bi}| << |E_{Ni\text{-}Ni}|$

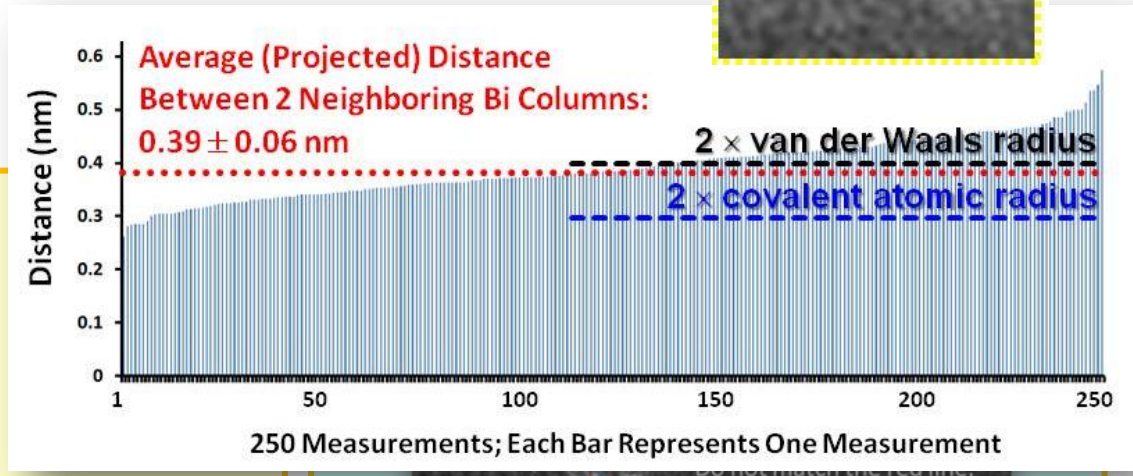


"High-Temperature Lipids"?

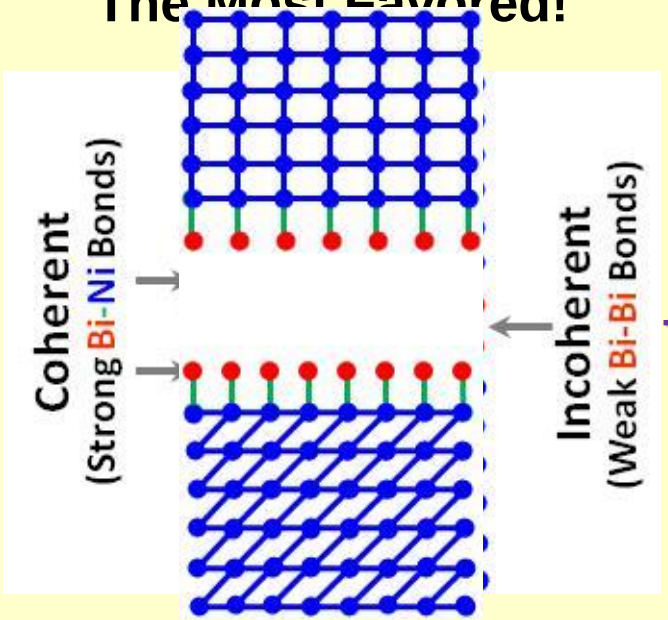




Bilayer Formation → Embrittlement



Energetically The Most Favored!

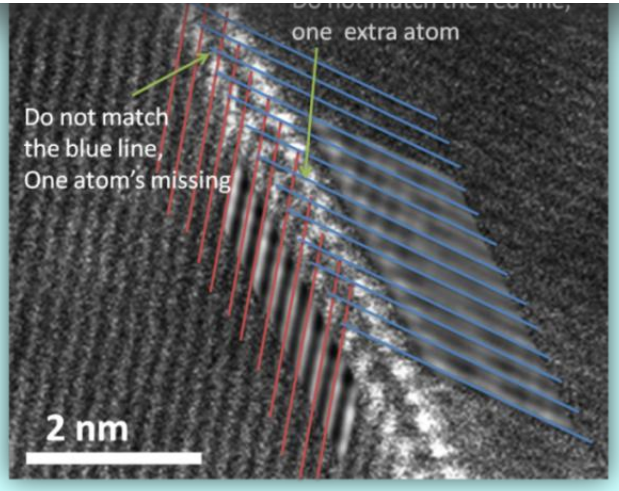


The Miedema Model:

$\Omega_{Ni\text{-}Bi}$ = -3.7 kJ/mol

Strong Ni-Bi: $\frac{1}{2}|E_{Ni\text{-}Ni}| + \frac{1}{2}|E_{Bi\text{-}Bi}| < |E_{Ni\text{-}Bi}|$

Weak Bi-Bi: $|E_{Bi\text{-}Bi}| << |E_{Ni\text{-}Ni}|$



- Each Bi layer **coherently** adsorbed on the adjacent Ni grain
- **Incoherent** between the 2 Bi layers

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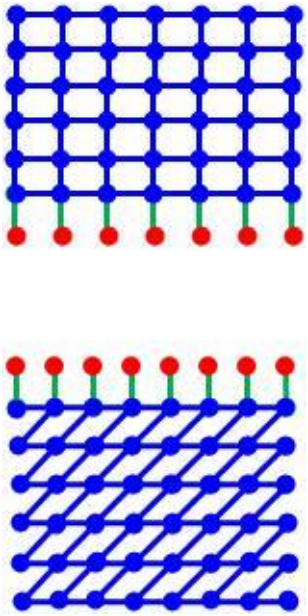
An Alternative Way to Better Quantify…



Surface monolayer adsorption because

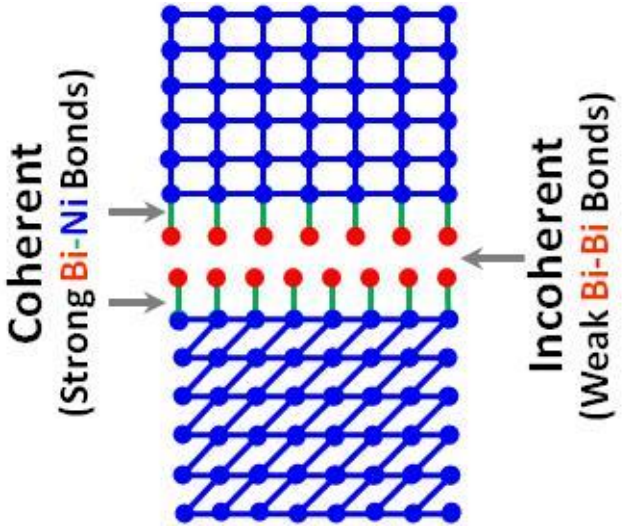
1) $\gamma_{Bi}^{surf} << \gamma_{Ni}^{surf}$
2) $\frac{1}{2}|E_{Ni\text{-}Ni}| + \frac{1}{2}|E_{Bi\text{-}Bi}| < |E_{Ni\text{-}Bi}|$

Bi are "surfactants"…

γ_s(Bi-mono)

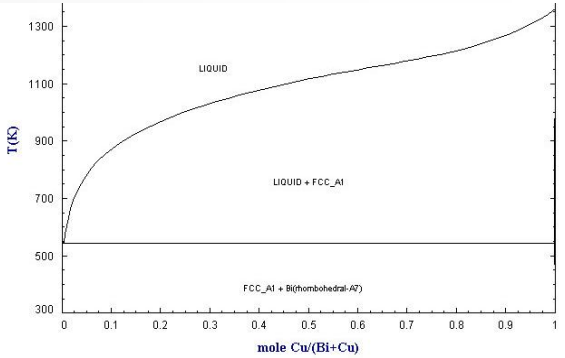
γ_s(Bi-mono)

$-\Delta\gamma_{decohesion}$



$$\gamma_{gb}^{(eq)} = 2\gamma_S^{(Bi-mono)} - \Delta\gamma_{decohesion}$$

How about Cu-Bi?



1) γ_{Bi}^{surf} (0.49 J/m^2) << γ_{Cu}^{surf} (1.83 J/m^2) √

2) ½|$E_{Cu\text{-}Cu}$| + ½|$E_{Bi\text{-}Bi}$| > |$E_{Cu\text{-}Bi}$| ×

$\Delta H_{mix}^{(50\%Cu\text{-}50\%Bi)}$ = +3.56 kJ/mol

Yet, Bi are known to be "surfactants" on Cu surfaces…

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Bi surfactant effects of Co/Cu multilayered films prepared by sputter deposition

Masao Kamiko*, Atsuhito Nakamura, Kazuaki Aotani, Ryoichi Yamamoto

Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan

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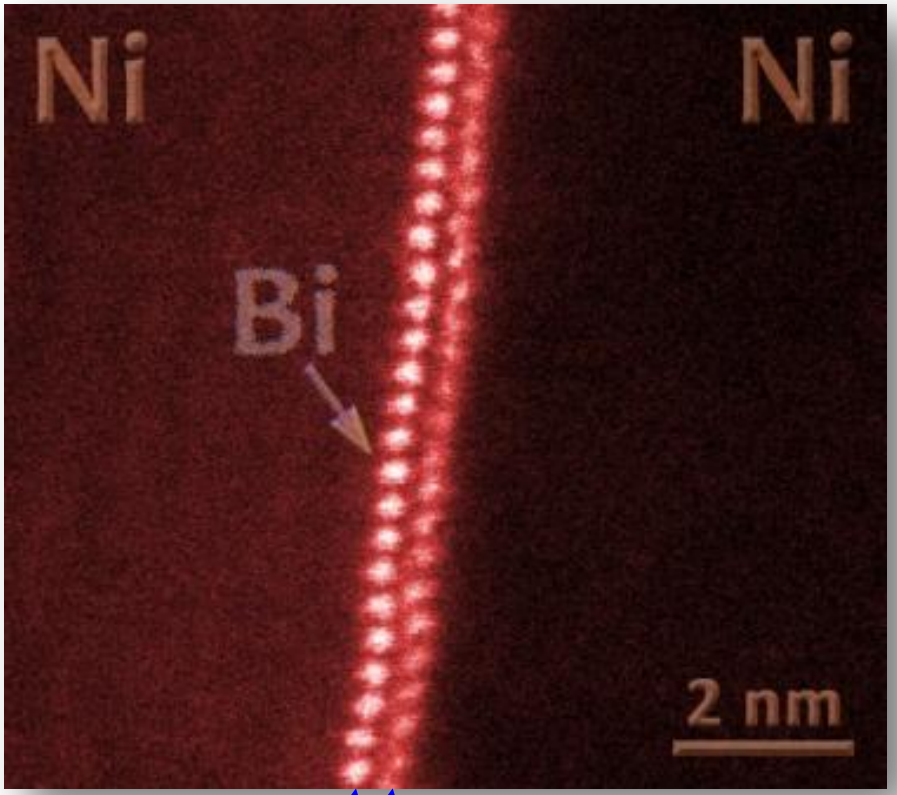
ABSTRACT

The influence of a Bi surfactant layer on the structural and magnetic properties of Co/Cu multilayers grown onto Cu(1 1 0) buffer layer by RF magnetron sputtering has been studied. The results of X-ray diffraction revealed the initial deposition of a 2.0 Å-thick Bi layer onto the Cu buffer layer prior to the deposition of the Co/Cu multilayer yielded high-quality fcc-(1 1 0) oriented epitaxial films. The X-ray photoelectron spectra revealed that Bi was segregated at around the top of the surface. Therefore, Bi was concluded to be an effective surfactant to enhance the epitaxial growth of Co/Cu(1 1 0) multilayer. The maximum giant magnetoresistance and antiferromagnetic interlayer coupling ratios of the Co/Cu multilayers were increased by using the Bi surfactant layer.

The Stability of Bilayers



Why different intensities (sometimes)?
..because the two grain surfaces of a "general GB" have different "densities" of adsorption sites…

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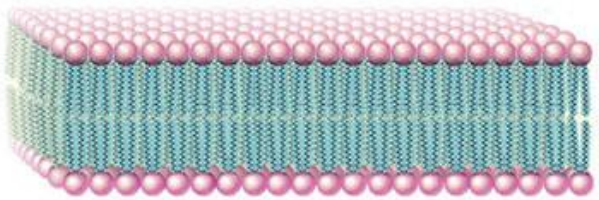
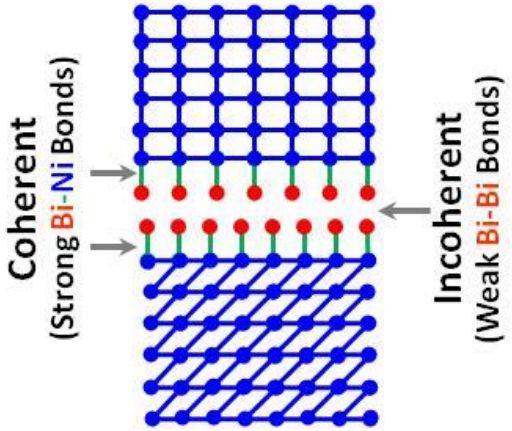
"High-Temperature Lipids"?





Strong Ni-Bi
Weak Bi-Bi

Shall we measure GB adsorption amount and correlate it with GB character?

Update on YSZ work
…Discussion of future directions

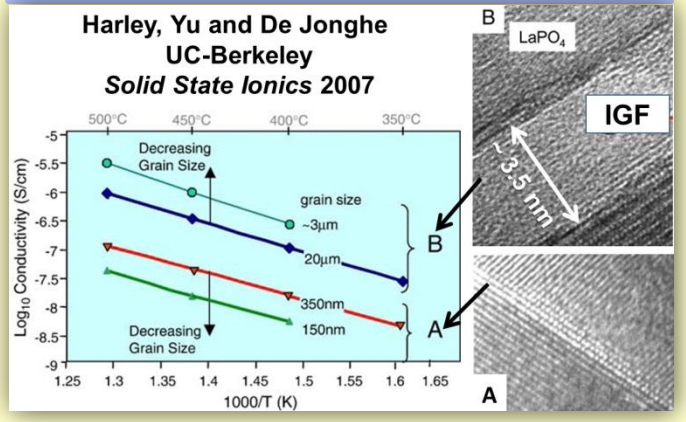
Roles of Complexions in Ionic Conduction?

Experimental Task II:
Roles of Complexions in Ionic Conduction

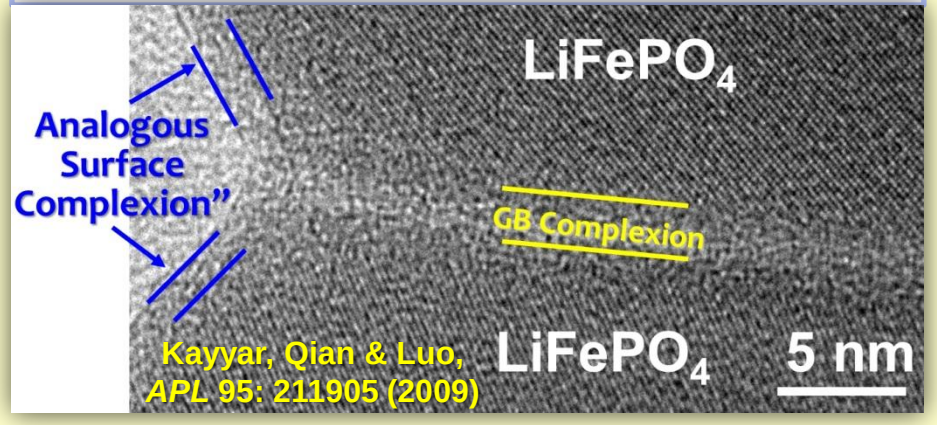
Background & Motivations

- Ionic conductors -- important for energy storage & generation.
- In ZrO_2-Y_2O_3-(SiO_2), certain GB complexions → severe "**blocking effects**" to ionic conduction
  - Practically, co-doping → alleviate the problem (selected empirically)
- Other GB complexion → enhance ion conductivity

Enhanced Proton Conduction



Lithium Ion Battery Cathodes???



Planned Research: Primary Model System: ZrO_2-Y_2O_3-(SiO_2)-M_xO_y

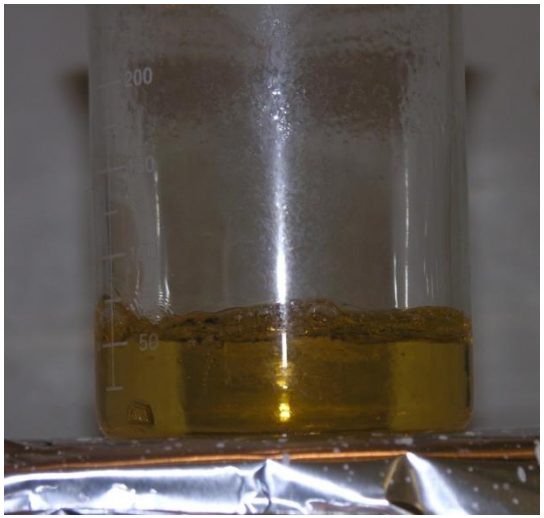
- Synthesis, high-*T* impedance, HRTEM/STEM (Lehigh) → To understand the complexion formation & roles in ionic conduction…
- To develop & experimentally validate physics-based predictive models

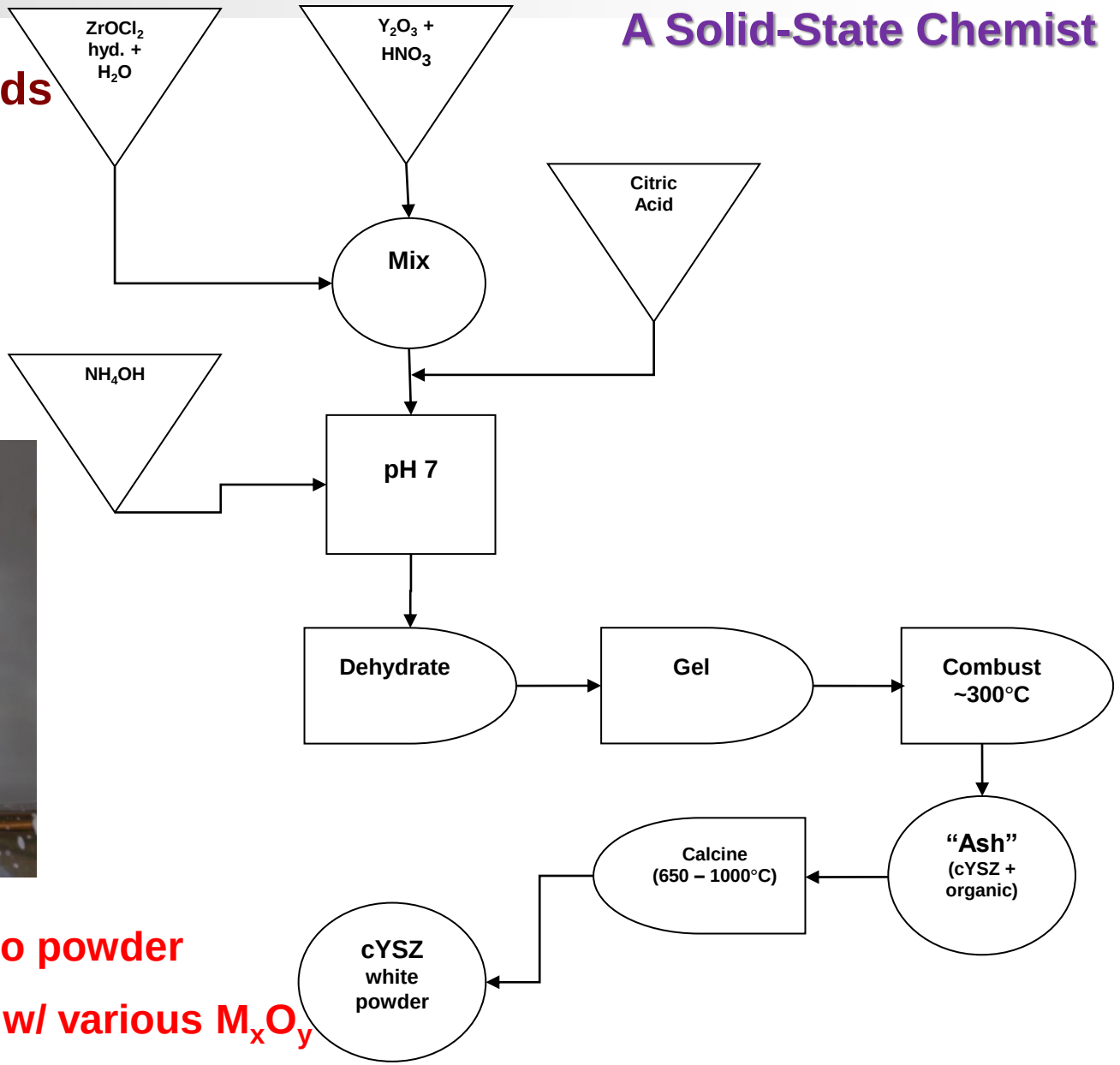
Synthesis

Work of
Dr. Matthew Williams
A Solid-State Chemist

Three synthetic methods examined

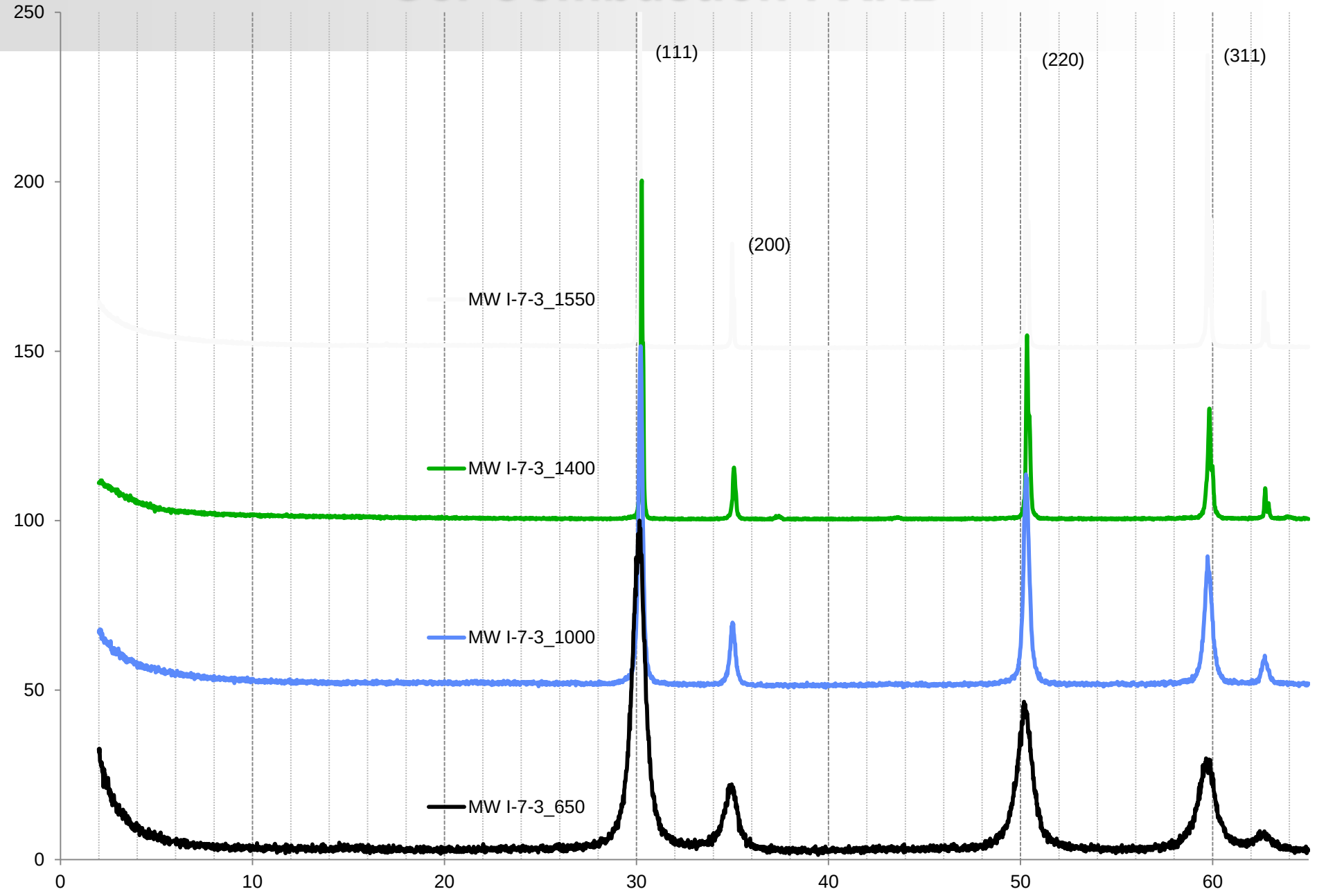
- Shake-n-bake
- Co-precipitation
- Gel-combustion √



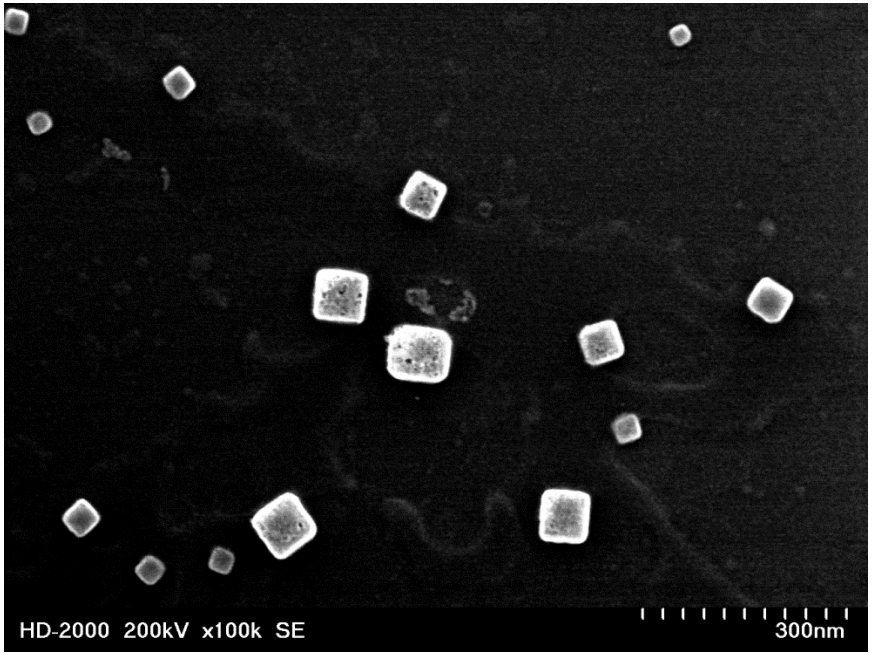


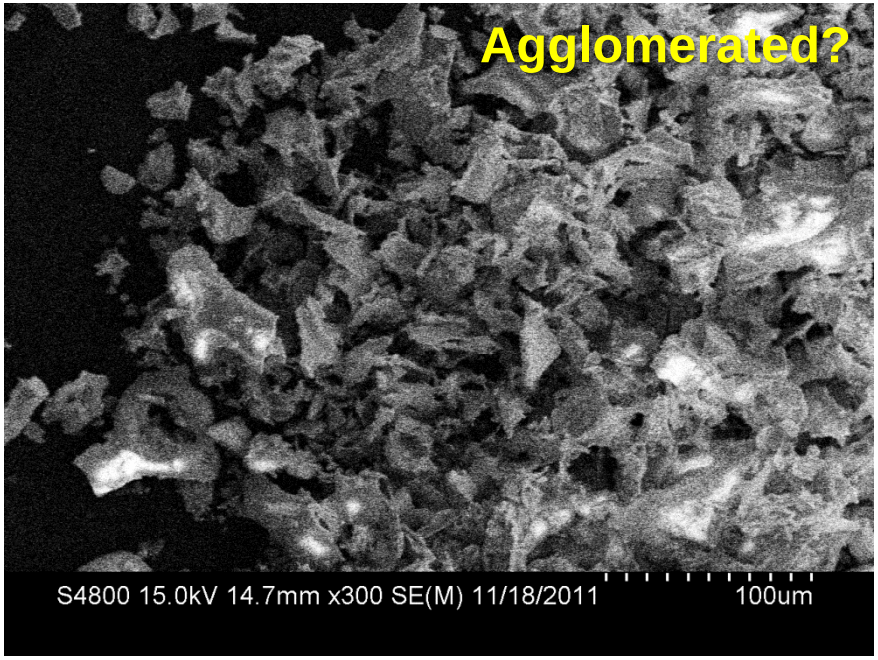
- Phase-pure YSZ nano powder
- Allow us to co-dope w/ various M_xO_y

Gel-Combustion PXRD

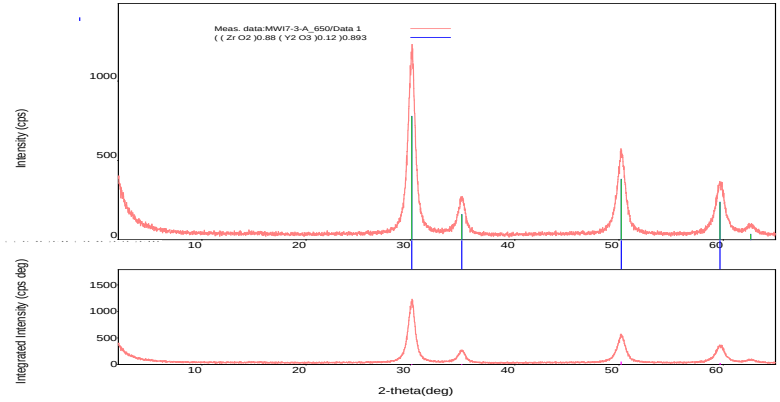


Gel-Combustion Powder (YSZ)





MW I-33-11S_650: powder calcined @ 650°C followed by sonication in EtOH



Avg. crystallite size (XRD): ~10 nm

Initial Pressureless Sintering Experiments Densification

Densities (g/cm^3) determined by either dimensional (D) analysis or Archimedes' (A) method

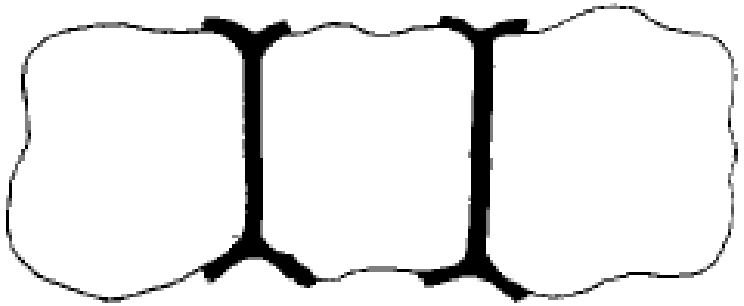
- MW I-5-3_1000 (D) – 2.486 (41.7%)
- MW I-7-3_1400 (A) – 4.63 (77.7%)
- MW I-24-9-1_1550 (A) – 4.959 (83.2%)
- MW I-24-9-2_1000_1550 (A) – 4.851 (81.4%)
- MW I-29-10_1550_1300 (D) – 5.24 (87.9%)
- MW I-29-10_1550 (D) – 5.094 (85.5%)
- MW I-29-10_PVA_1550_1300 (D) – 5.35 (89.8%)
- MW I-29-10_PVA_1550 (D) – 5.39 (90.5%)

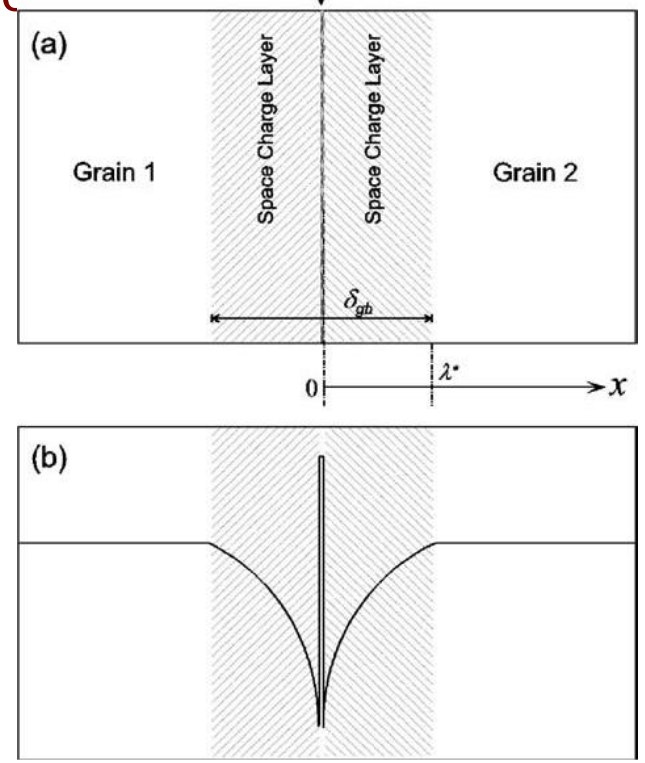
Next steps:

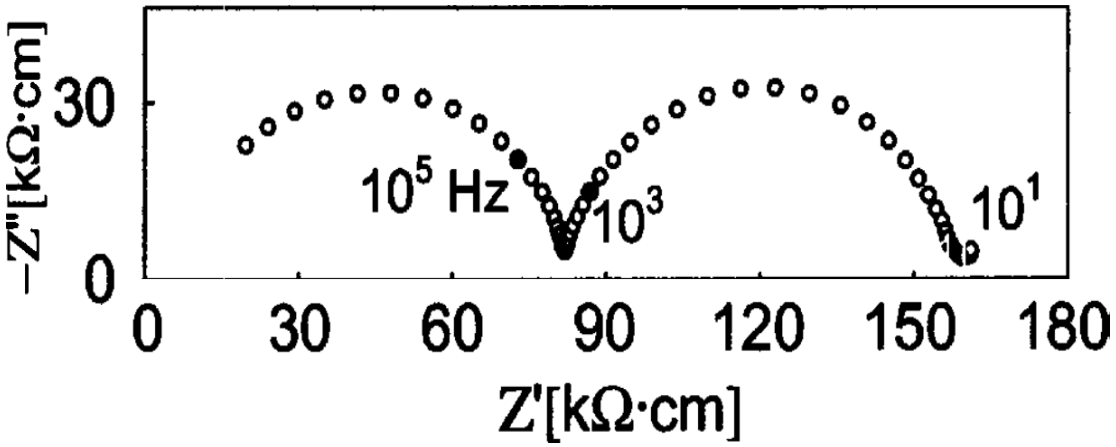
- **Continue to optimize the pressureless sintering recipes, and/or**
  - **Send some powder to Lehigh for SPS?**
  - **"Flash sintering"? (see discussion in a later slide)**
- **Systematically measure high-T impendence for specimens w/ different controlled doping**
- **Send selected specimens to Lehigh for STEM**
- **Goal – the systematic data that correlate doping (various M_xO_y to YSZ) – impedance – complexion structure – other properties for developing/validating models**
  - **Models focusing on interaction b/ complexions & space charges (a step forward compared w/ metals) – "interfacial doping" to control ionic conductivity**

Electrical Impedance Measurements – Set up

Standard measurements are run across a range of frequencies as a function of temperature and/or composition



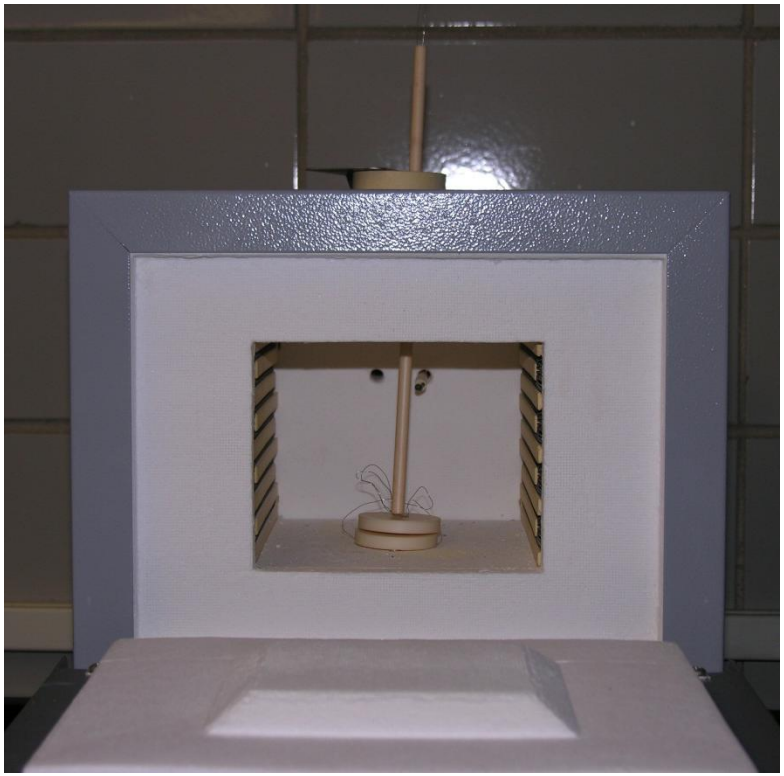




4. Jung, Y.-S., Lee, J.-H., Lee, J.-H., Kim, D.-Y., *J. Electrochem. Soc.* 150 (2003) J49 – J53.

Preliminary Impedance Testing Set

Utilizing Gamry Potentiostatic for Electrical Impedance Spectroscopy (EIS), we designed a high temperature impedance testing set for preliminary measurements…



We will also set up a more sophisticated tube furnace system (which will allow control of atmosphere and have better impedance range) at a later time…

Other Future Directions/Tasks To Be Concisdered…

- **"Flash sintering" of various doped YSZ (M_xO_y) – following Raj *et al.* – The roles of surface/grain boundary complexions?**

and/or (perhaps more interestingly…)

- **The effects of electrical field on grain growth – following NCSU (Conrad *et al.*) who propose that an applied electrical field can interact with space-charges and reduce GB energy to stabilize nano grain size**
  - **The roles of surface/grain boundary complexions are certainly important**
  - **Coherent theme with the metal size (if we decide to work on stabilizing nano grain size in Ni via complexions)**

- **We selected YSZ because this is perhaps one of the most well-characterized model systems**
  - **Include/expand to other "new" (less-studied, but more interesting) ionic materials?**