AGENDA

8:15-8:30	Self introductions
8:30-8:45	David Shifler, Introductory remarks
8:45-9:30	Martin Harmer, Overview of MURI project
9:30-11:45	Presentations by individual MURI team members plus guest scientist, Alexis Lewis.
Note: Anthony Rollett from Carnegie Mellon University will be in Europe, but will participate remotely.	
9:30-9:45	Andrea Harmer, Kutztown University
9:45-10:00	Helen Chan, Lehigh University
10:00-10:15	Jeffrey Rickman, Lehigh University
10:15-10:30	Michael Widom, Carnegie Mellon University
10:30-10:45	Break
10:45-11:00	Jian Luo, Clemson University
11:00-11:15	Greg Rohrer, Carnegie Mellon University
11:15-11:30	Shen Dillon, University of Illinois
11:30-11:45	Alexis Lewis, Naval Research Laboratory
12:00-1:00	Lunch and discussion, Tower Room, Mountaintop Campus
1:00-1:45	Alan Pense, * Tour of ATLSS national earthquake testing laboratory and composite ship building laboratory, Mountaintop Campus.
1:45-2:15	Private meeting for review team -ATLSS Conference Room B144
2:15-2:30	Feedback and discussion
2:45-3:00	Demonstration of Spark Plasma Sintering, 3rd floor Whitaker Lab
3:00-3:30	Tour of Electron Microscopy Laboratory, 1st floor Whitaker Lab
3:30	Depart

Office of Naval Research Multidisciplinary University Research Initiative Project
Kickoff Meeting, Thursday June 23rd 2011
ONR Topic Chief: David Shifler

Tailoring of Atomic-Scale Interphase Complexions for Mechanism-Informed Material Design

Martin P. Harmer

Outline

- Participants in MURI Program
- Introduction to Interphase Complexions (IC's) Concept
    - Examples of IC's in Ceramic and Metal Systems
- Objectives and Goals of the MURI Program
    - Thrust 1: Creation of New Classes of Materials with Tailored Properties
    - Thrust 2: Exploitation of Complexions in the Processing of Bulk Nano-grain Materials
    - Thrust 3: Exploitation of Complexions in Controlling Properties in Strategic Engineering Materials
- Management/Future Meetings
- Recruitment
- MURI-Related Affiliations

Participating Institutions

Lehigh University

Martin P. Harmer (PI), Helen M. Chan, Jeffrey M. Rickman, Ed Webb

Carnegie Mellon University

Gregory S. Rohrer, Anthony D. Rollett, Michael Widom

Clemson University

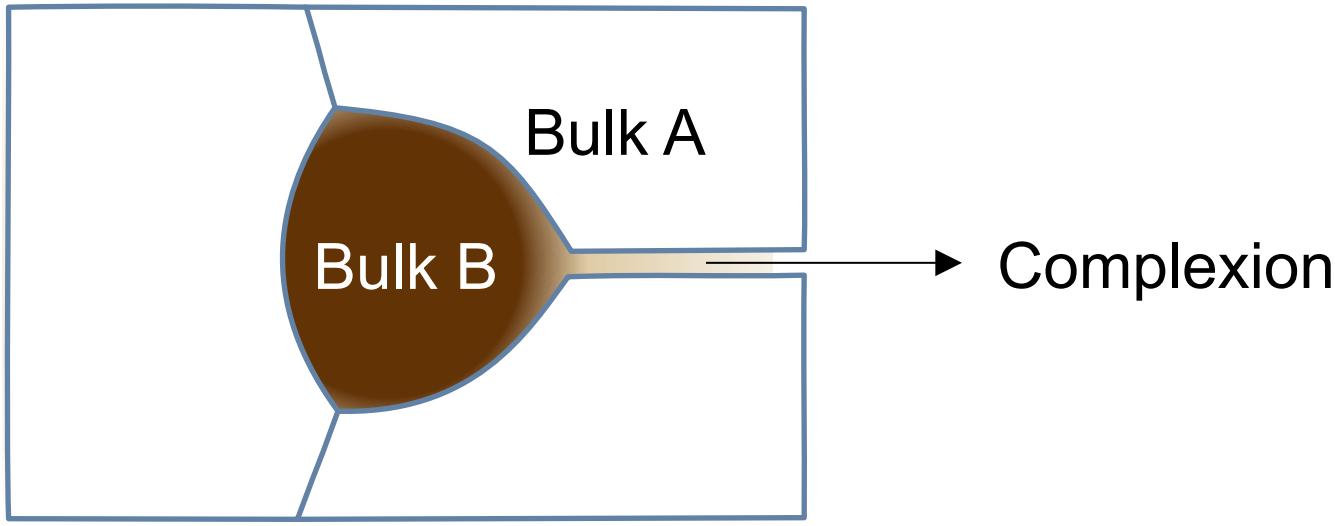
Jian Luo

University of Illinois Urbana-Champaign

Shen J. Dillon

Kutztown University of Pennsylvania

Andrea J. Harmer



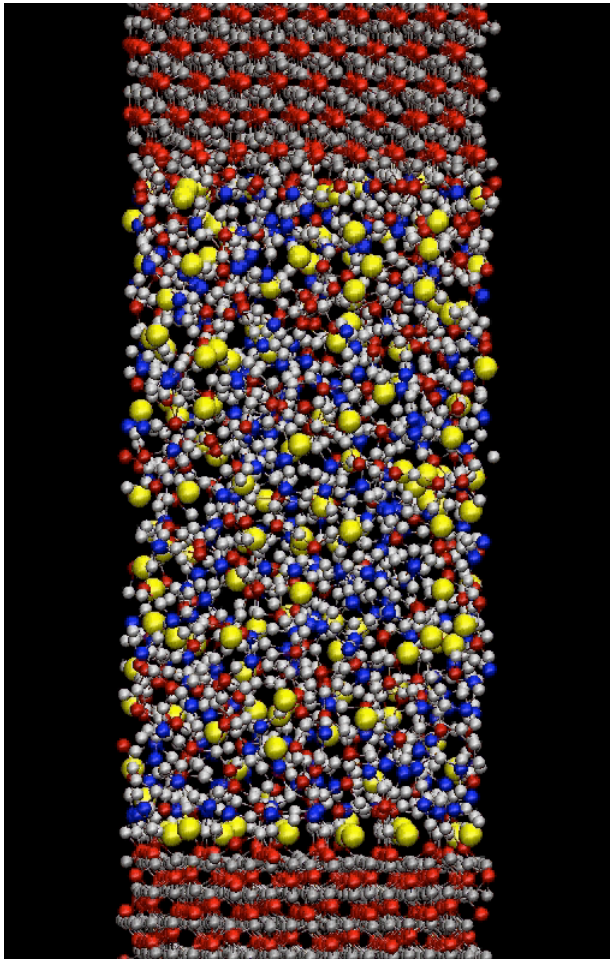
Complexion

com·plex·ion ***noun*** **\kəm-ˈplek-shən**

Atomic scale (0.2 – 2 nm) thermodynamically stable interface-stabilized phase (interphase) that does not exist in bulk form.

"The Phase Behavior of Interfaces", Science, 332 [6026] 182-183 (8 April 2011).

Complexions: Characteristics



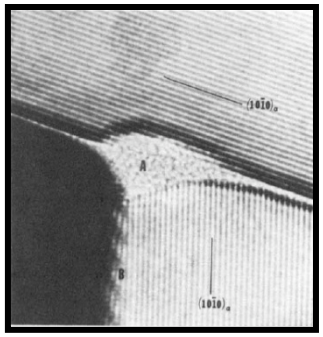
Courtesy of Steve Garofalini

- Complexions are transformable like phases (crystallography, chemistry, temperature important).
- Characteristic thickness with varying degree of disorder (6 distinct layering transitions) – new taxonomy.
- Superimposable onto bulk phase diagrams – Complexion Diagrams.
- Different complexions have vastly different kinetics and probably physical properties.

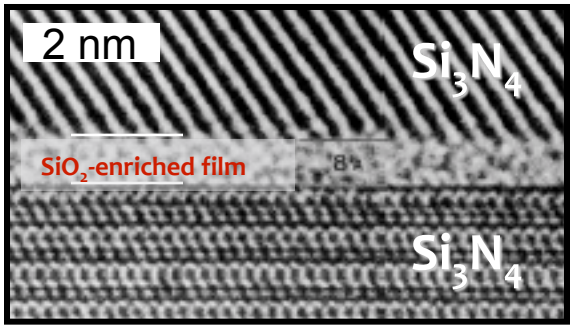
"Interfacial Kinetic Engineering: How Far Have We Come Since Kingery's Inaugural Sosman Address?", J. Am. Ceram. Soc., 93 [2] 301–317 (2010)

Example - Intergranular Films (IGF)

Ceramic Grain Boundaries (GBs)



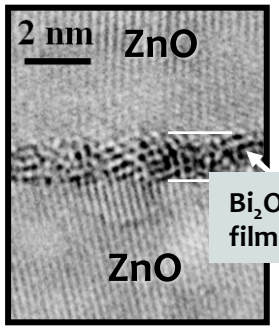
Equilibrium thickness
D. Clarke,
J. Am. Ceram. Soc. 1977



Kleebe et al, *J. Am. Cer. Soc.* 1993

Widespread Existence of Similar IGFs:

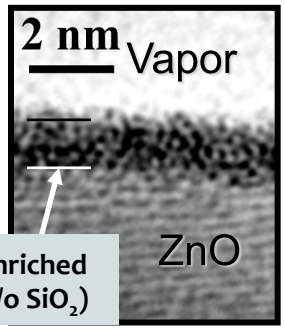
SiC,
AlN,
SIALON,
Al_2O_3,
(Sr, Ba)TiO_3,
ruthenate thick film resistors,
TiO_2, ZrO_2, YBCO,
Synroc, etc.
(all with additives)



$T < T_{eutectic}$

No SiO_2, (Wang & Chiang, *J. Am. Cer. Soc.* 1998)

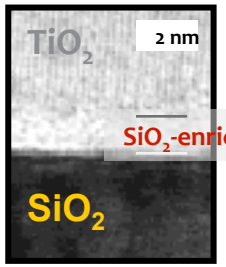
Free Surfaces



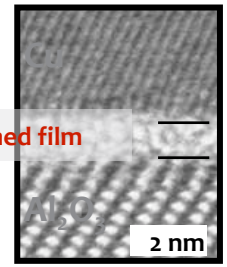
$T < T_{eutectic}$

(Luo & Chiang,
Annu. Rev. Mater. Res. 2008)

Hetero-Interfaces

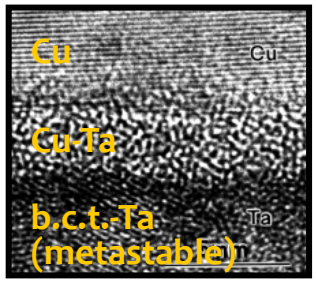


Oxide-Oxide Hetero-Interface
(Ackler & Chiang, *J. Am. Cer. Soc.* 1997)

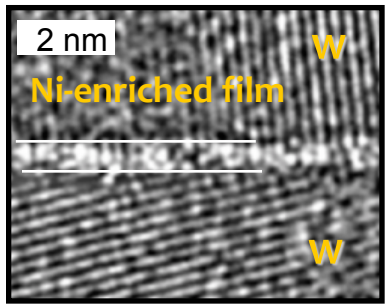


Metal-Oxide Interface
(Kaplan et al, *Acta Mater.* 2000)

Metals



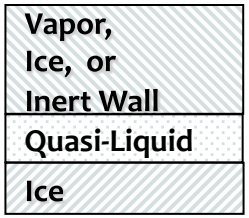
(Kwon et. al, *APL* 1999)
NOT classical solid-state amorphization



$T < T_{eutectic}$

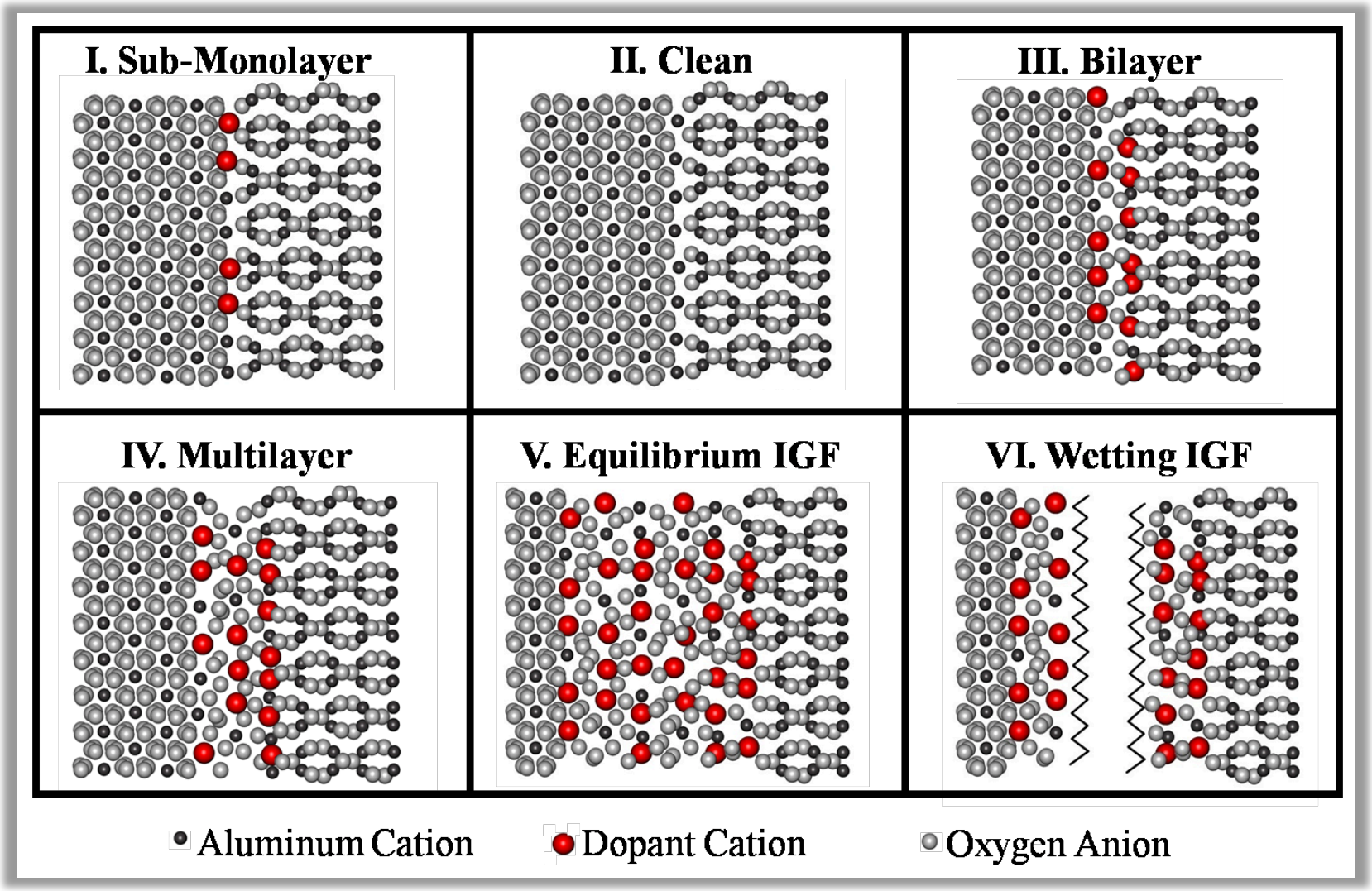
(Luo, et al., *APL* 2005)

Ice + Impurities, e.g. NaCl (Molecular Solids)



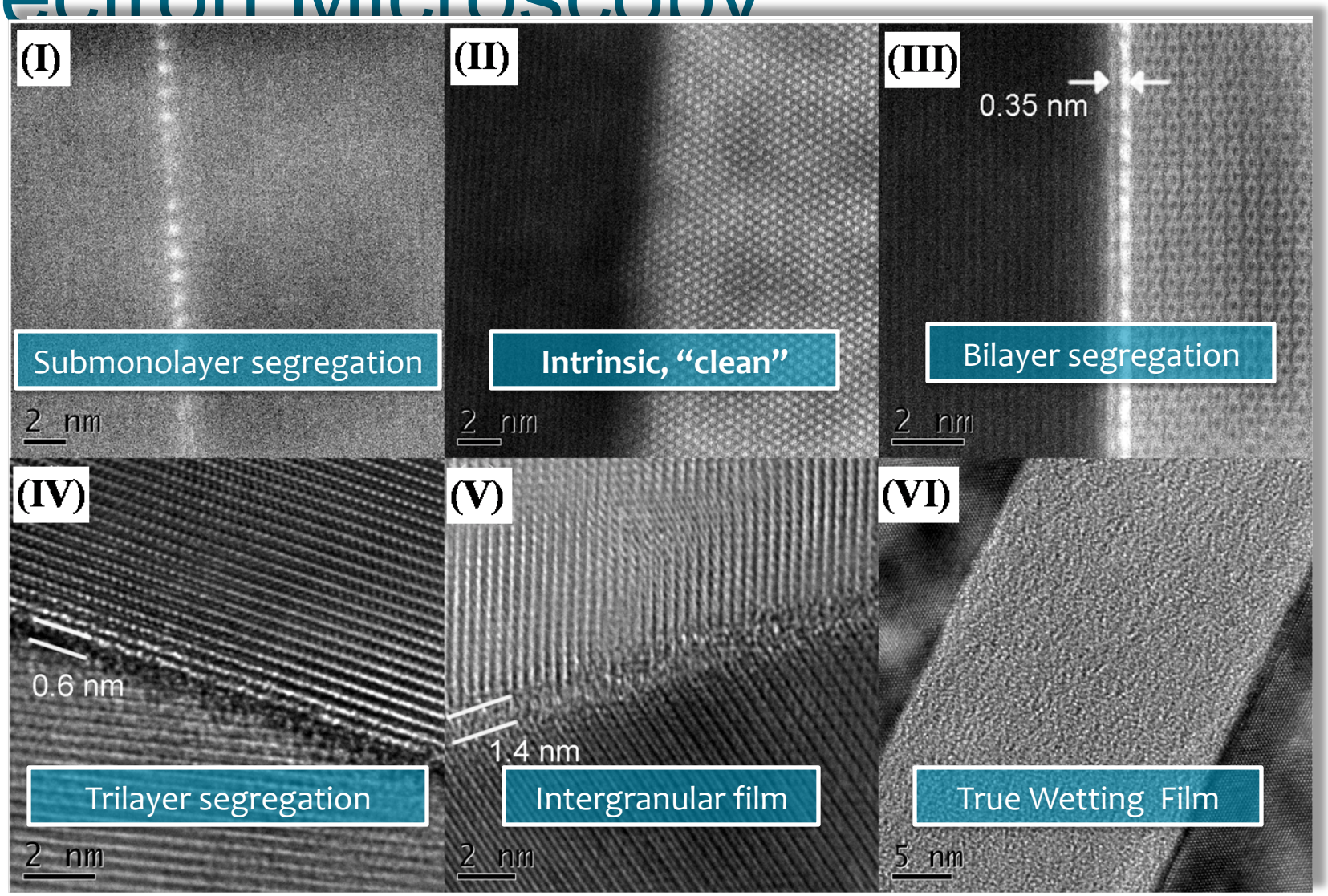
Surface
(Wettlaufer, PRL 1999)
GB & interface
(Wettlaufer et al., PRE 2005)

Schematic of Complexion Types



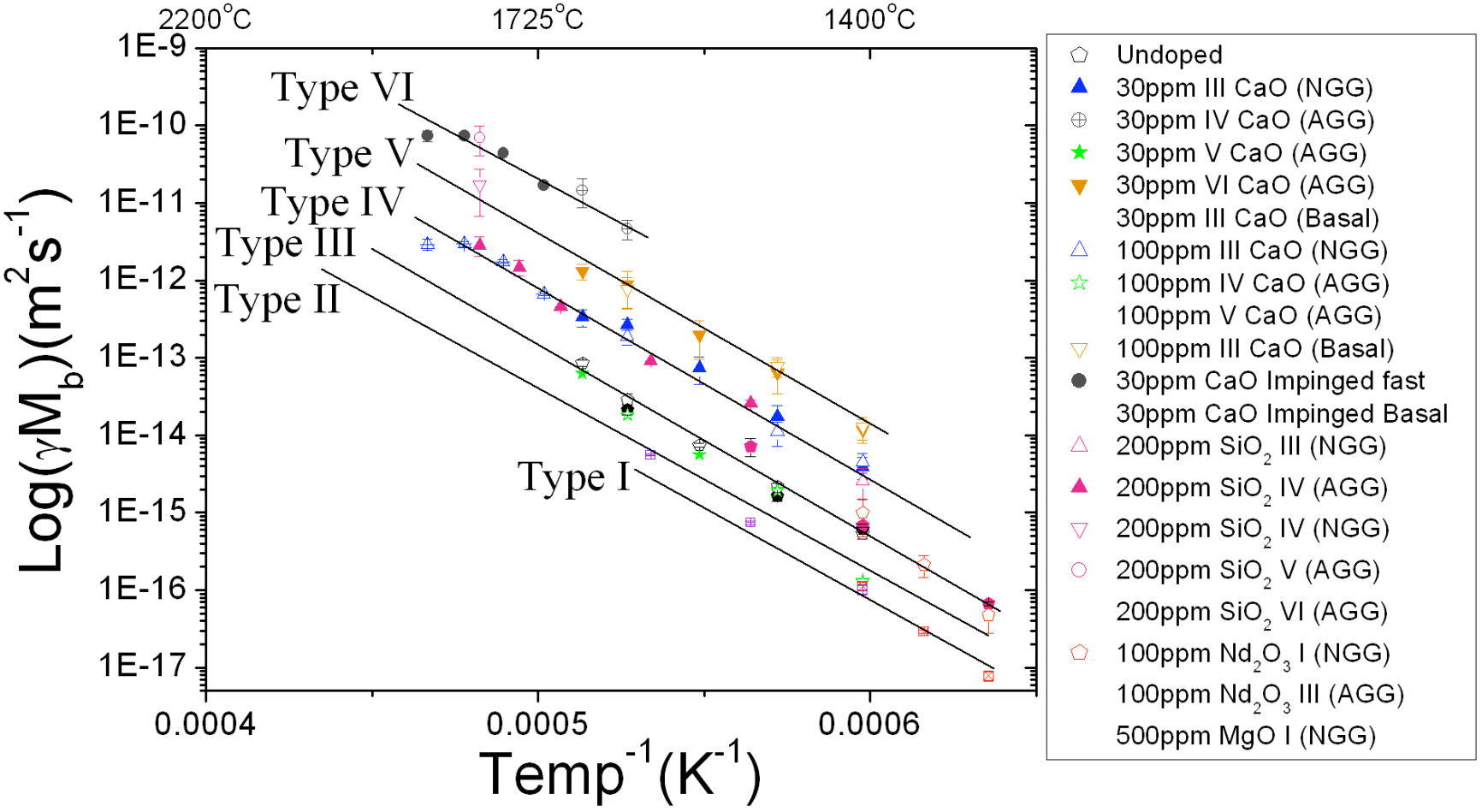
S.J. Dillon, M. Tang, W.C. Carter, M.P. Harmer, Acta Mater. 2007

Complexions - High Resolution Electron Microscopy



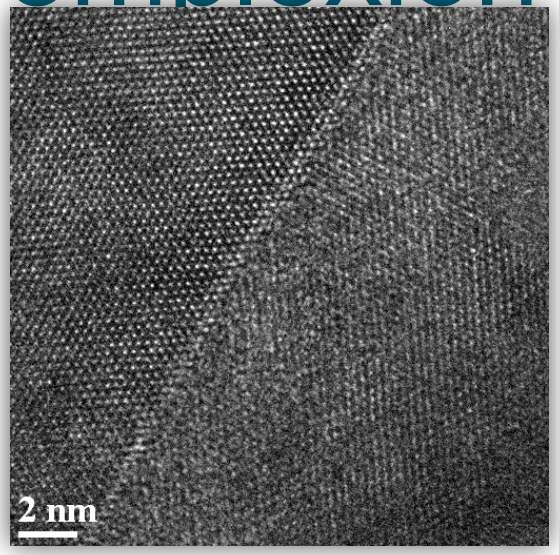
S.J. Dillon, M. Tang, W.C. Carter, M.P. Harmer, Acta Mater. 2007

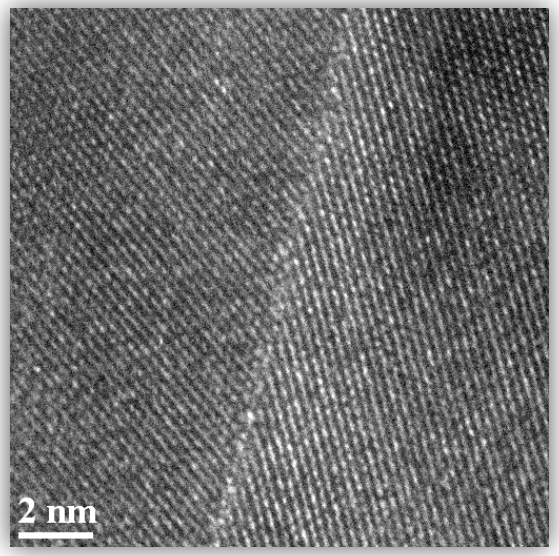
Transport Properties of Complexions (Alumina)



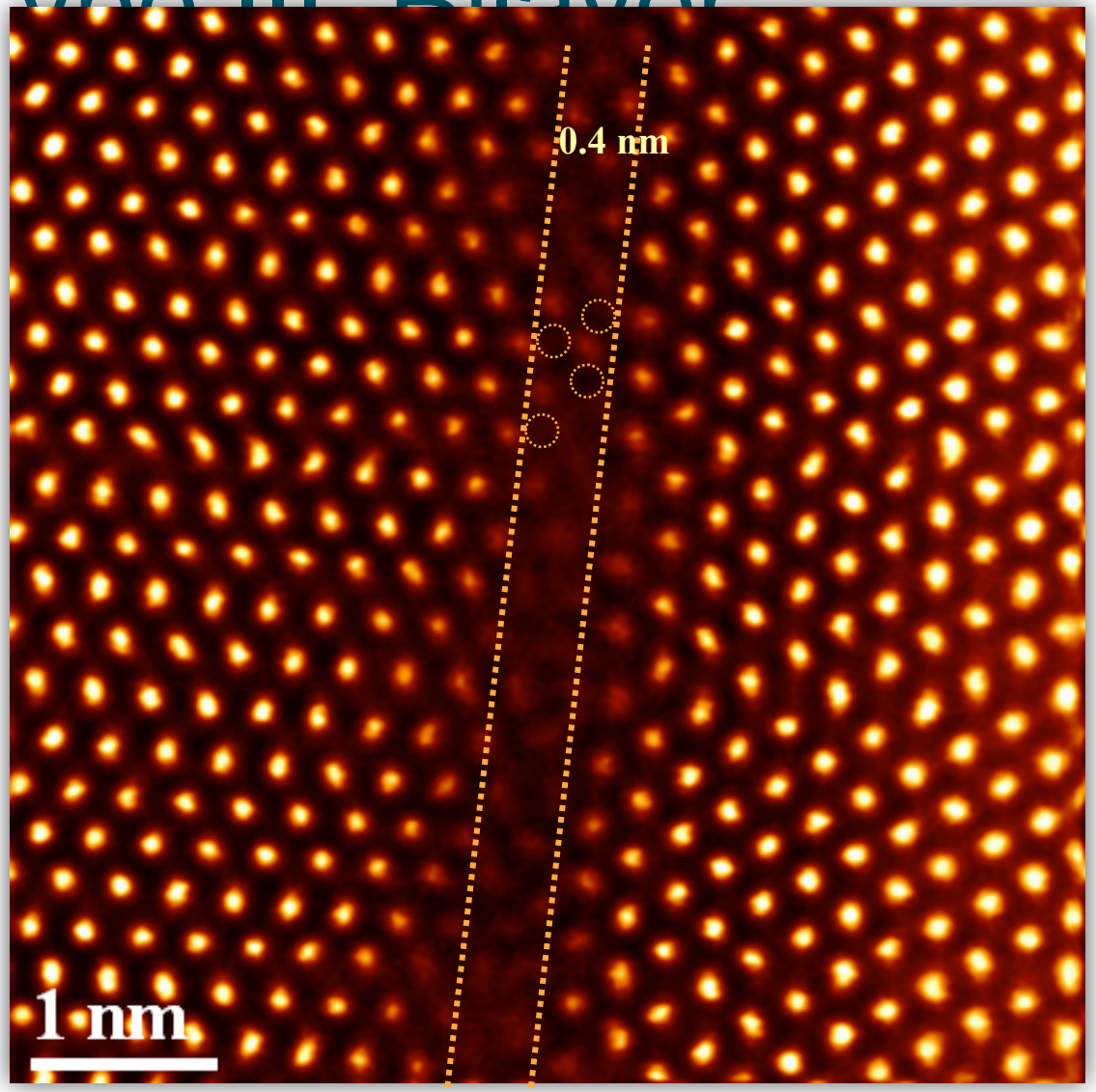
S.J. Dillon, M. Tang, W.C. Carter, M.P. Harmer, Acta Mater. 2007

Copper Oxide Doped Titania-complexion Type III Bilayer





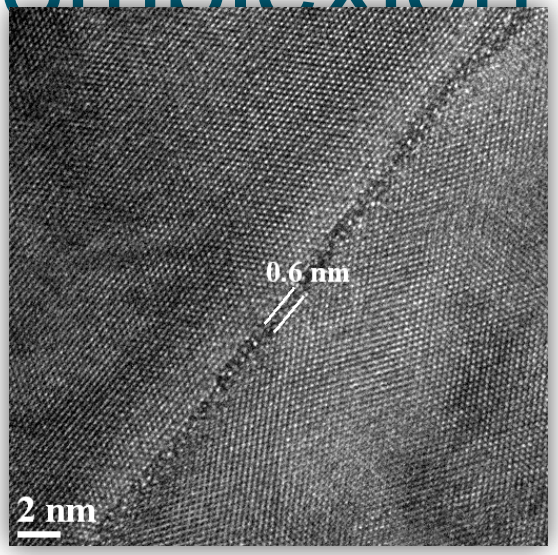
HRTEM

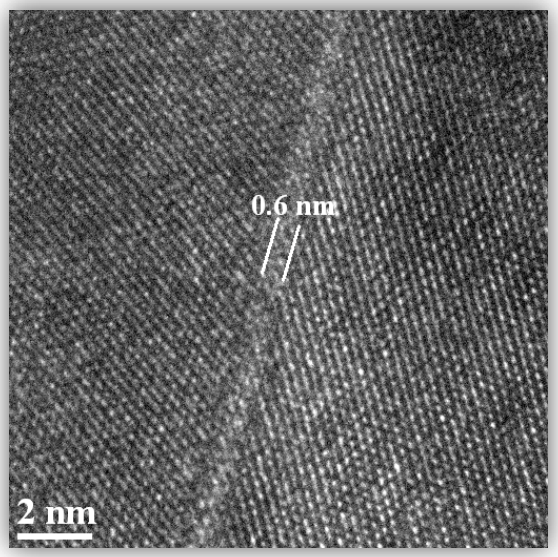


HAADF-STEM (smoothed and deconvoluted)

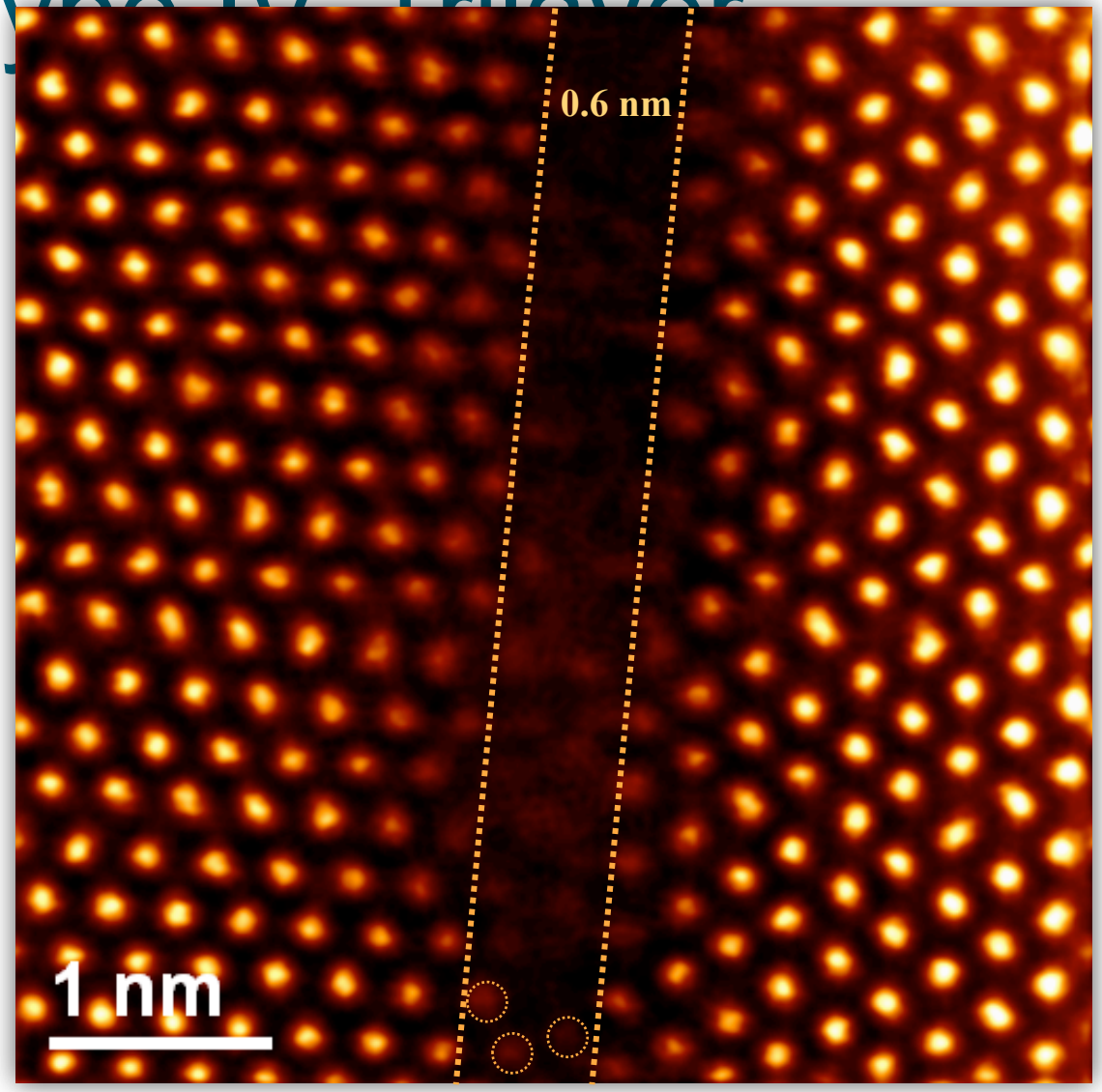
Courtesy of ShuaiLei Ma

Copper Oxide Doped Titania-complexion Type IV Trilayer





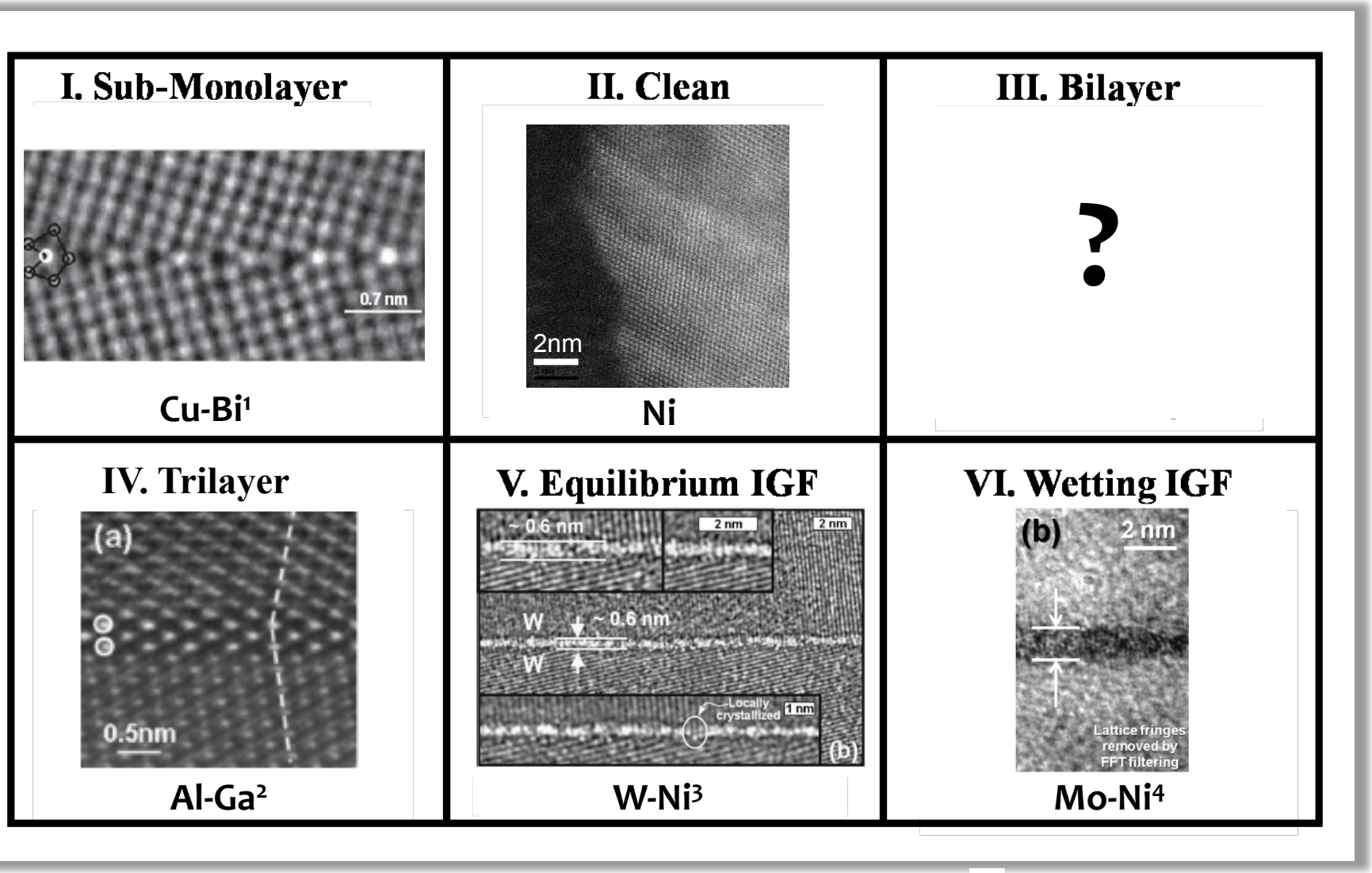
HRTEM



HAADF-STEM (smoothed and deconvoluted)

Courtesy of ShuaiLei Ma

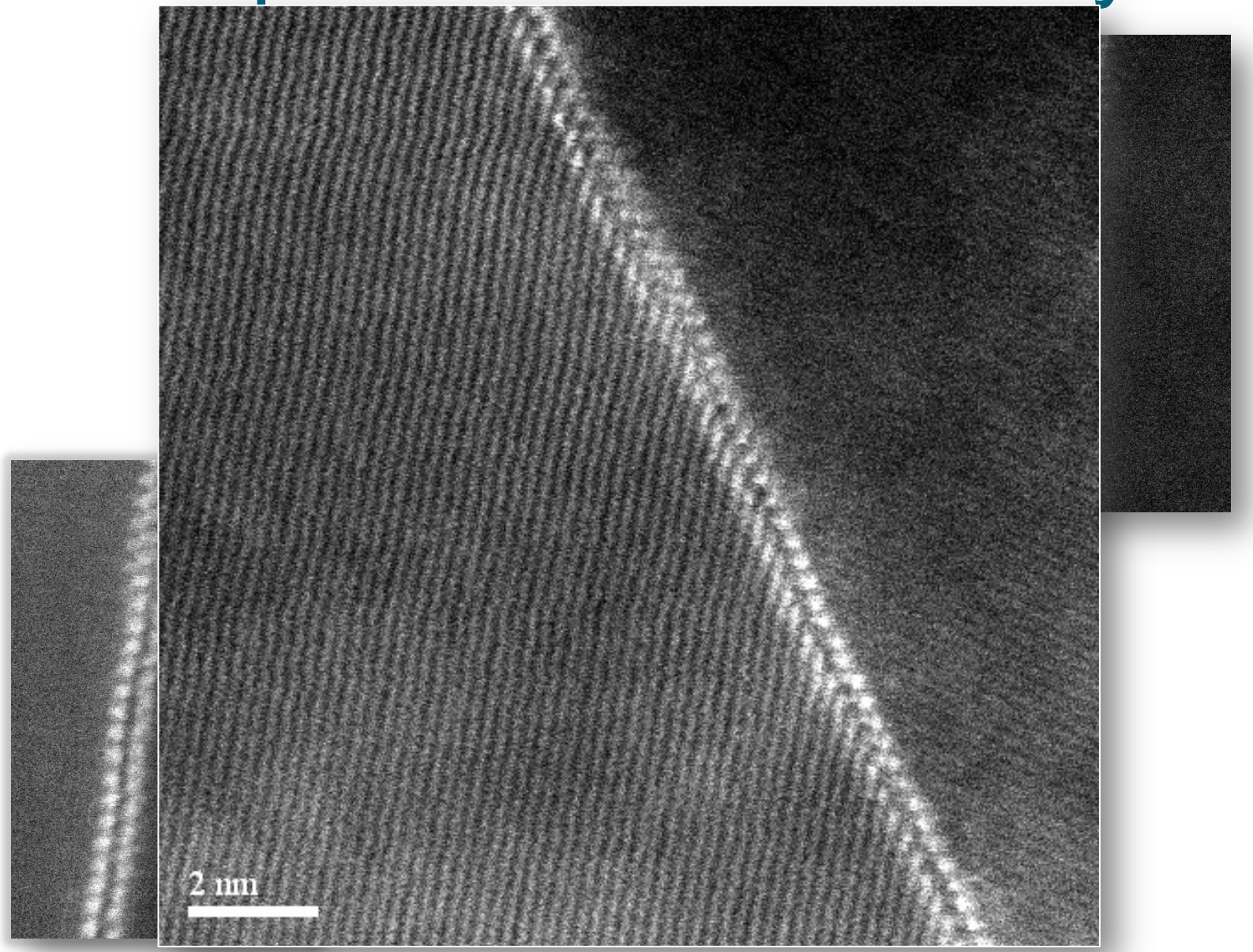
GB Complexions In Metal Systems



1. G. Duscher et al. Nature Materials, 2004

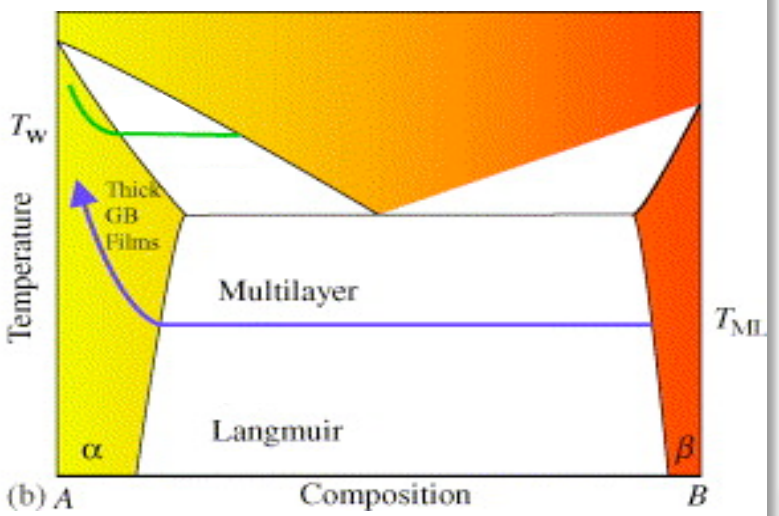
2. W. Sigle et al. Applied Physics Letters, 2006
3. J. Luo et al. Applied Physics Letters, 2005
4. X. Shi et al. Applied Physics Letters, 2009

GB Complexions in Ni-Bi Alloys



J. Luo, H. Cheng, K. Meshinchi Asl, C. J. Kiely, M. P. Harmer, submitted to Science

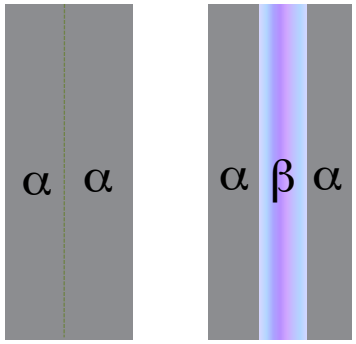
Thermodynamic Modelling



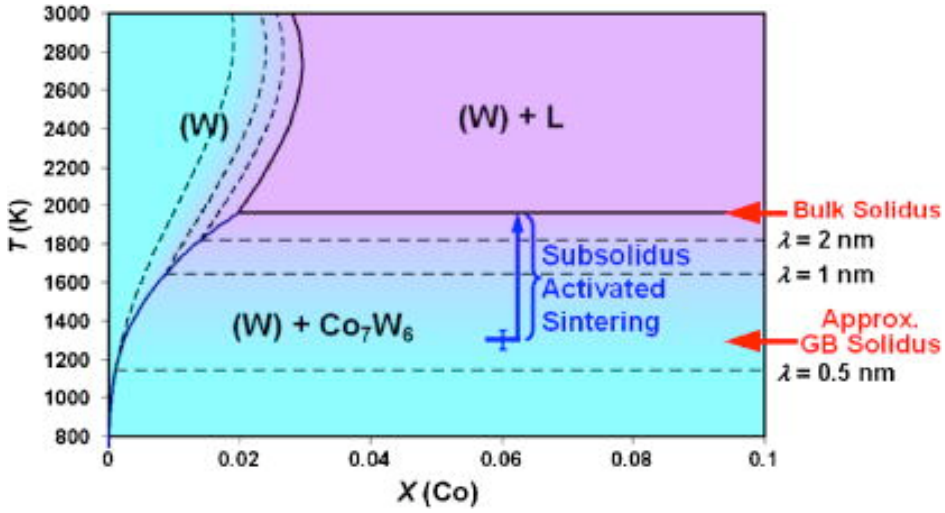
C. Bishop et al., Mat. Sci. Eng. A., 2006.

Stability Condition

$$h\Delta G_\beta = \gamma_{\alpha\alpha} - 2\gamma_{\alpha\beta}$$



No Atomistic/First Principles Calculations of IC's and their transitions to date

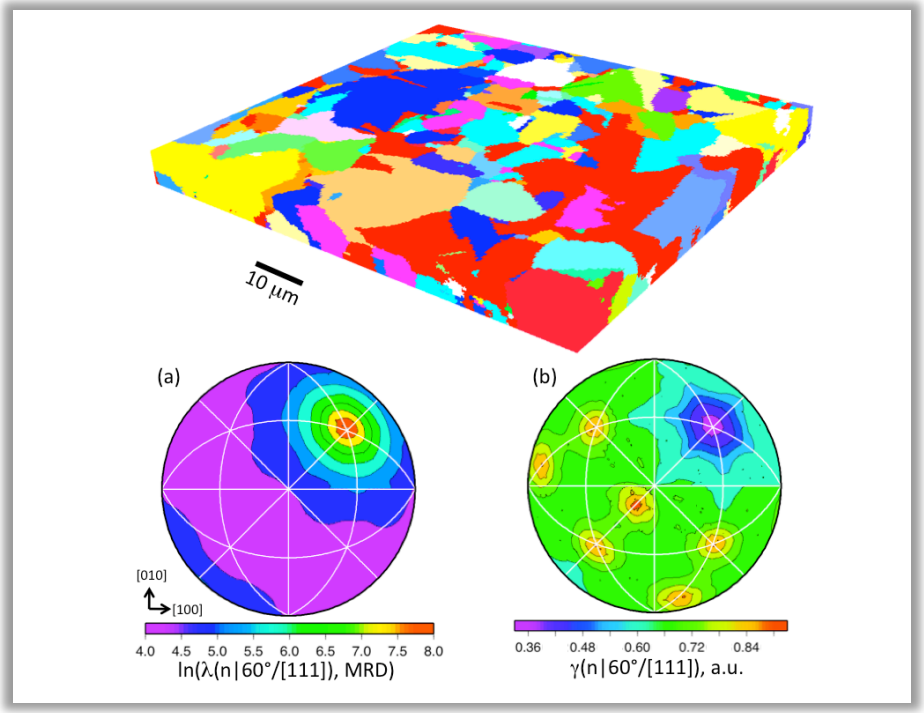


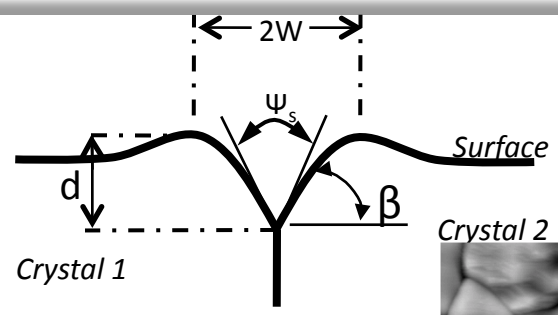
J. Luo, X. Shi, Appl. Phys. Lett., 2008.

Selection Rules

Complexion formation favored by:

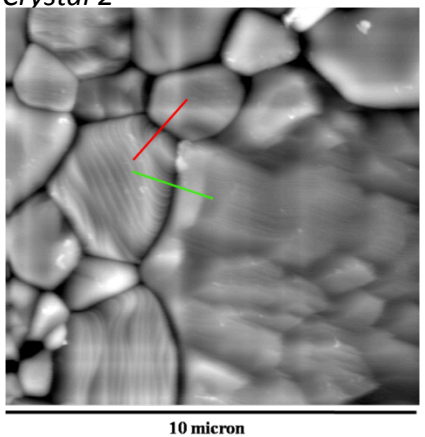
- High energy grain boundaries in the host
- Compositions near deep eutectics
- Systems that produce second phases with large interphase boundary energies
- Alloy systems with low solubility and high segregation

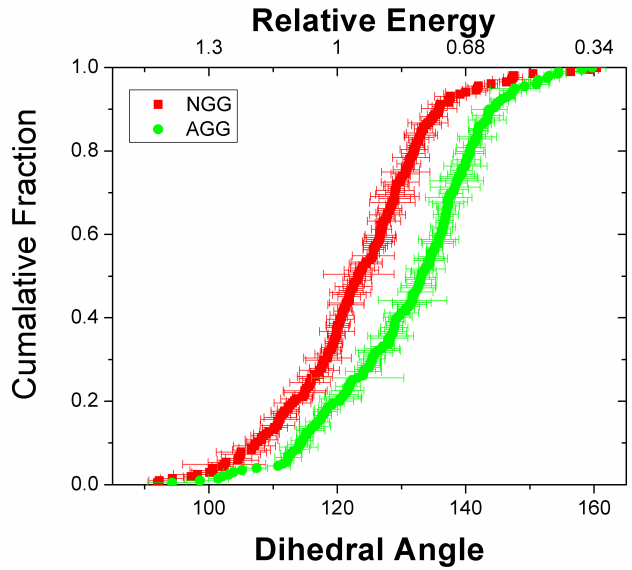




$$\frac{\gamma_{Gb}}{\gamma_S} = 2Cos\left(\frac{\Psi_S}{2}\right)$$

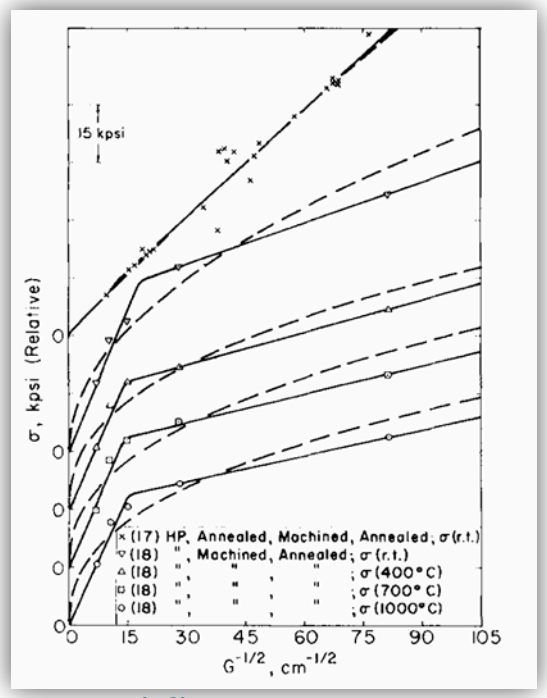
$$\frac{W}{d} = \frac{4.73}{\tan\beta}$$



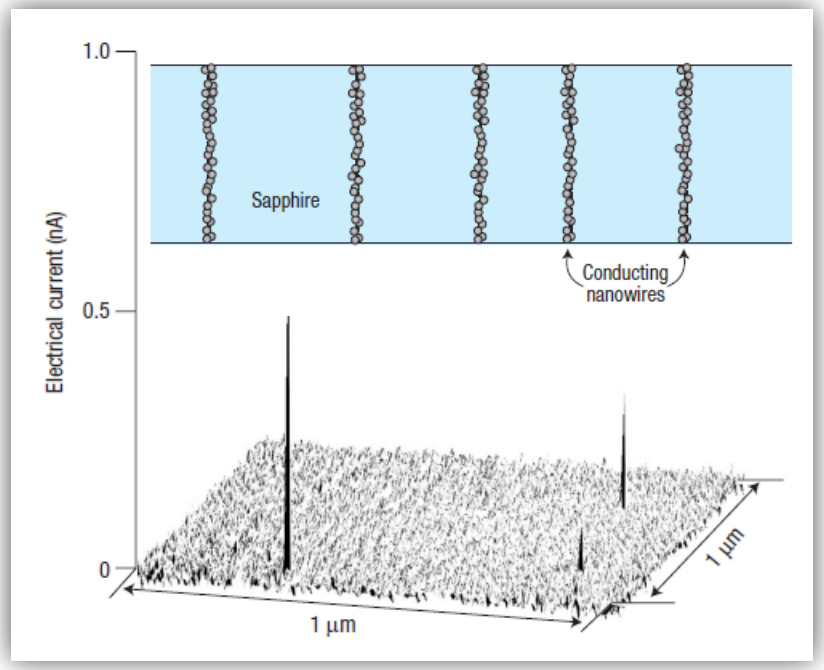


Tailorable Properties - Examples

Phenomenon	Properties	Examples
Grain Growth	Atomic diffusivity, $D_b^{\perp}$	Al_2O_3
Creep, Oxidation, Densification	Atomic Diffusivity, $D_b^{\parallel}$	Refractory Metals (W, Mo), Al_2O_3, Si_3N_4
Electrical Conduction	Conductivity, σ	Al_2O_3-Ti
Mechanical	Strength, Toughness	Al_2O_3, WC-Co

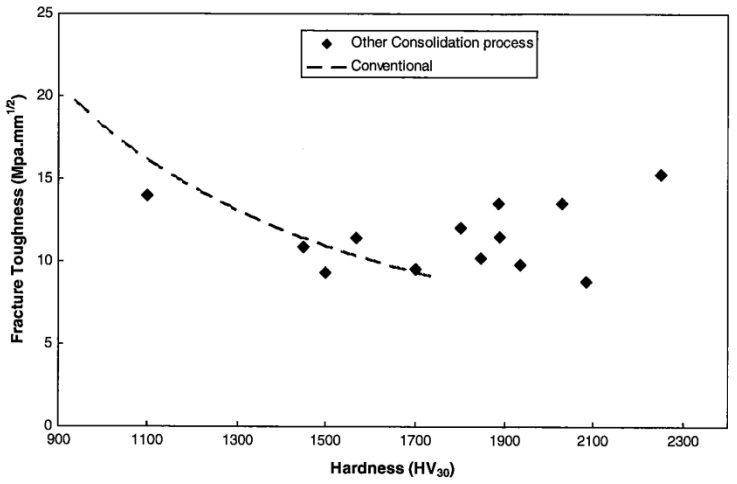


S.C. Carniglia, J. Am. Cer. Soc., 1972

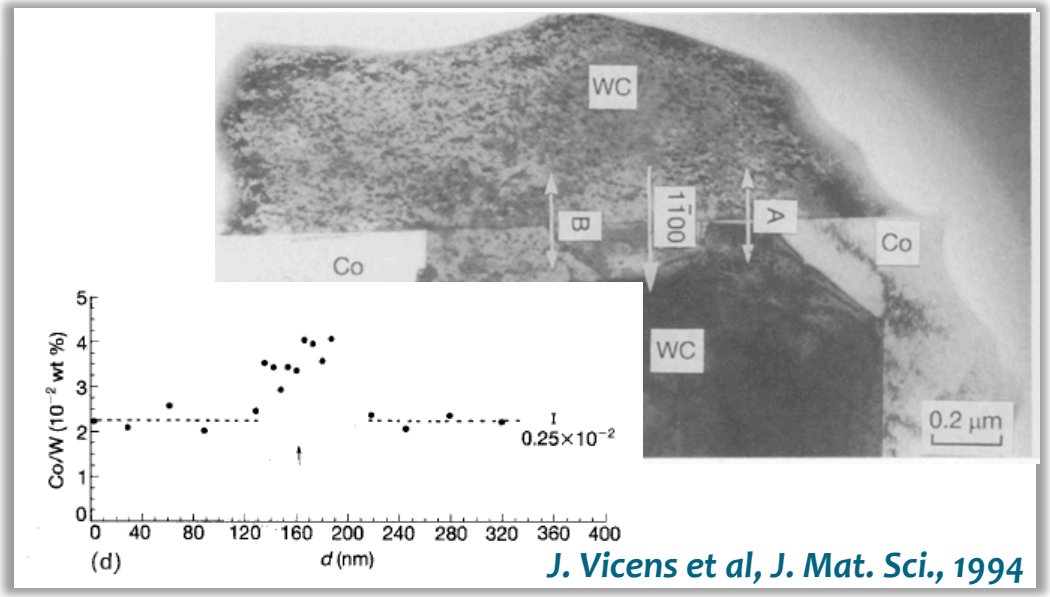


Nakamura et al, Nature Materials (2003)

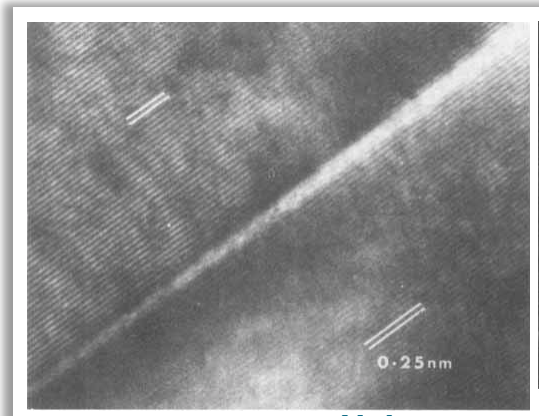
WC - Co Complexion-Property Relationship?

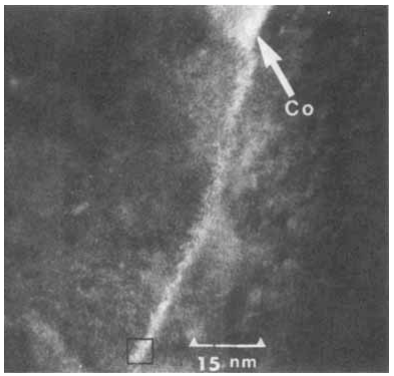


Z. Z. Fang et al, Int. J. Refr. Met. & Hard Mat., 2009

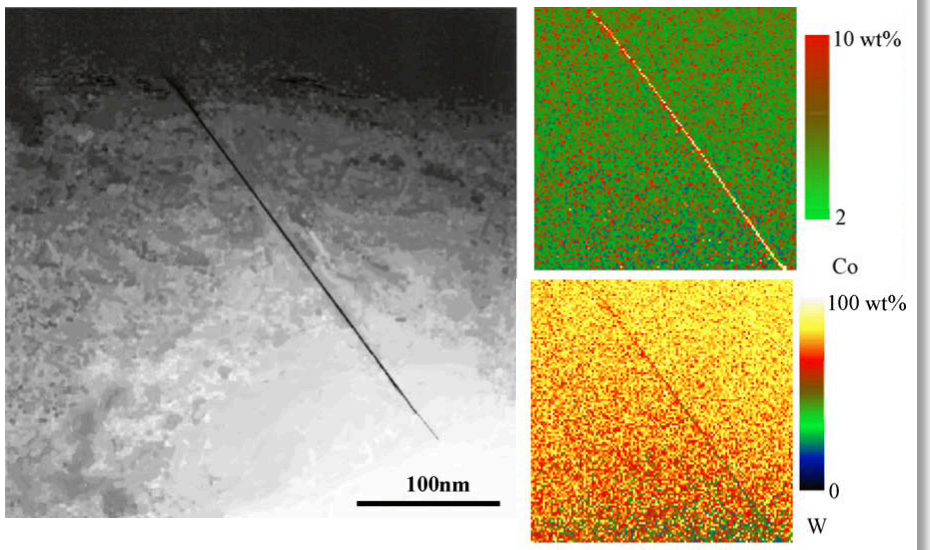


J. Vicens et al, J. Mat. Sci., 1994



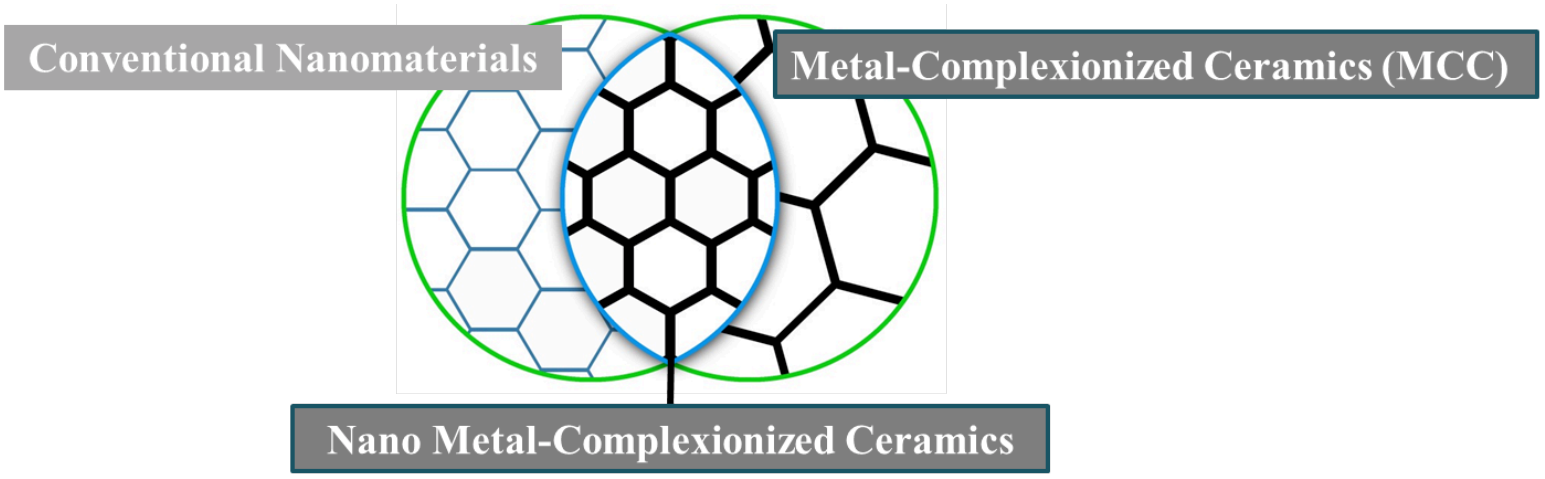


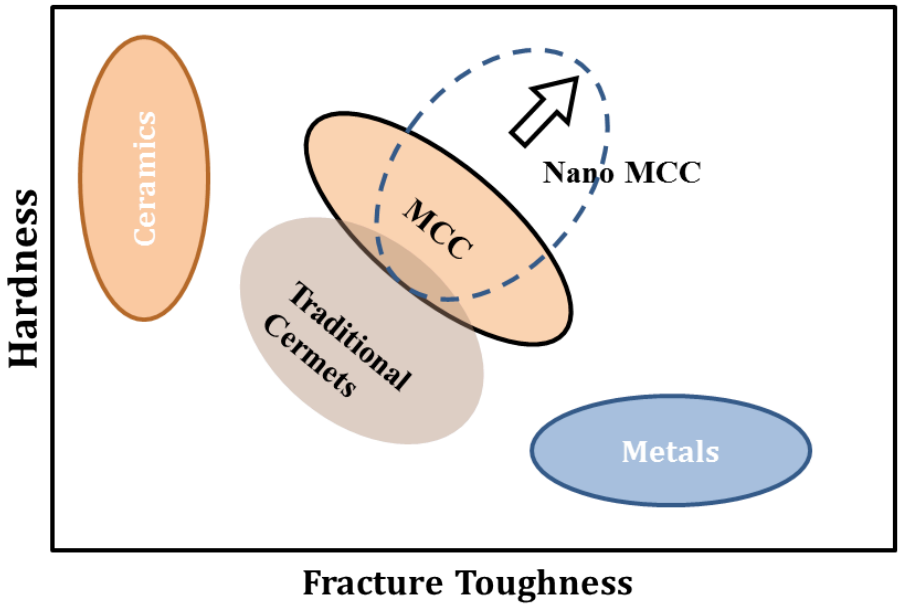
V. Jayaram et al, J. Am. Cer. Soc., 1983



E. Breval et al, Mat. Sci. & Engg., 2005

Proposed Approach





Tailorable Properties in MCC

Thermal Conductivity (k),
Thermal Expansion (α)
Electrical Conductivity (σ_i)
Mechanical Strength (σ)
Hardness (H)
Fracture Toughness (K_{IC})
Atomic Diffusivity ($D^{\parallel}$,$D^{\perp}$)

THRUST 1: OBJECTIVES

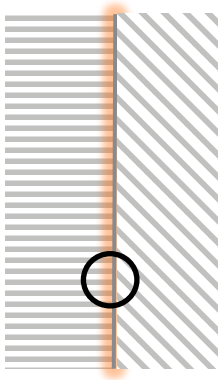
Creation of New Classes of Materials with Tailored Properties

- **Establish a set of "Selection Rules" for metal-complexionized ceramics (MCC).**
- **Develop complexion phase diagrams for MCC.**
- **Correlate individual complexion types with each of their associated physical properties (thermo-mechanical, diffusivity).**
- **Develop Ashby-type property maps incorporating important grain size (nanoscale) effects.**
- **Correlate individual boundary effects with distributions in polycrystalline microstructures.**
- **Develop processing strategies for controlling polycrystalline grain structures (e.g. unimodal vs. multi-modal, nano grain size vs. micron grain size etc).**

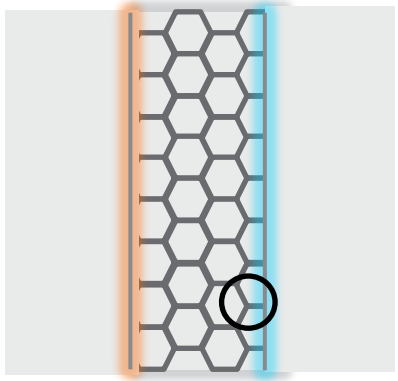
THRUST 1: TECHNICAL APPROCH

Creation of New Classes of Materials with Tailored Properties

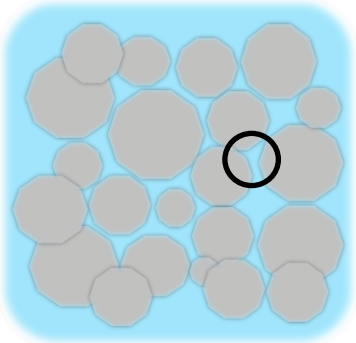
MCC material system: Alumina – (Cu, Cu-Ti, Ni)



Bicrystals



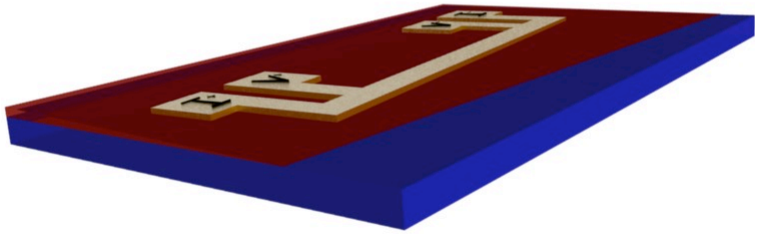
Model Sandwich Structures



Nanophase MCCs

Characterization

- HREM (structure, chemistry), ELNES (local bonding)
- SPM - Conduction Mode (conductivity of individual IC's)
- Nano-indentation
- GB character and energy distribution
- Thermal Properties
- SIMS, GB diffusivity



THRUST 1: MODELLING

Creation of New Classes of Materials with Tailored Properties

First-Principles Calculations

Ab-Initio

Developing Interatomic Potentials

- *-- Phase Stability*
- *-- Segregation Energies*
- *-- GB Energies*
- *-- Diffusion Barriers*

Atomic Level Modelling & Simulations

Monte Carlo, Molecular Dynamics

- *-- Transport Properties*
- *-- Mechanical Behavior*

Interphase Thermodynamic Modelling

Phenomenological, Sharp-Interface Model

- *-- Compute Complexion Phase Diagrams*

Mesoscale Simulations

Potts Model, Phase-field Method

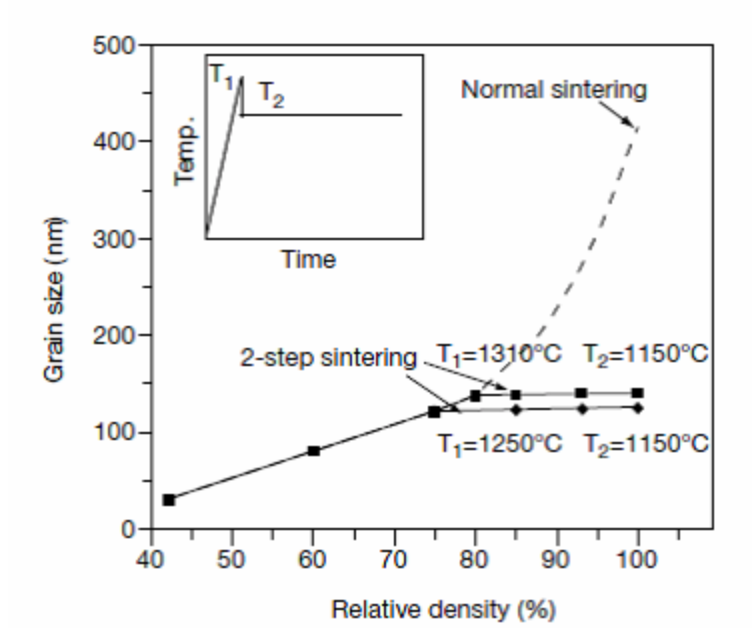
- *-- Abnormal Grain Growth*

THRU

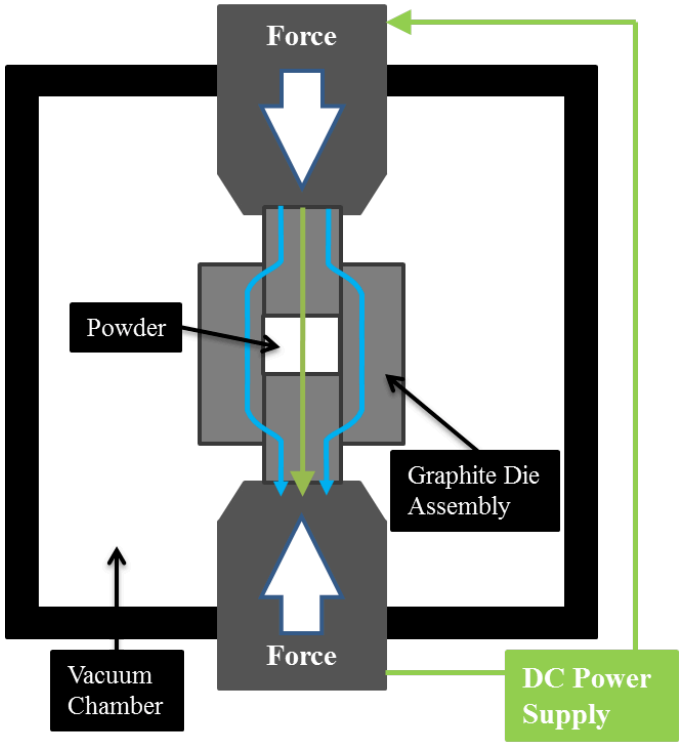
STP2 Exploitation of Complexions in the Processing of Bulk Nano-grain Materials

- **Determine the critical role of IC's in the application of fabrication processes for producing bulk nano-grain materials.**

Two Step Sintering

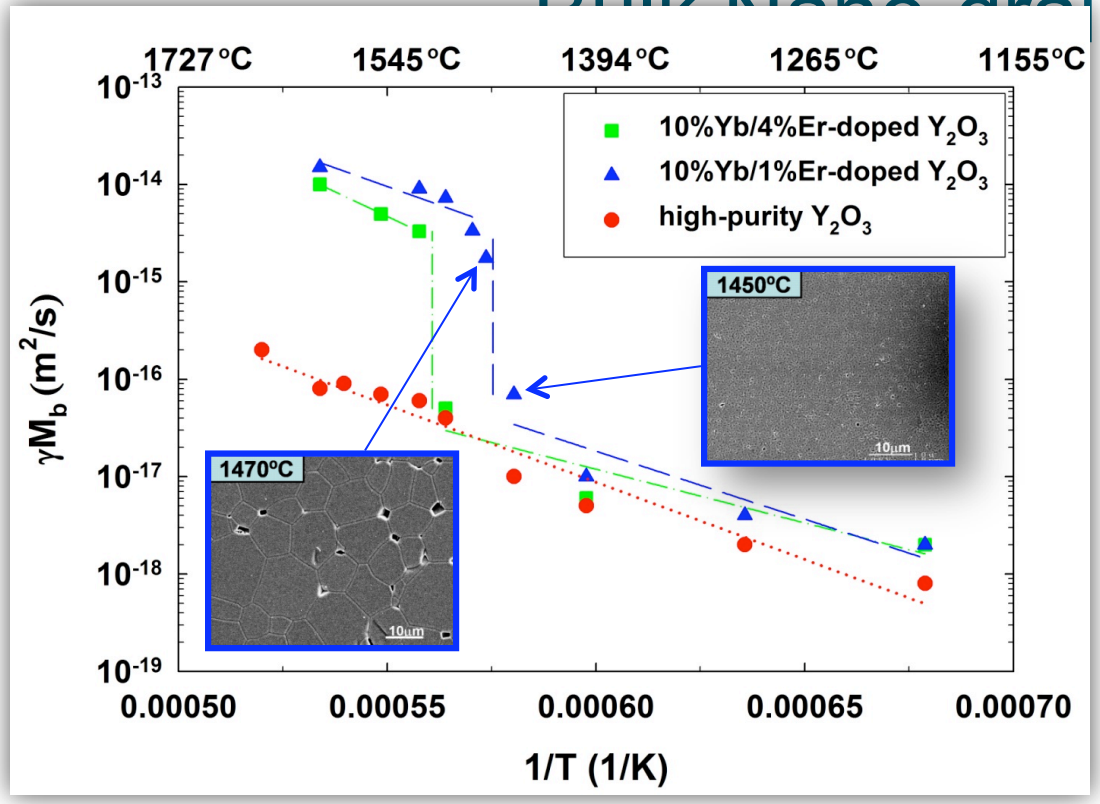


Spark Plasma Sintering



THRU

ST 2 Exploitation of Complexions in the Processing of Bulk Nano-grain Materials



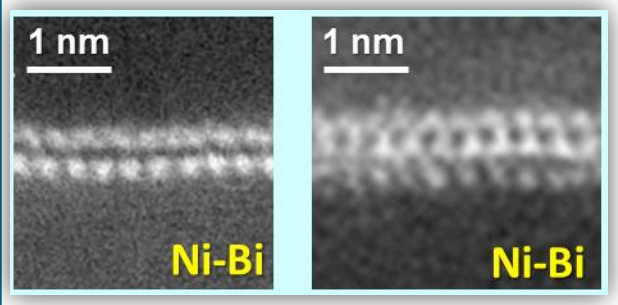
Material Systems for Thrust 2	
Model Systems:	Alumina – silica/yttria
New Materials:	Nano metal-complexionized ceramics
Challenging Conventional Materials:	WC-Co, YSZ

THRU ST 3 Exploitation of Complexions in Controlling Properties in Strategic Engineering Materials

Revisit WC-Co

- Systematic investigation of grain boundary mobility and the formation and stability of complexion as a function of temperature chemistry
- Develop interphase engineered nano MCC of WC-Co.

Embrittlement of Ni & Cu Alloys



- Systematic Co-doping
- Characterization

Other Systems

- Sn and Sb doped ZnO
- Al-B_4C
- ....

Ionic Conductivity of Oxides

- Model System: ZrO_2-Y_2O_3-(SiO_2)-M_xO_y
- Co-dope to control GB resistance
- Synthesis of specimens
- High-T impedance measurements
- HRTEM, HAADF-STEM (Lehigh)...

Management

http:\\muri.cc.lehigh.edu

MURI Research Group Meetings

- **Monthly teleconference**
- **Biyearly face to face meetings: December and Mid-June**

Annual ONR Review Meeting

Bear Creek International Conference on Interfaces October 2-6, 2012

Reporting Requirements?

US Student/PostDoc Recruitment

LEHIGH UNIVERSITY

Abigail Lawrence (US citizen), Michael Kracum (US citizen), Denise Yin (US citizen), Patrick Cantwell (US citizen), Suxing Wu (US citizen), Animesh Kundu

CLEMSON UNIVERSITY

Yuanyao Zhang, Matthew Williams (US citizen)

CARNEGIE MELLON UNIVERSITY

Stephanie Bojarski (US citizen)

UNIVERSITY of ILLINOIS AT URBANA-CHAMPAIGN

MURI-RELATED AFFILIATIONS

DOD PARTNERSHIPS

ARL

- James Sands
- Michael (Mick) Maher
- Gary Gilde

ARO

- David Stepp
- Doug Kiserow

ARDEC Picatinny

- John Theis
- Stacey Kerwein
- Chris Haines

AFOSR/WPAFB

- Ali Sayir/Randall Hay

NRL

- Alexis Lewis

POTENTIAL INDUSTRY PARTNERS

- Material Complexions Inc.
- TA&T
- Thermal Technologies Inc
- Dupont
- GE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