Development of Nanostructured Metallic Systems – Progress and Challenges

Presented by

P. R. Subramanian

Ceramic and Metallurgy Technologies

GE Global Research

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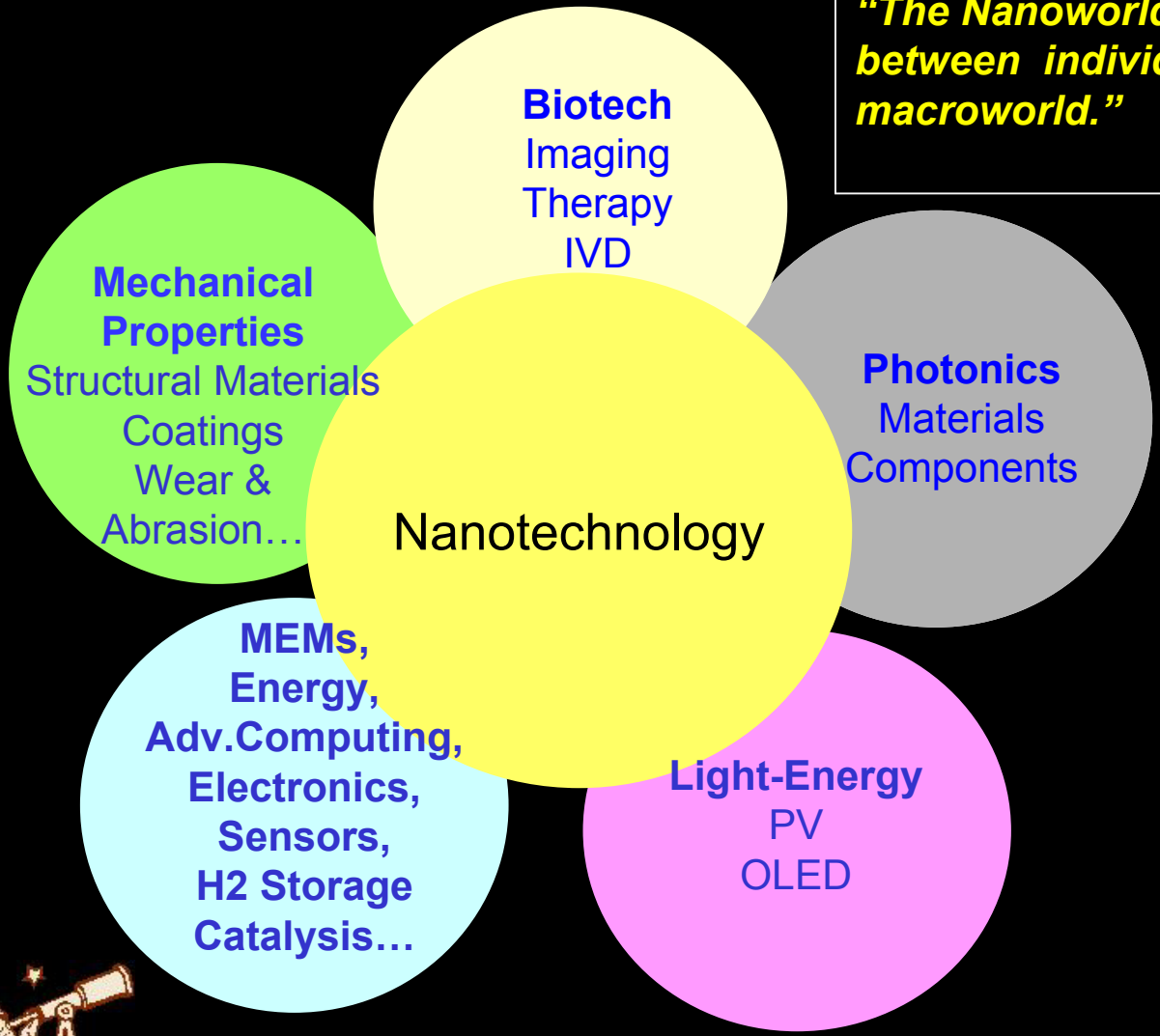
The Nanotechnology Challenge

> *"The Nanoworld is a weird borderland between individual molecules and the macroworld."*
>
> *Scientific American, 9/01*

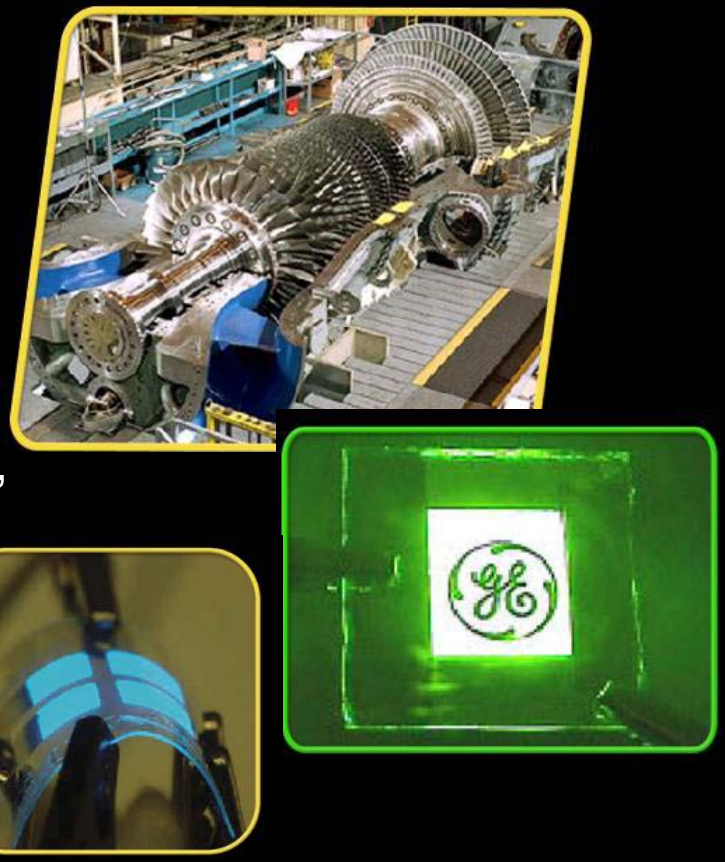


Too Many Opportunities: Where do we start?

Nanotechnology Opportunities in GE

GE Technology…

- Saving Energy & the Environment
  - GE Aircraft Engines, GE Power Systems, GE Specialty Materials, GE Industrial Systems, GE Transportation
- Household Innovations
  - GE Consumer Products, GE Plastics
- The Future of Healthcare
  - GE Medical Systems



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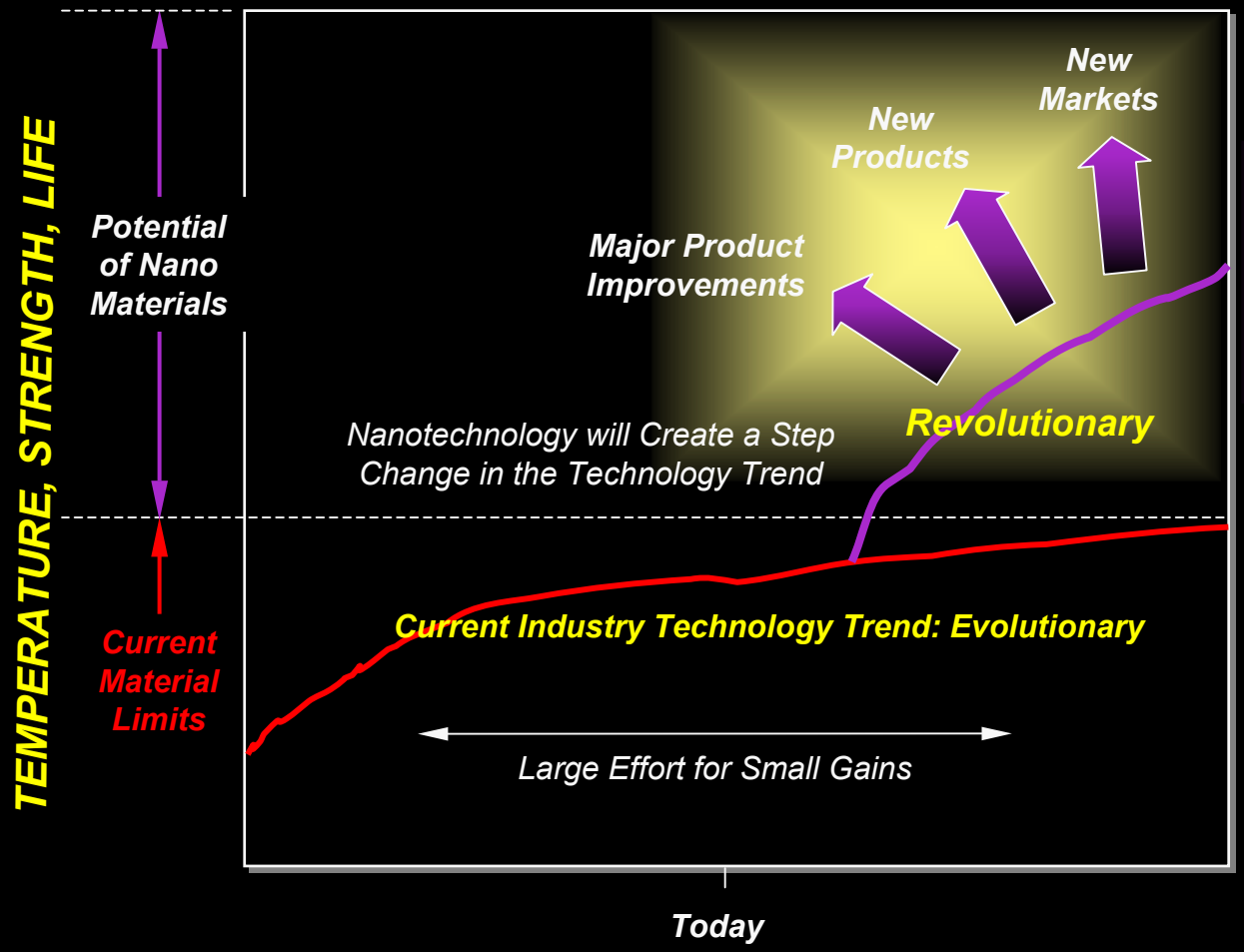
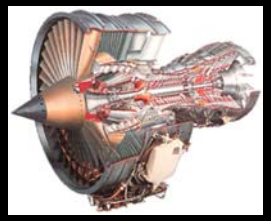
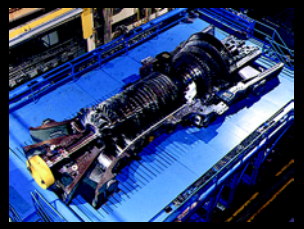
Why is GE Investing in Nanotechnology?





Higher Thrust to Weight Ratio Engines

Aircraft Engines



Higher Efficiency Turbines

Land Based Turbines

Increased Diagnostic Speed for Medical Systems

Medical Systems

All of the GE Businesses will benefit from the current investments being made in nanomaterials and nanotechnology

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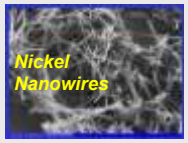
GE's Nanotechnology Program

NanoMaterials

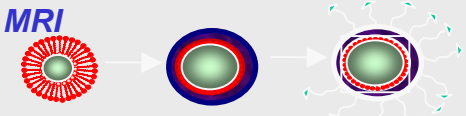
Nanotubes & Nanowires Platform

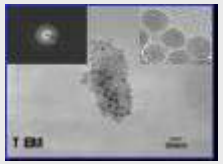
Leverage existing & invent novel materials In targeted application areas

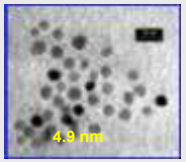


Magnetic Nano-Particles Platform

Develop expertise in functionalized magnetic nano-particles via contrast agents for MRI



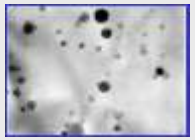




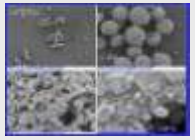
NanoComposites

NanoStructures in Metals & Ceramics Platform

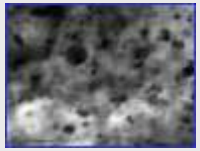
Develop fundamental structure-property relationships to design novel structural materials



ODS Alloys



Thermal Spray

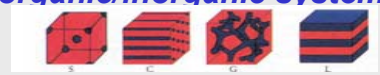


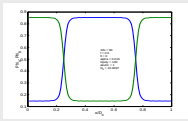
EB-PVD

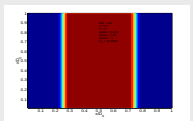
Ordered NanoStructures

Hybrid Materials Platform

Exploit self-assembly to engineer complex organic/inorganic systems

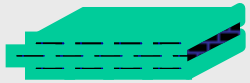






Ceramics Platform

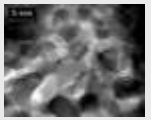
Leverage biomimetic syntheses to produce high toughness, high T structural ceramics



Soft Lithography, Micro-casting
(0.1-1mm)

Field Induced, Sol-ge
(1-10 μm)

Surfactant / Polymer Based Synthesis
(~10 nm)



Broad Based Materials Foundation

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Nanostructured Metallic Systems

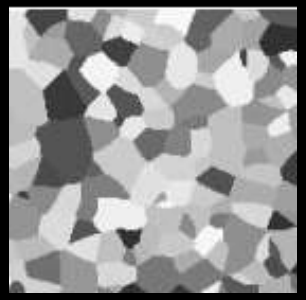
Develop fundamental structure-property relationship to design nanostructural materials & coatings with superior properties

Nano structure

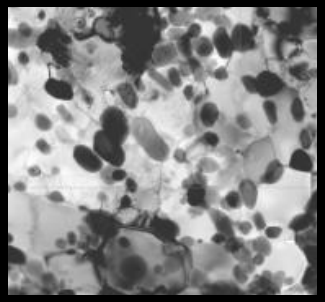
Processing

Properties

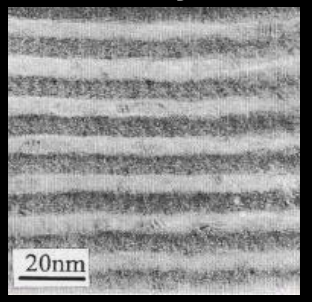
Nano grains



Nano-Dispersoids

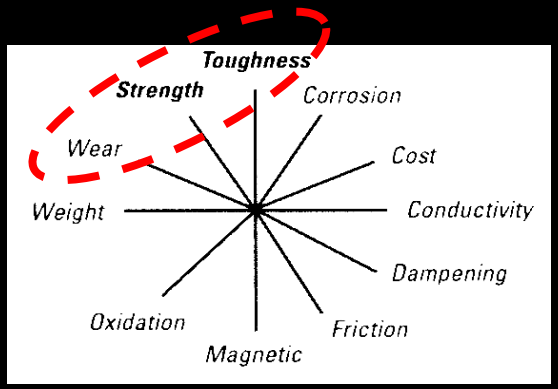


Nanolayers



Scaleable, Bulk Processes
Casting, Powder processing, Deformation processing

Structure-stability -property fundamentals
Physical Vapor Deposition



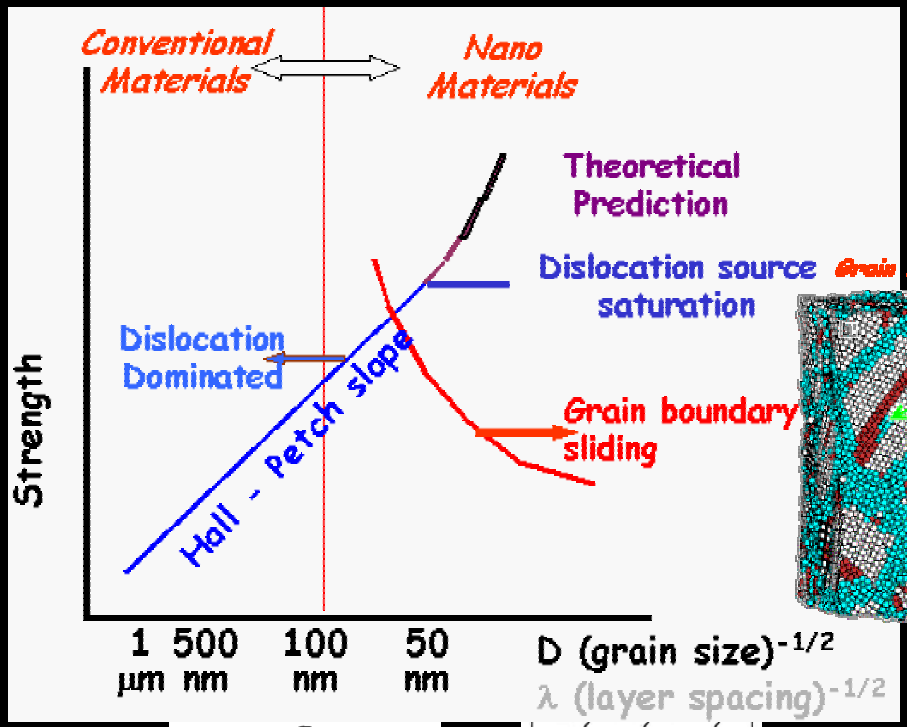
Focus

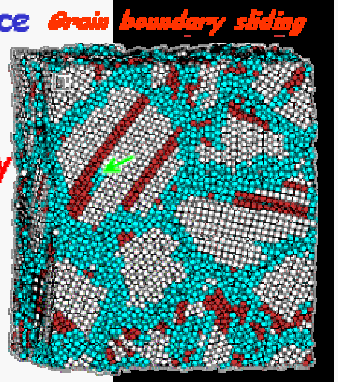
- *Create & control nanostructures*
- *Stabilize structures*
- *Optimize structures for properties*

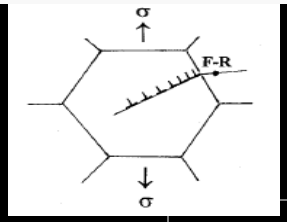
Opportunities for exceptional stability & strength enhancement in metallic materials

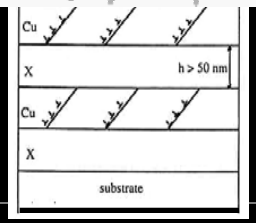
Strengthening Mechanisms

Effect of Microstructural Scale

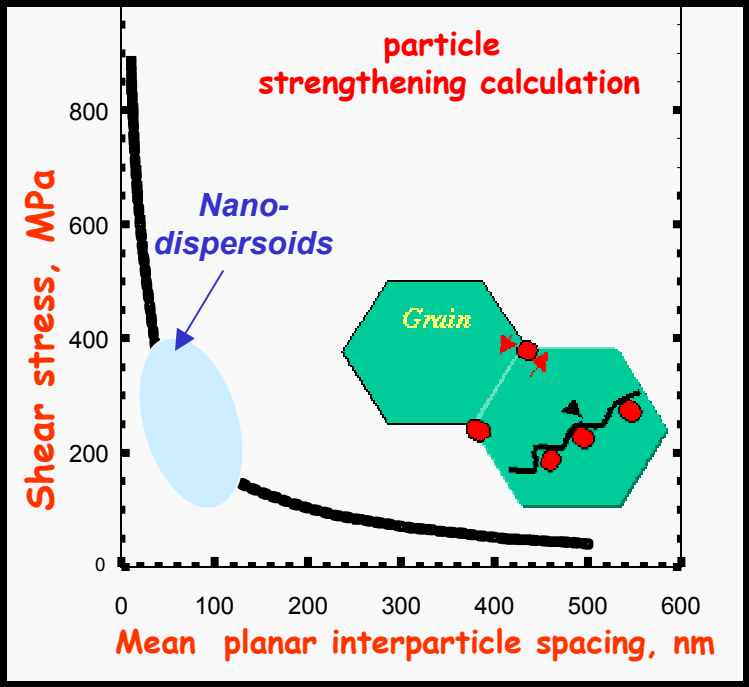








Effect of Dispersoid Reinforcement



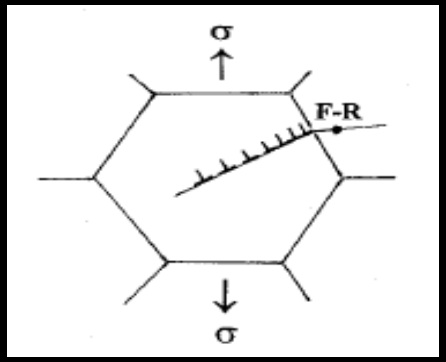
Order of magnitude increase in strength over micron size predicted

Issues:

- *Dislocation source saturation at nano-scale*
- *Competition between strengthening from nano-scale vs. weakening by gb sliding*
- *Thermal stability*

Strengthening Mechanisms: Dislocation Pile-up Model

Single phase Nanocrystalline Materials



- Large grains: many dislocations in pile-up →continuum theory of Hall-Petch works ($\sigma \propto d^{-1/2}$)
- Small grains: question is how many dislocations in pile-up?

# of dislocations in pile-up (using circular pile-up model)

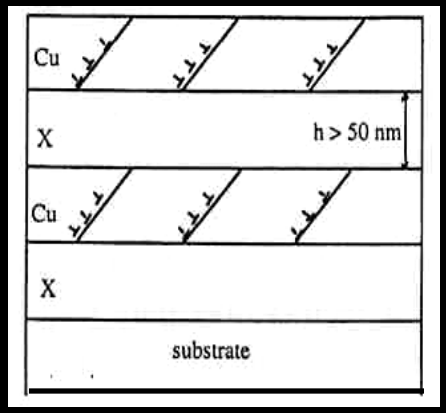
$$n = \left(\frac{\tau^*}{G}\right)^{1/2}\left(\frac{D}{b}\right)^{1/2}$$

~20-100 nm grain size: dislocations cross gbs one at a time & there is no pile-up (dislocation source saturation)

➔ Easier to deform by Coble creep instead of dislocation glide

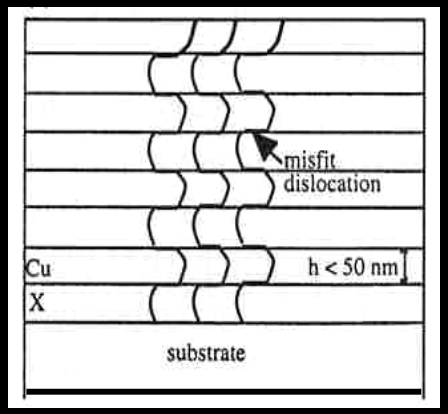
Layered Structures

Large h (λ/2)

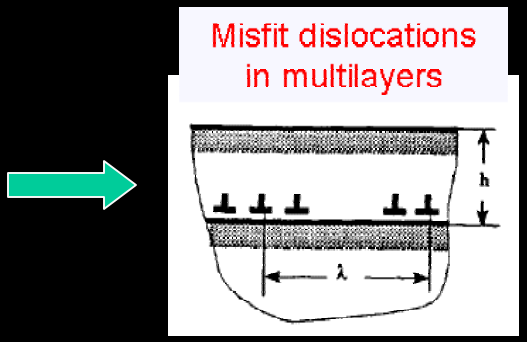


Hall-Petch behavior - dislocation pile-ups at interface

Small h (λ/2)



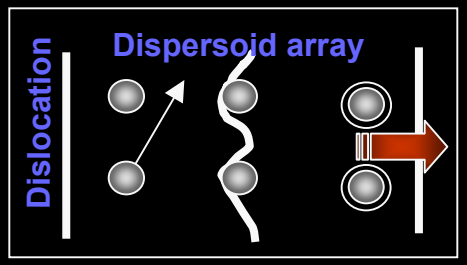
Plastic flow by single dislocations moving by bowing within layers



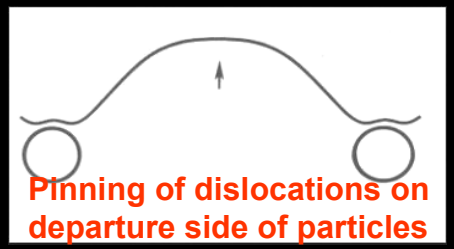
Leaves misfit dislocations at interface

Effect of Dispersoid Reinforcement: Strengthening

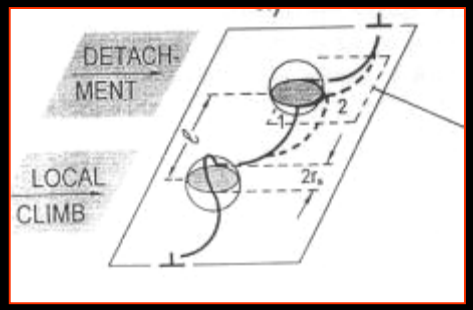
Dislocation-particle interactions



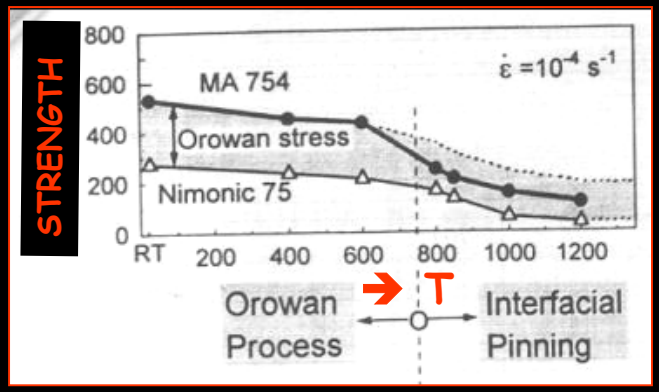
Orowan mechanism

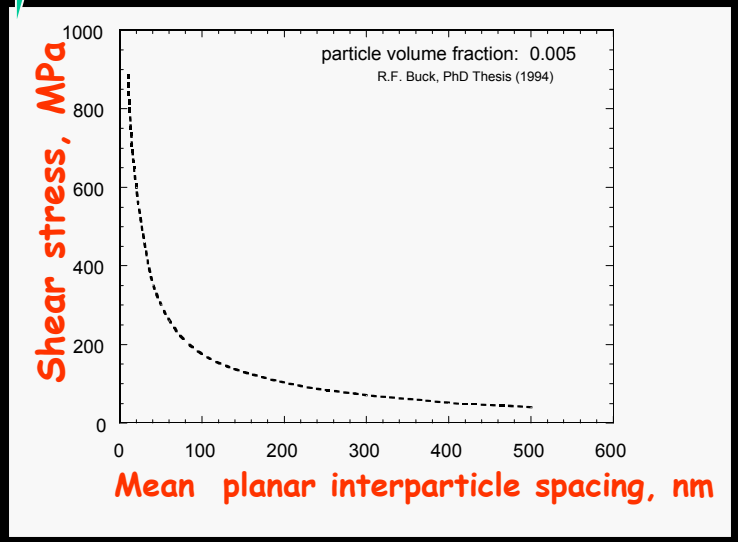


Pinning of dislocations on departure side of particles



Interfacial pinning mechanism



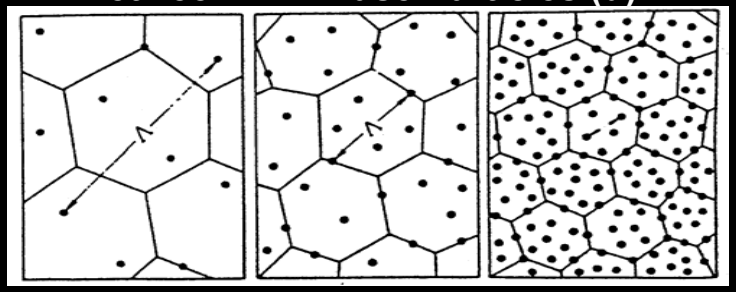


Issues:

- *Thermally assisted climb at high Ts*
- *Microstructural stability at high Ts and high stresses*
- *Dispersoid volume fraction: Tradeoff for strengthening vs. ductility ? What is needed for wear resistance?*

Dispersoid Reinforcement - Grain Boundary Pinning

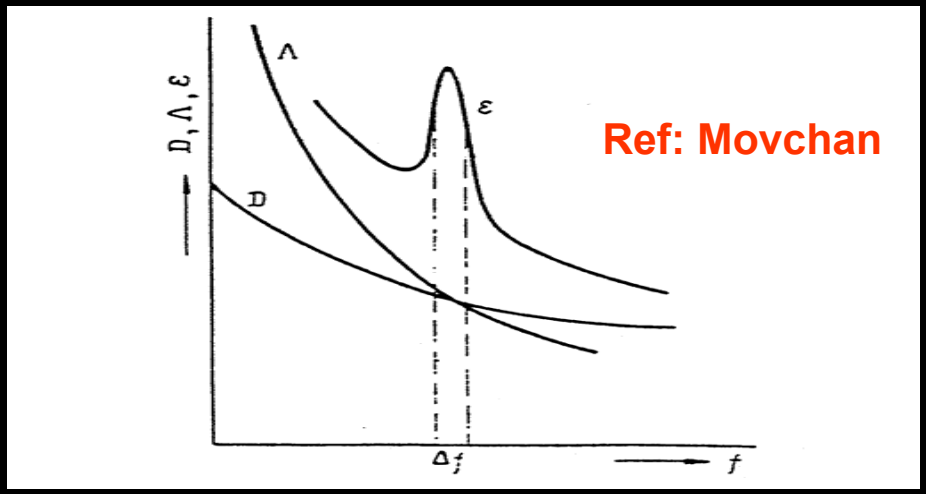
Grain Size (D) vs. Mean Free Path (Λ)
Between 2nd Phase Particles (d)



D < Λ D = Λ D > Λ

INCREASING DISPERSOID CONTENT

Zener Pinning



Ref: Movchan

Issues:

- *Microstructural stability at high Ts and high stresses*
- *Dispersoid volume fraction: Tradeoff for strengthening vs. ductility ? What is needed for wear resistance?*

Wear of Dispersoid Structures: Microstructural Effects

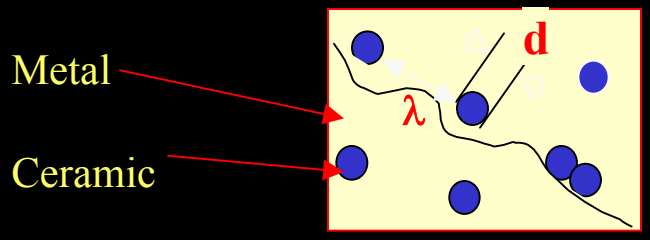
Dispersoid Structures

Nano strengthening mechanisms can be used to leverage superior wear properties while retaining higher toughness

Wear = f (H, K_c)

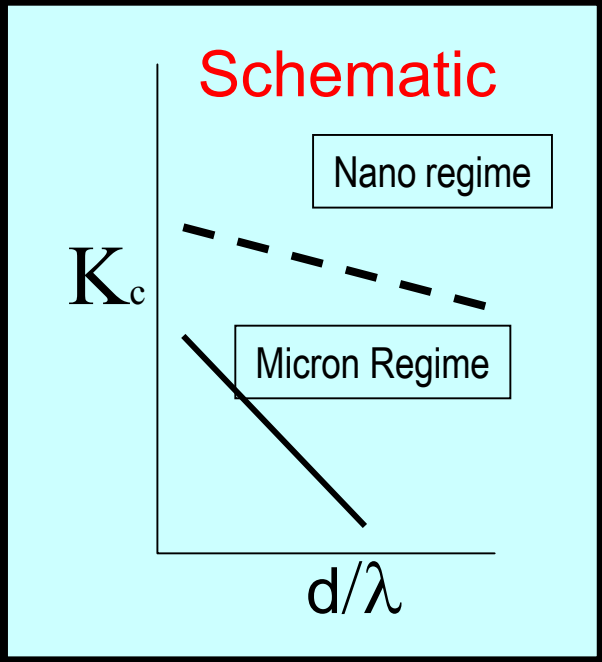
H = Hardness: f($\lambda^{-1/2}$)

K_c = Fracture toughness: f(λ/d)



7 X reduction in wear by reducing λ from 0.4 to 0.15 microns

- ***Higher hardness through lower mean free spacing λ***
- ***Better toughness through fine particle size d, and d/λ ratio***



High wear resistance and toughness obtained by dispersoid structure

Nanostructured Pure Metals: Background

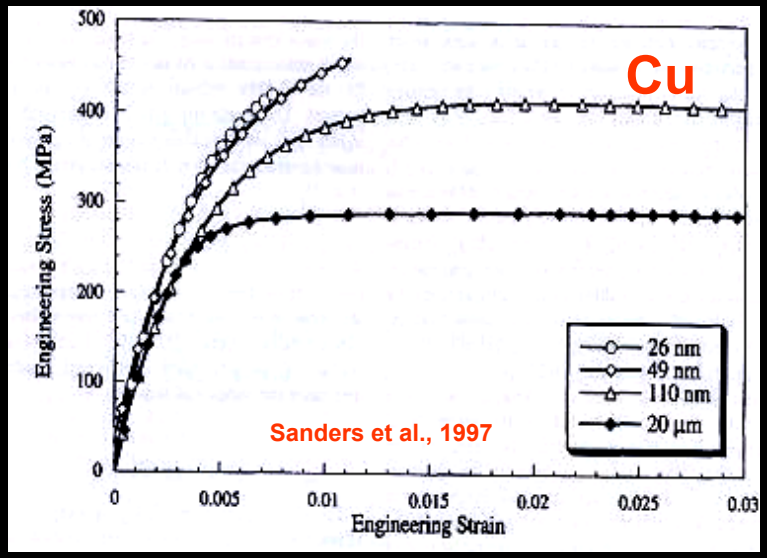
- *Strength (nanocrystalline metals) >> Strength (conv. metals)*
- *Ductility (nanocrystalline metals) << Strength (conv. metals)*

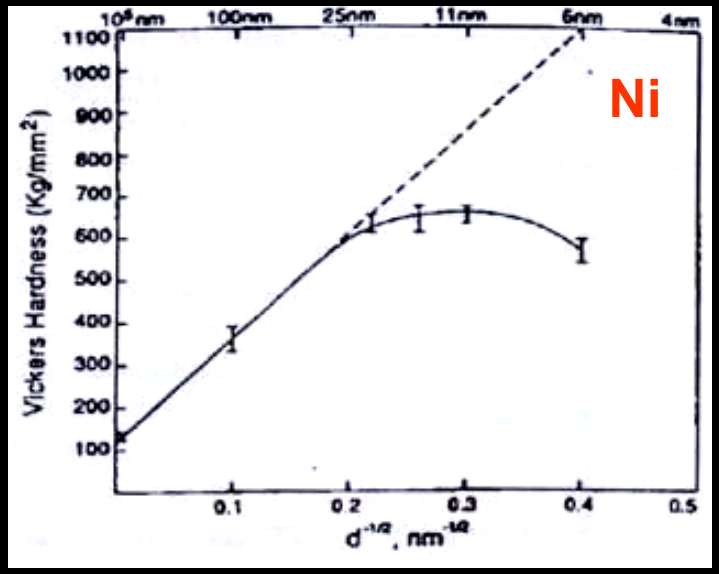
- *Hardness & wear resistance = strong function of gs*

- *Modulus & thermal expansion = mostly grain-size independent*

- *Softening at ~ 5-50 nm grain size due to grain boundary sliding + diffusional creep*

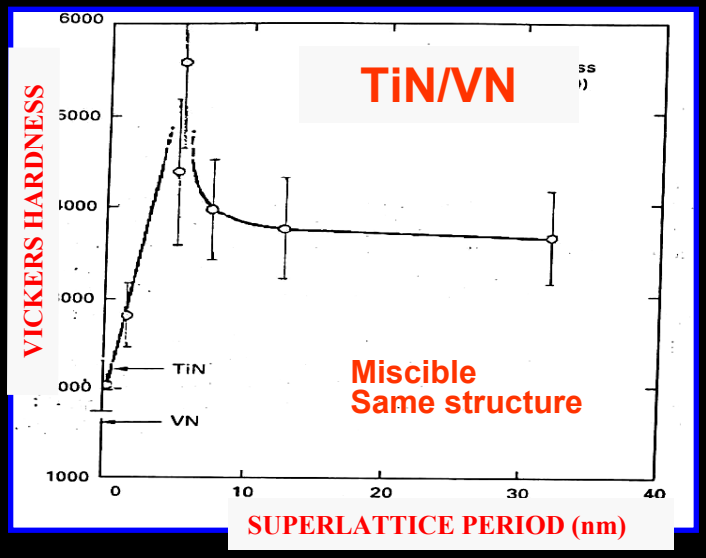
- *Properties = strong function of processing*

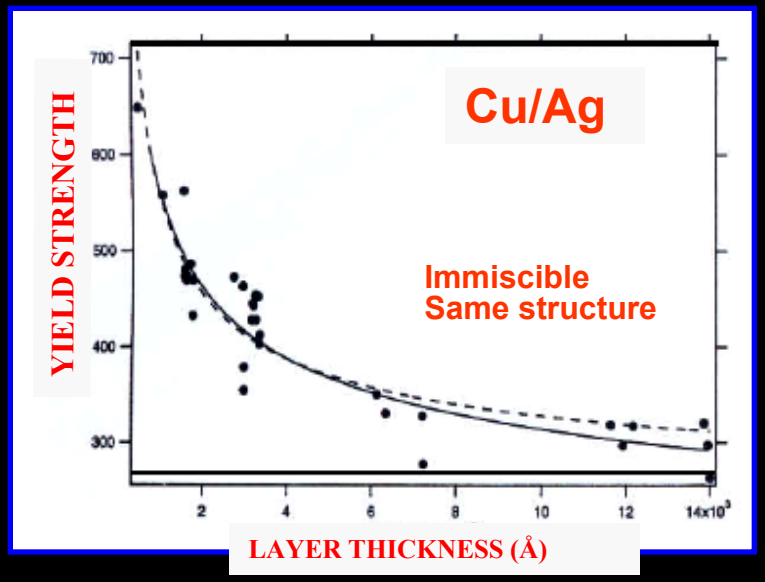




Multilayer Strengthening: Background

- *Parameters influencing strength*
  - *Layer spacing (λ)*
    - ➔ Large spacings: Hall-Petch behavior (Dislocation pile-up model)
    - ➔ Low spacings: individual dislocation motion in layers
    - ➔ Very low spacings: superlattice strength (>> harder component)
  - *Miscibility*
  - *Slip systems (Crystal structure)*
  - *Shear modulus*
  - *Coherency strains (δ)*





- *Metal/ceramic multilayers show good combination of toughness + hardness => wear application*
- *Significant strengthening observed in nanolayered structures*

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Summary of Mechanisms at Nano-Scale

CURRENT FOCUS

Mechanisms/Factors	Dispersed Structures			Layered Structures			Parameters
	Strength	Creep	Thermal Stability	Strength	Creep	Thermal Stability	
Dislocation-particle interaction (Orowan effect, attachment, detachment, shear)	√	√					Particle size, spacing,distribution
GB-particle interaction (Zener pinning)	√	√					Particle size, spacing,distribution
Hall-Petch effect (Dislocation-boundary interaction)	√			√			Matrix grain size /layer spacing
Grain boundary sliding	√	√	√				Matrix grain size & aspect ratio
Microstructural Evolution	√	√	√	√	√	√	Thermo/kinetics
Interfacial energy		√	√		√		
Dislocation sources & generation stresses	√?			√			Matrix grain size /layer spacing
Dislocation substructure	√						Matrix grain size
Koehler Stress or Image Stress				√			Modulus mismatch
Interface coherency	√			√			Crystallographic mismatch
GB segregation of solutes & particles	√	√	√				
Misciblity	√		√	√		√	Solubilty/diffusivity/ Thermodynamics

GOAL: Differentiate mechanisms giving rise to unique properties

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Stability & Structure-Property Understanding

Stability

Predictive tool development

- Phase Field
- Analytical

§ *Grain growth*

§ *Alloying effects on stability*

§ *Thermal stability of layered structures*

§ *Exptl. validation*

Atomistics

Strengthening mechanism prediction & fundamental quantities

- Embedded Atom Method
- Analytical

§ *Interfacial strength*

§ *Dislocation-interface interaction mechanisms*

§ *Exptl. validation*

Mechanical Behavior

Deformation behavior understanding

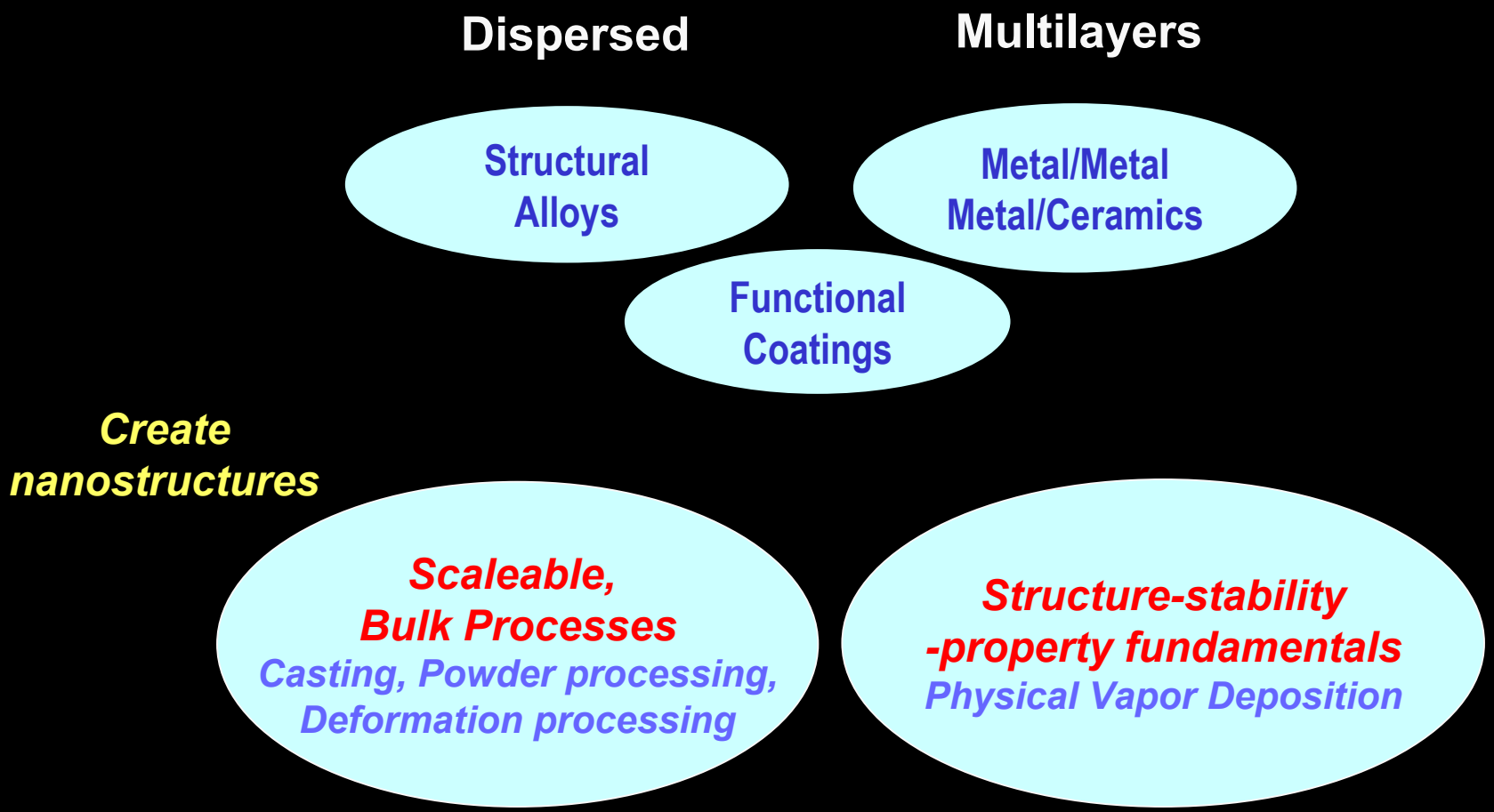
- Analytical
- Numerical

§ *Nano-structural effects on deformation behavior*

§ *HT creep mechanisms in nanostructures*

Modeling across multiple-length scales for structure-to-property understanding in metallic nanostructures

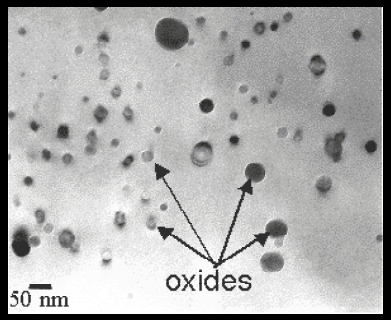
Model Material Systems

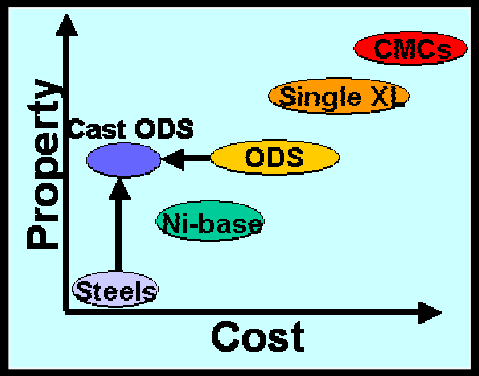


Produce controlled & tailored systems for structure-property understanding
Learn what controls grain growth; high T stability; gb sliding

Cast Oxide Dispersion Strengthened (ODS) Alloys

Objective: Develop technology for dispersion of nano oxides in molten metal castings.





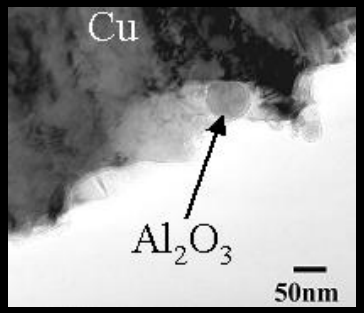
Opportunity
- Lower cost
- Higher strength
- Higher T capability

Technical Barriers:

- ***Wettability & reactivity at particle/matrix interface***
- ***Dispersion, initially and during solidification***

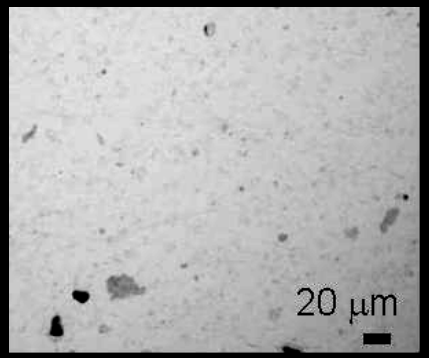
Dispersion Technologies
- **Coatings**
- Active Elements

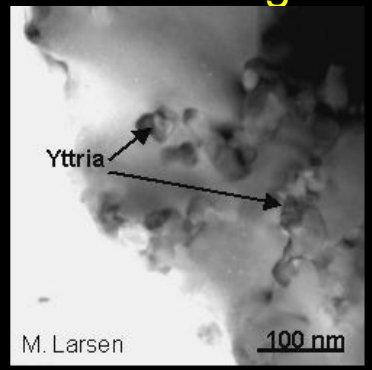
Power feedstock



Coat feedstock

Melt and Solidified casting





Agglomerated n-yttria + detached n-oxides

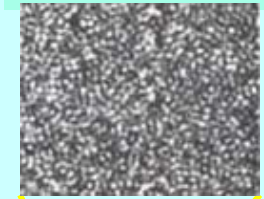
Initial results showed some wetting and dispersion of nano-oxides in molten metal

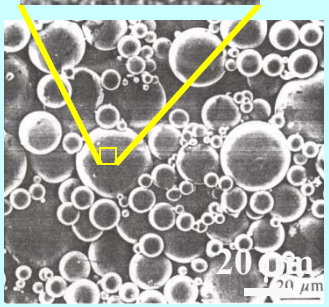
Amorphous-Induced Nanocrystalline Materials

Bulk Amorphous Phase
- Non-crystalline
- Isotropic
- No segregation
- **Producible in bulk by conventional methods**

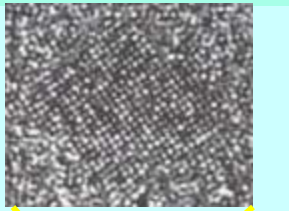
\+ Heat Treat =

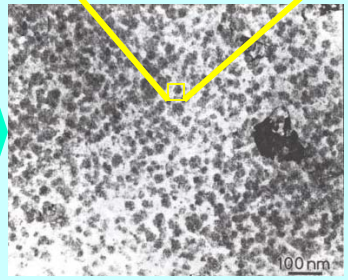
Nano-crystalline Materials
- Ultra-fine grains
- Uniform distribution
- Nano-particles
- **Varieties of primary/second phases possible**





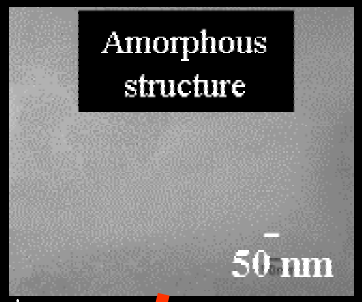
Powder Deposition, Consolidation

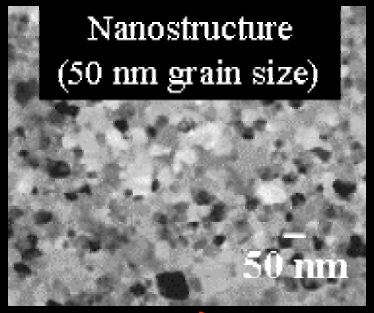


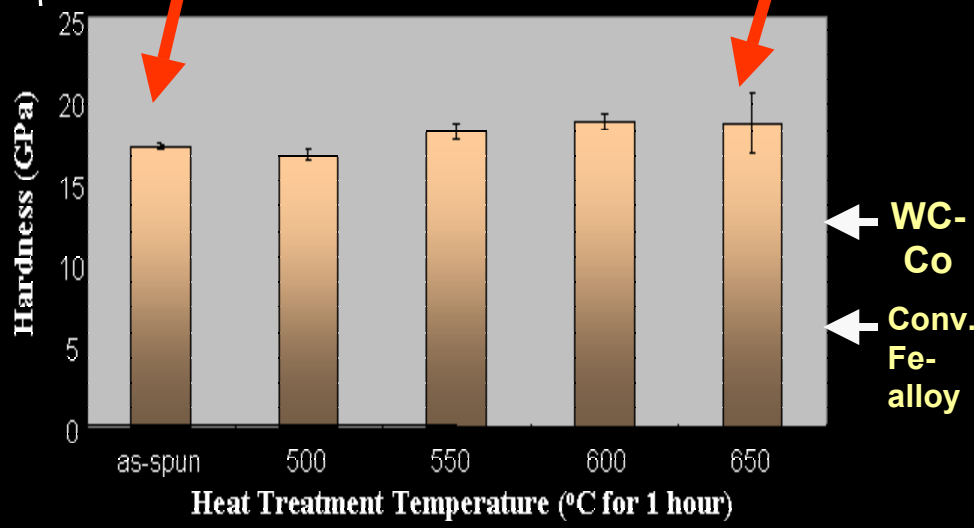


- **High Strength**
- **Corrosion Resistant**
- **Damage tolerant**

Nanostructured Fe-Based Materials







Nanostructures created in Fe-based alloys exhibit hardness 4x conventional alloys

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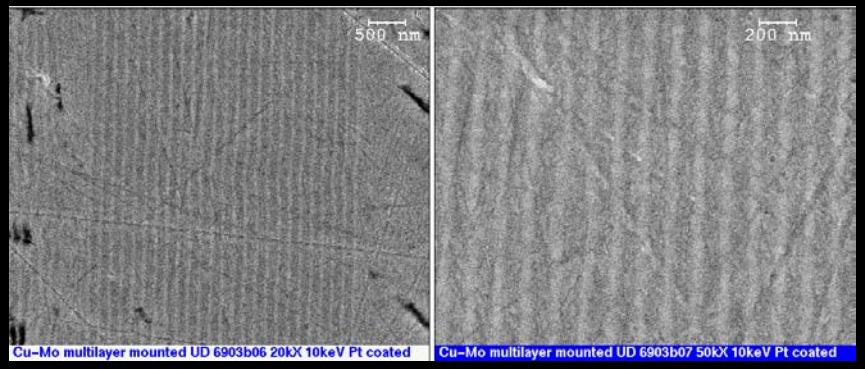
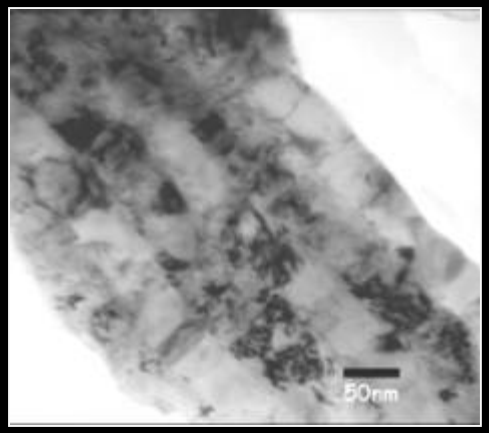
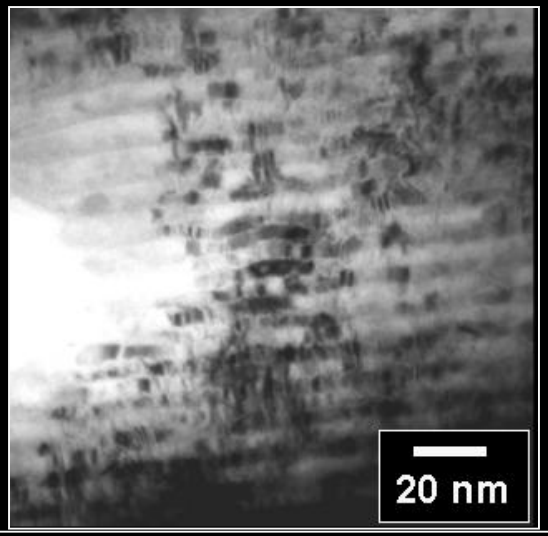
Layered Structures by PVD

(50nm Cu/50nm Mo) x 50

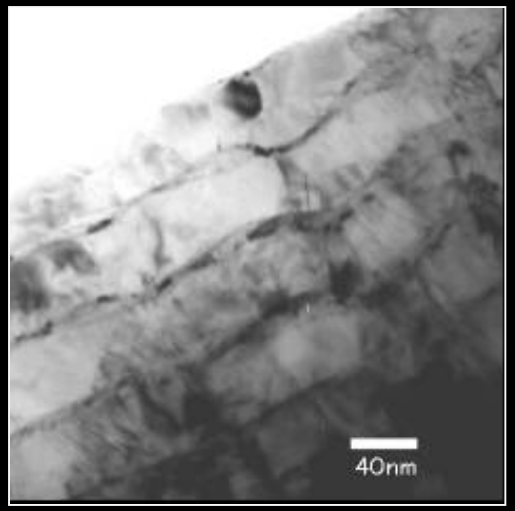




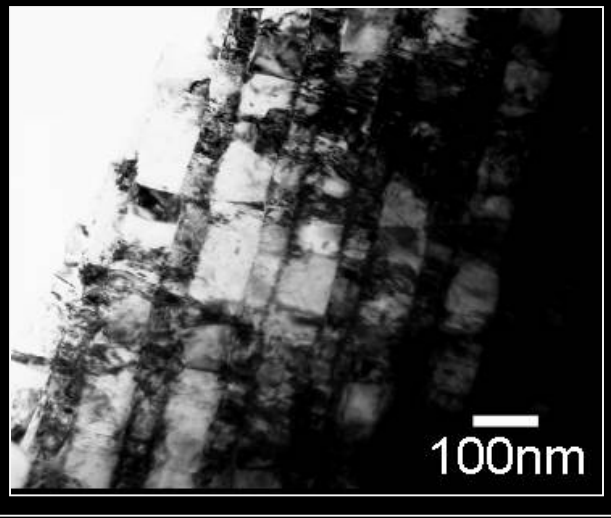
(5nm Cu/5nm Mo) x 50



(50nm Cu/5nm Mo) x 50



(100nm Cu/50nm Mo) x 50



- *Controlled nanolayer systems can be fabricated by PVD*
- *Experiments planned to study variables affecting strength in layered systems*

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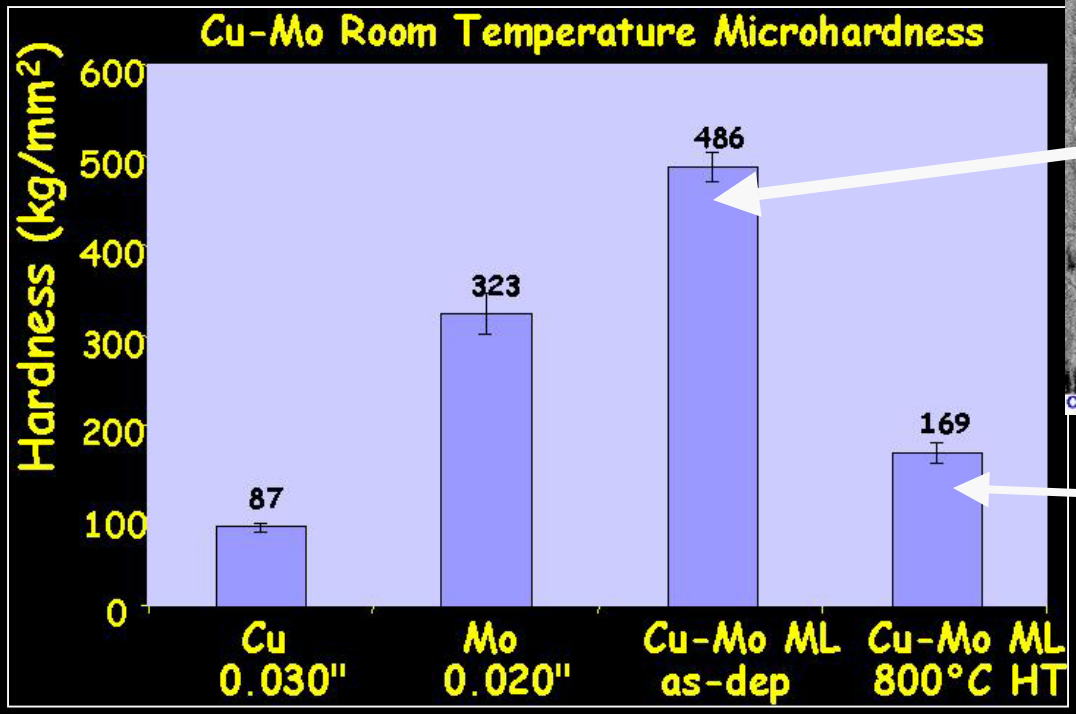
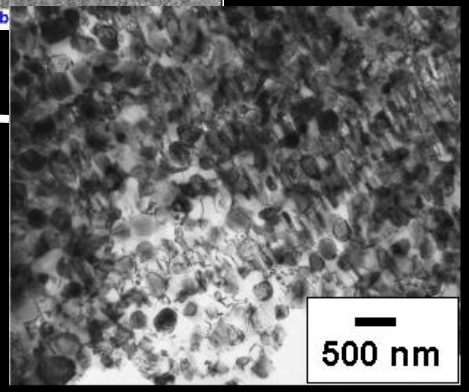
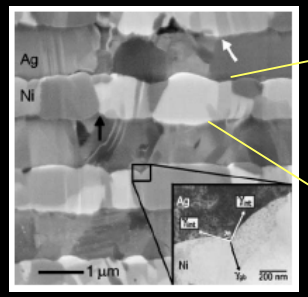
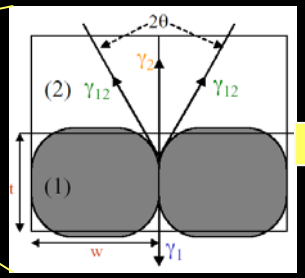
Cu/Mo Sputtered Nanocomposite Multilayers

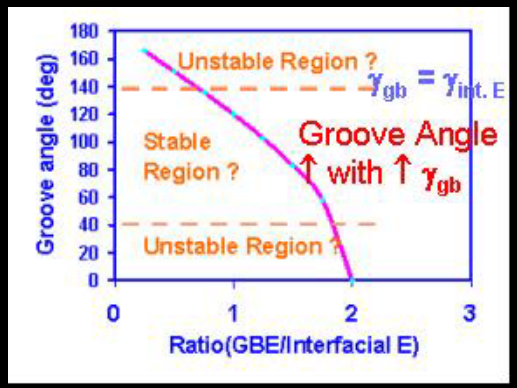






Thermal grooving of GB





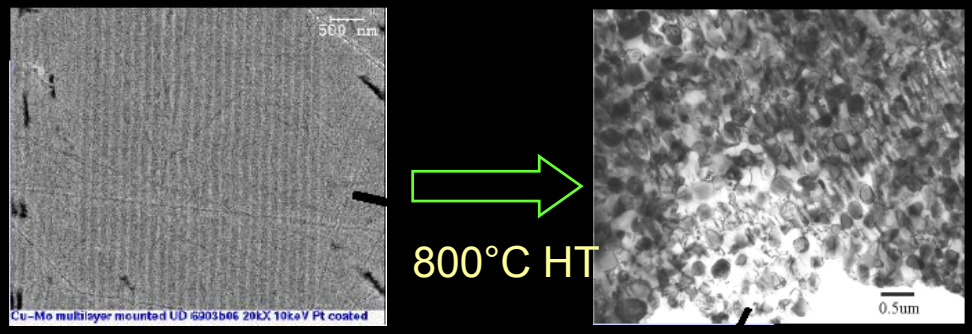
Need predictive model for thermal stability from microstructural variables

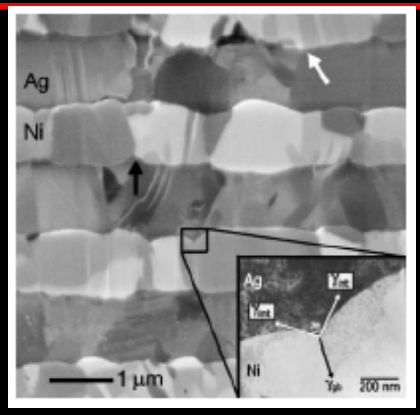
Stability Diagrams

- *Significant increase in hardness demonstrated in nano multilayers*
- *~60% drop in strength for unstable spherodized structure*

Progress on ML stability : Kinetics of grooving

Cu-Mo





Thermal stability of Multilayers :

➔ Instability mechanism: thermal grooving

Kinetic Model:

Evolution of groove depth 'd ' with time 't' :

$$d = (0.78)\ (\tan\beta)[(\Omega^{4/3} D_{int})\frac{\gamma_{int}}{kT}]^{1/4}\ t^{1/4}$$

For a (50 nm/50 nm) Cu-Mo multilayer, time taken for grooving :

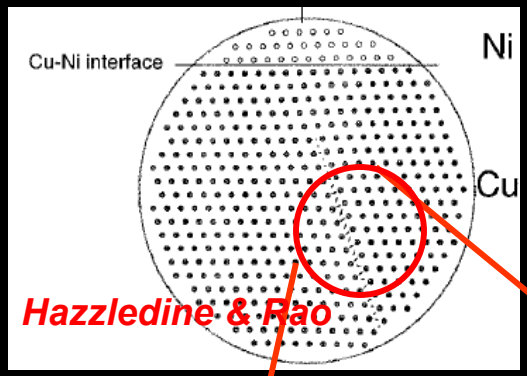
T= 800°C → time ~ 0.006 h
T= 500°C → time ~ 0.16 h
T= 300°C → time ~ 12 h

Refinements Needed:

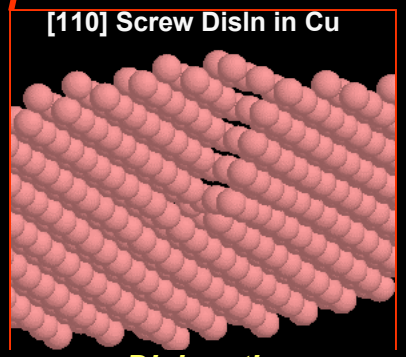
- ***Interface Diffusivity of Cu-Mo***
- ***GBE/interfacial energies dependence with T***

- *HT & TEM to determine groove angle in Cu-Mo multilayers*
- *Refinement of kinetics model needed*

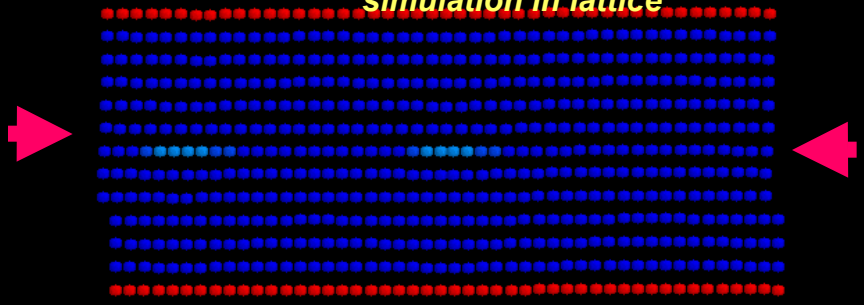
Atomistic Modeling – Barrier Strength in Multilayers



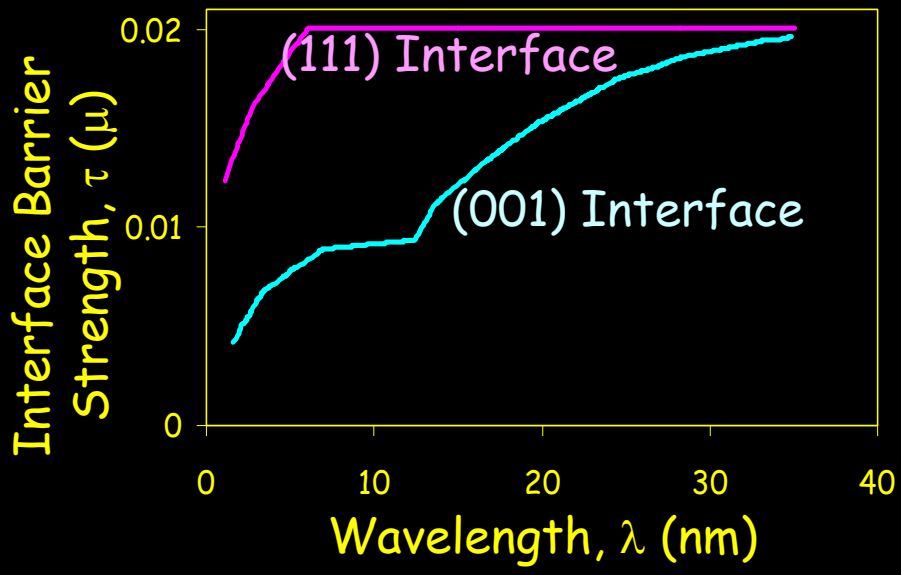
Dislocation vs. Interface in Nanolayers



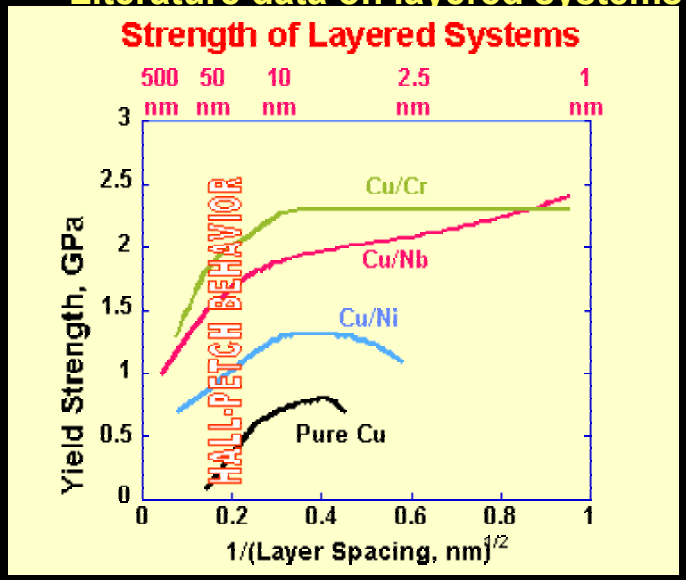
Dislocation simulation in lattice



Dislocation motion under applied stress in Ni lattice

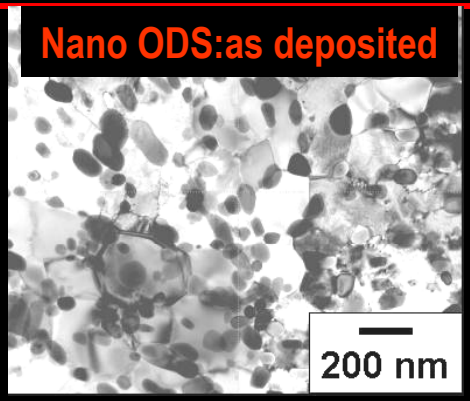


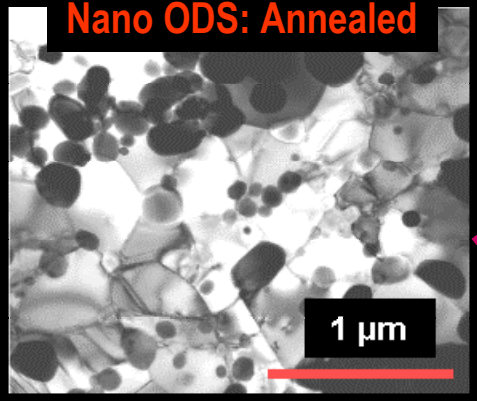
Literature data on layered systems

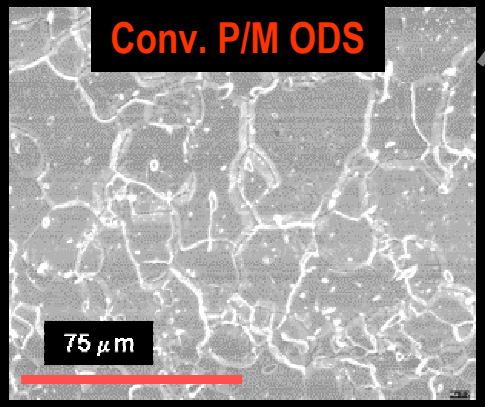


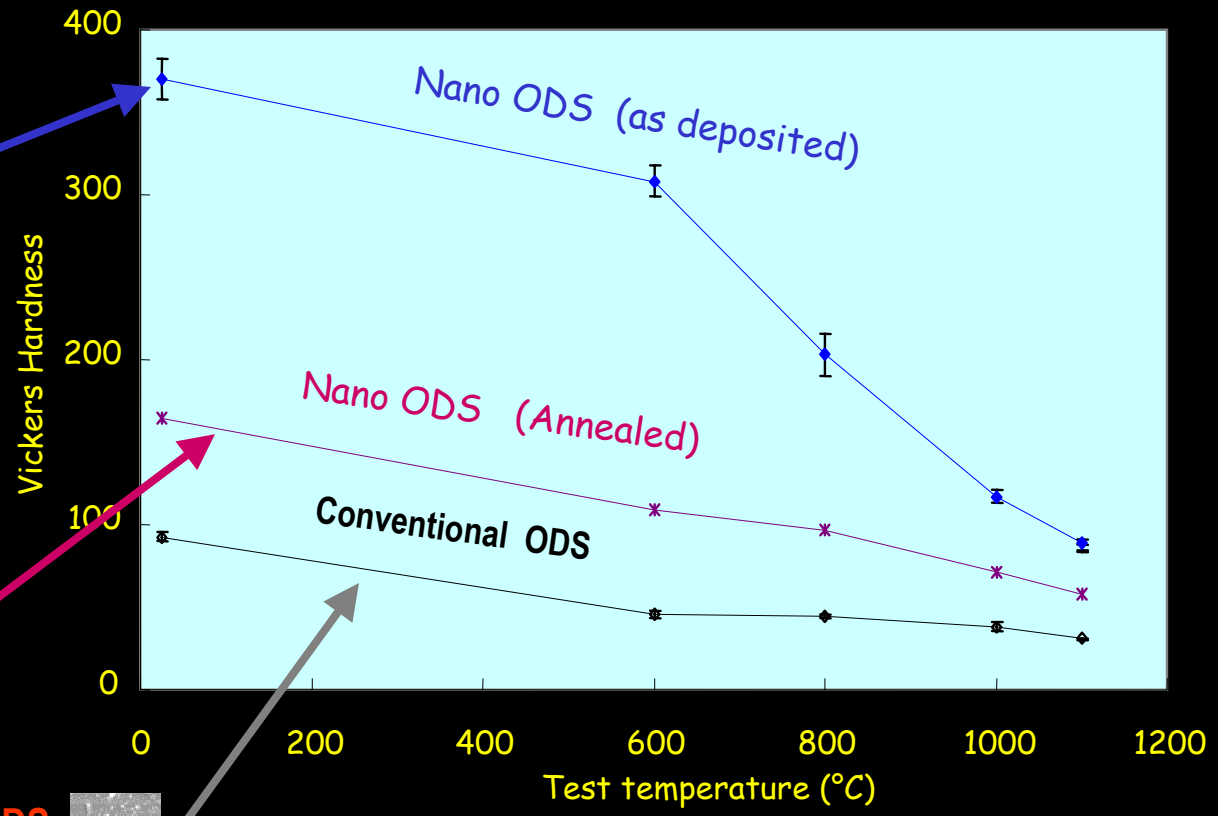
GOAL: Prediction of strength in nanolayered structures

Vapor Deposited ODS Nanocomposites



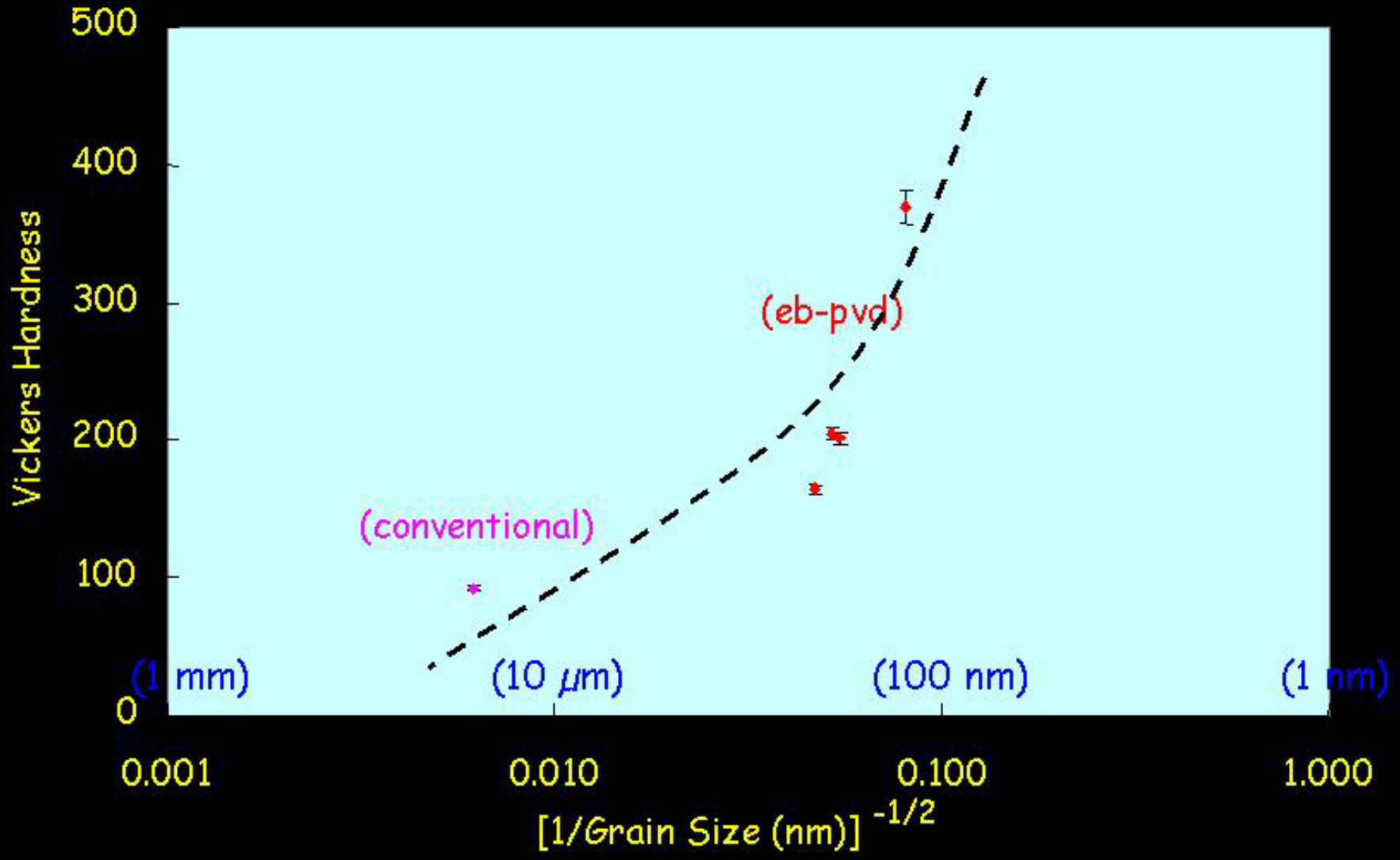






- *Nano ODS structures over 2 times harder than conventional ODS structures*
- *Nano ODS stronger than conventional ODS at all temperatures*

Vapor Deposited ODS Nanocomposites



Nano ODS has ~2-3x greater hardness (strength) than conventional material

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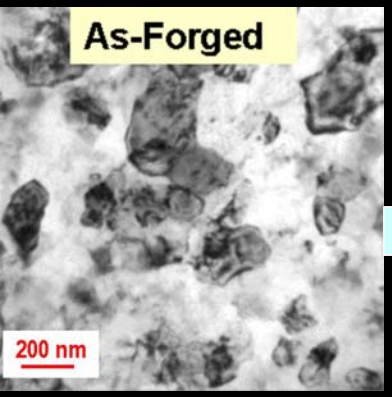
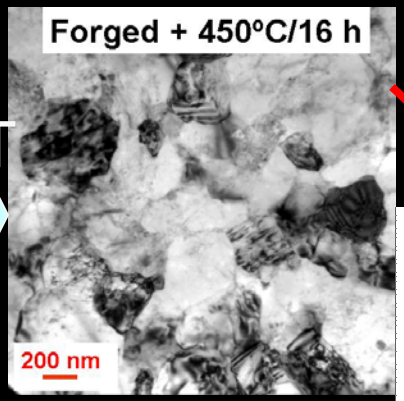
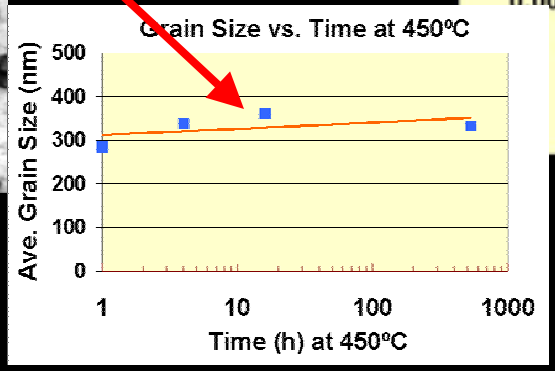
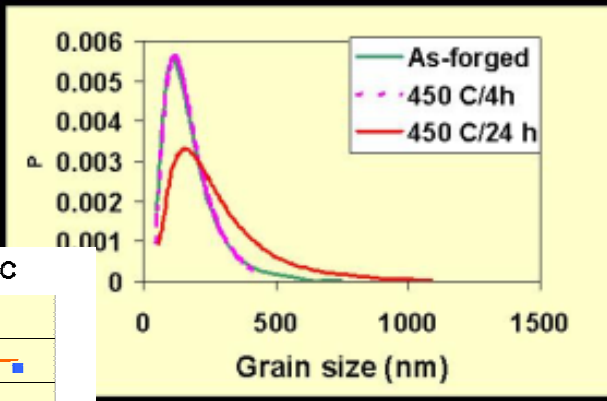
Mechanically Alloyed Nano-Al



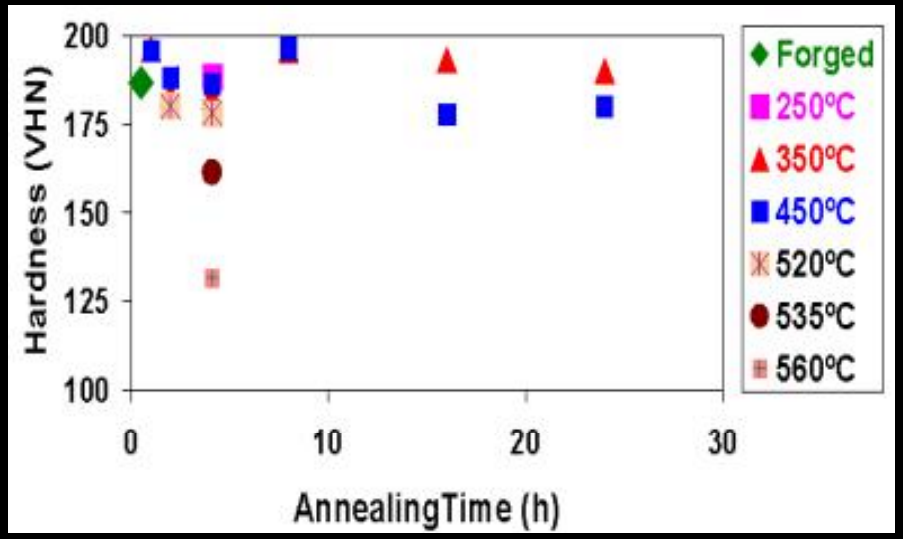
HT



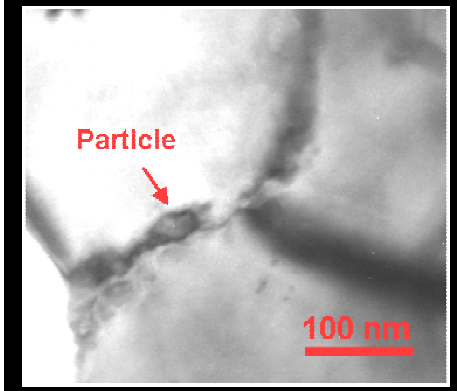


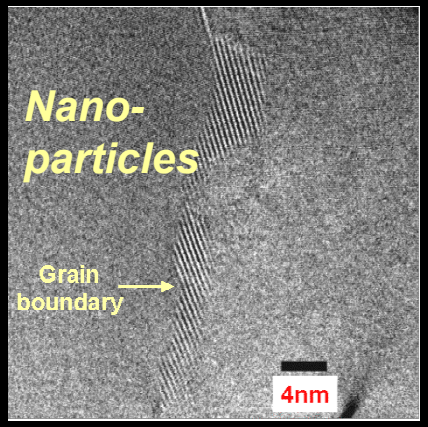


RT Hardness vs. Annealing Temperature & Time



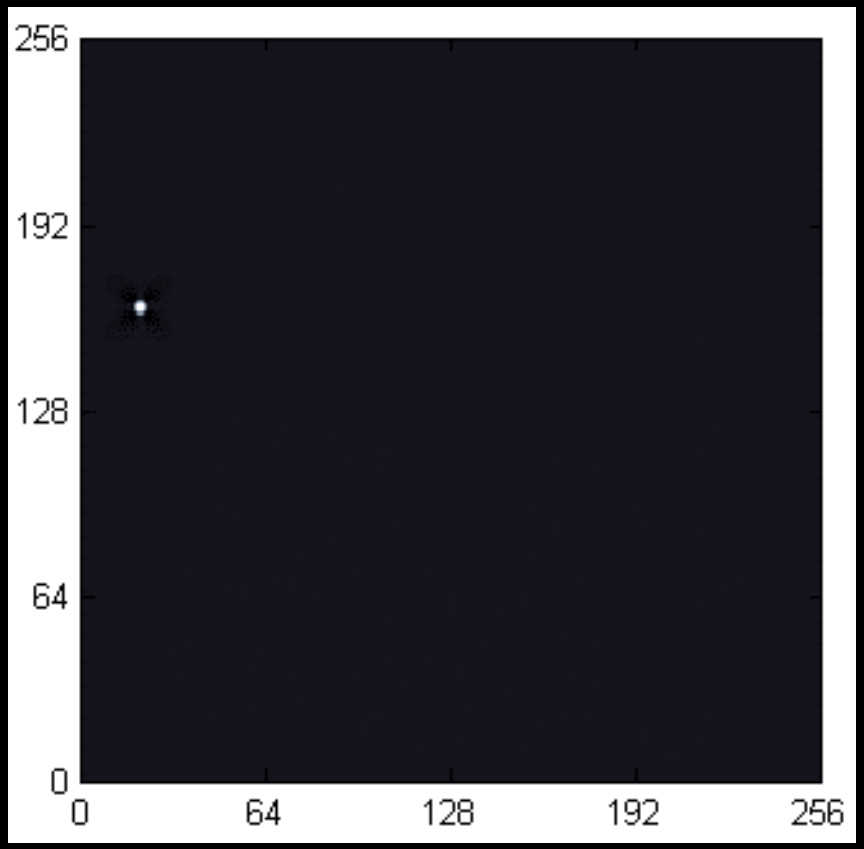
Grain Boundary (GB) Pinning by Particles: Zener Pinning?



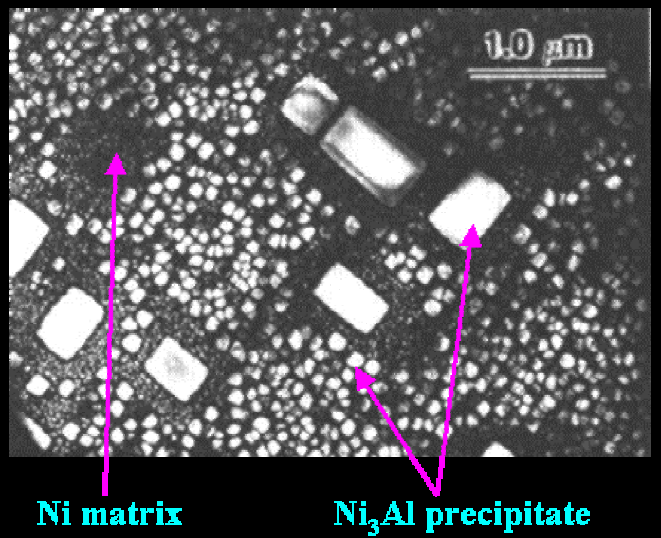


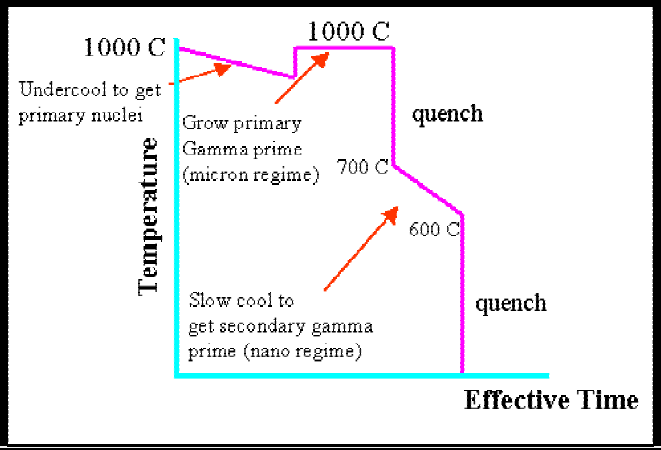
Early stages of understanding of potential stability mechanisms in Nano-Al

Multiscale Modeling: Phase-field Approach



Experimental structure
Micron and nano scales





Phase-field approach is applicable at micron and nano size scales

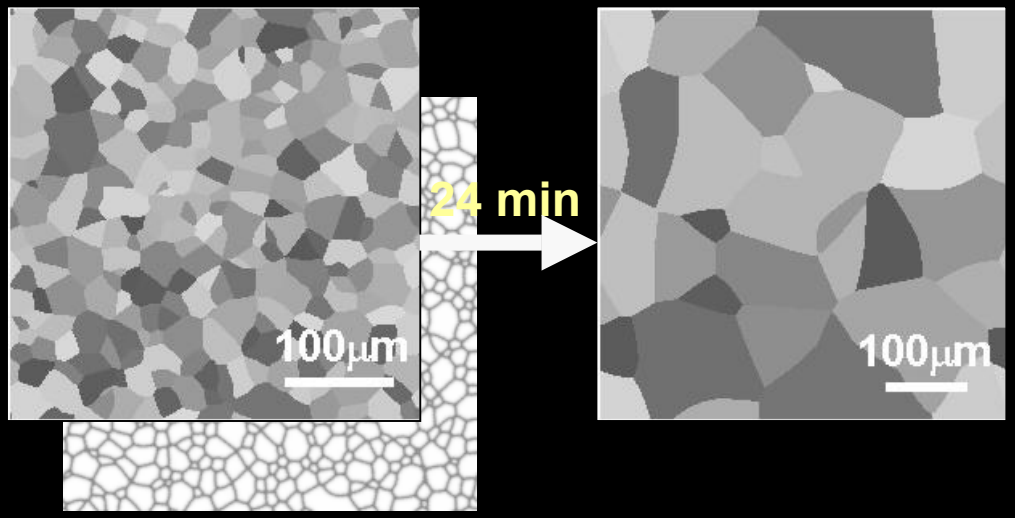
Acknowledgment: Yunzhi Wang, Ohio State University

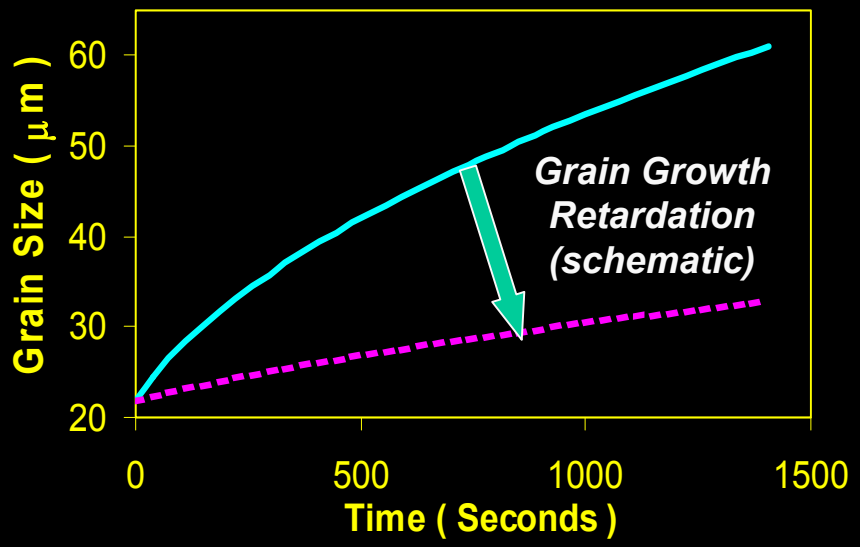
Thermal Stability– Microstructural Evolution Modeling

Thermodynamics
Diffusion
Strain energy
Surface Energy
Morphology

- *How much of second phase (V_f)*
- *Size (d_p)*
- *Shape*
- *Crystal structure & orientation relationship*
- *Stability*

Initial modeling efforts: Ni @ 800 °C



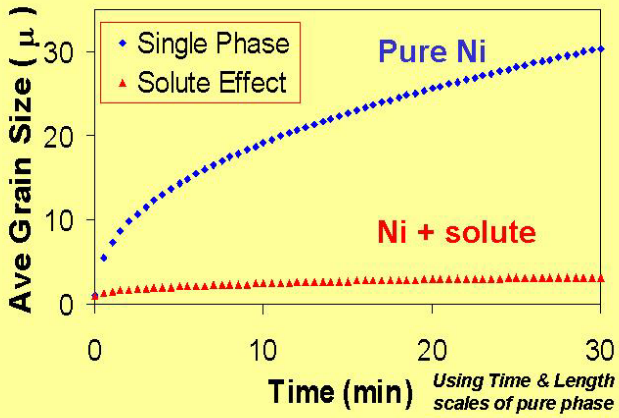


Grain growth model in place for predicting thermal stability of nano-structures

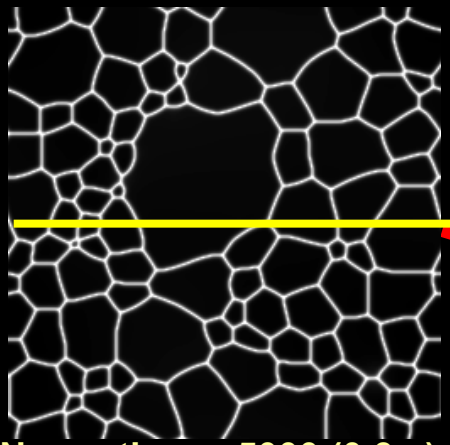
Thermal Stability– Microstructural Evolution Modeling

Grain growth in pure Ni: Model vs. Validation

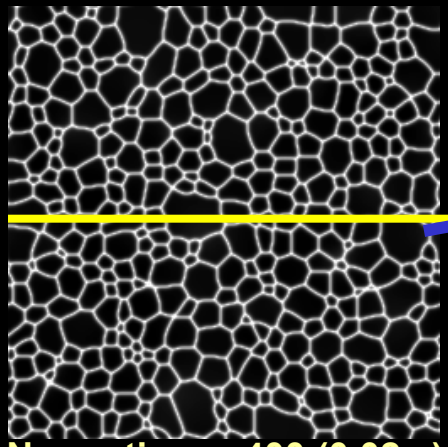
T (°C) / t (min)	Grain Size (μ) Starting GS = 16.4 μ	
	Model	Expt
800/30	35.5	35.1
800/60	44.2	37.9
1000/30	102.1	91.9



Model solute Diffusivity = ½ (self diffusion of Ni)



Norm. time = 5000 (0.3 s)



Norm. time = 400 (0.02 s)

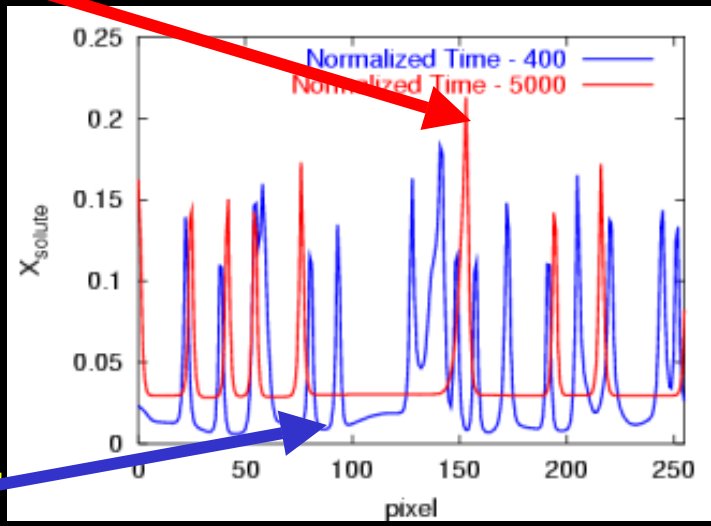
1μm

Solute Segregation (at%)

τ=0: Grain = 5 % GB = 5 %

τ =400: Grain ≈ 1 % GB ≈ 16 %

τ =5000: Grain ≈ 3 % GB ≈ 18 %



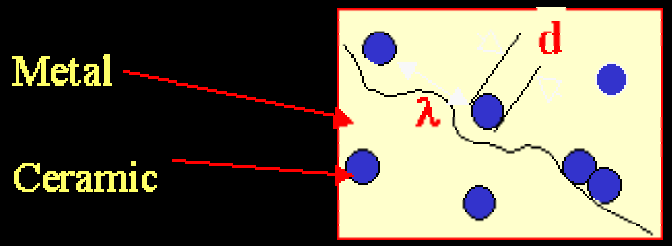
Model predicts significant grain growth retardation with 20% solute at gb
Experimental validation planned with PVD structures

Wear of Dispersoid Structures: Microstructural Effects

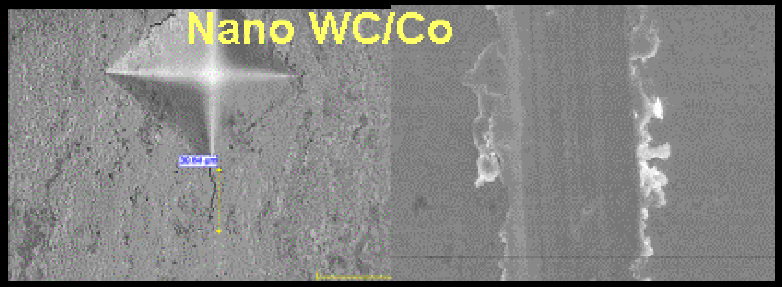
Wear resistance = f (H, K_c)

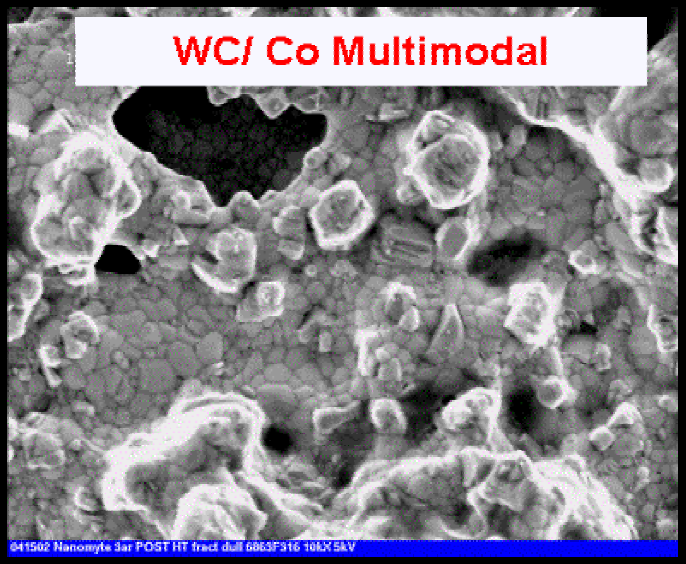
H = Hardness: $f(\lambda^{-1/2})$

K_c = Fracture toughness: $f(\lambda/d)$

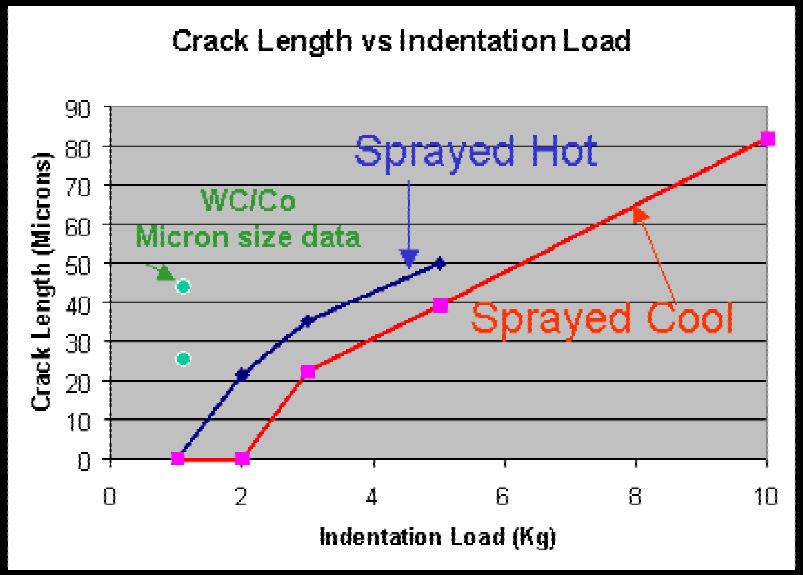


Thermal Sprayed WC/Co Coating





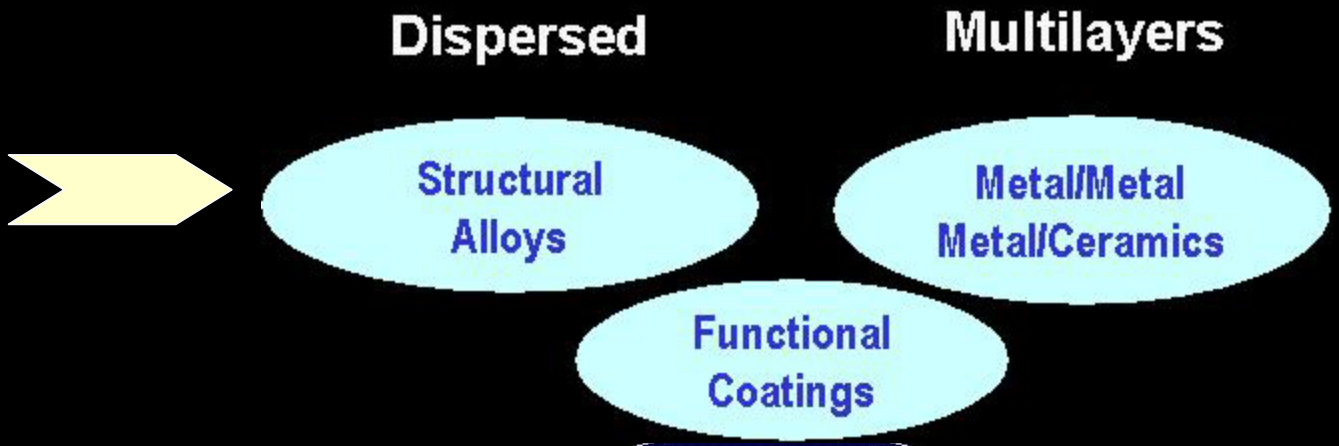
SEM of Fracture surface



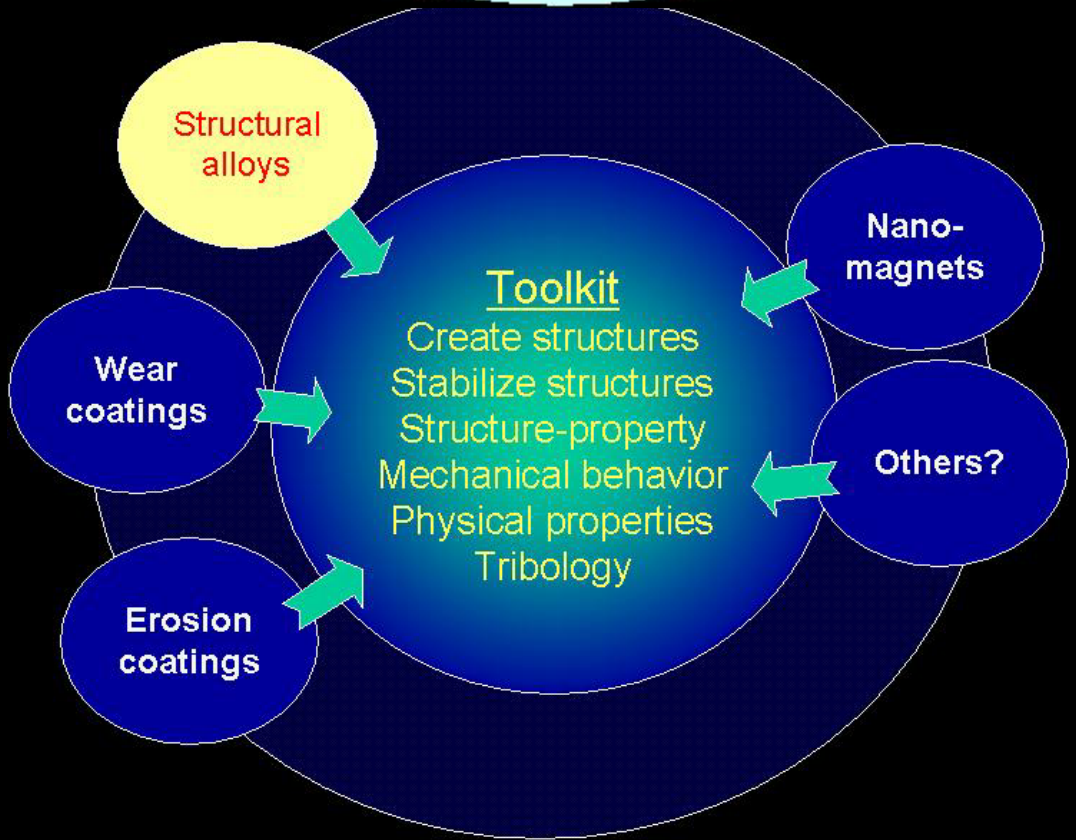
High wear resistance and toughness obtained by nanostructured coatings

What next?

Explore stability & strength in materials with broad-based impact

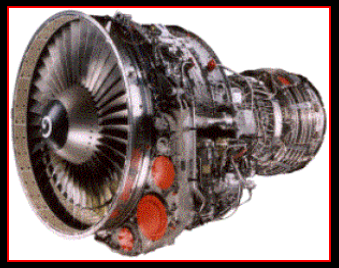


Beyond structural applications??



GE Global Research

Nanocomposites - Breaking Design Limitations



Aircraft Engines

Gas Turbines

Medical Systems

Structural alloys

Nano-magnets

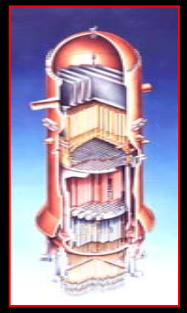
GE Hydro

Wear coatings

Toolkit

Create structures
Stabilize structures
Structure-property
Mechanical behavior
Physical properties
Tribology

Others?



GENE

Erosion coatings

Transportation Systen

Enabler for Multiple Applications

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