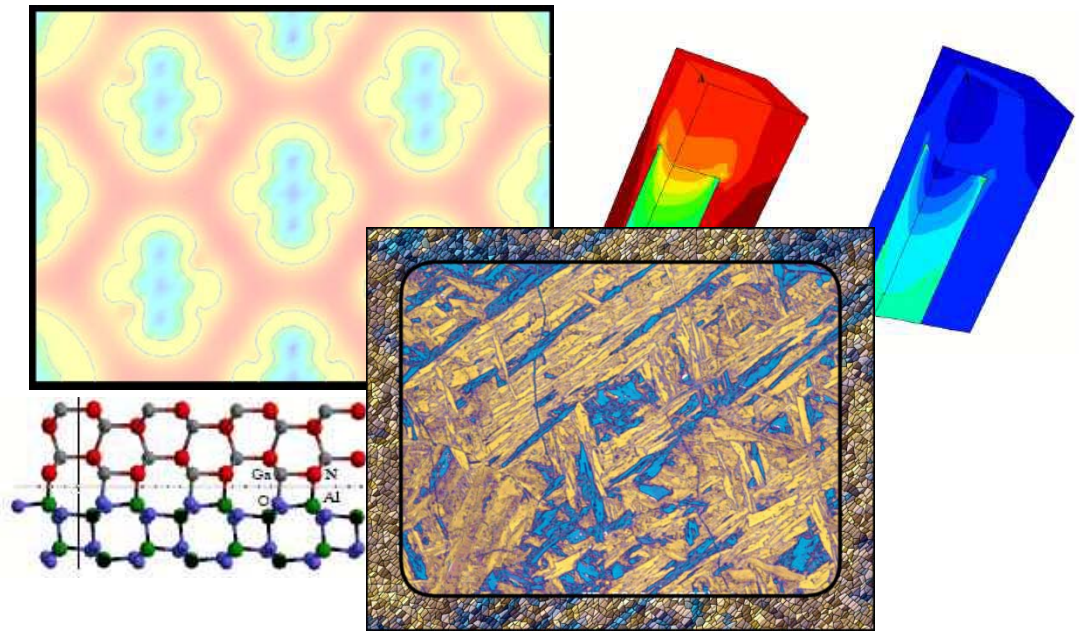
NATIONAL ENERGY TECHNOLOGY LABORATORY

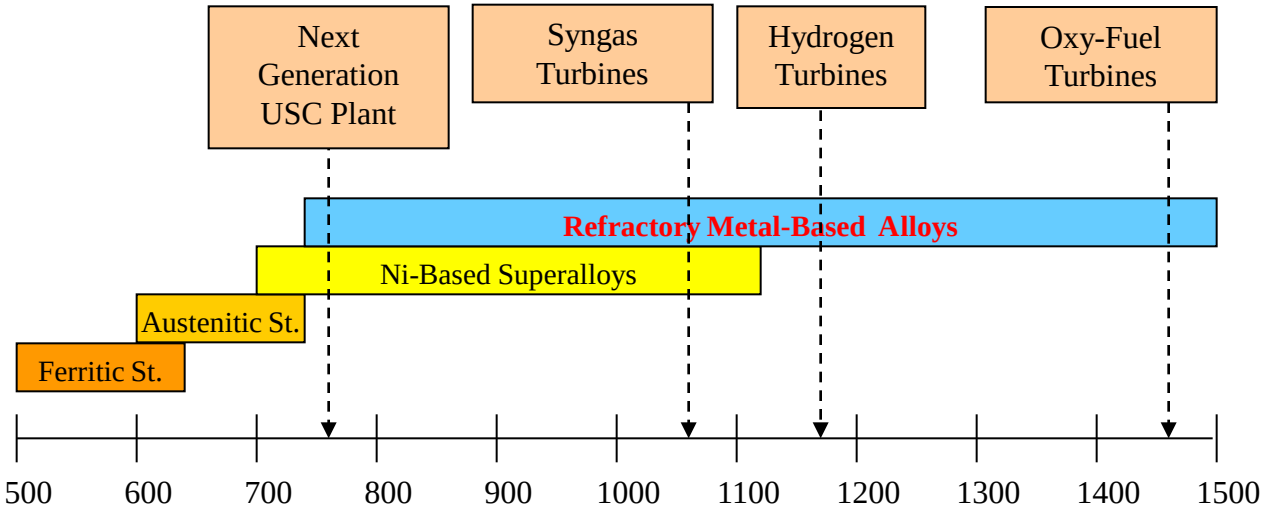


Computational Design and Experimental Verification of Refractory Metal-Based Alloys

Ömer Doğan, Michael Gao, Kaisheng Wu

24th Annual Conference on Fossil Energy Materials – May 25-27, 2010 – Pittsburgh, PA

New Energy Conversion Technologies and High-Temperature Structural Materials



Turbine blade substrate metal temperature (°C) and temperature capability of structural materials

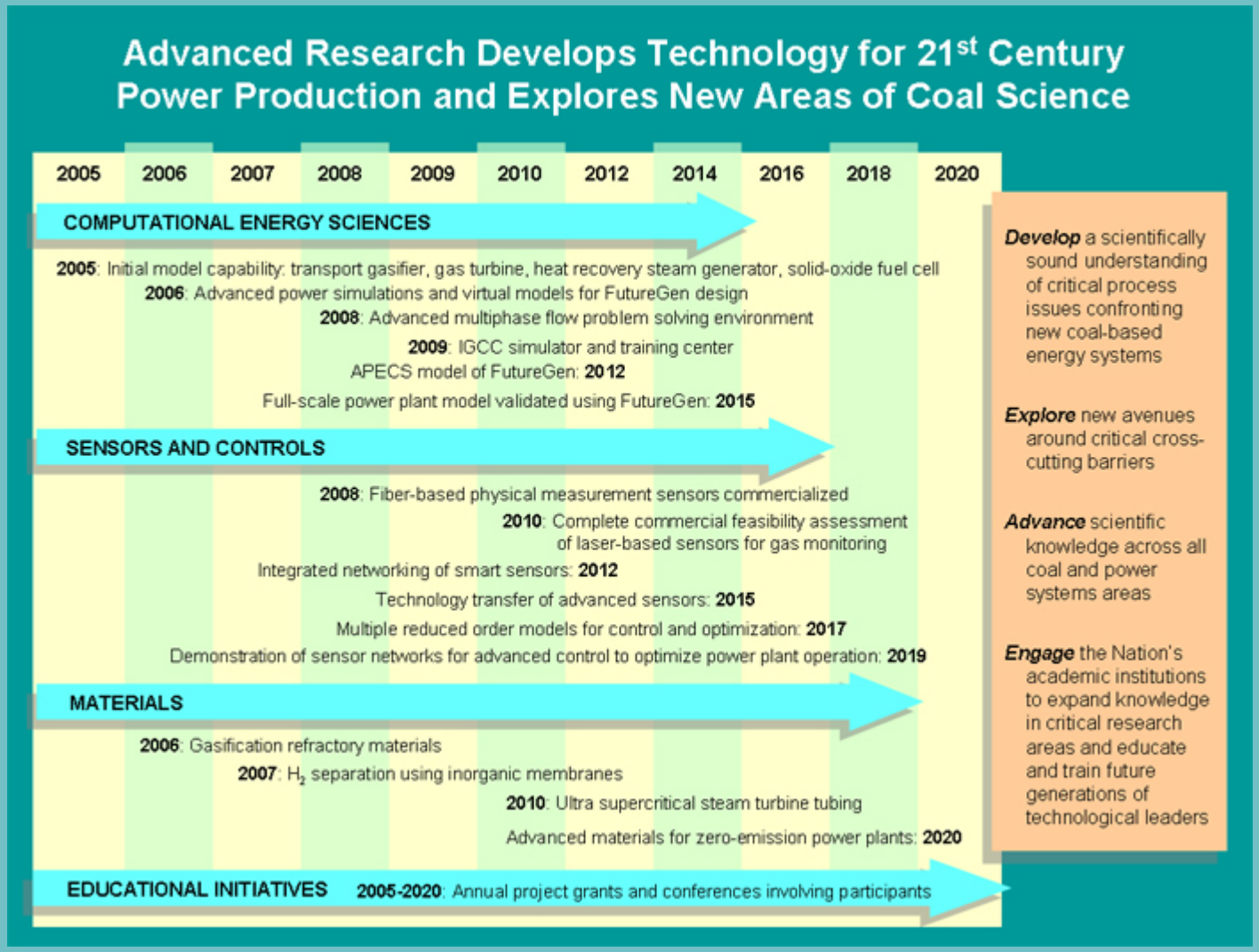
Project Goals

To demonstrate that computational methods and experimental techniques together can be appropriately used to develop novel materials

To improve room temperature ductility of Cr-based alloys, the primary barrier for chromium to be considered as a viable high temperature material for fossil energy applications.

Accelerated development and commercialization of novel materials to enable advanced fossil energy systems

Alignment with FE AR-Materials Program



Why Chromium?

Advantages

- High melting point (1873°C)
- Good strength up to 1300-1400°C
- Low density (7.1 g/cm^3)
- Low CTE (4x10^{-6} /°C)
- High thermal conductivity
- Most abundant refractory element

Challenges

- Room temperature ductility and fracture toughness
- Oxidation resistance above 1000°C
- Creep strength

How do we use computational methods to develop new materials?

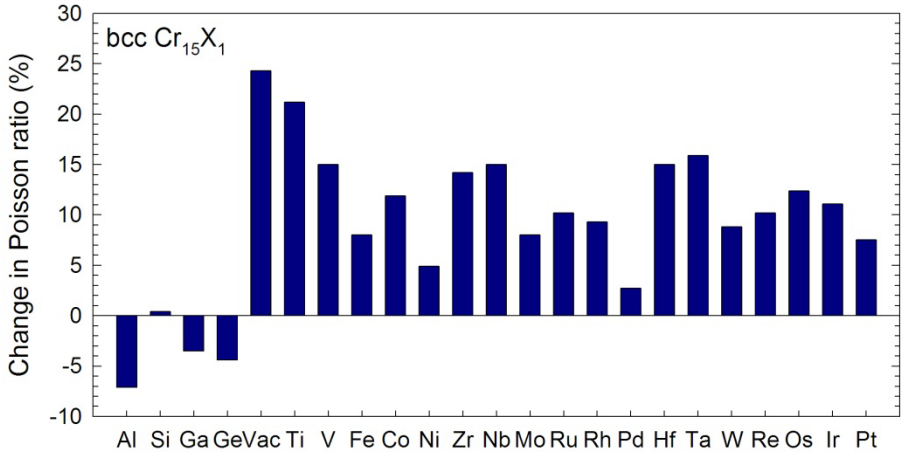
Ductility

Grain boundary segregation

Creep strength

IMPROVING DUCTILITY OF CHROMIUM

Modifying Poisson's ratio of Cr by alloying

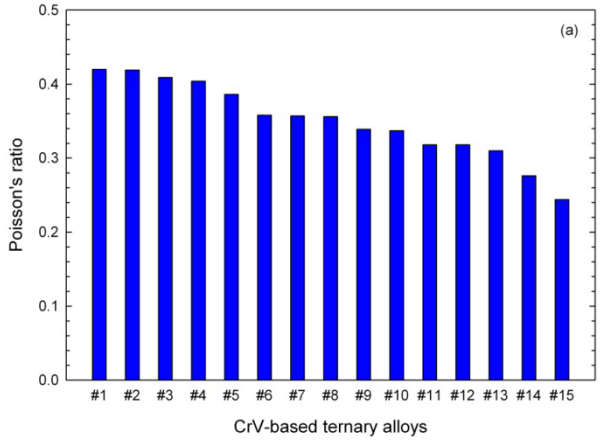


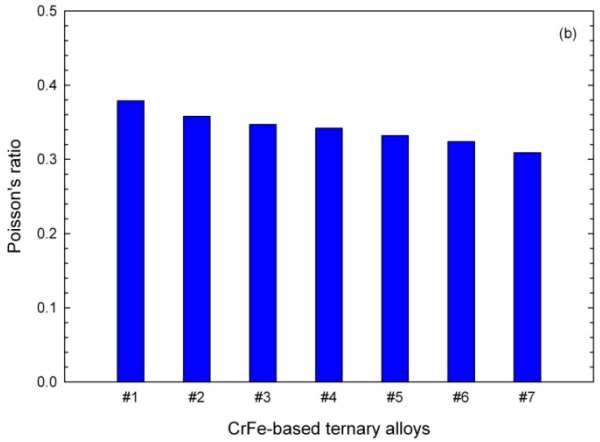
M.C. Gao et al., JOM, 60 (2008), 7, pp. 61-65

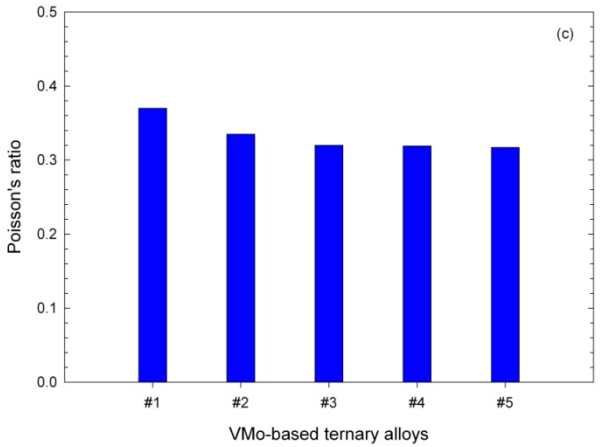
First-Principles DFT Computations

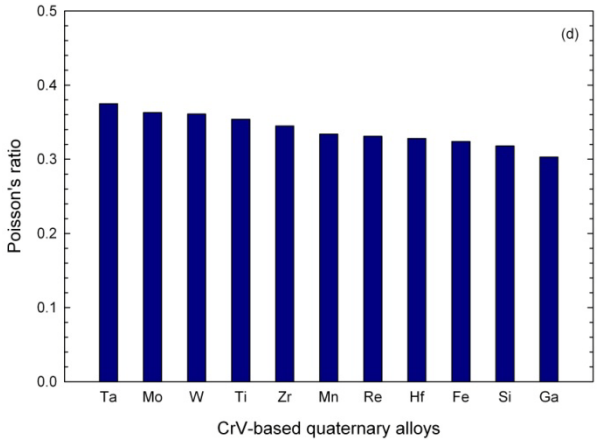
- *VASP package*
- *Projector augmented-wave pseudopotentials*
- *Perdew-Burke-Ernzerhof gradient approximation to the exchange-correlation functional*
- *Energy cutoff = 500 eV*
- *Convergence w.r.t. K-points:1 meV*
- *Precision "high"*
- *semi-core 3p, 4p and 5p electrons treated as valence*
- *Spin polarization considered (antiferromagnetism)*
- *2x2x2 supercell bcc lattice*
- *Binary: composition of $Cr_{15}X_1$ (X=6.25at%) in bcc structure*

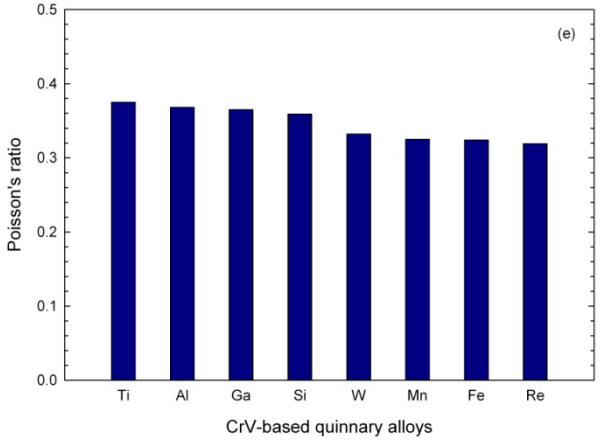
Modifying Poisson's ratio of Cr by alloying

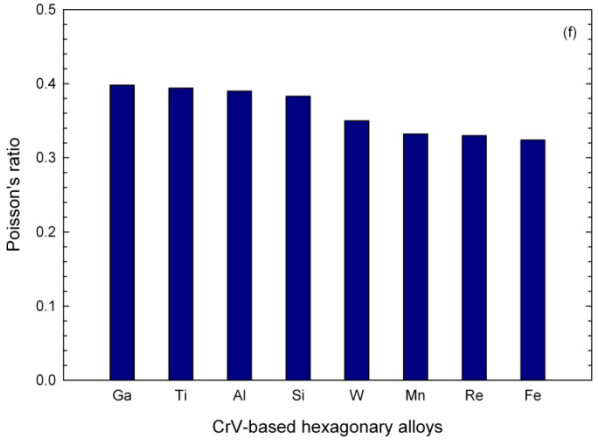




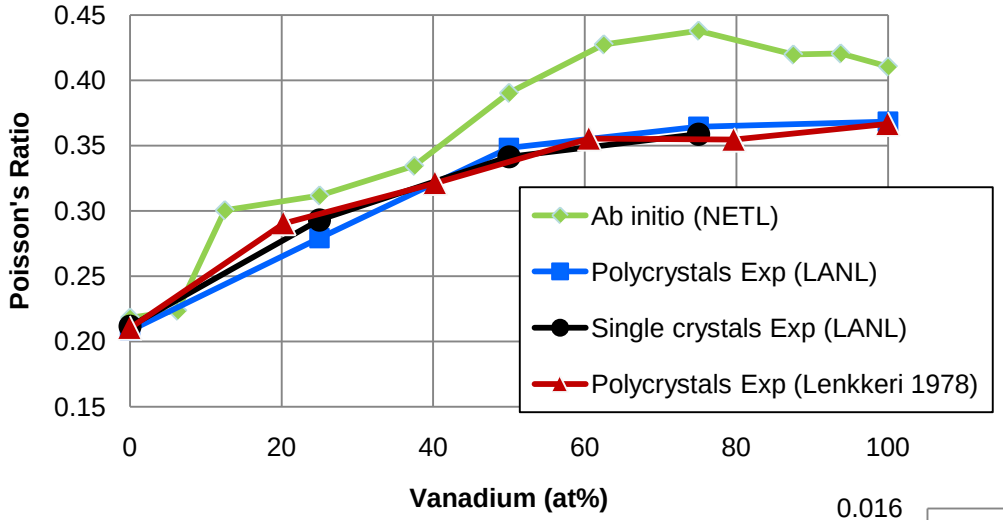






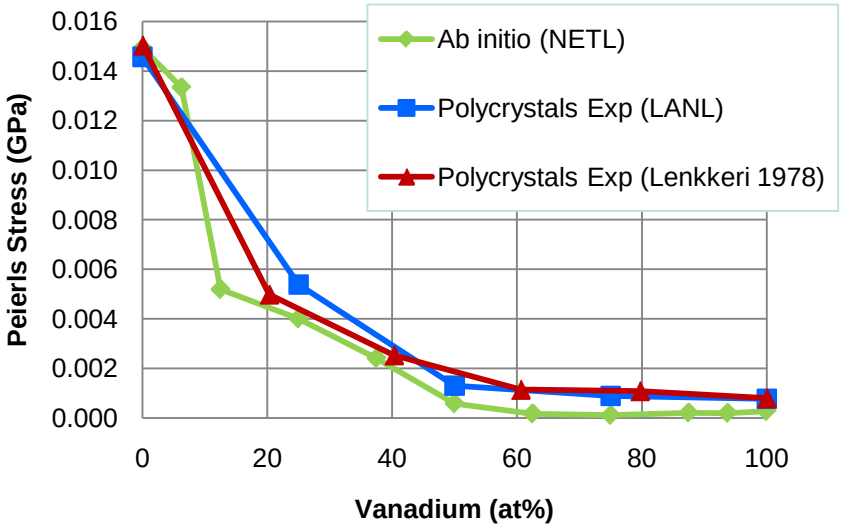


Modification of elastic properties of Cr via alloying with V



$$\sigma_{P-N} = \frac{G}{1-\nu} e^{-\frac{2\pi a}{b(1-\nu)}}$$

$$b = \frac{1}{2}[111]$$



RUS measurements were made at LANL (Y. Suzuki,J. Betts)
Single crystals were grown at Ames Lab (T. Lograsso, D. Schlagel)

Cr-V Alloys
Fabrication and Testing

Blending of powders

HIP
(1250 C – 103 MPa

Heat Treatment
1300 C, 120 h

Extrusion
1200 C, 6:1 ratio

Diffusion Study

Mechanical testing

	Atomic (%)		
Sample	Cr	V	Y
R7	99.96%		.04%
R8	74.29%	25.40%	.31%
R9	48.92%	50.50%	.58%
R10	23.75%	75.40%	.85%

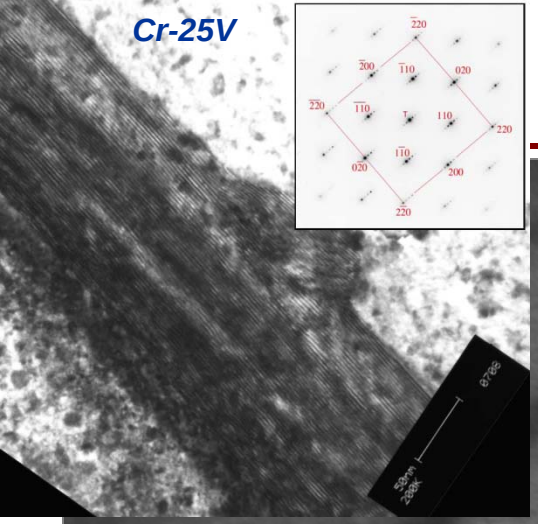
BDTT Determination

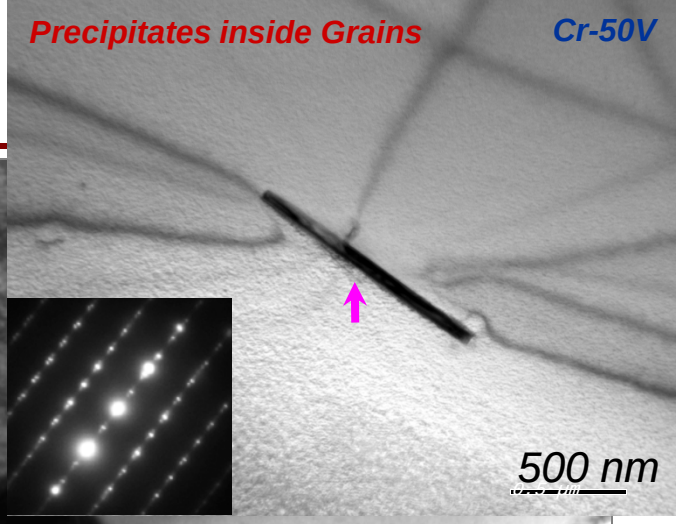
- *3-Point Bend Tests (-40 C – 400 C)*
- *Tensile Tests (-40 C – 400 C)*

Hailey Murdock
Jay Kruzic

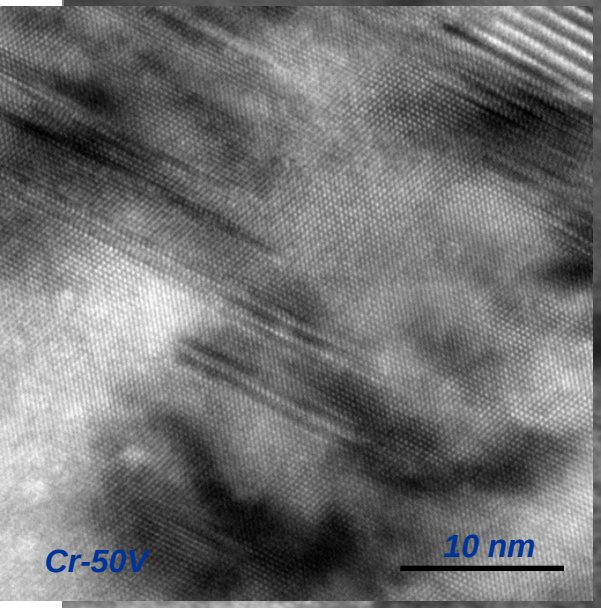
Oregon State University OSU College of Engineering

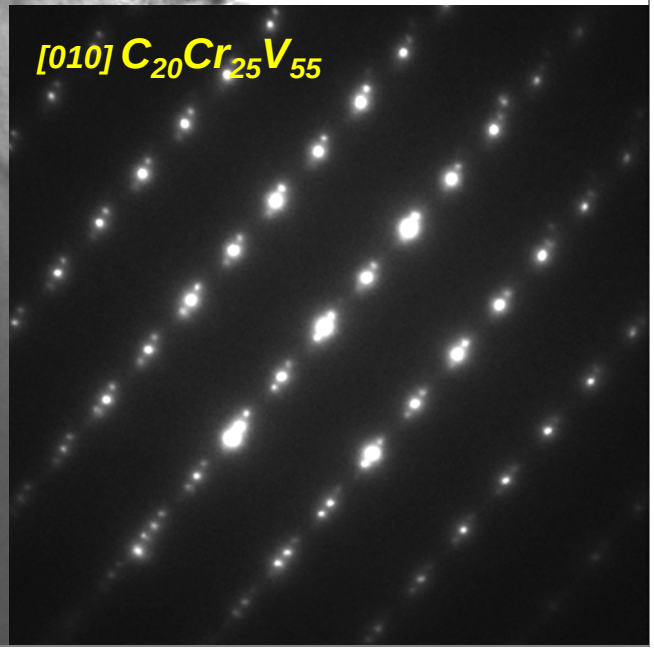
X. Song, West Virginia Univ.
J. Sears, NETL





Precipitates at GB





0.5 μm

Cr-50V

We are developing capability of modeling microstructures using Phase Field Method

Creep mechanisms

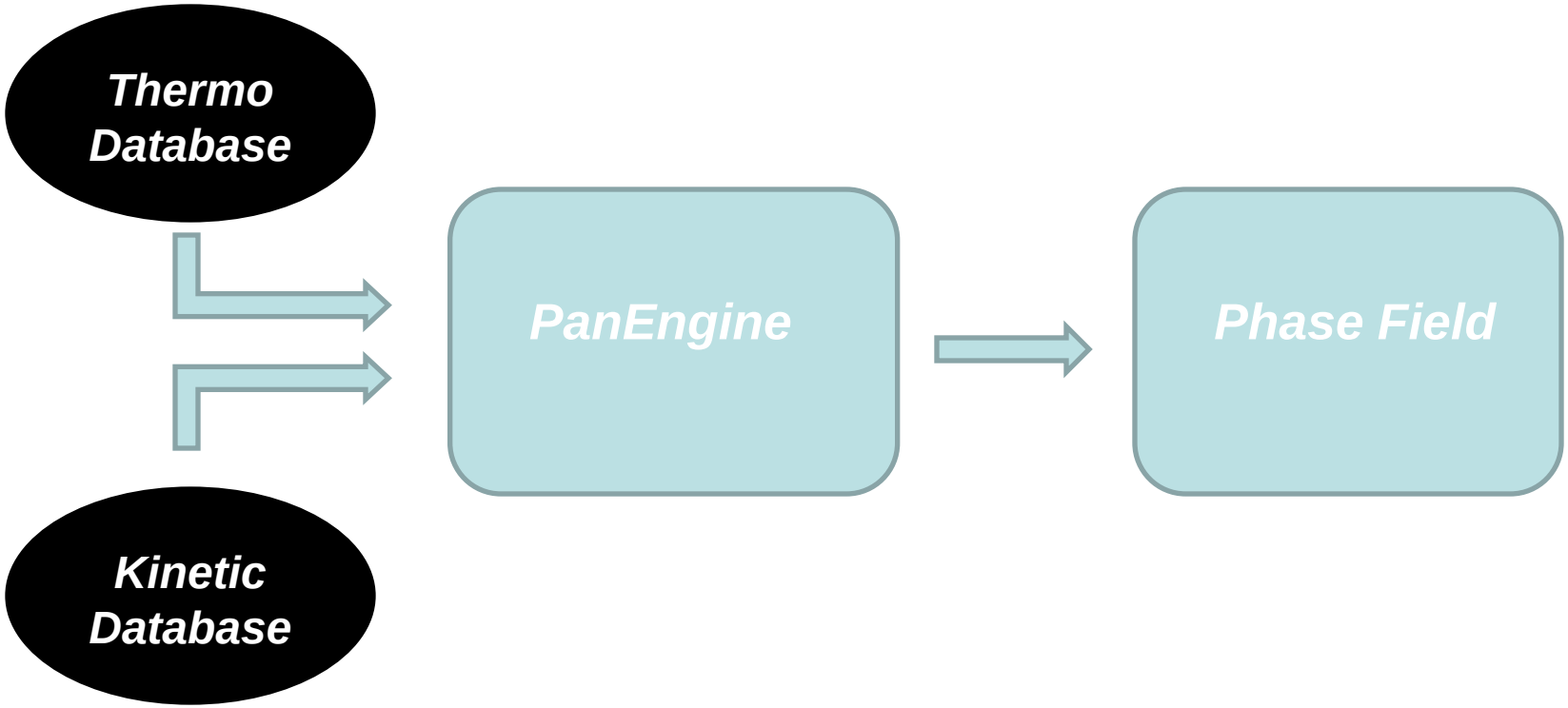
Oxidation scale growth

TBC/Bond Coat/Substrate degradation

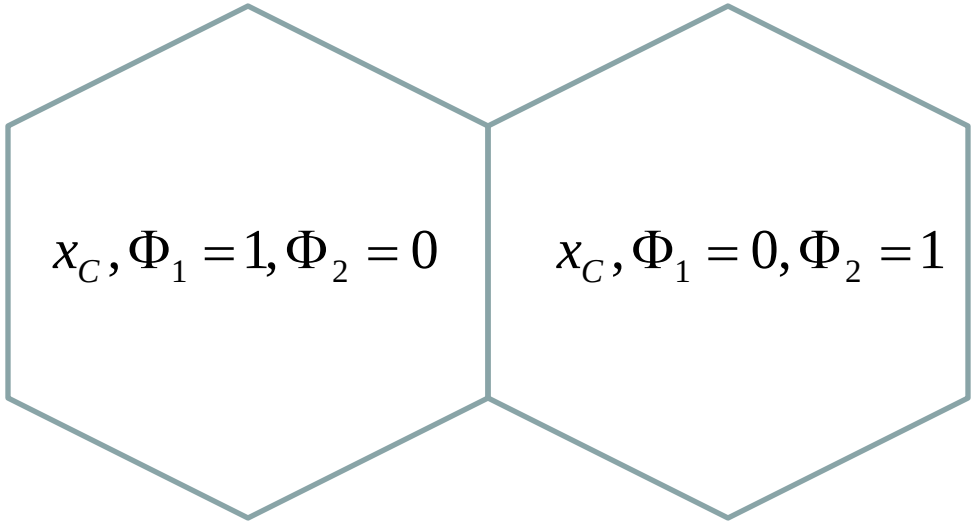
Phase Field Modeling

GRAIN BOUNDARY SEGREGATION

Program



Interstitial Segregation



$$F = \int_V \left\{ \frac{G_m(X_C, T)}{V_M} + f(X_C, \phi_1, \phi_2, T) + \frac{\epsilon^2}{2} \left[\phi_1 (\nabla \phi_2)^2 + \phi_2 (\nabla \phi_1)^2 \right] \right\} dV$$

Sublattice Model

e.g. ***$Fe(C,Va)_3$*** *for BCC(α-Fe)*

Segregation Energy

Segregation Parameters

GB Barrier & Segregation Energy

$$f(X_C, \phi_1, \phi_2, T) = \frac{W_c(T) y_c + W_v(T) y_{v_a}}{2} \phi_1^2 \phi_2^2$$

Chemical Potential of Interstitial

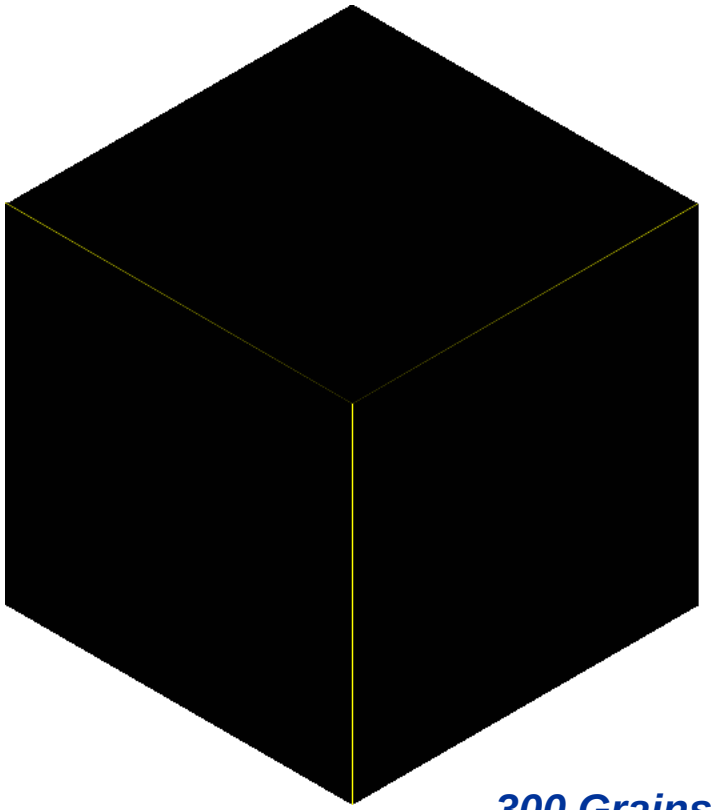
$$\mu_C = \mu_C^h + [W_c(T) - W_v(T)] \phi_1^2 \phi_2^2$$

Diffusion Flux of Interstitial

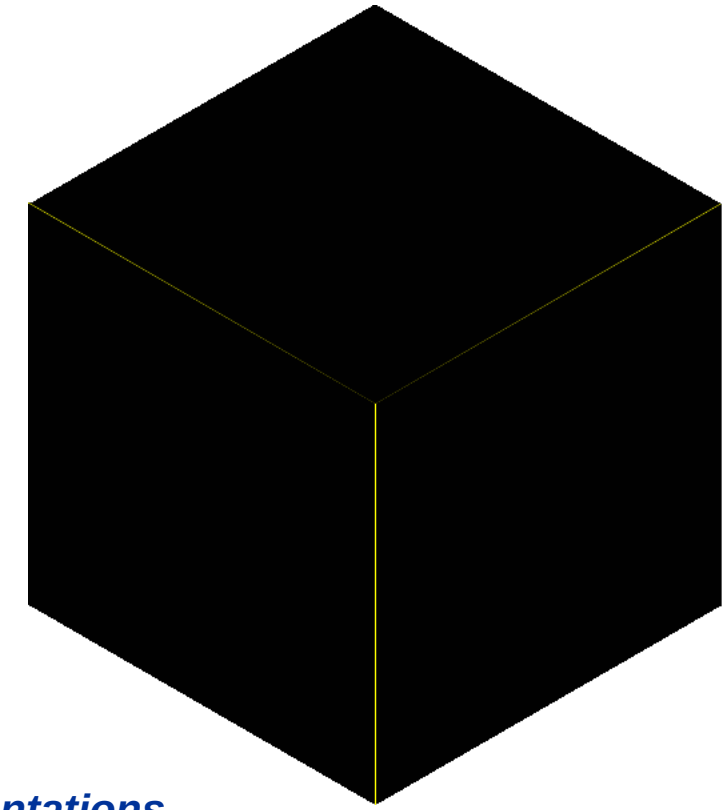
$$J_C = -\frac{c_c}{c_A} (c_c M_A + c_A y_{v_a} M_C) \nabla \mu_C$$

GB Segregation-3D

Grains



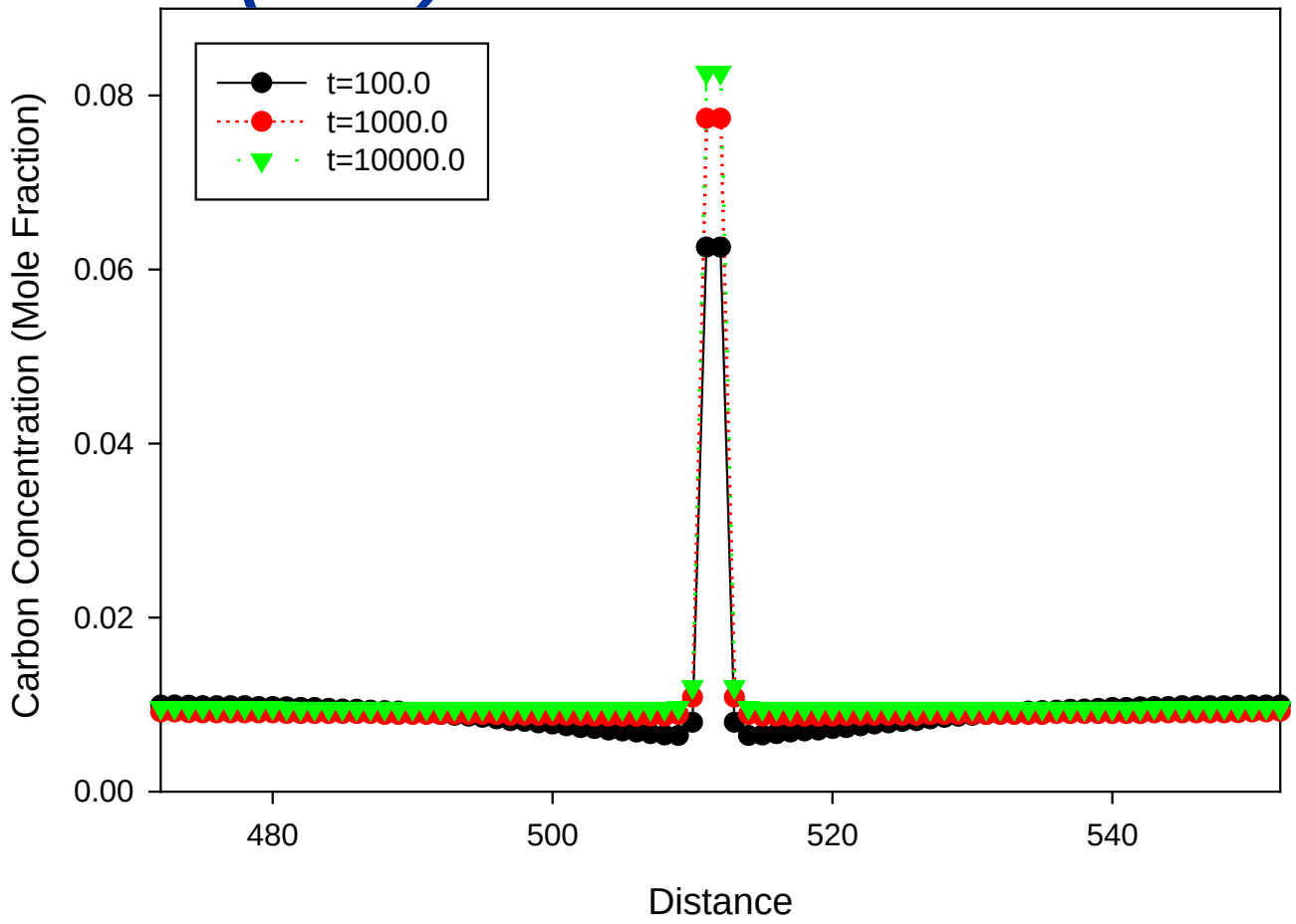
Concentration



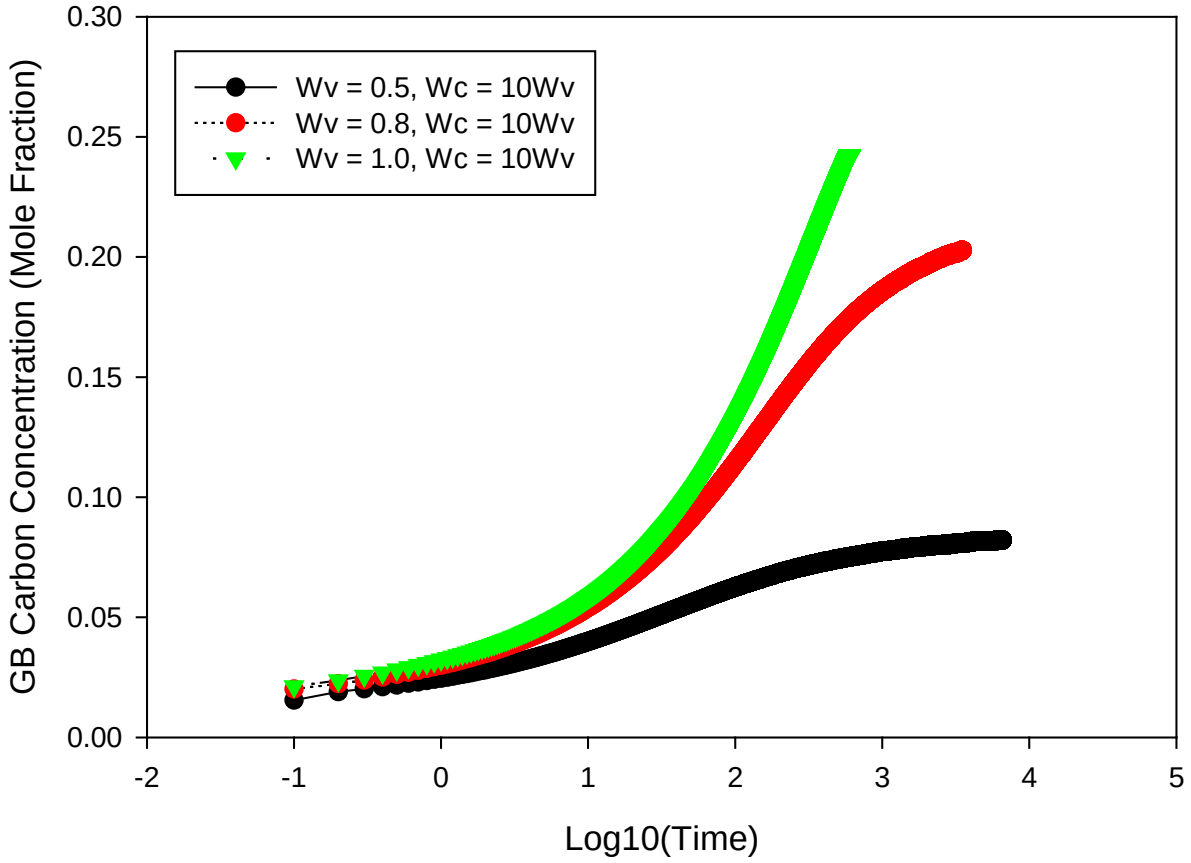
300 Grains, 200 Orientations

Segregation Kinetics

Fe-C BCC (α-Fe)



Effect of Segregation Parameters



$$f(X_C, \phi_1, \phi_2, T) = \frac{W_c(T)y_c + W_v(T)y_{v_a}}{2}\phi_1^2\phi_2^2$$

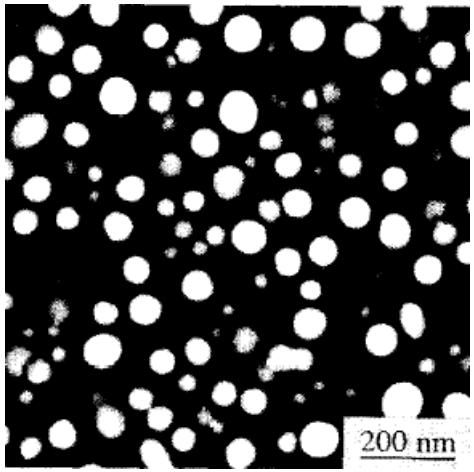
Summary on Phase Field Modeling

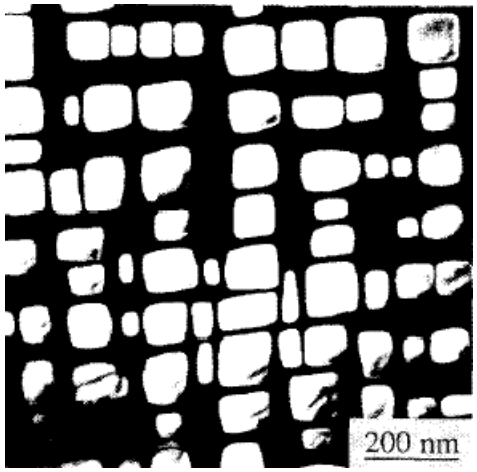
- **Completed**
  - Parallel code
  - Multi-component, Multi-orientation, Polycrystal
  - GB Segregation of Interstitial Solutes
  - Integration with CALPHAD Databases
  - Ready for Real Systems

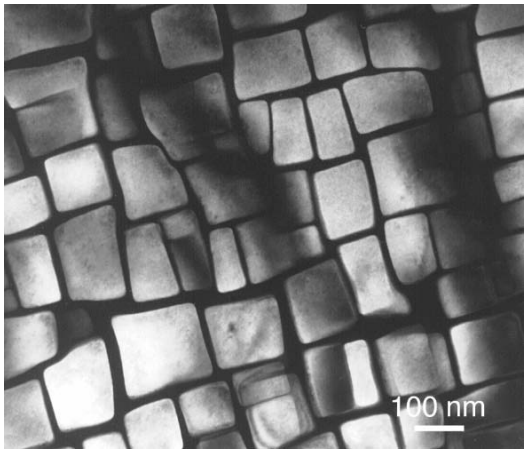
- In Progress
  - Integration with FFT for Mechanical Property Evaluation
  - Integration with First-Principles DFT and KMC Calculations

CREEP STRENGTH IN CHROMIUM ALLOYS

SEARCHING FOR ORDERED PHASES



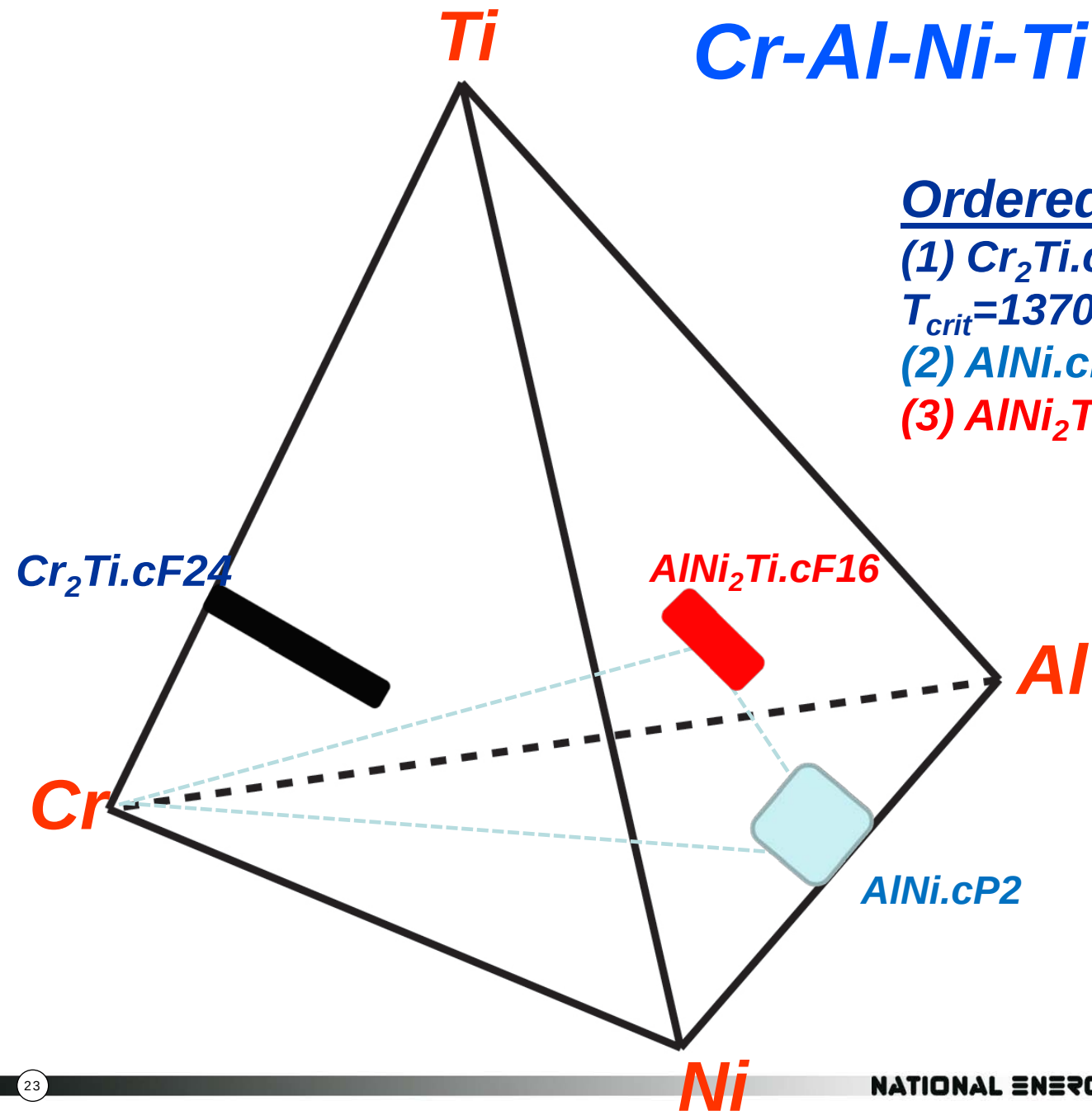




Something like these microstructures

For improved creep resistance
And ideally contribute to the oxidation resistance

Cr-Al-Ni-Ti Quaternary



Ordered phases:

(1) $Cr_2Ti.cF24$ (Laves), $T_{crit}=1370^oC$

(2) AlNi.cP2 (CsCl), $T_m=1638^oC$

(3) $AlNi_2Ti.cF16$, $T_m=1500^oC$

Cr.cI2	$AlNi_2Ti.cF16$	AlNi.cP2
a = 2.87 [cal]	a = 5.8898 [cal]	a = 2.8890 [cal]
a = 2.91 [exp]	a = 5.87 [exp]	a = 2.88 [exp]
C_{11} = 426 GPa	C_{11} = 218 GPa	C_{11} = 214 GPa
C_{12} = 56 GPa	C_{12} = 145 GPa	C_{12} = 138 GPa
C_{44} = 95 GPa	C_{44} = 94 GPa	C_{44} = 119 GPa
B = 179 GPa	B = 169 GPa	B = 163 GPa
G = 124 GPa	G = 65 GPa	G = 75 GPa
ν = 0.219	ν = 0.330	ν = 0.300
	misfit = 0.9%	misfit = 1.0%

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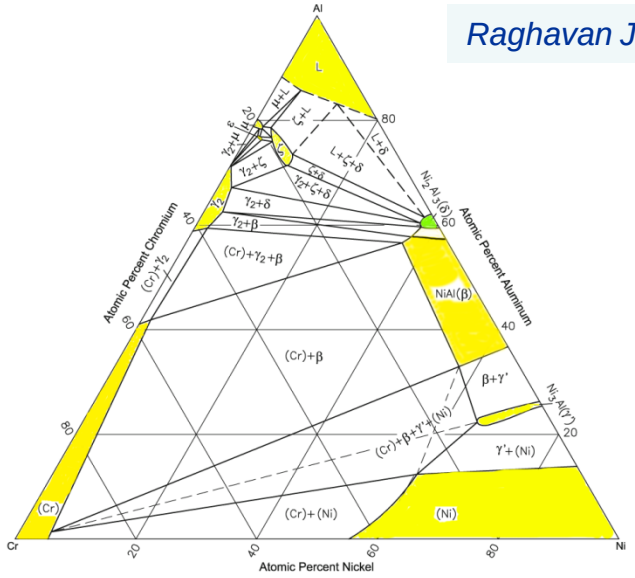

Fig. 4 Al-Cr-Ni isothermal section at 1000 °C [2008Gru1]

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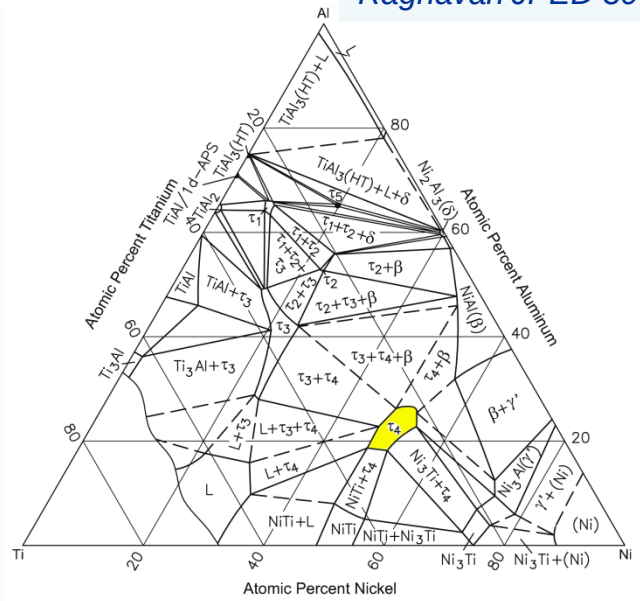

Fig. 1 Al-Ni-Ti isothermal section at 1000 °C [2007Sch]

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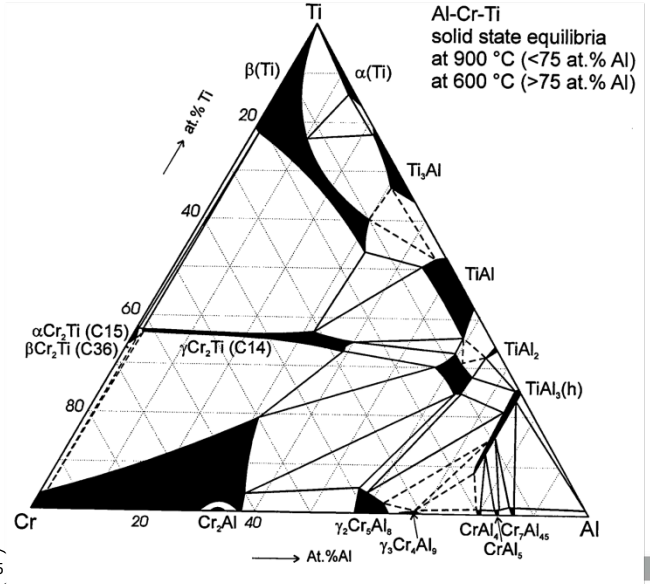
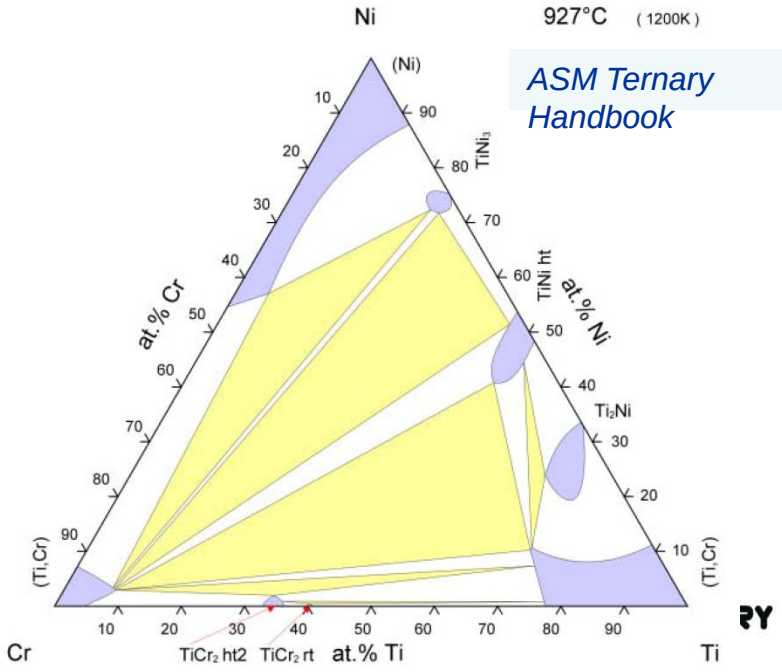
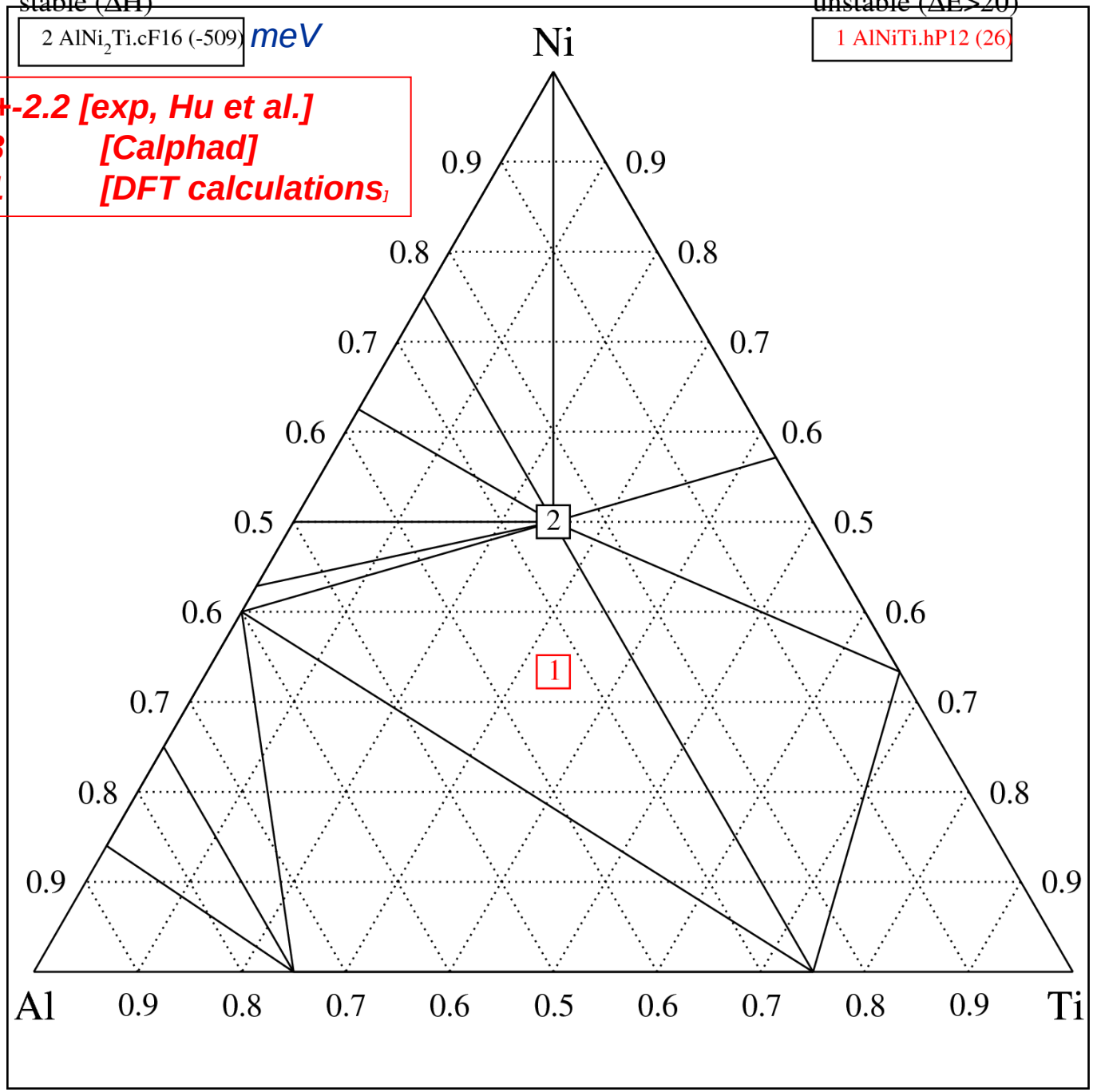


Fig. 1—Solid-state phase equilibria at 900 °C (for ≤75 at. pct Al) and 600 °C (for >75 at. pct Al).

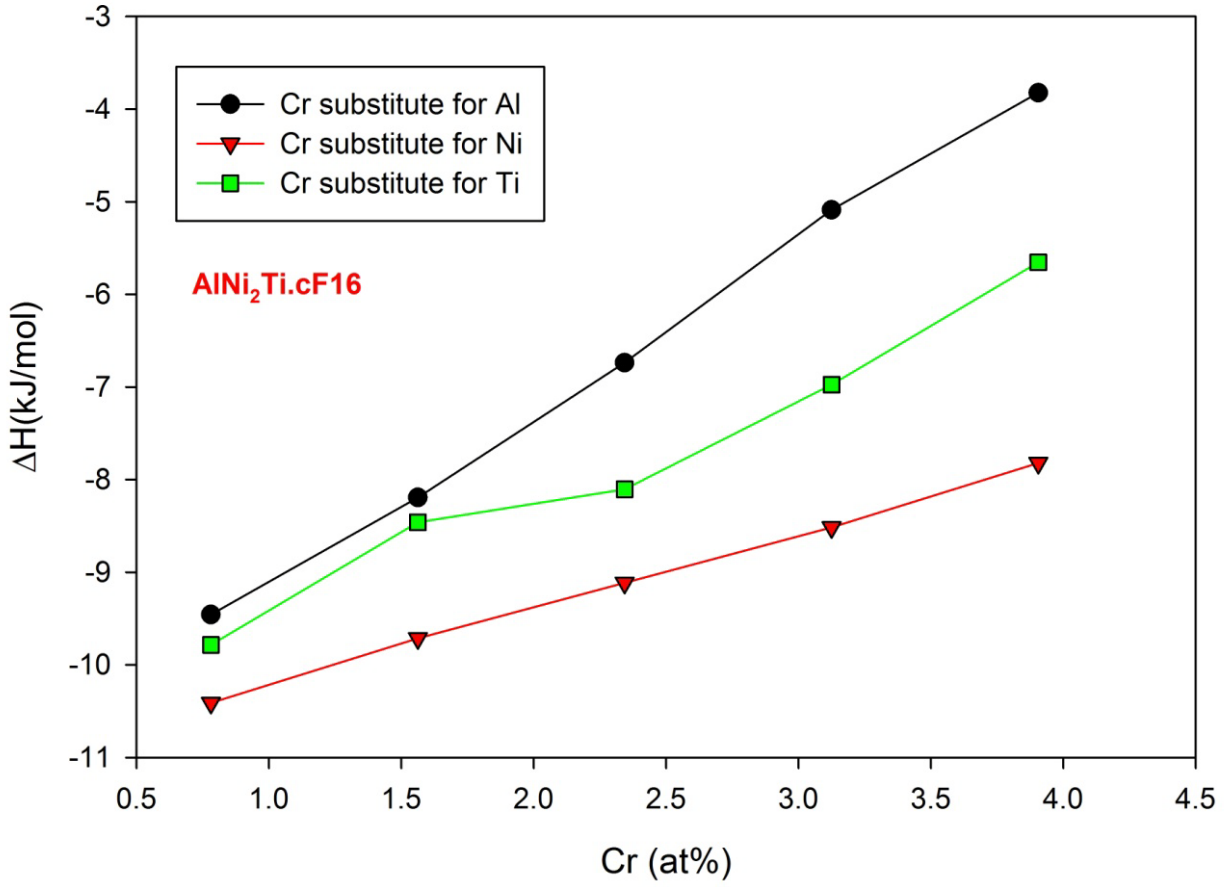
ASM Ternary Handbook





ΔH_f=-55.8+-2.2 [exp, Hu et al.]
-63.8 [Calphad]
-49.1 [DFT calculations]

Cr Solubility in $AlNi_2Ti.cF16$



DFT: 2x2x2 supercell (128 atoms); electronic spin polarization considered.

Experimental Work

Process Cr-Ni-Al-Ti alloys

Characterize microstructure

Verification of $AlNi_2Ti$ second phase

Milestones	Milestone Date
Establish computational methods to study (i) effects of alloying elements on dislocation mobility (ii) segregation of impurities at grain boundaries, (iii) formation of ordered phases.	12/31/2009
Preliminary results of computational work on the three tasks above.	03/31/2010
Experimental results on identification of ordered phases predicted by computations	06/30/2010
Demonstrated improved ductility for Cr alloys	09/30/2010

Deliverables

- **Thermodynamic Assessment of Mo-Ce and Mo-Y Systems,W. Chan, M.C. Gao, Ö. N. Doğan, P. King, accepted, *Journal of Phase Equilibria and Diffusion*.**
- **Thermodynamic Assessment of V-Rare Earth Systems, W. Chan, M. C. Gao, Ö. N. Doğan, P. King, submitted to *Journal of Phase Equilibria and Diffusion*.**
- **Thermodynamic Assessment Of Cr-Rare Earth Systems, W. Chan, M. C. Gao, Ö.N. Doğan, P. King, A. D. Rollett, *Journal of Phase Equilibria and Diffusion*, (2009) 30 578-586.**
- **Integrated Design of Chromium Based Alloys for Fossil Energy Applications, M.C. Gao, Ö.N. Doğan, P. King, Proceedings of The 17th Plansee Seminar, Reutte, Austria, May 25-29, 2009, RM31.**
- **First Principles Design of Ductile Refractory Alloys, M.C. Gao, O.N. Dogan, P. King, A.D. Rollett, M. Widom, *JOM*, 60 (2008), 7, pp. 61-65.**

Future Plans

Further improve computational methods to realistically simulate complex alloy systems and coatings.

Apply the computational methods that we have developed to other high temperature alloys.

Develop high temperature materials for FE applications to support AR goal of “Advanced Materials for Zero-Emission Power Plants”.