NATIONAL ENERGY TECHNOLOGY LABORATORY

Integrated Design and Rapid Development of Refractory Metal Based Alloys for Fossil Energy Applications

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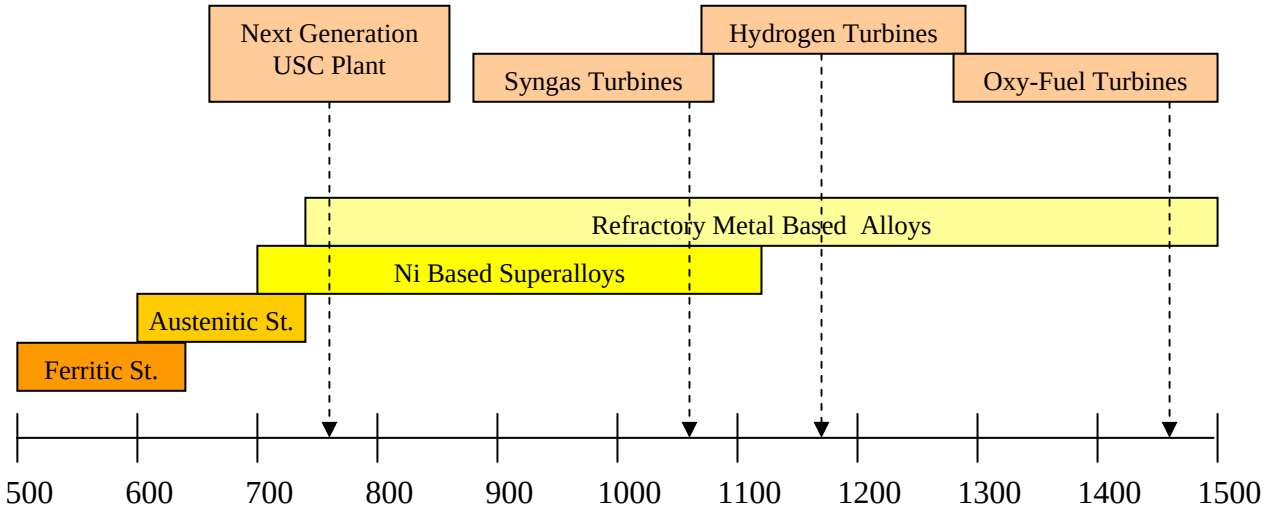
22nd Annual Conference on Fossil Energy Materials, Pittsburgh, PA, July 8-10, 2008

New Energy Generating Technologies and High-Temperature Structural Materials



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

Refractory Metals and Ni

	Melting T °C	Density g/cm³
Ni	1455	8.9
Cr	1863	7.2
V	1910	6.1
Rh	1963	12.4
Hf	2231	13.3
Ru	2334	12.4
Ir	2447	22.6
Nb	2469	8.6
Mo	2623	10.2
Ta	3020	16.6
Os	3033	22.6
Re	3186	21.0
W	3422	19.3

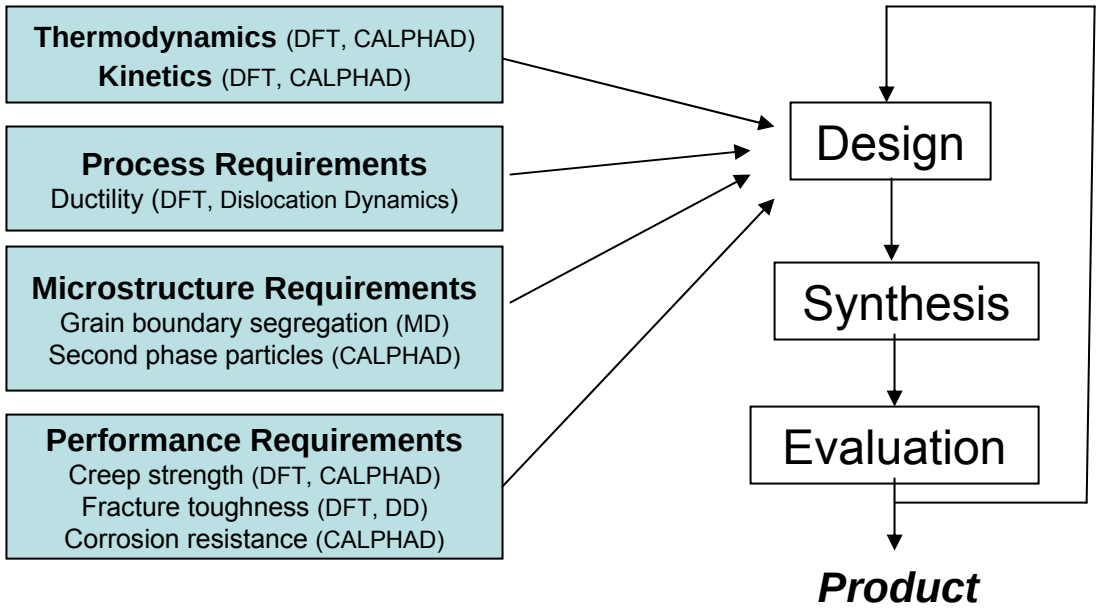
Major issues with refractory metals

- Low ductility and fracture toughness at low temperatures
- Poor oxidation resistance at high temperatures

Integrated Design of Refractory Metal Based Alloys For Fossil Energy Applications

The project goal is to develop refractory metal based alloys utilizing integrated design approach.

Integrated design uses computational methods with experimental verification and available knowledge base to design alloys according to the requirements of processing, microstructure and properties.



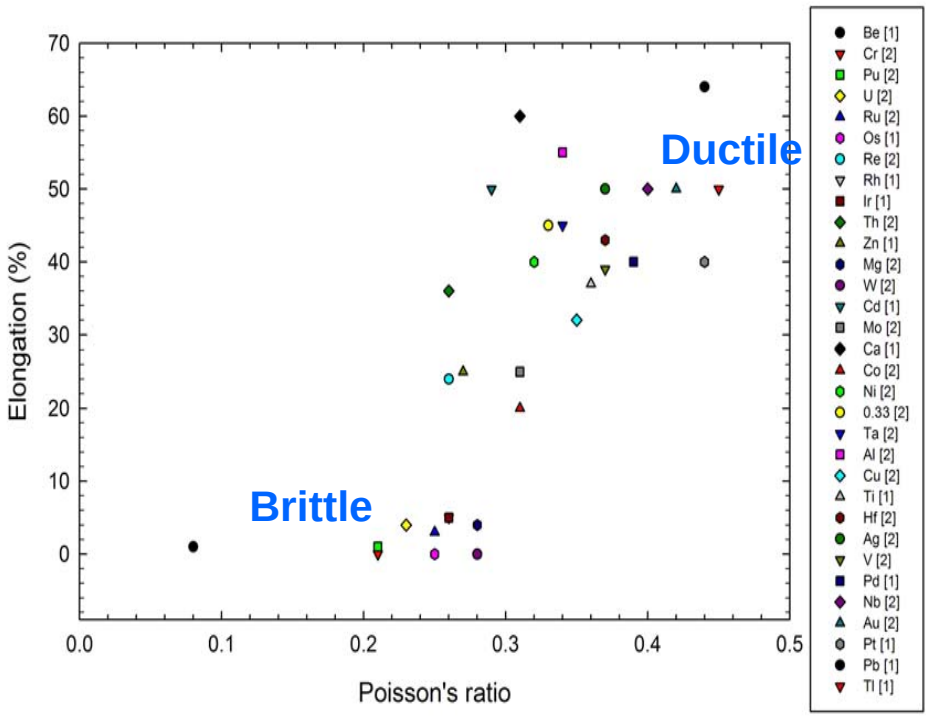
As a result of integrated design, the efficient development of materials requires much less experimental work, thus reducing the time and cost involved in alloy development.

Integrated Design of Refractory Metal Based Alloys for Fossil Energy Applications

- Improving ductility and fracture toughness through substitutional alloying
- Thermodynamic evaluation of promising systems
- Kinetic evaluation of relevant alloy systems
- Grain boundary segregation of C, N, O, and S in the refractory alloys
- Ductile – Brittle transition (DBT) in refractory alloys
- Improving creep strength
- Improving high temperature oxidation resistance

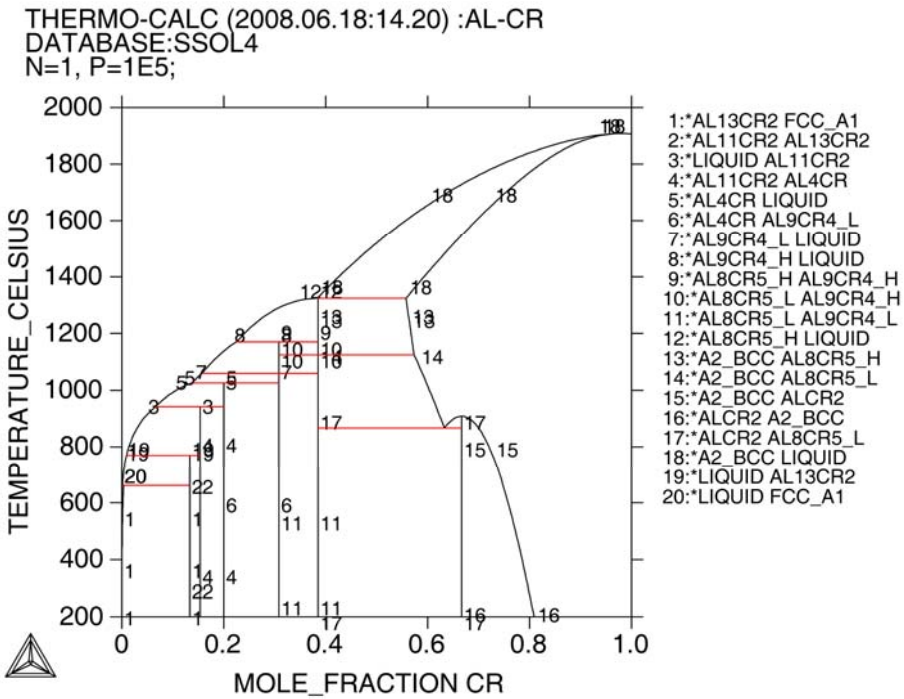
Improving ductility and fracture toughness through substitutional alloying

- First principles quantum mechanical calculations
- Experimental verification: tensile & fracture toughness

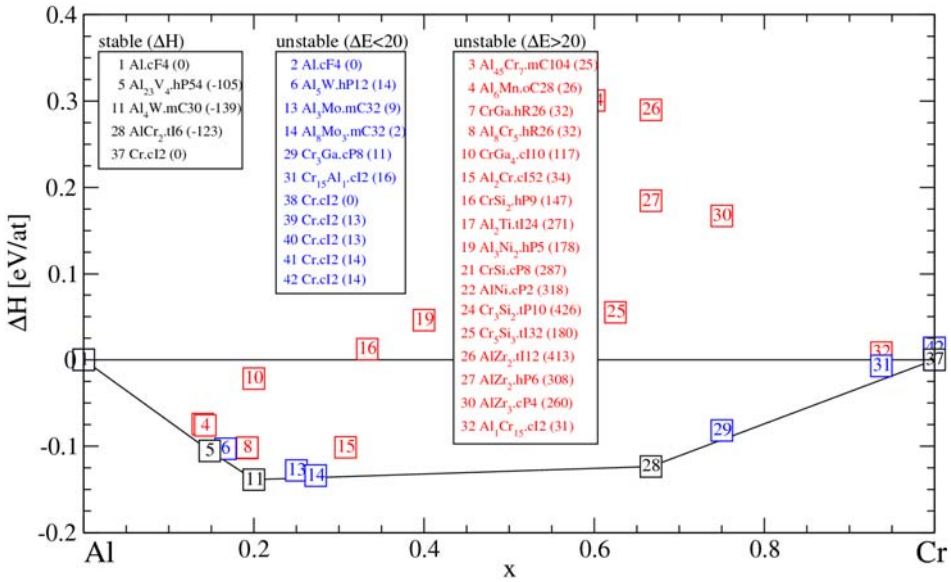


Thermodynamic evaluation of promising systems

- **DFT calculations & CALPHAD modeling**
- **Experimental verification: Thermal analysis, XRD, TEM, SEM**



Al-Cr from CALPHAD modeling



Enthalpy convex hull plot of Al-Cr from first principles DFT calculations

An efficient and reliable way to study phase diagrams is to combine first principles DFT calculations, critical experiments and CALPHAD modeling.

Kinetic evaluation of relevant alloy systems

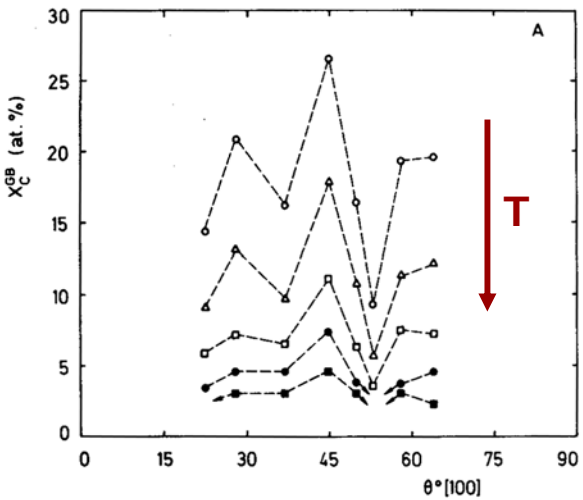
- **DFT calculations of diffusivities (CMU)**
  - Interstitial (O, N and C) diffusion in refractory metal based alloys will be studied using first-principles quantum-mechanical calculations

- **Experimental diffusivity measurements (CMU)**
  - Substitutional diffusion coefficients for promising systems will be measured and incorporated into the DICTRA kinetic database

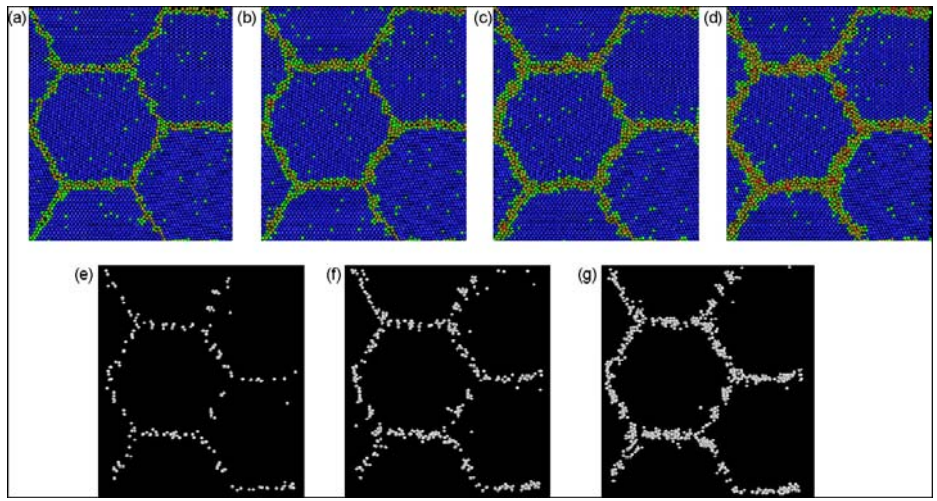
Grain boundary segregation of C, N, O, and S in the refractory alloys

- **Molecular dynamic simulations coupled with DFT calculations**
- **Experiments: HRTEM, Analytical TEM**

Carbon concentration as a function of misorientation of adjacent grains



Hofman: Surf interf Ana 19 (1992) 601



(a–d) Simulations of Al-Pb microstructures for 0–3 at.% Pb, respectively. (e–g) The Pb atom positions highlighted for frames (b–d), respectively.

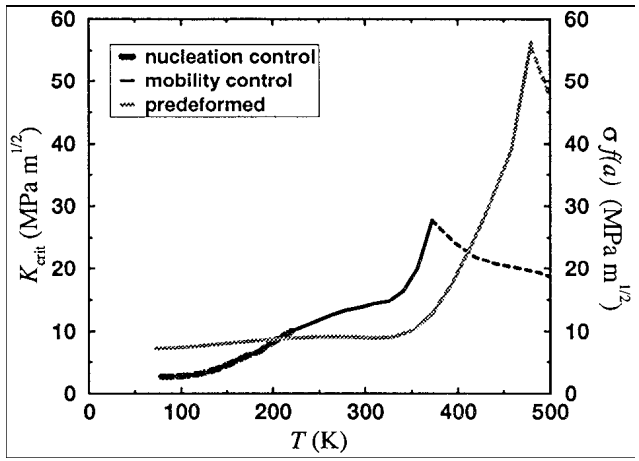
S. Jang, et al., Mater. Sci. Eng. A (2008), doi:10.1016/j.msea.2007.05.130

Ductile – Brittle Transition (DBT) in Refractory Metal Based Alloys

- **Dislocation dynamics simulations to study interactions between the crack tip and dislocations**

- **Experimental study to understand the ductile-brittle transition**

DBT
Is it lack of dislocation nucleation?
Is it lack of dislocation mobility?

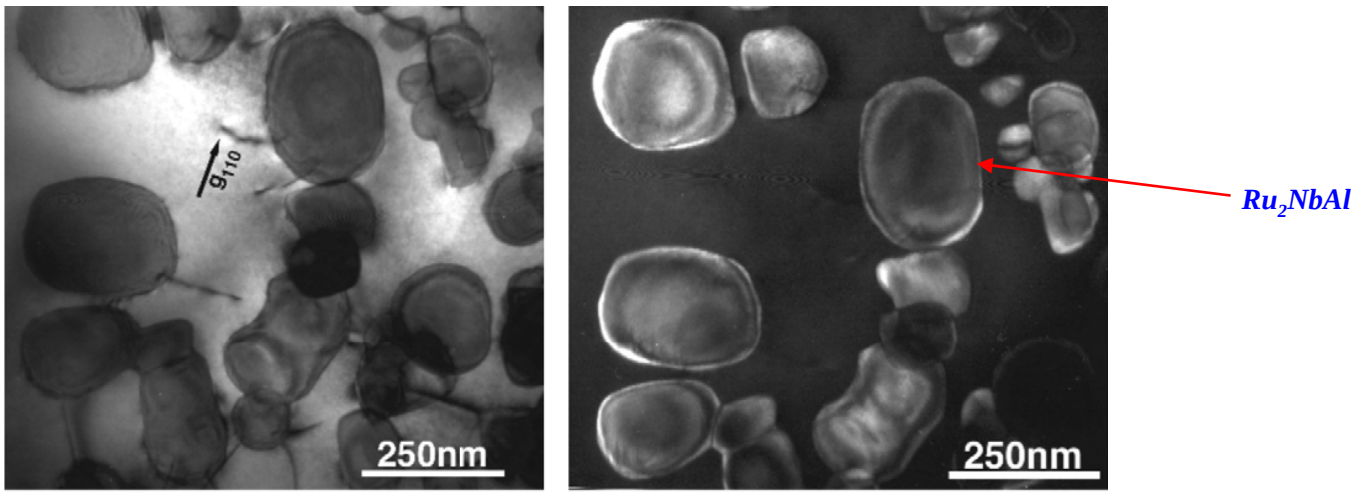


Hartmaier 1999 – j. Comp.-Aided Mat. Des., 6, 145

Improving Creep Strength of Refractory Metal Based Alloys

- **Explore strengthening second phase particles in terms of high temperature stability, lattice coherency, and coarsening behavior in candidate alloy systems**
- **Fabricate designated binary/ternary/higher degree alloys and characterize them using XRD, TEM, SEM, and optical microscopy**

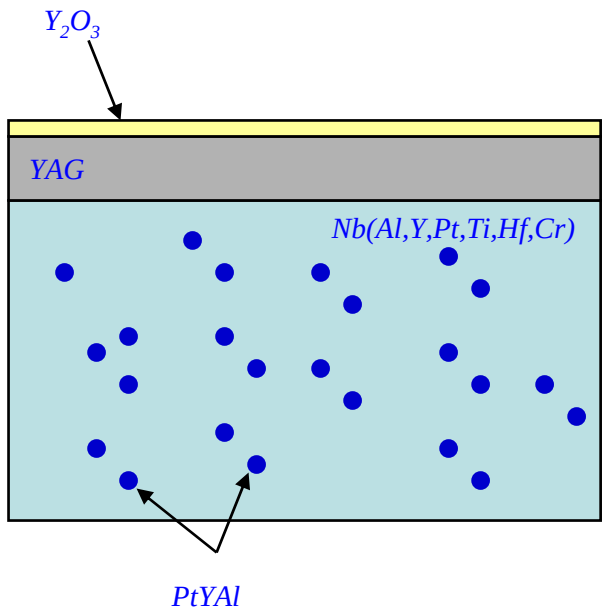
82Nb-8Al-10Ru



G. Ghosh, G.B. Olson, Acta Mat., 55, 2007, 3281-3303.

Improving High Temperature Oxidation Resistance of Refractory Metal Based Alloys

- **Thermodynamic calculations to identify stable oxides at high temperatures, to determine solubility of alloying elements and elements entering from the environment both in the scale and in the bulk alloy**
- **Kinetic computations will be performed to determine growth rates of the oxide scales**
- **High temperature oxidation experiments (continuous and cyclic) will be performed and oxide scales will be characterized using XRD, ESCA, Auger spectroscopy, and SEM**

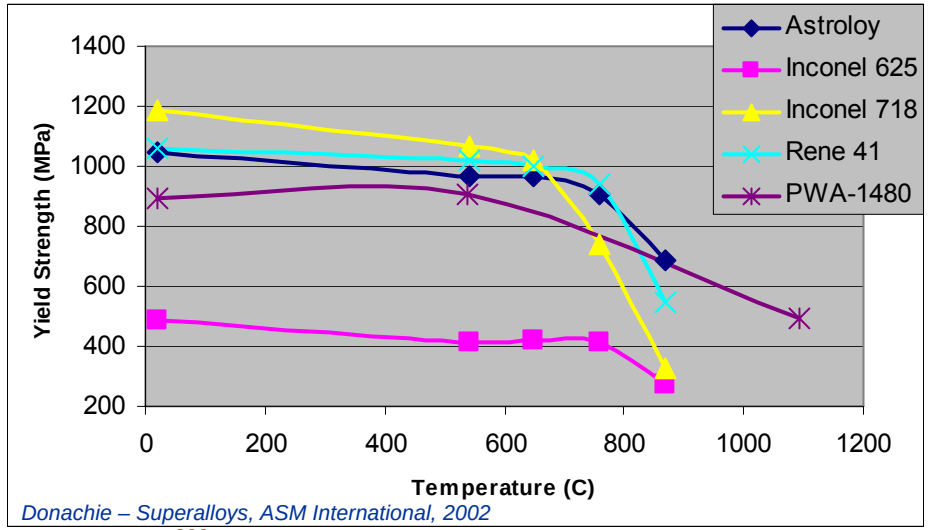


Nb-15Al-8Y-7Pt-6Ti-3Hf-3Cr

Olson 2006, U.S. Patent No. US 2006/0172142

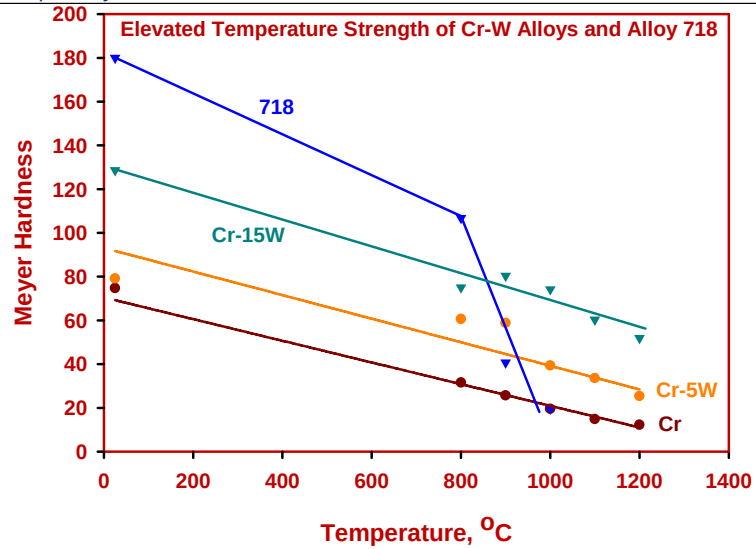
Integrated Design of Chromium Based Alloys for Fossil Energy Applications

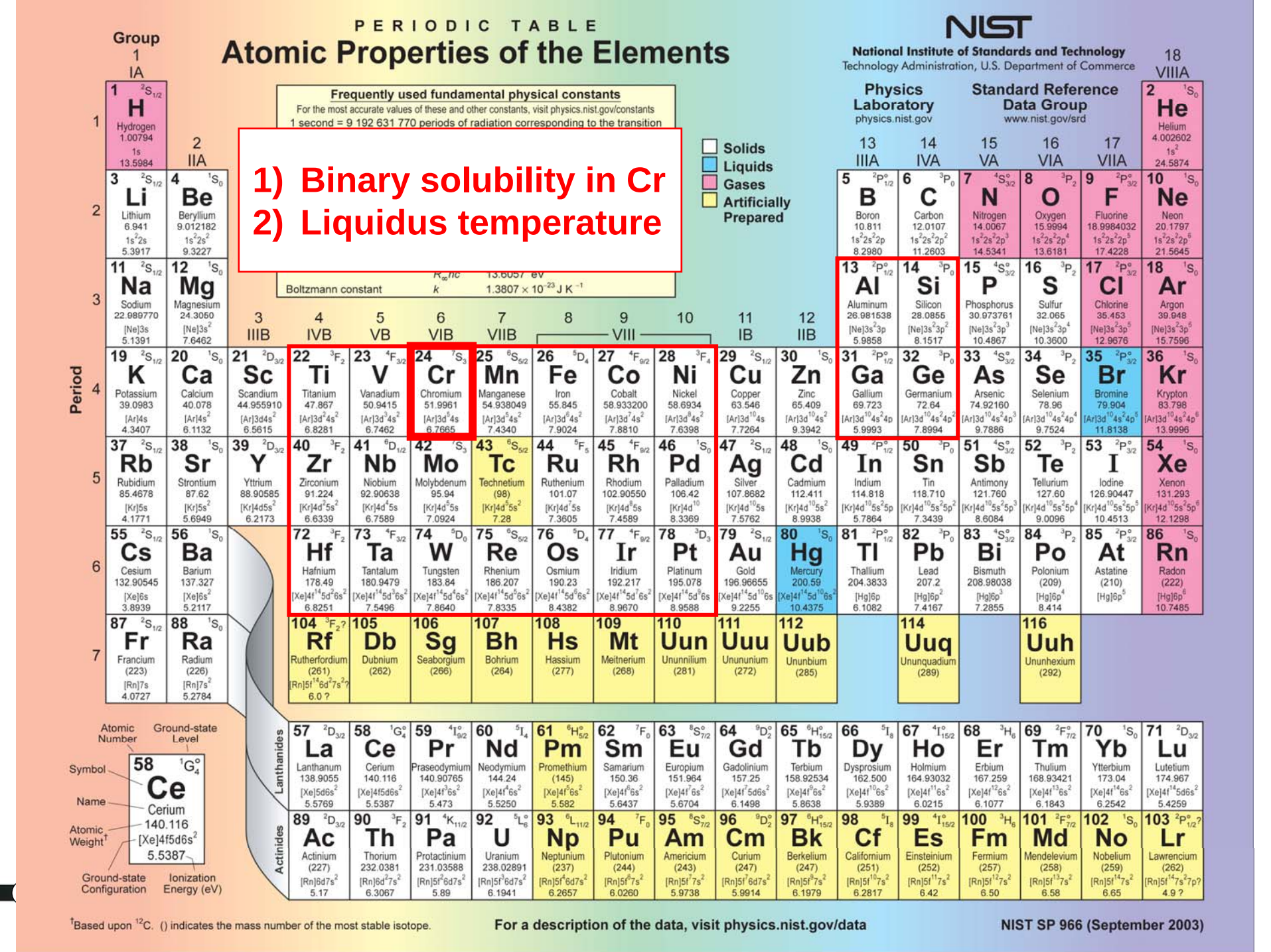
- **We selected Cr to demonstrate that integrated design methodology works well in developing new high temperature materials based on refractory metals.**
- **Cr based alloys show considerable promise due to**
  - relatively low cost
  - relatively low density
  - good high temperature strength



Donachie – Superalloys, ASM International, 2002

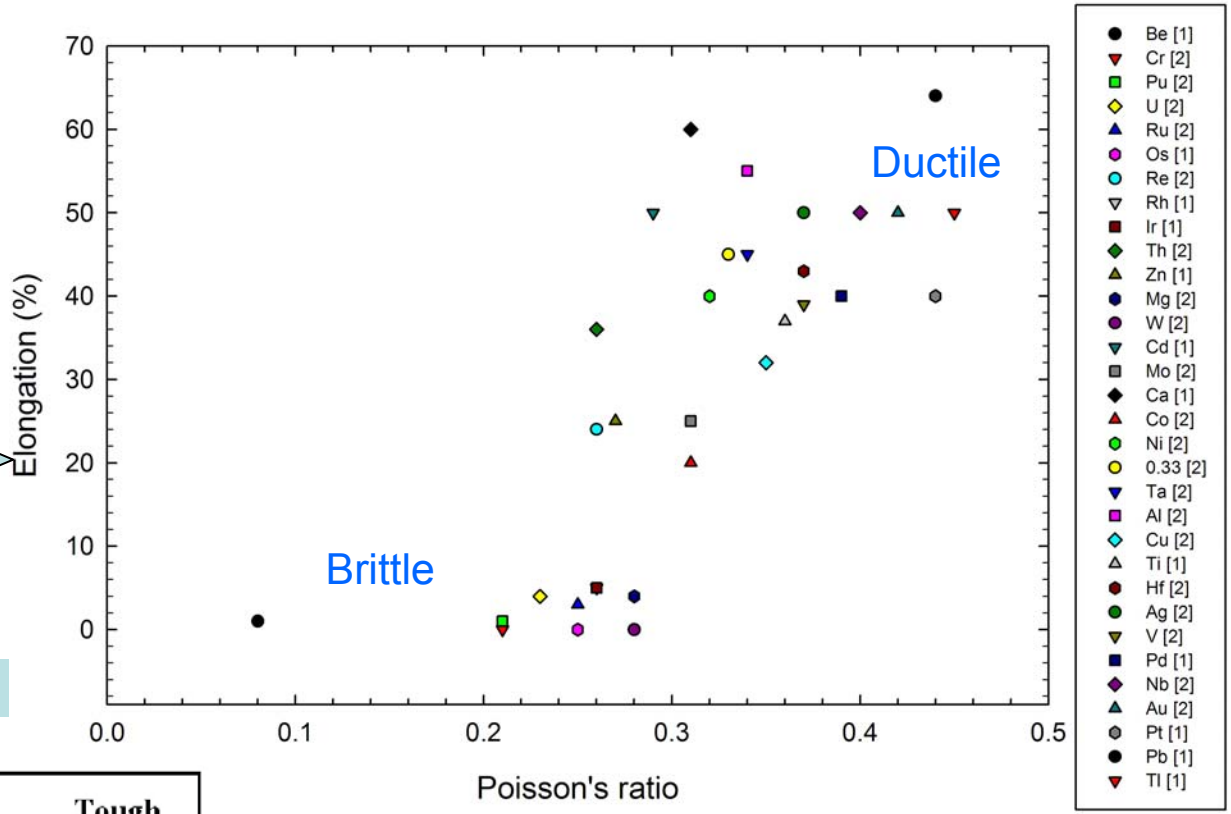
	Density g/cm^3
Ni	8.9
Cr	7.2
Nb	8.6
Mo	10.2
W	19.3




PERIODIC TABLE
Atomic Properties of the Elements
NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce
Physics Laboratory
physics.nist.gov
Standard Reference Data Group
www.nist.gov/srd
Frequently used fundamental physical constants
For the most accurate values of these and other constants, visit physics.nist.gov/constants
1 second = 9 192 631 770 periods of radiation corresponding to the transition
Boltzmann constant
1.3807 × 10^-23 J K^-1
1) Binary solubility in Cr
2) Liquidus temperature
Solids
Liquids
Gases
Artificially Prepared
Group
Period
Lanthanides
Actinides
Atomic Number
Ground-state Level
Symbol
Name
Atomic Weight†
Ground-state Configuration
Ionization Energy (eV)
†Based upon ¹²C. () indicates the mass number of the most stable isotope.
For a description of the data, visit physics.nist.gov/data
NIST SP 966 (September 2003)

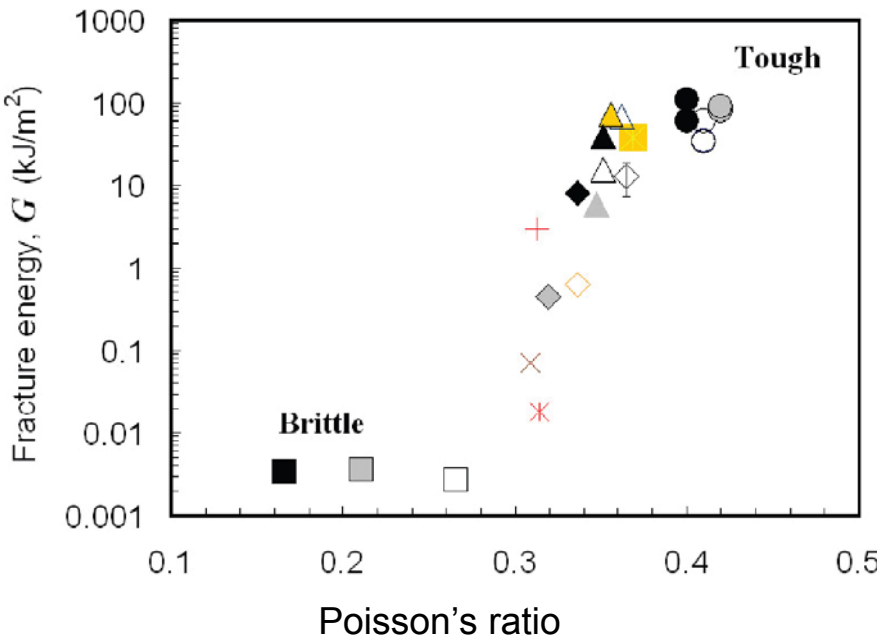
Ductility and Toughness vs. Poisson ratio

crystalline metals (purity≥ 99.9%)



[1]. S.F. Pugh, Phil. Mag., 45 (1954) 823

[2]. Smithells Metals Ref. Book, 7th Ed. 1992



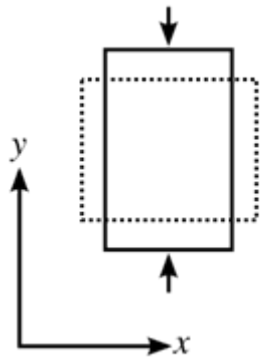
Amorphous alloys
Amorphous+crystalline composite

Phil. Mag. Lett. ***85*** *(2005) 77*

What Is Poisson's Ratio?

Poisson's ratio is the ratio of the relative contraction strain, or transverse strain (normal to the applied load), divided by the relative extension strain, or axial strain (in the direction of the applied load).

$$\nu = \frac{3 - 2(G/B)}{6 + 2(G/B)}$$



Uniaxial compression

$$\nu = -\frac{\varepsilon_{tran}}{\varepsilon_{axial}}$$

■ is the resulting Poisson's ratio

ε_{tran} is transverse strain

ε_{axial} is axial strain.

G = polycrystalline shear modulus

B = bulk modulus

Poisson ratio is all about G/B ratio

Desirable: high B, low G

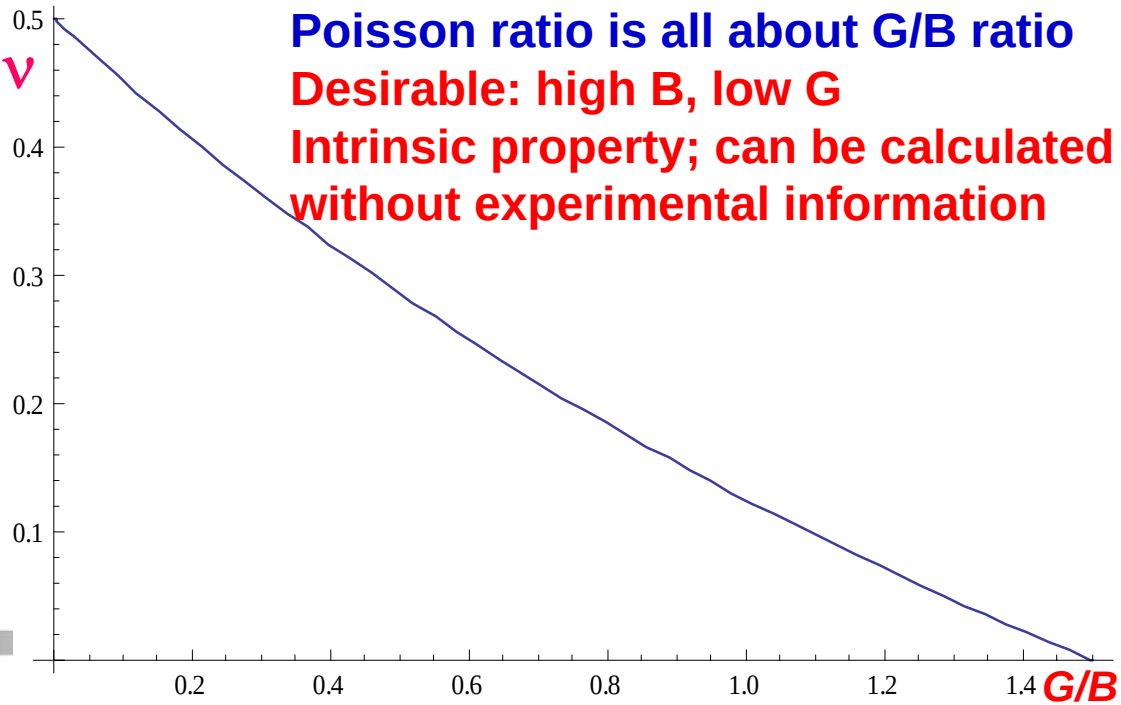
Intrinsic property; can be calculated without experimental information

General Hook's law

$$\varepsilon_x = \frac{1}{E}\left[\sigma_x - \nu\left(\sigma_y + \sigma_z\right)\right]$$

$$\varepsilon_y = \frac{1}{E}\left[\sigma_y - \nu\left(\sigma_x + \sigma_z\right)\right]$$

$$\varepsilon_z = \frac{1}{E}\left[\sigma_z - \nu\left(\sigma_x + \sigma_y\right)\right]$$



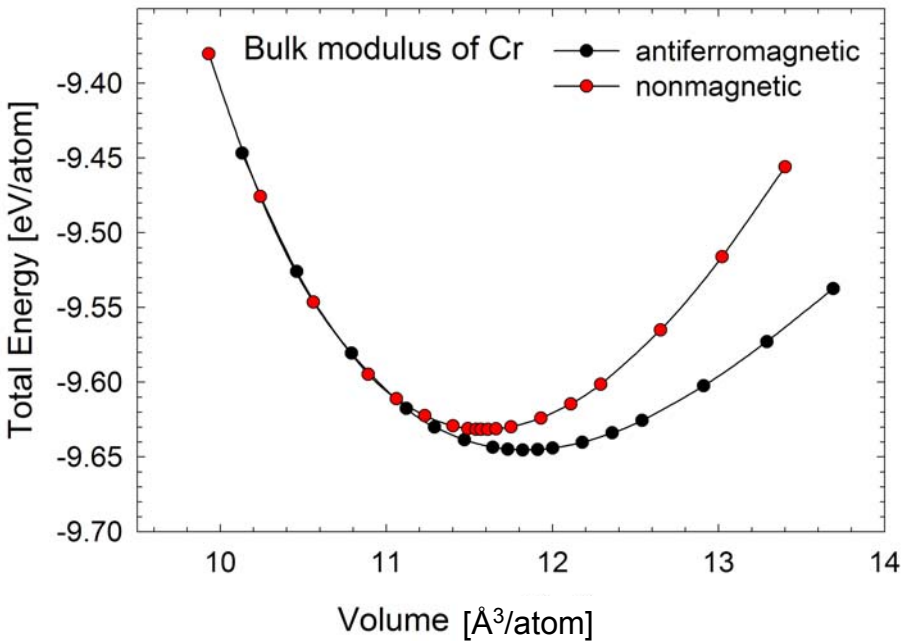
Computational Details

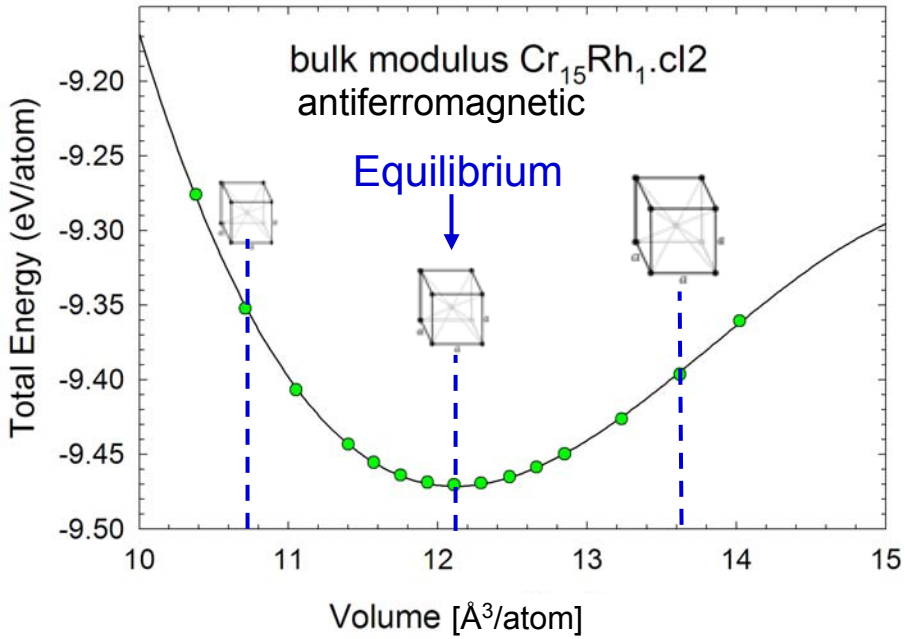
- **VASP package is used**
- **Projector augmented-wave pseudopotentials**
- **Perdew-Burke-Ernzerhof gradient approximation to the exchange-correlation functional**
- **Energy cutoff = 500 eV**
- **Convergence w.r.t. K-points:1 meV**
- **Precision “high”**
- **semi-core 3p, 4p and 5p electrons treated as valence**
- **Spin polarization considered (antiferromagnetism)**
- **2x2x2 supercell bcc lattice**
- Binary **compositions**
- Ternary **compositions in bcc structure**

Bulk Modulus Calculations

$$B = -\left(V\frac{\partial P}{\partial V}\right)_{E_{\min}} = V\frac{\partial^2 E}{\partial V^2}\bigg|_{E_{\min}}$$

Cubic polynomial fitting. There are other EOS (equation of state) such as Murnaghan equation, Birch-Murnaghan equation.





Antiferromagnetism of Cr must be included into calculations to validate the predicated physical properties

Antiferromagnetism is considered in all bcc $Cr_{15}X_1$ alloys

Polycrystalline Shear Modulus

Hershey's averaging method: Taga et al. Phys Rev B 71 (2005) 014201

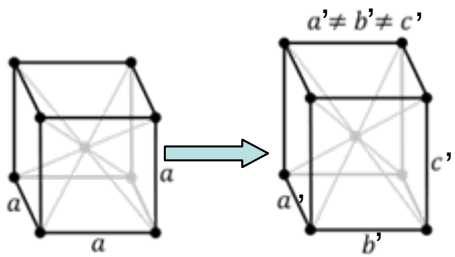
$$G^3 + \frac{9B+4C'}{8}G^2 - \frac{3C_{44}(B+4C')}{8}G - \frac{3C_{44}C'B}{4} = 0 \qquad C' = \frac{1}{2}(C_{11} - C_{12}) \qquad B = \frac{1}{3}(C_{11} + 2C_{12})$$

G=shear; B=bulk modulus; C_{11}, C_{12} and C_{44} are elastic constants

Applying orthorhombic strain

Mehl et al, Phys Rev B 41 (1990) 10311

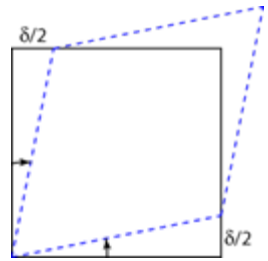
$$\varepsilon_o = \begin{pmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \delta^2/(1-\delta^2) \end{pmatrix}$$



$$\Delta E(\delta) = E(0) - E(\delta) = (C_{11} - C_{12})V_0\delta^2 + O[\delta^4]$$

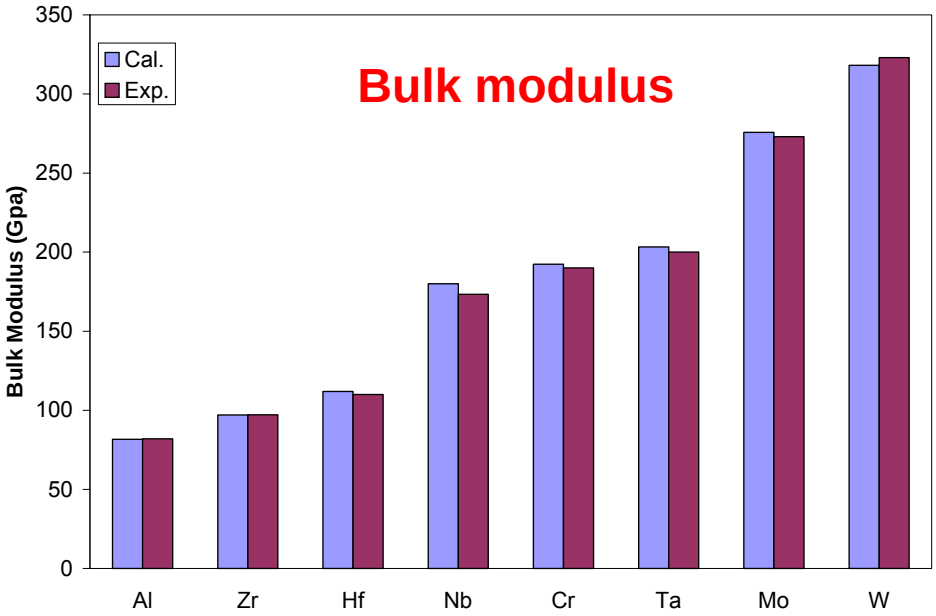
Applying monoclinic strain

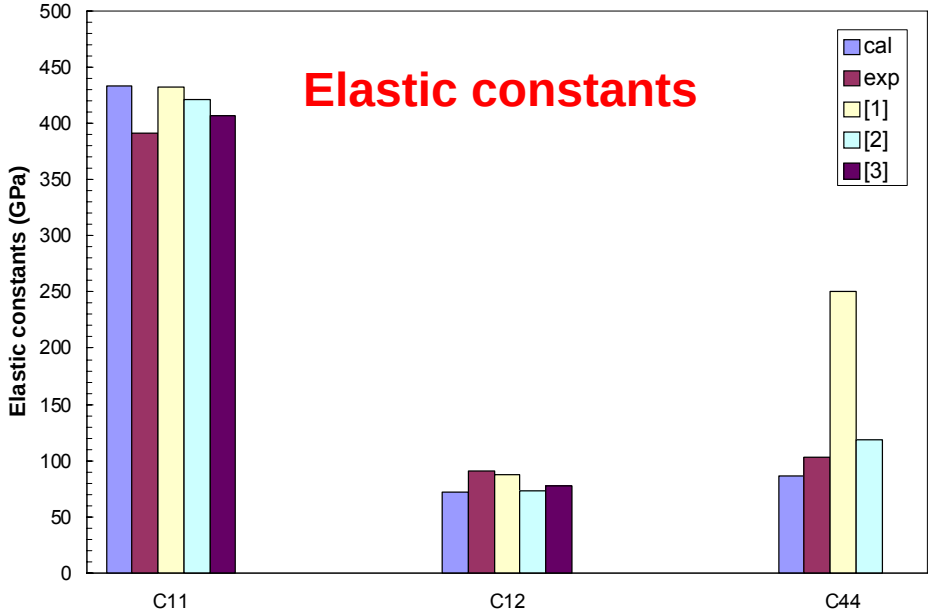
$$\varepsilon_m = \begin{pmatrix} 0 & \delta/2 & 0 \\ \delta/2 & 0 & 0 \\ 0 & 0 & \delta^2/(4-\delta^2) \end{pmatrix}$$

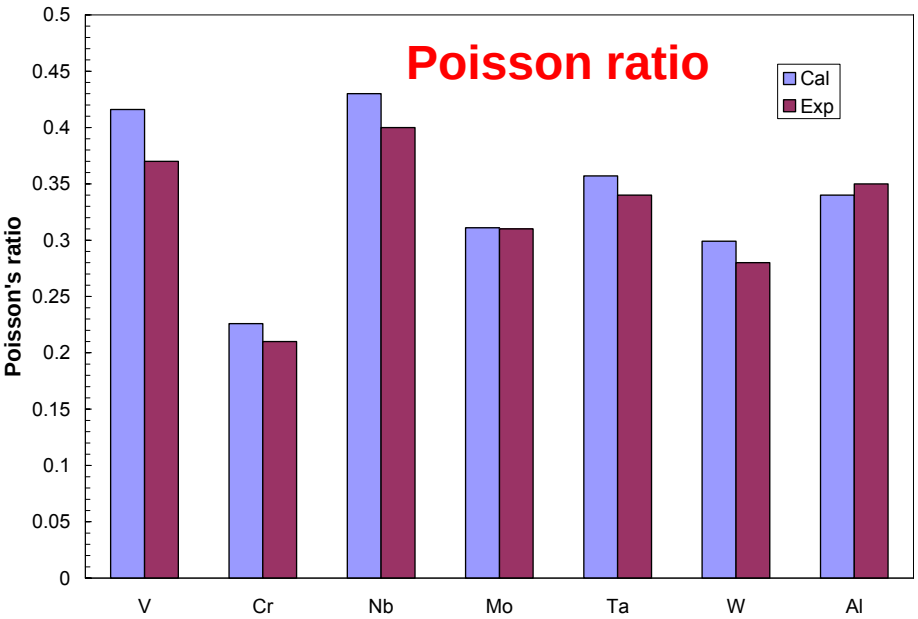


$$\Delta E(\delta) = E(0) - E(\delta) = \frac{1}{2}C_{44}V_0\delta^2 + O[\delta^4]$$

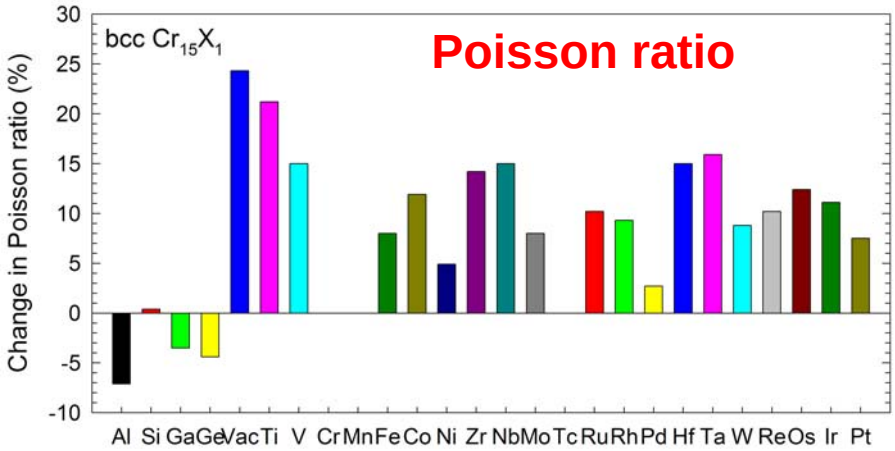
Validation of Computation

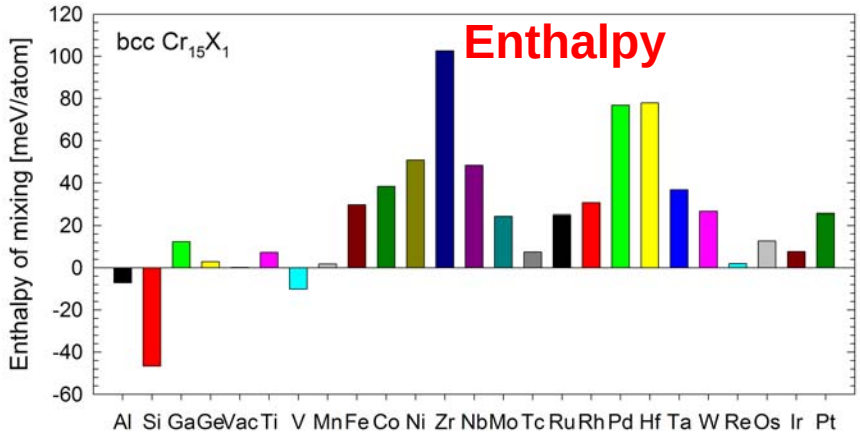


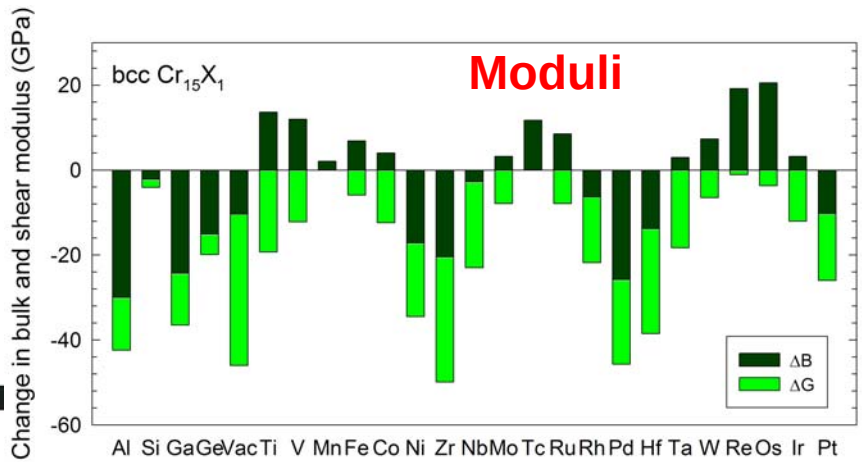




*[1] Phys Rev B **54** (1996) 4519 (tight binding)*
*[2] Phys Rev B **62** (2000) 5136 (DFT full potential)*
*[3] Phys Rev B **67** (2003) 134204 (DFT full potential)*







~~Al~~
~~Ga~~
~~Ge~~

Current Calculations

Ti, V, Fe, Co, Ni, ~~Zr~~, ~~Nb~~, Mo, Ru, Rh, ~~Pd~~, ~~Hf~~, ~~Ta~~, W, Re, Os, Ir, Pt

Solubility

Ti, V, Fe, Co, Ni, Mo, ~~Ru~~, ~~Rh~~, W, ~~Re~~, ~~Os~~, ~~Ir~~, ~~Pt~~

Economy

Ti, V, Fe, Co, Ni, Mo, W

Current status

- We have done similar calculations on ternary systems based on the promising binaries
- Currently, we are working on establishing phase diagrams for the promising ternary systems

Future Work

- Continue thermodynamic investigation to identify a promising multi-component system
- Kinetic studies on the identified multi-component system
- Designing an alloy with sufficient creep strength within the multi-component system
- Further modifying the alloy composition for high-temperature oxidation resistance

Above tasks will be accomplished utilizing various computational tools and experimental work