NATIONAL ENERGY TECHNOLOGY LABORATORY

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

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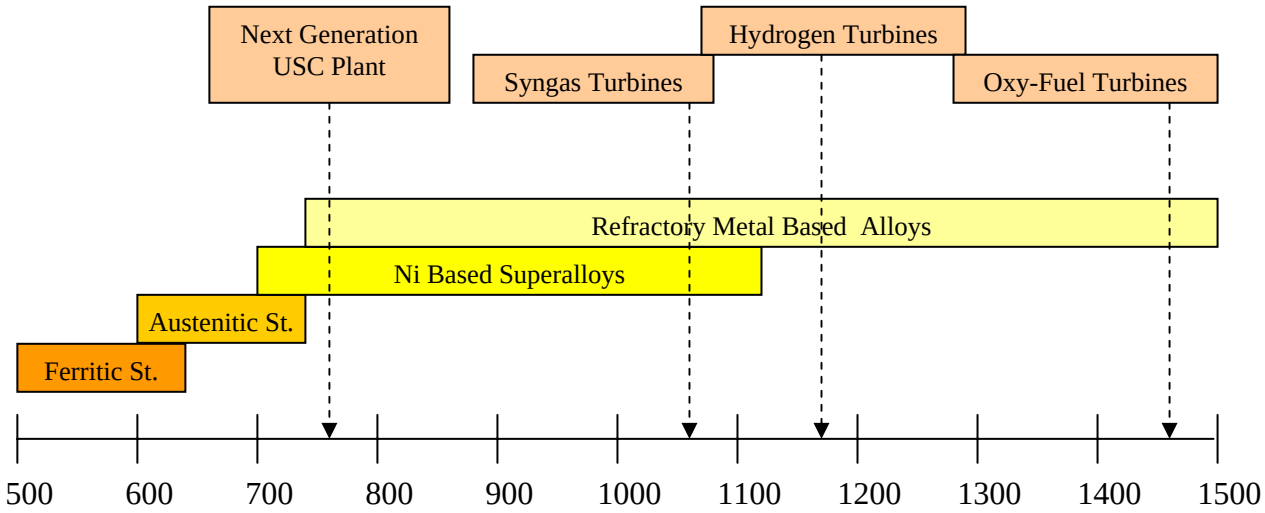
22nd Annual Conference on Fossil Energy Materials, Pittsburgh, PA, July 8-10, 2008

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

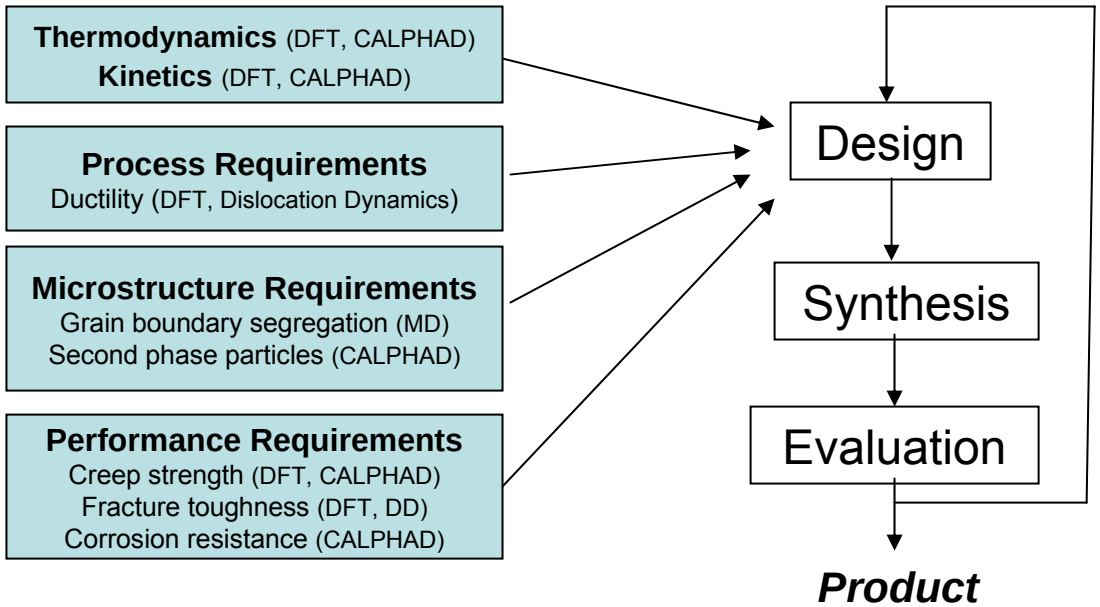
Major issues with refractory metals

- 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.



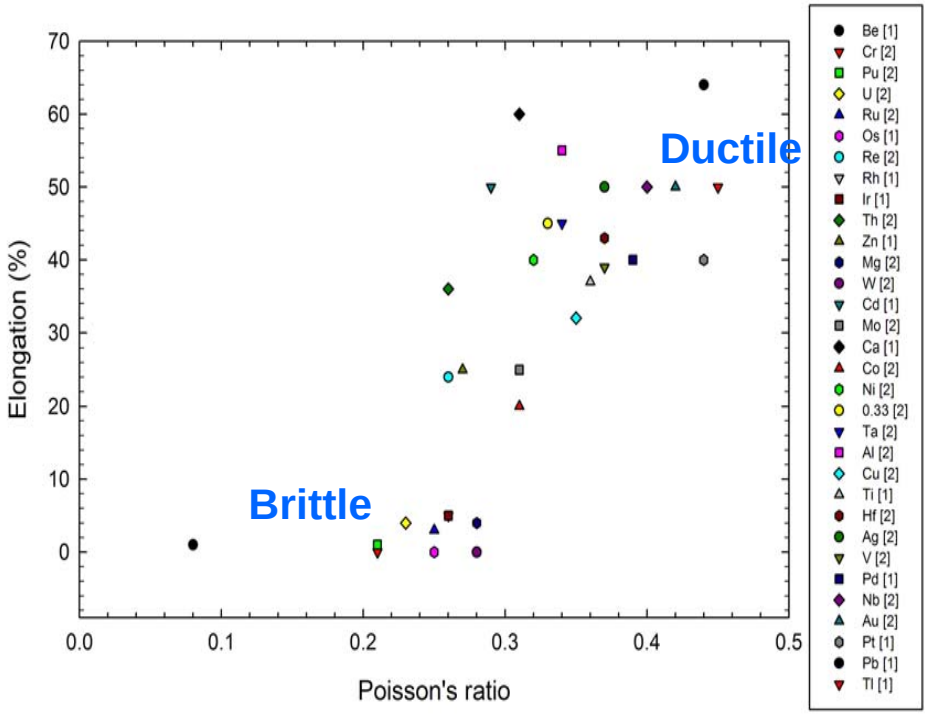
As a result of integrated design, the efficient development of materials requires much less experimental work, thus reducing the time and cost involved in alloy development.

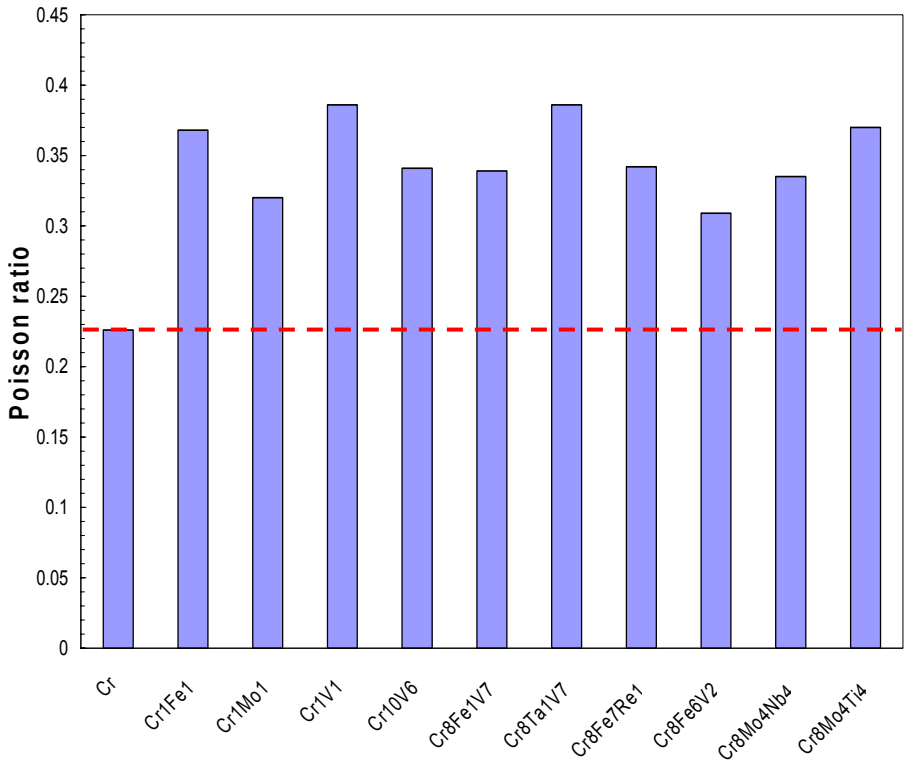
Integrated Design of Refractory Metal Based Alloys for Fossil Energy Applications

- 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

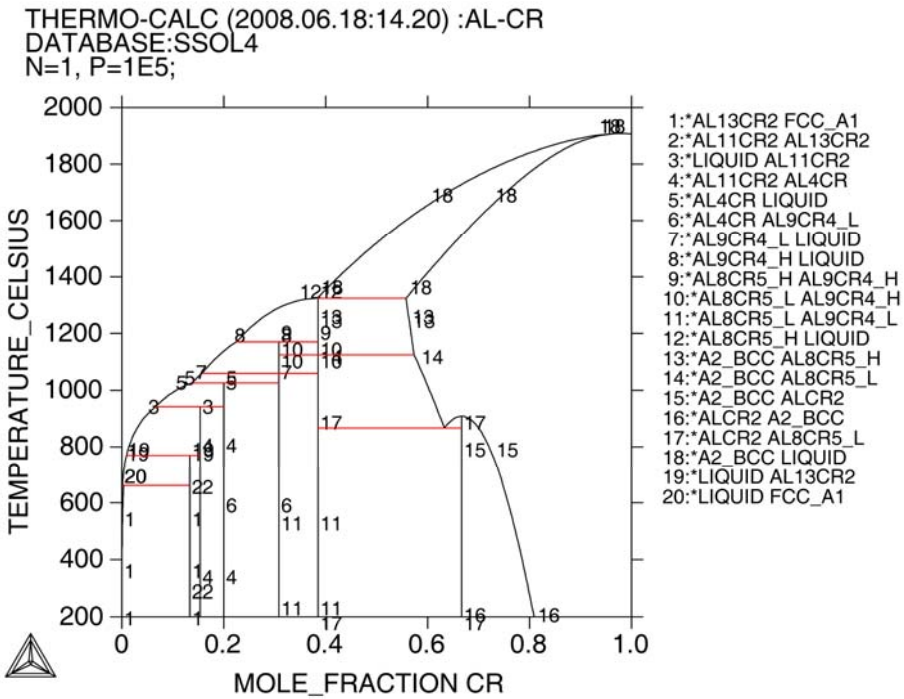
- **First principles quantum mechanical calculations**
- **Experimental verification: tensile & fracture toughness**



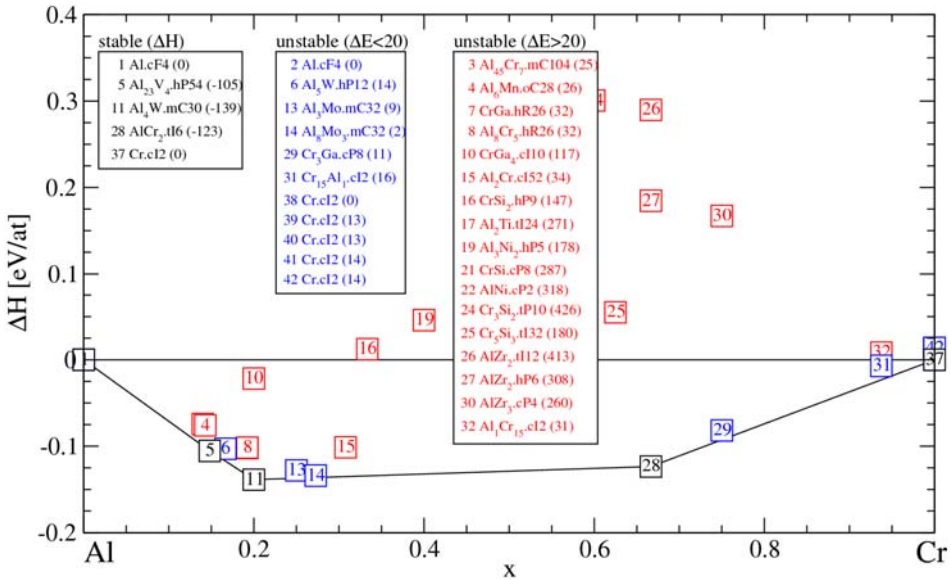


Thermodynamic evaluation of promising systems

- **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

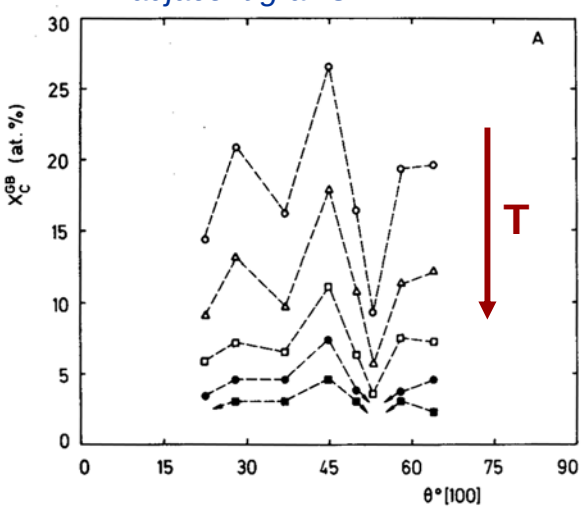
- **DFT calculations of diffusivities (CMU)**
  - Interstitial (O, N and C) diffusion in refractory metal based alloys will be studied using first-principles quantum-mechanical calculations

- **Experimental diffusivity measurements (CMU)**
  - Substitutional diffusion coefficients for promising systems such as Cr-Mo-Al-V quaternary system will be measured and incorporated into the DICTRA kinetic database

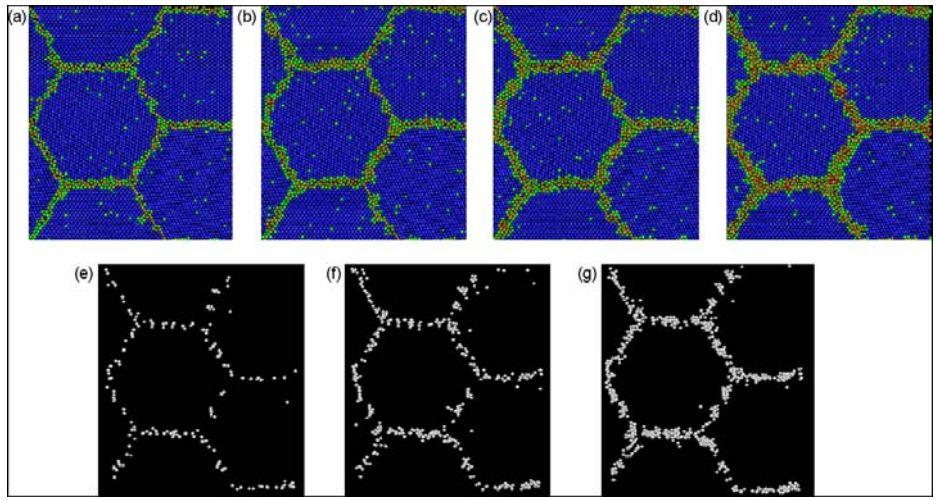
Grain boundary segregation of C, N, O, and S in the refractory alloys

- **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.

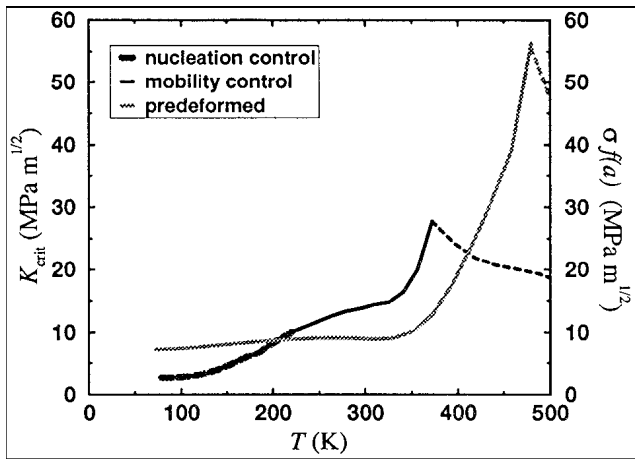
S. Jang, et al., Mater. Sci. Eng. A (2008), doi:10.1016/j.msea.2007.05.130

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?

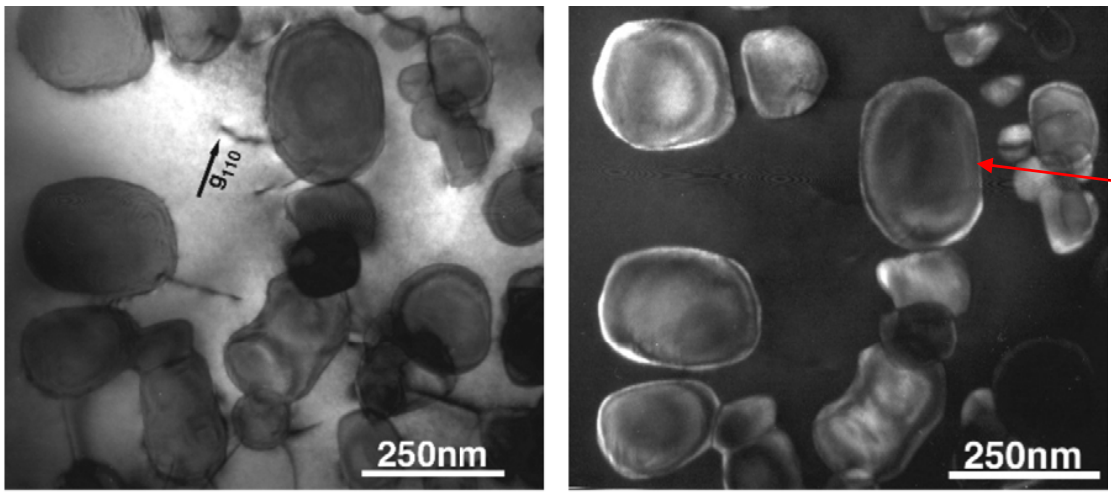


Hartmaier 1999 – j. Comp.-Aided Mat. Des., 6, 145

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

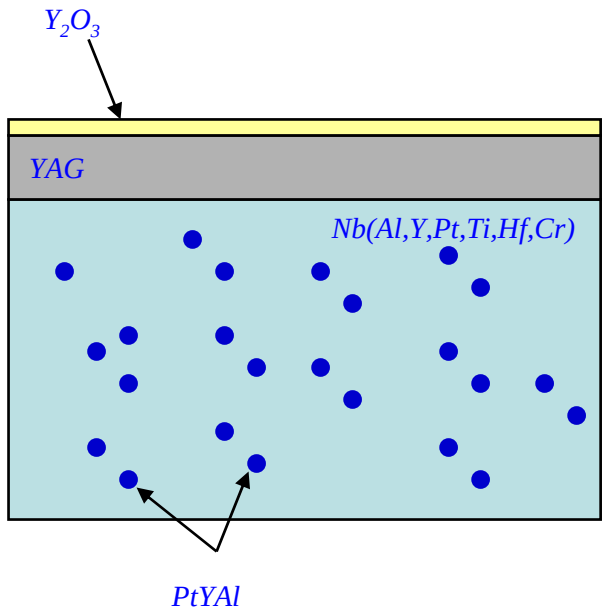


Ru_2NbAl

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**

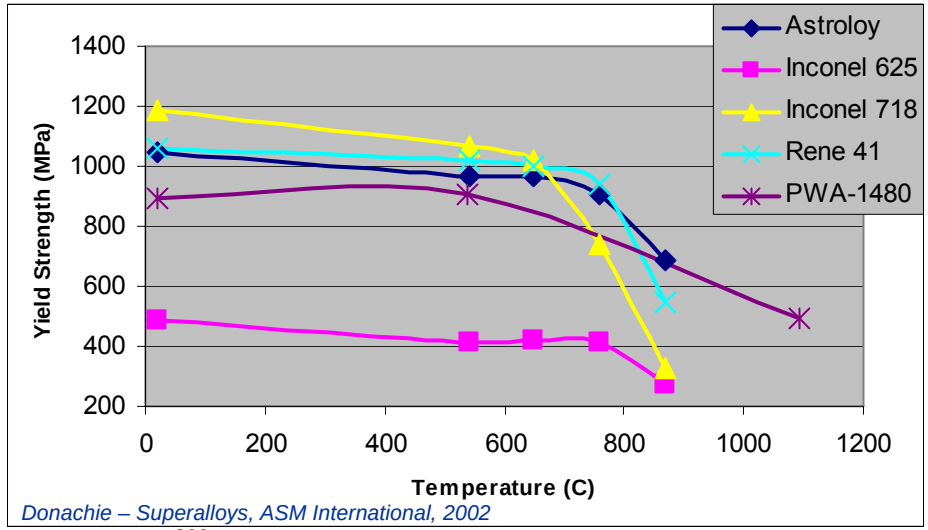


Nb-15Al-8Y-7Pt-6Ti-3Hf-3Cr

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

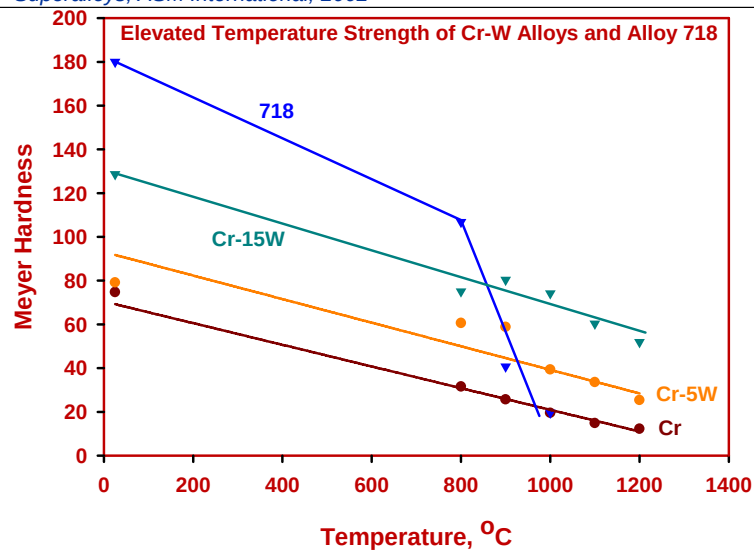
Integrated Design of Chromium Based Alloys for Fossil Energy Applications

- **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

$R_\infty hc$	13.6057 eV	
Boltzmann constant	k	1.3807×10^{-23} J K^{-1}

1) Binary solubility in Cr
2) Liquidus temperature

Solids
Liquids
Gases
Artificially Prepared

Period	Group 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 $^2S_{1/2}$ **H** Hydrogen 1.00794 1s 13.5984																	2 $^1S_0$ **He** Helium 4.002602 $1s^2$ 24.5874
2	3 $^2S_{1/2}$ **Li** Lithium 6.941 $1s^22s$ 5.3917	4 $^1S_0$ **Be** Beryllium 9.012182 $1s^22s^2$ 9.3227											5 $^2P^\circ_{1/2}$ **B** Boron 10.811 $1s^22s^22p$ 8.2980	6 $^3P_0$ **C** Carbon 12.0107 $1s^22s^22p^2$ 11.2603	7 $^4S^\circ_{3/2}$ **N** Nitrogen 14.0067 $1s^22s^22p^3$ 14.5341	8 $^3P_2$ **O** Oxygen 15.9994 $1s^22s^22p^4$ 13.6181	9 $^2P^\circ_{3/2}$ **F** Fluorine 18.9984032 $1s^22s^22p^5$ 17.4228	10 $^1S_0$ **Ne** Neon 20.1797 $1s^22s^22p^6$ 21.5645
3	11 $^2S_{1/2}$ **Na** Sodium 22.989770 [Ne]3s 5.1391	12 $^1S_0$ **Mg** Magnesium 24.3050 $[Ne]3s^2$ 7.6462											13 $^2P^\circ_{1/2}$ **Al** Aluminum 26.981538 $[Ne]3s^23p$ 5.9858	14 $^3P_0$ **Si** Silicon 28.0855 $[Ne]3s^23p^2$ 8.1517	15 $^4S^\circ_{3/2}$ **P** Phosphorus 30.973761 $[Ne]3s^23p^3$ 10.4867	16 $^3P_2$ **S** Sulfur 32.065 $[Ne]3s^23p^4$ 10.3600	17 $^2P^\circ_{3/2}$ **Cl** Chlorine 35.453 $[Ne]3s^23p^5$ 12.9676	18 $^1S_0$ **Ar** Argon 39.948 $[Ne]3s^23p^6$ 15.7596
4	19 $^2S_{1/2}$ **K** Potassium 39.0983 [Ar]4s 4.3407	20 $^1S_0$ **Ca** Calcium 40.078 $[Ar]4s^2$ 6.1132	21 $^2D_{3/2}$ **Sc** Scandium 44.955910 $[Ar]3d4s^2$ 6.5615	22 $^3F_2$ **Ti** Titanium 47.867 $[Ar]3d^24s^2$ 6.8281	23 $^4F_{3/2}$ **V** Vanadium 50.9415 $[Ar]3d^34s^2$ 6.7462	24 $^7S_3$ **Cr** Chromium 51.9961 $[Ar]3d^54s$ 6.7665	25 $^6S_{5/2}$ **Mn** Manganese 54.938049 $[Ar]3d^54s^2$ 7.4340	26 $^5D_4$ **Fe** Iron 55.845 $[Ar]3d^64s^2$ 7.9024	27 $^4F_{9/2}$ **Co** Cobalt 58.933200 $[Ar]3d^74s^2$ 7.8810	28 $^3F_4$ **Ni** Nickel 58.6934 $[Ar]3d^84s^2$ 7.6398	29 $^2S_{1/2}$ **Cu** Copper 63.546 $[Ar]3d^{10}4s$ 7.7264	30 $^1S_0$ **Zn** Zinc 65.409 $[Ar]3d^{10}4s^2$ 9.3942	31 $^2P^\circ_{1/2}$ **Ga** Gallium 69.723 $[Ar]3d^{10}4s^24p$ 5.9993	32 $^3P_0$ **Ge** Germanium 72.64 $[Ar]3d^{10}4s^24p^2$ 7.8994	33 $^4S^\circ_{3/2}$ **As** Arsenic 74.92160 $[Ar]3d^{10}4s^24p^3$ 9.7886	34 $^3P_2$ **Se** Selenium 78.96 $[Ar]3d^{10}4s^24p^4$ 9.7524	35 $^2P^\circ_{3/2}$ **Br** Bromine 79.904 $[Ar]3d^{10}4s^24p^5$ 11.8138	36 $^1S_0$ **Kr** Krypton 83.798 $[Ar]3d^{10}4s^24p^6$ 13.9996
5	37 $^2S_{1/2}$ **Rb** Rubidium 85.4678 [Kr]5s 4.1771	38 $^1S_0$ **Sr** Strontium 87.62 $[Kr]5s^2$ 5.6949	39 $^2D_{3/2}$ **Y** Yttrium 88.90585 $[Kr]4d5s^2$ 6.2173	40 $^3F_2$ **Zr** Zirconium 91.224 $[Kr]4d^25s^2$ 6.6339	41 $^6D_{1/2}$ **Nb** Niobium 92.90638 $[Kr]4d^45s$ 6.7589	42 $^7S_3$ **Mo** Molybdenum 95.94 $[Kr]4d^55s$ 7.0924	43 $^6S_{5/2}$ **Tc** Technetium (98) $[Kr]4d^55s^2$ 7.28	44 $^5F_5$ **Ru** Ruthenium 101.07 $[Kr]4d^75s$ 7.3605	45 $^4F_{9/2}$ **Rh** Rhodium 102.90550 $[Kr]4d^85s$ 7.4589	46 $^1S_0$ **Pd** Palladium 106.42 $[Kr]4d^{10}$ 8.3369	47 $^2S_{1/2}$ **Ag** Silver 107.8682 $[Kr]4d^{10}5s$ 7.5762	48 $^1S_0$ **Cd** Cadmium 112.411 $[Kr]4d^{10}5s^2$ 8.9938	49 $^2P^\circ_{1/2}$ **In** Indium 114.818 $[Kr]4d^{10}5s^25p$ 5.7864	50 $^3P_0$ **Sn** Tin 118.710 $[Kr]4d^{10}5s^25p^2$ 7.3439	51 $^4S^\circ_{3/2}$ **Sb** Antimony 121.760 $[Kr]4d^{10}5s^25p^3$ 8.6084	52 $^3P_2$ **Te** Tellurium 127.60 $[Kr]4d^{10}5s^25p^4$ 9.0096	53 $^2P^\circ_{3/2}$ **I** Iodine 126.90447 $[Kr]4d^{10}5s^25p^5$ 10.4513	54 $^1S_0$ **Xe** Xenon 131.293 $[Kr]4d^{10}5s^25p^6$ 12.1298
6	55 $^2S_{1/2}$ **Cs** Cesium 132.90545 [Xe]6s 3.8939	56 $^1S_0$ **Ba** Barium 137.327 $[Xe]6s^2$ 5.2117		72 $^3F_2$ **Hf** Hafnium 178.49 $[Xe]4f^{14}5d^26s^2$ 6.8251	73 $^4F_{3/2}$ **Ta** Tantalum 180.9479 $[Xe]4f^{14}5d^36s^2$ 7.5496	74 $^5D_0$ **W** Tungsten 183.84 $[Xe]4f^{14}5d^46s^2$ 7.8640	75 $^6S_{5/2}$ **Re** Rhenium 186.207 $[Xe]4f^{14}5d^56s^2$ 7.8335	76 $^5D_4$ **Os** Osmium 190.23 $[Xe]4f^{14}5d^66s^2$ 8.4382	77 $^4F_{9/2}$ **Ir** Iridium 192.217 $[Xe]4f^{14}5d^76s^2$ 8.9670	78 $^3D_3$ **Pt** Platinum 195.078 $[Xe]4f^{14}5d^96s$ 8.9588	79 $^2S_{1/2}$ **Au** Gold 196.96655 $[Xe]4f^{14}5d^{10}6s$ 9.2255	80 $^1S_0$ **Hg** Mercury 200.59 $[Xe]4f^{14}5d^{10}6s^2$ 10.4375	81 $^2P^\circ_{1/2}$ **Tl** Thallium 204.3833 [Hg]6p 6.1082	82 $^3P_0$ **Pb** Lead 207.2 $[Hg]6p^2$ 7.4167	83 $^4S^\circ_{3/2}$ **Bi** Bismuth 208.98038 $[Hg]6p^3$ 7.2855	84 $^3P_2$ **Po** Polonium (209) $[Hg]6p^4$ 8.414	85 $^2P^\circ_{3/2}$ **At** Astatine (210) $[Hg]6p^5$	86 $^1S_0$ **Rn** Radon (222) $[Hg]6p^6$ 10.7485
7	87 $^2S_{1/2}$ **Fr** Francium (223) [Rn]7s 4.0727	88 $^1S_0$ **Ra** Radium (226) $[Rn]7s^2$ 5.2784		104 $^3F_2$? **Rf** Rutherfordium (261) $[Rn]5f^{14}6d^27s^2$? 6.0 ?	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (266)	107 **Bh** Bohrium (264)	108 **Hs** Hassium (277)	109 **Mt** Meitnerium (268)	110 **Uun** Ununnilium (281)	111 **Uuu** Unununium (272)	112 **Uub** Ununbium (285)		114 **Uuq** Ununquadium (289)		116 **Uuh** Ununhexium (292)		

Lanthanides	57 $^2D_{3/2}$ **La** Lanthanum 138.9055 $[Xe]5d6s^2$ 5.5769	58 $^1G^\circ_4$ **Ce** Cerium 140.116 $[Xe]4f5d6s^2$ 5.5387	59 $^4I^\circ_{9/2}$ **Pr** Praseodymium 140.90765 $[Xe]4f^36s^2$ 5.473	60 $^5I_4$ **Nd** Neodymium 144.24 $[Xe]4f^46s^2$ 5.5250	61 $^6H^\circ_{5/2}$ **Pm** Promethium (145) $[Xe]4f^56s^2$ 5.582	62 $^7F_0$ **Sm** Samarium 150.36 $[Xe]4f^66s^2$ 5.6437	63 $^8S^\circ_{7/2}$ **Eu** Europium 151.964 $[Xe]4f^76s^2$ 5.6704	64 $^9D^\circ_2$ **Gd** Gadolinium 157.25 $[Xe]4f^75d6s^2$ 6.1498	65 $^6H^\circ_{15/2}$ **Tb** Terbium 158.92534 $[Xe]4f^96s^2$ 5.8638	66 $^5I_8$ **Dy** Dysprosium 162.500 $[Xe]4f^{10}6s^2$ 5.9389	67 $^4I^\circ_{15/2}$ **Ho** Holmium 164.93032 $[Xe]4f^{11}6s^2$ 6.0215	68 $^3H_6$ **Er** Erbium 167.259 $[Xe]4f^{12}6s^2$ 6.1077	69 $^2F^\circ_{7/2}$ **Tm** Thulium 168.93421 $[Xe]4f^{13}6s^2$ 6.1843	70 $^1S_0$ **Yb** Ytterbium 173.04 $[Xe]4f^{14}6s^2$ 6.2542	71 $^2D_{3/2}$ **Lu** Lutetium 174.967 $[Xe]4f^{14}5d6s^2$ 5.4259
Actinides	89 $^2D_{3/2}$ **Ac** Actinium (227) $[Rn]6d7s^2$ 5.17	90 $^3F_2$ **Th** Thorium 232.0381 $[Rn]6d^27s^2$ 6.3067	91 $^4K_{11/2}$ **Pa** Protactinium 231.03588 $[Rn]5f^26d7s^2$ 5.89	92 $^5L^\circ_6$ **U** Uranium 238.02891 $[Rn]5f^36d7s^2$ 6.1941	93 $^6L_{11/2}$ **Np** Neptunium (237) $[Rn]5f^46d7s^2$ 6.2657	94 $^7F_0$ **Pu** Plutonium (244) $[Rn]5f^67s^2$ 6.0260	95 $^8S^\circ_{7/2}$ **Am** Americium (243) $[Rn]5f^77s^2$ 5.9738	96 $^9D^\circ_2$ **Cm** Curium (247) $[Rn]5f^76d7s^2$ 5.9914	97 $^6H^\circ_{15/2}$ **Bk** Berkelium (247) $[Rn]5f^97s^2$ 6.1979	98 $^5I_8$ **Cf** Californium (251) $[Rn]5f^{10}7s^2$ 6.2817	99 $^4I^\circ_{15/2}$ **Es** Einsteinium (252) $[Rn]5f^{11}7s^2$ 6.42	100 $^3H_6$ **Fm** Fermium (257) $[Rn]5f^{12}7s^2$ 6.50	101 $^2F^\circ_{7/2}$ **Md** Mendelevium (258) $[Rn]5f^{13}7s^2$ 6.58	102 $^1S_0$ **No** Nobelium (259) $[Rn]5f^{14}7s^2$ 6.65	103 $^2P^\circ_{1/2}$? **Lr** Lawrencium (262) $[Rn]5f^{14}7s^27p$? 4.9 ?

Atomic Number
Ground-state Level
Symbol
Name
Atomic Weight†
Ground-state Configuration
Ionization Energy (eV)

58 $^1G^\circ_4$
Ce
Cerium
140.116
$[Xe]4f5d6s^2$
5.5387

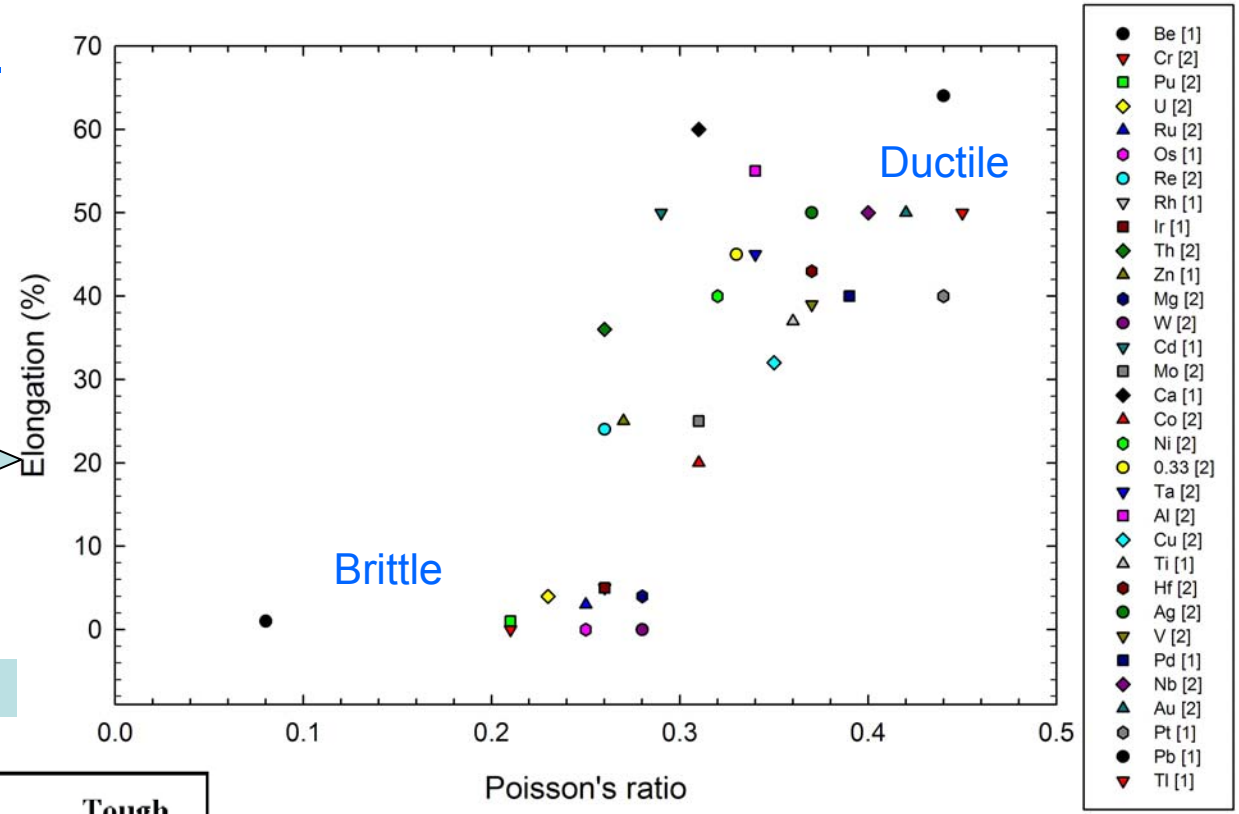
†Based upon ^{12}C. () indicates the mass number of the most stable isotope.

For a description of the data, visit physics.nist.gov/data

NIST SP 966 (September 2003)

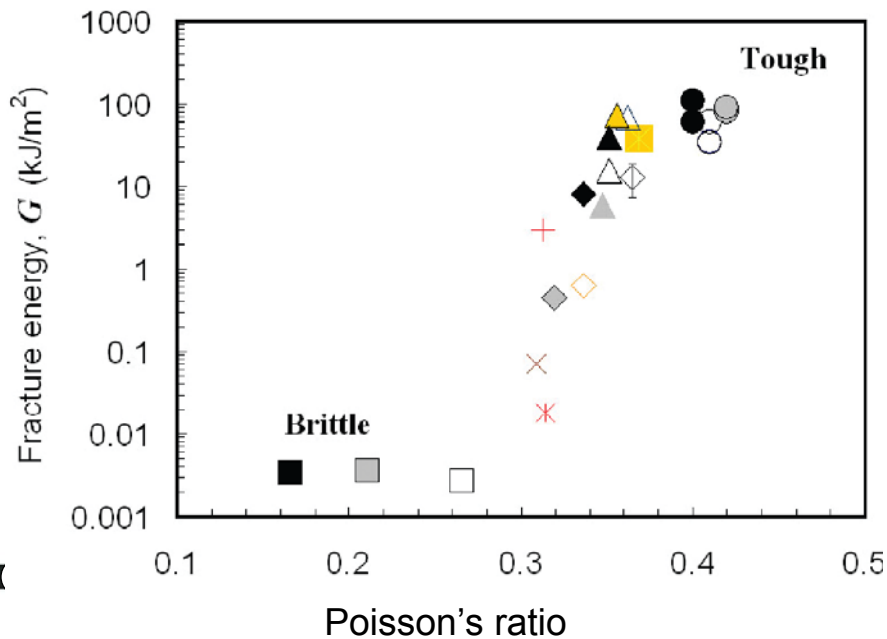
Ductility and Toughness vs. Poisson ratio

crystalline metals (purity≥ 99.9%)



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

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



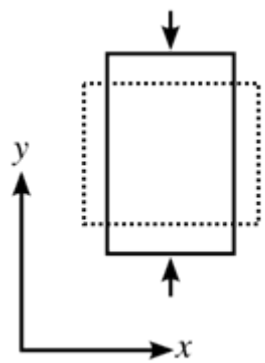
Amorphous alloys
Amorphous+crystalline composite

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

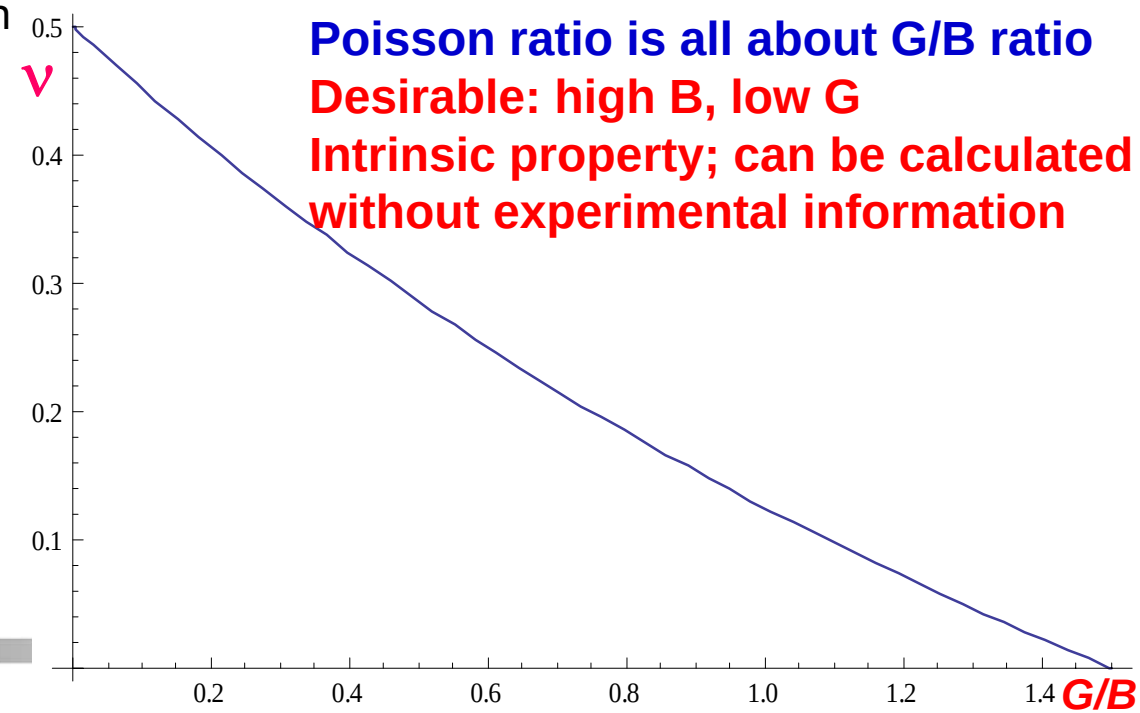
B = bulk modulus

General Hook's law

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

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

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



Poisson ratio is all about G/B ratio

Desirable: high B, low G

Intrinsic property; can be calculated without experimental information

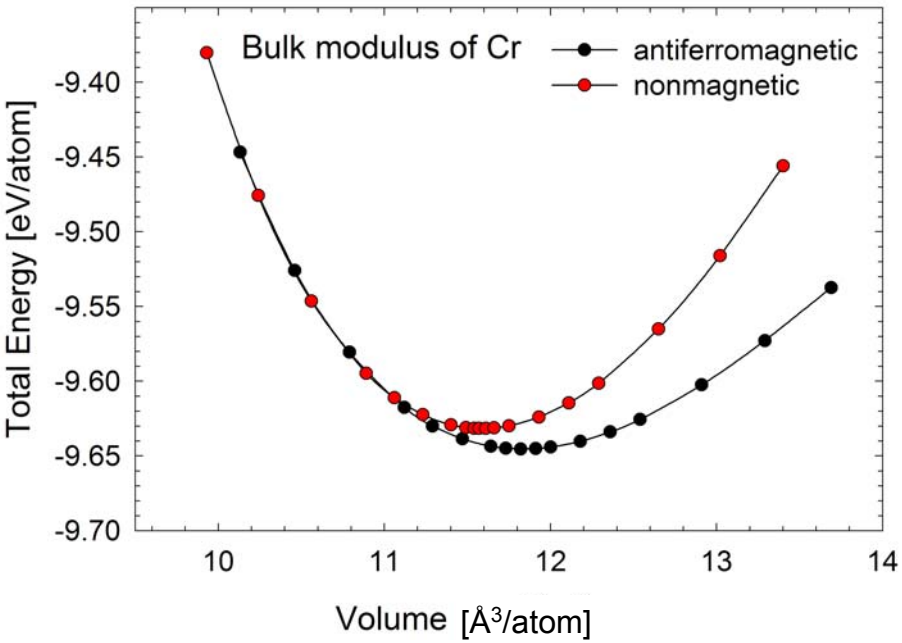
Computational Details

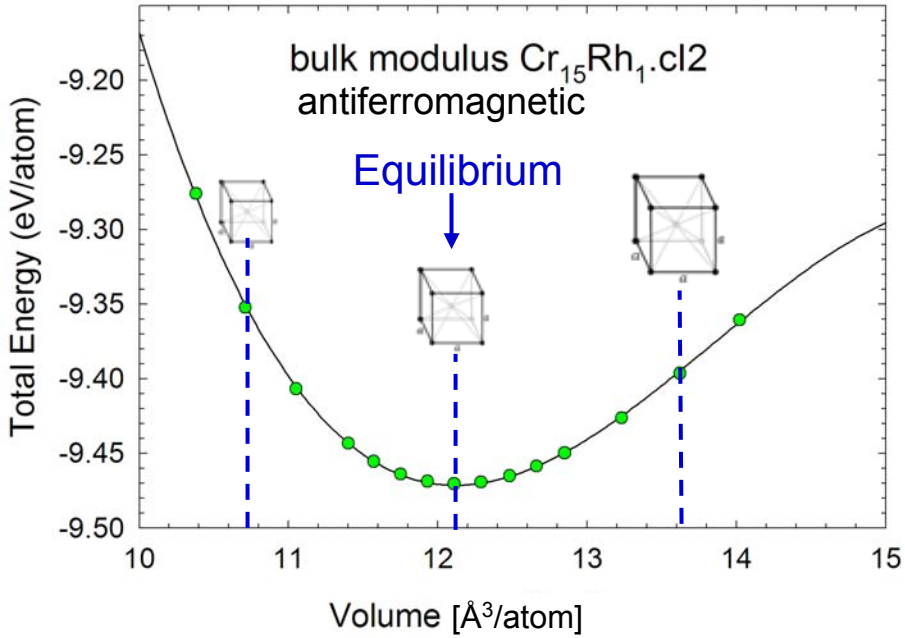
- **VASP package is used**
- **Projector augmented-wave pseudopotentials**
- **Perdew-Burke-Ernzerhof gradient approximation to the exchange-correlation functional**
- **Energy cutoff = 500 eV**
- **Convergence w.r.t. K-points:1 meV**
- **Precision "high"**
- **semi-core 3p, 4p and 5p electrons treated as valence**
- **Spin polarization considered (antiferromagnetism)**
- **2x2x2 supercell bcc lattice**
- Binary: **composition of** $Cr_{15}X_1$ (X=6.25at%) **and** Mo_1X_1 (X=50at%) **in bcc structure**
- Ternary**: composition** $Cr_8V_7X_1$, $Cr_8Mo_7X_1$, $Cr_8Fe_7X_1$ **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

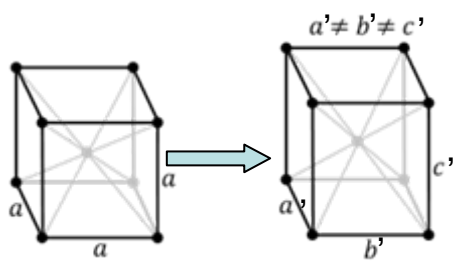
$$G^3 + \frac{9B+4C'}{8}G^2 - \frac{3C_{44}(B+4C')}{8}G - \frac{3C_{44}C'B}{4} = 0 \qquad C' = \tfrac{1}{2}(C_{11} - C_{12}) \qquad B = \tfrac{1}{3}(C_{11} + 2C_{12})$$

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

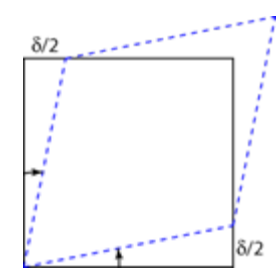
$$\varepsilon_o = \begin{pmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & \delta^2/(1-\delta^2) \end{pmatrix}$$



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

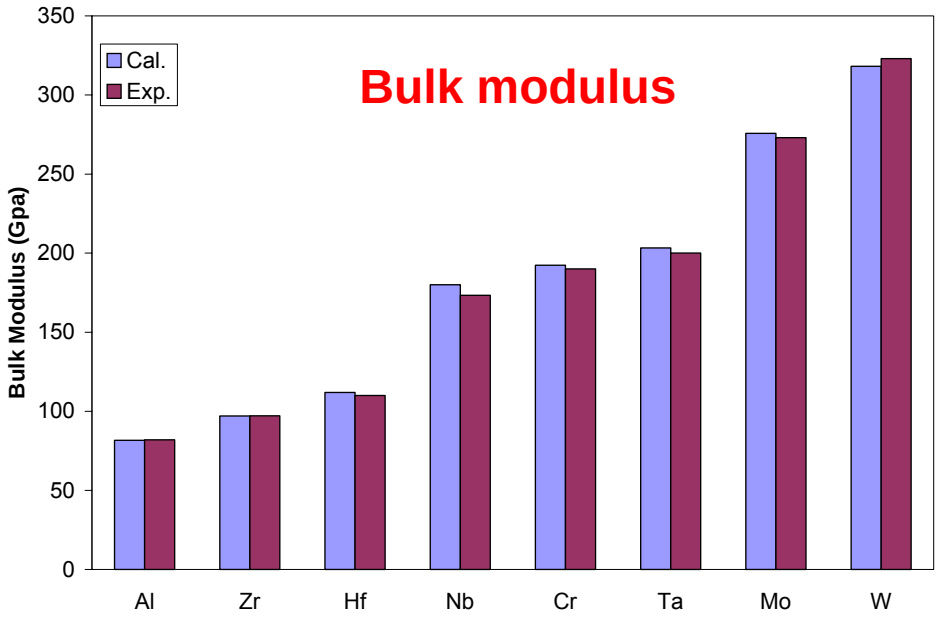
Applying monoclinic strain

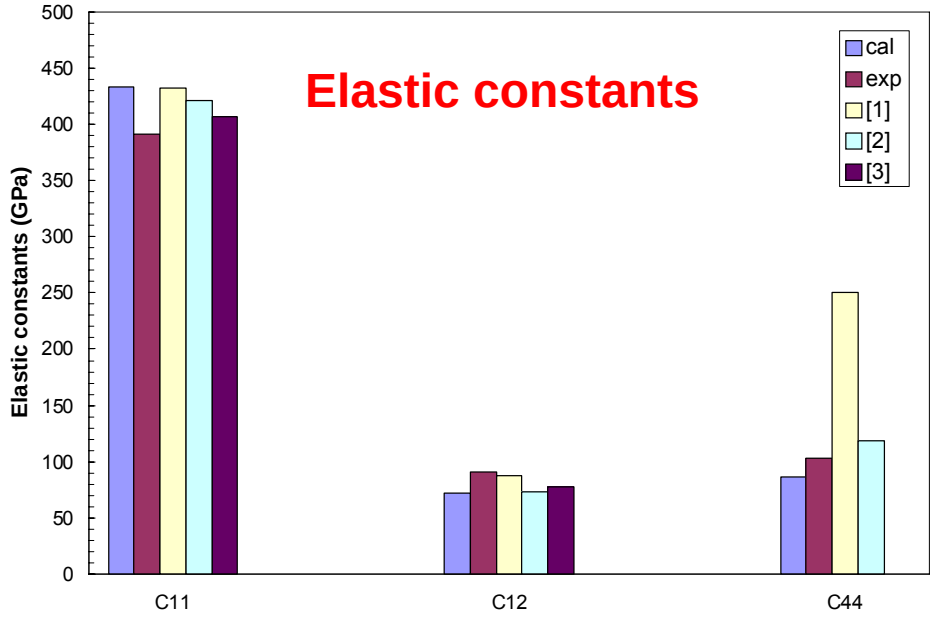
$$\varepsilon_m = \begin{pmatrix} 0 & \delta/2 & 0 \\ \delta/2 & 0 & 0 \\ 0 & 0 & \delta^2/(4-\delta^2) \end{pmatrix}$$

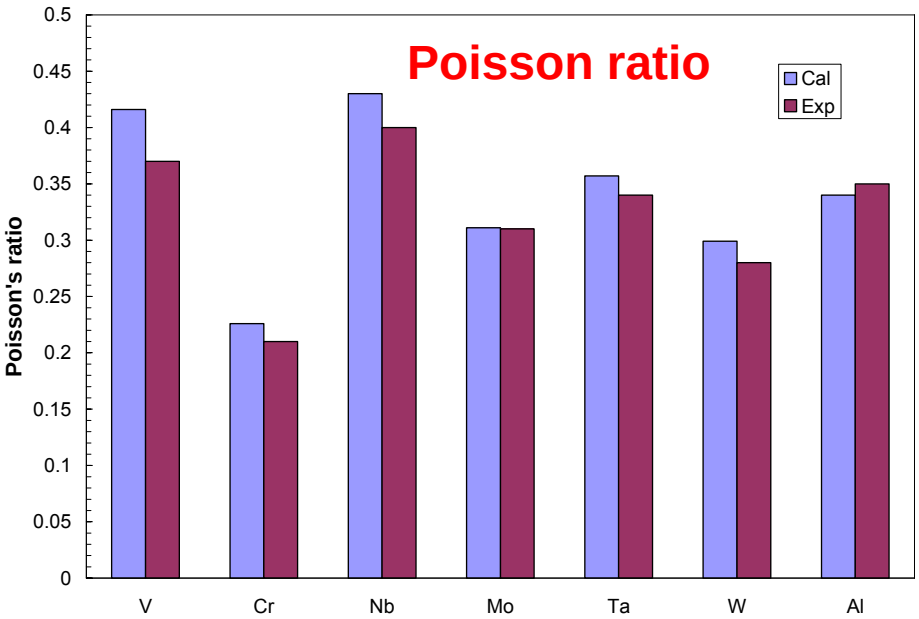


$$\Delta E(\delta) = E(0) - E(\delta) = \tfrac{1}{2}C_{44}V_0\delta^2 + O[\delta^4]$$

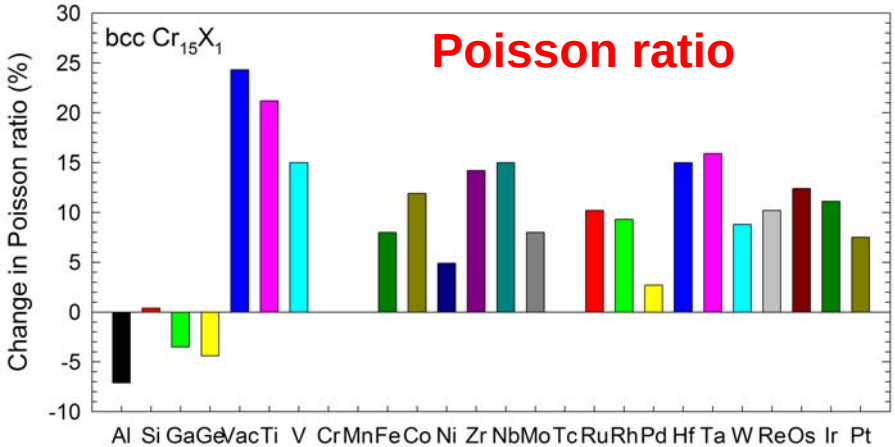
Validation of Computation

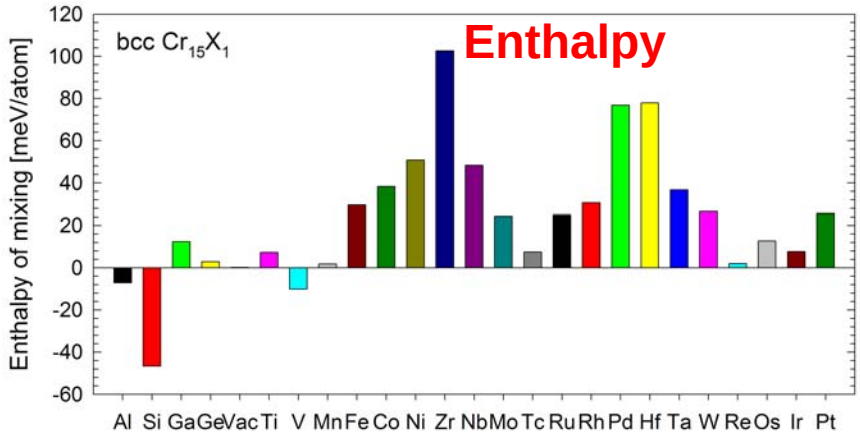


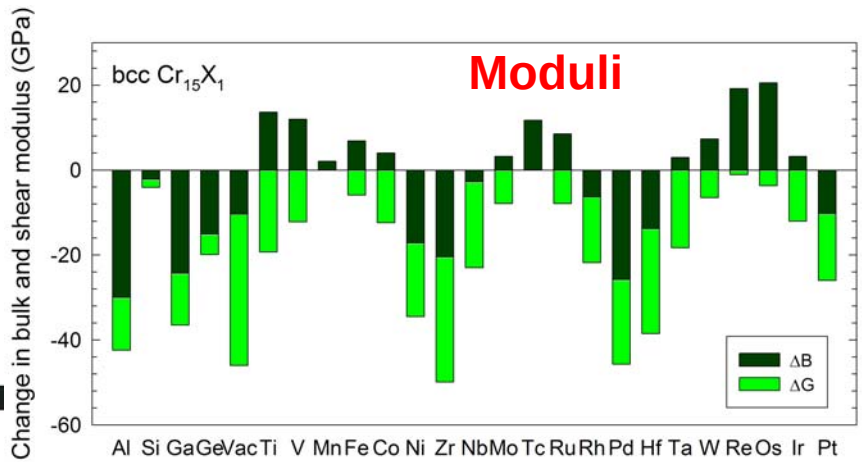




*[1] Phys Rev B **54** (1996) 4519 (tight binding)*
*[2] Phys Rev B **62** (2000) 5136 (DFT full potential)*
*[3] Phys Rev B **67** (2003) 134204 (DFT full potential)*







~~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 (CrVX, CrFeX, CrMoX) 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