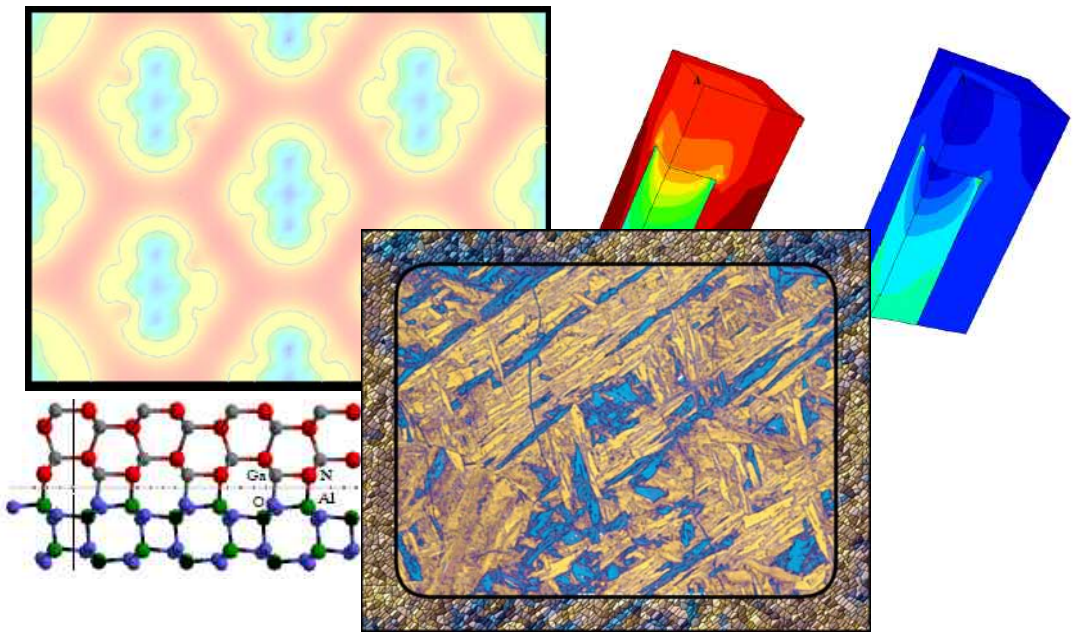
NATIONAL ENERGY TECHNOLOGY LABORATORY

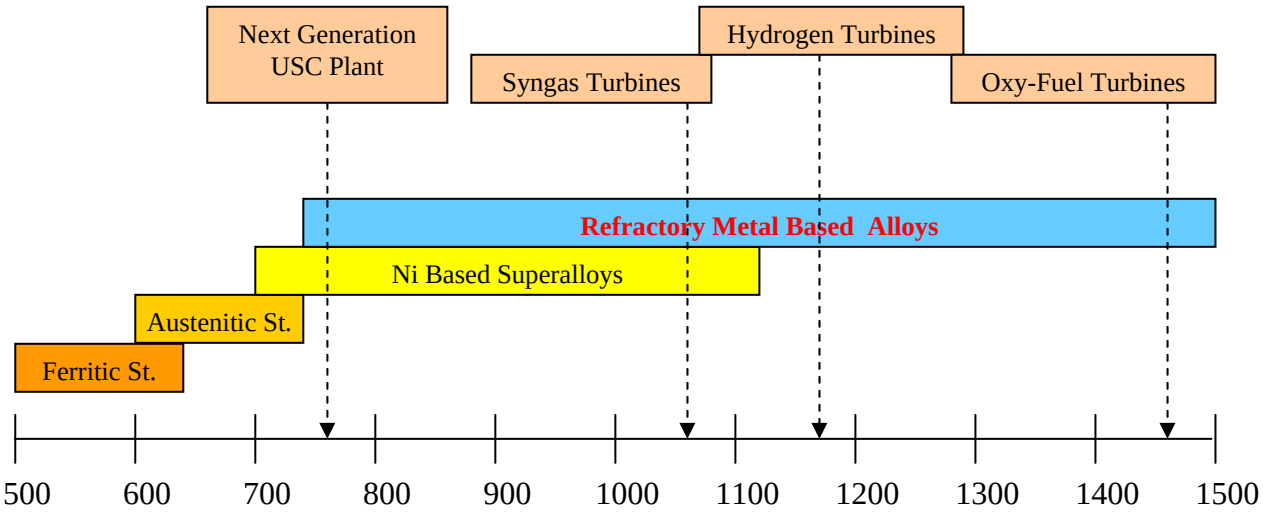


Computational Design and Experimental Verification of Refractory Metal-Based Alloys

Ömer Doğan, Michael Gao, Wren Chan, Paul King

23rd Annual Conference on Fossil Energy Materials – May 12-14, 2009 – Pittsburgh, PA

New Energy Conversion 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

Pros and Cons of Refractory Metals

- ❖ **Good high-temperature strength**
- ❖ **High thermal conductivity, low CTE**
- ➢ **Low ductility at low temperatures thus difficult to fabricate**
- ➢ **Poor oxidation resistance at high temperatures**
- ❑ **Cr has good corrosion resistance due to formation of Cr_2O_3 scale**
- ❑ **Cr is relatively abundant; Cr has low density; high thermal conductivity**

Key Property Requirements

- **Ductility at low temperatures**
  - ⇨ Required for processing e.g. machining, rolling.
  - ⇨ Elongation
  - ⇨ Area reduction
- **Fracture toughness (i.e., resistance against crack propagation)**
  - ⇨ Minimum: 15-20MPa√m; preferred: ≥20-25MPa√m for structural applications
- **Creep resistance at high temperatures**
- **Corrosion resistance against internal and external oxidation and nitridation at high temperatures**

Cr Alloys Development

Holzwarth et al. J. Nucl. Mat. 300 (2002) 161

- Cr-5Fe-1Y_2O_3: 6.4MPa√m; DBTT 400-500^oC
- Cr-44Fe-5Al-0.3Ti-0.5Y_2O_3: forms dense Al_2O_3 surface layer, very brittle

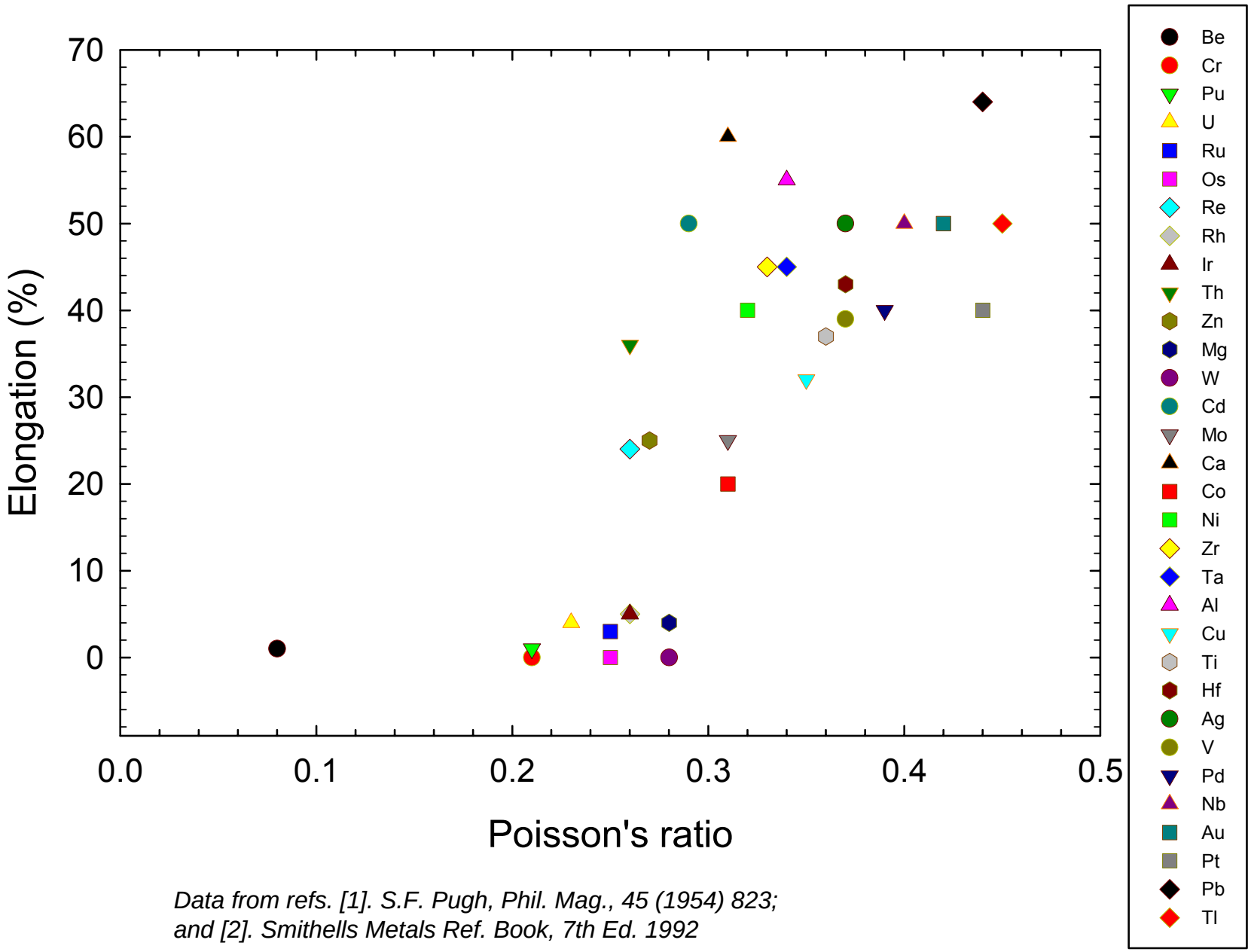
Brady et al, ORNL, Script. Mater. 52 (2005) 815 and more

- Various Cr-Nb, Cr-Ta, Cr-Ni, Cr-Fe alloys
- Cr-30Fe-6.3Ta-4Mo-0.5Ti-0.3Si-0.1La, 20MPa√m and 350 MPa at 1100^oC
- Cr-6wt%MgO-0.75wt%Ti: 10% elongation at RT (hot pressed and extruded)
- Cr-45Fe-6MgO-0.75Ti (wt%): 1% elongation and 650MPa@RT

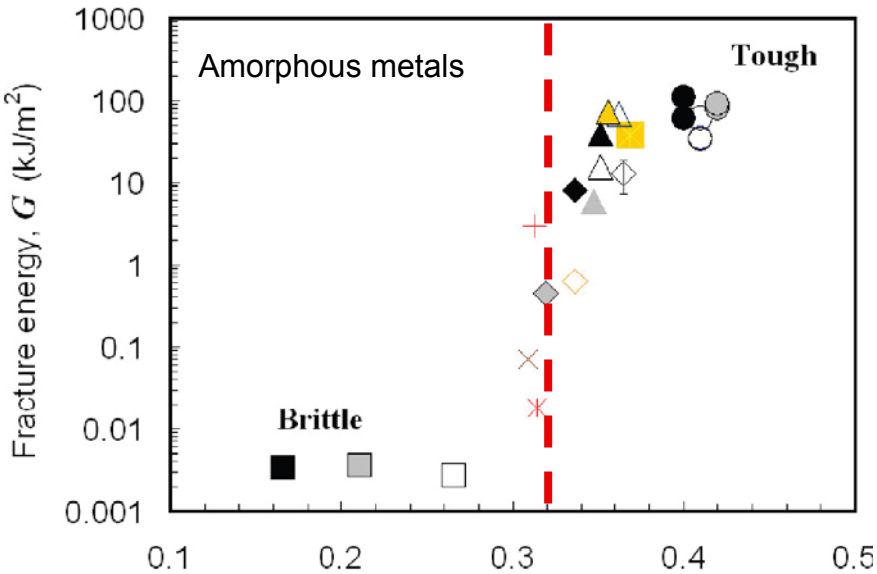
What Controls Ductility of Metals?

- Electronic properties of a solid determine its intrinsic mechanical property.
- Delocalized, mobile electrons contribute to high ductility; localized, immobile electrons cause low ductility.
- Formation of flexible bonds contribute to high ductility; strong directionality of bonds causes low ductility.
- Poisson's ratio is commonly used as a ductility indicator. Metals with higher Poisson's ratio tend to be more ductile.
- Rice-Thompson parameter is another ductility criterion. It considers the ease of dislocation emission compared to crack growth. The lower its value is, more ductile the metal will be.
- Other parameters include unstable twinning, dislocation mobility, etc.

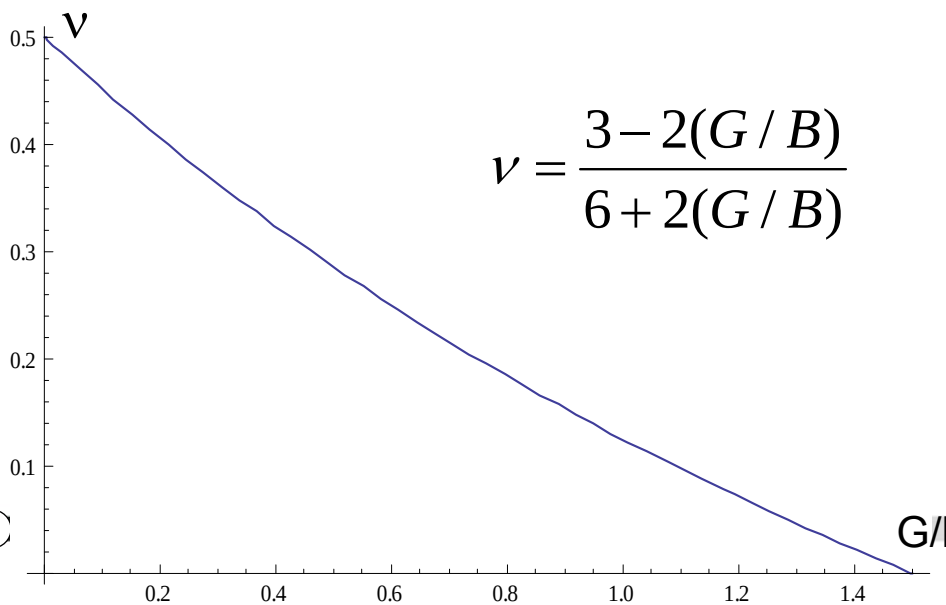
Elongation vs. Poisson's Ratio



Data from refs. [1]. S.F. Pugh, Phil. Mag., 45 (1954) 823; and [2]. Smithells Metals Ref. Book, 7th Ed. 1992



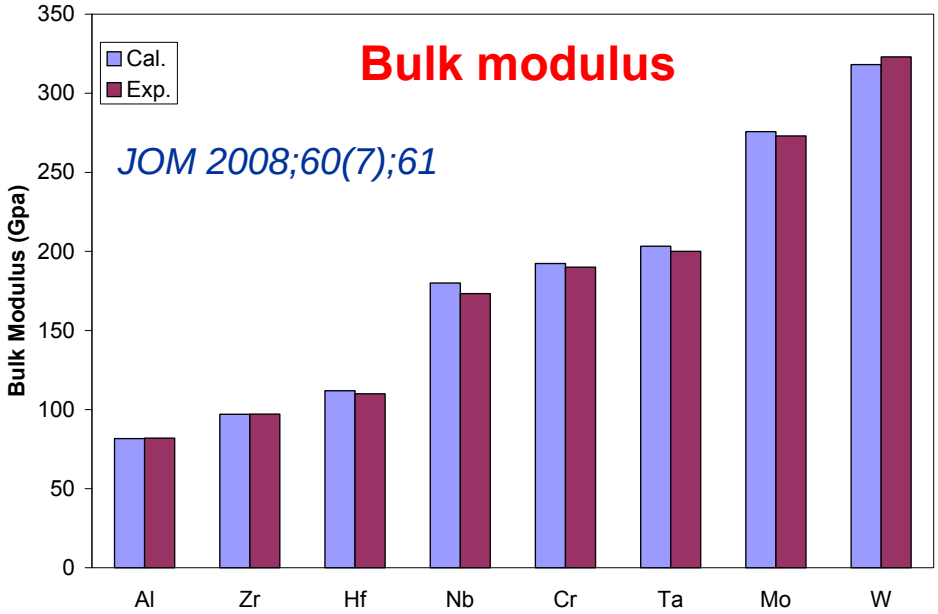
Phil. Mag. Lett. ***85*** *(2005) 77*

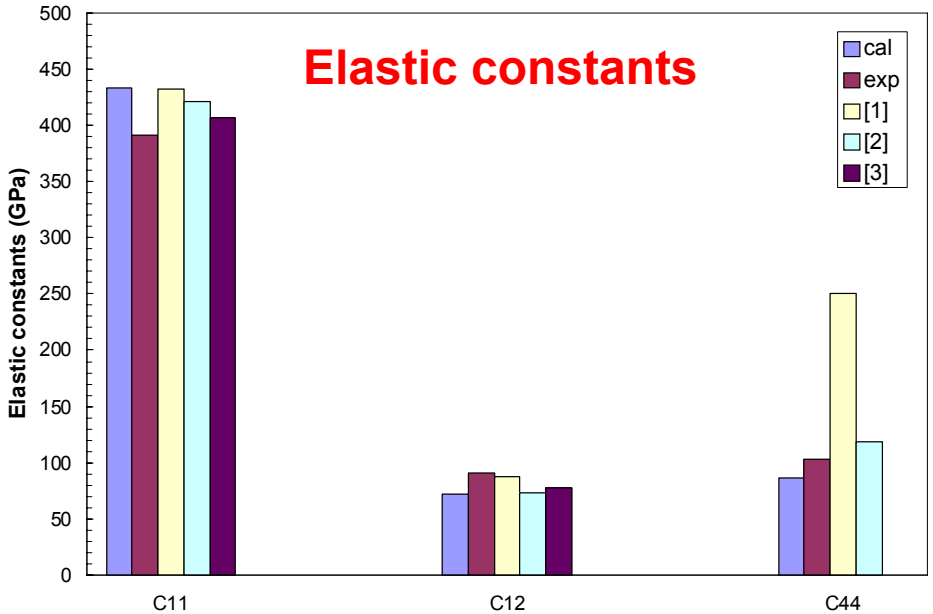


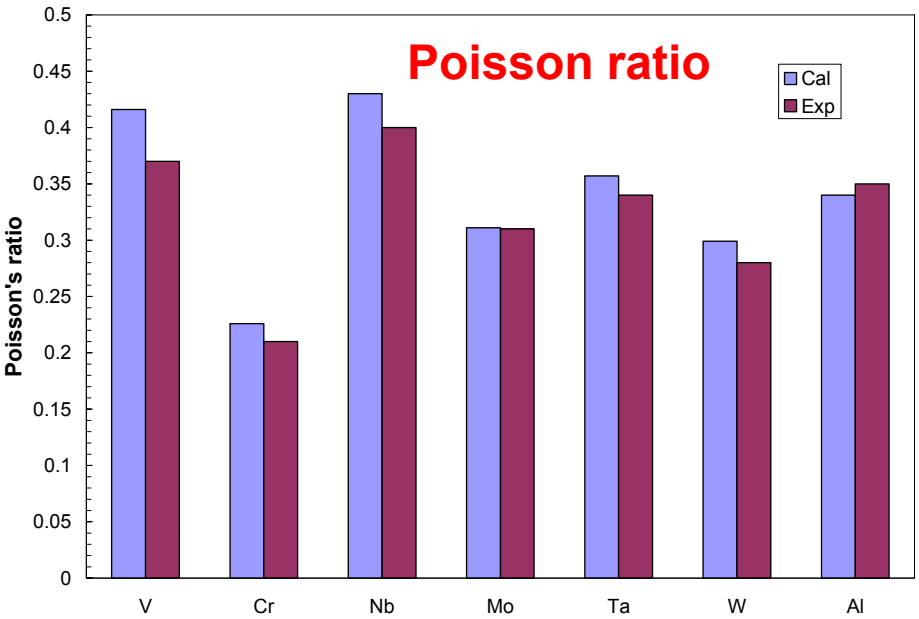
$$\nu = \frac{3 - 2(G/B)}{6 + 2(G/B)}$$

Desirable: high B, low G
Poisson ratio measures the intrinsic properties of a solid.
It can be predicted from first principles DFT calculations.

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)*

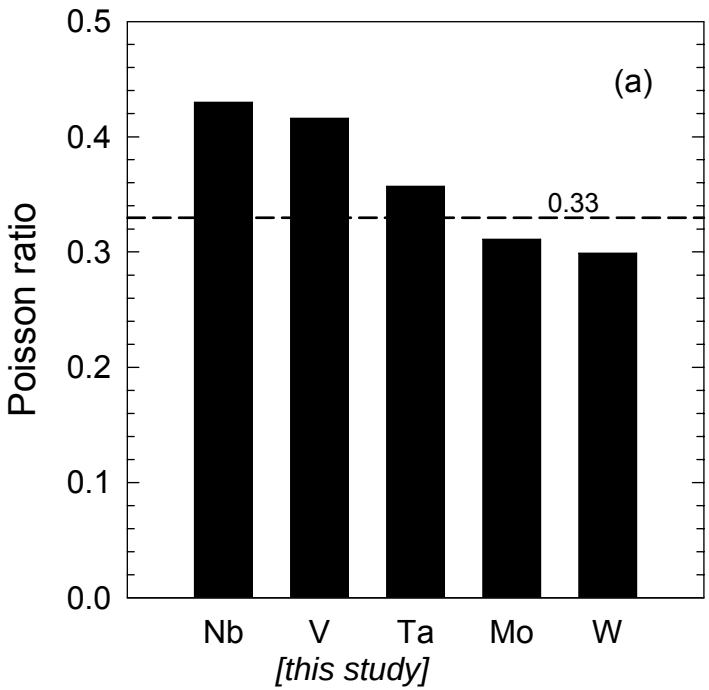
Poisson's Ratio

Poisson's ratio is the ratio of the relative contraction strain divided by the relative extension strain

General Hook's law

$$\varepsilon_{ii} = \frac{1}{E}\left[\sigma_{ii} - \nu(\sigma_{kk} + \sigma_{jj})\right]$$

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



[this study]

Rice-Thompson Parameter

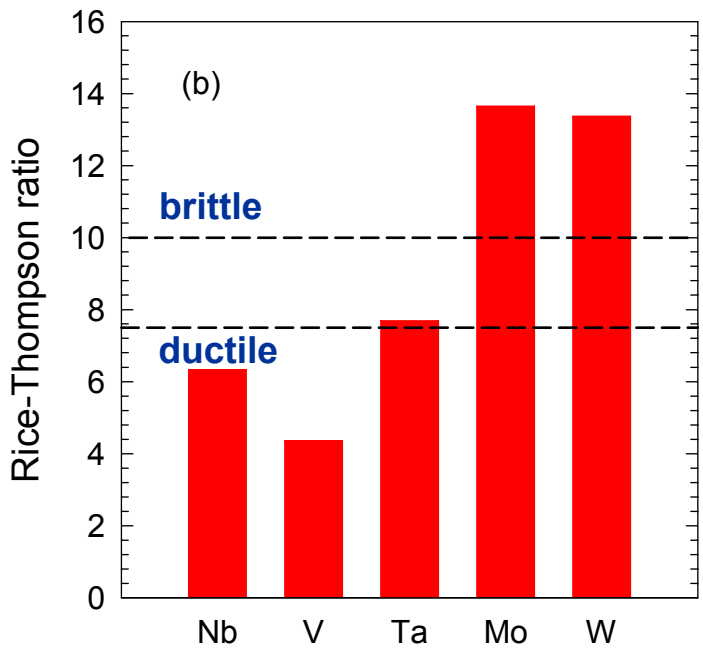
J.R. Rice and R. Thomson: Ductile versus brittle behavior of crystals, Philosophical Magazine, 1974, 29, p.78.

$$R - T_{paramter} = \frac{G^{\{110\}} b^{<[111>}}{\gamma^{\{110\}}}$$

$G^{\{110\}}$ Shear modulus of (110) plane

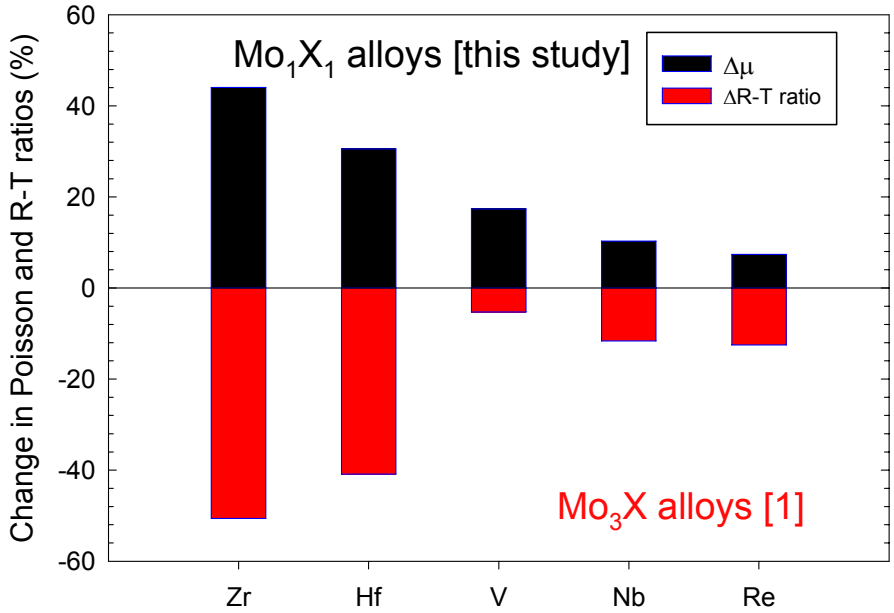
$b^{<111>}$ Burgers vector along [111] direction

$\gamma^{\{110\}}$ Surface energy of (110) plane

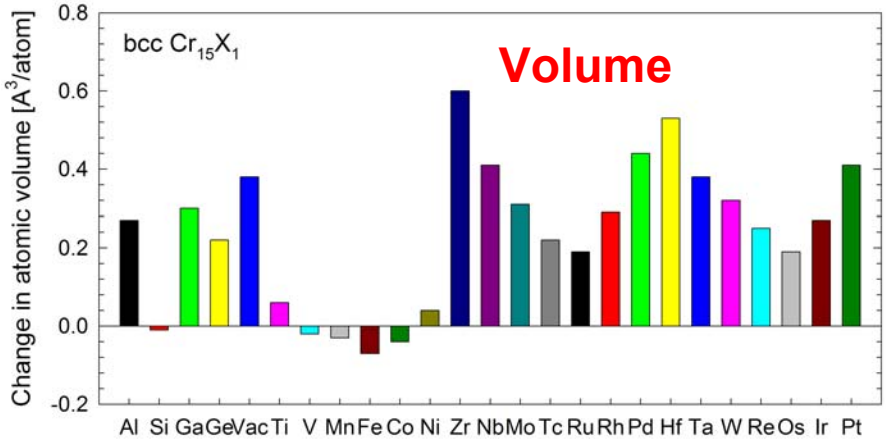


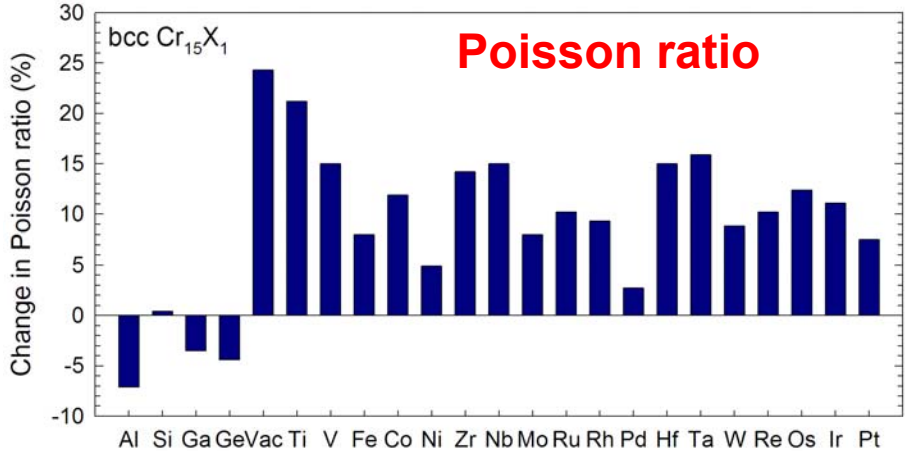
CB.Geller et al, Scripta Mater 52 (2005) 205, "A computational search for ductilizing additives to Mo)"

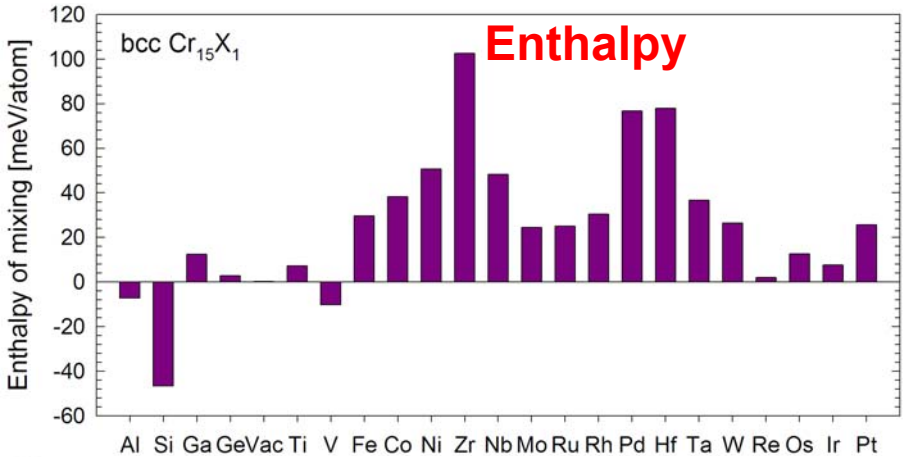
Ductilizing Mo via alloying

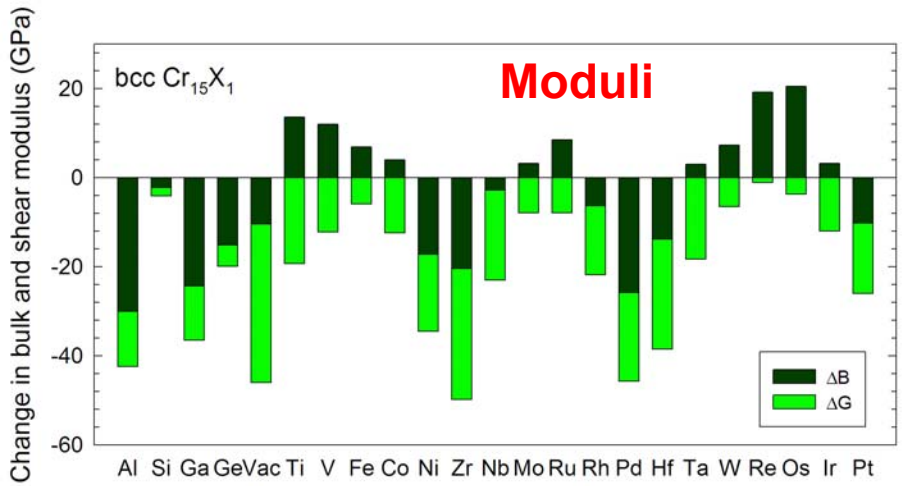


[1] CB.Geller et al, Scripta Mater 52 (2005) 205, "A computational search for ductilizing additives to Mo)"









Major Constituents

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

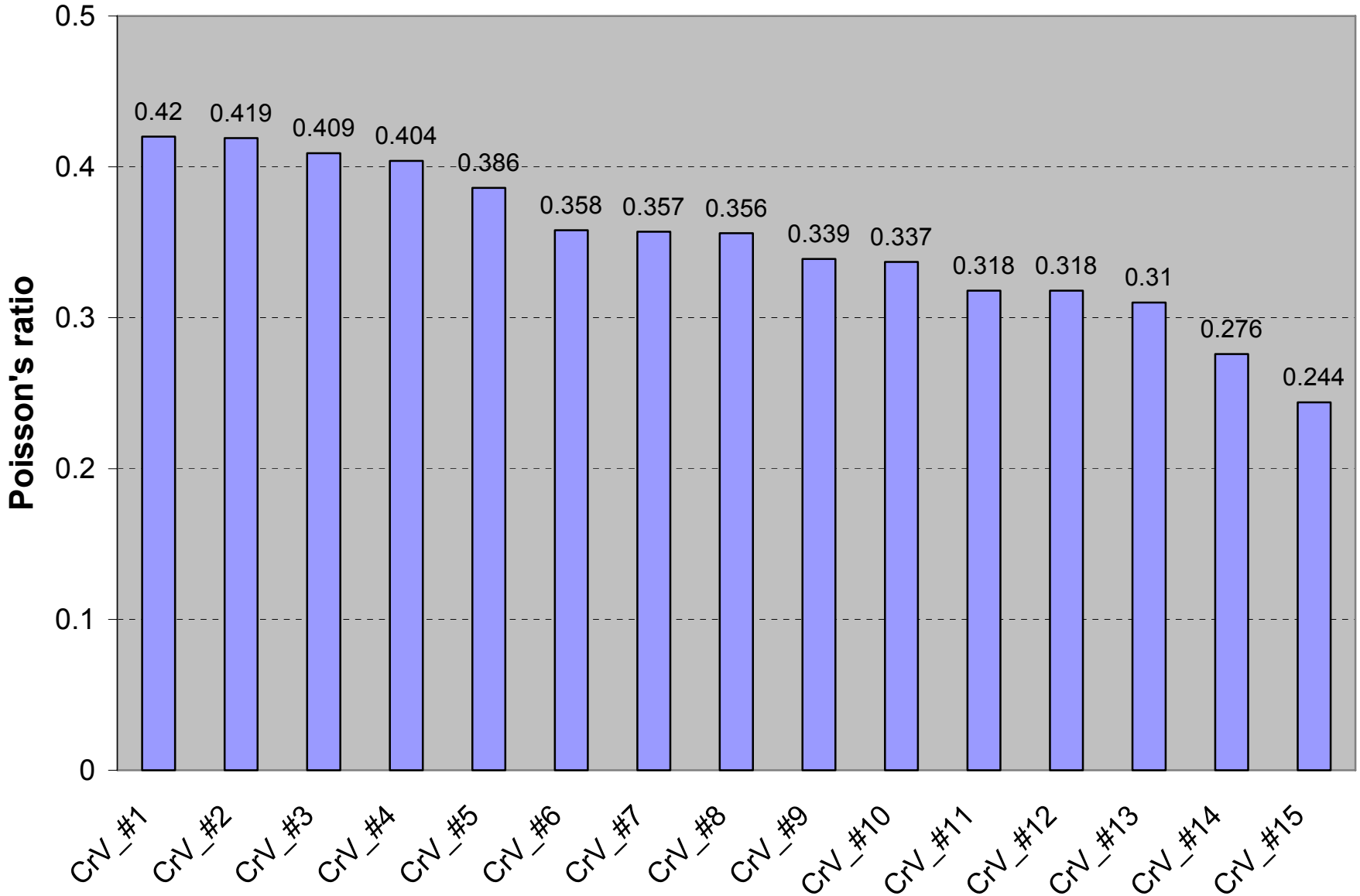
Solubility

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

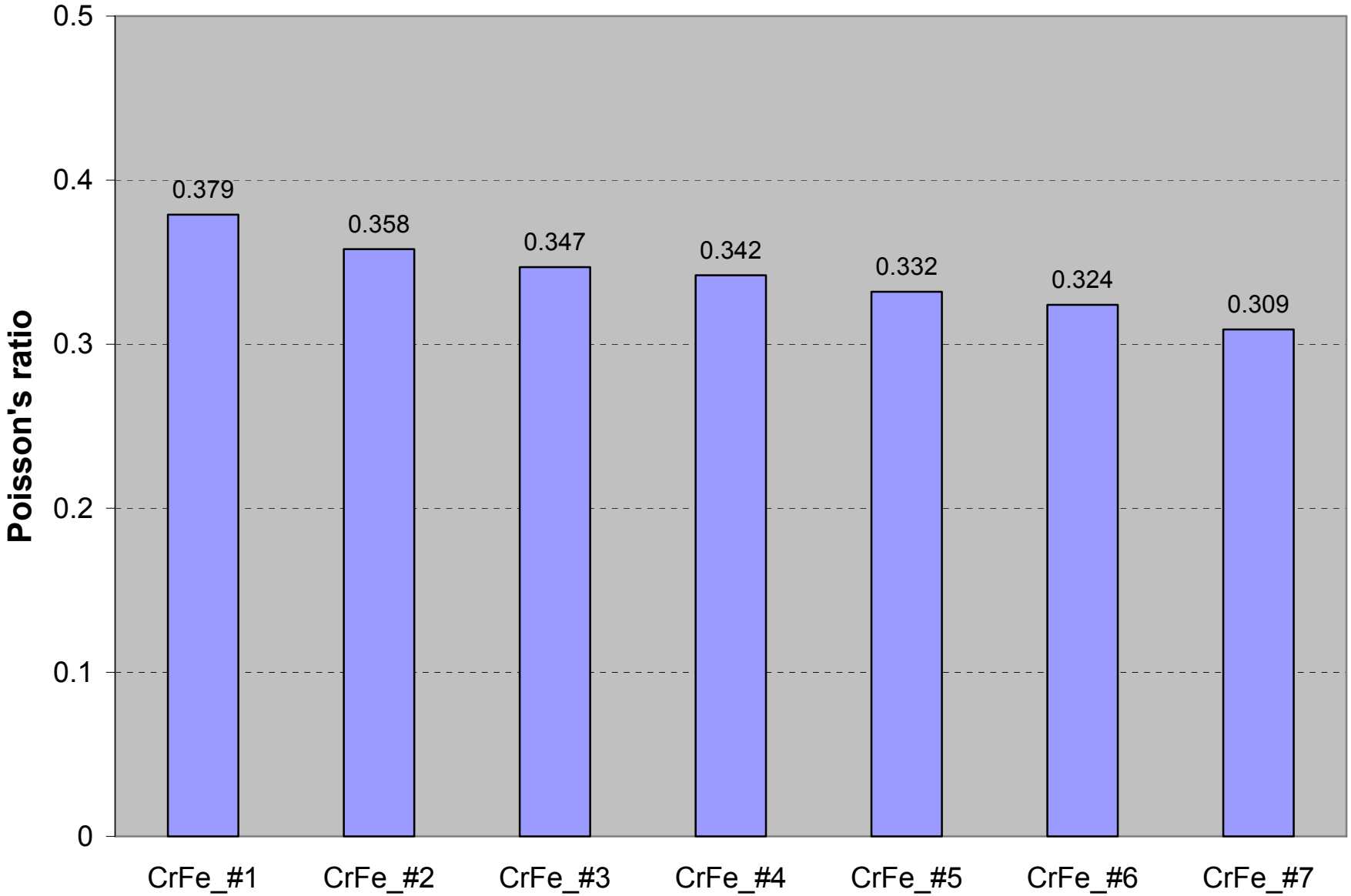
Cost

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

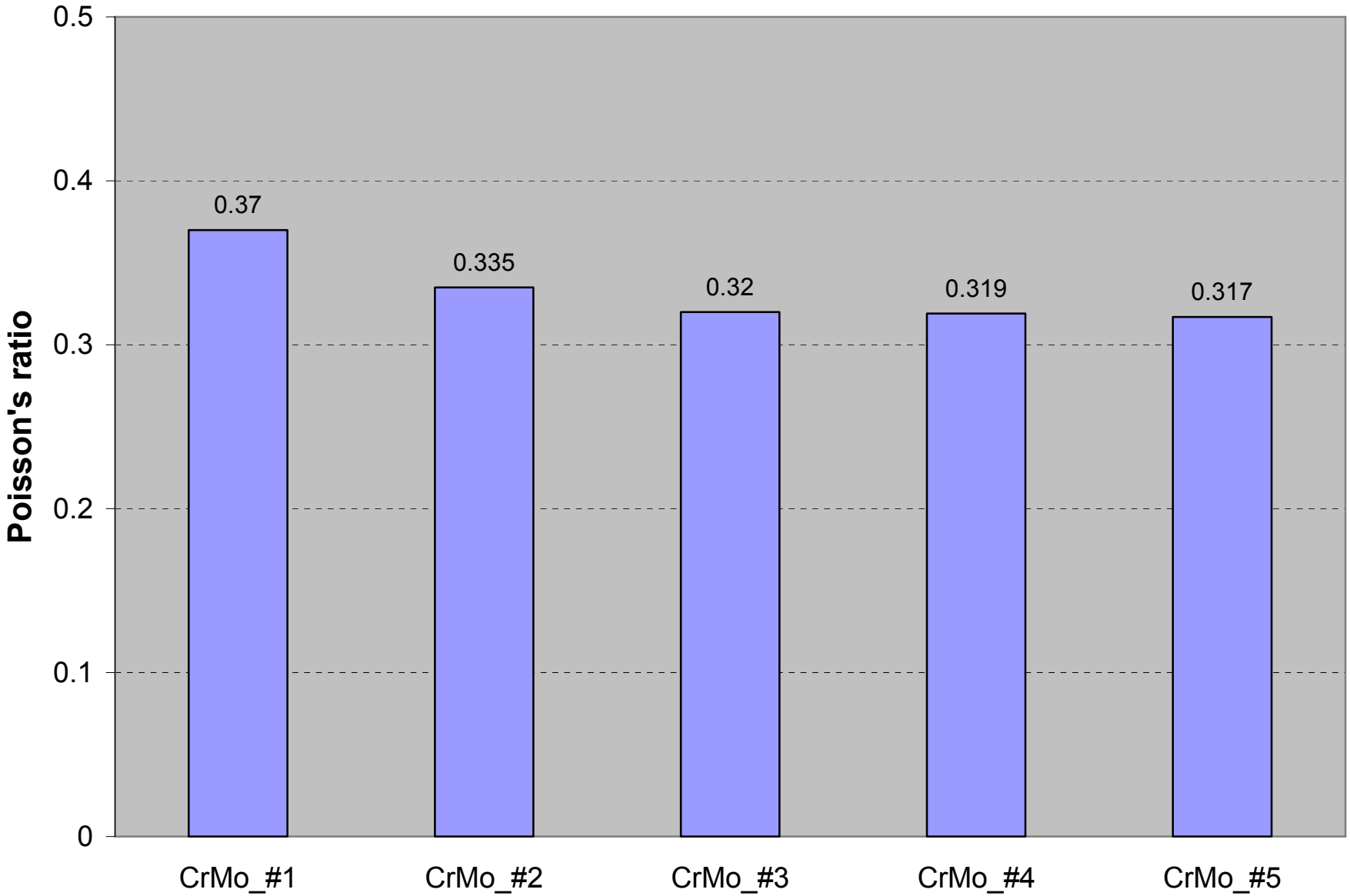
Cr-V-X Ternary Alloys



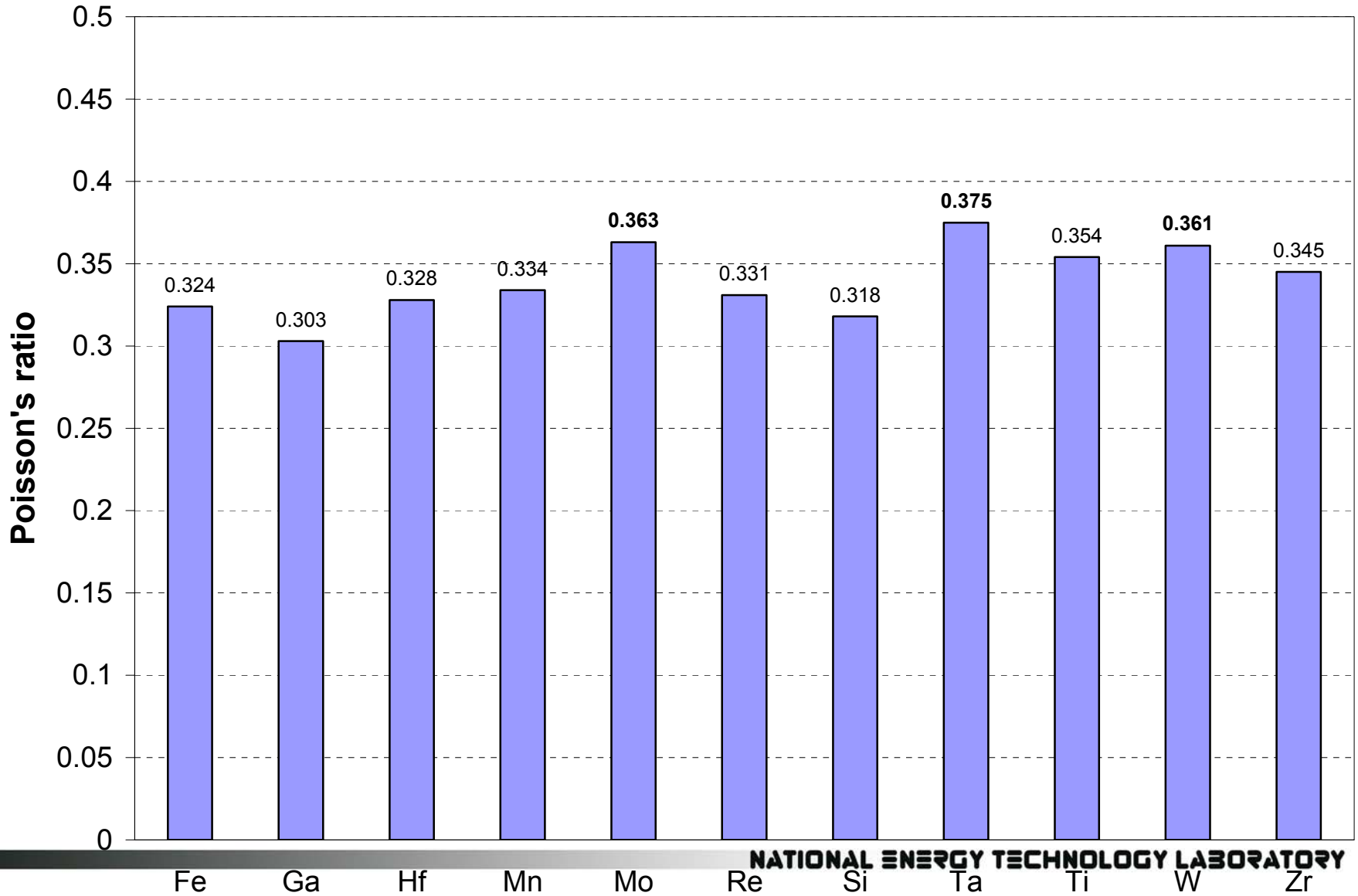
Cr-Fe-X Ternary Alloys



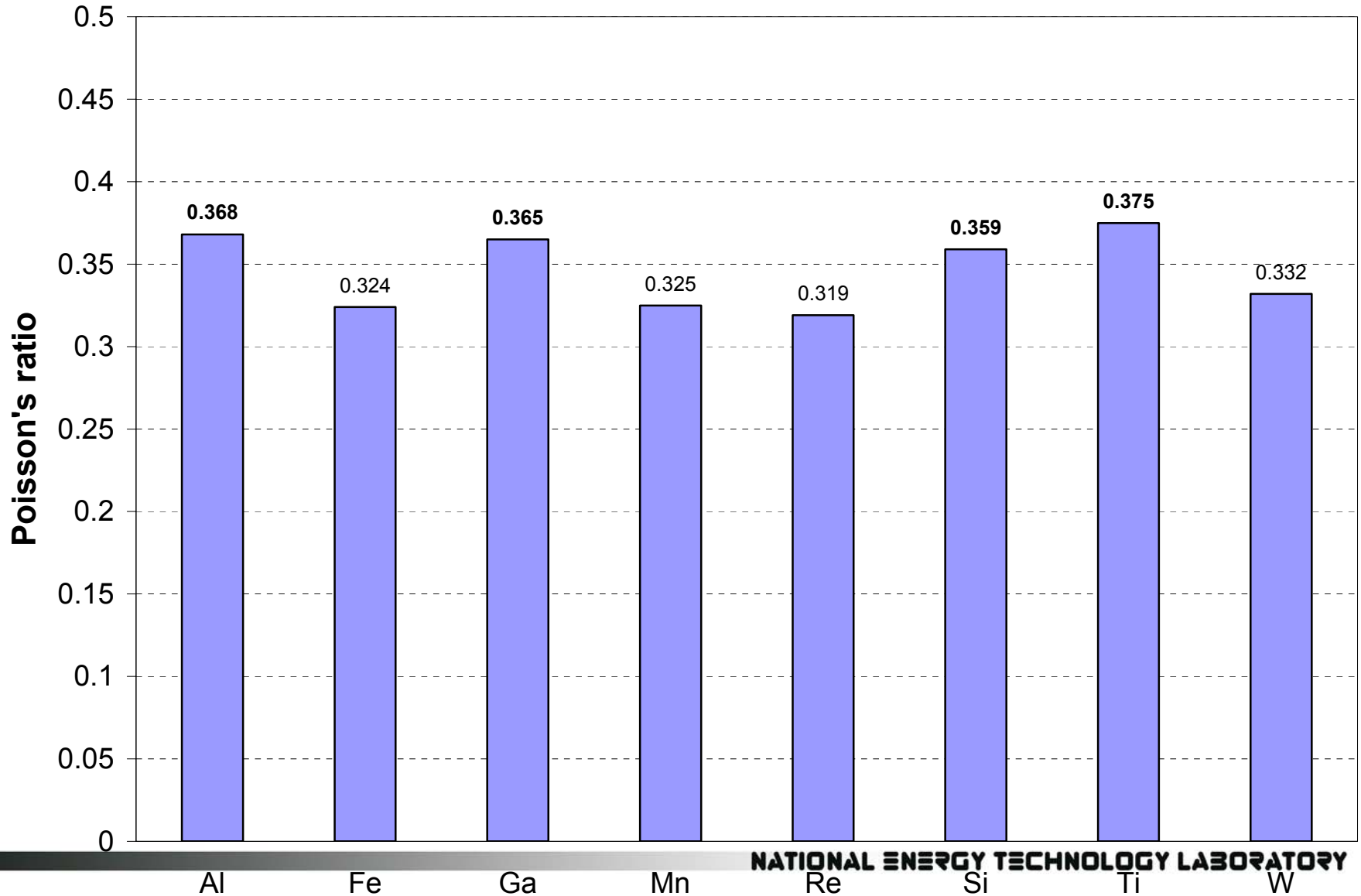
Cr-Mo-X Ternary Alloys



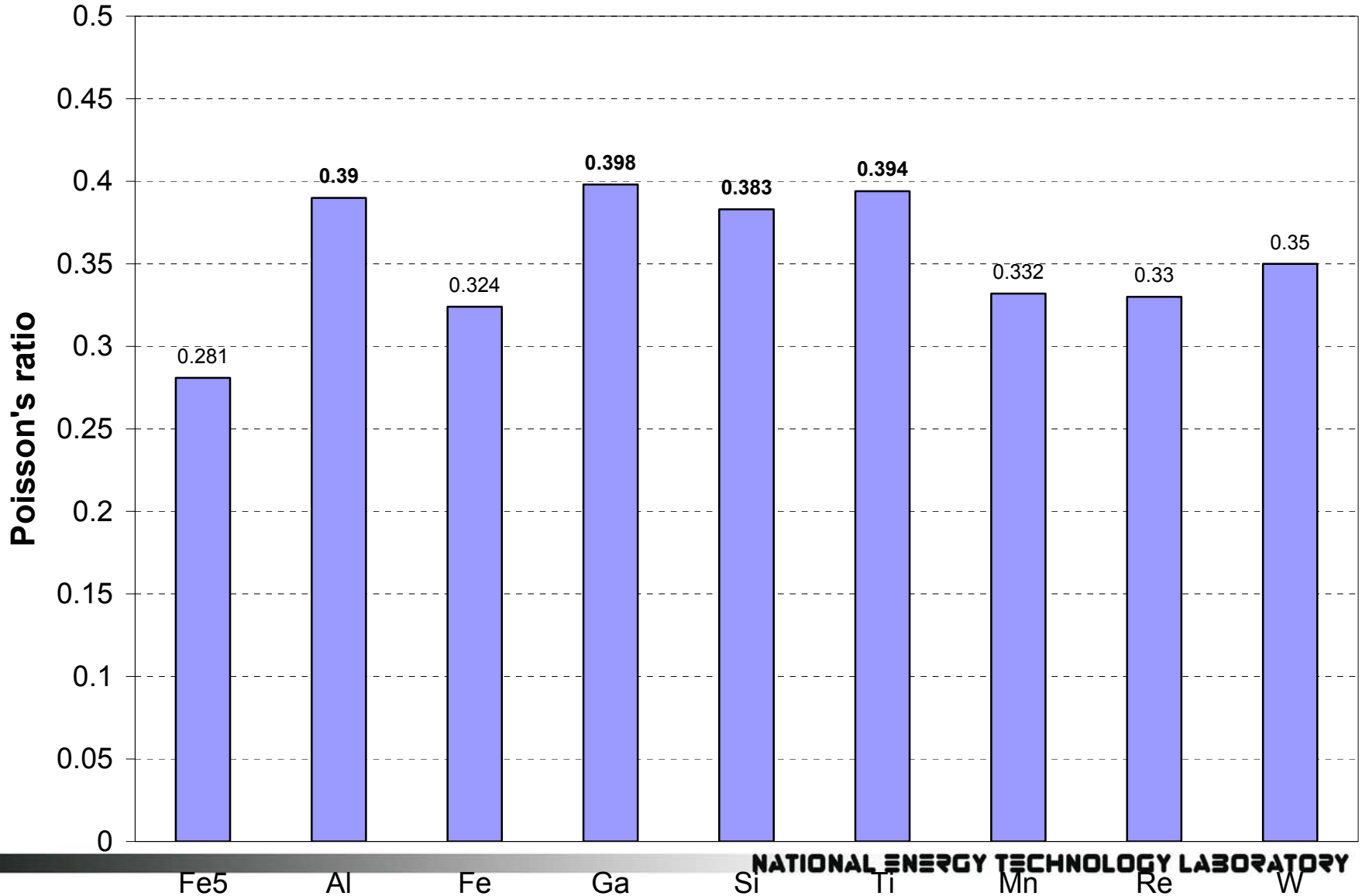
Cr-Quartenary Alloys

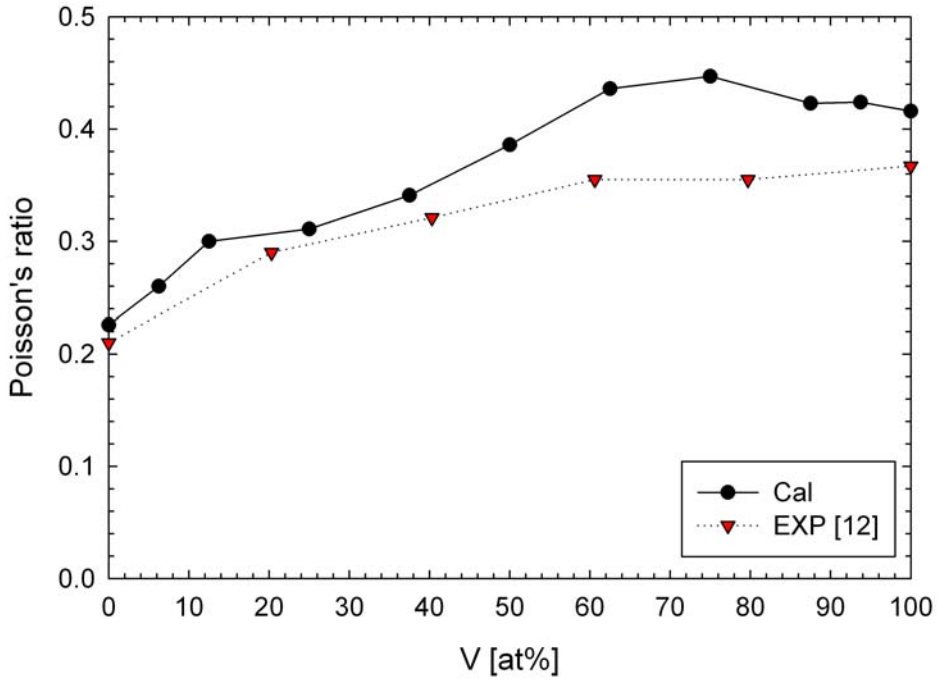


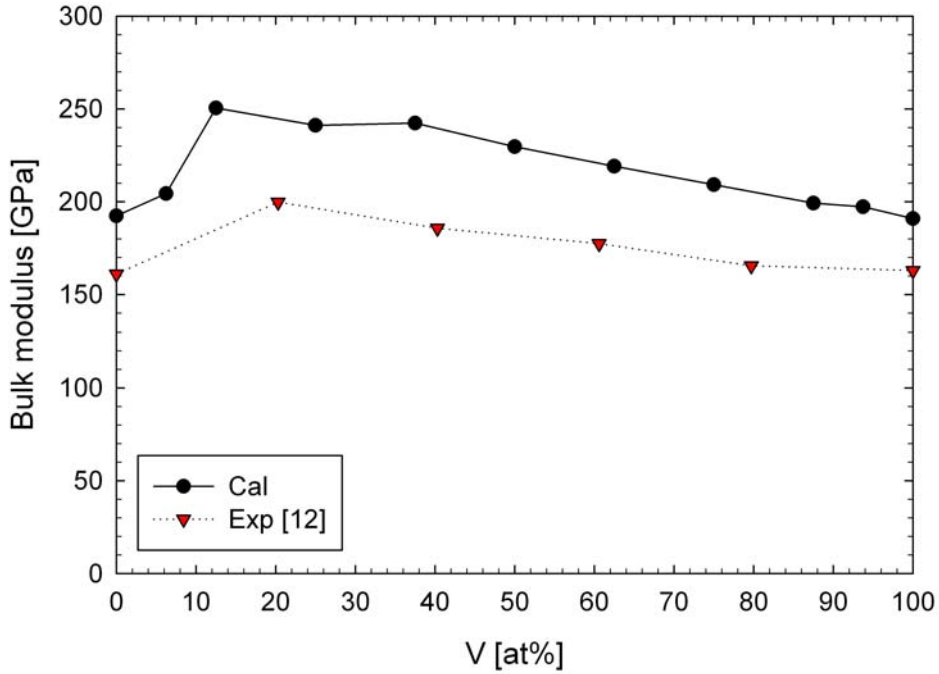
Cr-Quinnary Alloys



Cr-Hexagonary Alloys

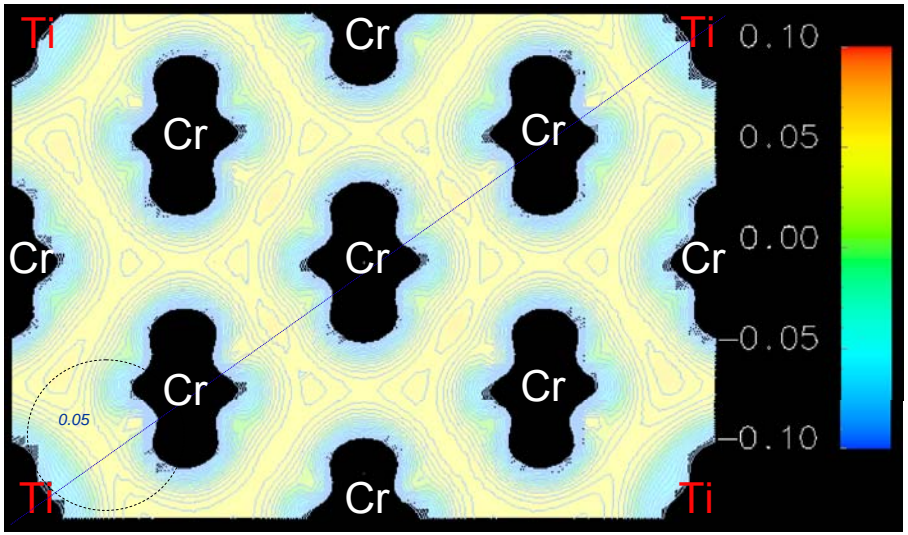




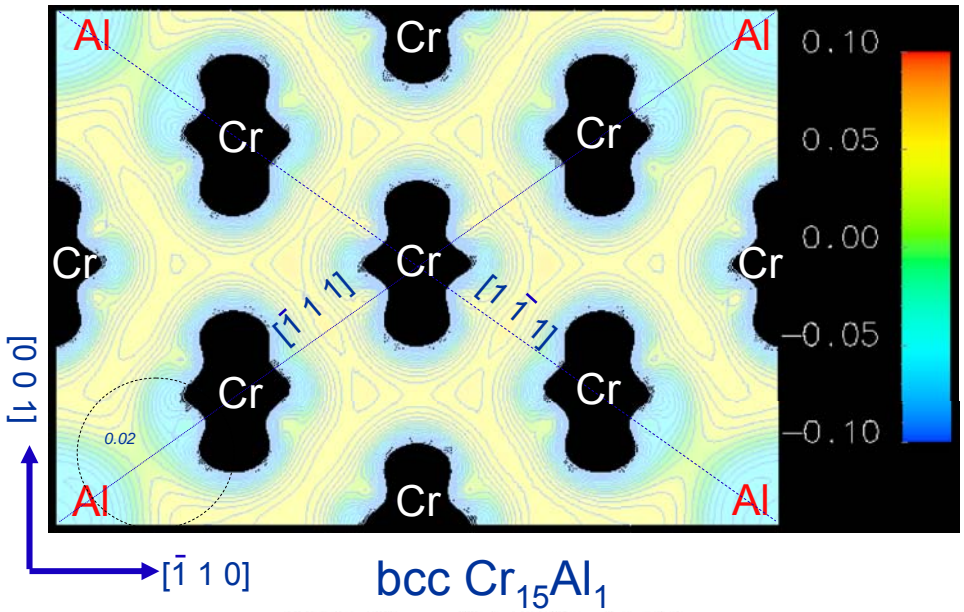


[12] J T Lenkkeri and E E Lahteenkorva, J. Phys. F: Metal Phys.. Vol. 8, No. 8, 1978, “An investigation of elastic moduli of vanadium-chromium alloys”

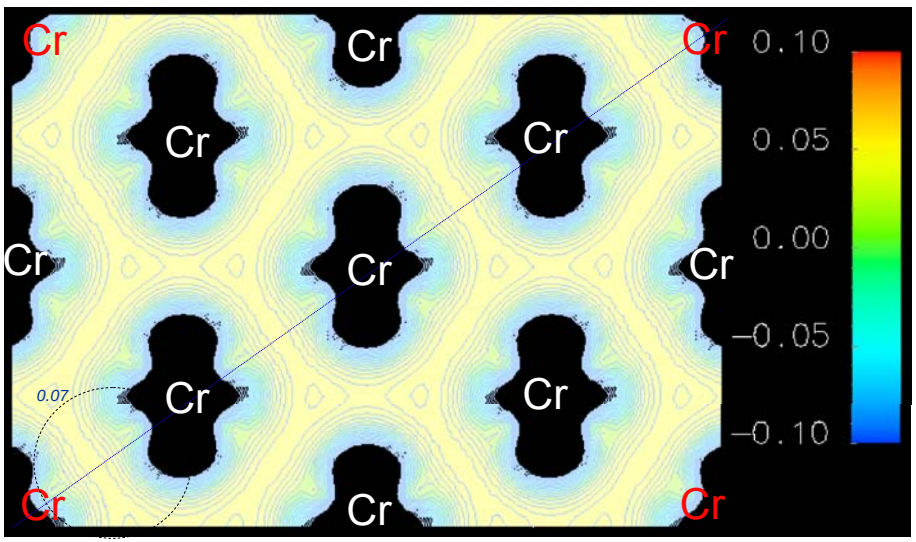
Charge Density Plot: (1 1 0) Plane



bcc $Cr_{15}Ti_1$

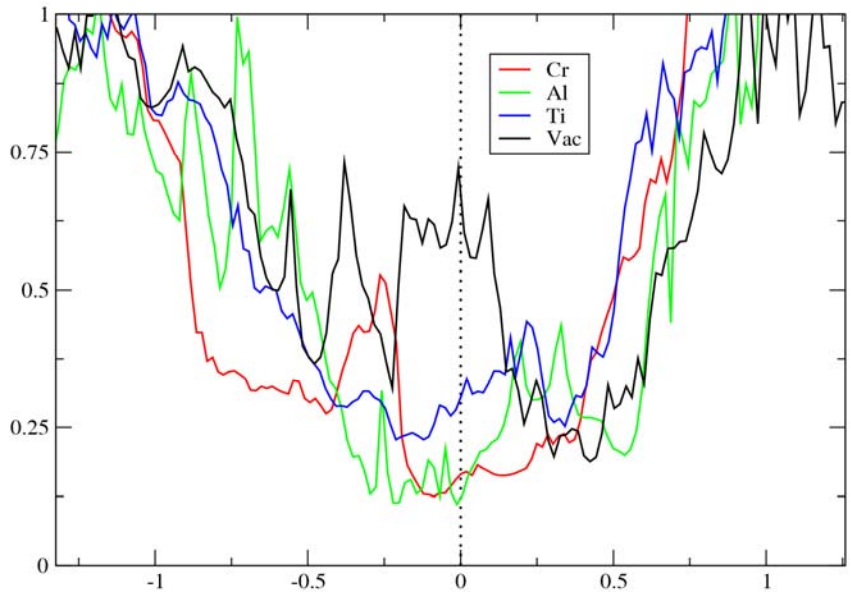


bcc $Cr_{15}Al_1$



bcc Cr

DOS Plots of Cr15X1.cI2 Alloys



Summary

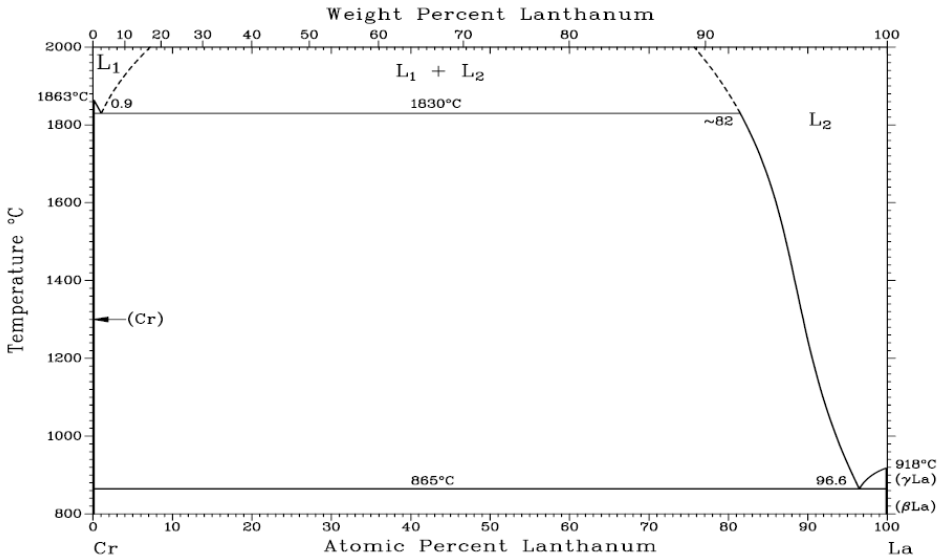
- **Poisson ratio calculations agree with Rice-Thompson parameter calculations on selected pure elements and Mo binary alloys**
- **Elastic properties of 25 binary, 27 ternary, 28 higher order Cr alloys were theoretically examined:**
  - all transition metals selected enhance ductility of binary Cr alloys while IIIA/IVA elements lower it
  - Calculation method verified
- **Most favorable elements in binary alloys are Ti, Zr, Hf, Nb, V, Ta**
  - These alloys have a higher DOS at Fermi level
  - They tend to delocalize electrons.
- **Al tends to lower the ductility:**
  - The alloy has lower DOS at Fermi level
  - Possible bond formation along <1 1 1> in the {1 1 0} plane. Enhancement in bond directionality usually deteriorates ductility.

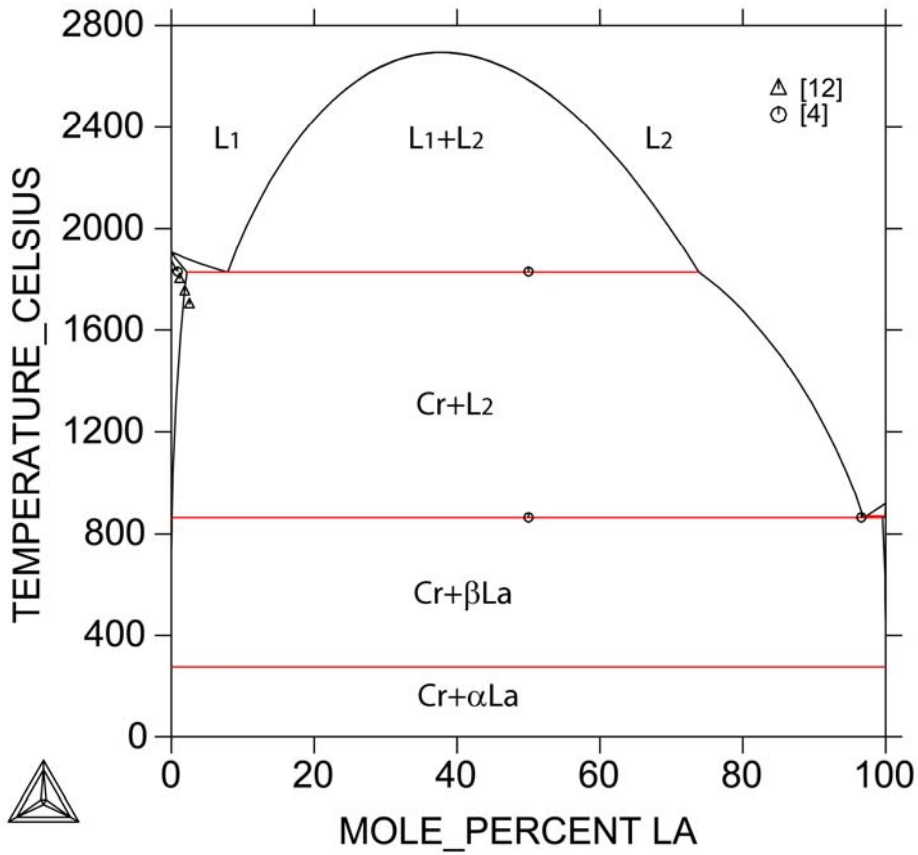
Thermodynamic Assessment of Cr-RE, Mo-RE and V-RE Systems

Cr-Rare Earth Elements Alloys

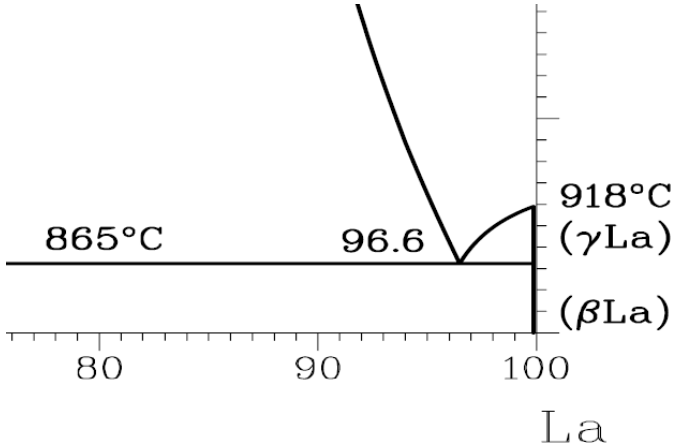
- **Rare earth elements are added to:**
  - Absorb residual oxygen contents in the matrix and thus enhance ductility.
  - Form rare earth oxides that strengthen the matrix and enhance creep resistance
- **There are no accurate thermodynamic databases for Cr-rare earth systems**
- **There are no compound formation in these systems.**
- **Insufficient experimental data on terminal solubility**
- **Discrepancy in melting point of Cr**
  - 1907 or 1863^{o}C?

Calculated Cr-La System





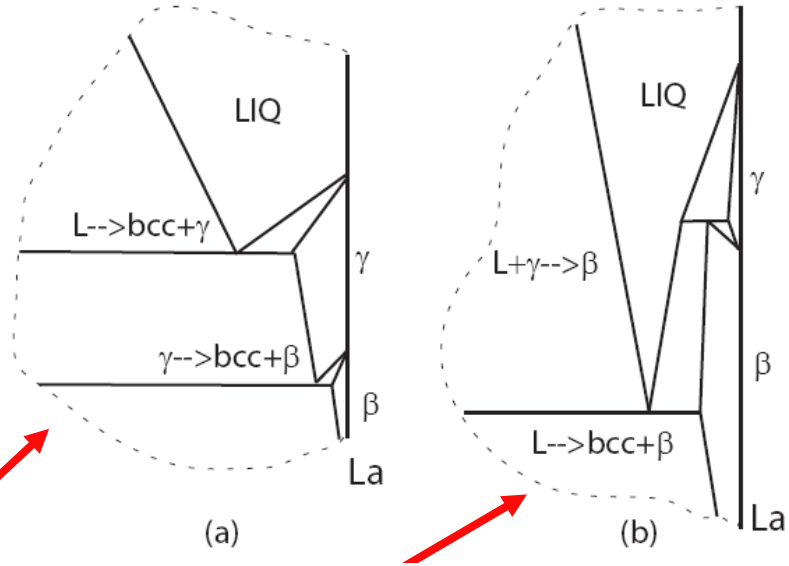
Problems with La-rich Cr-La System

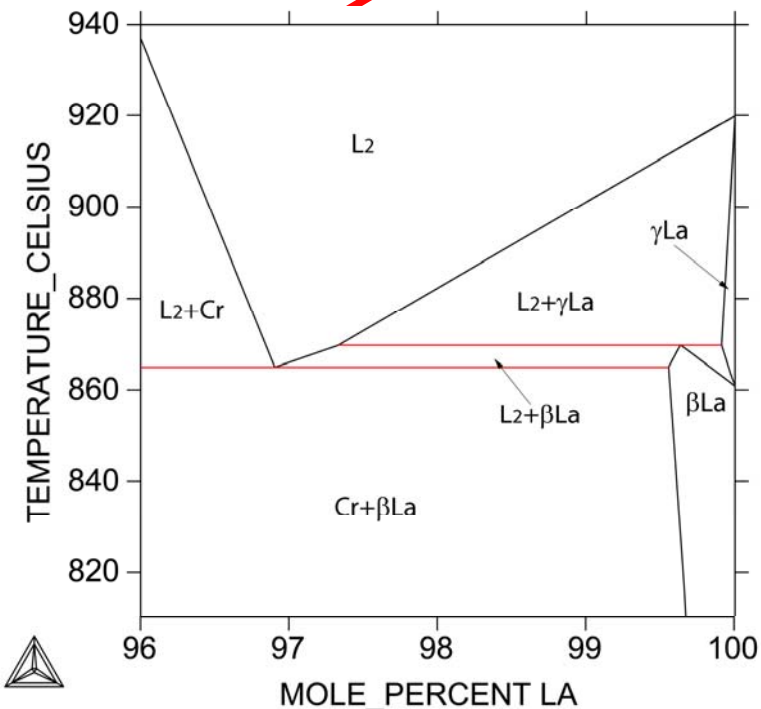


4-phase equilibria at 865°C: L, γLa, βLa, and Cr

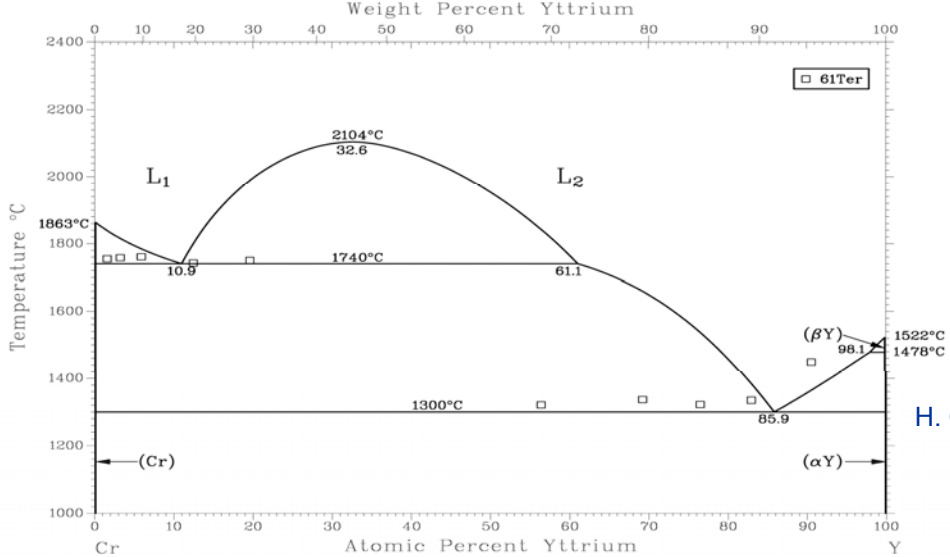
Case a: Eutectic reaction: L→ Cr+γLa
Eutectoid reaction: γLa→Cr+βLa

Case b: Eutectic reaction: L→ Cr+βLa
Peritectic reaction: L+ γLa→βLa

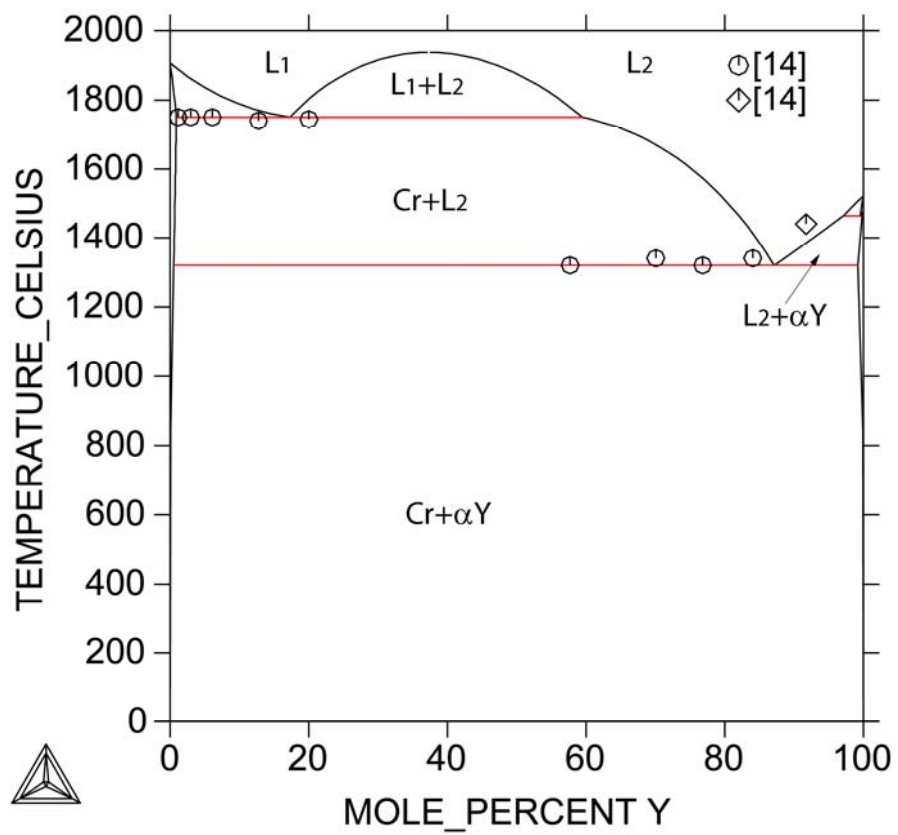


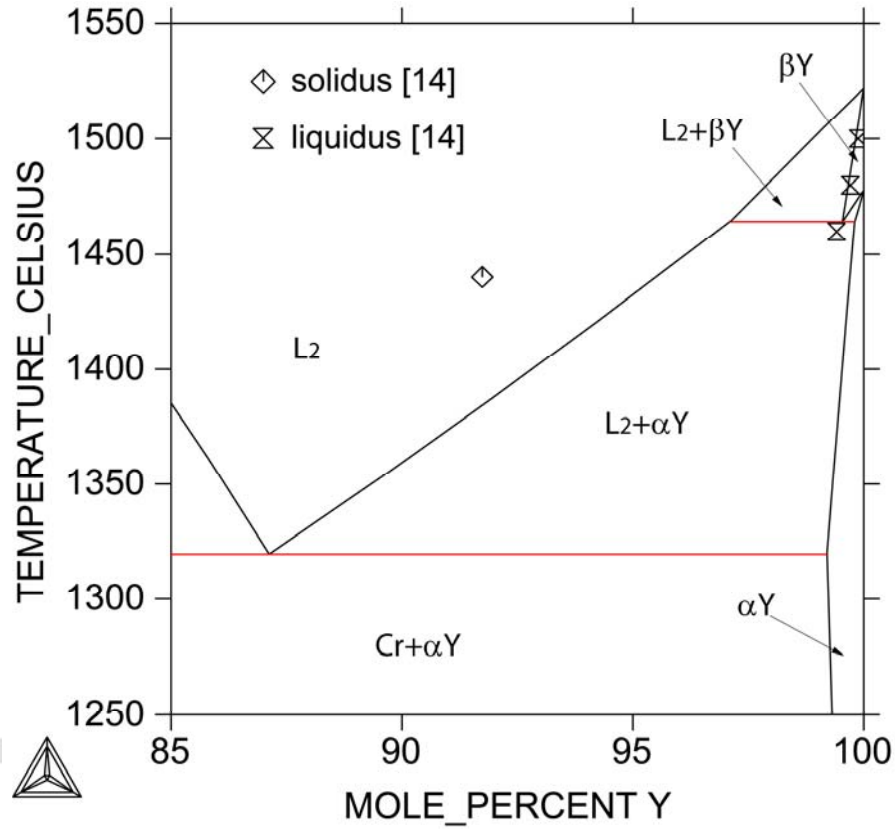


Calculated Cr-Y System

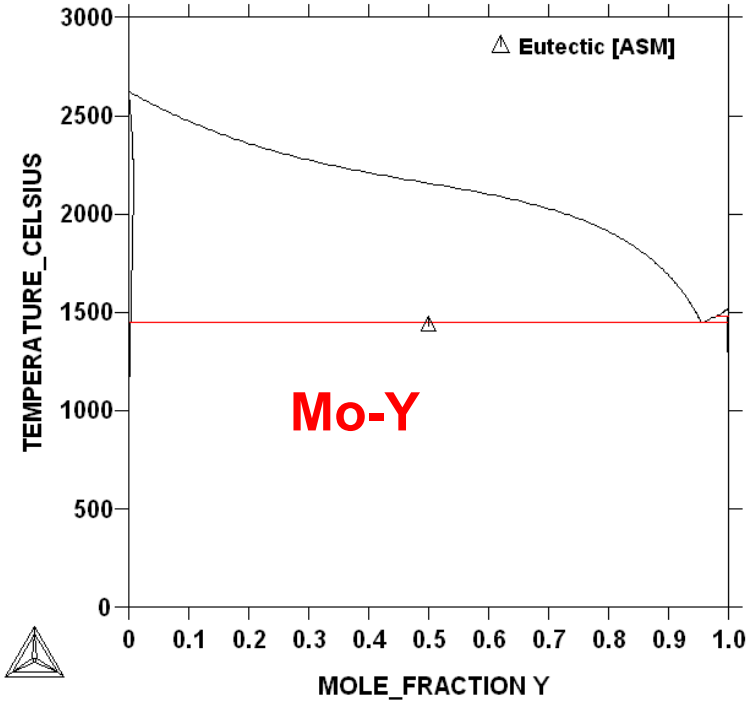


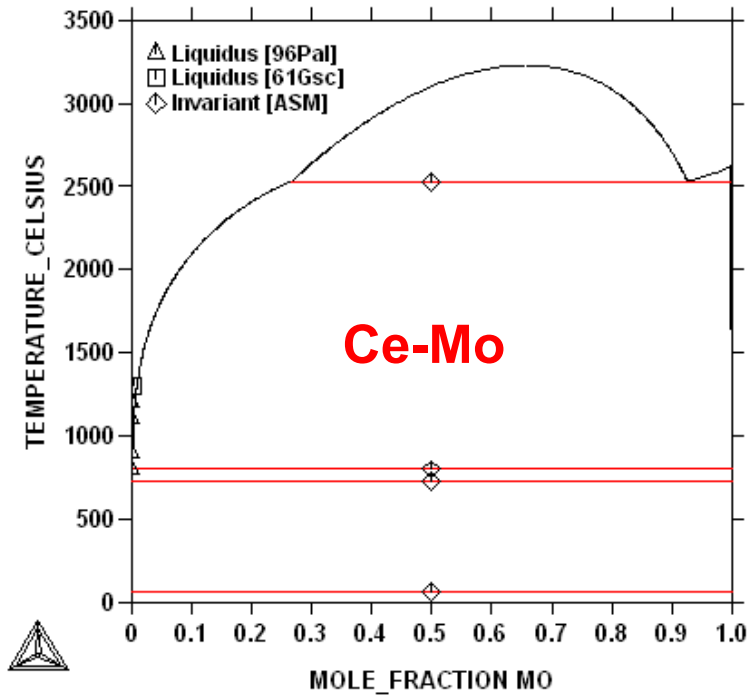
H. Okamoto: *Journal of Phase Equilibirum*, 1992, vol. 13, no. 1, pp. 100-101.

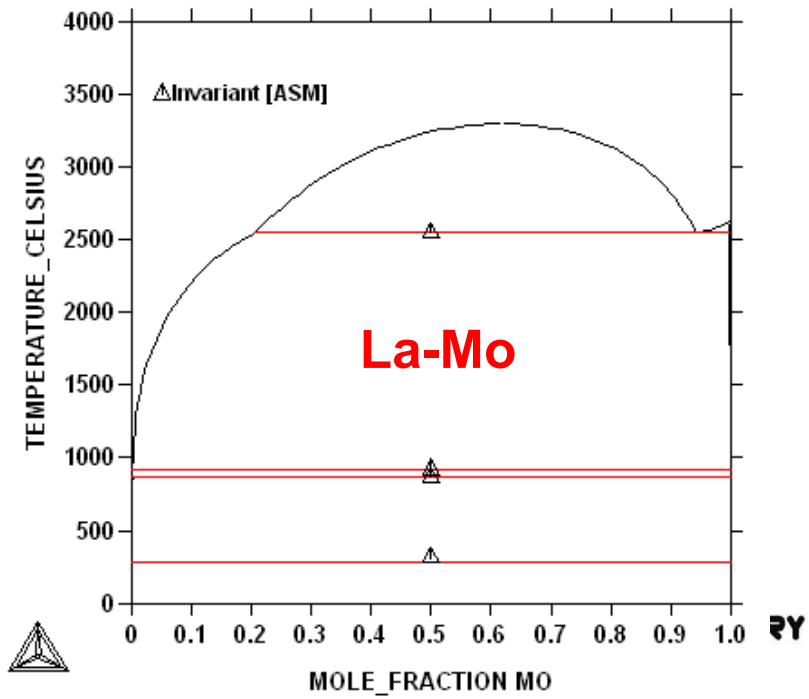




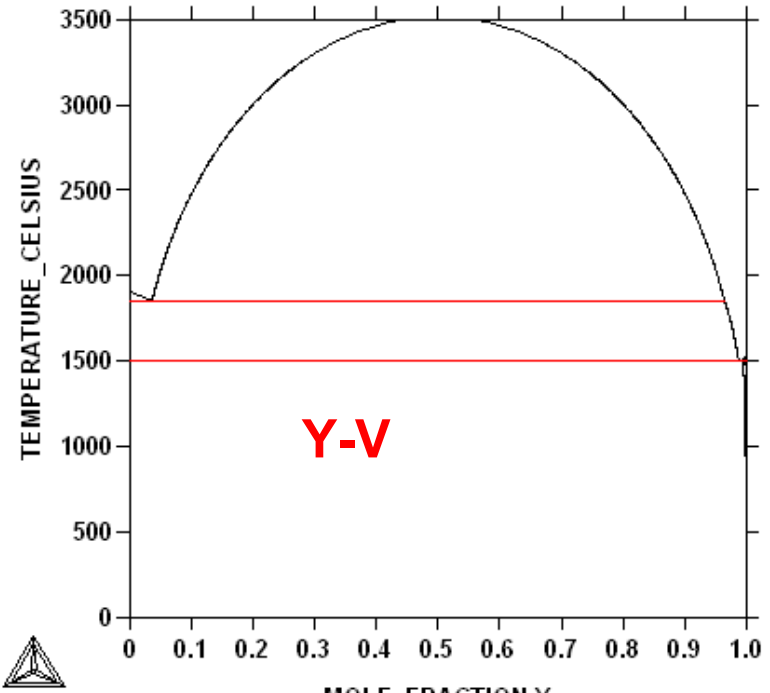
Mo-RE Systems







V-RE Systems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3500
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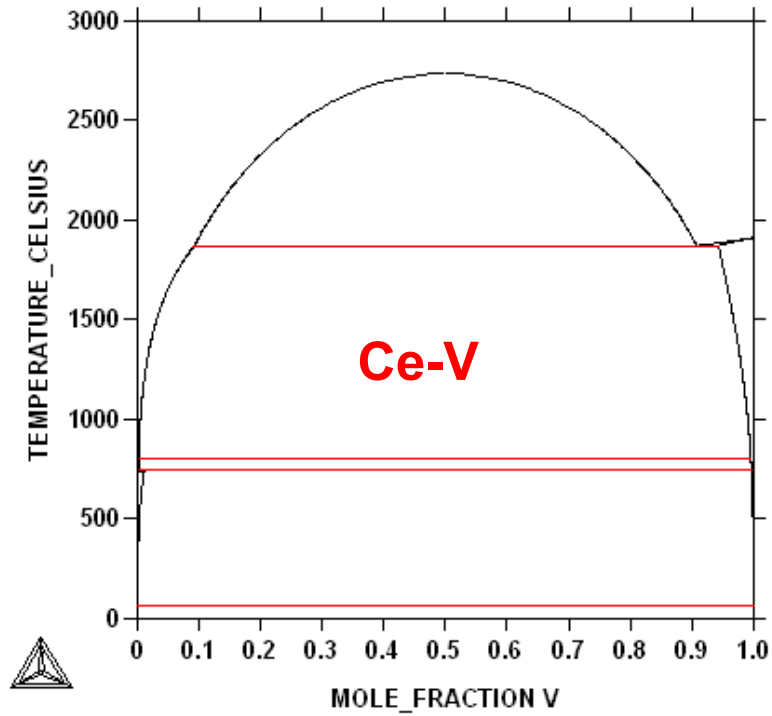
MOLE_FRACTION Y
Y-V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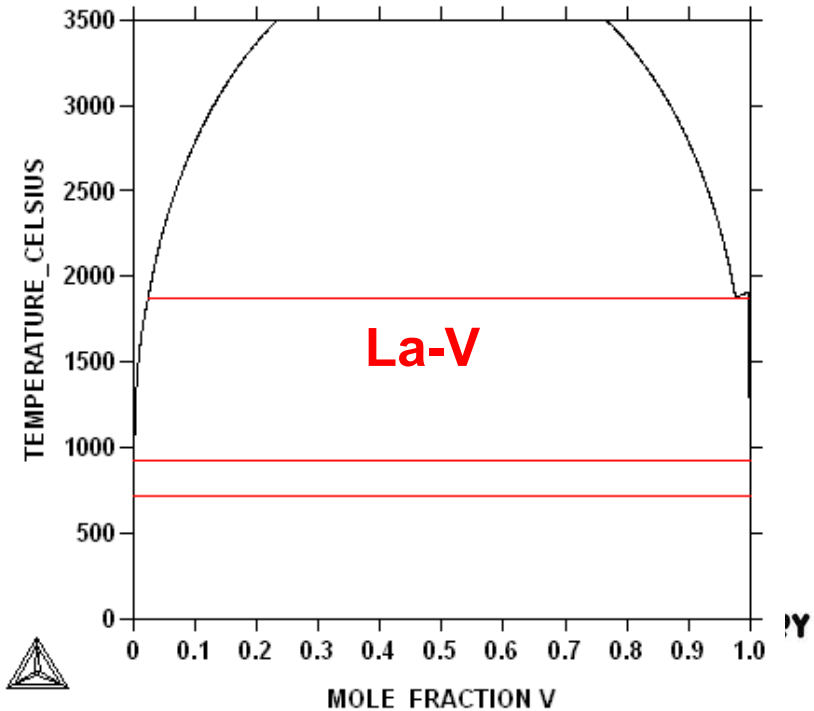
Ce-V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3000
2500
2000
1500
1000
500
0
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
MOLE_FRACTION V
La-V

Summary

- **Cr-Ce, Cr-La and Cr-Y are thermodynamically assessed**
  - Self-consistent thermodynamic databases are obtained.
  - Current study predicts a likely peritectic reaction in the La-rich side of the Cr-La system: $L_2+\delta La \rightarrow \beta La$, which resolves the ambiguity of the currently accepted phase diagram.
  - It also predicts a possible catetectic reaction in the Y-rich side of the Cr-Y system: $\beta Y \rightarrow L_2+\alpha Y$.
  - Work on the Mo-RE and V-RE systems is continuing.
- **Future work needed:**
  - Melting point of high-purity Cr.
  - Polymorphic transformation temperature of $\gamma Ce \leftrightarrow \beta Ce$.
  - La-rich side Cr-La phase diagram.
  - Y-rich side of Cr-Y phase diagram

Milestones

- **Evaluate promising Cr ternary systems using CALPHAD modeling, DFT total energy calculations, and experiments (09/30/2009)**
  - In progress.
- **Complete ductility calculations and experimental verifications on Cr based ternary and higher order alloys (09/30/2009).**
  - Computational work is complete.
  - Experimental work is in progress.
- **Identify second phase particles potentially increasing creep strength in a promising Cr based multi component system (09/30/2009).**
  - In progress.

Deliverables

Peer-reviewed journal articles

- **First Principles Study of the Mechanical Properties of Mo-50at%X (X=Zr, Hf, V, Nb, Re) Alloys,** Michael C. Gao, Ömer N. Doğan, Paul King, Michael Widom, To be submitted to Scripta Materialia (May 2009).
- **Elastic and Thermodynamic Properties of Cr-V Binary Alloys Predicted from First Principles Calculations**, Michael C. Gao, Ömer N. Doğan, Paul King, To be submitted to Scripta Materialia (May 2009).
- **Thermodynamic Assessment of Cr-Rare Earth Systems**, Wren Chan, Michael C. Gao, Ömer N. Doğan, Paul King, Anthony D. Rollett, Accepted for publication in Journal of Phase Equilibria and Diffusion (2009).
- **The First-Principles Design of Ductile Refractory Alloys**, Michael C. Gao, Ömer N. Doğan, Paul King, Anthony D. Rollett, Michael Widom, Journal of Metals, 2008, 7, 61-65.

Deliverables

Articles in Conference Proceedings

- **Integrated Design of Chromium Based Alloys for Fossil Energy Applications**, Michael C. Gao, Ömer N. Doğan, Paul King, Proceedings of The 17th Plansee Seminar, Reutte, Austria, May 25-29, 2009.
- **Computational Design and Experimental Verification of Refractory Metal-Based Alloys**, Proceedings of the 23rd Annual Conference on Fossil Energy Materials, Pittsburgh, PA, May 12-14, 2009.
- **First Principles Design of Ductile Refractory Alloys: Ductility Criteria**, Michael C. Gao, Ömer N. Doğan, Paul King, Supplemental Proceedings of the 138th Annual Meeting: Volume 1: Fabrication, Materials, Processing and Properties, TMS, 2009, 157-163.
- **Thermodynamic Assessment of Cr-Rare Earth Systems**, Wren Chan, Michael C. Gao, Ömer N. Doğan, Paul King, Supplemental Proceedings the 138th Annual Meeting: Volume 2: Materials Characterization, Computation and Modeling, TMS, 2009, 55-61.
- **Integrated Design and Rapid Development of Refractory Metal-Based Alloys for Fossil Energy Applications**, Proceedings of the 22nd Annual Conference on Fossil Energy Materials, Pittsburgh, PA, July 8-10, 2008.
- **First Principles Design of Ductile Refractory Alloys**, Michael C. Gao, Anthony D. Rollett, Michael Widom, Ömer N. Doğan, Paul King, Supplemental Proceedings of the 137th Annual Meeting: Volume 1: Materials Processing and Properties, TMS, 2008.

Deliverables

Presentations

- **Computational Design of High Performance Refractory Alloys for Ultra-High Temperature Applications: a Bottom-up Approach**, Michael C. Gao, Ömer N. Doğan, Paul King, AeroMat'09, Dayton, OH, June 6-11, 2009.
- **Integrated Design of Chromium Based Alloys for Fossil Energy Applications**, Michael C. Gao, Ömer N. Doğan, Paul King, the 17th Plansee Seminar, Reutte, Austria, May 25-29, 2009.
- **Computational Design and Experimental Verification of Refractory Metal-Based Alloys, the 23rd Annual Conference on Fossil Energy Materials**, Pittsburgh, PA, May 12-14, 2009.
- **Materials Development for Future Energy Conversion Systems**, Ömer N. Doğan, Michael C. Gao, Paul King, presented at Materials Science Seminars at Oregon State University, Corvallis, OR, February 26, 2009.
- **First Principles Design of Ductile Refractory Alloys: Ductility Criterion**, Michael C. Gao, Ömer N. Doğan, Paul King, presented at TMS Annual Meeting & Exhibition, February 15-19, 2009, San Francisco, CA.
- **Thermodynamic Assessment of Cr-Ce, Cr-La, and Cr-Y Systems**, Wren Chan, Michael C. Gao, Ömer N. Doğan, Paul King, Anthony D. Rollett, presented at TMS Annual Meeting & Exhibition, February 15-19, 2009, San Francisco, CA.
- **Computational Design of Refractory Alloys for Fossil Energy Applications**, M.C. Gao, O.N. Dogan, P. King, presented at the 4th International Conference of Multiscale Materials Modeling, Tallahassee, FL, USA, October 27-31, 2008.
- **Multiscale Computational Design of Ductile Refractory Alloys for Moderrn Fossil Energy Applications**, M.C. Gao, O.N. Dogan, P. King, presented at the Materials Science & Technology 2008 Conference and Exhibition (MS&T'08), Pittsburgh, PA, USA, October 5-9, 2008.
- **Integrated Design and Rapid Development of Refractory Metal-Based Alloys for Fossil Energy Applications**, the 22rd Annual Conference on Fossil Energy Materials, Pittsburgh, PA, July 8-10, 2008.
- **First Principles Design of Ductile Refractory Alloys**, Michael C. Gao, Anthony D. Rollett, Michael Widom, Ömer N. Doğan, Paul King, presented at TMS Annual Meeting & Exhibition, March 9-13, 2008, New Orleans, LA.