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Title: Multiscale Simulations of Alloy Phase Stability

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MULTISCALE SIMULATIONS OF ALLOY PHASE STABILITY

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Abstract
First principles, atomic scale and continuum level models are combined to predict thermodynamic properties of alloys and stability of phases. Many-body interactions, as well as vacancies, defects, and non-stoichiometry are included in the modeling process and the structural stability of hypothetical phases is evaluated. The resulted thermodynamic functions and phase diagrams are integrated in a casting simulation computer program.
The process of relating microscopic modeling results to the macroscopic heat transfer and phase equilibrium calculations is detailed to emphasize the self-consistency of the approach and to identify the potential sources of errors. The sequence: data acquisition, modeling, prediction, experimental validation, is illustrated for several recent results in actinide based alloys.

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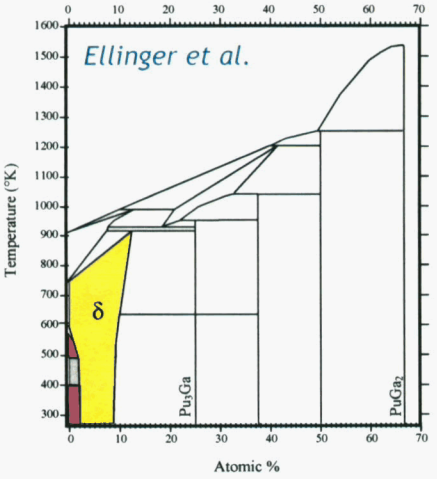
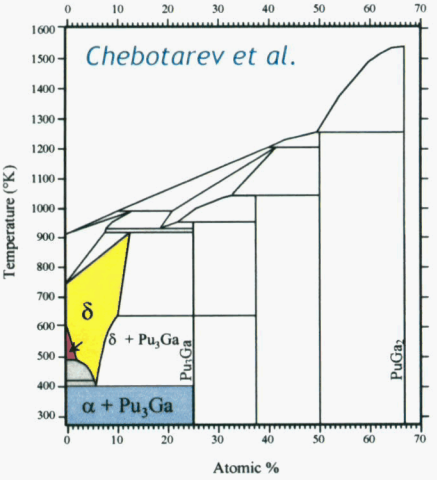
Comparison of Portions of the Pu-Ga Phase Diagrams





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* N. T. Chebotarev, E. S. Smotriskaya, M. A. Adrianov, and O. E. Kostyuk, In Plutonium 1975 and Other Actinides, Proceedings of the Fifth International Conference on Plutonium and Other Actinides, Baden Baden, Germany, September 10-13, 1975, Edited by North-Holland Publishing Company, New York, 1976, p.37-45.

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A Good Plan

- Get thermodynamic data for perfect and imperfect structures from:
  - First principle calculations (Generalized Gradient Approximation)
  - Atomic-scale models (Modified Embedded Atom Method)
  - Molecular dynamics simulations (Cascade Models for defects)
  - Experimental measurements (Calorimetry, Dilatometry)
- Check the thermodynamic data sets for thermodynamic self-consistency.
- Evaluate uncertainty (Bayesian statistics, Genetic Algorithms, Markov Chain Monte Carlo).
- Calculate the equilibrium phase diagram (CALPHAD method).
- Incorporate the phase diagram into a casting simulation software.

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First Principles Calculations

- VASP
- Generalized Gradient Approximation
- Ultra-soft pseudopotentials or Projected Augmented Wave method
- Spin-polarized
- Monkhorst-Pack special k points
- Structural relaxations

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Results for $PuGa_3$

- $L1_2$ structure
- a_0 = 4.2880 Angstrom
- Bulk Modulus = 71.78 Gpa
- B' = dB/dp = 4.8
- Magnetic moment = 5.4 Bohr magneton
- Ferromagnetic state is more stable

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Atomic Scale Modeling

Embedded Atom Method (EAM)

$$E = \sum_i \left(F(\bar{\rho}_i) + \tfrac{1}{2} \sum_{j \neq i} \phi(R_{ij}) \right)$$

Embedding Function

$$F(\bar{\rho}) = AE_c \frac{\bar{\rho}}{\rho_0} \ln \frac{\bar{\rho}}{\rho_0}$$

Pair Potential

$$\phi(R) = \frac{2}{Z} \left\{ E^u(R) - F(\bar{\rho}^0(R)) \right\}$$

Background Electron Density

$$\bar{\rho} = \rho^{(0)} \sqrt{1 + \Gamma}$$

$$\Gamma = \sum_{l=1}^{3} t^{(l)} \left(\rho^{(l)} / \rho^{(0)} \right)^2$$

angle dependent electron density (MEAM)

Universal EOS

$$E^u(R) = -E_c \left(1 + a^* + \delta a^{*3} \frac{r_e}{R} \right) e^{-a^*}$$

$$a^* = \alpha \left(\frac{R}{r_e} - 1 \right) \qquad \alpha^2 = \frac{9\Omega B}{E_c}$$

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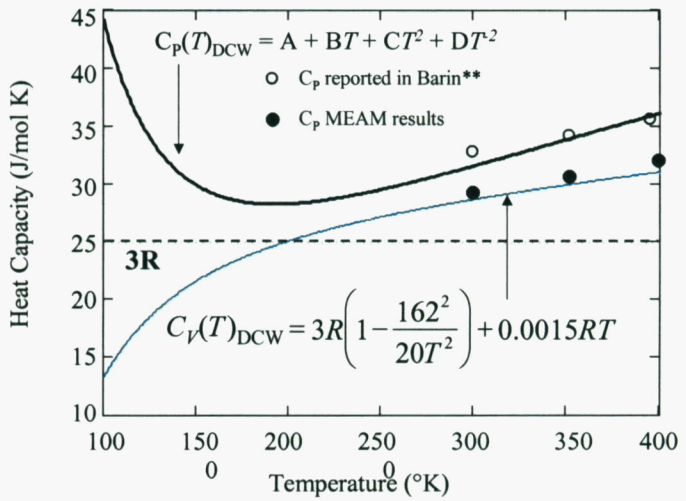
C_p of alpha-Pu (MEAM calculations)



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Thermodynamic Modeling

$$C_p(T) = A + BT + CT^2 + DT^{-2}$$

$$H(T) = H_{298.15} + \int_{298.15}^{T_1} C_{p1}(\tau)\, d\tau + \Delta H_{T_1} + \int_{T_1}^{T} C_{p2}(\tau)\, d\tau$$

$$H(T) = H_0 + AT + B\frac{T^2}{2} + C\frac{T^3}{3} - DT^{-1}$$

$$S(T) = S_{298.15} + \int_{298.15}^{T_1} \frac{C_{p1}(\tau)}{\tau} d\tau + \frac{\Delta H_{T_1}}{T_1} + \int_{T_1}^{T} \frac{C_{p2}(\tau)}{\tau} d\tau$$

$$S(T) = S_0 + A\ln T + BT + C\frac{T^2}{2} - D\frac{T^{-2}}{2}$$

$$G(T) = H(T) - T \cdot S(T)$$

$$G(T) = G_1 + G_2 T - AT\ln T - B\frac{T^2}{2} - C\frac{T^3}{6} - D\frac{T^{-1}}{2}$$

$$Cp(T) = -T\frac{\partial^2 G}{\partial T^2}$$

$$H(T) = \frac{\partial\left(\frac{G}{T}\right)}{\partial\left(\frac{1}{T}\right)}$$

$$S(T) = -\frac{\partial G}{\partial T}$$

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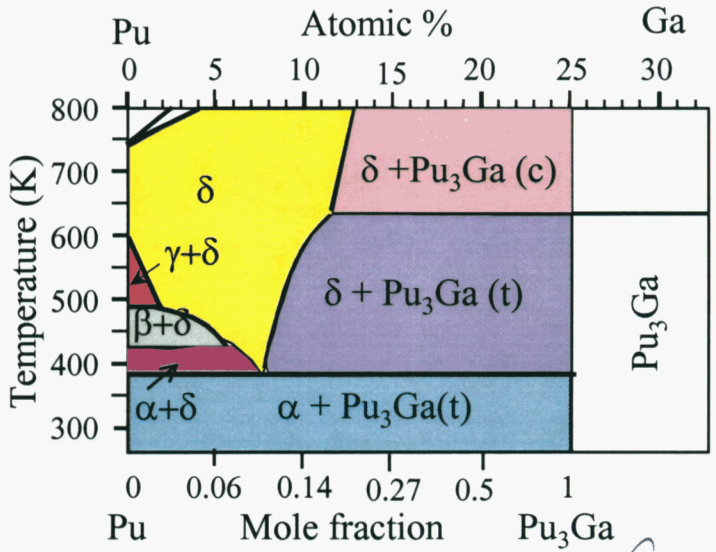
Equivalent representations of the eutectoid point in the Pu-Ga and Pu-Pu_3Ga systems



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A model consistent with the Pu-Ga eutectoid point

We propose a subregular model for the Gibbs free energy of the stabilized delta phase in the Pu-Pu_3Ga pseudo-binary system (all values in kJ/mol). The model is intended to emphasize the possibility of the existence of an eutectoid point in the Pu-Ga phase diagram at:

$T^E = 370$ K and $x^E = 7.9$ % in Pu-Ga

$x^E = 0.104$ in Pu-Pu_3Ga

$$G_\delta(T,x) = (1-x)G_{Pu}(T) + xG_{Pu3Ga}(T) + RT[(1-x)\ln(1-x) + x\ln x] + \\ + (1-x)x[(1-x)\Omega_{Pu} + x\Omega_{Pu3Ga}]$$

$$G_{Pu_3Ga\ cubic}(T) = -40 - (T - 298.15)0.185$$

$T^{transf} = 638$ K

$$G_{Pu_3Ga\ tetragonal}(T) = -30 - (T - 298.15)0.215$$

When referenced to delta Pu: $\Delta G_{Pu_3Ga}(T) = -72.4 - 0.0138T$

Interaction parameters: $\Omega_{Pu} = -42$ $\Omega_{Pu3Ga} = -102$

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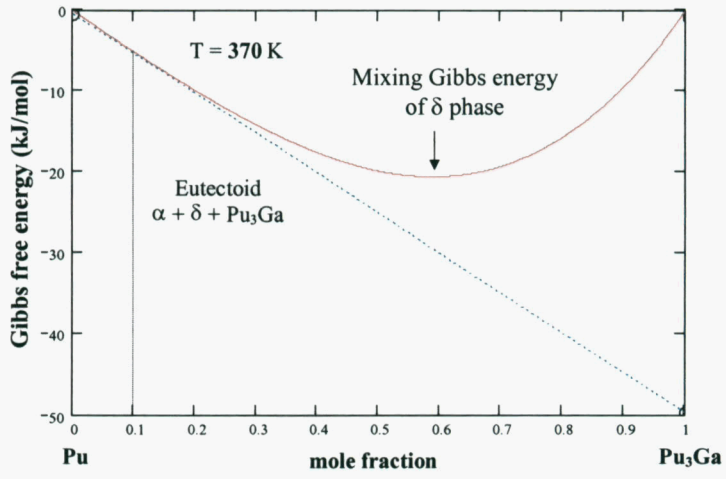
Free Energies of Selected Phases at the Eutectoid Point

$\Delta G_{Pu_3Ga}(T) = -72.4 - 0.0138T \quad \Omega_{Pu} = -42 \quad \Omega_{Pu3Ga} = -102$ (kJ/mole)



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Radiation Damage Modeling

Technique

- Empirical modified embedded atom potential for all phases of Pu (Baskes)
- Molecular dynamics simulations at constant volume and temperature
- Cells periodic in x,y,z
- Pure metal (no alloying)

Conditions (fcc Pu)

- 512 Pu atoms in relaxed, distorted, δ-lattice (Sickafus)
- 300 K, constant volume to mimic alloy stabilization
- 20 eV Primary Knock-on Atom (PKA) energy; (121) direction

Results (fcc Pu)

- Estimate of displacement threshold energy: 8-10 eV
- Modified dumbbell defect structures suggested
- Nascent defect loops

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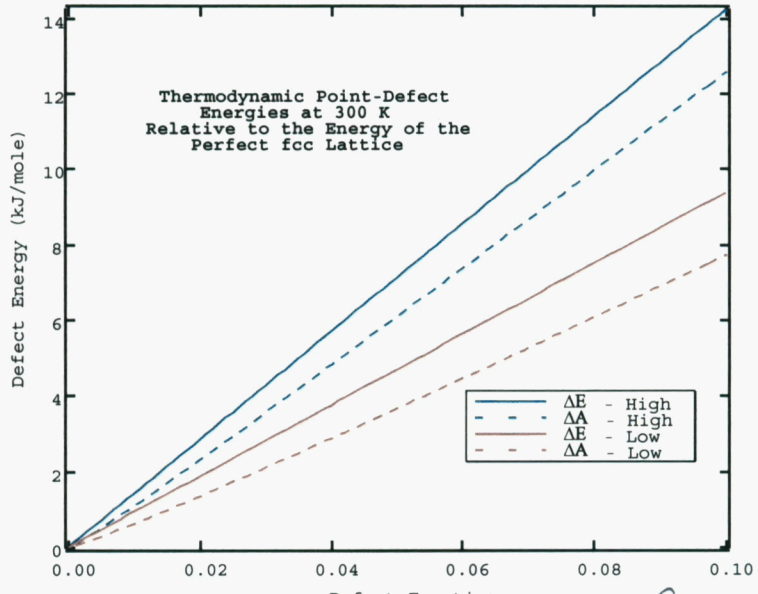

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Truchas

Complex code for simulation of casting and related phenomena. (ASCI project)

Simulation capabilities:

- Mass transfer (flow)
- Heat transfer (conduction, convection, and radiation)
- Phase change (pure materials, alloys)
- Chemical reactions (curing)
- Thermo-mechanical (stress-strain)
- Electro-magnetic fields

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