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Thermodynamics

MEAM Potential and Its Application

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Semi-Empirical Atomic Potentials

- **Elastic Constants**
  - ▷ **B, C11, C12, C44, ...**
- **Defect Energy**
  - ▷ **Surface Energy**
  - ▷ **Heat of Vacancy Formation, …**
- **Structural Energy**
  - ▷ **Energy and Lattice Parameters in Different Structures**
- **Thermal Property**
  - ▷ **Specific Heat**
  - ▷ **Thermal Expansion Coefficient**
  - ▷ **Melting Temperature, ...**

Semi-Empirical Atomic Potentials – History of Development

- **EAM Potentials (1983, M.S. Daw and M.I. Baskes)**
  ▷ **Successful mainly for FCC elements**
  - many other many-body potentials show similar performance

- **1NN MEAM Potentials (1987,1992, M.I. Baskes)**
  ▷ **Show Possibility for description of various structures**
  - important to be able to describe multi-component system

- **2NN MEAM Potentials (2000, B.-J. Lee & M.I. Baskes)**
  ▷ **Applicable to fcc, bcc, hcp, diamond structures and their alloys**

Second Nearest Neighbor Modified EAM (2NN MEAM)

- Second Nearest-Neighbor Modified Embedded-Atom Method Potential
  Byeong-Joo Lee and M.I. Baskes, Phys. Rev. B. 62, 8564-8567 (2000).
  Formalism of the 2NN MEAM

- Second Nearest-Neighbor Modified Embedded Atom Method Potentials for BCC Transition Metals
  B.-J. Lee, M.I. Baskes, H. Kim and Y. K. Cho, Phys. Rev. B. 64, 184102 (2001).
  Potential for Fe, Cr, Mo, W, V, Nb, Ta

- Semi-Empirical Atomic Potentials for the FCC metals Cu, Ag, Au, Ni, Pd, Pt, Al and Pb based on first and second nearest-neighbor modified embedded atom method
  Byeong-Joo Lee, J.-H. Shim and M.I. Baskes, Phys. Rev. B. 68, 144112 (2003).
  Potential for Cu, Ag, Au, Ni, Pd, Pt, Al, Pb

- Potential for other Elements: ***Si, Ge***
- Potential for Alloy Systems: **Fe-Cr**, **Ni-W**, ***Fe-Cu, Cu-Ni, Fe-Ni, Ni-Si, Ge-Si***

Semi-Empirical Atomic Potentials – EAM/MEAM : General

$$E = \sum_i \left[F_i(\overline{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(r_{ij}) \right]$$

E : Total Potential Energy
F : Embedding Energy
ρ : Electron Density (Considering Bonding Directionality)
ϕ : Pair Interaction Energy

Semi-Empirical Atomic Potentials – EAM : Electron Density

$$E = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(r_{ij}) \right]$$

$$\rho_i^{a(h)}(R) = C\, e^{-\beta^{(h)}(R/r_e - 1)}$$

$$\bar{\rho}_i = \rho_i^{(0)} \left(= \sum_j \rho_j^{a(0)}(r_{ij}) \right)$$

$$\overline{\rho}_i = \rho_i^{(0)} \left(= \sum_j \rho_j^{a(0)}(r_{ij})\right)$$ + Angular contribution

$$(\rho_i^{(0)})^2 = \left[\sum_{j\neq i} \rho_j^{a(0)}(R_{ij})\right]^2$$

$$(\rho_i^{(1)})^2 = \sum_{\alpha} \left[\sum_{j\neq i} \frac{R_{ij}^{\alpha}}{R_{ij}} \rho_j^{a(1)}(R_{ij})\right]^2$$

$$(\rho_i^{(2)})^2 = \sum_{\alpha,\beta} \left[\sum_{j\neq i} \frac{R_{ij}^{\alpha} R_{ij}^{\beta}}{R_{ij}^2} \rho_j^{a(2)}(R_{ij})\right]^2 - \frac{1}{3}\left[\sum_{j\neq i} \rho_j^{a(2)}(R_{ij})\right]^2$$

$$(\rho_i^{(3)})^2 = \sum_{\alpha,\beta,\gamma} \left[\sum_{j\neq i} \frac{R_{ij}^{\alpha} R_{ij}^{\beta} R_{ij}^{\gamma}}{R_{ij}^3} \rho_j^{a(3)}(R_{ij})\right]^2 - \frac{3}{5}\sum_{\alpha} \left[\sum_{j\neq i} \frac{R_{ij}^{\alpha}}{R_{ij}} \rho_j^{a(3)}(R_{ij})\right]^2$$

Semi-Empirical Atomic Potentials – MEAM : Electron Density

$$\overline{\rho}_i = \rho_i^{(0)} \left(= \sum_j \rho_j^{a(0)}(r_{ij})\right)$$ + Angular contribution

$$(\overline{\rho}_i)^2 = \sum_{h=0}^{3} t_i^{(h)} (\rho_i^{(h)})^2 = (\rho_i^{(0)})^2 \left(1 + \sum_{h=1}^{3} t_i^{(h)} \left(\frac{\rho_i^{(h)}}{\rho_i^{(0)}}\right)^2\right) \quad \text{with } t_i^{(0)} = 1$$

$$\Gamma = \sum_{h=1}^{3} t_i^{(h)} \left[\frac{\rho_i^{(h)}}{\rho_i^{(0)}}\right]^2$$

$$\overline{\rho}_i = \rho_i^{(0)} G(\Gamma)$$

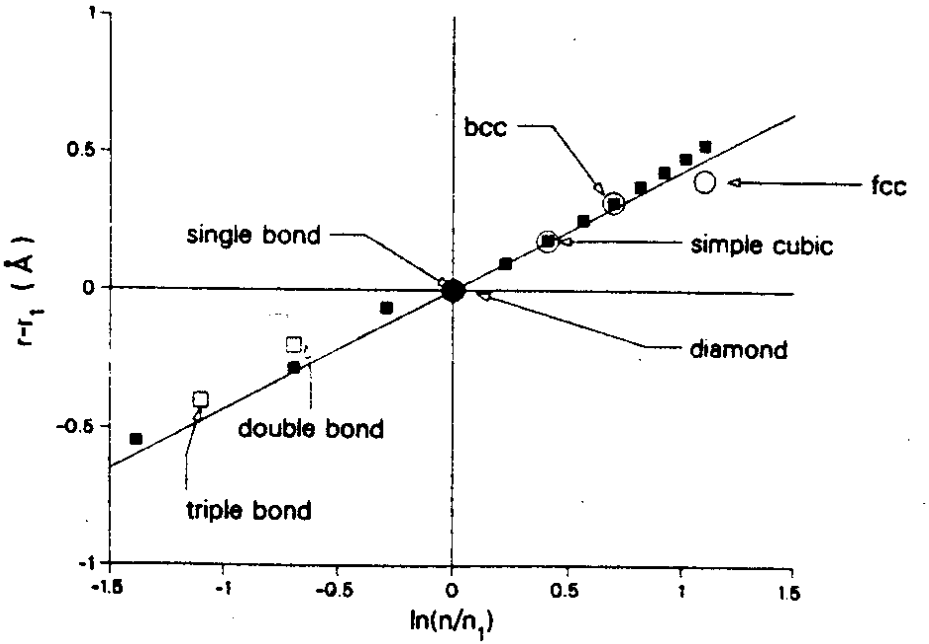
$$G(\Gamma) = \frac{2}{1 + e^{-\Gamma}}$$

Semi-Empirical Atomic Potentials – MEAM : Embedding Function

$$E = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(r_{ij}) \right]$$

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

$$r - r_e \cong \frac{-\rho^q(r_e)'}{\alpha^2 \rho^a(r_e)} \ln\left(\frac{n}{n_e}\right)$$



M.I. Baskes et al., Phys. Rev. B, 40, 6085 (1989)

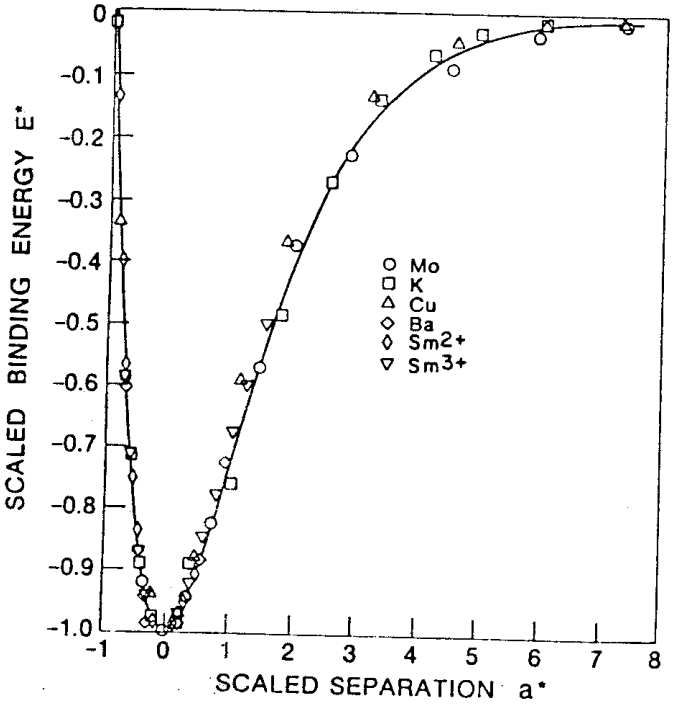
Semi-Empirical Atomic Potentials – MEAM : Universal EOS

$$E = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(r_{ij}) \right]$$

$$E^u(r) = -E_c(1 + a^*)e^{-a^*}$$

$$a^* = \alpha(r / r_e - 1)$$

$$\alpha = \left(\frac{9B\Omega}{E_c} \right)^{1/2}$$



J.H. Rose et al., Phys. Rev. B, 29, 2963 (1984)

$$E = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(r_{ij}) \right]$$

$$F(\bar{\rho}^{o}(r)) + \tfrac{1}{2}\sum \phi(r) = E^{u}(r) = -E_c(1+a^{*})e^{-a^{*}}$$

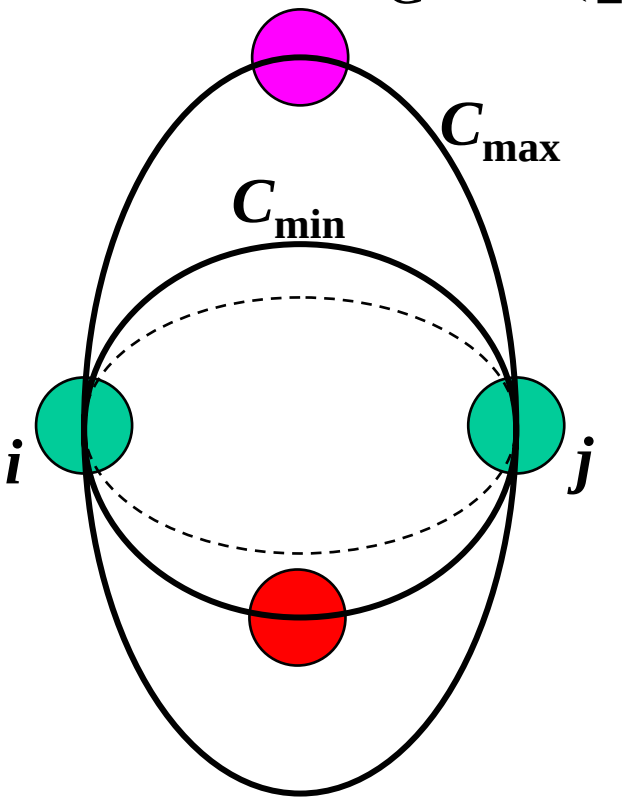
$$\phi(r) = \frac{2}{Z_1}[E^{u}(r) - F(\bar{\rho}^{o}(r))]$$

1NN MEAM vs. 2NN MEAM – Many-Body Screening

$$C = \frac{2(X_{ik} + X_{kj}) - (X_{ik} - X_{kj})^2 - 1}{1 - (X_{ik} - X_{kj})^2}$$

$$x^2 + \frac{1}{C}y^2 = \left(\frac{1}{2}R_{ij}\right)^2$$

$X_{ik}=(R_{ik}/R_{ij})^2$ and $X_{kj}=(R_{kj}/R_{ij})^2$



$$S_{ikj} = f_c\left[\frac{C - C_{\min}}{C_{\max} - C_{\min}}\right]$$

$$f_c(x) = \begin{cases} 1 & x \geq 1 \\ \left[1-(1-x)^4\right]^2 & 0 < x < 1 \\ 0 & x \leq 0 \end{cases}$$

$$S_{ij} = \prod_{k \neq i,j} S_{ikj}$$

Semi-Empirical Atomic Potentials – 2NNMEAM

$$E = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(r_{ij}) \right]$$

$$E^u(R) = F(\bar{\rho}^o(R)) + \frac{Z_1}{2}\phi(R) + \frac{Z_2 S}{2}\phi(aR)$$

$$\bar{\rho}^o(R) = Z_1 \rho^{a(0)}(R) + Z_2 S \rho^{a(0)}(aR)$$

$$E^u(R) = F(\bar{\rho}^o(R)) + \frac{Z_1}{2}\psi(R)$$

$$\psi(R) = \phi(R) + \frac{Z_2 S}{Z_1}\phi(aR)$$

$$\phi(R) = \psi(R) + \sum_{n=1} (-1)^n \left(\frac{Z_2 S}{Z_1} \right)^n \psi(a^n R)$$

Semi-Empirical Atomic Potentials – 2NNMEAM for Alloy Systems

$$E = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2} \sum_{j(\neq i)} \phi_{ij}(r_{ij}) \right]$$

Select a Reference Phase: FCC_A1, BCC_B2, L12, $M(Va,C)_3$,

▷ Potential Energy per Atom, for BCC_B2 (CsCl type)

$$E_{ij}^{u}(R) = \frac{1}{2}\{F_i(\bar{\rho}_i(R)) + F_j(\bar{\rho}_j(R))\}$$

$$+ \frac{1}{2}\left\{Z_1\phi_{ij}(R) + \frac{Z_2}{2}[S_{ii}\phi_{ii}(aR) + S_{jj}\phi_{jj}(aR)]\right\}$$

$$E_{ij}^{u}(R) = -E_c^{ij}(1+a^*)e^{-a^*}$$

$$a^* = \alpha\left(\frac{R}{r_e^{ij}} - 1\right), \qquad \alpha = \left(\frac{9B_{ij}\Omega_{ij}}{E_c^{ij}}\right)^{1/2}$$

Evaluation of MEAM Potential Parameters

- E_c, R_e, B, A, d, $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, $\beta^{(3)}$, $t^{(1)}$, $t^{(2)}$, $t^{(3)}$, C_{max}, C_{min}

  - ▷ Cohesive Energy of Stable and Metastable Structure
  - ▷ Nearest Neighbor Distance
  - ▷ Bulk Modulus, Elastic Constants (C11, C12, C44)
  - ▷ Stacking Fault Energy
  - ▷ Vacancy Formation Energy
  - ▷ Surface Energy

MEAM for BCC Transition Metals - Fitted Properties

Elem.	C11	C12	C44	$E_{(100)}$	$E_{(110)}$	$E_{(111)}$	E_v^f	$E_{bcc/fcc}$	$E_{fcc/hcp}$
Fe	2.430	1.380	1.219	2510	2356	2668	1.75	0.069	-0.023
	2.431	*1.381*	*1.219*		*2360**		*1.79*	*0.082*	*-0.023*
Cr	3.909	0.897	1.034	2300	2198	2501	1.91	0.070	-0.02
	3.910	*0.896*	*1.032*		*2200**		*1.80*	*0.075*	*-0.029*
Mo	4.649	1.655	1.088	3130	2885	3373	3.09	0.167	-0.038
	4.647	*1.615*	*1.089*		*2900**		*3.10*	*0.158*	*-0.038*
W	5.326	2.050	1.631	3900	3427	4341	3.95	0.263	-0.047
	5.326	*2.050*	*1.631*		*2990**		*3.95*	*0.200*	*-0.047*
V	2.323	1.194	0.460	2778	2636	2931	2.09	0.084	-0.011
	2.324	*1.194*	*0.460*		*2600**		*2.10*	*0.078*	*-0.036*
Nb	2.527	1.331	0.319	2715	2490	2923	2.75	0.176	-0.012
	2.527	*1.332*	*0.310*		*2300**		*2.75*	*0.140*	*-0.036*
Ta	2.664	1.581	0.875	3035	2778	3247	2.95	0.148	-0.023
	2.663	*1.582*	*0.874*		*2780**		*2.95*	*0.166*	*-0.041*

MEAM for BCC Transition Metals - Defect Properties

Elem.	E_v^f		Q		self-interstitial	
	MEAM	exp.	MEAM	exp.	E_I	structure
Fe	1.75	1.79	2.28	2.5	4.23	[110] dumbbell
Cr	1.91	1.80	2.61	3.1	3.90	[110] dumbbell
Mo	3.09	3.10	4.22	4.5	5.97	[110] dumbbell
W	3.95	3.95	5.56	5.5	8.98	[110] dumbbell
V	2.09	2.10	2.47	3.2	2.49	[110] dumbbell
Nb	2.75	2.75	3.32	3.6	2.56	[110] dumbbell
Ta	2.95	2.95	3.71	4.3	4.88	[110] dumbbell

MEAM for BCC Transition Metals - Thermal Properties

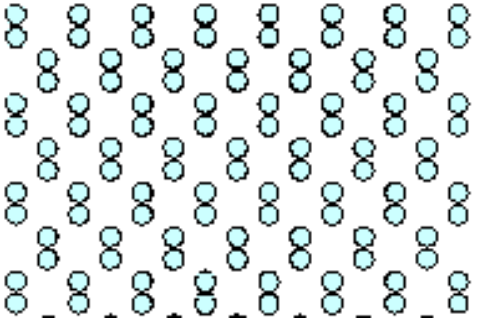
Ele.	ε (0-100°C)		C_P(0-100°C)		T_m		ΔH_m		$\Delta V_m/V_{solid}$	
	MEAM	exp.	MEAM	exp.	MEAM	exp.	MEAM	exp.	MEAM	exp.
Fe	12.4	12.1	26.1	25.5	2200	1811	13.2	13.8	3.4	3.5
Cr	9.0	6.5	26.8	24.0	2050	2180	18.8	21.0	4.4	-
Mo	5.3	5.1	25.9	24.1	3100	2896	20.1	37.5	3.0	-
W	4.2	4.5	25.4	25.4	4600	3695	33.0	52.3	3.2	-
V	8.7	8.3	26.1	25.4	1800	2183	11.7	21.5	1.3	-
Nb	6.4	7.2	26.1	24.9	1900	2750	13.5	30.0	1.0	-
Ta	5.8	6.5	25.7	25.7	3200	3290	22.3	36.6	2.1	-

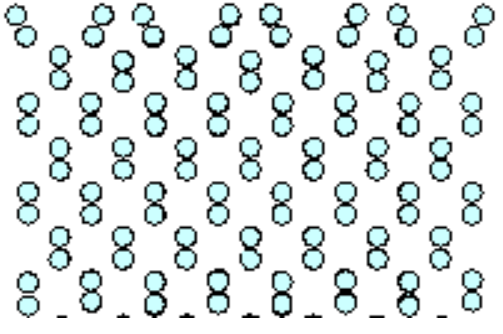
Semi-Empirical Potentials for Fe

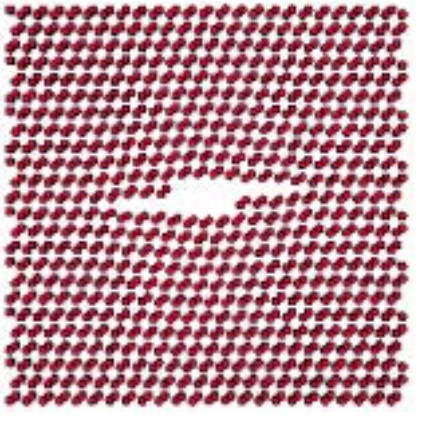
Property	Fe-I	Fe-II	Fe-III	FS	MEAM	Experiment/FP
C11	2.12	2.33	2.42	2.43	2.43	2.43
C12	1.53	1.37	1.47	1.45	1.38	1.38
C44	1.15	1.18	1.12	1.16	1.22	1.22
C’	0.29	0.48	0.48	0.49	0.53	0.53
Hf_vac	2.14	1.41	1.63	1.83	1.75	1.5-2.0
Hm_vac	0.10	1.45	0.66	0.91	0.53	0.55
Hf_SIA	2.59 <111>cr	6.77 <111>cr	3.54 <111>cr	4.76 <110>du	4.23 <110>du	- <110>du
ΔE_fcc/bcc	0.056	0.032	0.027	0.054	0.069	0.08/0.035,0.08
ΔE_hcp/fcc	0.000	0.000	0.000	0.000	-0.023	-0.023/0.085,0.03
MP	1400	3850	2200	2200	2200	1811

MEAM for Silicon

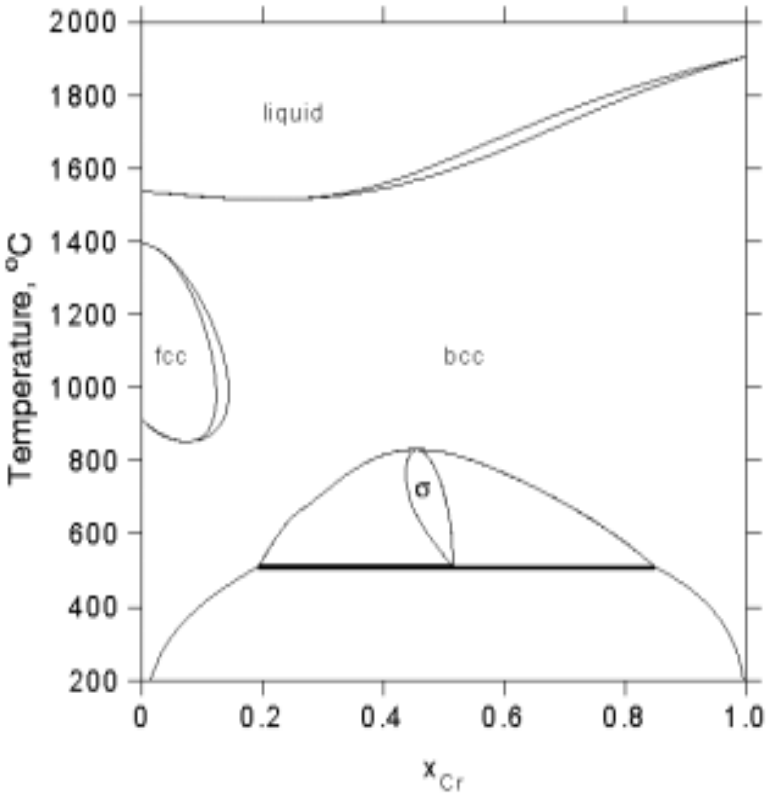
C_{11}	C_{12}	C_{44}	$E_{(100)}$	$E_{(110)}$	$E_{(111)}$	E_v^f	$E_{dia/fcc}$	$E_{dia/hcp}$	$E_{dia/bcc}$	ε
(10^{12}dyne/cm^2)			(erg/cm^2)			(eV)		(eV)		(0-100°C)
1.67	0.65	0.80	2631	1766	1442	3.67	0.57	0.55	0.52	2.65
1.68	0.65	0.80		1135*		3.3-4.3	0.57	0.55	0.53	2.69

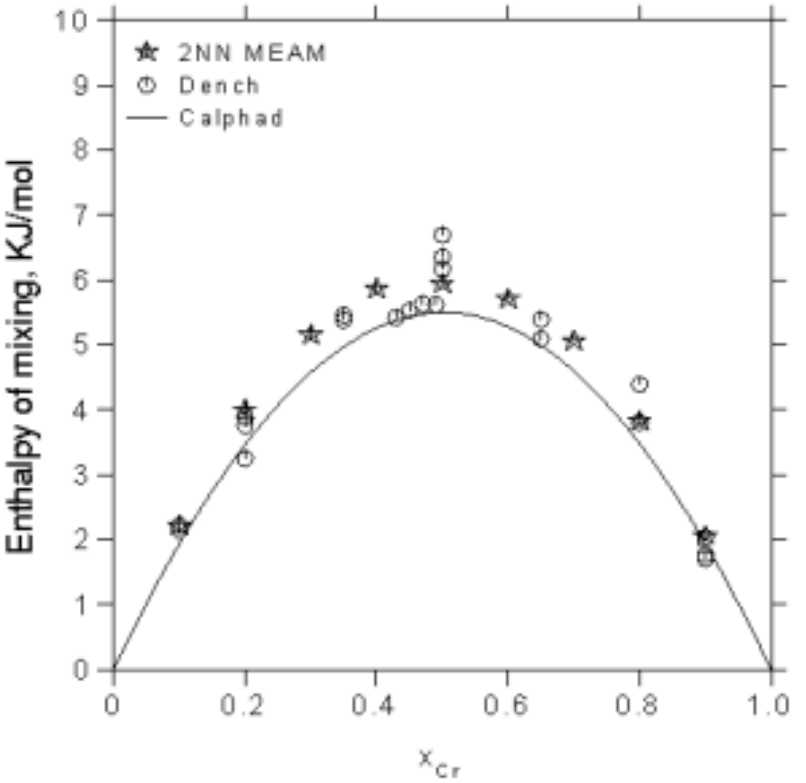




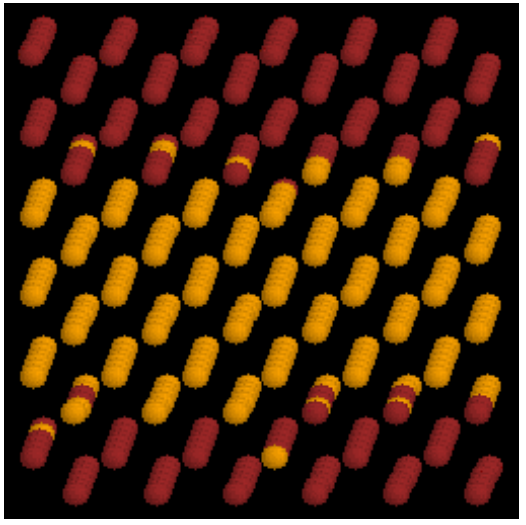


MEAM for Fe-Cr Binary System

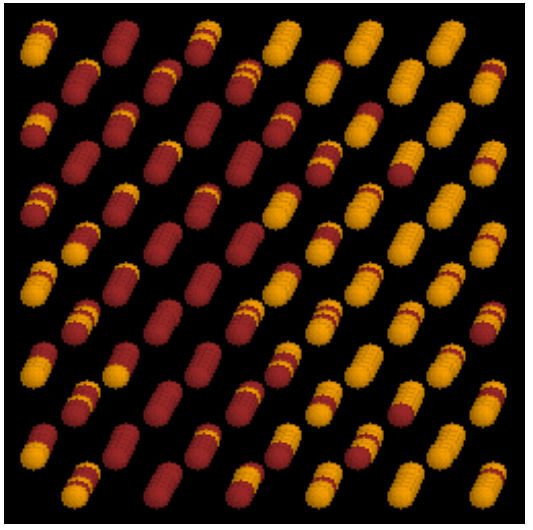




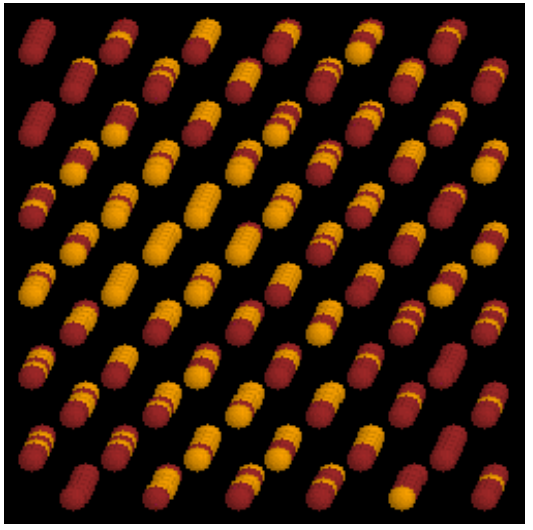
MEAM for Fe-Cr Binary System - Simulation of Phase Separation



200K

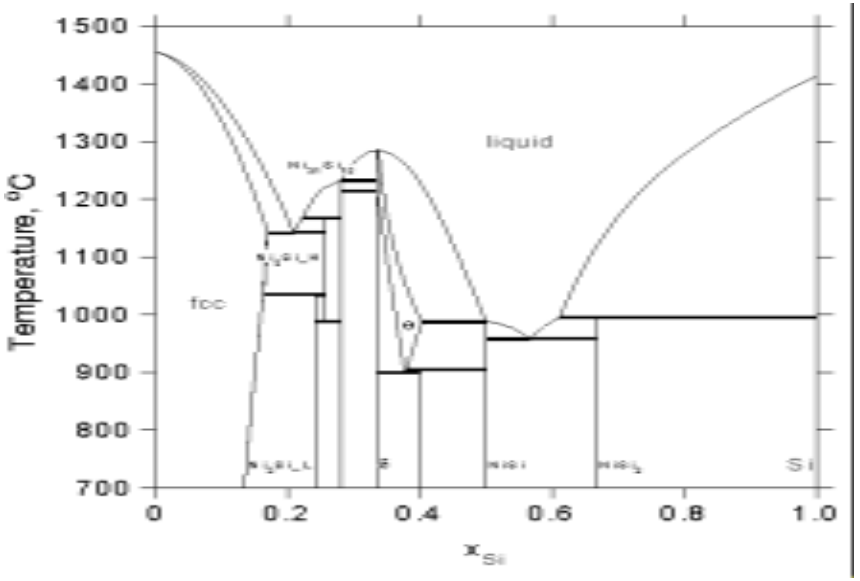


850K



1000K

MEAM for Ni-Si Binary System

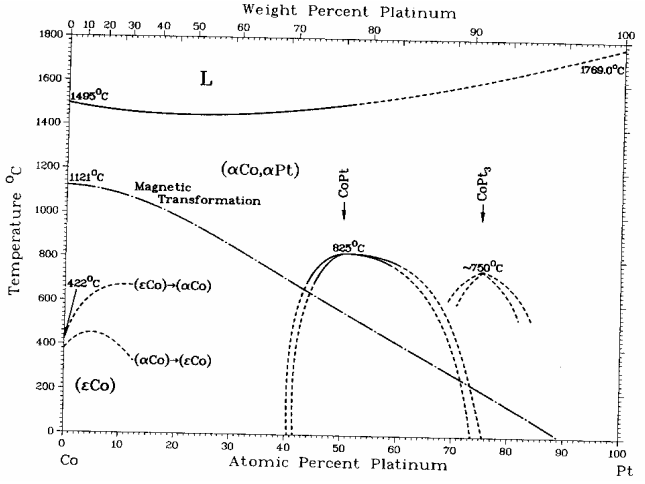


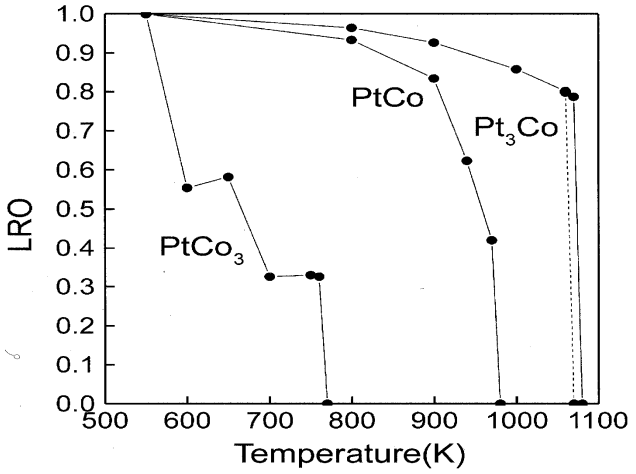
Dilute Heat of Solution (eV/atom)

Si in (Ni)	-1.50 (-1.37)
Ni in (Si)	+0.50

	Ni_3Si	$NiSi_2$
Enthalpy of Formation (eV/atom)	0.36 (0.36)	0.28 (0.28)
Lattice constant (Å)	3.504 (3.504)	5.391 (5.406)
Bulk Modulus (100 GPa)	2.64	1.93 (1.60)
C11 (100 GPa)	3.67 (3.63-3.75)	2.39
C12 (100 GPa)	2.13 (2.00-2.05)	1.69
C11-C12 (100 GPa)	1.54	0.70 (0.58)
C44 (100 GPa)	1.96 (1.67-1.72)	0.32
(100) fracture energy ($J \cdot m^{-2}$)	5.3 (7.2)	8.0

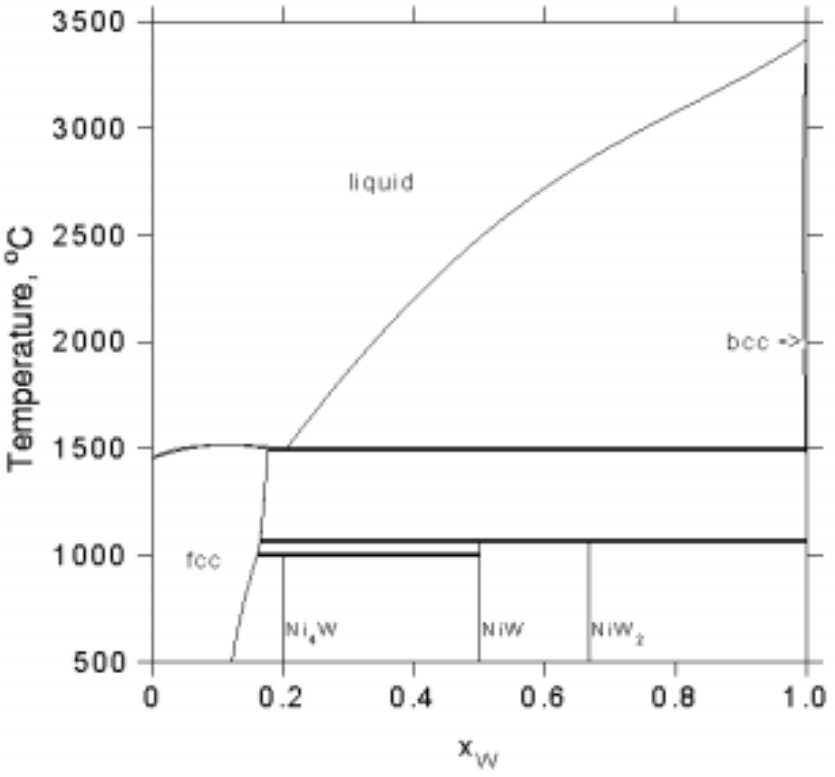
MEAM for Co-Pt Binary System - S.I. Park et al., Scripta Mater., 2001.

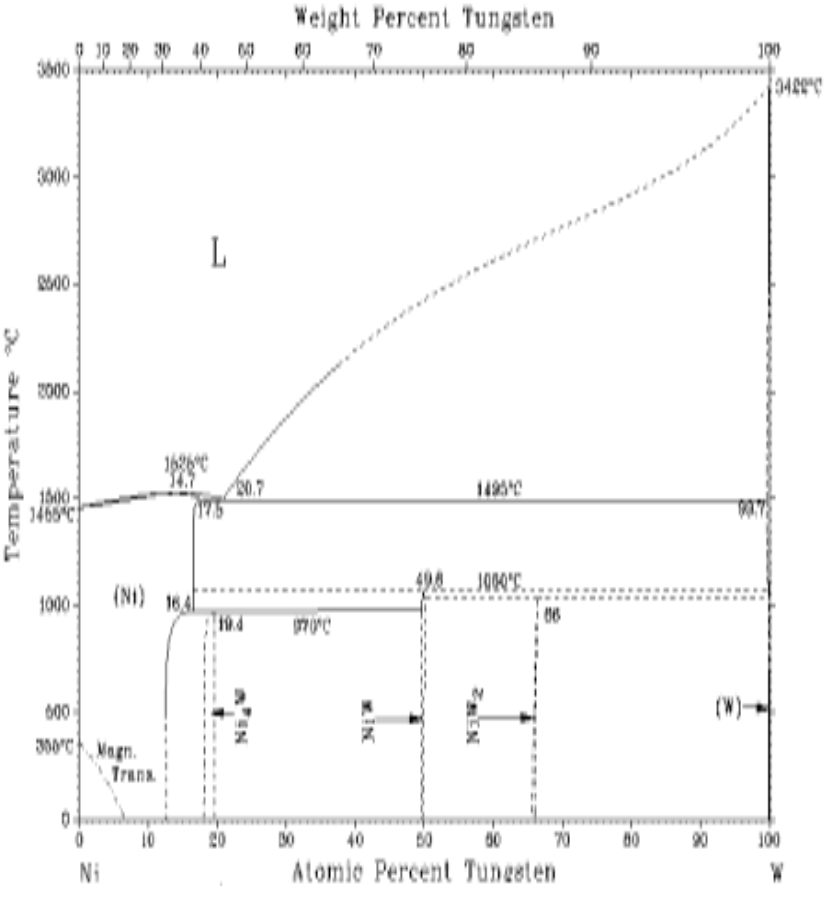




Property	Pt_3Co	PtCo	$PtCo_3$
Cohesive Energy (eV/atom)	5.500 *5.555 ±0.017*	5.215 *5.228 ±0.005*	4.873
Lattice Constant (Å)	a=3.833 *a=3.831*	3.754, c/a=.98 *3.745, c/a=.98*	3.625 *3.668*
Transition Temperature (K)	1070-1080 *1000*	970-980 *1100*	760-770 *840*

Phase Diagram of the Ni-W Binary System





P. Gustafson et al., 1987
A. Fernandez Guillermet, 1986

MEAM for Tungsten

Property	MEAM	Experiment/FP
B	3.14	3.14
$(\partial B/\partial P)_{0K}$	4.79	4.50
C11	5.326	5.326
C12	2.050	2.050
C44	1.631	1.631
ΔE_fcc/bcc	0.26	0.20
ΔE_hcp/fcc	-0.047	-0.047
H_vac	3.95	3.95
Q_D	5.56	5.5
E(100)/(110)/(111)	3900/3427/4341	2990, 3468
% relaxation	-3.2/-3.0/-13.2	-3.1/ -5.9/ -15.1
MP	4600	3695
ΔH /ΔV_f	33.0/3.2	52.3/ -
Cp/ε (0-100°C)	25.4/4.2	25.4/4.5

MEAM for Nickel

Property	MEAM	Experiment/FP
B	1.876	1.876
$(\partial B/\partial P)_{0K}$	4.90	4.89
C11	2.612	2.612
C12	1.508	1.508
C44	1.317	1.317
ΔE_fcc/bcc	0.16	0.11
H_vac	1.51	1.60
Q_D	2.98	2.87
E(100)/(110)/(111)	1943/2057/1606	2240
% relaxation	-1.8/-6.0/-1.4	-3.2~1.1/ -8 ±1 / -1 ±1
E_SF(111)	125	125
MP	2013	1728
ΔH / ΔV_f	24.6/9.1	17.5/4.5
Cp/ε (0-100°C)	25.4/12.6	26.5/13.3

- Calphad Assessment Results

- First Principles Calculation
  on stabilities, lattice constants
  and bulk moduli
  of stable/non-stable compounds

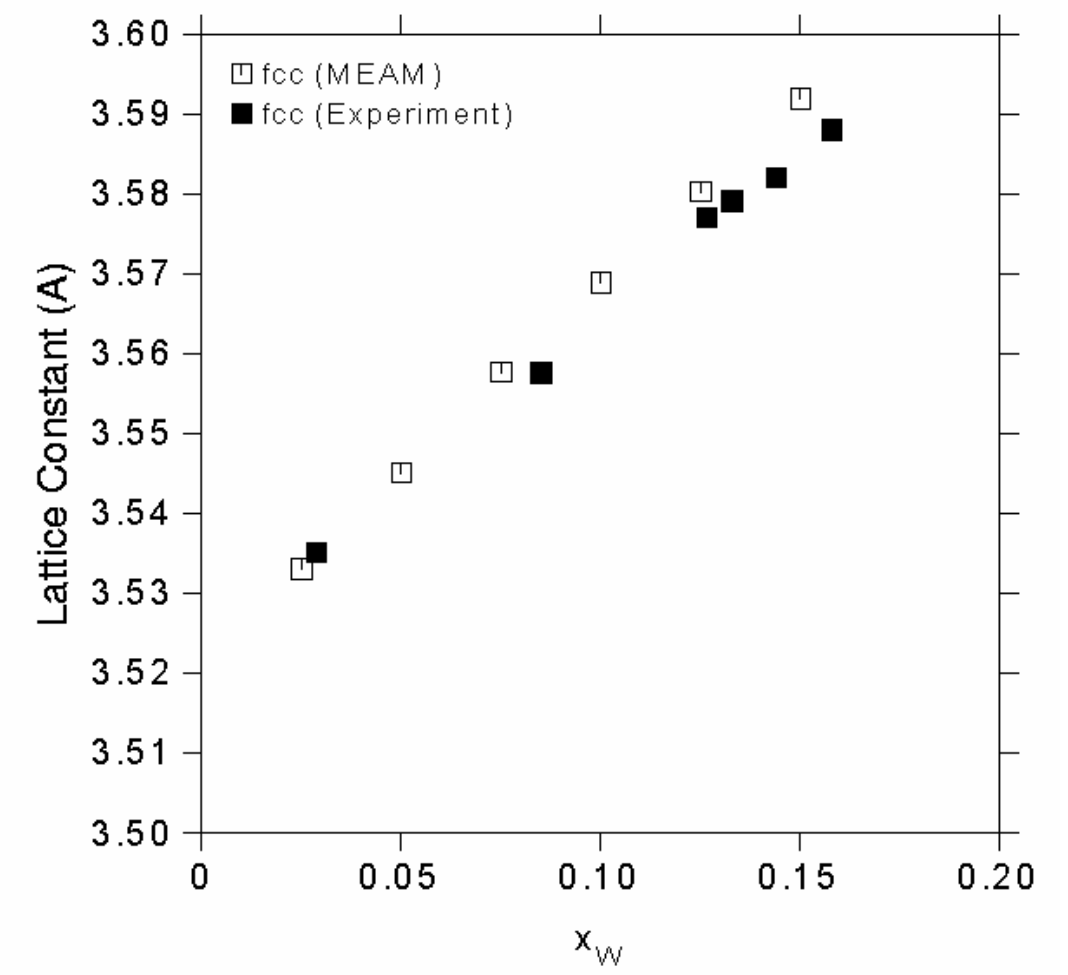
MEAM parameters for the Ni-W Binary System

	Selected value	Procedure for the determination
E_c^{Ni3W}	$E_c^{Ni}+E_c^{W}$ + 0.08	Fitting
r_e^{Ni3W}	2.557	Fitting
B^{Ni3W}	3.189	Fitting
d	$0.75d^{Ni} + 0.25d^{W}$	Assumption
C_{min} (Ni-W-Ni)	0.81 (0.81)	Fitting
C_{min} (W-Ni-W)	0.52 (0.49)	Fitting
C_{min} (Ni-Ni-W)	2.25	Fitting
C_{min} (Ni-W-W)	2.25	Fitting
ρ_0	$\rho_0^{Ni}= \rho_0^{W}$ = 1	Assumption

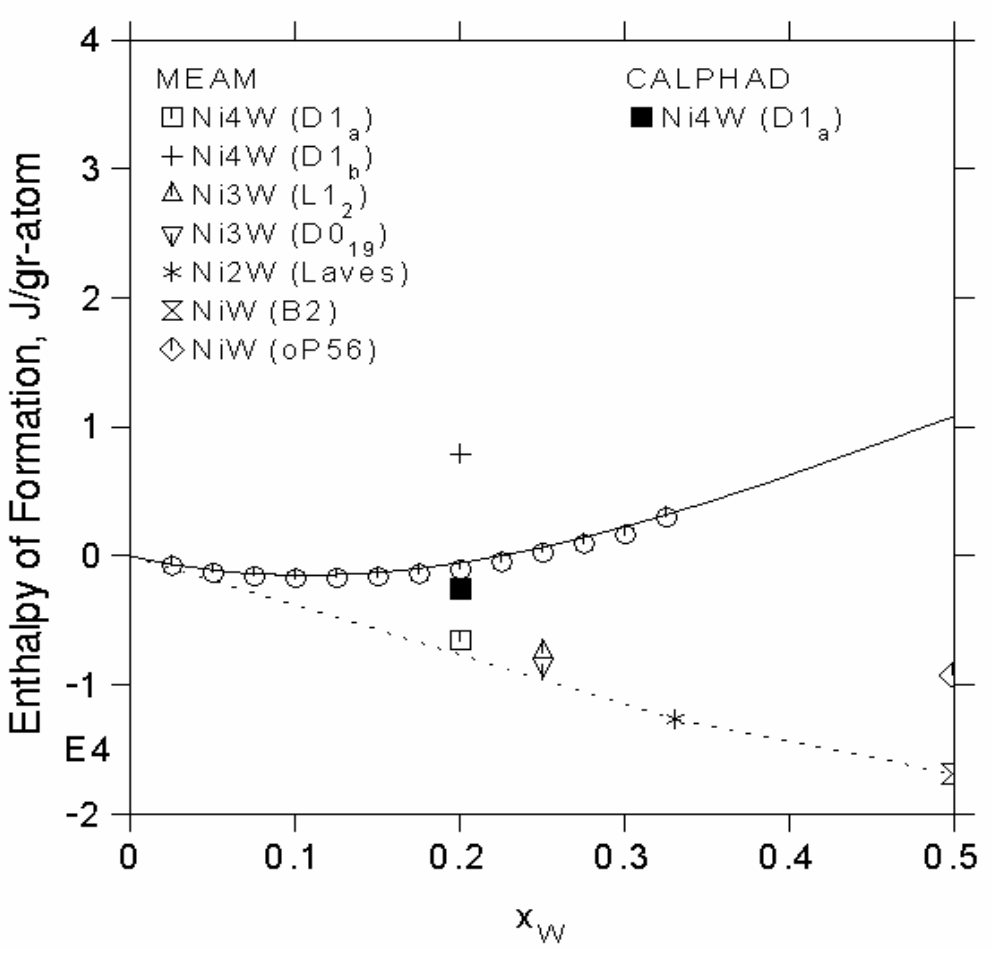
MEAM for Ni-W Binary System

	a (Å)	c (Å)	Ec (eV)	B (Gpa)
Ni_4W (D1a)	5.73	3.553	5.36	292
	5.73	3.553	5.40	293
Ni_3W ($L1_2$)	3.62	-	5.58	319
	3.58	-	5.65	287
Ni_3W ($D0_{19}$)	2.56	4.05	5.59	316
	2.53	-	5.42	289
NiW_3 ($L1_2$)	3.86	-	7.29	316
	3.84	-	7.55	283
NiW_3 ($D0_{19}$)	2.76	4.44	7.36	321
	2.76	-	7.70	304

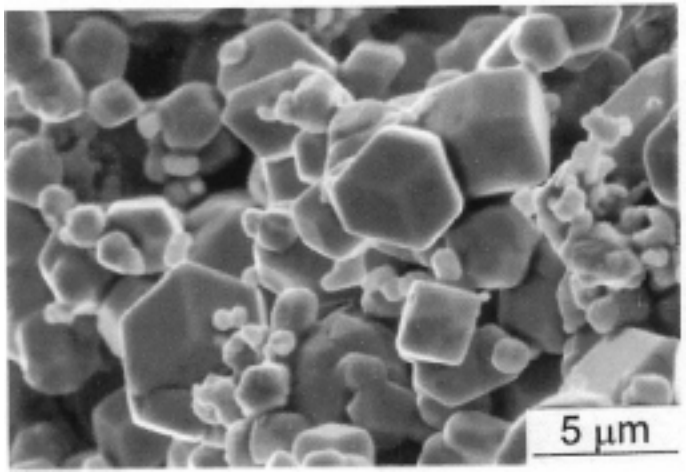
MEAM for Ni-W Binary System



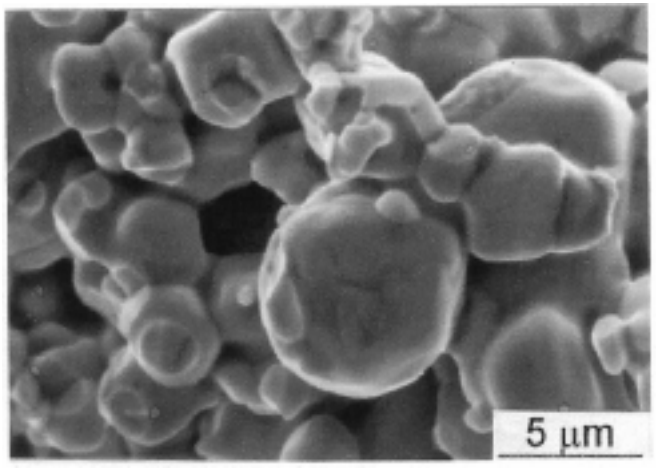
MEAM for Ni-W Binary System



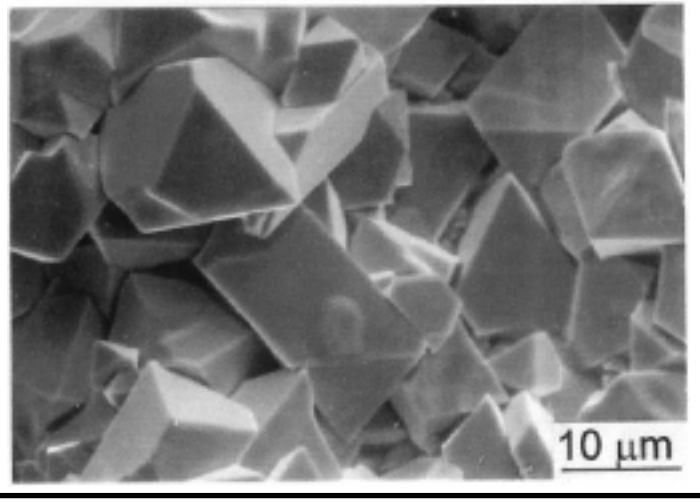
Surface Transition and Alloying Effect – N.M. Hwang et al., 2000.



Pure W

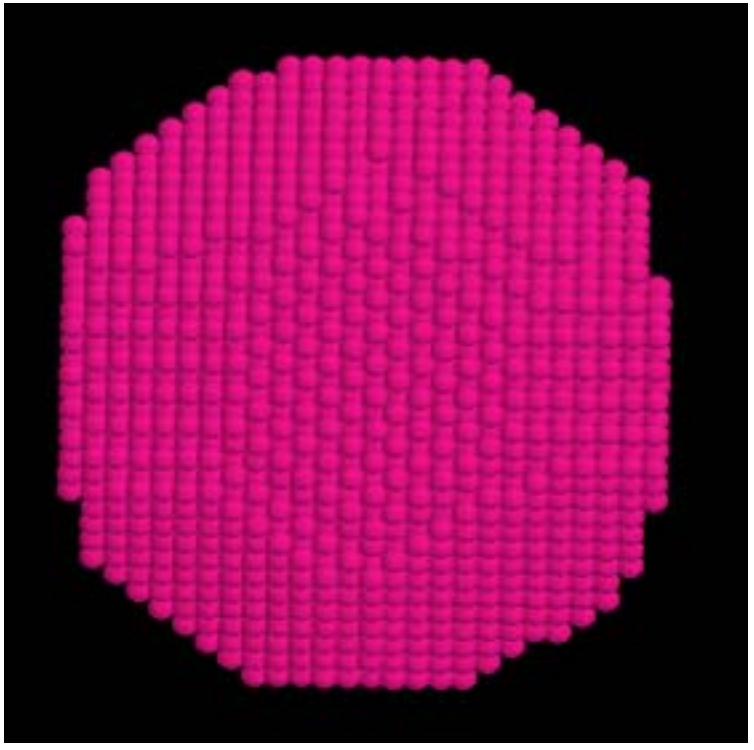


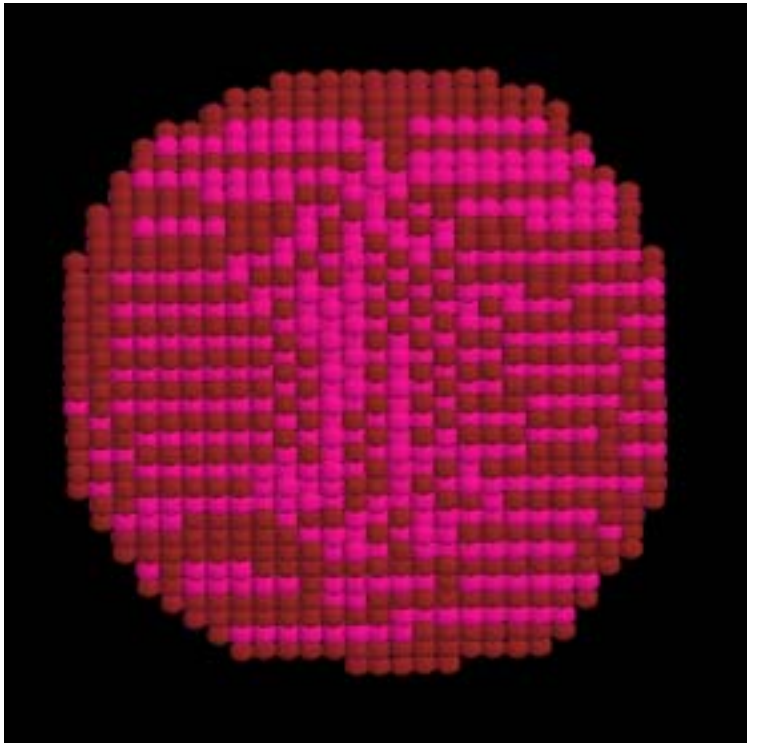
W + 0.4wt% Ni



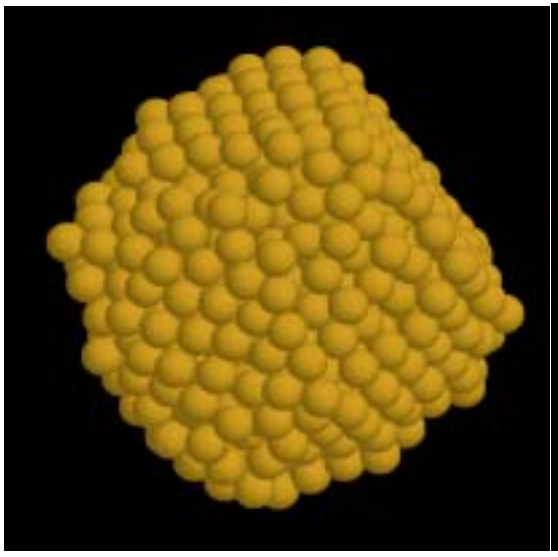
Vaccum Annealing

Simulated Surfaces of pure W and W-Ni alloy Powders - 6nm

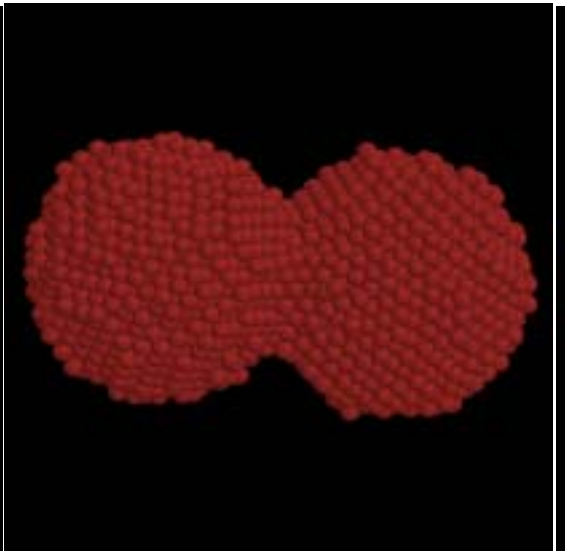




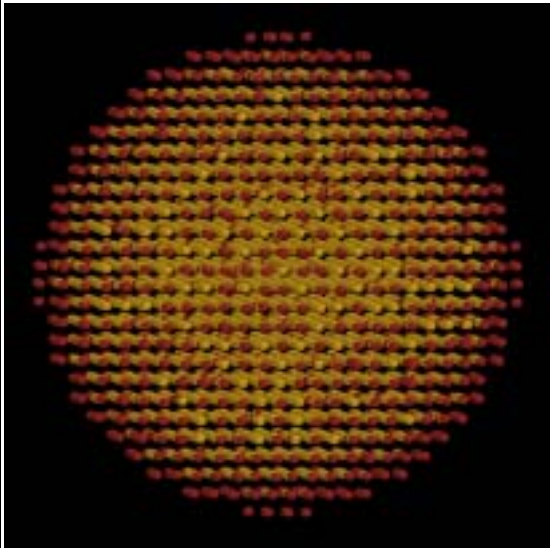
Application to Nano Powder



Surface Facet, Au

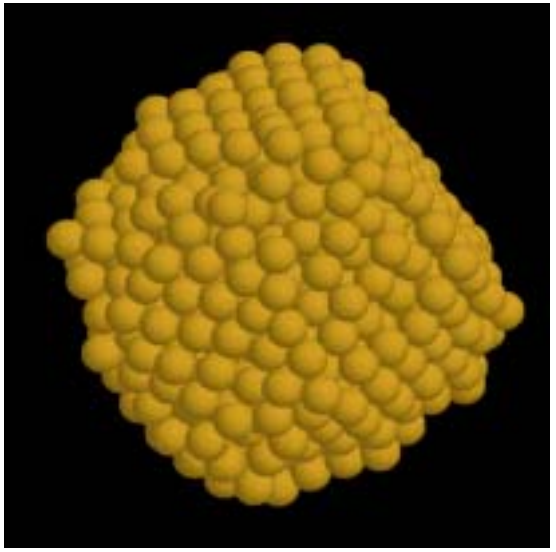


Sintering, Ni

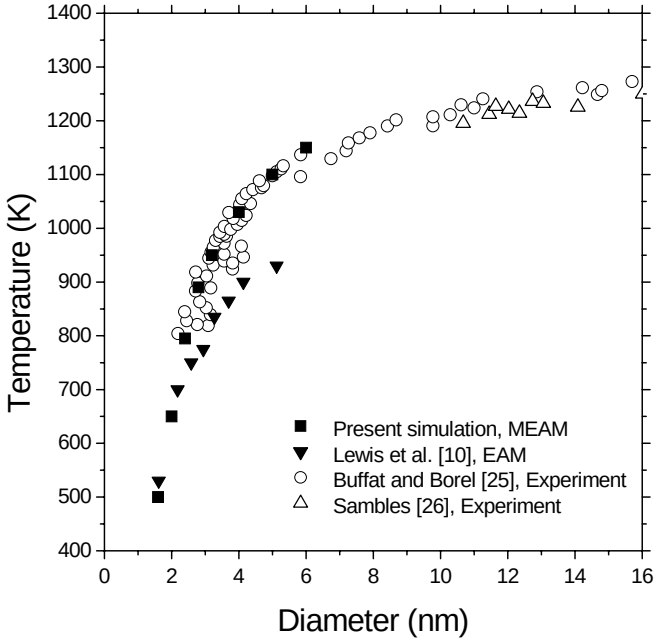


Surface Segregation, Cu-Ni

Size Effect on the Melting Point - J.-H. Shim et al., Surface Science, 2002.



Surface Facet, Au



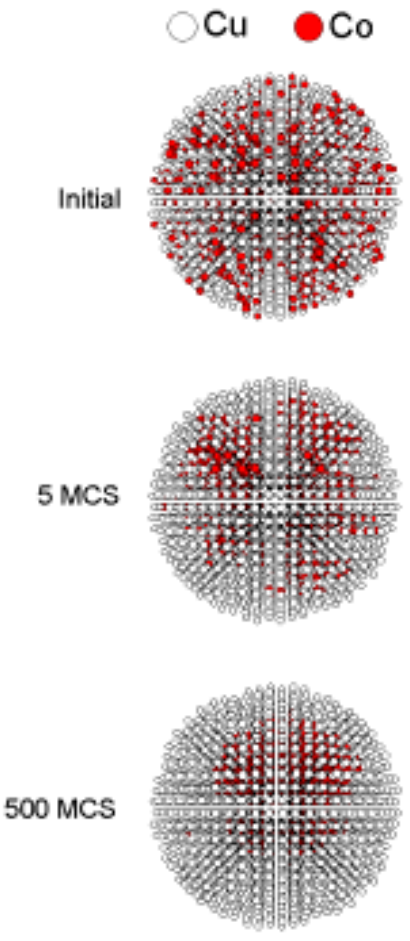
Size dependence of Melting point

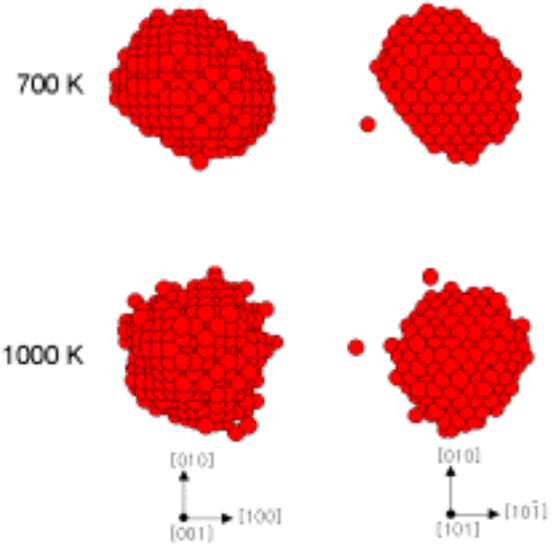
Surface Segregation and Phase Separation in Cu-Ni Nano Powder - III

Bulk, 100K Thin Film, 100K Thin Film, 298K

Surface Segregation and Phase Separation

Precipitation of Co in a Cu-Co Nano Powder - J.-H. Shim et al., JMR, 2002.





Energetics of Dot Formation during Thin Film Growths : Ge on Si

I **II** **III**



Coverage (Dot-size)	E_{II}-E_I	E_{III}-E_I
Double-Layer (5nm)	0.010 eV/atom	0.025 eV/atom
Triple-Layer (5nm)	0.017 eV/atom	0.031 eV/atom
Triple-Layer (10nm)	0.007 eV/atom	0.016 eV/atom
Double-Layer (10nm)	0.004 eV/atom : (100) side	
Double-Layer (10nm)	0.002 eV/atom : (110) side	
Double-Layer (12nm)	0.003 eV/atom : (100) side	

Future Plan

- **C, H, O, N**
- **Si, Ge, Ga, In, As, N**
- **Oxide Systems**
- **First Principles Calculation**