Thermodynamics

Thermodynamics of Surfaces & Interfaces

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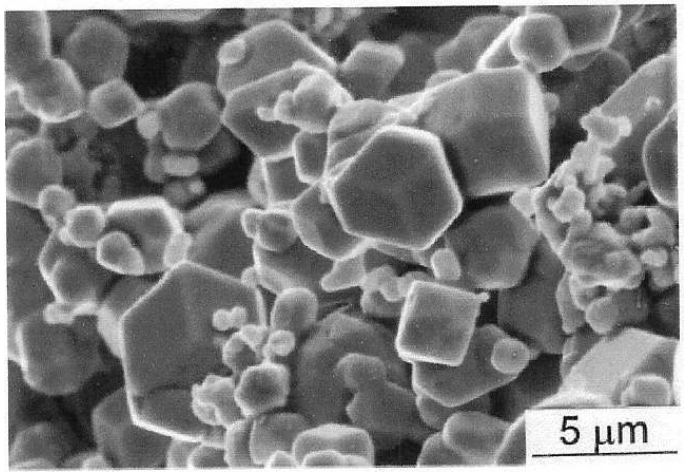
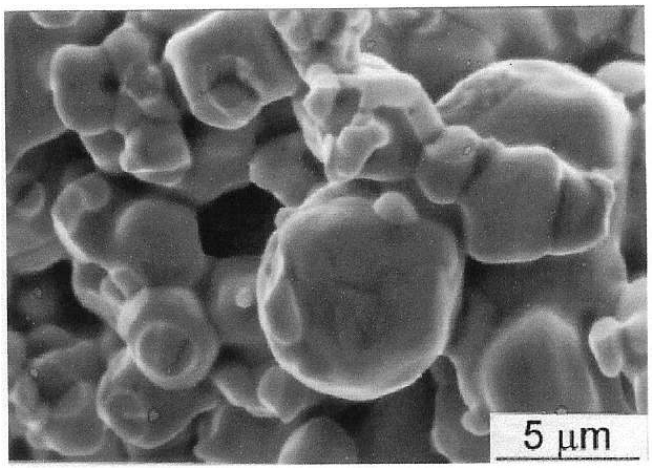
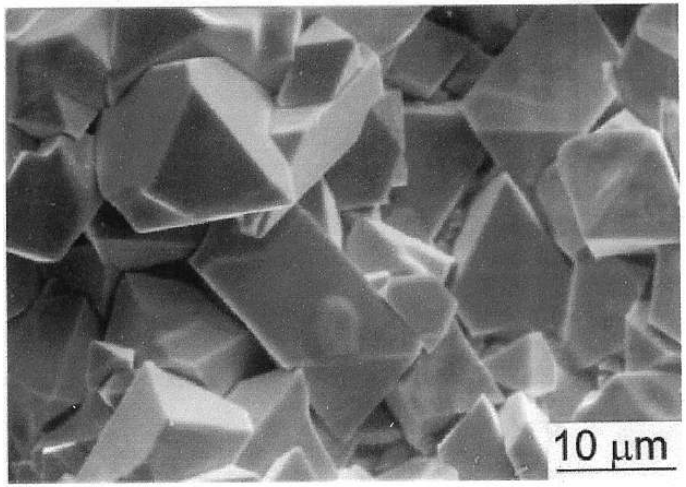
Surface Transition and Alloying Effect – N.M. Hwang et al., 2000.



Pure W

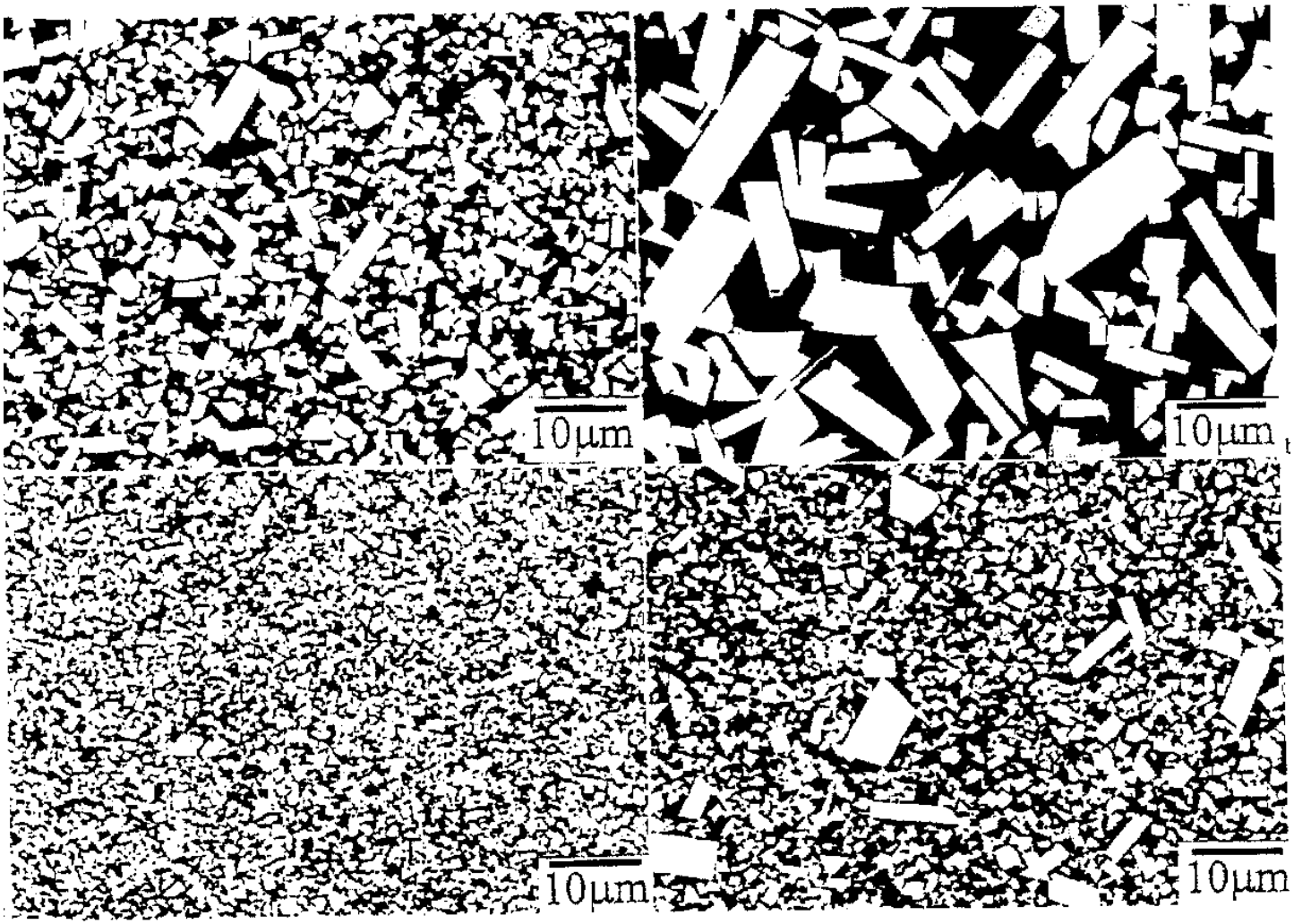


W + 0.4wt% Ni

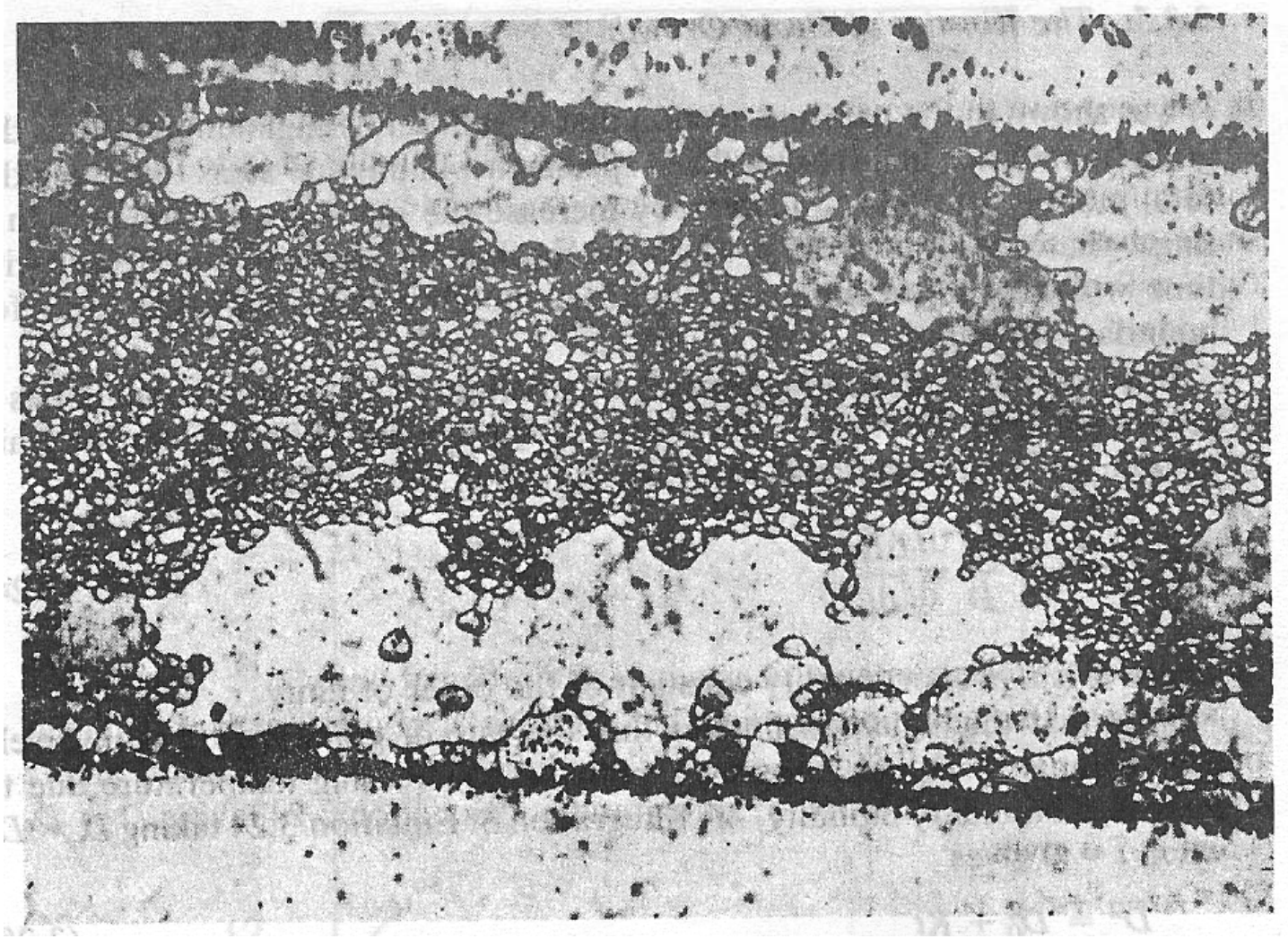


Vaccum Annealing

Abnormal Grain Growth – from N.M. Hwang



Abnormal Grain Growth – from N.M. Hwang



Scope

Fundamentals

1. Concept of Surface Energy
2. A Rough Estimation of Solid Surface Energy
3. Anisotropy of Surface Energy
4. Curvature Effect
   - Capillary Pressure
   - Vapor Pressure
   - Solubility
   - Melting Point
5. Measurement of Surface/Interface Energy

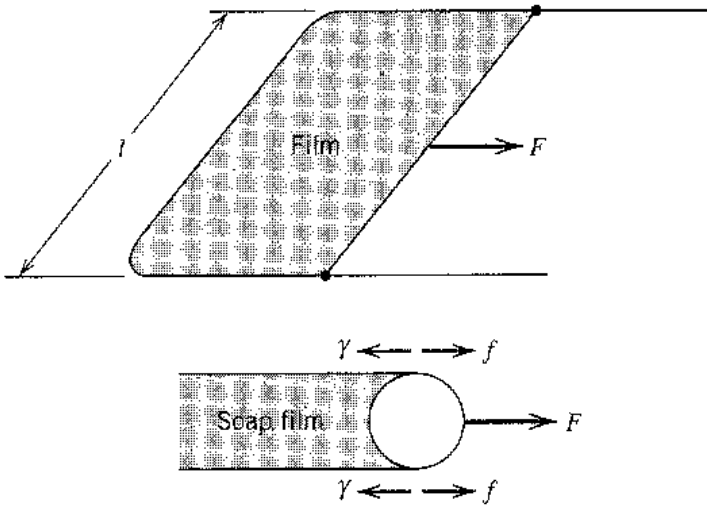
Interface Phenomena

1. Adsorption
2. Segregation
3. Crystal Shape
4. Grain Growth

Concept of Surface Energy and Surface Tension

$$dG = -SdT + VdP + \gamma \; dA$$

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{T,P}$$



Stretching a film—increasing area.

$$2l\gamma \; dx = Fdx$$

$$\gamma = \frac{F}{2l}$$

※ **Surface Energy and Tension for Liquids and Solids**

Rough Estimation of Solid Surface Energy

Pair approximation

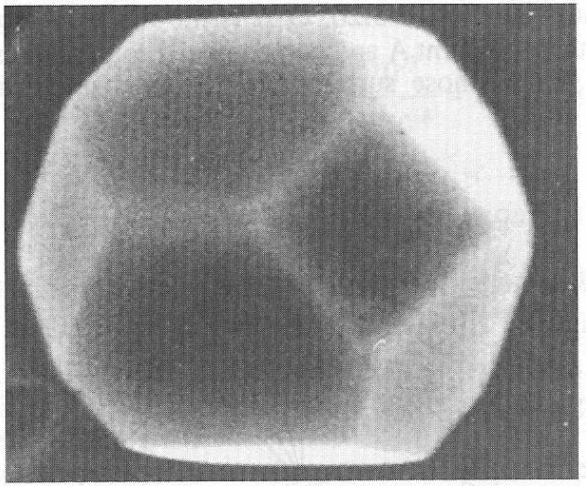
$$\Delta H_s = 0.5 Z N_A \varepsilon$$

Necessary Work for Creation of (111) surface in fcc (/atom)

$$w = \frac{3}{2}\varepsilon = \frac{\Delta H_s}{4N_A} \qquad \gamma = \frac{\Delta H_s}{4N_A}\left(\frac{N}{A}\right)$$

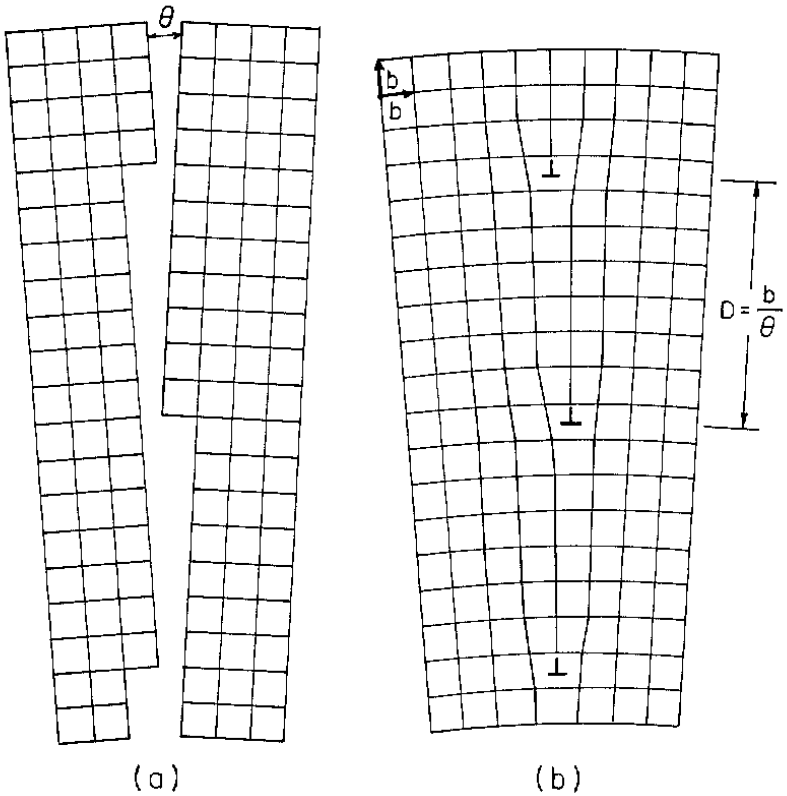
For fcc (111): $N/A = 4/(3^{1/2}a^2)$
fcc (100): $N/A = 2/a^2$

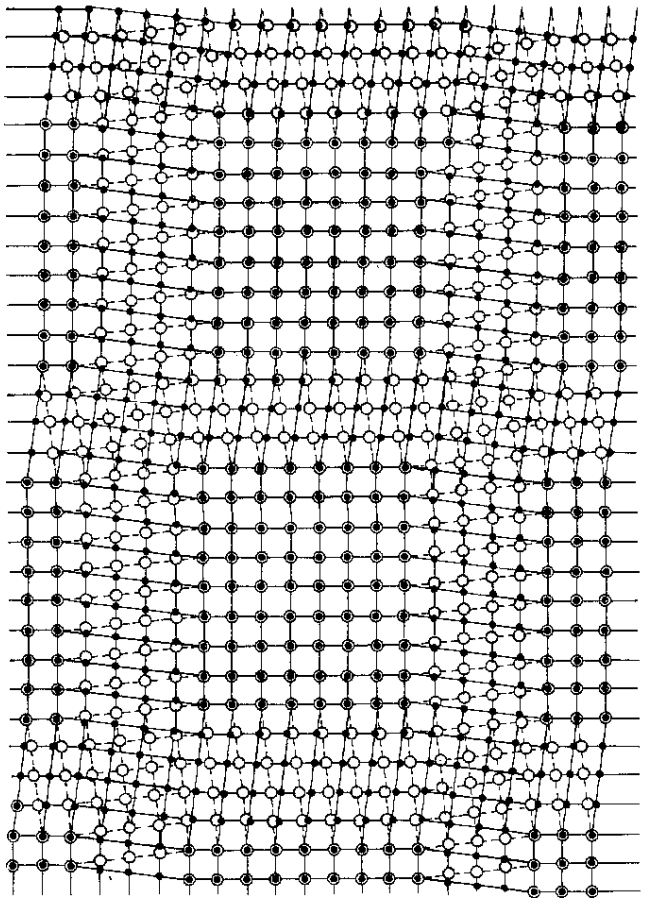
For Cu: a = 3.615 Å △Hs =337.7J/mol
$\gamma_{(111)}$ = 2460 erg/cm^2 (1700 by expt.)



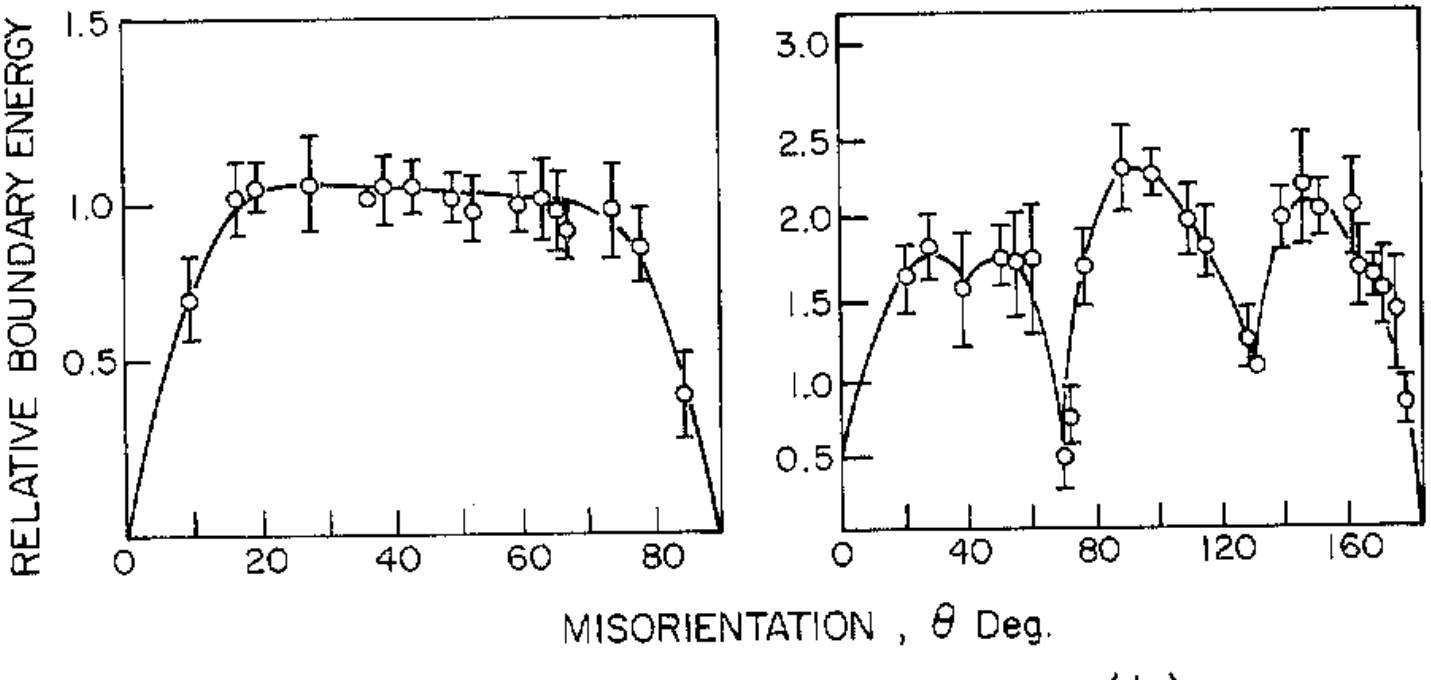
For fcc
※ Origin of Anisotropy $\dfrac{\gamma_{(100)}}{\gamma_{(111)}} = \dfrac{2}{\sqrt{3}} = 1.15$

Approximation for Estimation of Grain Boundary Energy

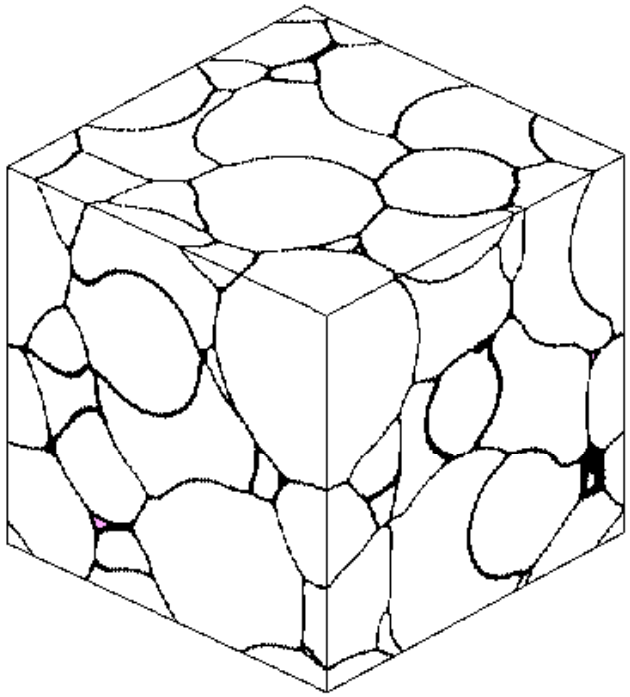




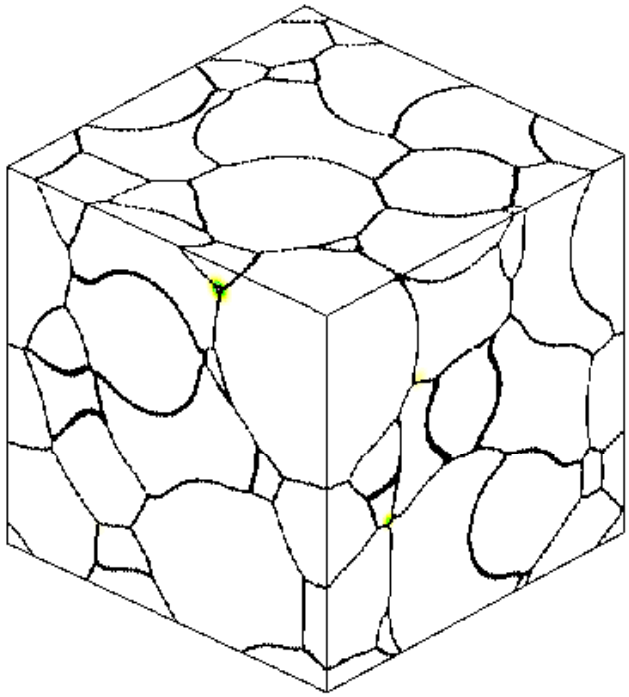
Anisotropy of Grain Boundary Energy – [100] and [110] tilt Bd. of Al



Why Interface/Grain Boundary Properties?



Wetting angle : 36°

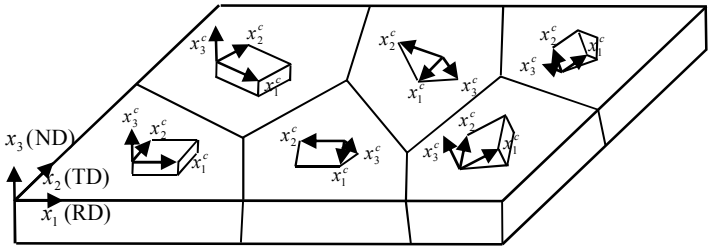


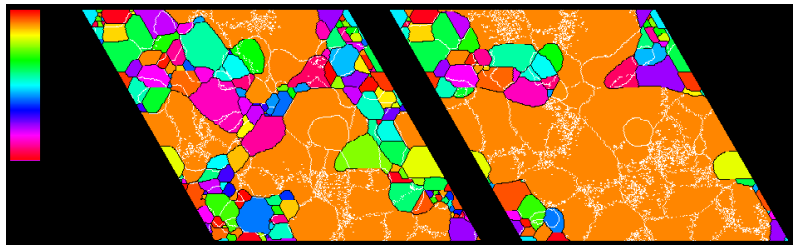
Wetting angle : 120°

Fe - 0.5% Mn – 0.1% C, dT/dt = 1 °C/s

from SG Kim, Kunsan University

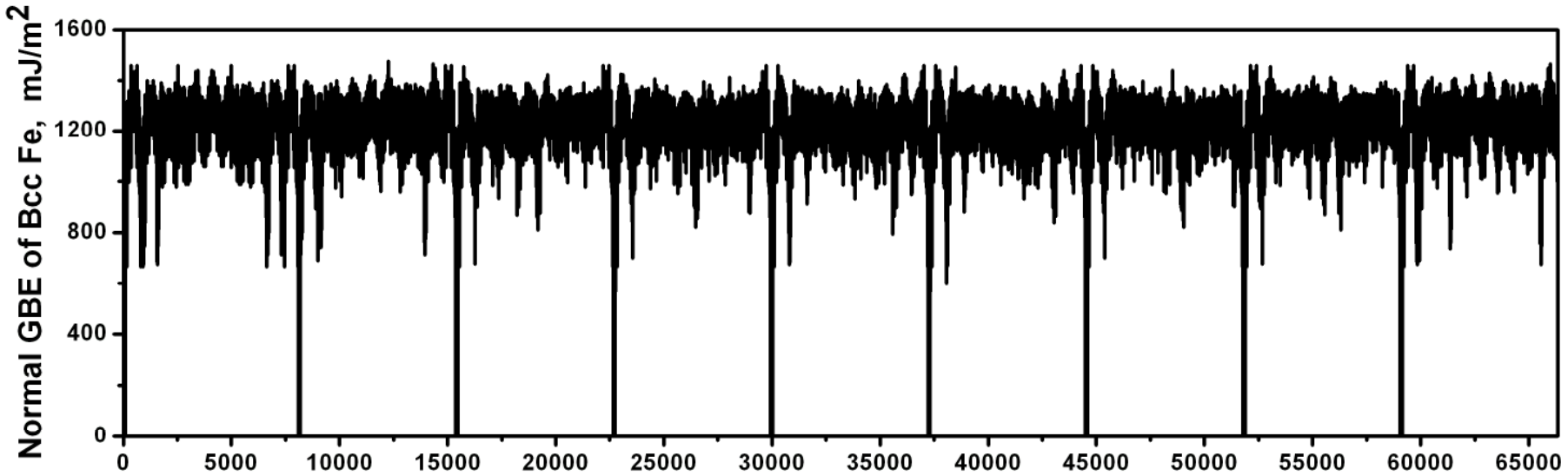
Grain Boundary Identification Scheme

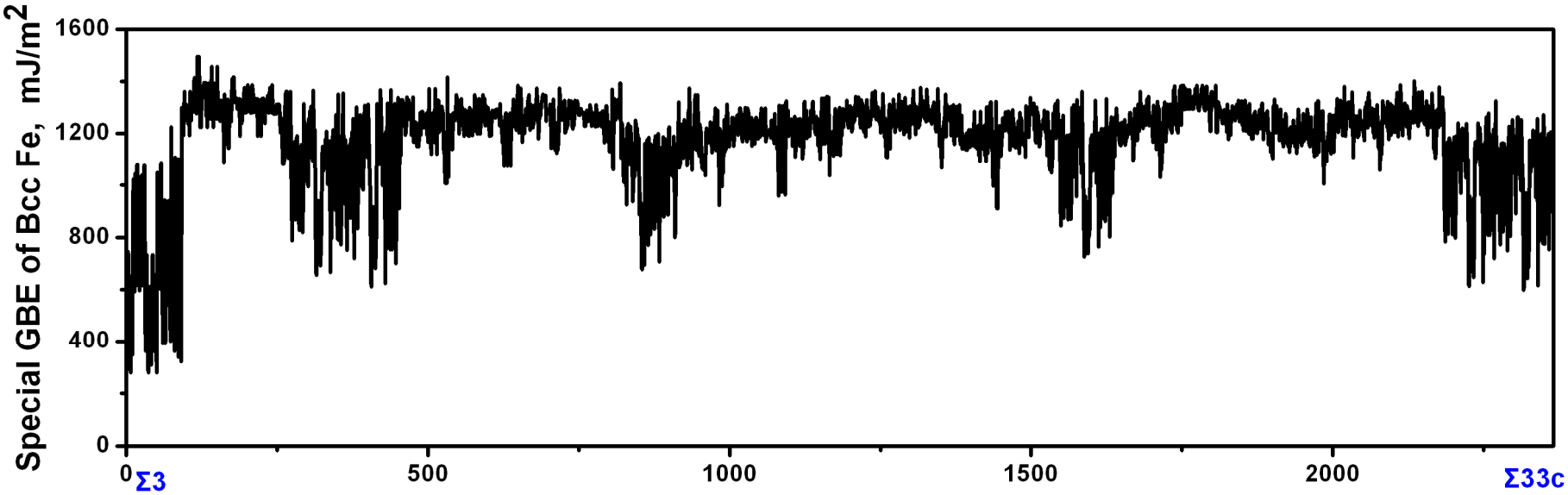




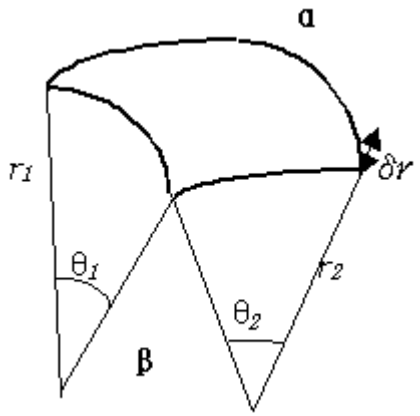
How to uniquely define misorientation and inclination between two neighboring grains

Grain Boundary Energy of BCC Fe





Curvature Effect – Capillary Pressure



System condition

T = constant

$V^{\alpha} = V^{\beta} = V$ = constant

$$dF = -SdT - PdV + \gamma dA$$
$$= -P^{\beta}dV^{\beta} - P^{\alpha}dV^{\alpha} + \gamma dA$$
$$= -(P^{\beta} - P^{\alpha})dV^{\beta} + \gamma dA$$

@ equilibrium

$$\Delta P = (P^{\beta} - P^{\alpha}) = \gamma \frac{dA}{dV^{\beta}}$$

$$dA = (r_1 + \delta r)\theta_1 \cdot (r_2 + \delta r)\theta_2 - r_1\theta_1 \cdot r_2\theta_2 = (r_1 + r_2)\delta r\theta_1\theta_2 + (\delta r)^2\theta_1\theta_2 \cong (r_1 + r_2)\delta r\theta_1\theta_2$$

$$dV^{\beta} = r_1 r_2 \delta r \theta_1 \theta_2$$

$$\Delta P = (P^{\beta} - P^{\alpha}) = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

$$\Delta G = G_m^{\beta} - G_m^{\alpha} = V_m \Delta P = \gamma\ V_m\left(\frac{1}{r_1} + \frac{1}{r_2}\right) = \mu^{\beta} - \mu^{\alpha}$$

Curvature Effect – Capillary Pressure Effect on Vapor Pressure and Solubility

Vapor Pressure

$$\mu_{c,r} - \mu_{c,\infty} = \frac{2}{r}\gamma\ V_m = \mu_{v,r} - \mu_{v,\infty} = RT \ln \frac{P_r^o}{P_\infty^o}$$

$$\ln \frac{P_r^o}{P_\infty^o} = \frac{V_m}{RT} \cdot \frac{2\gamma}{r}$$

Solubility of pure B phase in a dilute solution

$$\mu_{B,r} - \mu_{B,\infty} = \frac{2\gamma_{A-B}}{r} V_m = RT \ln a_B = RT \ln k x_{B,r} \qquad k \cdot x_{B,\infty} = 1$$

$$\mu_{B,r} - \mu_{B,\infty} = RT \ln \frac{x_{B,r}}{x_{B,\infty}}$$

$$\ln \frac{x_{B,r}}{x_{B,\infty}} = \frac{V_m}{RT} \cdot \frac{2\gamma_{A-B}}{r}$$

Curvature Effect – Capillary Pressure Effect on Melting Point

$$P_S = P_L + \frac{2\gamma_{S-L}}{r}$$

$$d\mu_L = -S_L dT + V_L dP_L \qquad d\mu_S = -S_S dT + V_S dP = -S_S dT + V_S d\left(P_L + \frac{2\gamma_{L-S}}{r}\right)$$

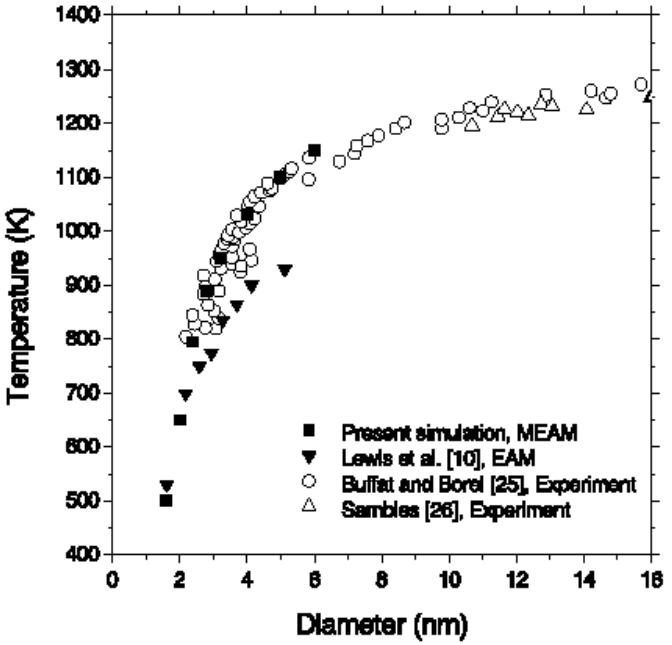
$$(S_L - S_S)dT - (V_L - V_S)dP_L - 2\gamma_{L-S}V_S\frac{dr}{r^2} = 0$$

$$\Delta S_m dT = 2\gamma_{S-L}V_m\frac{dr}{r^2}$$

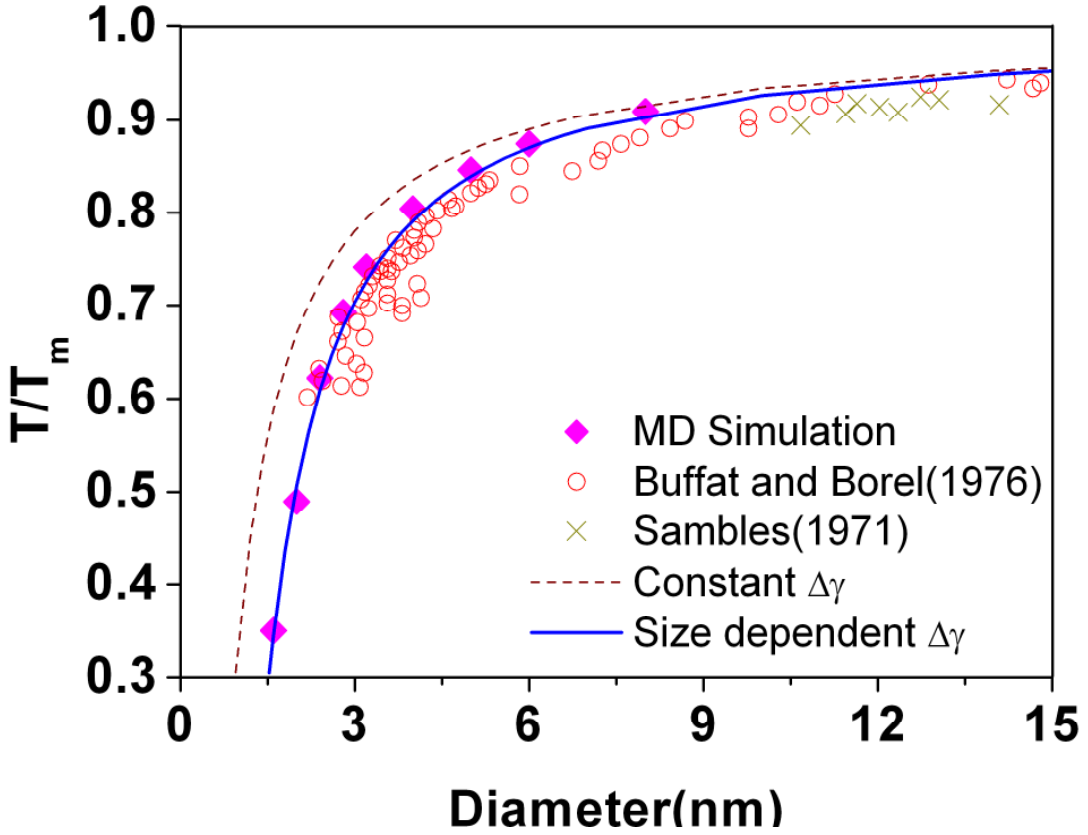
$$\Delta S_m \int_{T_\infty}^{T_r} dT = 2\gamma_{S-L}V_m \int_{T_\infty}^{T_r} \frac{dr}{r^2}$$

$$\Delta S_m (T_r - T_\infty) = \Delta S_m \Delta T_m = -\frac{2\gamma_{S-L}V_m}{r}$$

$$\Delta T_m = -\frac{2\gamma_{S-L}V_m}{\Delta S_m r} = -\frac{2\gamma_{S-L}V_m T_m}{\Delta H_m}\cdot\frac{1}{r}$$

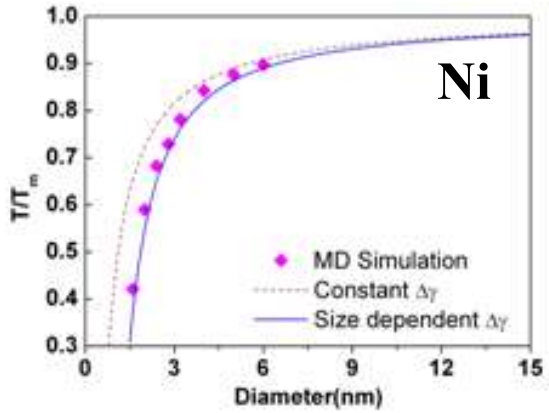


Thermodynamics of Nano Particles or Nanowires

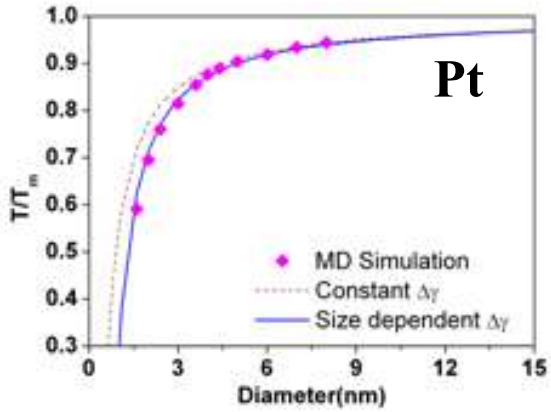


Size dependence of melting points of Au nano particles.

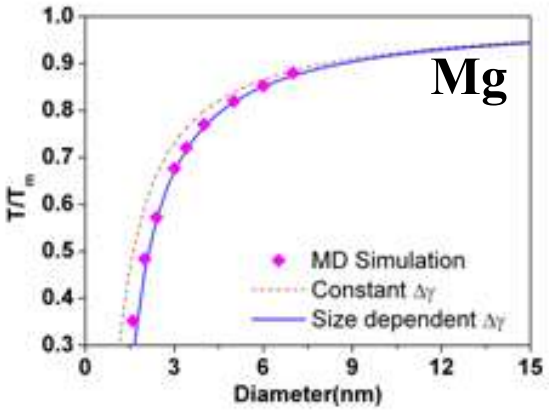
Melting points of Nano Particles



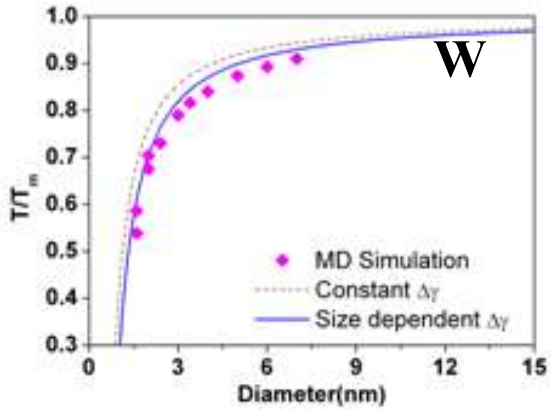
(a)



(b)

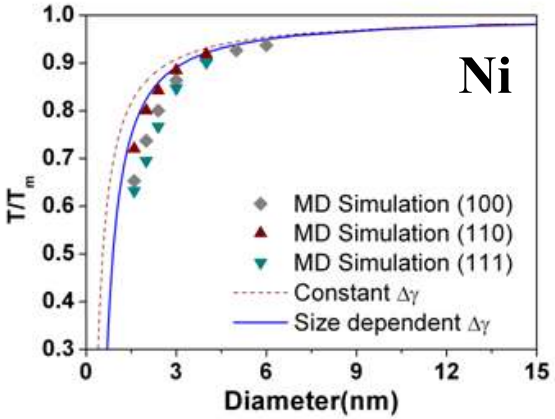


(c)

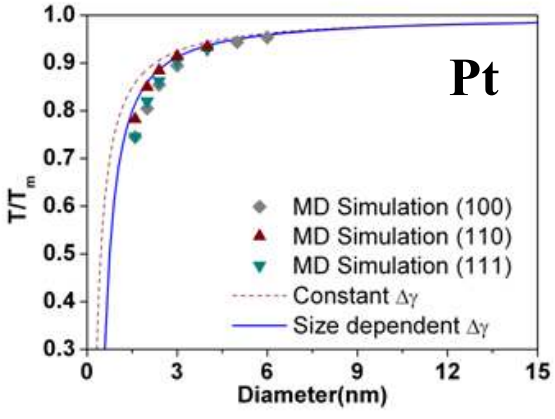


(d)

Melting points of Nano Wires



(a)



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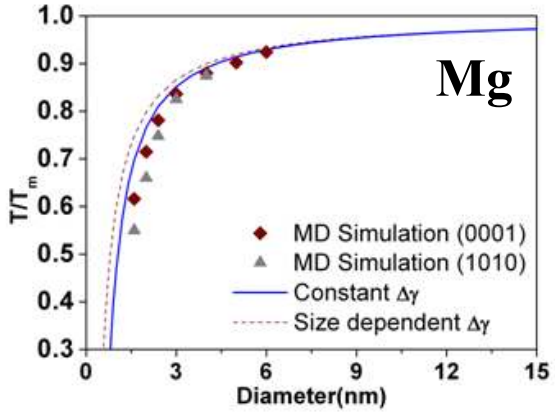

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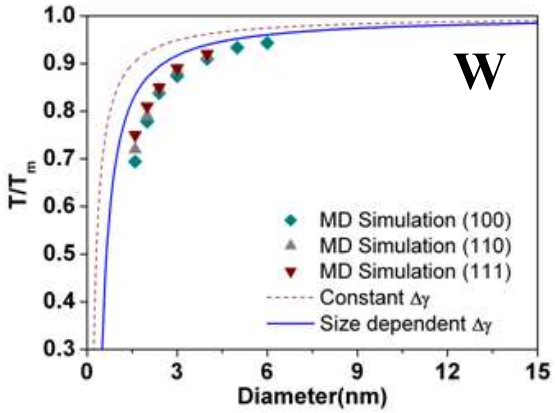
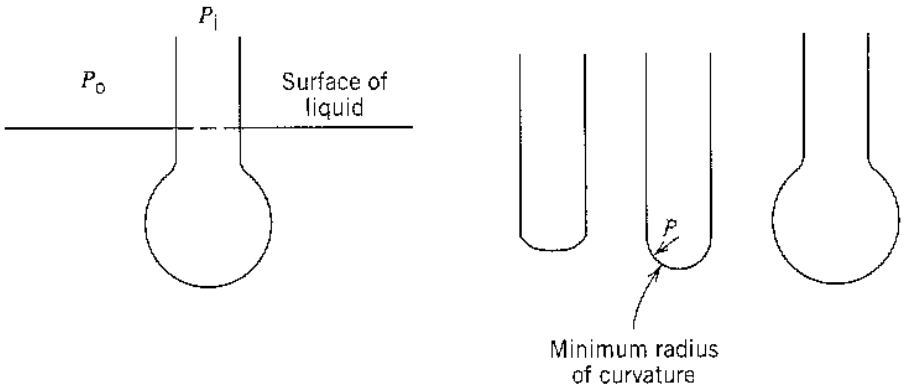
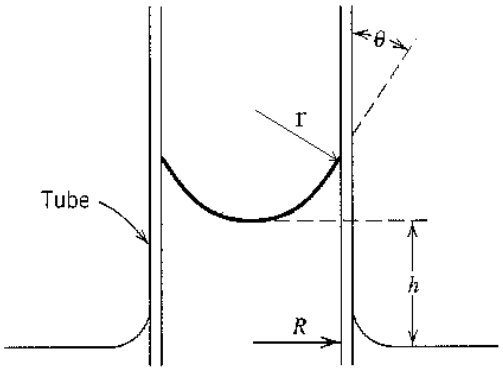


(d)

Measurement of Surface Energy – Surface Energy of Liquid



Bubble method for surface energy determination



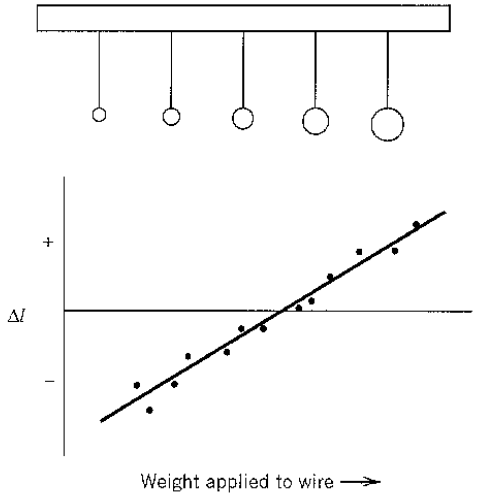
Capillary rise method for surface energy measurement

$$\Delta P = P_i - P_o = \frac{2\gamma}{r}$$

$$r = R / \cos\theta$$

$$\rho g h = \frac{2\cos\theta \cdot \gamma}{R}$$

Measurement of Surface Energy – Surface Energy of Solid



Elongation method for measurement of surface energy of solids

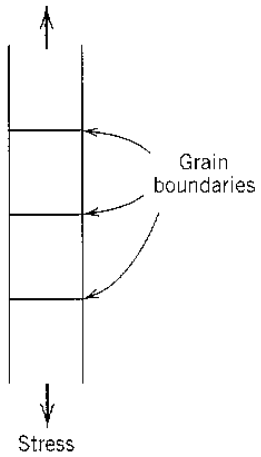
$$\delta w_{rev} = mg \cdot dl = \gamma \cdot dA$$

$$A = 2\pi rl \qquad dA = 2\pi(rdl + ldr)$$

$$V = \pi r^2 l = const.$$

$$dV = 2\pi\ ldr + \pi r_2 dl = 0 \qquad dr = -\frac{1}{2}\frac{r}{l}dl$$

$$\gamma = \frac{mg}{\pi r}$$



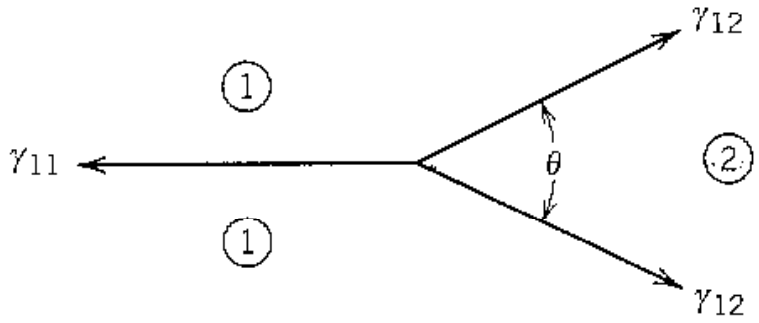
$$mg \cdot dl = \gamma \cdot dA + \gamma_{gb} dA_{gb}$$

$$dA_{gb} = d\left(n\pi r^2\right)$$

$$mg = \pi\ r\gamma\ - \pi\ r^2 \frac{n}{l}\gamma_{gb}$$

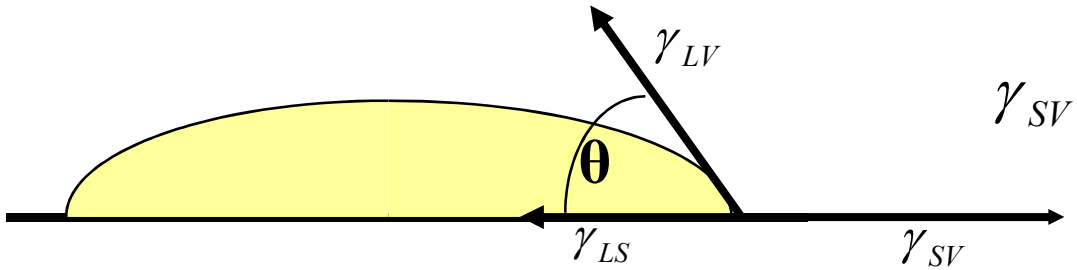
Measurement of Surface Energy – Relative Interface Energy of Solid

$$\frac{\gamma_{23}}{\sin\theta_1} = \frac{\gamma_{12}}{\sin\theta_3} = \frac{\gamma_{31}}{\sin\theta_2}$$



Two-phase equilibrium

$$\gamma_{11} = 2\gamma_{12}\cos\left(\frac{\theta}{2}\right)$$



$$\gamma_{SV} = \gamma_{LS} + \gamma_{LV}\cos\theta$$

Physisorption : Van der Waals
Chemisorption : Chemical Bonding

Langmuir adsorption : monolayer chemisorption

θ : fraction of surface site covered

$$R_a = K_a P(1-\theta)$$
$$R_d = K_d \theta$$

@ equilibrium $K_a P(1-\theta) = K_d \theta$

$$\frac{\theta}{P(1-\theta)} = \frac{K_1}{K_2} = K(T)$$

$$\theta = \frac{KP}{1+KP}$$

θ_A : fraction of coverage of A
θ_B : fraction of coverage of B

- A(g) + S ↔ AS
- B(g) + S ↔ BS

For A :

$$R_a = K_a P_A (1 - \theta_A - \theta_B)$$
$$R_d = K_d \theta_A$$

$$\frac{\theta_A}{P_A(1 - \theta_A - \theta_B)} = K_A(T)$$

For B :

$$R_a = K_a P_B (1 - \theta_A - \theta_B)$$
$$R_d = K_d \theta_B$$

$$\frac{\theta_B}{P_B(1 - \theta_A - \theta_B)} = K_B(T)$$

$$\frac{\theta_A}{\theta_B} = \frac{K_A(T)P_A}{K_B(T)P_B}$$

1. $A(g) + S \leftrightarrow AS$ $\quad\quad \theta_1 = \theta_0 K_1 P$
2. $A(g) + AS \leftrightarrow A_2S$ $\quad\quad \theta_2 = \theta_1 K_2 P$
3. ….
n. $A(g) + A_{n-1}S \leftrightarrow A_nS$ $\quad\quad \theta_n = \theta_{n-1} K_n P$

K_1 : chemisorption

$K_2, \ldots, K_n$: the same physisorption (interface)

assume $K_2 = K_3 = \ldots = K_n = K$

$$\theta_n = \theta_1 (KP)^{n-1}$$

Assume a one atomic layer surface phase and consider equilibrium between bulk and surface

$$ {}^{o}G_i^{\phi} + RT\ln\gamma_i^{\phi}X_i^{\phi} = \mu_i^{\phi} + \sigma\omega_i \qquad {}^{o}G_i^{B} + RT\ln\gamma_i^{B}X_i^{B} = \mu_i^{B} $$

where ω_i is the molar surface area
Assume $\omega_i = \omega_j = \ldots = \omega$

from $\mu_i^{\phi} = \mu_i^{B}$

$$ \sigma\omega = [{}^{o}G_i^{\phi} - {}^{o}G_i^{B}] + RT\ln\frac{\gamma_i^{\phi}}{\gamma_i^{B}} + RT\ln\frac{X_i^{\phi}}{X_i^{B}} $$

$$ \frac{X_i^{\phi}}{X_n^{\phi}} = \frac{X_i^{B}}{X_n^{B}}\, e^{-\Delta G^{seg}/RT} $$

$$ \Delta G^{seg} = [{}^{o}G_i^{\phi} - {}^{o}G_i^{B}] - [{}^{o}G_n^{\phi} - {}^{o}G_n^{B}] + RT\ln\frac{\gamma_i^{\phi}\gamma_n^{B}}{\gamma_n^{\phi}\gamma_i^{B}} $$

for multicomponents

$$ X_i^{\phi} = \frac{X_i^{B} e^{-\Delta G_i^{seg}/RT}}{1 + \sum_{j=1}^{n-1} X_j^{B}\left(e^{-\Delta G_j^{seg}/RT} - 1\right)} $$

$$\Delta G^{seg} = [{}^{o}G_i^{\phi} - {}^{o}G_i^{B}] - [{}^{o}G_n^{\phi} - {}^{o}G_n^{B}] + RT \ln \frac{\gamma_i^{\phi}\gamma_n^{B}}{\gamma_n^{\phi}\gamma_i^{B}}$$

$$= \omega^{o}\sigma_i - \omega^{o}\sigma_n + [\Delta^{xs}\overline{G}_i^{\phi} - \Delta^{xs}\overline{G}_n^{\phi}] - [\Delta^{xs}\overline{G}_i^{B} - \Delta^{xs}\overline{G}_n^{B}]$$

from $\mu_i^{\phi} = \mu_i^{B}$

$$\sigma\omega_i = [{}^{o}G_i^{\phi} - {}^{o}G_i^{B}] + RT \ln \frac{\gamma_i^{\phi}}{\gamma_i^{B}} + RT \ln \frac{X_i^{\phi}}{X_i^{B}}$$

$$\sigma = \frac{1}{\omega_i}[{}^{o}G_i^{\phi} - {}^{o}G_i^{B}] + \frac{1}{\omega_i}[\Delta^{xs}\overline{G}_i^{\phi} - \Delta^{xs}\overline{G}_i^{B}] + \frac{RT}{\omega_i} \ln \frac{X_i^{\phi}}{X_i^{B}}$$

- $\omega_i \neq \omega_j = \cdots$

$$\sigma = \frac{1}{\omega_i}[{}^{o}G_i^{\phi} - {}^{o}G_i^{B}] + \frac{1}{\omega_i}[\Delta^{xs}\overline{G}_i^{\phi} - \Delta^{xs}\overline{G}_i^{B}] + \frac{RT}{\omega_i}\ln(X_i^{\phi}/X_i^{B})$$

$$= \cdots$$

$$= \frac{1}{\omega_n}[{}^{o}G_n^{\phi} - {}^{o}G_n^{B}] + \frac{1}{\omega_n}[\Delta^{xs}\overline{G}_n^{\phi} - \Delta^{xs}\overline{G}_n^{B}] + \frac{RT}{\omega_n}\ln(X_n^{\phi}/X_n^{B})$$

$$-\left\{\frac{1}{\omega_i}[{}^{o}G_i^{\phi} - {}^{o}G_i^{B}] - \frac{1}{\omega_n}[{}^{o}G_n^{\phi} - {}^{o}G_n^{B}] + \frac{1}{\omega_i}[\Delta^{xs}\overline{G}_i^{\phi} - \Delta^{xs}\overline{G}_i^{B}] - \frac{1}{\omega_n}[\Delta^{xs}\overline{G}_n^{\phi} - \Delta^{xs}\overline{G}_n^{B}]\right\} = \frac{RT}{\omega_i}\ln(X_i^{\phi}/X_i^{B}) - \frac{RT}{\omega_n}\ln(X_n^{\phi}/X_n^{B})$$

$$\ln\left[\left(X_i^{\phi}/X_i^{B}\right)^{\frac{1}{\omega_i}} / \left(X_n^{\phi}/X_n^{B}\right)^{\frac{1}{\omega_n}}\right] = -\Delta G_i^{seg'}/RT$$

$$X_i^{\phi}/X_i^{B} = \left(X_n^{\phi}/X_n^{B}\right)^{\frac{\omega_i}{\omega_n}} \cdot e^{-\Delta G_i^{seg}/RT}$$

$$\Delta G_i^{seg} = [{}^{o}G_i^{\phi} - {}^{o}G_i^{B}] - \frac{\omega_i}{\omega_n}[{}^{o}G_n^{\phi} - {}^{o}G_n^{B}] + [\Delta^{xs}\overline{G}_i^{\phi} - \Delta^{xs}\overline{G}_i^{B}] - \frac{\omega_i}{\omega_n}[\Delta^{xs}\overline{G}_n^{\phi} - \Delta^{xs}\overline{G}_n^{B}]$$

Interfacial Phenomena – Segregation (Example)

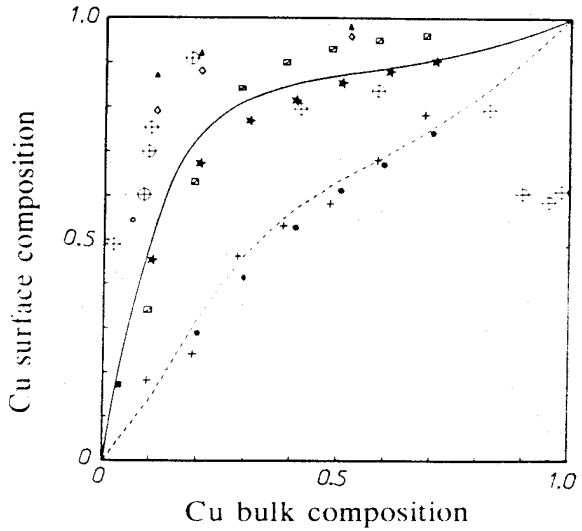
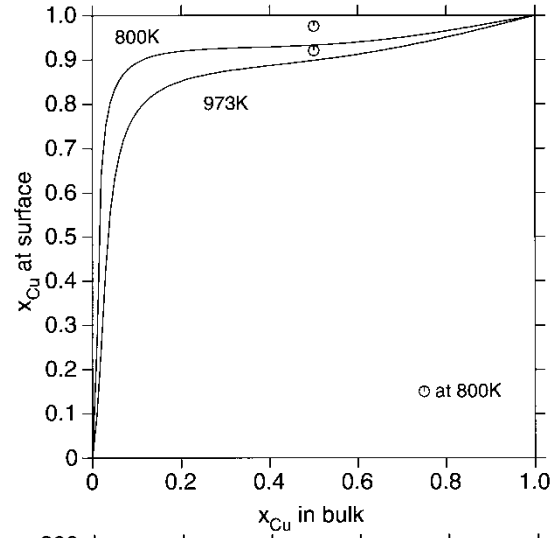
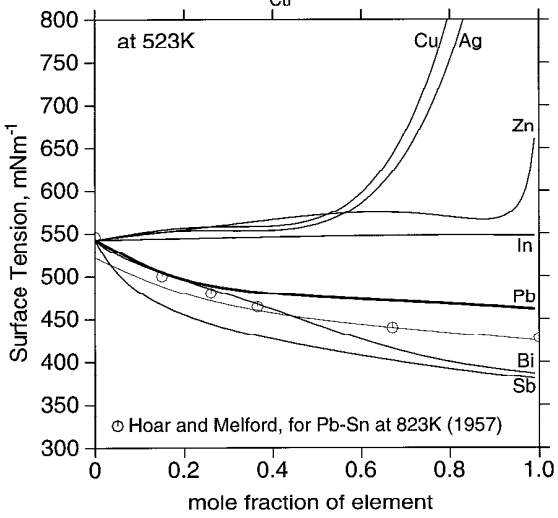
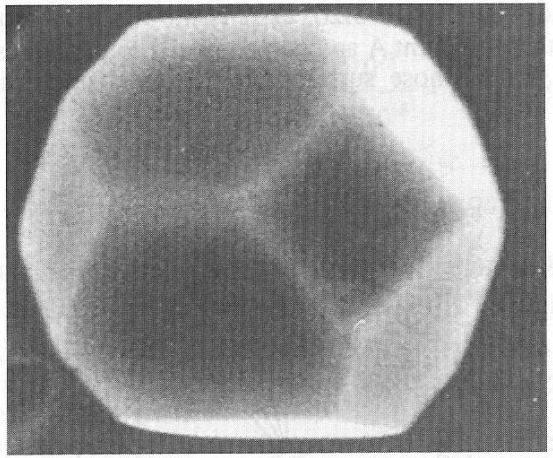
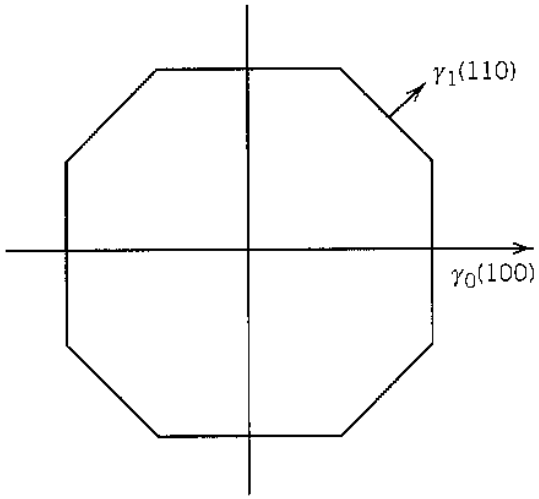


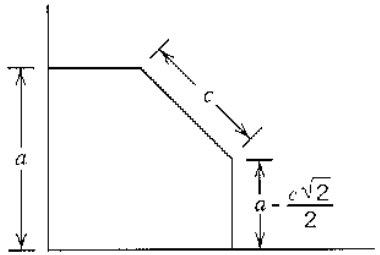
Fig. 3. Cu(111) surface composition versus Cu bulk composition for Cu–Ni alloys: comparison between the experimental and theoretical results. Regular model: $T = 973$ K, (———) surface; (— — —) 2nd plane. Monte Carlo calculations: $T = 973$ K, (★) surface; (∗) 2nd plane. Experimental results: (⧄) AES, $T = 873$ K, ref. [18]; (+) AES, $T = 873$, 2nd plane, ref. [18]; (▲) ISS, $T = 773$ K, ref. [19]; (◇) ISS, $T = 673$ K, ref. [19], (○) AP FIM, $T = 823$ K, refs. [20,21]; (■) AP FIM, $T = 923$ K, refs. [20,21]; (⊕) AP, $T = 870$–920 K, ref. [22].











$$E_S = 2\left(a - \frac{c\sqrt{2}}{2}\right)\gamma_0 + c\gamma_1$$

$$A = a^2 - \frac{c^2}{4} = const.$$

$$\frac{c}{a} = 2\left(\sqrt{2} - \frac{\gamma_1}{\gamma_2}\right)$$

$$for \quad \gamma_0 = \gamma_1 \qquad 2\left(a - \frac{c\sqrt{2}}{2}\right) = c$$

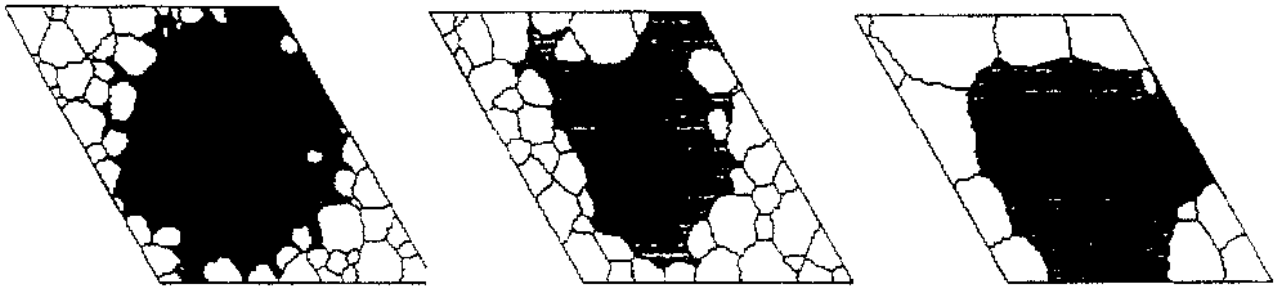


Figure 2 Microstructure evolution after (a) 500 MCS, (b) 500 MCS and (c) 2000 MCS with the percentages of type II grains, (a) 100%, (b) 70% and (c) 40%. The grain boundary between AGG and type I grains has energy 3 times that between AGG and type II grains or between type I and type II grains.

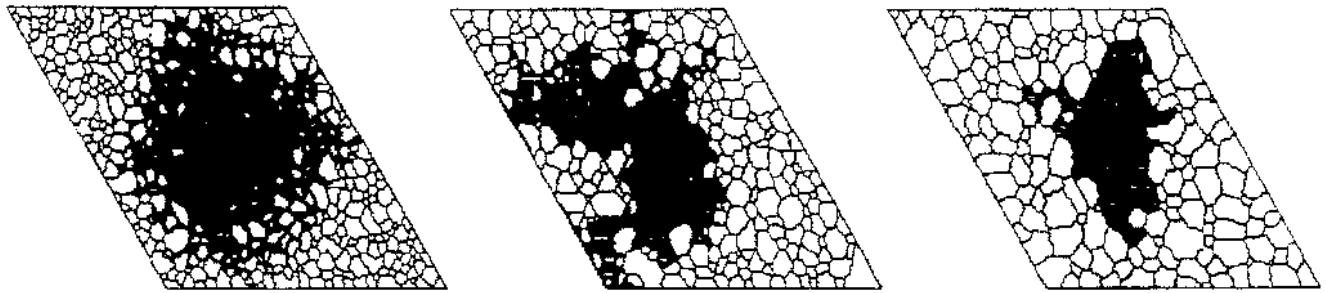


Figure 3 Microstructure evolution after (a) 500 MCS, (b) 500 MCS and (c) 1000 MCS with percentages of type II grains, (a) 100%, (b) 80% and (c) 60%. The overall mobility except at the triple junction is reduced by 10 times. Conditions for anisotropy in grain boundary energy are the same as Fig. 2.