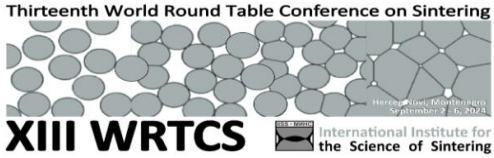


Aug. 30, 2024
Herceg Novi, Montenegro

Fundamentals of Sintering

Lecturer: Suk-Joong L. Kang (강석중),
sjkang@kaist.ac.kr

Textbook: "Sintering: densification, grain growth and microstructure" Elsevier (2005)

Supporting materials: selected papers and book chapters

Main Sequence:

Part I. Basis of Sintering Science

- Brief description of sintering processes and their parameters
- Interfacial energy and driving force of sintering
- Sintering and polycrystalline microstructure

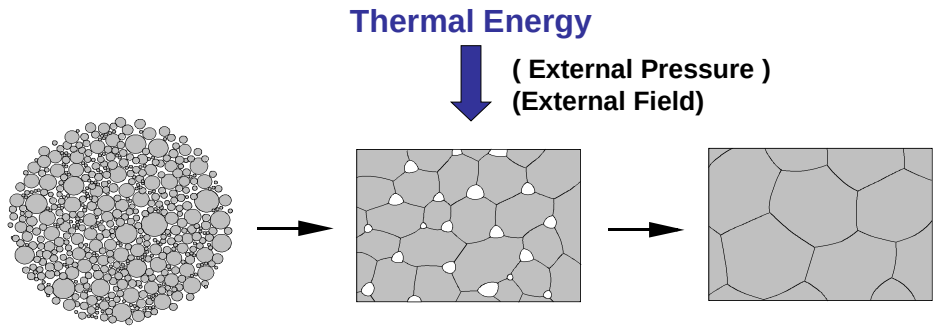
Part II. Bonding and Densification

- Solid state sintering (SSS) Models and Densification
  - Models and kinetics - Effects of processing variables
- Liquid phase sintering (LPS) Models and Densification
  - Role of liquid in densification - Densification kinetics (effects of processing variables)

Part III. Grain Growth and Microstructural Evolution

- Liquid phase sintering
  - Grain growth in a matrix (Ostwald ripening)
  - Effect of interfacial energy anisotropy
- Solid state sintering
  - Grain growth in a pure dense system
  - Effects of second phase particles and solute segregation
  - Effect of pores on microstructure development
  - Effect of boundary energy anisotropy

What is Sintering?



- Densification
- Grain Growth

} Microstructural Design

A processing technique of materials to produce density and microstructure controlled materials and components from metallic or ceramic powders by applying, in general, thermal energy.

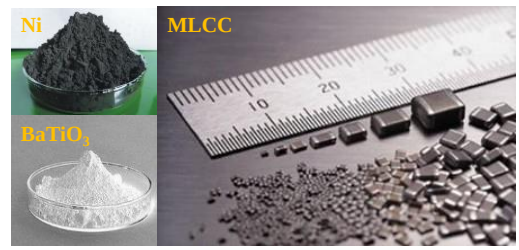
Sintering:

the oldest, but probably an everlasting technique in materials and components fabrication

Prehistoric era

Firing of pottery

21st century



Fabrication of MLCC

PI: Basis of Sintering Science

Outline:

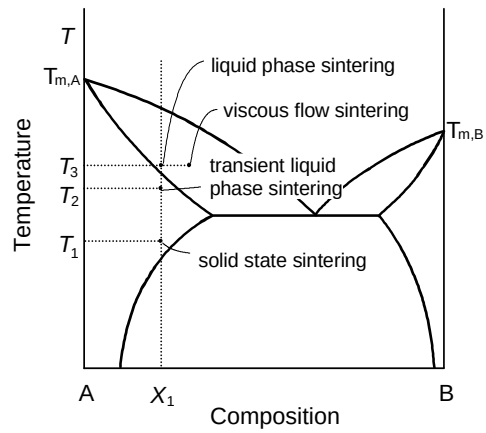
- Brief description of sintering processes and their parameters
- Interfacial energy and driving force of sintering
- Characteristics of polycrystalline microstructure

KAIST, S-J L. Kang

Chap. Sintering Processes

Categories of sintering:

SSS; LPS; TLPS; VFS



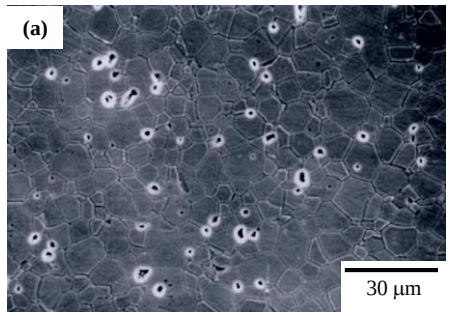
S.-J. L. Kang, "*Sintering : Densification, Grain Growth and Microstructure*", Elsevier, Oxford (2005).

KAIST, S-J L. Kang

Typical microstructures observed during SSS and LPS

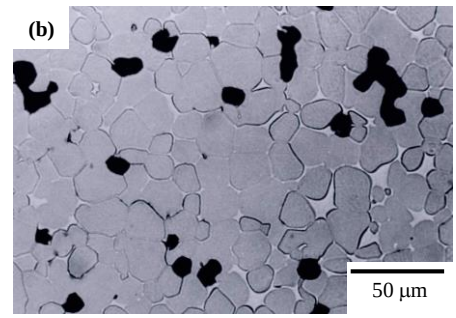
SSS

Al_2O_3



LPS

98W-1Ni-1Fe(wt%)



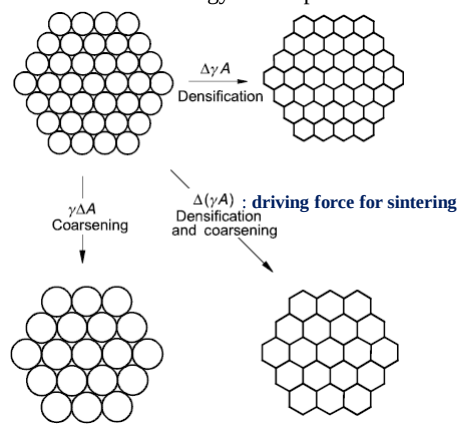
S.-J. L. Kang, "*Sintering : Densification, Grain Growth and Microstructure*", Elsevier, Oxford (2005).

KAIST, S-J L. Kang

Driving Force for Sintering

Reduction of the total surface energy

0.5 ~ 500J/mole (100μm ~ submicron size)
(cf. chemical free energy of compound formation)



Note: the meaning of sintering

S.-J. L. Kang, "*Sintering : Densification, Grain Growth and Microstructure*", Elsevier, Oxford (2005).

KAIST, S-J L. Kang

Exercise:

- Energy change with the sintering of cube-shaped powder with an edge of *l* with no grain growth

$$6L^2\gamma_s \frac{1}{L^3} \rightarrow \frac{6}{2}L^2\gamma_b \frac{1}{L^3}$$

$$\Delta E = \frac{6}{L}\left(\frac{\gamma_b}{2} - \gamma_s\right)$$

- Meaning of γ_s and γ_b
- Sintering of SiC (addition of C and B)

Qn:

Total surface energy = f(particle size)

Densification and Coarsening

- The two processes are themselves complex.
- Multiple mechanisms can be operative for each process (parallel processes) cf. serial processes
- Simultaneous and mutually interactive processes (The choice of processing condition is important)
- We usually want to prepare materials with high density and fine grain size by increasing the densification rate relative to coarsening rate.

$$\left(\dot{\rho}/\dot{G}\right)\uparrow$$

Directions for attaining $(\dot{\rho}/\dot{G})\uparrow$

- Modification of powder characteristic
  (shape, size and size distribution, etc.)
- Modification of chemistry
  - Use of additives in solid solution Why?
    eg) Al_2O_3 + MgO, WC-Co + VC
  - Use of a second phase, commonly liquid
  - Atmosphere control (Po2 control) Why?
    eg) BaTiO3, SrTiO3, Ni, Cu
- Modification of the sintering process
  Unconventional sintering processes
  eg) HP, HIP, Fast Firing, Two-step sintering, SPS, Flash sintering, Cold sintering

Sintering Variables

i) Variables inherent to raw powders (material variables)

- Powder : shape, size, size dist, agglomeration (hard and soft), mixedness
- Chemistry : composition, impurity, nonstoichiometry-atomosphere, homogeneity

i) Variables related to sintering condition (process variables)

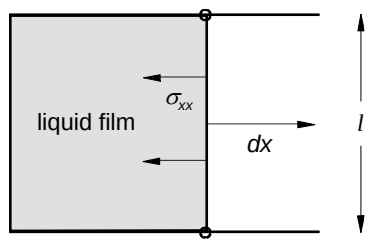
- T, t, P, atmosphere, heating and cooling rate, E, B (magnetic field)
  eg) P: HP, GPS, HIP and SPS(with E)
  eg) E: SPS and Flash sintering
  eg) Atmosphere : Po2 (oxidizing or reducing), inert

Chap. Thermodynamics of the Interface

- Qn: Why does bonding occurs between particles?
  - (i) Two particle model, (ii)Surface and Geometry
  - (iii) Driving force (difference in chemical potential)

Surface Tension (stress) and Surface Energy

Qn: How do we know that there is a tension force on a surface?



Work : $W = 2\sigma_{xx} l dx$

Energy : $\Delta E = \Delta A \cdot \gamma = 2\gamma l dx$

$\sigma_{xx} = \gamma$

$\sigma = (\sigma_{xx} + \sigma_{yy})/2 = \gamma$

σ // to the surface

$\gamma \perp$ to surface

Nature of surface tension:

surface configuration of atoms

Qn: Cases of liquid and solid

Qn: Case of a thin film or 2-D material

Relation btw. γ and σ

- $\sigma_{ij} = \delta_{ij}\gamma + d\gamma/d\varepsilon_{ij}$

  δ_{ij} : Kronecker's delta

  for $i = j$, $\delta_{ij} = 1$

  for $i \neq j$, $\delta_{ij} = 0$

  - The equality of σ and γ ← mobility of atoms
  - Driving force of sintering

    Thermodynamics: $\Delta(\gamma A)$

    Kinetics: σ and geometry
  - Case of sintering

    T_{sinter} is usually ~2/3 T_m. T_{sinter} ↓ as a ↓.

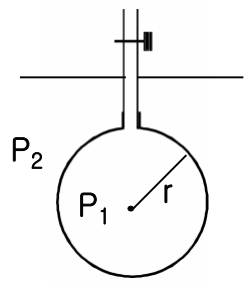
    At usual sintering temperatures, γ≈σ.

Thermodynamics of curved interface

Qn: Pressure difference btw two adjacent phases with a curved interface

- Blow of a soap bubble
- Inflate a balloon
- Water droplet and Gas bubble

Curved interface



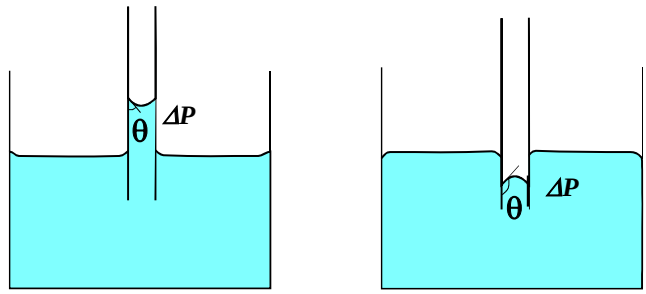
$$PdV = \gamma dA$$

$$P_1 - P_2 = \frac{2\gamma}{r}$$

Young-LaPlace Eq.

Capillary Pressure

Capillary action of a glass tube



$\theta < 90^o$ $\theta > 90^o$

Capillrity and Chemical Potential

System with two incompressible phases that are separated by a curved interface

$$d\Omega = 0 = d\Omega^{\alpha} + d\Omega^{\beta} + d\Omega^{\sigma}$$
$$= -P^{\alpha}dV^{\alpha} - P^{\beta}dV^{\beta} + \gamma dA$$
$$P^{\alpha} - P^{\beta} = \gamma\frac{dA}{dV^{\alpha}}$$
$$= \gamma K \qquad K = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$
$$P^{\alpha} - P^{\beta} = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)\gamma$$

Cf: Energy change of compressible fluid due to a curved interface

Deformation energy

$$W = -\int_0^P P dV = -\int_0^P P\left(\frac{\partial V_m}{\partial P}\right)_T dP = V_m K\int_0^P P dP$$
$$= \frac{1}{2}V_m K P^2$$

$$\mu_r^{\alpha} = \mu_{\infty}^{\alpha} + \gamma K V_m^{\alpha}$$ **Gibbs-Thompson Eq.** Only to phase α
$$\mu_r^{\beta} = \mu_{\infty}^{\beta}$$

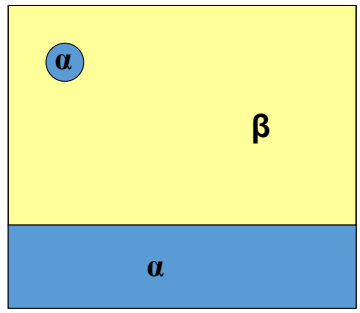
Freezing point of liq. ↓ Melting point of fine powder ↓

For r $<10^{-8}$m, the size effect becomes significant (~0.1).

For r > 0.1μm, the size effect is insignificant.

Capillarity and Atom Activity

Curved Interface and Solubility



$$a_r = a_\infty \exp(\frac{2\gamma V_m}{RTr})$$

$$a_r = a_\infty (1+\frac{2\gamma V_m}{RTr})$$

Gibbs -Thompson Eq.

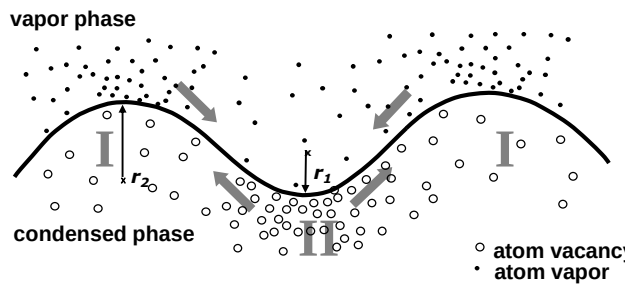
Condensed and Dispersed Phase

α : a condensed phase
β : a dispersed phase

$P^\alpha - P_\infty = (2\gamma/r)\cdot V^\beta_m/(V^\beta_m - V^\alpha_m) = 2\gamma/r$ for condensed phase

$p^\beta - p_\infty = (2\gamma/r)\cdot V^\alpha_m/(V^\beta_m - V^\alpha_m) = p_\infty(1+2\gamma V^\alpha_m/RTr)$ for dispersed phase

As P increases, p increases. (equality of μ)



Differences in i) Pressure, ii) Vacancy concentration, and iii) Vapor pressure (solubility).

Chap. Polycrystalline Microstructure

A few Questions:

Qn: What are the factors that affect microstructure and microstructural evolution?

Qn: What are the characteristics of a polycrystalline microstructure?

Representative (equilibrium) shape of grains?

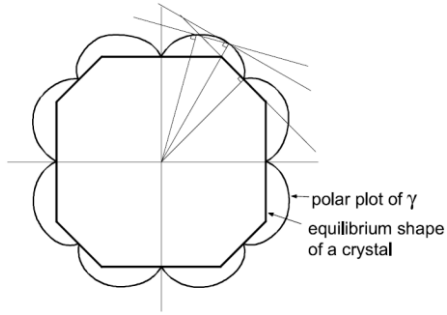
A stationary microstructure?

- Polycrystal: an Aggregate of Single Crystals

Equilibrium Shape of a Single Crystal

Equilibrium Shape: $\sum(\gamma_i A_i)_{\min}$

Polar plot of surface energy γ (γ-plot)



Wulff construction

(γ of a plane ∝ the distance from the center to the corresponding γ point)

Herring, Phys. Review, 82, 87 (1951)

Kang, in *Sintering: Densification, Grain Growth and Microstructure*, Elsevier, Oxford (2005)

Wulff Theorem

Under equilibrium

$$dF = \sum_i \gamma_i dA_i + \left(\frac{\partial F}{\partial n^c}\right)_{T,V} dn^c + \left(\frac{\partial F}{\partial V^c}\right)_{T,V} dV^c + \left(\frac{\partial F}{\partial n^s}\right)_{T,V} dn^s + \left(\frac{\partial F}{\partial V^s}\right)_{T,V} dV^s = 0$$

$$\sum \gamma_i dA_i + (\mu^c - \mu^s) dn^c - (P^c - P^s) dV^c = 0$$

$$\sum_i \left[\gamma_i - \frac{h_i}{2}(P^c - P^s)\right] dA_i + (\mu^c - \mu^s) dn^c = 0$$

$$P^c - P^s = \frac{2\gamma_i}{h_i} \equiv K_w$$

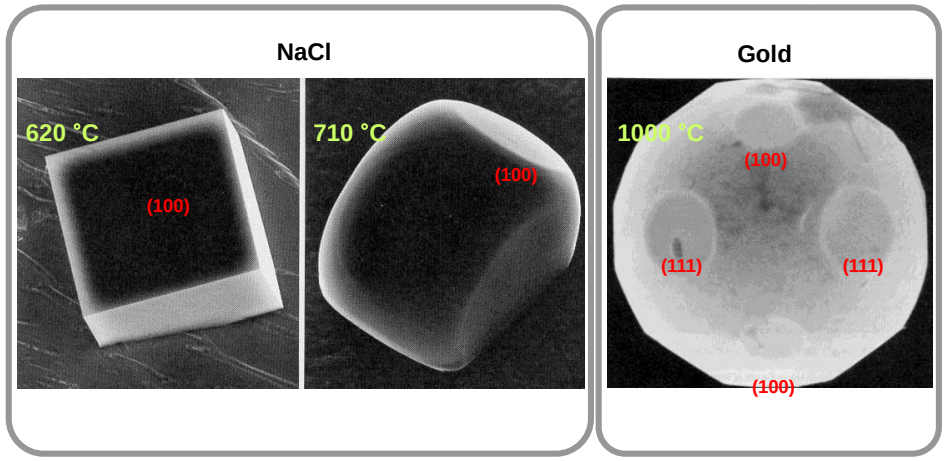
K_w:Wulff constant

$$\mu = \mu^o + \frac{2\gamma_i V_m}{h_i}$$

cf. Gibbs-Thompson eq.

Equilibrium Shape of Single Crystals

Examples



Simple calculation of surface energy using the broken bond model

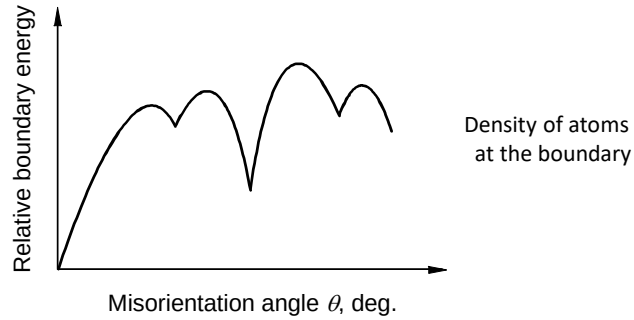
$$\gamma_\theta = \frac{U_b}{2a}(\cos\theta + \sin\theta) = \frac{U_b}{a\sqrt{2}}\cos(\theta - \frac{\pi}{4})$$

Heyraud and Métois, *J. Crystal Growth*, **84,** 503 (1987).
Heyraud and Métois, *J. Crystal Growth*, **50,** 571 (1980).

KAIST, S-J L. Kang

Single Phase Microstructure

$\gamma_b = f(\text{orientation})$



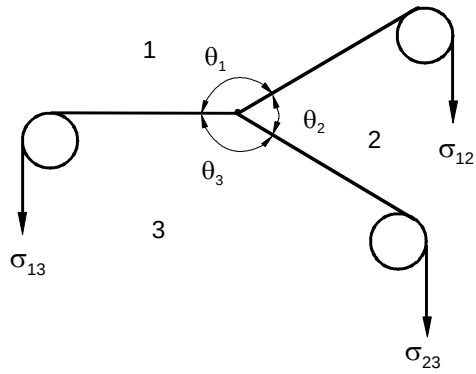
Simplification : γ_b = const. (a foam structure)

Grain shape is determined by
i) Local geometrical requirement
(minimization of the total interface energy and the equilibrium condition of surface tensions)
ii) Overall requirement of space filling

KAIST, S-J L. Kang

Interfacial Tension and Microstructure

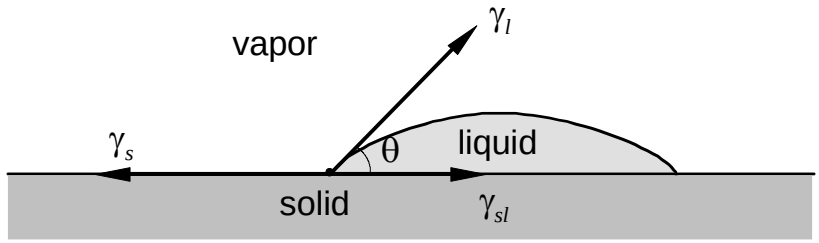
Equilibrium state btw three interfacial tensions



The sine law is satisfied. $\frac{\sigma_{12}}{\sin\theta_3} = \frac{\sigma_{23}}{\sin\theta_1} = \frac{\sigma_{31}}{\sin\theta_2}$

Wetting Angle

3-phase system, s/l/v



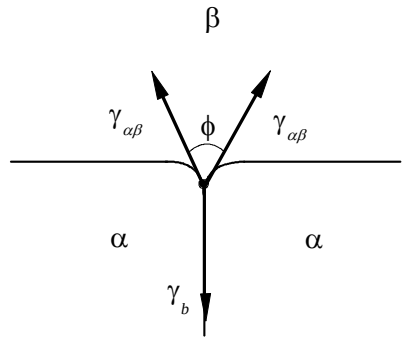
$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta$

Complete wetting at $\theta = 0$

$\gamma_s \geq \gamma_{sl} + \gamma_l$

Dihedral Angle

2-phase system, s/v or s/l



$$\gamma_b = 2\gamma_{\alpha\beta}\cos\frac{\phi}{2}$$

grain boundary

Usually, $\gamma_s > \gamma_b$ Ø > 120°

$\gamma_s \approx 3\gamma_b$ Ø ~ 160°

KAIST, S-J L. Kang

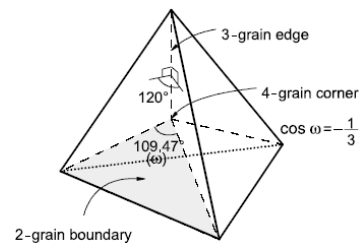
Equilibrium Grain Shape

2-dim: hexagon consider triangle and square

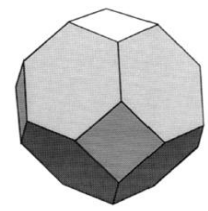
3-dim:

Soap film equilibrium in a tetrahedral frame

C = 22.794 vertices



- Pentagonal dodecahedron (12 pentagons)
  with 20 corners (close-packing of spheres)
- Tetrakaidecahedron (Regularly truncated octahedron)
  with 24 corners (bcc packing)
  (8 hexagons and 6 squares)



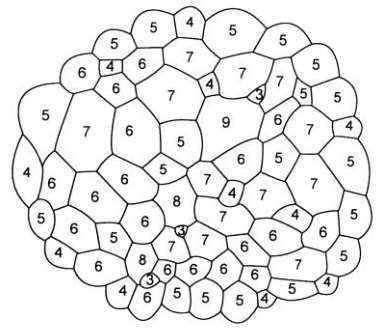
KAIST, S-J L. Kang

Topological Relationship

Euler's Law describes the relationship btw. features of different dimensionality

$$n_0-n_1+n_2-n_3=1 \text{ (C-E+P-B=1)}$$ eg.

- 2-dim:
  av. number of sides of polygons = 6



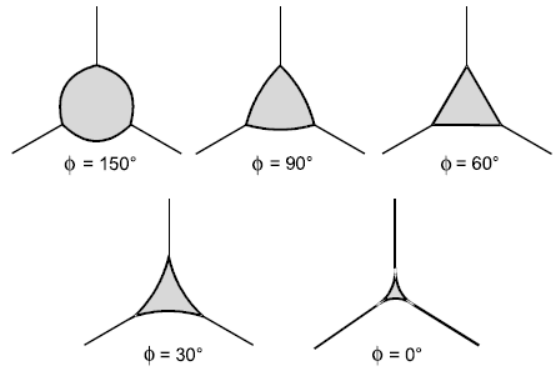
Case of NGG
AGG

- 3-dim:
  av. number of sides of polygons < 6

2-Phase Microstructure

Shape of a second phase = f(ϕ)

In 2-dim



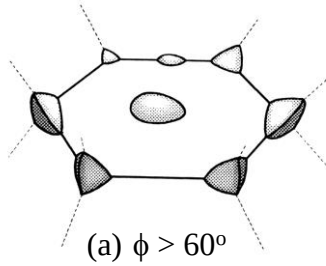
ex. Dihedral angle and physical properties

Qn: Distribution?

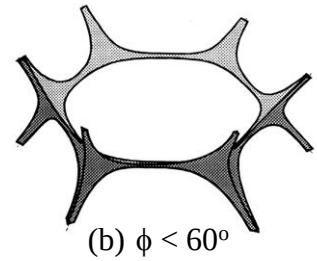
2-Phase Microstructure

Shape of a second phase = f(ϕ)

In 3-dim



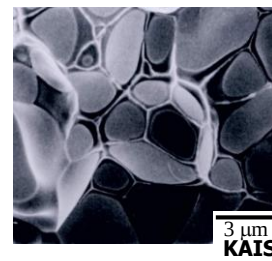
(a) $\phi > 60^o$



(b) $\phi < 60^o$

Qn: Measurement of dihedral angle?

Qn: Thickness of liquid film?



KAIST, S-J L. Kang

Kinetic thickening of liquid film

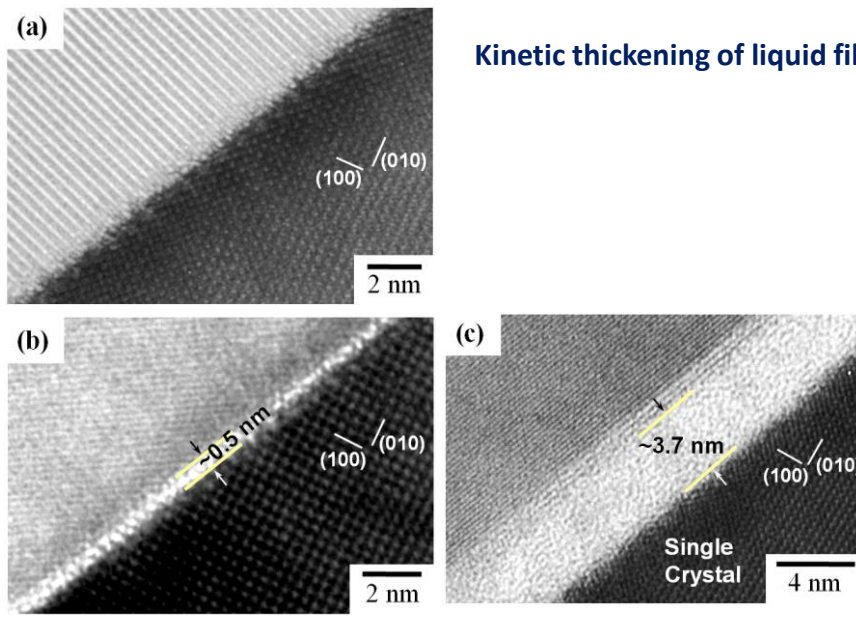


Figure 3-12. HREM images of the boundaries between a single crystal and a fine matrix grain. (100) single crystal/polycrystal bi-layer samples with 0.4-mol%-TiO_2 addition annealed at 1350°C for (a) 5, (b) 20, and (c) 50 h in air after H_2-treatment at 1250°C for 10 h.[22]

Choi, et al., *Acta Mater.*, **52**, 3721 (2004)

KAIST, S-J L. Kang

2-Phase Microstructure

Equilibrium Microstructure

Qn: Conditions that govern the equilibrium microstructure of mono-size grains?

Qn: Effective pressure of a powder compact?

eg) Elimination of pores during sintering
Redistribution of liquid between two samples in contact with different amounts of liquid

Minimum Interfacial Energy Configuration = f(ϕ, amt of matrix)

For an infinitesimal change under equilibrium,

work done = $P_e \cdot dV_m$

= total interfacial energy change ($\Delta(\gamma A)$)

$$P_e = -\frac{(1-f_m)^2}{V_g}\left[\frac{\partial E}{\partial f_m}\right]_{V_g}$$

Calculated variation of total interfacial energy

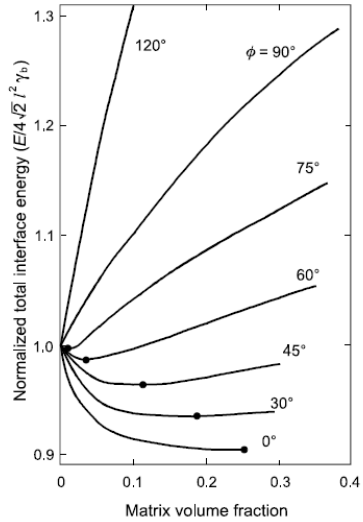
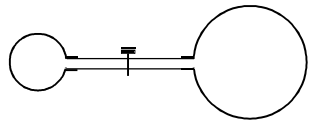


Figure 3.13. Calculated variation of total interfacial energy, *E*, with the matrix volume fraction (at constant grain volume) for various dihedral angles.[24] The minimum *E* values are shown by filled circles.

H. H. Park and D. N. Yoon, *Metall. Trans. A*, 16A, 923 (1985)

Exercises:

- Elastic balloons



- Equilibrium shape of an entrapped pore
- Measurement of $\gamma_{\alpha/\alpha}/\gamma_{\beta/\beta}$