

5.2 Heterogeneous Nucleation

Nucleation in solids is almost always heterogeneous.

Possible sites are

1. Vacancies
2. Dislocations
3. Grain boundaries
4. Stacking faults
5. Inclusions
6. Free surfaces

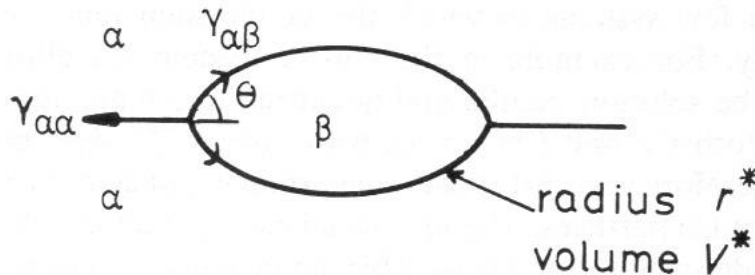
$$\Delta G_{het} = -V(\Delta G_V - \Delta G_S) + A\gamma - \Delta G_d$$

Heterogeneous nucleation에 의해 감소된 energy barrier

5.2 Heterogeneous Nucleation

1. Nucleation on Grain Boundaries

- ignore misfit strain energy, then the minimization of total interfacial free energy
- incoherent ppt, $\gamma_{\alpha\beta}$ is isotropic and equal for both grains,)



$$\cos \theta = \gamma_{\alpha\alpha} / 2\gamma_{\alpha\beta}$$

$$\Delta G = -V \Delta G_V + A_{\alpha\beta} \gamma_{\alpha\beta} - A_{\alpha\alpha} \gamma_{\alpha\alpha}$$

Analogous to solidification on a substrate

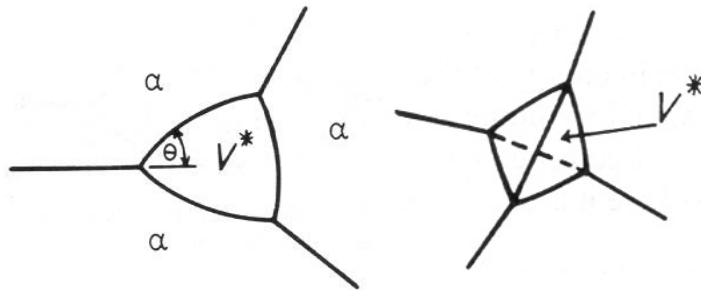
$$r^* = 2\gamma_{\alpha\beta} / \Delta G_V$$

$$\frac{\Delta G^*_{het}}{\Delta G^*_{hom}} = \frac{V^*_{het}}{V^*_{hom}} = S(\theta)$$

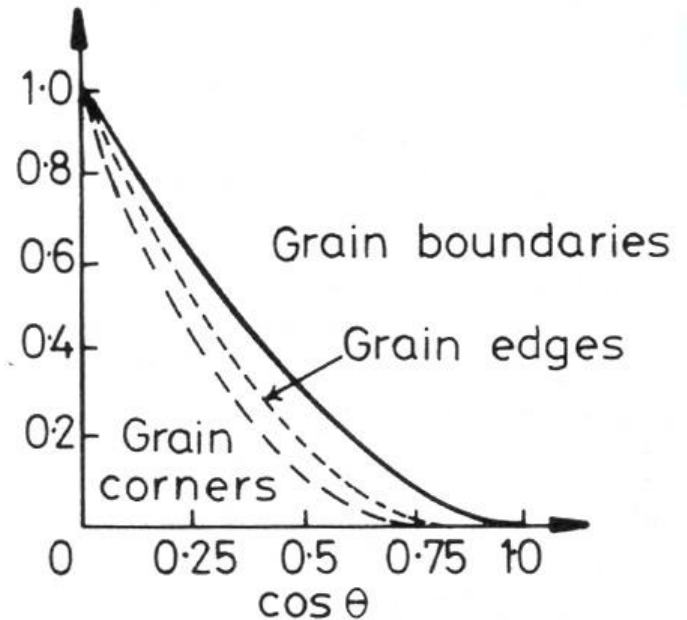
$$S(\theta) = \frac{1}{2}(2 + \cos \theta)(1 - \cos \theta)^2$$

5.2 Heterogeneous Nucleation

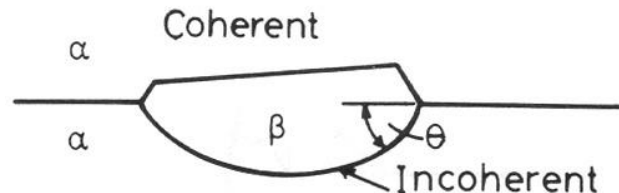
* Nucleation on Grain Edge or Grain Corner



$$\frac{\Delta G_{het}^*}{\Delta G_{hom}^*}$$



- High angle grain boundary 에서 incoherent ppt이 생성되기 쉽다.
- Low energy interface 를 가질 경우 더 쉽게 생성
- Such nucleation will be expected whenever possible with smallest nucleation barrier.



5.2 Heterogeneous Nucleation

2. Dislocations

$$\Delta G_{het} = -V(\Delta G_V - \Delta G_S) + A\gamma - \Delta G_d$$

- ✓ $\Delta G_d \approx \Delta G_s$ reducing total strain energy

ex) Coherent nucleus with a negative misfit

=> smaller volume than the matrix

=> Can reduce nucleation barrier by forming in the compressive strain region at the edge dislocation

- ✓ Solute segregation at the dislocation core
- ✓ Diffusion pipe with a lower ΔG_m
- ✓ Interface energy를 낮추는 데는 별로 도움이 되지 않음
- ✓ 따라서 적어도 하나는 coherent or semi-coherent interface 가 필요

5.2 Heterogeneous Nucleation

3. Excess Vacancies

$$\Delta G_{het} = -V(\Delta G_V - \Delta G_S) + A\gamma - \Delta G_d$$

- ✓ When alloy is quenched from a high temperature, excess vacancies are retained.
- ✓ Can assist nucleation by increasing diffusion rate or by relieving misfit strain E .
- ✓ Since ΔG_d is relatively small, following conditions are required
 - Low interfacial E (fully coherent)
 - Small volume strain energy
 - High driving forces

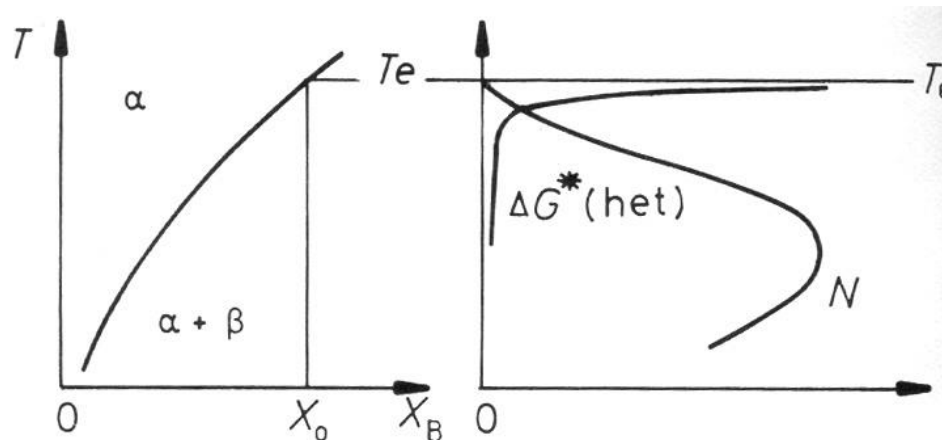
5.2.1 Rate of Heterogeneous Nucleation

- Decreasing order of ΔG^*
- 1) homogeneous sites
 - 2) vacancies
 - 3) dislocations
 - 4) stacking faults
 - 5) grain boundaries and interphase boundaries
 - 6) free surfaces

Relative concentration of the sites should be considered!!

$$N_{het} = \omega C_1 \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right) \quad \text{nuclei } m^{-3} s^{-1}$$

C_1 : concentration of heterogeneous nucleation sites



5.2.1 Rate of Heterogeneous Nucleation

$$N_{het} = \omega C_1 \exp\left(-\frac{\Delta G_m}{kT}\right) \exp\left(-\frac{\Delta G^*}{kT}\right) \quad \text{nuclei } m^{-3} s^{-1}$$

$$\frac{N_{het}}{N_{hom}} = \frac{C_1}{C_0} \exp\left(\frac{\Delta G^*_{hom} - \Delta G^*_{het}}{kT}\right)$$

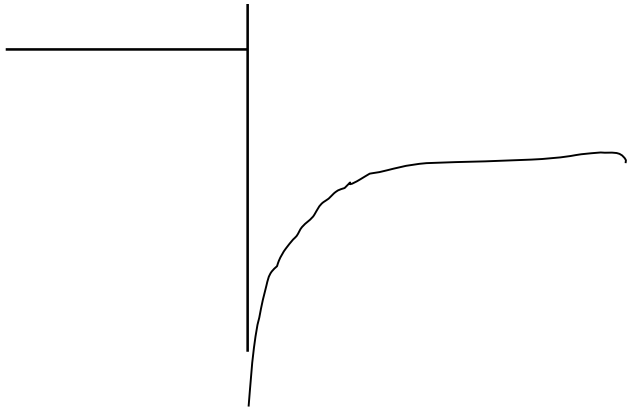
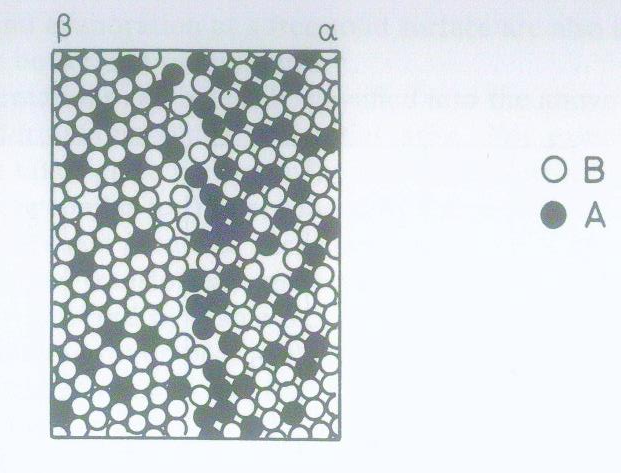
for grain boundary nucleation

$$\frac{C_1}{C_0} = \frac{\delta}{D} \approx 10^{-5}$$

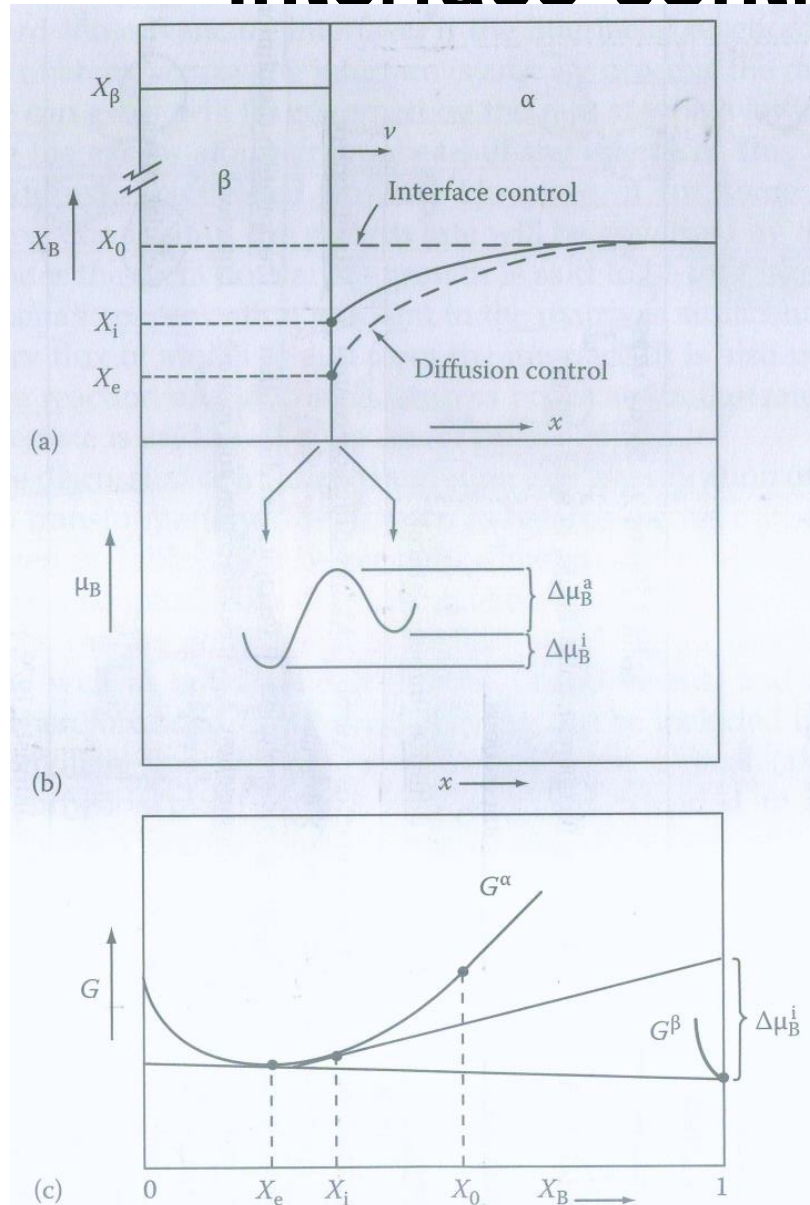
Grain boundary	Grain edge	Grain corner	Dislocations		Excess vacancies
$D = 50 \mu\text{m}$	$D = 50 \mu\text{m}$	$D = 50 \mu\text{m}$	10^5 mm^{-2}	10^8 mm^{-2}	$X_v = 10^{-6}$
10^{-5}	10^{-10}	10^{-15}	10^{-8}	10^{-5}	10^{-6}

5.3 Precipitate Growth

(3.5.1 Interface Migration)



3.5.1 Diffusion-controlled and interface-controlled growth



- ❖ β ppt (almost pure B) grows behind a planar interface into A-rich α of X_0 composition.
 - ① α near interface: $X_i < X_0$ (bulk conc.)
 - ② β growth: $\Delta\mu_B^i (> 0)$ (driving force)

Origin of the driving force for growth:

$$X_i > X_e$$

3.5.1 Diffusion-controlled, Interface-Controlled

- ✓ With net flux of B, the interface velocity

$$v = M \cdot F = M \cdot \frac{\Delta\mu_B^i}{V_m}$$

M : interface mobility

V_m : molar volume of B

A flux of B atoms towards the interface

= corresponding flux across the interface

$$J_B^\alpha = -D \left(\frac{\partial C_B}{\partial x} \right)_{interface}$$

$$J_B^i = C_B v_i = -M \Delta\mu_B^i X_B / V_m^2 \quad [\text{moles of B m}^2/\text{sec}] \quad \left(C_B = \frac{X_B}{V_m} \right)$$

At a steady state, those equations must be balanced.

$$J_B^i = J_B^\alpha$$

3.5.1 Diffusion-controlled, Interface-Controlled

- ① If M (interface mobility) is very high (e.g., incoherent interface):
 $\Delta\mu_B^i$ is very small

$$X_i = X_e \quad \text{Local equilibrium at the interface}$$

The interface moves as fast as diffusion allows → **diffusion controlled**

Growth rate can be evaluated as a function of time by solving diffusion equation with boundary condition

$$X_i = X_e \quad X_B(\infty) = X_0$$

- ② If the mobility of the interface is low, it needs a chemical potential gradient ($\Delta\mu_B^i$) and there will be a departure from local equilibrium at the interface.

X_i will satisfy $J_B^i = J_B^\alpha$ Then the interface will migrate under **mixed control**

3.5.1 Diffusion-controlled, Interface-Controlled

- ③ In the limit of a very low mobility: $X_i = X_o$,
$$\left(\frac{\partial C}{\partial x}\right)_{int} = 0$$

=> **interface controlled**

- In a dilute or ideal solution, the driving force $\Delta\mu_B^i$ (composition vs. $\Delta\mu_B$)

$$\begin{aligned}\Delta\mu_B^i &= (\mu_B^i - \mu_B^0) = RT \ln \frac{X_i}{X_e} \\ &= RT \ln \left(1 + \frac{X_i - X_e}{X_e}\right) = \frac{RT}{X_e} (X_i - X_e) \quad \text{when } (X_i - X_e) \ll X_e\end{aligned}$$

$$v = M \cdot \frac{\Delta\mu_B^i}{V_m} \propto (X_i - X_e)$$

∴ the rate of the interface that moves under interface control

$$\propto (X_i - X_e)$$

(the deviation of the interface concentration from the equilibrium)