3.3 Boundaries in Single-Phase Solids ($\alpha/\alpha$)

- **Special High Angle Grain Boundaries**
  - Some special high angle boundaries have significantly lower energy than ordinary high angle boundaries.

1. **Twin Boundary**

- If the twin boundary is // to the twining, the atoms in the boundaries fit perfect!!
- undistorted position
- coherent
- Extremely low energy

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Coherent twin boundary energy</th>
<th>Incoherent twin boundary energy</th>
<th>Grain boundary energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>21</td>
<td>498</td>
<td>623</td>
</tr>
<tr>
<td>Ag</td>
<td>8</td>
<td>126</td>
<td>377</td>
</tr>
<tr>
<td>Fe-Cr-Ni</td>
<td>19</td>
<td>209</td>
<td>835</td>
</tr>
</tbody>
</table>

(stainless steel type 304)
3.3 Boundaries in Single-Phase Solids ($\alpha/\alpha$)

✓ In fcc twin, mistorientation of 70.5 degree about a $<110>$ axis.

Special Grain Boundary
3.3 Boundaries in Single-Phase Solids ($\alpha/\alpha$)

- **Equilibrium in Polycrystalline Materials**
  
  
  \[
  \frac{\gamma_{23}}{\sin \theta_1} = \frac{\gamma_{13}}{\sin \theta_2} = \frac{\gamma_{12}}{\sin \theta_3}
  \]

- **Intersection of Grain Boundary with Free Surface**

  \[
  \gamma^b = 2 \gamma_{sv} \cos \frac{\theta}{2}
  \]
3.3 Boundaries in Single-Phase Solids ($\alpha/\alpha$)

Crystallographic View of Grain Boundary

Transformation matrix

$$M = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

Orthogonality

$$a_{ij}a_{ik} = \delta_{jk}$$

3 independent variables

$$\cos \theta = \frac{(a_{11} + a_{22} + a_{33} - 1)}{2}$$

$$U : V : W = a_{32} - a_{23} : a_{31} - a_{13} : a_{21} - a_{12}$$
3.3 Boundaries in Single-Phase Solids ($\alpha/\alpha$)

Lattice orientations of two grains

Crystal coordinate

Specimen coordinate

2 independent variables

Grain boundary plane or inclination angles

Phase Transformation in Materials
3.3 Boundaries in Single-Phase Solids ($\alpha/\alpha$)

- **Thermally Activated Grain Boundary Migration**
  - Net Force due to Surface Tension

- **Direction of Grain Boundary Migration during Grain Growth (2-D)**
  - Junction angle: 120°
  - Grains with # of boundary > 6 → grain growth
  - Grains with # of boundary < 6 → grain shrink, disappear

- Reduce the # of grains, increase the mean grain size, reducing the total g.b. energy
- Called **Grain growth, grain coarsening**
3.3 Boundaries in Single-Phase Solids ($\alpha/\alpha$)

- **Thermodynamic Consideration**

\[ \Delta G = \frac{2\gamma V_m}{R} = \Delta \mu \]

: effect of pressure difference by curved boundary

- For grain growth, $\Delta G$ is due to the grain boundary curvature.
- For recrystallization, $\Delta G$ is due to the difference of strain energy

Free Energy Released \( = \Delta G \cdot \delta x / V_m = F \delta x \)

\( F = \frac{\Delta G}{V_m} \quad N \cdot m^{-2} \)
3.3 Boundaries in Single-Phase Solids ($\alpha/\alpha$)

The effect of $\Delta G$ on Kinetics of Boundary Migration

- Effective Flux of Atoms

from grain 1 to 2:  
$$A_2 n_1 v_1 \exp \left( -\frac{\Delta G^a}{RT} \right) \quad m^{-2} s^{-1}$$

from grain 2 to 1:  
$$A_1 n_2 v_2 \exp \left( \frac{\Delta G}{RT} \right) \quad m^{-2} s^{-1}$$

If $\Delta G = 0$ and there is no net boundary movement

$$A_1 n_2 v_2 = A_2 n_1 v_1$$

If $\Delta G > 0$ and there is no net boundary movement

$$J_{net} = A_2 n_1 v_1 \exp \left( -\frac{\Delta G^a}{RT} \right) \left\{ 1 - \exp \left( -\frac{\Delta G}{RT} \right) \right\}$$
3.3 Boundaries in Single-Phase Solids ($\alpha/\alpha$)

If boundary velocity is $v$

\[ \text{Net flux} = \frac{v}{(V_m/N_a)} \]

\[ v = \frac{A_2n_1v_1V_m^2}{N_a RT} \exp \left(-\frac{\Delta G^\alpha}{RT}\right) \frac{\Delta G}{V_m} \]

or \[ v = M \cdot \Delta G/V_m \]

where \[ M = \left\{ \frac{A_2n_1v_1V_m^2}{N_a RT} \exp \left(\frac{\Delta S^\alpha}{R}\right) \right\} \exp \left(\frac{-\Delta H^\alpha}{RT}\right) \]

The boundary migration is a thermally activated process.

- High energy g. b. → Open g. b. structure → high mobility
- Low energy g. b. → closed (or dense) g. b. structure → low mobility
3.3 Boundaries in Single-Phase Solids ($\alpha/\alpha$)

- **Grain Boundary Segregation**
  - Impurities tend to stay at the grain boundary

\[ X_b = X_0 \exp \frac{\Delta G_b}{RT} \]

$\Delta G_b$ : free energy reduced when a solute is moved to GB from matrix.
3.3 Boundaries in Single-Phase Solids (α/α)

The Kinetics of Grain Growth

\[ \bar{v} = \alpha M \frac{2\gamma}{D} \approx \frac{d \bar{D}}{dt} \]

\[ \bar{D}^2 = D_0 + Kt \text{ where } K = 4\alpha M\gamma \]

- Experimental Observation
  \[ \bar{D} = K' t^n \]

- Interaction with Particles

\[ P = \frac{3f}{2\pi r^2} \cdot \pi r \gamma = \frac{3f \gamma}{2} \bar{D} \]

\[ \frac{2\gamma}{D} = \frac{3f \gamma}{2r} \]

\[ D_{\text{max}} = \frac{4r}{3f} \]

- Single phase
- With particle dispersion
3.4 Interphase Interfaces in Solids (α/β)

- Different X-tal structure and composition

❖ Interface Coherency

A. Fully coherent Interface: When two crystal match perfectly at interface.

\[ \gamma_{\text{coherent}} = \gamma_{\text{ch}} \ (1 - 200 \ \text{mJ/m}^2) \]

구조가 같기 때문에 chemical energy 만 존재한다
3.4 Interphase Interfaces in Solids (α/β)

✓ Lattice 가 같지 않아도 coherent interface를 만들 수 있다.
→ Lattice Distortion → Coherency Strain
3.4 Interphase Interfaces in Solids ($\alpha/\beta$)

B. Semi-coherent Interfaces

For sufficiently large atomic misfit

$$\delta = \frac{d_\beta - d_\alpha}{d_\alpha}$$

$$D = \frac{d_\beta}{\delta} \quad \text{or} \quad D = \frac{b}{\delta}$$

$$b = (d_\alpha + d_\beta)/2$$

(as $\delta \uparrow$, $D \downarrow$)

Interfacial Energy

$$\gamma (\text{semicoherent}) = \gamma_{ch} + \gamma_{st}$$

$$\gamma_{st} \propto \delta \quad \text{for small } \delta$$

$$\gamma(\text{semi-coherent}) = 200 - 500 \text{ mJ/m}^2$$
3.4 Interphase Interfaces in Solids (\(\alpha/\beta\))

C. Incoherent Interfaces

Very different atomic configuration (\(\delta > 0.25\))

\[ \gamma(\text{inherent}) = 500 - 1000 \text{ mJ/m}^2 \]

D. Complex Semicohrent Interfaces

Semicoh. Int. observed at boundaries formed by low-index planes (atom pattern and spacing are almost equal.)

Nishiyama-Wasserman (N-W) Relationship

\[(110)_{bcc} // (111)_{fcc}, [001]_{bcc} // [\overline{1}01]_{fcc}\]

Kurdjumov-Sachs (K-S) Relationships

\[(110)_{bcc} // (111)_{fcc}, [1\overline{1}1]_{bcc} // [0\overline{1}1]_{fcc}\]

Phase Transformation in Materials
3.4 Interphase Interfaces in Solids ($\alpha/\beta$)

- **Second-Phase Shape: Interface Energy Effects**

  $$\sum A_i \gamma_i = \text{minimum}$$

**A. Fully Coherent Precipitate**

- ✓ If $\alpha$, $\beta$ have the same structure
- ✓ Happens during early stage of many ppt hardening
- ✓ Good match $\rightarrow$ can have any shape $\rightarrow$ spherical

GP(Guinier-Preston) Zone in Al–Ag Alloys

$$\varepsilon_a = \frac{r_A - r_B}{r_A} = 0.7\%$$
3.4 Interphase Interfaces in Solids ($\alpha/\beta$)

B. Partially Coherent Precipitates

- $\alpha$, $\beta$ have different structure and one plane which provide close match

Coherent or Semi-coherent in one Plane; Disc Shape (also plate, lath, needle-like shapes are possible)

$\gamma'$ Precipitates in Al–4% Ag Alloys

$\theta'$ Phase Al–Cu Alloys
3.4 Interphase Interfaces in Solids (α/β)

C. Incoherent Precipitates

✓ When $\alpha$, $\beta$ have completely different structures $\rightarrow$ Incoherent interfaces
✓ Interface energy is high for all planes $\rightarrow$ spherical shape
✓ Polyhedral shapes from coher. or semi-coher. interfaces

\[ \theta \text{ phase in Al} - \text{Cu alloys} \]

D. Precipitates on Grain Boundaries
3.4 Interphase Interfaces in Solids ($\alpha/\beta$)

- **Second-Phase Shape in**: Misfit Strain Effects

\[ \sum A_i \gamma_i + \Delta G_S = \text{minimum} \]

**A. Fully Coherent Precipitates**

Coherency strain

- **Unconstrained Misfit**
  \[ \delta = \frac{a_\beta - a_\alpha}{a_\alpha} \]

- **Constrained Misfit**
  \[ \varepsilon = \frac{a'_\beta - a_\alpha}{a_\alpha} \]  \quad (\alpha'_\beta: \text{strained para.})

\[ \varepsilon = \frac{2}{3} \delta \quad E_\beta = E_\alpha \quad \nu = 1/3 \quad 0.5 \delta \leq \varepsilon \leq \delta \]
3.4 Interphase Interfaces in Solids ($\alpha/\beta$)

Elastically Isotropic Materials

$$\Delta G_S = 4 \mu \delta^2 \cdot V$$

Elastically Anisotropic Materials

- **Atom radius (Å)**: Al : 1.43, Ag : 1.44, Zn : 1.38, Cu : 1.28
- **Zone Misfit ($\delta$)**: –, + 0.7%, – 3.5%, – 10.5%
- **Zone Shape**: –, sphere, sphere, disc
### 3.4 Interphase Interfaces in Solids ($\alpha/\beta$)

#### B. Plate-Like Precipitates

Volume Misfit

$$\Delta = \frac{\Delta V}{V}$$

Phase Transformation in Materials

$$\frac{x^2}{a^2} + \frac{y^2}{a^2} + \frac{z^2}{c^2} = 1$$

$$\Delta G_s = \frac{2}{3} \mu \Delta^2 \cdot V \cdot f(c/a)$$
3.4 Interphase Interfaces in Solids ($\alpha/\beta$)

C. Plate-Like Precipitates
3.4 Interphase Interfaces in Solids ($\alpha/\beta$)

- **Coherency Loss**

\[
\Delta G(\text{coherent}) = 4\mu\delta^2 \cdot \frac{4}{3} \pi r^3 + 4\pi r^2 \cdot \gamma_{ch}
\]

\[
\Delta G(\text{non-coherent}) = 4\pi r^2 \cdot (\gamma_{ch} + \gamma_{st})
\]

\[
r_{\text{crit}} = \frac{3\gamma_{st}}{4\mu\delta^2}
\]

\[
r_{\text{crit}} \propto \frac{1}{\delta} \quad \text{for small } \delta \quad \gamma_{st} \propto \delta
\]