

Lecture 13: Heterogeneous Nucleation: Effects of Grain Boundaries and Surface Defects

Today's topics

- Effects of grain boundaries on solid-solid phase transformation: various types of grain boundaries.
- Defects of container wall like pinholes, cavities, cracks, have significant effect on the liquid-solid phase transformation, e.g., solidification of metals.
- For metal solidification in a container, the supercooling temperature required for the freezing is dependent on the superheating temperature. Understanding such an interesting phenomenon demands consideration of the small cavities within the container wall. These tiny sites serve as catalytic sites for the heterogeneous nucleation and the superheating and supercooling temperature is correlated to the size (radius) of the cavity.

About grain boundaries

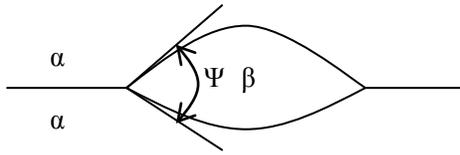
- A grain boundary is a general planar defect that separates regions of different crystalline orientation (i.e. grains) within a polycrystalline material.
- Grain boundaries are usually the result of uneven growth when the solid is crystallizing. The atoms in the grain boundary will not be in perfect crystalline arrangement. Grain sizes vary from 1 μm to 1 mm.
- Since grain boundaries are defects in the crystal structure they tend to decrease the electrical and thermal conductivity of the material.
- The high interfacial energy and relatively weak bonding in most grain boundaries often make them preferred sites for heterogeneous nucleation (precipitation of new phases from the solid).

Today's Lecture: we will learn how to apply the general theory of heterogeneous nucleation as described in Lectures 10-12 onto some specific practical cases, e.g., the solidification of metals in a container, where the surface defects play important roles in facilitating the nucleation.

Different geometries of grain boundaries:

Consider a second phase of β precipitates out of the matrix, α . It usually occurs at grain boundaries, which act as the nucleation sites facilitating the phase transformation. The potential sites for nucleation include: 1.) Grain facets (two grain junctions - faces) 2.) Grain edges (three grain junction - lines) 3.) Grain corners (four grain junctions - points)

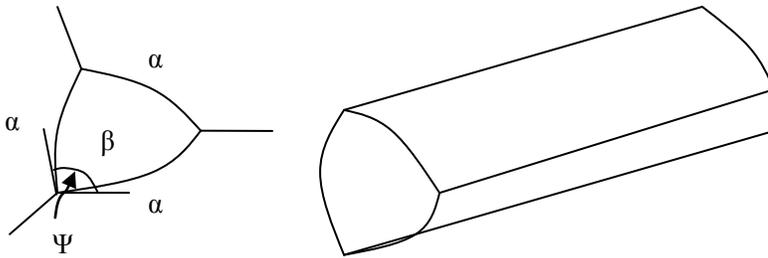
1) At a grain facet:



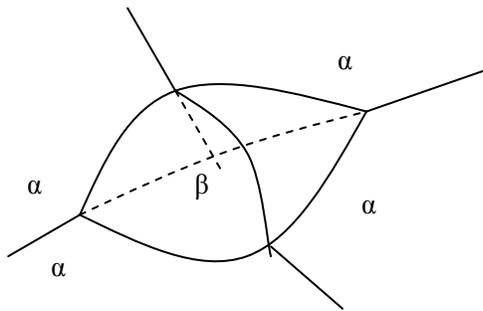
The angle Ψ can be determined by minimizing surface free energy, or force balance as we learned in Lecture 8.

$$2 \gamma_{\alpha\beta} \cos\left(\frac{\Psi}{2}\right) = \gamma_{\alpha\alpha}$$

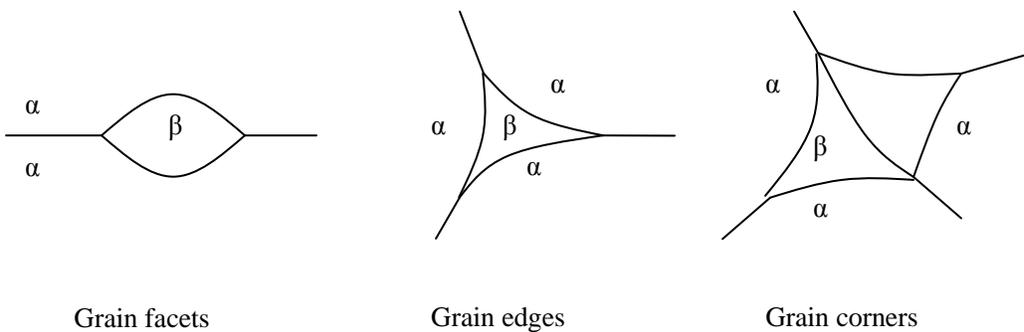
2) At the grain edge: along three grain junction



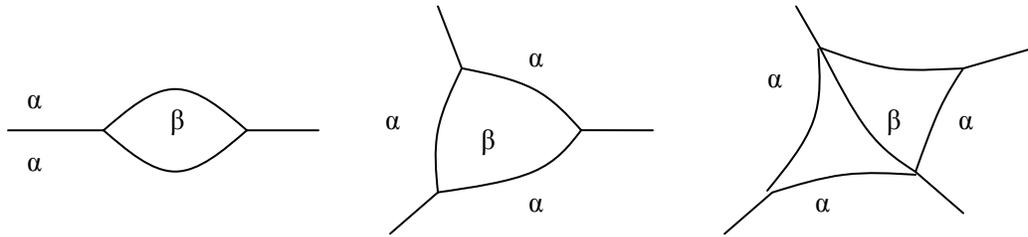
3) At four grain corners, — tetrahedral



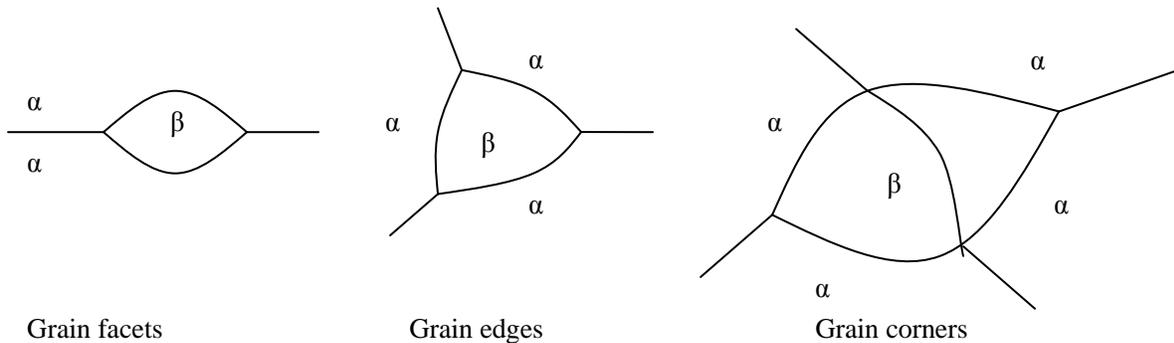
For $\Psi < 60^\circ$, the β precipitate shape takes the following shape depending on the location



For $60^\circ < \Psi < 70.5^\circ$



For $\Psi > 70.5^\circ$

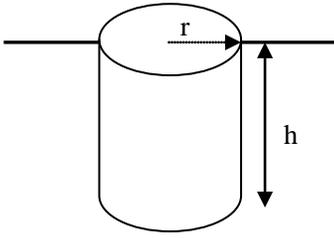


Different geometries have different implications for phase transformation: The second β phase is always thermodynamically **unstable** at grain facet, because the chemical potential is greater under a **convex** surface than under a flat surface (see Lecture 8). For $\Psi < 60^\circ$, β phase is **stable** at grain edges and corners because the chemical potential is lower under a **concave** surface than under a flat surface (see Lecture 8); for $60^\circ < \Psi < 70.5^\circ$, β phase is **stable** at grain corners only; for $\Psi > 70.5^\circ$, β phase is **unstable** everywhere inside α -phase, and given enough time, will be expelled outside the body onto the surface.

Freezing of a metal in a container: the effect of superheating (imposed) on supercooling required for freezing to occur

Most container walls have defects, such as pinholes, cavities, etc. These defects have a significant effect on the freezing of a liquid metal. Specifically, if the container is heated to T^+ , a temperature above the equilibrium melting point, T_M (i.e., superheating by $\Delta T^+ = T^+ - T_M$), then during the subsequent cooling step, *the supercooling temperature T* (i.e., the temperature below T_M by $\Delta T^- = T_M - T$ to enable the metal freezing to occur) *is interestingly dependent on ΔT^+* . This phenomenon can be explained by heterogeneous nucleation affected by the defects within the container wall.

Let's assume defects be cavities of various radii of cylindrical shape, such that $h \gg r$.



α —liquid metal, β —solid metal, δ —container surface

As solid wets the container better than liquid,

i.e., $\gamma_{\beta\delta} < \gamma_{\alpha\delta}$, then the contact angle

$$\cos\theta = \frac{\gamma_{\alpha\delta} - \gamma_{\beta\delta}}{\gamma_{\alpha\beta}} \quad (\text{Lecture 12})$$

Above T_M ,

- if the cavity contains liquid phase, the free energy is $G_{\text{cav}}(\alpha) = \pi r^2 \cdot h \cdot G_v(\alpha) + 2\pi r h \cdot \gamma_{\alpha\delta}$
- if it is solid phase, the free energy is $G_{\text{cav}}(\beta) = \pi r^2 \cdot h \cdot G_v(\beta) + 2\pi r \cdot h \gamma_{\beta\delta}$

where $G_v(\alpha)$ and $G_v(\beta)$ are the volumetric free energy for the liquid and solid phase, $\gamma_{\alpha\beta}$, $\gamma_{\alpha\delta}$ and $\gamma_{\beta\delta}$ are the surface energy of the liquid-solid boundary of metal, liquid-container surface, and solid-constrainer surface, respectively.

At $T > T_M$, $G_v(\alpha) < G_v(\beta)$, but, $\gamma_{\alpha\delta} > \gamma_{\beta\delta}$, then it is possible to have $G_{\text{cav}}(\alpha) > G_{\text{cav}}(\beta)$ --- *that is, the rest of the container have liquid, but the cavity has the solid.*

Consider an liquid-solid equilibrium at T in the cavity, where $G_{\text{cav}}(\alpha) = G_{\text{cav}}(\beta)$

$$\text{Then } G_{\text{cav}}(\alpha) = \pi r^2 \cdot h \cdot G_v(\alpha) + 2\pi r h \cdot \gamma_{\alpha\delta} = G_{\text{cav}}(\beta) = \pi r^2 \cdot h \cdot G_v(\beta) + 2\pi r \cdot h \gamma_{\beta\delta}$$

$$\text{Then, } G_v(\beta) - G_v(\alpha) = \frac{2}{r}(\gamma_{\alpha\delta} - \gamma_{\beta\delta}) = \frac{2\gamma_{\alpha\beta} \cos\theta}{r}$$

$$\text{Also from Lecture 11, } G_v(\beta) - G_v(\alpha) = [S_v(\beta) - S_v(\alpha)] (T_M - T) = [S_v(\alpha) - S_v(\beta)] (T - T_M)$$

$$\text{Then, } G_v(\beta) - G_v(\alpha) = \Delta G_v (L \rightarrow S) = \Delta S_v (L \rightarrow S) (T_M - T) = \Delta S_v (S \rightarrow L) (T - T_M)$$

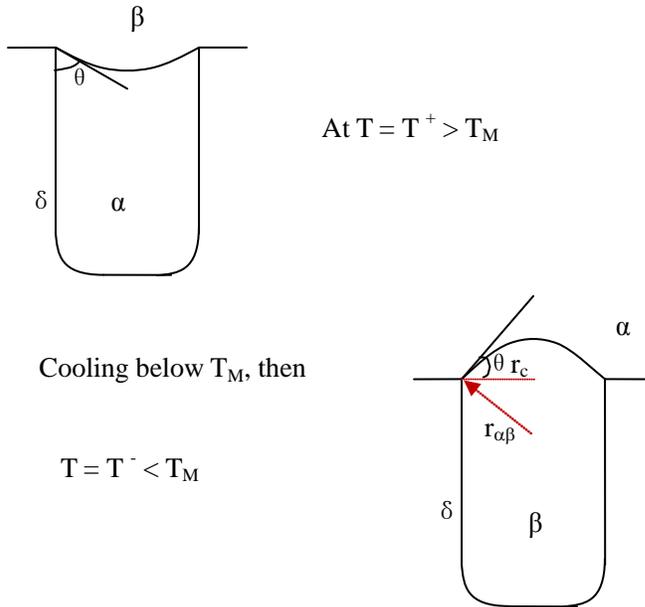
$$\text{Then, } G_v(\beta) - G_v(\alpha) = \Delta S_v (S \rightarrow L) (T - T_M) = \frac{2\gamma_{\alpha\beta} \cos\theta}{r}$$

$$\text{Then, } T = T_M + \frac{2\gamma_{\alpha\beta} \cos\theta}{r \Delta S_v (S \rightarrow L)} = T^+ \quad (\text{superheating due to cavity})$$

At T^+ , liquid-solid equilibrium is reached within the cavity. Defining the cavity radius as r_c , then we have

$$T^+ = T_M + \frac{2\gamma_{\alpha\beta} \cos\theta}{r_c \Delta S_v (S \rightarrow L)} \quad \text{or} \quad r_c = \frac{2\gamma_{\alpha\beta} \cos\theta}{(T^+ - T_M) \Delta S_v (S \rightarrow L)}$$

Thus, for $r > r_c$, $G_{cav}(\alpha) < G_{cav}(\beta)$ at T^+ , liquid in cavity (α phase)
 for $r < r_c$, $G_{cav}(\alpha) > G_{cav}(\beta)$ at T^+ , solid in cavity (β phase)



As the container is cooled farther, spontaneous freezing will occur when the radius of α/β interface ($r_{\alpha\beta}$) reaches the critical radius (r^*).

For the solid nucleus (a truncated sphere) shown in the diagram above,

$r_{\alpha\beta} \sin\theta = r_c$, when $r_{\alpha\beta} = r^*$ (critical nucleus for freezing to occur), then we have, $r^* \sin\theta = r_c$

$$r^* = -\frac{2\gamma_{\alpha\beta}}{\Delta G_V(L \rightarrow S)} = -\frac{2\gamma_{\alpha\beta}}{\Delta S_V(L \rightarrow S)(T_M - T^-)} \quad (\text{see Lecture 10-12})$$

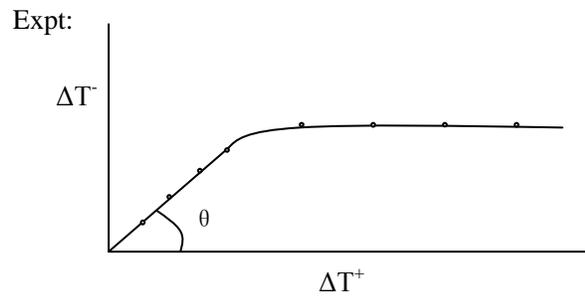
T^- is the temperature needed to cool, at which the freezing occurs inside a cavity of radius of r_c .

$$\text{Then, } r_c = r^* \sin\theta = \frac{2\gamma_{\alpha\beta} \sin\theta}{\Delta S_V(S \rightarrow L)(T_M - T^-)}$$

$$\text{Also, as shown above, } r_c = \frac{2\gamma_{\alpha\beta} \cos\theta}{\Delta S_V(S \rightarrow L)(T^+ - T_M)}$$

$$\text{Then, } \frac{2\gamma_{\alpha\beta} \sin\theta}{\Delta S_V(S \rightarrow L)(T_M - T^-)} = \frac{2\gamma_{\alpha\beta} \cos\theta}{\Delta S_V(S \rightarrow L)(T^+ - T_M)}$$

$$\text{Then, } \frac{T_M - T^-}{T^+ - T_M} = \frac{\Delta T^-}{\Delta T^+} = \tan\theta$$



Beyond a certain ΔT^+ , the required ΔT^- becomes constant ($\theta \rightarrow 0$, or fully wetting for the solid on the surface), because the heterogeneous nucleation starts to occur on flat container walls.