Lecture 16: Kinetics of Phase Growth in a Two-component System:

*dilute-solution approximation*

**Today’s topics**

- Kinetics of phase growth (transformation) in a two-component system: atom A and B form two phases $\alpha$ and $\beta$, which are dominated by A and B, respectively. Upon cooled from a pure $\alpha$ phase to a low temperature, $\beta$ particles precipitate in the $\alpha$ matrix. How fast these particles can grow depends on the diffusion of B atoms towards to the particle, as well as the diffusion of A atoms away from the particle.
- To make the kinetics analysis simple, we assume a dilute solution of $\alpha$ phase containing small molar fraction of $\beta$ phase, i.e., molar fraction of B ($X_B$) $\ll$ molar fraction of A ($X_A$). In such a case, the growth of $\beta$ particle depends on only the diffusion of B atoms.
- The overall kinetics of the $\beta$ particle growth is determined by the diffusion flux of B atoms across the $\alpha/\beta$ interface around the particle. The diffusion flux is primarily driven by the chemical potential difference of B atoms within the $\beta$ phase and that in the proximity $\alpha$ matrix around the particle, $\mu_B^\alpha(C_\alpha) - \mu_B^\beta(C_\beta) = \mu_B^\alpha(C_\alpha) - \mu_B^\alpha(C_\alpha)$.
- When the $\beta$ particle grows sufficiently large so that the surface energy can be ignored, the diffusion flux of B atoms across the $\alpha/\beta$ interface can be simply described to be proportional to the concentration difference between the concentration of B atoms within the proximity $\alpha$ matrix around the particle ($C_i$) and the equilibrium concentration of B atoms within the bulk $\alpha$ matrix ($C_e$).

The following kinetics treatment applies only to the dilute-solution of $\alpha$ phase containing small molar fraction of $\beta$ phase, i.e., molar fraction of B ($X_B$) $\ll$ molar fraction of A ($X_A$).

Consider a binary phase diagram of the type shown in the above figure, where $\alpha$ phase is assumed to be dilute solid solution containing small fractions of $\beta$ phase.

Initially, the sample is a homogeneous, single phase $\alpha$ of composition $x_0$ (mole fraction of B). The
corresponding concentration of B, **number of B atoms/unit volume** is \( C_0 \). The alloy is then cooled to a temperature \( T_1 \), at which the equilibrium composition of \( \alpha \) and \( \beta \) are respectively \( C_\alpha \) and \( C_\beta \), where \( C_0 > C_\alpha \).

The free energy (G) vs. composition diagram at \( T_1 \) can be drawn as below.

--- Please refer to the “**additional readings**” (provided online at our course website) for how to draw a molar free energy curve (\( G \) vs. \( X_B \)) for a binary phase system \( \alpha/\beta \), and its relationship with phase diagram, as well as how to get chemical potential \( \mu \) of each of the two component A and B in the \( \alpha \) and \( \beta \) phase.

\[
\mu_B^{\alpha}(C_r) = \mu_B^{\beta}(C_\beta) + \frac{2\gamma_{\alpha B} V^M_{\alpha}}{r} \\
= \mu_B^{\beta}(\infty) + \frac{2\gamma_{\alpha B} V^M_{\alpha}}{r} \quad \text{(Lecture 9)}
\]

From this diagram, when the \( \beta \) particle grows to be large, the surface energy contribution \( \frac{2\gamma_{\alpha B} V^M_{\alpha}}{r} \) becomes negligible, and the curve of \( G(r) \) lowers down to be the same as the \( G(\infty) \) --- as a result, the tangent point at the \( G_\alpha \) curve (\( C_r \), determined by the common tangent line between the \( G_\alpha \) and \( G(r) \) curves) moves to the left to be the same as \( C_r \), i.e, \( C_r \rightarrow 0 \) or \( C_r \rightarrow C_\alpha \).

During the cooling, \( \beta \) particles precipitate in the \( \alpha \) matrix and grow. The growth of \( \beta \) particles requires that a flux of B atoms flow towards the growing \( \beta \) particles, and meanwhile, A atoms flow away from the growing \( \beta \) particles into the \( \alpha \) matrix. Thus, the diffusion flux must be described in terms of the interdiffusion coefficient,

\[
\tilde{D} = X_A D^C_B + X_B D^C_A
\]

for an atomic (e.g., metallic alloy) solid solution (see Lecture 6).
With the initial assumption \( X_A >> X_B \) (\( X_A ->1, X_B ->0 \)) we have \( \tilde{D} = X_A D_B^C + X_B D_A^C \equiv X_A D_B^C \equiv D_B^C \). For dilute solution of \( B \), \( D_B^C \equiv D_B \), so, \( \tilde{D} \equiv D_B \)

--- implying that we can simply consider the only diffusion flux of \( B \) (neglect the flux of \( A \)).

For \( \beta \) particles to grow, \( B \) atoms must diffuse to the growing \( \beta \) particles and then cross the \( \alpha/\beta \) interface to deposit onto the particle. Thus, there are two continuous processes: ① diffusion of \( B \) in \( \alpha \) ② transfer of \( B \) across the \( \alpha/\beta \) interface.

Assume the \( \beta \) particle growing as spherical shape, and essentially composing pure \( B \), then we can plot the concentration of \( B \) as a function of the radial coordinate \( \rho \) from the center of the \( \beta \) particle of radius \( r \):

Where \( C_r \) is the concentration of \( B \) in \( \alpha \) matrix in the proximity around the growing \( \beta \) particle of radius \( r \).

Assume \( \beta \) particle to be much larger than the critical size, i.e., \( r >> r^* \), so we neglect the effect of surface energy and chemical potential, i.e., \( \frac{2 \gamma_{\alpha\beta} V_M^\beta}{r} \) is very small, then \( \mu_B^a(C_\beta) \to \mu_B^a(C_\alpha) = \mu_B^0(C_\beta) \), or \( C_r \to 0 \) or \( C_r \to C \), as indicated above in the free energy curve.

Since \( \alpha \) is a dilute solution of \( B \) in \( A \), the Henry’s law applies,
\[
\mu_B^a = \mu_B^0 + RT \ln(\gamma_H C)
\]
where \( \gamma_H \) — Henrian activity coefficient in the unit of cm\(^3\), and the concentration is in the unit of # of atoms/cm\(^3\) instead of mole fraction.

Then we have the chemical potential for the three concentrations:
\[
\mu_B^a(C_0) = \mu_B^0 + RT \ln(\gamma_H C_0) \\
\mu_B^a(C_r) = \mu_B^0 + RT \ln(\gamma_H C_r) \\
\mu_B^a(C_\alpha) = \mu_B^0 + RT \ln(\gamma_H C_\alpha)
\]

since, \( C_0 > C_r > C_\alpha \), then we have
\[
\mu_B^0(C_0) > \mu_B^a(C_r) > \mu_B^a(C_\alpha) = \mu_B^0(C_\beta)
\]
Implied thermodynamic driving force for the diffusion of B atoms from the matrix α to the growing β particle. This diffusion flux occurs firstly by diffusion in the α phase from C₀ to Cᵣ. Once B atoms arrive at the α/β interface, they can cross the interface to deposit onto the β particle because \( \mu_B^\alpha(C_r) > \mu_B^\beta(C_\beta) = \mu_B^\alpha(C_\alpha) \).

**Description of the diffusion flux of B atoms across the α/β interface:**

Such flux, as marked as \( J \), must be proportional to the thermodynamic driving force:

\[
J \propto 1 - \exp\left\{ -\frac{[\mu_B^\alpha(C_r) - \mu_B^\beta(C_\beta)]}{RT} \right\} = 1 - \exp\left\{ -\frac{[\mu_B^\alpha(C_r) - \mu_B^\beta(C_\alpha)]}{RT} \right\} \quad \text{(see Lecture 2, 3)}
\]

If \( \mu_B^\alpha(C_r) - \mu_B^\beta(C_\alpha) \ll RT \), i.e., when \( r \) grows sufficiently big, \( C_r \to C_\alpha \), \( \mu_B^\alpha(C_r) \to \mu_B^\alpha(C_\alpha) \)

\[
\exp\left\{ -\frac{[\mu_B^\alpha(C_r) - \mu_B^\beta(C_\alpha)]}{RT} \right\} \approx 1 - \frac{\mu_B^\alpha(C_r) - \mu_B^\beta(C_\alpha)}{RT}
\]

So, \( J \propto \mu_B^\alpha(C_r) - \mu_B^\alpha(C_\alpha) \)

\[
\propto RT \ln \left( \frac{C_r}{C_\alpha} \right)
\]

\[
\propto RT \ln \left[ 1 + \frac{C_r - C_\alpha}{C_\alpha} \right]
\]

As discussed above, when the β particle grows to be much larger than the critical size, \( C_r - C_\alpha \ll C_\alpha \)

Then, \( \frac{C_r - C_\alpha}{C_\alpha} \ll 1.0 \)

So, \( J \propto RT \frac{C_r - C_\alpha}{C_\alpha} \), Or, \( J = \frac{M' RT}{C_\alpha} (C_r - C_\alpha) \), where \( M' \) depends on T but not on composition.

Define \( M = \frac{M' RT}{C_\alpha} \) defined as an interface parameter, a measure of the transport kinetics of atoms across the α/β interface.

Then, \( J = M \quad (C_r - C_\alpha) \quad (1) \)

Where C has the unit of #/cm³, M has the unit of cm/sec.

If the interface thickness is \( \delta \) (a few Å), the M equals to the diffusion coefficient across the interface divided by \( \delta \).

\( M = \frac{D}{\delta} \).

The process is clearly not a steady state process. However, we assume the changes with time is slow, i.e., a quasi-steady-state process.