# 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 α and β, which are dominated by A and B, respectively. Upon cooled from a pure α phase to a low temperature, β particles precipitate in the α 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 α phase containing small molar fraction of β phase, i.e., molar fraction of B (X_B) << molar fraction of A (X_A). In such a case, the growth of β particle depends on only the diffusion of B atoms.
- The overall kinetics of the β particle growth is determined by the diffusion flux of B atoms across the α/β interface around the particle. The diffusion flux is primarily driven by the chemical potential difference of B atoms within the β phase and that in the proximity α matrix around the particle, $\mu_B^{\alpha}(C_r)-\mu_B^{\beta}(C_{\beta}) = \mu_B^{\alpha}(C_r)-\mu_B^{\alpha}(C_{\alpha})$.
- When the β particle grows sufficiently large so that the surface energy can be ignored, the diffusion flux of B atoms across the α/β interface can be simply described to be proportional to the concentration difference between the concentration of B atoms within the proximity α matrix around the particle (C_r) and the equilibrium concentration of B atoms within the bulk α matrix (C_{α}).

The following kinetics treatment applies only to the dilute-solution of α phase containing small molar fraction of β phase, i.e., molar fraction of B (X_B) << molar fraction of A (X_A).
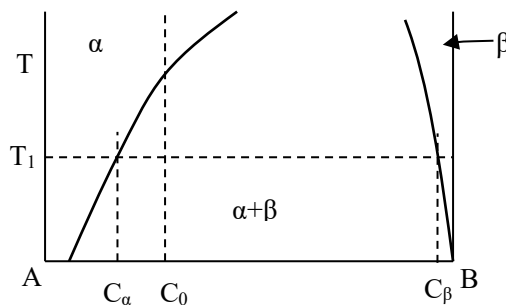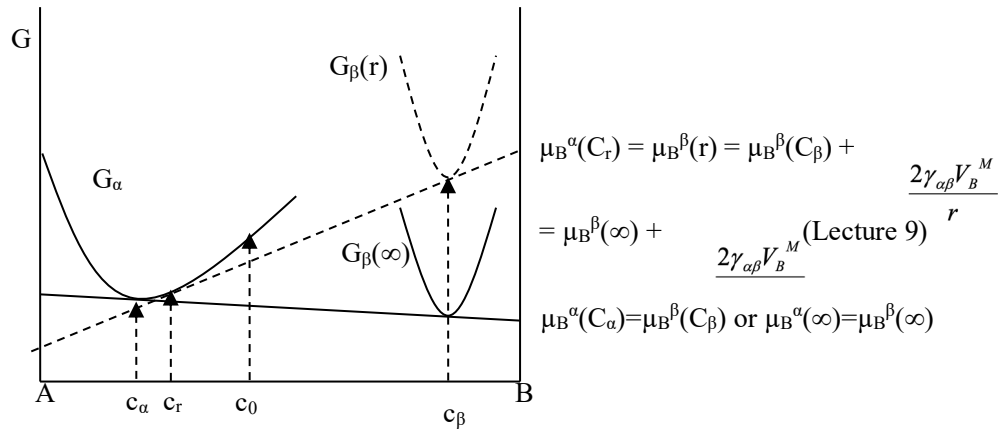

Consider a binary phase diagram of the type shown in the above figure, where α phase is assumed to be dilute solid solution containing small fractions of β phase.

Initially, the sample is a homogeneous, single phase α 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 α and β are respectively C_α and C_β, where $C_0 > C_\alpha$.

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

--- Please refer to the basics of thermodynamics that you learned before for how to draw a molar free energy curve (G vs. X_B) for a binary phase system α/β, and its relationship with phase diagram, as well as how to get chemical potential μ of each of the two component A and B in the α and β phase.

$$\mu_B^\alpha(C_r) = \mu_B^\beta(r) = \mu_B^\beta(C_\beta) + \frac{2\gamma_{\alpha\beta}V_B^M}{r}$$

$$= \mu_B^\beta(\infty) + \frac{2\gamma_{\alpha\beta}V_B^M}{?} \text{ (Lecture 9)}$$

$$\mu_B^\alpha(C_\alpha) = \mu_B^\beta(C_\beta) \text{ or } \mu_B^\alpha(\infty) = \mu_B^\beta(\infty)$$

From this diagram, when the β particle grows to be large, the surface energy contribution ($\frac{2\gamma_{\alpha\beta}V_B^M}{r}$) becomes negligible, and the curve of $G_\beta(r)$ lowers down to be the same as the $G_\beta(\infty)$ --- as a result, *the tangent point at the G_α curve (C_r, determined by the common tangent line between the G_α and $G_\beta(r)$ curves) moves to the left to be the same as C_α, i.e, $C_r - C_\alpha \to 0$ or $C_r - C_\alpha << C_\alpha$*
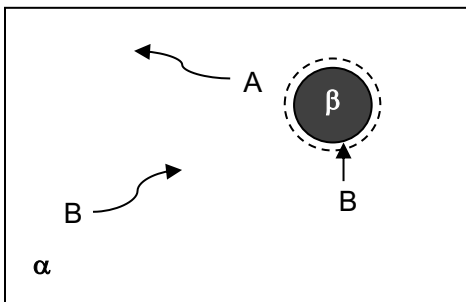
During the cooling, β particles precipitate in the α matrix and grow. The growth of β particles requires that a flux of B atoms flow towards the growing β particles, and meanwhile, A atoms flow away from the growing β particles into the α matrix. Thus, the diffusion flux must be described in terms of the interdiffusion coefficient,

$$\widetilde{D} = X_A D_B^C + X_B D_A^C \text{ for an atomic (e.g., metallic alloy) solid solution (see Lecture 6)}$$

With the initial assumption $X_A >> X_B$ ($X_A => 1$, $X_B => 0$) we have $\widetilde{D} = X_A D_B^C + X_B D_A^C \cong X_A D_B^C \cong D_B^C$. For

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dilute solution of B, $D_B^C \cong D_B$, so, $\widetilde{D} \cong D_B$

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

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

Assume the β 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 ' ρ ' from the center of the β particle of radius r:

ρ —— radial coordinate
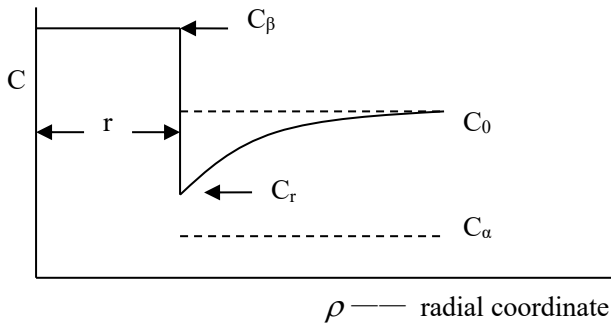
Where C_r is the concentration of B in α matrix in the proximity around the growing β particle of radius r.

Assume β 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., $\dfrac{2\gamma_{\alpha\beta}V_M^{\beta}}{r}$ is very small, then $\mu_B^{\alpha}(C_r)$ → $\mu_B^{\alpha}(C_{\alpha})=\mu_B^{\beta}(C_{\beta})$, or C_r - C_{α} → 0   *or* C_r

- C_{α} << C_{α} as indicated above in the free energy curve.

Since α is a dilute solution of B in A, the Henry's law applies,
$\mu_B^{\alpha} = \mu_B^0 + RT \ln(\gamma_H C)$
where γ_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:
$\mu_B^{\alpha}(C_0) = \mu_B^0 + RT \ln(\gamma_H C_0)$
$\mu_B^{\alpha}(C_r) = \mu_B^0 + RT \ln(\gamma_H C_r)$
$\mu_B^{\alpha}(C_{\alpha}) = \mu_B^0 + RT \ln(\gamma_H C_{\alpha})$

since, $C_0 > C_r > C_{\alpha}$, then we have
$\mu_B^{\alpha}(C_0) > \mu_B^{\alpha}(C_r) > \mu_B^{\alpha}(C_{\alpha}) = \mu_B^{\beta}(C_{\beta})$
--- implying 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 C_0 to C_r. Once B atoms arrive at the

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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:

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

If $\mu_B^\alpha(C_r) - \mu_B^\alpha(C_\alpha) \ll$ RT, i.e., when r grows sufficiently big, $C_r \rightarrow C_\alpha$, $\mu_B{}^\alpha(C_r) \rightarrow \mu_B{}^\alpha(C_\alpha)$

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

So, $J \propto [\mu_B{}^\alpha(C_r) - \mu_B{}^\alpha(C_\alpha)]/RT$

$$\propto \ln\ (\frac{C_r}{C_\alpha}) = \ln\ [1 + \frac{C_r - C_\alpha}{C_\alpha}]$$

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

Then, $\dfrac{C_r - C_\alpha}{C_\alpha} \ll 1.0$,

The with Taylor expansion, $\ln\ [1 + \dfrac{C_r - C_\alpha}{C_\alpha}] = \dfrac{C_r - C_\alpha}{C_\alpha}$

So, $J \propto \dfrac{C_r - C_\alpha}{C_\alpha}$, and since C_α is a constant under a given temperature, we have $J \propto (C_r - C_\alpha)$, or,

$$J = M\ (C_r - C_\alpha) \qquad\qquad \textbf{(1)}$$

where M is defined as an interface parameter, a measure of the transport kinetics of atoms across the α/β interface. M depends on T but not on composition. Concentrations C_r and C_α have the unit of #/cm³, M has the unit of cm/sec.

If the interface thickness is 'δ' (a few Å), the M equals to the diffusion coefficient across the interface divided by 'δ'. M = D/δ.
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.