Lecture 5: Diffusion–Controlled Growth

Rate–Controlling Processes

An electrical current i flowing through a resistor will dissipate energy in the form of heat (Fig. 1). When the current passes through two resistors in series, the dissipations are iv_1 and iv_2 where v_1 and v_2 are the voltage drops across the respective resistors. The total potential difference across the circuit is $v = v_1 + v_2$. For a given applied potential v, the magnitude of the current flow must depend on the resistance presented by each resistor. If one of the resistors has a relatively large electrical resistance then it is said to *control* the current because the voltage drop across the other can be neglected. On the other hand, if the resistors are more or less equivalent than the current is under *mixed* control.
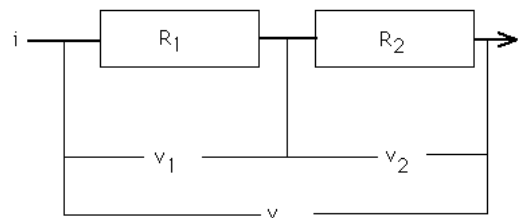

Fig. 1: Rate–controlling processes: electrical analogy.

This electrical circuit is an excellent analogy to the motion of an interface. The interface velocity and driving force (free energy change)

are analogous to the current and applied potential difference respectively. The resistors represent the processes which impede the motion of the interface, such as diffusion or the barrier to the transfer of atoms across the boundary. When most of the driving force is dissipated in diffusion, the interface is said to move at a rate *controlled* by diffusion. Interface–controlled growth occurs when most of the available free energy is dissipated in the process of transferring atoms across the interface.

These concepts are illustrated in Fig. 2, for a solute–rich precipitate β growing from a matrix α in an alloy of average chemical composition C_0. The equilibrium compositions of the precipitate and matrix are respectively, $C^{\beta\alpha}$ and $C^{\alpha\beta}$.
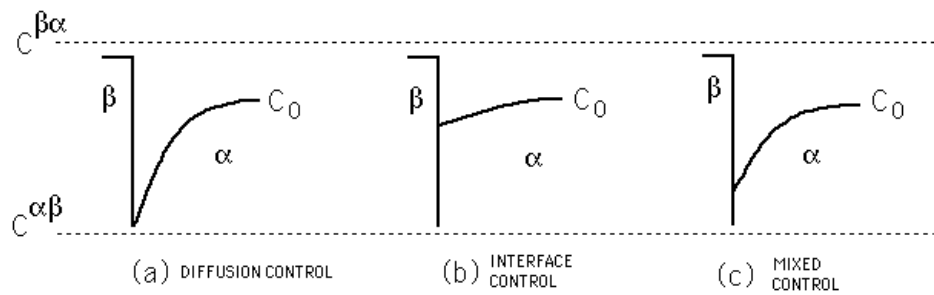

Fig. 2:Concentration profile at an α/β interface moving under: (a) diffusion–control, (b) interface–control, (c) mixed interface.

A reasonable approximation for diffusion–controlled growth is that local equilibrium exists at the interface. On the other hand, the concentration gradient in the matrix is much smaller with interface–controlled growth because most of the available free energy is dissipated in the

transfer of atoms across the interface.

Diffusion–Controlled Growth

Precipitates can have a different chemical composition from the matrix. The growth of such particles (designated β) is frequently controlled by the diffusion of solute which is partitioned into the matrix (designated α).

As each precipitate grows, so does the extent of its diffusion field. This slows down further growth because the solute has to diffuse over ever larger distances. As we will prove, the particle size increases with the square root of time, *i.e.* the growth rate slows down as time increases. We will assume in our derivation that the concentration gradient in the matrix is constant, and that the far–field concentration C_0 never changes (*i.e.* the matrix is semi–infinite normal to the advancing interface). This is to simplify the mathematics without loosing any of the insight into the problem.

For isothermal transformation, the concentrations at the interface can be obtained from the phase diagram as illustrated below. The diffusion flux of solute towards the interface must equal the rate at which solute is incorporated in the precipitate so that:

$$\underbrace{(C_\beta - C_\alpha)\frac{\partial x}{\partial t}}_{\text{rate solute absorbed}} = \underbrace{D\frac{\partial C}{\partial x}}_{\text{diffusion flux towards interface}} \simeq D\frac{C_0 - C_\alpha}{\Delta x}$$

A second equation can be derived by considering the overall conservation of mass:

$$(C_\beta - C_0)x = \frac{1}{2}(C_0 - C_\alpha)\Delta x \tag{1}$$
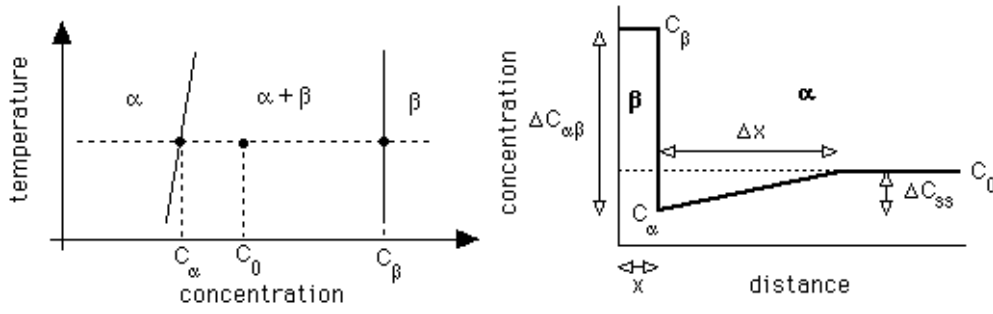
On combining these expressions to eliminate Δx we get:

$$\frac{\partial x}{\partial t} = \frac{D(C_0 - C_\alpha)^2}{2x(C_\beta - C_\alpha)(C_\beta - C_0)} \qquad (2)$$

If, as is often the case, $C_\beta \gg C_\alpha$ and $C_\beta \gg C_0$ then

$$2\int x\partial x = \left(\frac{C_0 - C_\alpha}{C_\beta - C_\alpha}\right)^2 D \int \partial t \quad \text{so that} \quad x \simeq \frac{\Delta C_{ss}}{\Delta C_{\alpha\beta}} \sqrt{Dt}$$

$$\text{and} \quad v \simeq \frac{1}{2} \frac{\Delta C_{ss}}{\Delta C_{\alpha\beta}} \sqrt{\frac{D}{t}} \qquad (3)$$

where v is the velocity. A more precise treatment which avoids the linear profile approximation would have given:

$$v \simeq \frac{\Delta C_{ss}}{\Delta C_{\alpha\beta}} \sqrt{\frac{D}{t}}$$

The growth rate decreases with time (Fig. 3). The physical reason why the growth rate decreases with time is apparent from equation 1, where the diffusion distance Δx is proportional to the precipitate size x (Fig. 3b). As a consequence, the concentration gradient decreases as the precipitate thickens, causing a reduction in the growth rate.
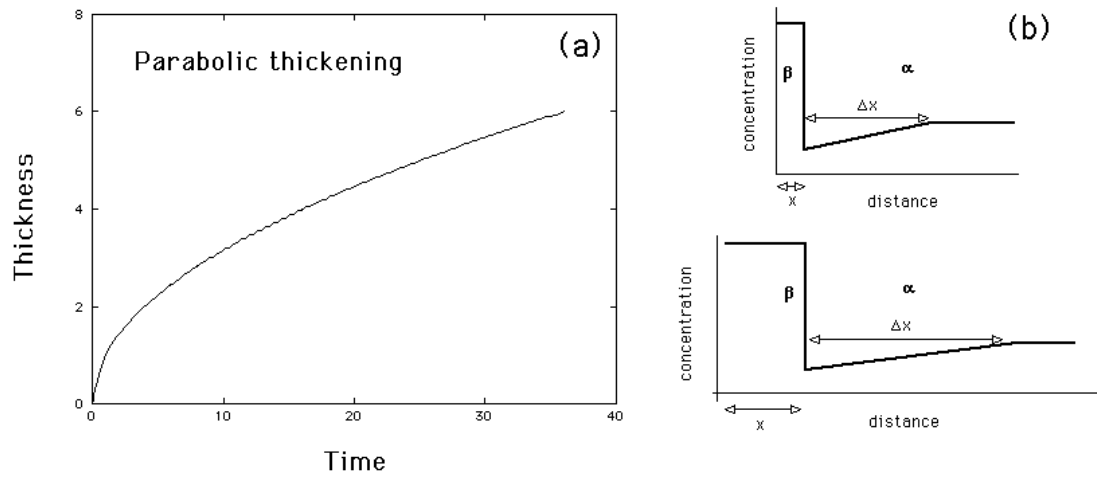
Fig. 3: (a) Parabolic thickening during one dimensional growth. (b) Increase in diffusion distance as the precipitate thickens.