Lecture 9: Overall Transformation Kinetics

Isothermal Transformation

To model transformation it is obviously necessary to calculate the nucleation and growth rates, but an estimation of the volume fraction requires *impingement* between particles to be taken into account.
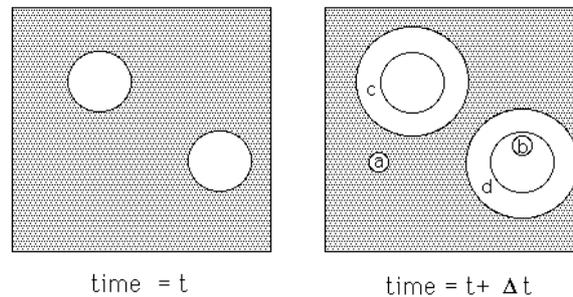

Fig. 1: An illustration of the concept of extended volume. Two precipitate particles have nucleated together and grown to a finite size in the time t. New regions c and d are formed as the original particles grow, but a & b are new particles, of which b has formed in a region which is already transformed.

This is done using the extended volume concept of Kolmogorov, Johnson, Mehl and Avrami. Referring to Fig. 1, suppose that two particles exist at time t; a small interval δt later, new regions marked a, b, c & d are formed assuming that they are able to grow unrestricted in extended space whether or not the region into which they grow is already transformed. However, only those components of a, b, c & d which lie in previously untransformed matrix can contribute to a change in the real volume of the product phase (α) :

$$dV^\alpha = \left(1 - \frac{V^\alpha}{V}\right) dV_e^\alpha \tag{1}$$

where it is assumed that the microstructure develops at random. The subscript e refers to extended volume, V^α is the volume of α and V is the total volume. Multiplying the change in extended volume by the probability of finding untransformed regions has the effect of excluding regions such as b, which clearly cannot contribute to the real change in volume of the product. For a random distribution of precipitated particles, this equation can easily be integrated to obtain the real volume fraction,

$$\frac{V^\alpha}{V} = 1 - \exp\left\{-\frac{V_e^\alpha}{V}\right\}$$

The extended volume V_e^α is straightforward to calculate using nucleation and growth models and neglecting completely any impingement effects. Consider a simple case where the α grows isotropically at a constant rate G and where the nucleation rate per unit volume, I_V. The volume of a particle nucleated at time $t = \tau$ (Fig. 2) is given by

$$v_\tau = \frac{4}{3}\pi G^3 (t - \tau)^3$$

The change in extended volume over the interval τ and $\tau + d\tau$ is

$$dV_e^\alpha = \frac{4}{3}\pi G^3 (t - \tau)^3 \times I_V \times V \times d\tau$$

On substituting into equation 1 and writing $\xi = V^\alpha/V$, we get

$$dV^\alpha = \left(1 - \frac{V^\alpha}{V}\right)\frac{4}{3}\pi G^3 (t - \tau)^3 I_V V \ \ d\tau$$

$$\text{so that} \quad -\ln\{1 - \xi\} = \frac{4}{3}\pi G^3 I_V \int_0^t (t - \tau)^3 \ d\tau \quad\quad (2)$$

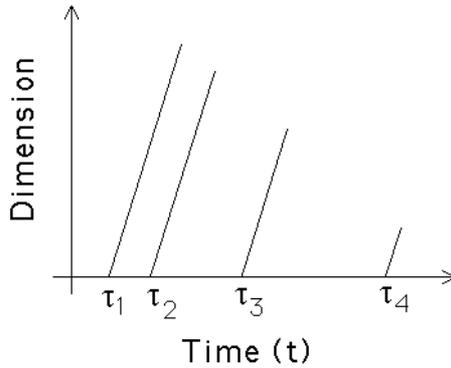$$\text{and} \quad \xi = 1 - \exp\{-\pi G^3 I_V t^4/3\}$$

Fig. 2: An illustration of the incubation time τ for each particle.

This equation has been derived for the specific assumptions of random nucleation, a constant nucleation rate and a constant growth rate. There are different possibilities but they often reduce to the general form:

$$\xi = 1 - \exp\{-k_A t^n\} \tag{3}$$

where k_A and n characterise the reaction as a function of time, temperature and other variables. The values of k_A and n can be obtained from experimental data by plotting $\ln(-\ln\{1-\xi\})$ versus $\ln\{t\}$. The specific values of k_A and n depend on the nature of nucleation and growth. Clearly, a constant nucleation and growth rate leads to a time exponent $n = 4$, but if it is assumed that the particles all begin growth instantaneously from a fixed number density of sites (*i.e.* nucleation is not needed) the $n = 3$ when the growth rate is constant. There are other scenarios and the values of the Avrami parameters are not necessarily unambiguous in the sense that the same exponent can represent two different mechanisms.

The form of equation 3 is illustrated in Fig. 3. Note that the effect of temperature is to alter the thermodynamic driving force for transformation, to alter diffusion coefficients and to influence any other thermally activated processes. The effect of manganese is via its influence on the stability of the parent and product phases.

The results of many isothermal transformation curves such as the ones illustrated in Fig. 3 can be plotted on at time–temperature–transformation diagram as illustrated in Fig. 4. The curves typically have a C shape because the driving force for transformation is small at high temperatures whereas the diffusion coefficient is small at low temperatures. There is an optimum combination of these two parameters at intermediate temperatures, giving a maximum in the rate of reaction. The curve marked *start* corresponds to a detectable limit of transformation (*e.g.* 5%), and that marked finish corresponds to say 95% transformation.

Simultaneous Transformations

There are many circumstances in which reactions do not happen in isolation. For example, a steel designed to serve at $600\,^\circ\mathrm{C}$ over a period of 30 years may contain
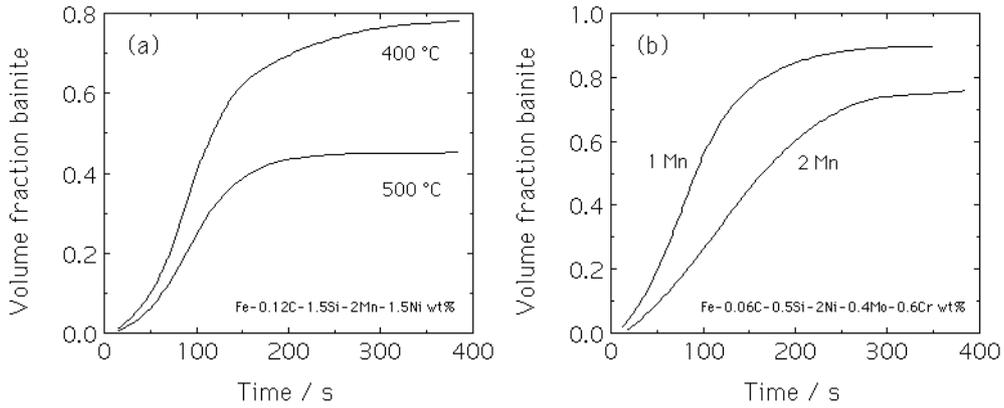
Fig. 3: The calculated influence of (a) transformation temperature and (b) manganese concentration on the kinetics of the bainite reaction (Singh, 1998). Bainite is a particular kind of solid–state phase transformation that occurs in steels.
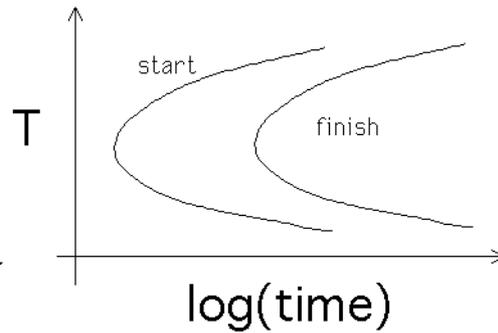

Fig. 4: A time–temperature–transformation (TTT) diagram.

more than six different kinds of precipitates so that it can sustain a load without creeping.

A simple modification for the simultaneous formation of two precipitates (α and β) is that equation 1 of Lecture MP6–8 becomes a coupled set of two equations,

$$dV^\alpha = \left(1 - \frac{V^\alpha + V^\beta}{V}\right)dV_e^\alpha \qquad \text{and} \qquad dV^\beta = \left(1 - \frac{V^\alpha + V^\beta}{V}\right)dV_e^\beta \qquad (4)$$

This can be done for any number of reactions happening together. The resulting set of equations must in general be solved numerically, although a few analytical solutions are possible for special cases, one of which is illustrated below.

Special Cases

For the simultaneous formation of two phases whose extended volumes are related linearly:

$$V_e^\beta = BV_e^\alpha + C \qquad \text{with} \qquad B \geq 0 \qquad \text{and} \qquad C \geq 0 \tag{5}$$

then with $\xi_i = V_i/V$, it can be shown that

$$\xi^\alpha = \int \exp\left\{-\frac{(1+B)V_e^\alpha + C}{V}\right\} \frac{dV_e^\alpha}{V} \qquad \text{and} \qquad \xi^\beta = B\xi^\alpha \tag{6}$$

If the isotropic growth rate of phase α is G and if all particles of α start growth at time $t = 0$ from a fixed number of sites N_V per unit volume then $V_e^\alpha = N_V \frac{4\pi}{3}G^3t^3$. On substitution of the extended volume in equation 6 gives

$$\xi^\alpha = \frac{1}{1+B}\exp\{-\frac{C}{V}\}\left[1 - \exp\left\{-\frac{(1+B)N_V\frac{4\pi}{3}G^3t^3}{V}\right\}\right] \qquad \text{with} \qquad \xi^\beta = B\xi^\alpha \tag{7}$$

The term $\exp\{-C/V\}$ is the fraction of parent phase available for transformation at $t = 0$; it arises because $1 - \exp\{-C/V\}$ of β exists prior to commencement of the simultaneous reaction at $t = 0$. Thus, ξ^β is the additional fraction of β that forms during simultaneous reaction. It is emphasised that $C \geq 0$. A case for which $C = 0$ and $B = 8$ is illustrated in Fig. 5.
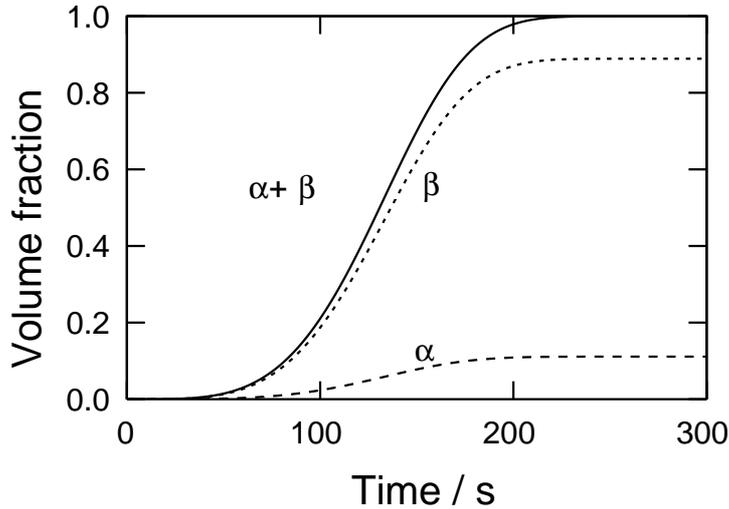

Fig. 5: Simultaneous transformation to phases $\alpha \equiv 1$ and $\beta \equiv 2$ with $C = 0$ and $B = 8$.