Lecture 10: Overall Transformation Kinetics II

Simultaneous Transformations

There are many circumstances in which reactions do not happen in isolation. For example, a steel designed to serve at 600 °C over a period of 30 years may contain more than six different kinds of precipitates so that it can sustain a load without creeping.

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

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

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:

$$V_e^\beta = BV_e^\alpha + C \qquad \text{with} \qquad B \geq 0 \qquad \text{and} \qquad C \geq 0 \tag{2}$$

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

$$\xi^\alpha = \int \exp\left\{-\frac{(1+B)V_e^\alpha + C}{V}\right\} \frac{dV_e^\alpha}{V} \qquad \text{and} \qquad \xi^\beta = B\xi^\alpha \tag{3}$$

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 $V_e^\alpha = N_V \frac{4\pi}{3} G^3 t^3$. On substitution of the extended volume in equation 3 gives

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

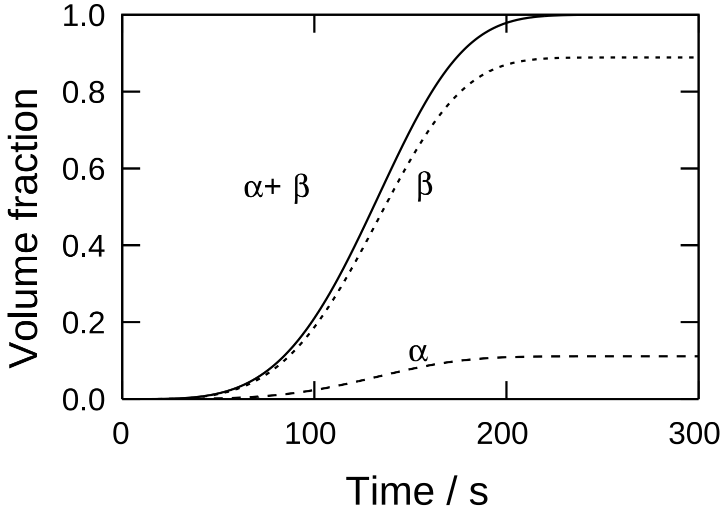

Fig. 1: Simultaneous transformation to phases $\alpha \equiv 1$ and $\beta \equiv 2$ with $C = 0$ and $B = 8$.

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. 1.

Anisothermal Transformation Kinetics

A popular method of converting between isothermal and anisothermal transformation data is the *additive reaction rule* of Scheil (1935). A cooling curve is treated as a combination of a sufficiently large number of isothermal reaction steps. Referring to Fig. 2, a fraction $\xi = 0.05$ of transformation is achieved during continuous cooling when

$$\sum_i \frac{\Delta t_i}{t_i} = 1 \tag{5}$$

with the summation beginning as soon as the parent phase cools below the equilibrium temperature.

The rule can be justified if the reaction rate depends solely on ξ and T. Although this is unlikely, there are many examples where the rule has been empirically applied to bainite with success. Reactions for which the additivity rule is justified are called

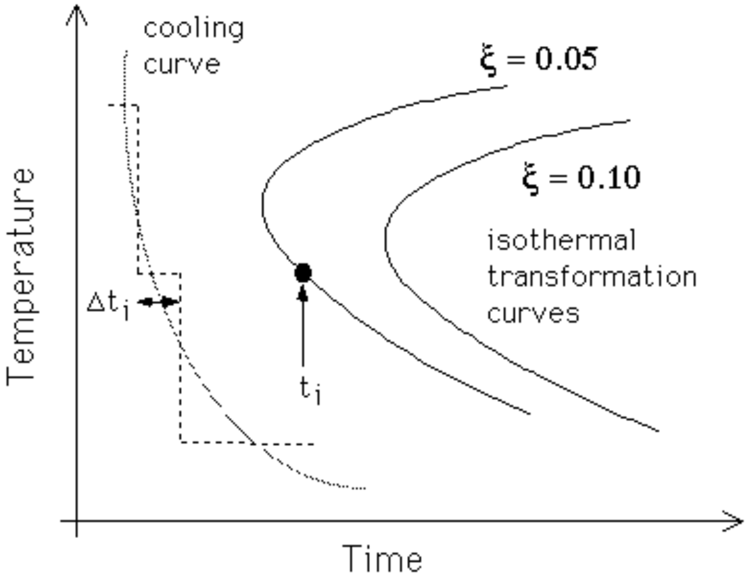

Fig. 2: The Scheil method for converting between isothermal and anisothermal transformation data.

isokinetic, implying that the fraction transformed at any temperature depends only on time and a single function of temperature.

Continuous Cooling Transformation (CCT) Diagrams

It is not common in industrial practice to conduct isothermal transformations. It is more convenient to generate the required properties during continuous cooling from the parent phase. Continuous–cooling–transformation (CCT) diagrams are then used to represent the evolution of microstructure (Fig. 3). We shall illustrate CCT diagrams using steels as an example, where the most important transformations are those that occur from austenite as the parent phase.

The rate of transformation in a given steel with a known austenite grain size can be described with just one TTT diagram. However, a different CCT diagrams is required for cooling function, *e.g.* whether the cooling rate is constant or Newtonian. It is therefore necessary to plot the actual cooling curves used in the derivation of the CCT diagram (Fig. 3). Each cooling curve must begin at the highest temperature where transformation becomes possible (the equilibrium or Ae_3 temperature).

Each CCT diagram requires a specification of the chemical composition of the steel, the austenitisation conditions, the austenite grain size and the cooling condition.

The diagrams are therefore specific to particular processes and lack the generality of TTT diagrams.

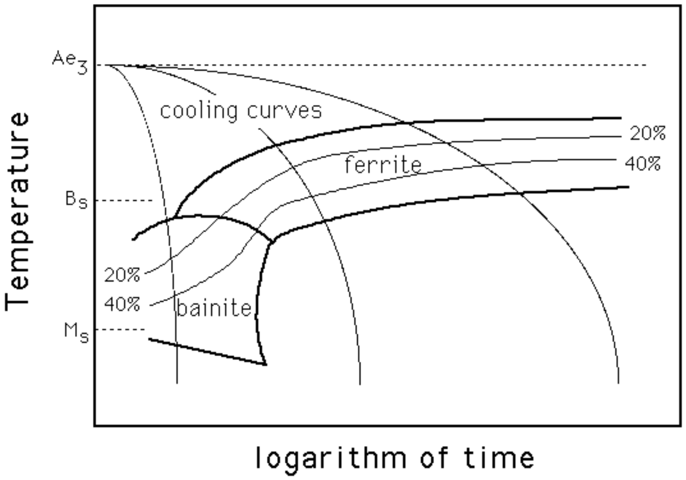

Fig. 3: CCT diagram illustrating the cooling curves, constant volume percent contours and transformation temperatures.

The CCT diagram is usually partitioned into domains of microstructure; Fig. 3 shows the conditions under which bainite and ferrite form (do not worry about the detailed meaning of these terms, just think of them as different transformation products of austenite). Mixed microstructures are obtained when a domain boundary is intersected by a cooling curve. The constant volume fraction contours must be continuous across the domain boundaries to avoid (incorrect) sudden changes in volume fraction as the boundary is crossed (*e.g.* points a, b on Fig. 4). The contours represent the fraction of austenite which has transformed into one or more phases.

Any transformation which precedes bainite alters the chemical composition of the residual austenite. The main changes occur in the region associated with the vertical line "c" in Fig. 5. The temperature at which the bainite first forms is depressed by the changed composition of the austenite. Because the ferrite and bainite domains are separated by a time gap, the continuity of constant volume fraction contours is interrupted. The contours must still be plotted so that their loose ends are connected by a cooling curve as illustrated by "ab" on Fig. 5.

Although bainite is depressed to lower temperatures by the prior formation of ferrite as the cooling rate decreases, the temperature range over which bainite forms

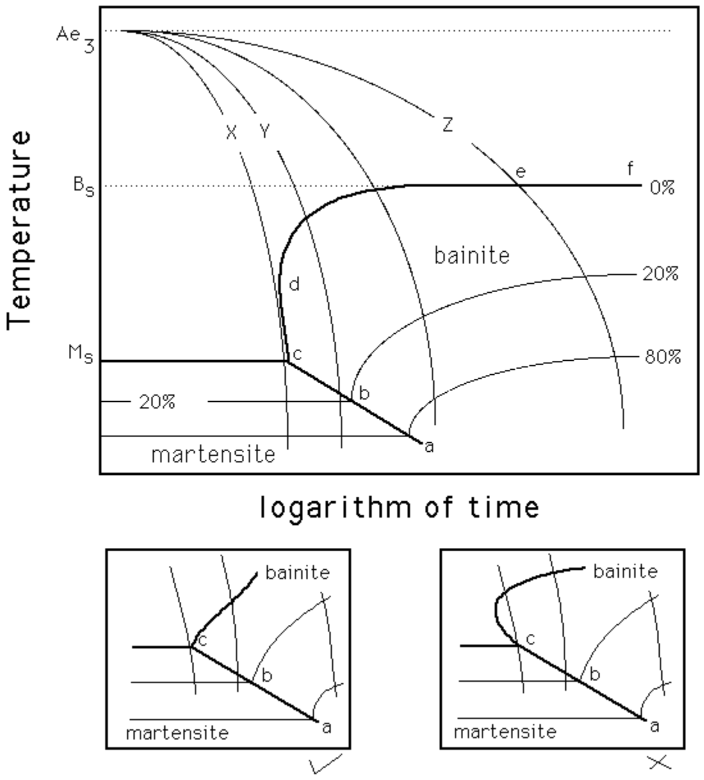

Fig. 4: Schematic CCT diagrams illustrating the continuity of constant volume percent contours across microstructure domain boundaries and the correct way in which the zero percent curves of different domains must meet at the point *c*.

is eventually reduced. This is because very slow cooling rates give ample opportunity for transformation to be completed over a smaller temperature range as illustrated by the rising curve "de" on Fig. 5.

All of the features described here can be found in actual TTT and CCT diagrams, for example, the measured diagrams for a '2.25Cr1Mo' steel which is used widely in the bainitic condition for power plant applications (Fig. 6).

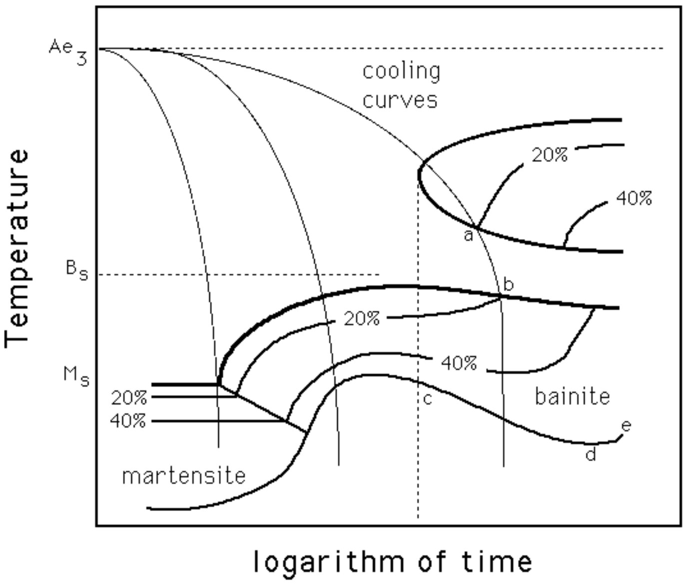

Fig. 5: TTT diagram in which the bainite region is strongly influenced by the initial formation of ferrite during continuous cooling transformation.

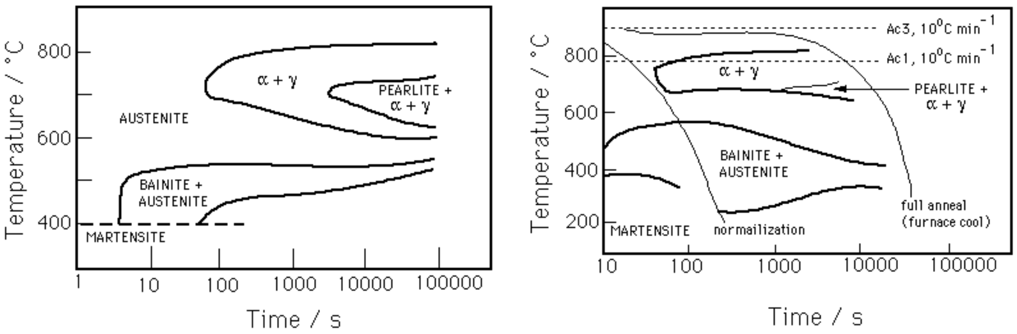

Fig. 6: Corresponding TTT and CCT diagrams for a 2.25Cr1Mo steel (Lundin *et al.*, 1982). The CCT diagram shows the terminology used in describing air–cooling from the austenitisation temperature (*i.e.* , normalising) and furnace cooling (*i.e.* annealing).