Last time

Morphological Stability of a Growing Spherical Precipitate

Kinetics of Nucleation and Growth Transformations — No Composition Change

Time Cone; Poisson Probability Distribution

3.21 Spring 2002: Lecture 35

Nucleation, Growth, Transformations, Coarsening, and Grain Growth: Reprise

It is useful to review how all of the kinetic processes associated with microstructural evolution relate to one another. We have been discussing how a transformation proceeds when a system is out of equilibrium, and how the kinetic processes affect the resulting microstructure.

An indication of *which* phase transformations may occur comes from the equilibrium phase diagram, for example:

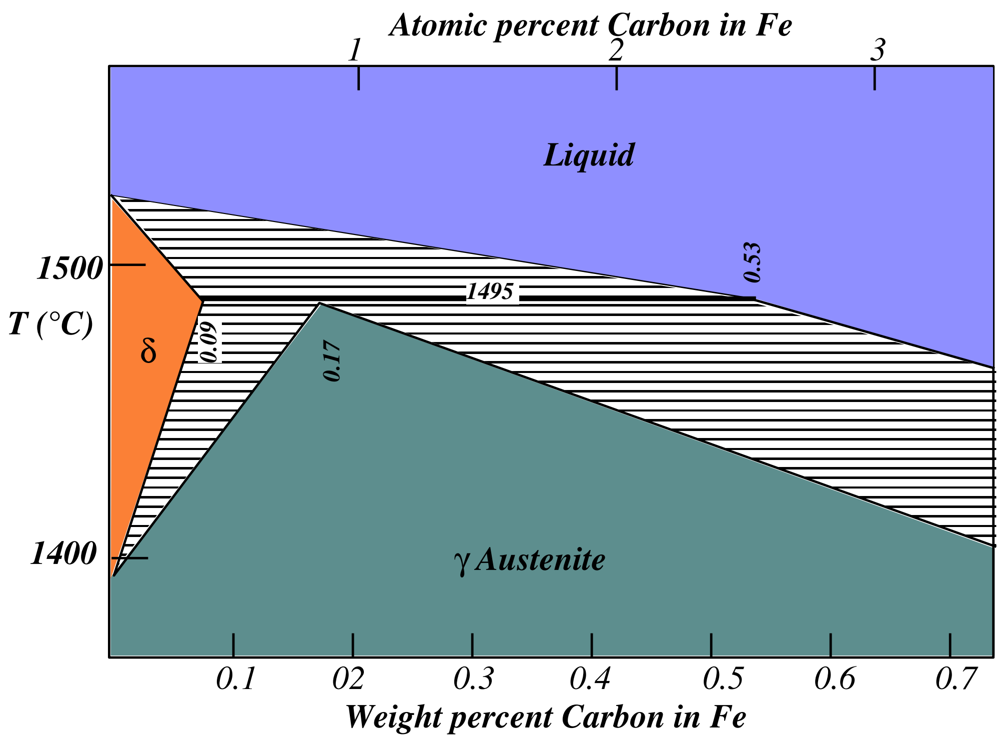

Figure 35-1: Example of the Iron-rich side of the Fe-C phase diagram.

Types of Transformations The kinetics of alloy phase transformations can be categorized into two fundamental categories.

- Transformations which **require long range diffusion** to the growing particles of the new phase.
- Transformations which only **local atomic rearrangement or local atomic structural changes**

Both kinds of transformations can be illustrated in the following figure which is taken from the iron-rich end of the Fe-C phase diagram.

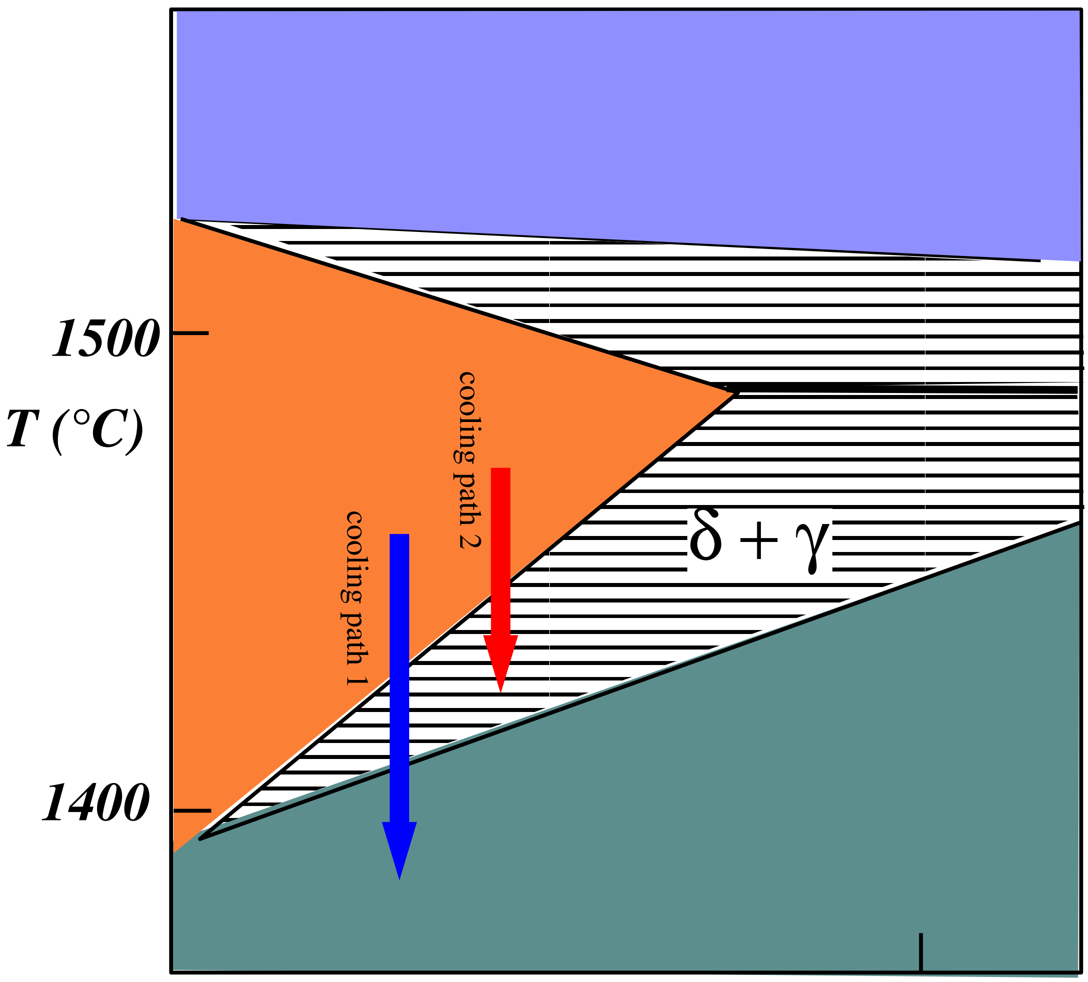

Figure 35-2: Example of two different processes that can initiate a phase transformation—however, the cooling path alone is insufficient to determine the type of microstructure that will result.

The two arrows represent quenching processes. The process on the left (iron-rich) side represents a quench from the single δ-phase into the single γ-phase region. The second cooling path represents a quench from the single δ-phase into the two phase $\delta - \gamma$ region.

It is important to realize that the cooling paths in the above equilibrium phase diagram are **not sufficient** for predicting what kinds of microstructures or even which phases will exist at the end of an experimental quench. If either the nucleation or the growth kinetics are slow—the usual case in solid-solid transformations—then the equilibrium phases that are predicted by the equilibrium phase diagram may not even appear. Furthermore, there may non-equilibrium phases that do not appear on the phase diagram and have lower molar free energy from than a currently existing phase. If the the non-equilibrium phase has faster nucleation kinetics, then it may appear during the quenching experiment. The essential information which does not appear in the cooling paths is the *rate* of quench.

Such cooling curves are illustrated in the following figure in plots of temperature versus time.

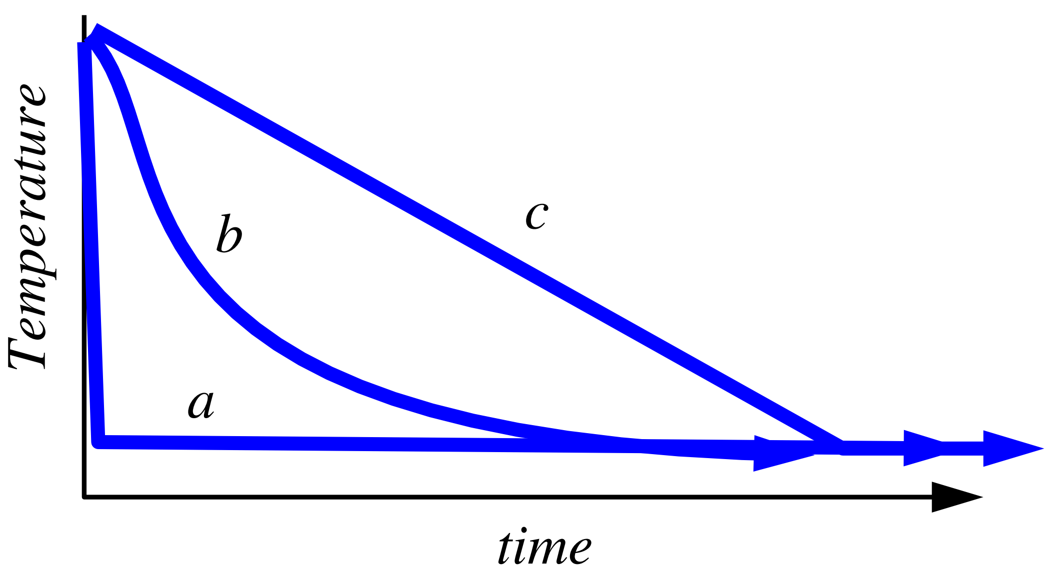

Figure 35-3: Three of a possible infinite number of cooling curves for one of the quenches illustrated in Fig. 35-2.

The three curves are each possible representations for one of the arrows illustrated on the equilibrium phase diagram. They differ in the rates of cooling. The curve a represents a very rapid quench, followed by an anneal at the final temperature. The curve c represents a constant cooling rate to the final temperature.

Consider the rapid quench illustrated by curve a. If the nucleation of the γ-phase is so slow that it cannot occur during the short time that the system spends at temperatures where the δ-phase is in equilibrium with γ, then δ can transform to γ with *no change in composition* at the lower, annealing, temperature. This is an example of a structural transformation which does not require long-range diffusion.

For an example of a phase transformation that requires long-range diffusion, consider the second quench experiment illustrated in the equilibrium phase diagram. If the same type of rapid quench is followed by a long anneal, then the new equilibrium γ-phase forms at a *different composition* which is given by the tie-lines in the phase diagram. In this case, carbon must diffuse out of the parent δ-phase and into the growing γ-phase. Of course, the limiting fraction of the γ-phase which can form is given by the lever rule in the phase diagram.

For both types of transformation, nucleation (or decomposition) of the new phase is required before growth can occur. The relationship between cooling curves, phase diagrams, and transformation kinetics are understood in terms of nucleation and growth kinetics.

Nucleation

Nucleation is a competition between capillary forces that resist the creation of new interfaces and a driving force to grow a more stable phase.

The rate of nucleation depends most strongly on two energetic factors:

- The activation energy required to produce a critical-size nucleus, ΔG^*;
- The rate at which atoms can attach to the growing incipient nucleus. When that nucleus requires a composition change then this rate will depend on an activation energy for migration: ΔG_m.

The equilibrium number of critical size nuclei is given by:

$$N^* = N_{site} \exp(\frac{-\Delta G^*_{site}}{kT}) \tag{35-1}$$

where N_{site} is the number of sites per unit volume at which nucleation can occur and ΔG^*_{site} is the critical nucleation activation energy at a particular *site*. For homogeneous nucleation, N_{site} is roughly the number of atomic sites per unit volume. For heterogenous nucleation, N_{site} is the number of atoms associated particular defects (i.e., surfaces, interfaces, dislocations) per unit volume and ΔG^*_{site} is the (usually reduced) nucleation activation energy.

The overall rate of nucleation, $\dot{N}$, is a product of the number of critical equilibrium nuclei and the frequency that atoms successfully transfer from the parent phase into the nucleus.

$$\dot{N} = (\text{frequency of successful jumps}) N_{site} \exp(\frac{-\Delta G^*_{site}}{kT}) \tag{35-2}$$

$$\dot{N} = \omega N_{site} \exp(\frac{-\Delta G_m}{kT}) \exp(\frac{-\Delta G^*_{site}}{kT}) \tag{35-3}$$

where ω is related to the atomic oscillation frequency.

Since the the activation energy ΔG^*_{site} is a linear combination of a barrier (i.e., surface energy γA) term plus a temperature dependent volumetric driving force $(\Delta G_V V)$ which depends on the undercooling, the activation energy is function of undercooling.

The transfer or migration activation energy is not a strong function of temperature. Therefore, according to equation 35-3, there is a maximum in the nucleation rate at finite undercoolings as illustrated in the figure below:

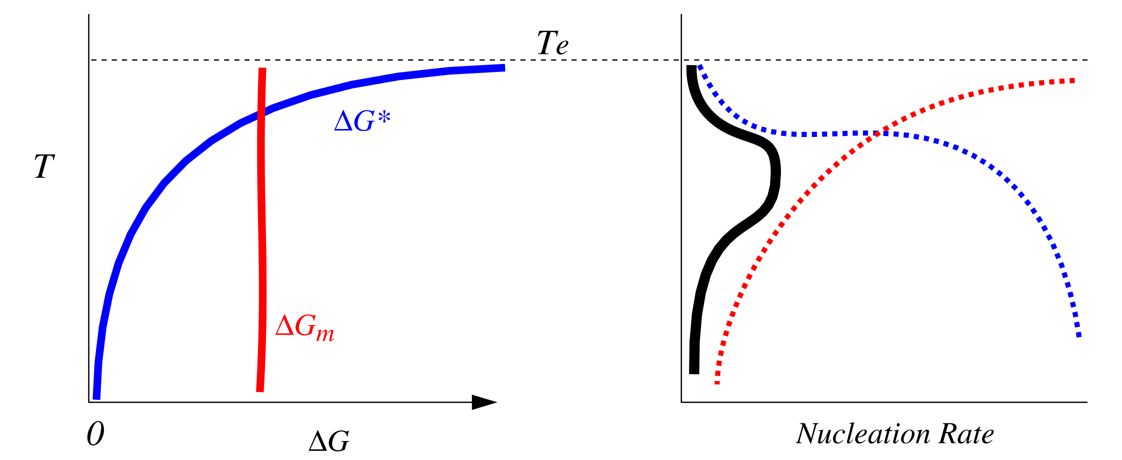

Figure 35-4: The competing effects of activated nucleation versus the rate of transfer to a nucleus.

Growth Once an incipient nucleus has reached its critical size, the capillary forces that restricted the development of the new phase become insignificant and the kinetics for growth are dominated by the limiting kinetic mechanism and the thermodynamic driving forces.

If the transformation is of the type that requires no long-range diffusion, then the rate of growth is controlled by the rate of atomic transfer across the growing phase interface.

However, if long-range diffusion is required, then two different rate-limiting processes can affect growth rate. Each of these are temperature dependent—typically the growth rate is Arrhenius type with growth becoming very slow at low temperatures.

1. **Interface Limited Growth**:In interface limited growth, growth is limited by how fast atoms can transfer across the interface and not the rate at which atoms can be transported to the growing interface. This is equivalent to growth where no long-range diffusion is required and the activation barrier is given by ΔG_m.

   This case applies when the time scale for diffusivity x/D^2 (where x is the distance over which mass is transported to the growing particles) is small compared to thecharacteristic time to transfer across the interface, $1/(\omega \exp -\Delta G_m/kT)$.

2. **Diffusion Limited Growth**: In the diffusion limited case, growth is limited by how fast the necessary chemical species are transfer from the matrix to the growing particles.

   In this case, the growth rate is limited by the diffusivity. As discussed previously in this course. diffusivity also has an Arrhenius relationship:

$$D = D_\circ \exp\left(-\frac{\Delta G_{form}}{kT}\right) \exp\left(-\frac{Q^*}{kT}\right) \tag{35-4}$$

   where the first exponential term gives the concentration of defects necessary for atomic migration and the second term is the activation energy for migration.

   In general, the rate of diffusional transport falls off very quickly with temperature.

Coarsening Consider a rapid quench for 'cooling path 2' in Fig. 35-2. At short times, the microstructural development is that of nucleation and growth of the γ-phase and the depletion of carbon from the δ-phase.. However, according to the phase diagram, all of the driving force for growth will be extinguished when a phase fraction of about 1/2 of the γ-phase is created.

Once the driving force for growth approaches zero, then the only remaining driving forces for microstructural evolution are the capillary driving forces. The capillary driving forces result in coarsening.

Note that the multiple phase region of an equilibrium phase diagram does not imply anything about how finely the phases are spatially configured—only the relative fractions and their compositions. The surface energy, through capillary driving forces, drives coarsening.

Note that the same limiting processes that were discussed for growth can also be applied to coarsening—however, with diminished driving forces. In both cases, a mean-field theory can be formulated for the rate of growth of an average particle.

Grain Growth Consider a quench for 'cooling path 1' in Fig. 35-2. Each bit of nucleated γ-phase will grow until the entire volume is transformed to γ—in other words, growth proceeds until impingement. If each γ-nucleus has a differing crystallographic orientation, then where impingement occurs, a grain boundary will result.

The grain boundaries also represent extra surface energy and a different type of coarsening can occur to reduce the extra surface energy. The process of grain growth is driven by capillary forces associated with grain boundary energy.

In two dimensions, for isotropic grain boundary energy, geometric considerations alone showed that grains with more sides than six would grow at the expense of grains with fewer sides.

By contrast, coarsening of isolated particles is driving by a size effect and grain growth is driven by a geometric effect.

TTT Diagrams

Practical application of nucleation and growth kinetics is often made from Time-Temperature-Transformation (TTT) diagrams. TTT diagrams contain several curves, each representing a particular constant value fraction of total transformed volume after a particular time for a fixed annealing temperature. The diagrams are usually determined by experiment, but their common "C"-shape follows from nucleation and growth kinetics.

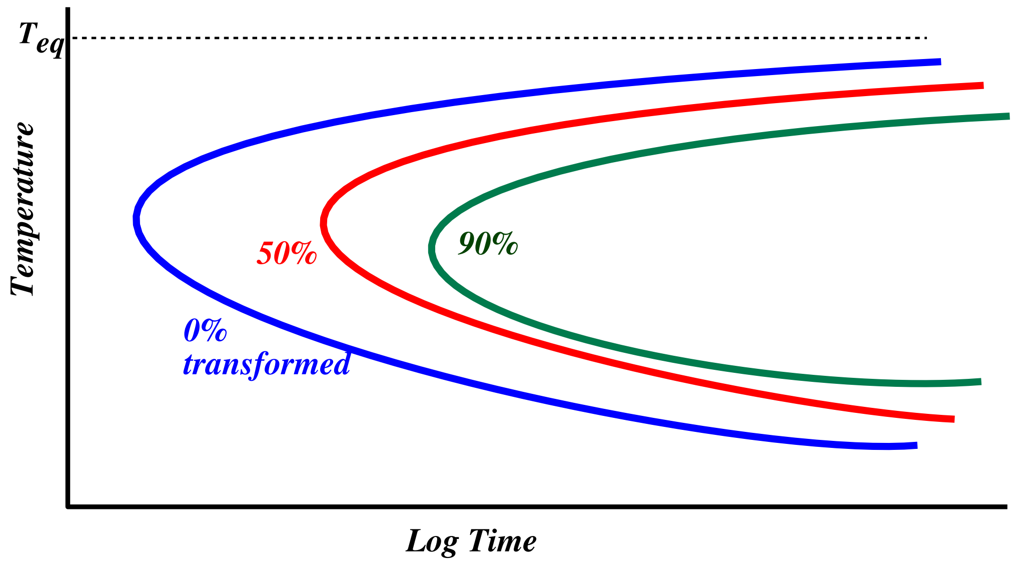

Figure 35-5: Schematic Illustration of a TTT diagram. Each curve represents the volume fraction transformed if held a a particular temperature.

At temperatures just below the equilibrium transformation temperature, transformations take a long time since the nucleation rate is low. (Remember that at low driving forces, that heterogeneous nucleation is expected to dominate.) At large undercoolings, transformation times are limited by transport or by motion of atoms across the transformaion interface.

The displacement of the curves of different volume fraction follow from both JMA kinetics (discussed in the next section) and from lever-rule considerations from the equilibrium phase diagram.

Among the questions that the TTT diagram can help answer are:

- The minimum critical cooling rate required to quench an alloy from a given temperature and suppress the appearance of the equilibrium phase. (*Find the tangent to the 0% transformation curve)*

- The anneal time or cooling schedule required to produce a particular amount of second phase.