eutectoid line is reached, about 0.4 of the sample is α already and 0.6 is still γ. As soon as the eutectoid line is crossed, this remaining γ is converted to the eutectoid microstructure. Note that the proeutectoid α tends to nucleate along the grain boundaries of the γ.

It is also quite common that a ferrous material has a composition above eutectoid, e.g. 1 wt % C. If we considered a cooling curve for that case, we would find something similar to path 2 above, except that the proeutectoid phase would be Fe_3C, but once again below the eutectoid line all the remaining γ would be converted to the eutectoid microstructure.

Note that the conversion of austenite to the eutectoid microstructure tends to originate along grain boundaries, and the layers tend to grow in a direction perpendicular to the grain boundaries. The process is illustrated schematically in Fig. 8.20.

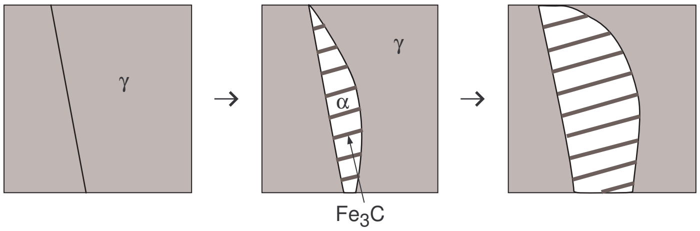

Figure 8.20: Schematic illustration of the growth of the pearlite microstructure.

The first panel in the figure above shows two neighboring grains of γ phase. In the other two panels, you should visualize the C atoms diffusing out of the austenite, away from ferrite, and towards the cementite, as the front of eutectoid material expands.

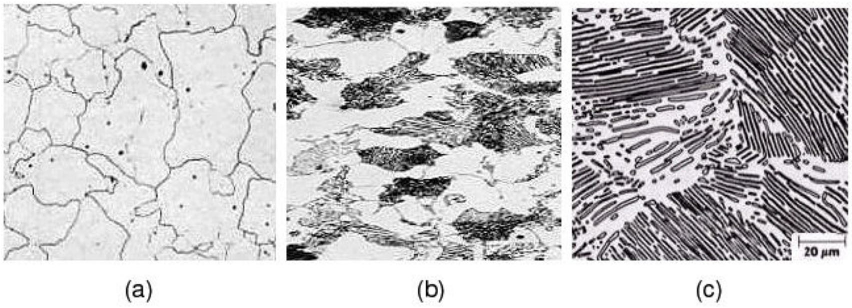

Figure 8.21: Microstructures of ferrite, hypoeutectoid, and eutectoid steel.

Fig. 8.21 displays micrographs of the microstructures of ferrite, a hypoeutectoid steel and a eutectoid steel. The first two panels on Fig. 8.21 are optical micrographs at a lower, unspecified resolution, and the third panel is an electron micrograph with a 20 μm scale bar. In Fig. 8.21a you can see the almost feature-less grain structure of single-phase α ferrite. Fig. 8.21b shows a roughly equal mix of proeutectoid α phase (light) and layered, eutectoid microstructure (dark). The individual pearlite layers are only barely resolved in a few dark areas. Fig. 8.21c shows the fully-developed pearlite microstructure of a eutectoid steel, ferrite being light in color and cementite dark.

8.5.3 Kinetics of Phase Transformation: TTT Diagrams

Previously I emphasized on several occasions that phase diagrams are associated with thermal equilibrium material conditions. That is, a phase diagram describes the state of a material at any point of composition and temperature (X_0, T) when we have waited long enough so that no further changes take place. This implies that if we want to use a phase diagram to follow a change in the state of the material, that change must occur very slowly.

On the other hand, when we cool a material from a higher to a lower temperature, by necessity the change in temperature occurs in a finite time. In practice the process may be too fast for the system to remain equilibrated. Hence we may well end up with the system in a **metastable state**, where it is not truly equilibrated yet not able to change further on a practically relevant time scale.

Moreover, if as a consequence of a change in temperature we observe a phase change, a transformation reaction takes place. This again takes time since the reaction evolves at a finite the rate. All these arguments are meant to show that time must be an important variable in phase transformations.

We encountered some examples of the importance of time in earlier discussions. The issue came up in connection with the solidification of pure substances in Chapter 7 (glass formation; nucleation and growth of crystals (Fig. 7.12)). We also noted briefly an effect of time in the formation of the eutectic microstructure in the Cu-Ag systems (see Fig. 8.12).

Avrami Phase Transformation Kinetics

Now we will have a closer look at the role time plays in phase transformations in general, and we will be particularly interested in transformations in the Fe-C system. First let me point out that the generic process outlined in Chapter 7 for a change of phase, namely the initial formation of independent nuclei of the new phase, followed by the growth of these nuclei, applies to any phase transformation, not just to solidification. For example, when austenite transforms into the pearlite microstructure of ferrite and cementite as the sample is cooled below the eutectoid temperature, nuclei of the new microstructure must form first and then take time to grow and convert the entire sample.

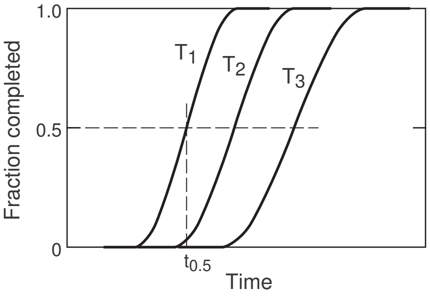

Figure 8.22: Generic time evolution of a phase transformation. Fraction completed vs. time for three different temperatures.

When one follows the progress of this kind of a reaction, a fairly universal behavior is observed (Fig. 8.22). The extent of the reaction typically follows an S-shape as a function of time. The reaction starts almost imperceptibly, with the nucleation phase. This is followed by a time of rapid growth. Finally, the reaction levels off and gradually approaches completion. The shape of this curve and its position on the time axis depend on temperature.

Curves of this type can be expressed conveniently in the form

$$y = 1 - \exp(-kt^n) \tag{8.24}$$

where y indicates the fraction of the transformation completed and k and n are suitable parameters depending on temperature. The parameter n is related to the dimensionality of the problem. In the simplest model of isotropic growth in three dimensions, n is equal to 4. Experimentally, when k and n are treated as empirical fitting parameters, values for n between 1 and 4 have been found. 8.24 is known as the **Avrami equation**.

If you think of the variable y as the amount of reaction product, then the reaction rate would be equal to $\frac{dy}{dt}$. This is displayed qualitatively in the left panel of Fig. 8.23 together with $y(t)$. The right panel of Fig. 8.23 shows the effect of n on the shape of $y(t)$.

You can see that the lower the value of n, the lower is the maximum slope in the middle of the $y(t)$ curve, and thus the lower is the maximum reaction rate. At the same time, for a fixed $t_{0.5}$, the lower the value of n, the longer the reaction takes to go to completion.

From these graphs it is apparent that the most important characteristic of the curve is its midpoint $t_{0.5}$. It is a measure of the time scale over which the transformation occurs. If you set $y = 0.5$ in Eq. 8.24 and take the natural log on both sides, you obtain after some simple algebra:

$$t_{0.5} = \left(\frac{\ln 2}{k}\right)^{\frac{1}{n}} \tag{8.25}$$

Of course, for a more complete characterization of the process, one would also

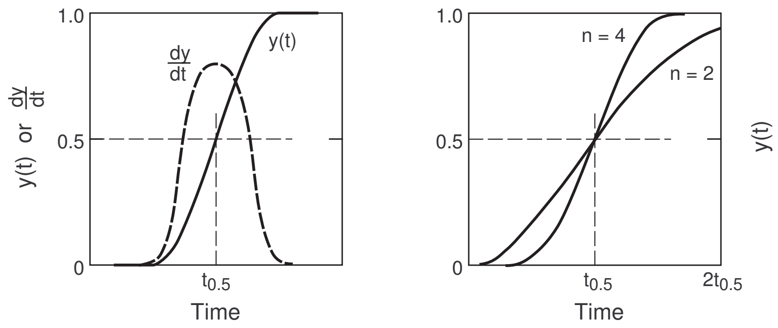

Figure 8.23: Extent of phase transformation, $y(t)$, rate of phase transformation, $\frac{dy}{dt}$, and the effect of the parameter n on the shape of $y(t)$.

need to know, for example, the width of the curve in Fig. 8.22, or the slope at the midpoint.

Generic Time-Transformation Curves

Since the rate of a reaction, in an average sense, is inversely proportional to the time the reaction takes, we will simply identify the inverse of $t_{0.5}$ with *the rate* of the transformation as envisioned in Fig. 7.12:

$$\text{transformation rate} = \frac{1}{t_{0.5}} \tag{8.26}$$

The implication is that if we plotted $t_{0.5}$ vs. T, we would obtain a curve similar to the transformation rate of Fig. 7.12, but flipped upside down (Fig. 8.24). From an experimental point of view, this is more convenient because the extent of a transformation vs. time, i.e. the function $y(t)$, is often easier to observe than the transformation rate.

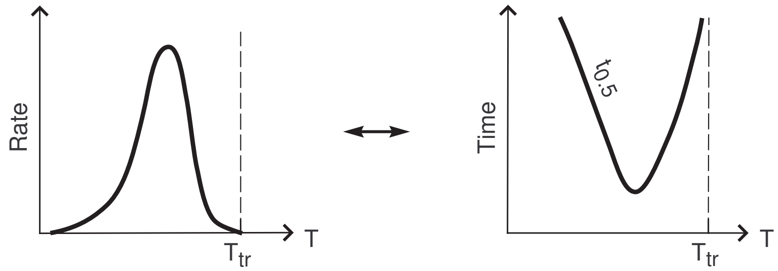

Figure 8.24: Generic phase transformation reaction rate and reaction time curves vs. temperature.

The left panel in Fig. 8.24 reproduces the reaction rate vs. T from Fig. 7.12, and the right panel displays its "inverse", i.e. the time it takes to reach the point of 50% conversion, $y = 0.5$, vs. T. Also note that T_{tr} denotes the temperature below which the transformation can take place.

The form in which such plots are typically used differs slightly from the one displayed in Fig. 8.24. It is common to have the x- and y-axes switched even though the temperature is the real independent variable. In addition, as we are interested in the progress of a transformation with time, we wish to keep track of when the transformation starts and when it ends. These terms are, of course, not very precise. So we will define them with a practical sense: The beginning of the transformation is set to the time when 1 % has been converted, and the end to when 99 % has been converted. Both these conditions can be represented by curves similar to the time curve in Fig. 8.24, as is illustrated in Fig. 8.25:

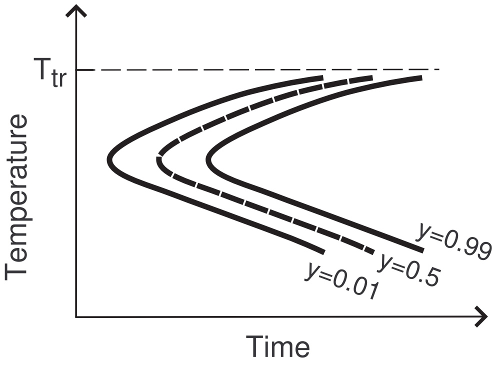

Figure 8.25: Generic time-transformation curves describing the progress of a phase transformation as a function of temperature.

Plots such as the one of Fig. 8.25 are referred to as isothermal transformation diagrams, or **TTT-diagrams** (for time-temperature-transformation). The set of three curves depicts in a somewhat simplified way how a phase transformation proceeds at a given, constant temperature. For example, any point (T,t(T)) on the $y = 0.5$ curve indicates the time t(T) which it takes for the transformation to go to 50% completion at the temperature T.

TTT Diagrams and Microstructures for the Fe-C System

We are now ready to examine the most important TTT-diagram for this book, namely the diagram for the eutectoid reaction of austenite (the γ phase) to the pearlite microstructure made up of ferrite (the α phase) and cementite (the Fe_3C phase). Just as a brief reminder: Austenite is the phase present above 727°C, and we are interested in the alloy with the eutectoid composition of 0.76 wt % C (cf. Fig. 8.19). The TTT-diagram is shown in Fig. 8.26.

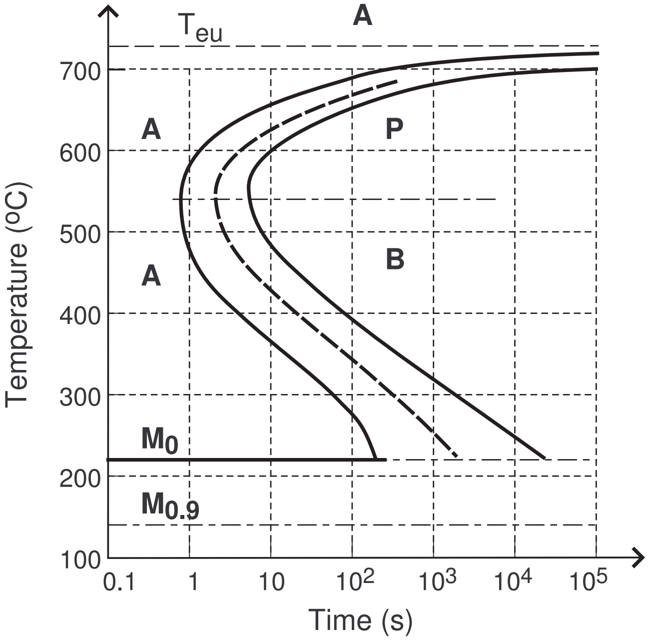

Figure 8.26: TTT diagram for the isothermal transformation of an Fe-C alloy with eutectoid composition from austenite to a low-temperature microstructure.

The main part of the diagram are the three curves indicating the beginning, 50% completion, and the end of the transformation (cf. Fig. 8.25). The curves show a "knee", i.e. a minimum for the time to convert, at around 540°C, where the transformation will be completed in about 7 s. At the eutectoid temperature T_{eu} of 727°C the curves approach infite time, meaning that exactly at T_{eu} no nucleation takes place, and thus no transformation occurs. Nucleation must be initiated by a certain amount of undercooling, just as in the case of solidification in Chapter 7.

Please note the logarithmic scale on the time axis Fig. 8.26. This is chosen so that the figure can display the large range of time necessary to cover this type of transformation.

Fig. 8.26 also incorporates new information regarding this phase transformation. First, the symbol A denotes the austenite phase, and the symbols P, B, and M denote possible microstructures. P stands for ***pearlite***, and the other two will be explained shortly. The dash-dotted horizontal line at the "knee" indicates that only at temperatures of around 540°C or above will the pearlite microstructure P be formed.

The figure is to be read from left to right, at a given temperature. For exam-