

Chapter 10.

Phase Transformations in Metals

10.1 Introduction

- ❖ We may use time and temperature dependencies to **modify** some phase diagrams to develop phase transformation diagrams.
- ❖ It is important to know how to use these transformation diagrams in order **design a heat treatment** for some alloy that will yield the desired room-temperature mechanical properties.
- ❖ Inasmuch as most phase transformations do not occur instantaneously, consideration is given to the dependence of the **reaction progress on time**, or the transformation rate.

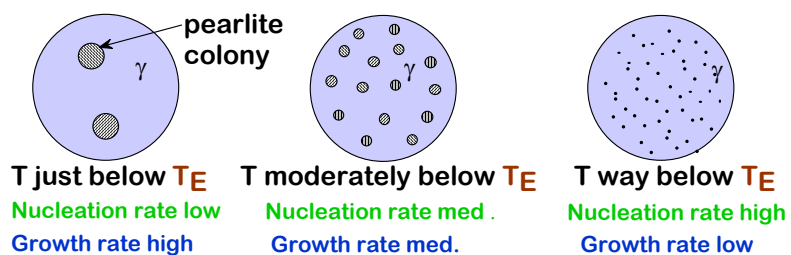
PHASE TRANSFORMATIONS

10.2 Basic Concepts

- ❖ Phase transformations are important in the processing of materials, and usually they involve some **alteration of microstructure**.
- ❖ Three classifications of transformations; three groups:
 1. Simple diffusion-dependent transformation in which there is **no changes** in either the number or composition of the phases present. These include solidification of a pure metal, allotropic transformations, and crystallization and grain growth.
 2. Another diffusion-dependent transformation, there is **some alteration** in phase compositions and often in the number of phases present, the final microstructure ordinarily consists of two phases. The eutectoid reaction is of this type.
 3. Diffusionless transformation, wherein a **metastable** phase is produced.

10.3 The Kinetics of Solid-State Reactions

- ❖ Since most transformations involve the formation of at least one new phase that has a composition (and/or new crystal structure), **some atomic rearrangements via diffusion are required** (diffusion is time dependent).
- ❖ A second impediment to the formation of a new phase is the **increase in energy associated with the phase boundaries** that are created between parent and developed phases.
- ❖ From a microstructural standpoint, phase transformation requires two processes: nucleation and growth. **Nucleation** involves the formation of very small particles (submicroscopic), or nuclei of the new phase, which are capable of growing. **Favorable positions** for the formation of these nuclei are **imperfection sites**, specially grain boundaries.
- ❖ The second stage is **growth**, in which the nuclei increase in size; during this process some volume of the **parent phase disappears**. The transformation reaches completion if growth of these new phase particles is allowed to proceed until the equilibrium fraction is attained.
- ❖ As would be expected, **the time dependency of the transformation rate** (often termed the kinetics of a transformation) is an important consideration in the heat treatment of materials.



- ❖ Figure shown represents the typical kinetic behavior (S shape) for most **solid-state reaction**. Nucleation and growth stage are indicated.

- ❖ For solid-state transformation displaying the kinetic behavior in the figure, the fraction of the transformation (function of time) is (Avrami equation):

$$y = 1 - e^{-kt^n} \quad (10.1)$$

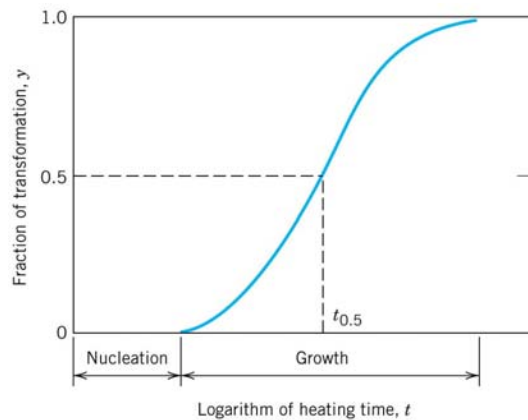


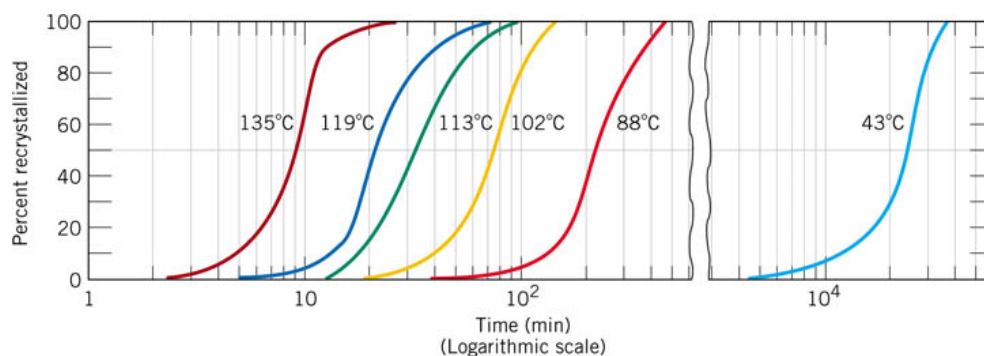
FIGURE 10.1 Plot of fraction reacted versus the logarithm of time typical of many solid-state transformations in which temperature is held constant.

Where k and n are time-independent constants for the particular reaction.

- ❖ **By convention**, the rate of a transformation r is taken as the reciprocal of time required for the transformation to proceed halfway to completion, $t_{0.5}$, or

$$r = \frac{1}{t_{0.5}} \quad (10.2)$$

- ❖ **Temperature** is one variable in a heat treatment process that is subject to control, and it may have a profound influence on the kinetics and thus on the **rate of a transformation**.
- ❖ Figure shown represents the S-shape curves at several temperatures for the recrystallization of pure copper as a function of time.



- ❖ For most reactions and over specific temperature ranges, rate increases with temperature according to

$$r = A e^{-Q/RT} \quad (10.3)$$

Where

R = gas constant

T = absolute temperature (K)

A = preexponential factor (temp-independent constant)

Q = activation energy

10.4 Multiphase Transformations

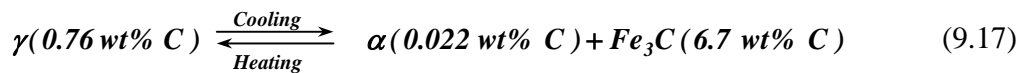
- ❖ To describe phase transformations that occur during cooling, equilibrium phase diagrams are inadequate if the transformation rate is slow compared to the cooling rate.
- ❖ The rate of approach to equilibrium for solid system is so slow that true equilibrium structures are **rarely** achieved.
- ❖ Equilibrium conditions are maintained only if heating or cooling is carried out at extremely slow and unpractical rates. For other than equilibrium cooling, transformations are shifted to lower temperatures than indicated by the phase diagram.
- ❖ These phenomenon are termed supercooling and superheating, respectively.
- ❖ For example, for normal cooling rate the iron-carbon eutectoid reaction is typically displaced 10 to 20°C below the equilibrium transformation temperature.

MICROSTRUCTURAL AND PROPERTY CHANGES IN IRON-CARBON ALLOYS

10.5 Isothermal Transformation Diagrams (Time-temperature-transformation diagrams)

A. Pearlite

- ❖ Consider again the iron-iron carbide **eutectoid** reaction



which is fundamental to the development of microstructure in steel alloys.

- ❖ Upon cooling, **austenite transforms** to a ferrite phase and cementite.
- ❖ Temperature plays an important role in the rate of the austenite-to-pearlite transformation. The temperature dependence for an iron-carbon alloy of eutectoid composition is indicated in the figure shown (S shape curves of the percentage transformation versus the logarithm of time) at three different temperatures for each curve.

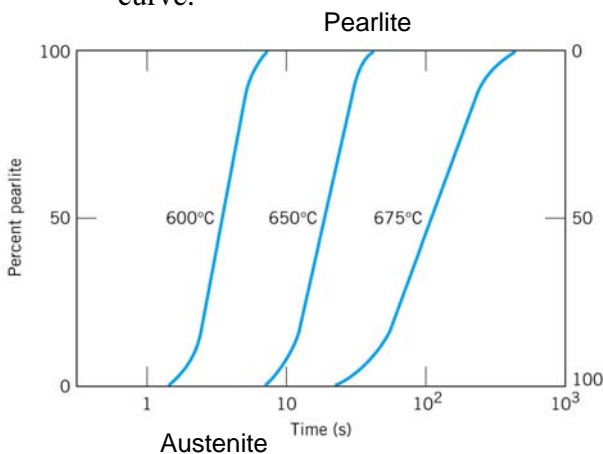
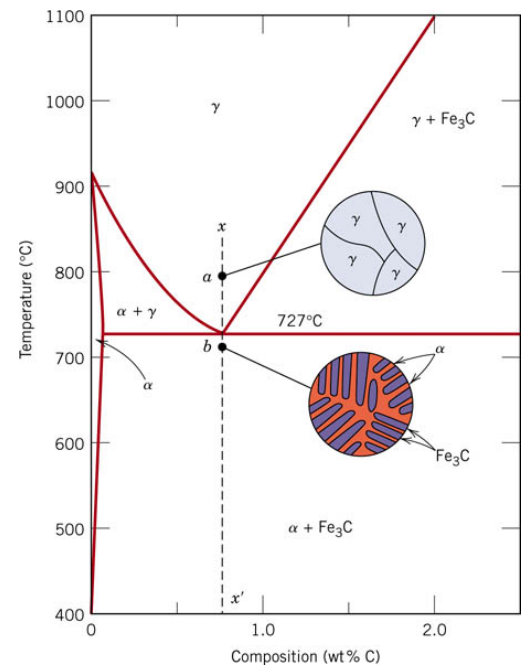


FIGURE 10.3 For an iron-carbon alloy of eutectoid composition (0.76 wt% C), isothermal fraction reacted versus the logarithm of time for the austenite-to-pearlite transformation.



- ❖ For **each curve**, data were collected after rapidly cooling a specimen composed of 100% austenite to the temperature indicated, the temperature was maintained constant throughout the course of the reaction.

- ❖ A more convenient way of representing both the time and temperature dependence of this transformation is in the bottom part of the figure shown.
- ❖ Two solid curves are plotted: one represents the time required at each temperature for the start of the transformation; the other is for the transformation conclusion.
- ❖ The dashed curve corresponds to 50% of transformation completion.
- ❖ These curves were generated from a series of plots of the percentages transformation versus the logarithm of time taken over a range of temperatures.

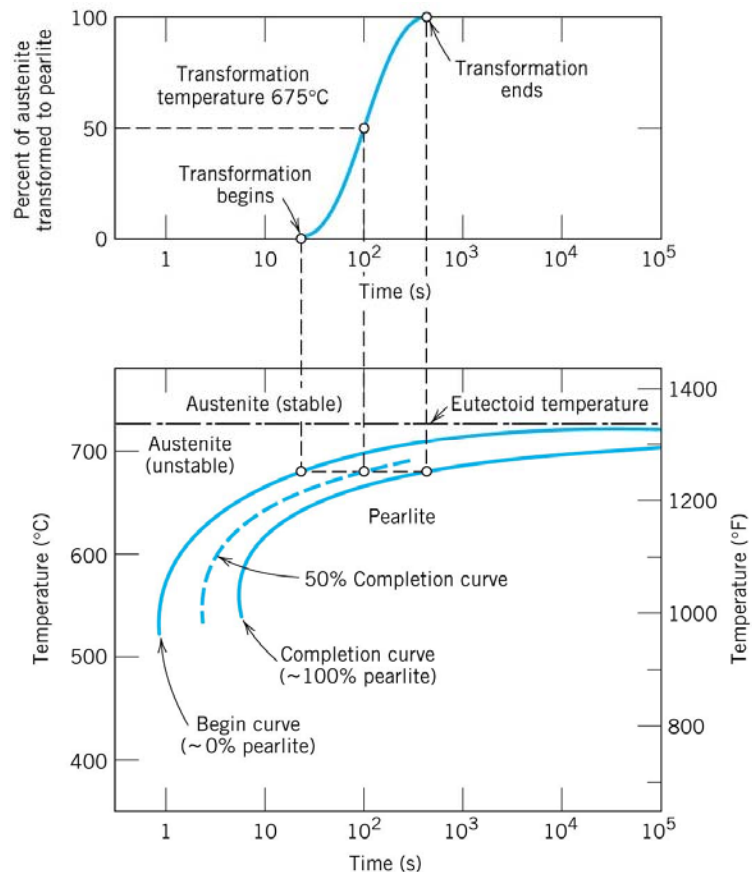


FIGURE 10.4 Demonstration of how an isothermal transformation diagram (bottom) is generated from percentage transformation-versus-logarithm of time measurements (top). [Adapted from H. Boyer, (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 369.]

- ❖ Interpretation of this diagram: note first that the eutectoid temperature (727°C) is indicated by a horizontal line; at temperatures above the eutectoid and for all times, only austenite will exist.
- ❖ The start and finish curves are nearly parallel, and they approach the eutectoid line asymptotically.
- ❖ To the left of the start curve, only austenite (unstable) will be present whereas to the right of the finish curve, only pearlite will exist. In between, the austenite is in the process of transforming to pearlite, and thus both microstructures will be present. The dashed curve corresponds to 50% of transformation completion.
- ❖ The shorter the time the higher the rate of transformation (inversely proportional, Eq. 10.2). So at temperature just below the eutectoid, very long times are required for the 50% transformation, and therefore the reaction rate is very slow (order of 10⁵ s).
- ❖ The transformation rate increases with decreasing temperature such that at 540°C only 3s is required for the reaction to go to 50% completion.

- ❖ **Constraints:** above plot is valid only for and iron-carbon alloy of **eutectoid composition**; also, plots accurate only for transformations in which the **temperature of the alloy is held constant throughout the duration of the reaction.**
- ❖ Conditions of constant temperature are termed **isothermal**. So, above diagram is referred to as **isothermal transformation diagrams (IT)**; or sometimes as **time-temperature transformation (TTT)** diagrams.
- ❖ Example for actual isothermal heat treatment curve (ABCD) is shown next:
 - Eutectoid composition, $C_o = 0.76 \text{ wt\% C}$
 - Begin at $T > 727^\circ \text{C}$
 - Rapidly cool of austenite to 625°C and hold isothermally (BCD).
- ❖ Transformation of austenite to pearlite begins at point C (after $\sim 3.5\text{s}$) and reaches completion by about 15s at point D.
- ❖ The thickness ratio of the ferrite and cementite layers in pearlite is ~ 8 to 1. However, layer thickness depends on the temperature at which isothermal transformation occurs:
 - At temperatures just below the eutectoid, thick layers of both ferrite and cementite are produced; called **coarse pearlite**, forming at the right of the completion curve. Here, diffusion rates are relatively high.
 - With decreasing temperature, carbon diffusion rate decreases, and the layers become progressively thinner, in the vicinity of 540°C , termed **fine pearlite**.

- Eutectoid composition, $C_o = 0.76 \text{ wt\% C}$.
- Begin at $T > 727^\circ \text{C}$
- Rapidly cool to 625°C and hold isothermally.
- Cooling to lower temperatures results in finer microstructures

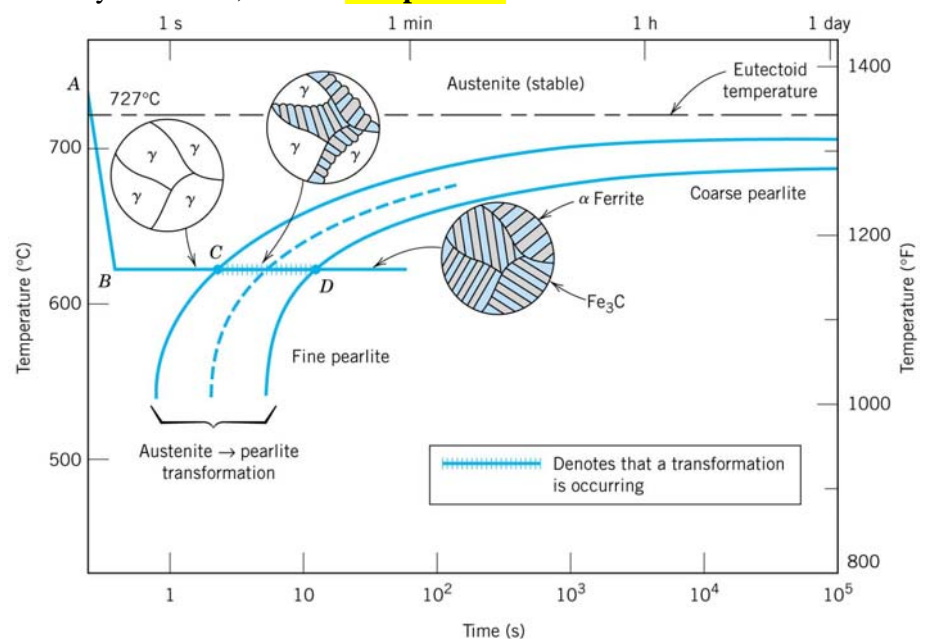
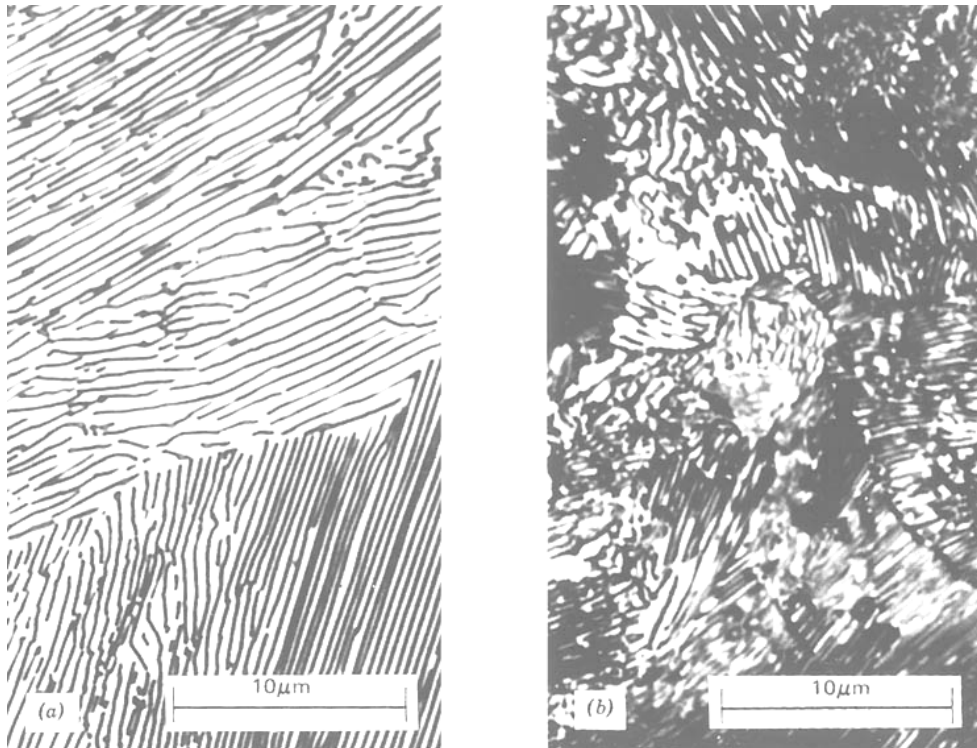
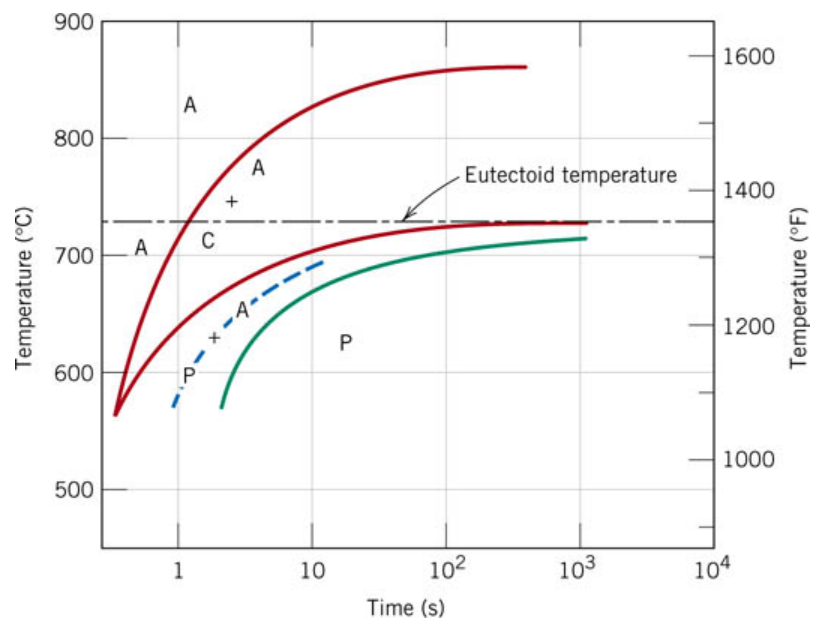


FIGURE 10.5 Isothermal transformation diagram for a eutectoid iron-carbon alloy, with superimposed isothermal heat treatment curve (ABCD). Microstructures before, during, and after the austenite-to-pearlite transformation are shown. [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 28.]

- ❖ Figure next shows photomicrographs of a) coarse pearlite and b) fine pearlite for eutectoid composition. (3000x).



- ❖ For iron-carbon alloys of other composition, a proeutectoid phase (either ferrite or cementite) will coexist with pearlite (section 9.18). Thus additional curves corresponding to a proeutectoid transformation must be included on the isothermal transformation diagram. Next figure shows a portion of one such diagram for 1.13 wt% alloy.



B. Bainite

- ❖ Other microconstituents may be produced from austenite transformation, such as **bainite**, which consists of **ferrite and cementite phases**, and thus diffusional processes are involved in its formation.
- ❖ Bainite forms as needles or plates; depending on the temperature of transformation; Very **fine microstructure** (visible only by using electron microscopy).
- ❖ Shown is an **electron micrograph** that shows a grain of bainite (positioned diagonally from lower left to upper right); it is composed of needles of ferrite that are separated by elongated particles of the Fe_3C phase.
- ❖ The phase that surrounds the needles is martensite. No proeutectoid phases forms with bainite.
- ❖ In the IT diagram, bainite forms at temperatures below those at which pearlite forms.
- ❖ The IT diagram of iron-carbon alloy of eutectoid composition has been extended to lower temperatures, as shown, C-shaped curves have a "**nose**" at point N where the rate of transformation is a maximum.

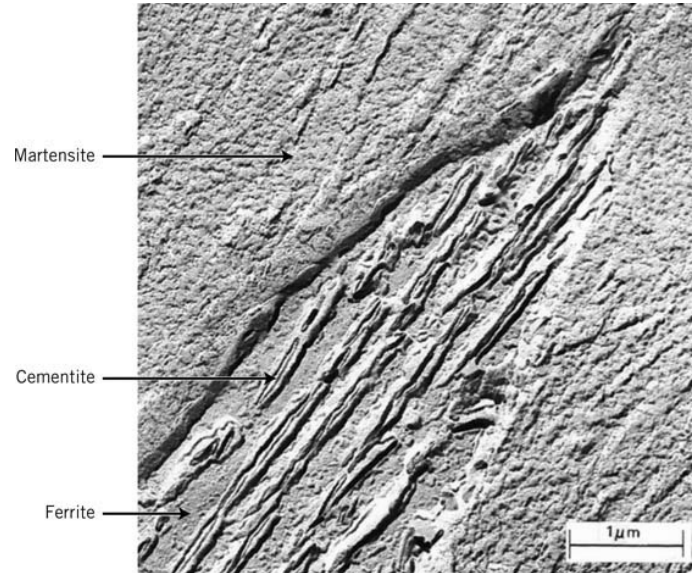
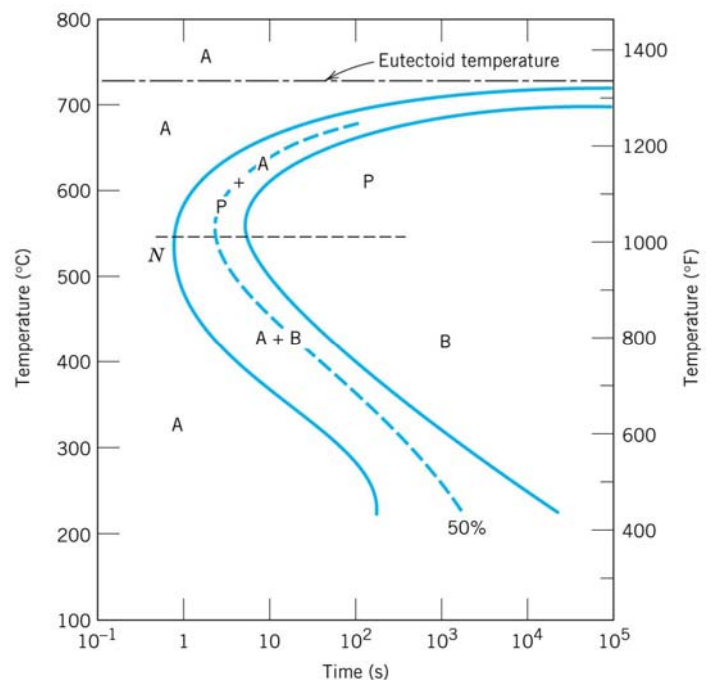


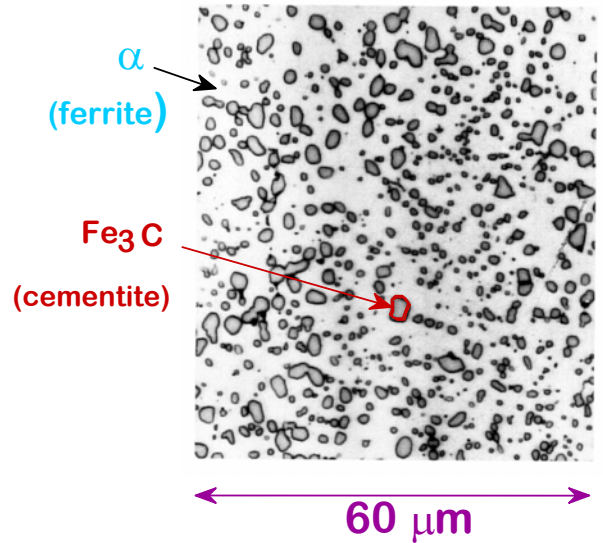
FIGURE 10.9
Isothermal transformation diagram for an iron-carbon alloy of eutectoid composition, including austenite-to-pearlite (A-P) and austenite-to-bainite (A-B) transformations. [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 28.]



- ❖ Note that **pearlite** forms between **540 and 727°C**; **bainite** forms between **215 to 540°C**.
- ❖ Once some portion of an alloy has transformed to either pearlite or bainite, transformation to the other microconstituent **is not possible** without reheating back to **austenite**.

C. Spheroidite

- ❖ If a steel alloy having either pearlite or bainite microstructure is **heated to, and left at**, a temperature **below** the eutectoid for a sufficiently long period of time – for example, at about **700°C for between 18 and 24 hrs** – yet other microstructure will form; called spheroidite; as shown.
- ❖ Instead of forming pearlite or bainite, The Fe₃C phase appears as sphere-like particles embedded in a continuous α phase matrix. This transformation has occurred by additional carbon diffusion with no change in the composition or relative amounts of ferrite and cementite phases.



D. Martensite

- ❖ When austenitized iron-carbon alloys are rapidly cooled (or quenched) to a relatively low temperature (in the vicinity of the ambient) martensite is formed.
- ❖ Martensite is a nonequilibrium single phase structure that results from a diffusionless transformation of austenite.
- ❖ Martensitic transformation occurs when the quenching rate is rapid enough to prevent carbon diffusion. Any diffusion whatsoever will result in the formation of ferrite and cementite phases.
- ❖ This transformation occurs in such a way that the FCC austenite experiences a polymorphic transformation to a body-centered tetragonal (BCT) martensite. See the unit cell.
- ❖ Many steels retain their martensitic structure almost indefinitely at room temperature.
- ❖ Since the martensitic transformation does not involve diffusion, it occurs almost instantaneously; the martensite grains nucleate and grow at a very rapid rate. Thus the martensitic transformation rate, for all practical purposes, is time independent.
- ❖ Martensite grains take on a plate-like or needle-like appearance, as indicated in the figure. The white phase is austenite that failed to transform during the rapid quench.

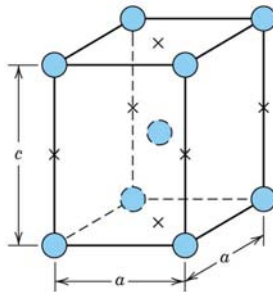
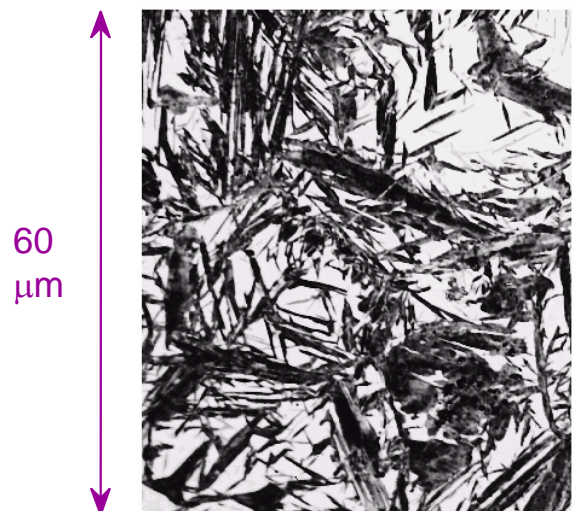


FIGURE 10.11 The body-centered tetragonal unit cell for martensitic steel showing iron atoms (circles) and sites that may be occupied by carbon atoms (crosses). For this tetragonal unit cell, $c > a$.

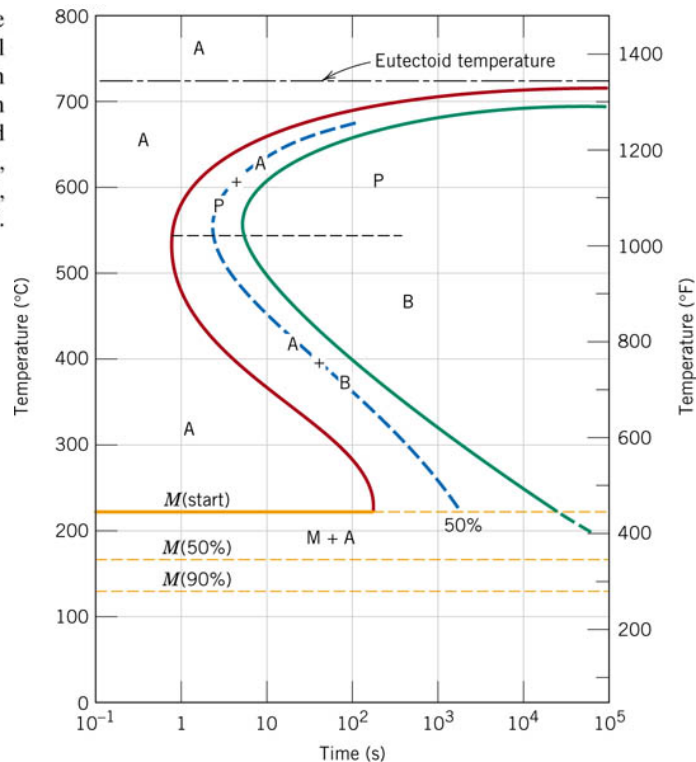


Martensite needles

Austenite

- ❖ The austenite-to-martensite transformation is presented in the IT diagram shown.

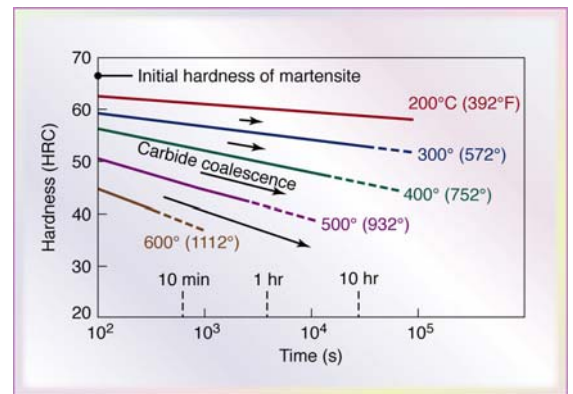
FIGURE 10.13 The complete isothermal transformation diagram for an iron–carbon alloy of eutectoid composition: A, austenite; B, bainite; M, martensite; P, pearlite.



- ❖ The beginning of this transformation is presented by a horizontal line designated M(start). Two other dashed lines labeled M(50%) and M(90%) indicating the percentages of austenite-to-martensite.
- ❖ The horizontal and linear character of these lines indicates that the martensitic transformation is independent of time, it is a function only of the temperature to which the alloy is quenched or rapidly cooled. Such a transformation is termed an athermal transformation.
- ❖ Consider an alloy of eutectoid composition is very rapidly cooled from a temperature above 727°C to say 165°C. From the IT diagram we note that 50% of the austenite will immediately transform to martensite; and as long as this temperature is maintained, there will be no further transformation.
- ❖ Steels in which carbon is the prime alloying element are termed **plain carbon steels**, whereas **alloy steels** contain appropriate concentration of other elements (e.g., Cr, Ni, Mo, and W).
- ❖ **E. Retained Austenite:**
 - ✓ If the temperature to which the alloy is quenched is not sufficiently low, only a portion of the structure is transformed to martensite. The rest is **retained austenite**, which is visible as white areas in the structure along with the dark, needlelike martensite.
 - ✓ Retained austenite can cause dimensional instability and cracking, and it lowers the hardness and strength of the alloy.
- ❖ **F. Tempered Martensite:**
 - ✓ Martensite is tempered in order to improve its mechanical properties.
 - ✓ Tempering is a heating process by which hardness is reduced and toughness is improved.

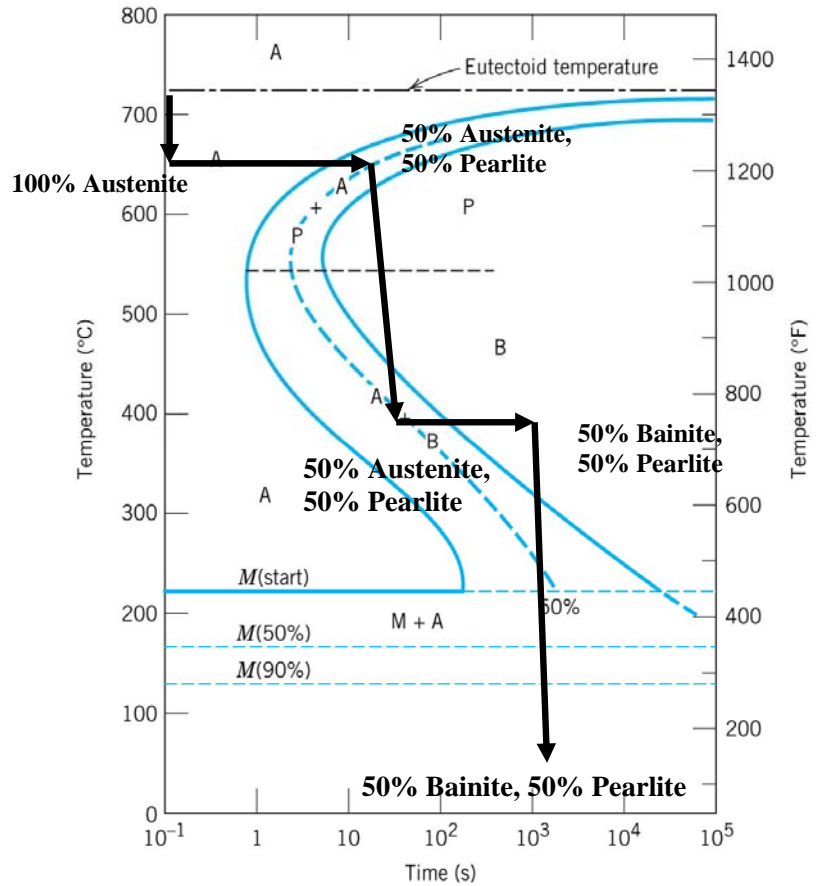
- ✓ The BCT martensite is heated to an intermediate temperature, typically $150^{\circ}\text{C} - 650^{\circ}\text{C}$, where it decomposes to a two-phase microstructure consisting of BCC alpha ferrite and small particles of cementite.
- ✓ With increasing tempering time and temperature, the hardness of the tempered martensite decreases (see Fig next). The reason is that the cementite particles coalesce and grow, and the distance between the particles in the soft ferrite matrix increases as the less stable and smaller carbide particles dissolve.

Figure shows that hardness of tempered martensite as a function of tempering time for the 1080 steel quenched to 65 HRC. Hardness decreases because the carbide particles coalesce and grow in size, thereby increasing the interparticle distance of the softer ferrite



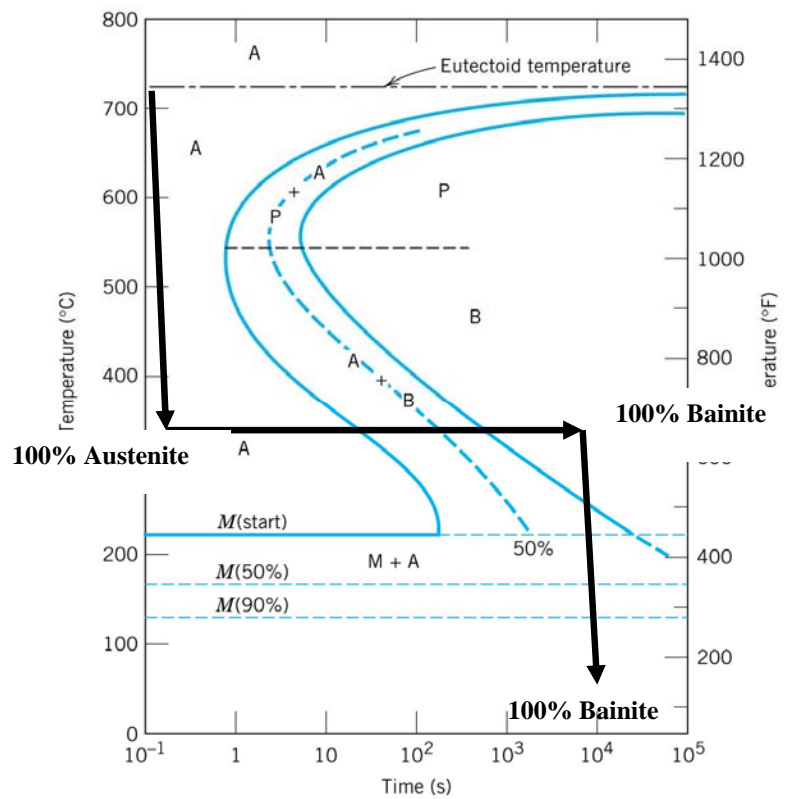
COOLING EX:

- ✓ Rapidly cool to 650o C
- ✓ Hold for 10 seconds
- ✓ Rapidly cool to 400o C
- ✓ Hold for 1000 seconds
- ✓ Rapidly cool to room T



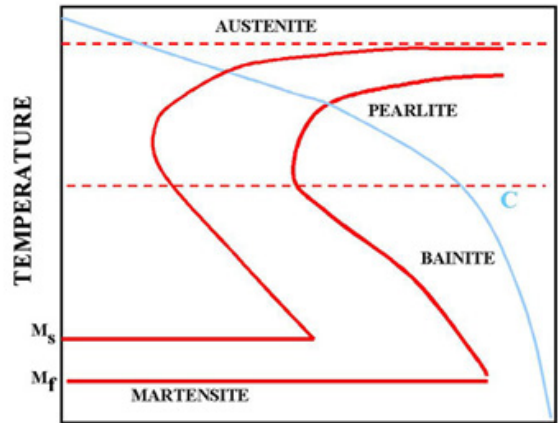
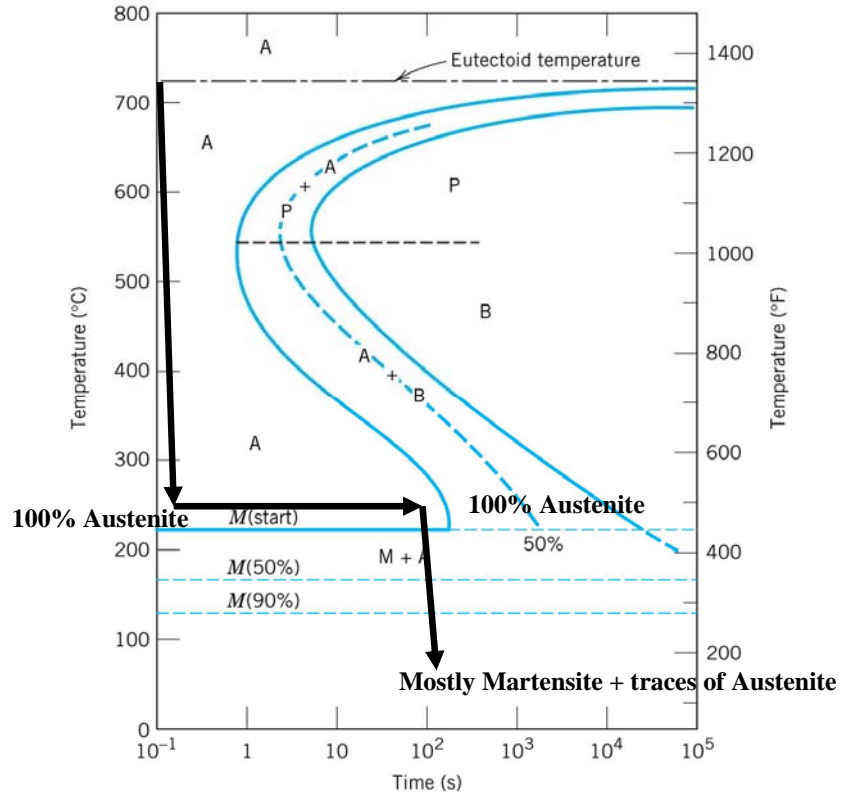
❖ COOLING EX:

- ✓ Rapidly cool to 350o C
- ✓ Hold for 10000 seconds
- ✓ Rapidly cool to room T

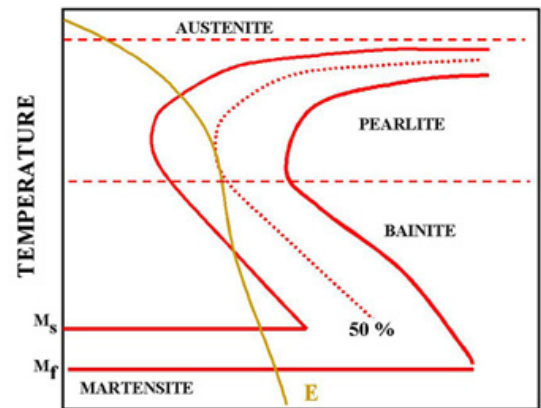


❖ **COOLING EX:**

- ✓ Rapidly cool to 250o C
- ✓ Hold for 100 seconds
- ✓ Rapidly cool to room T



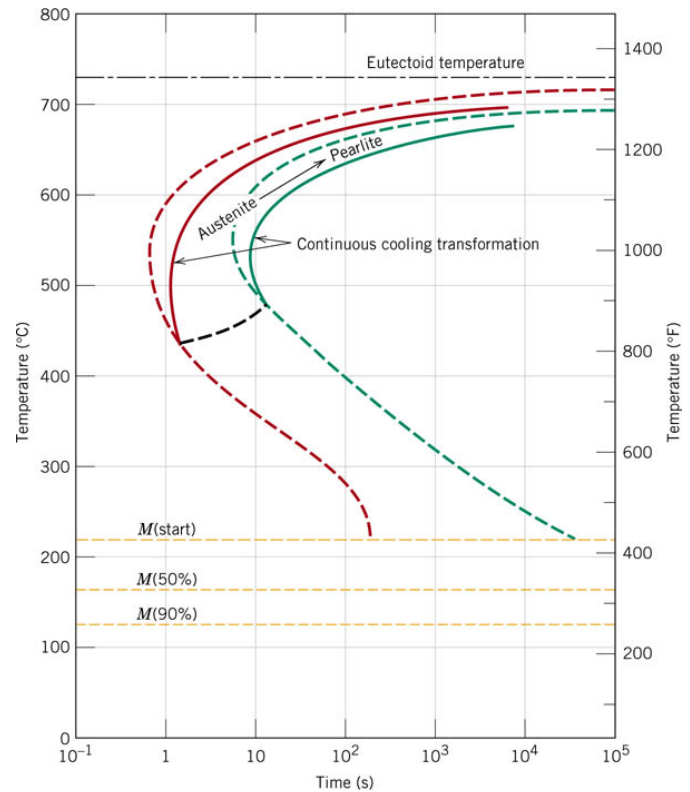
PRODUCT OF COOLING CURVE (C) : PEARLITE



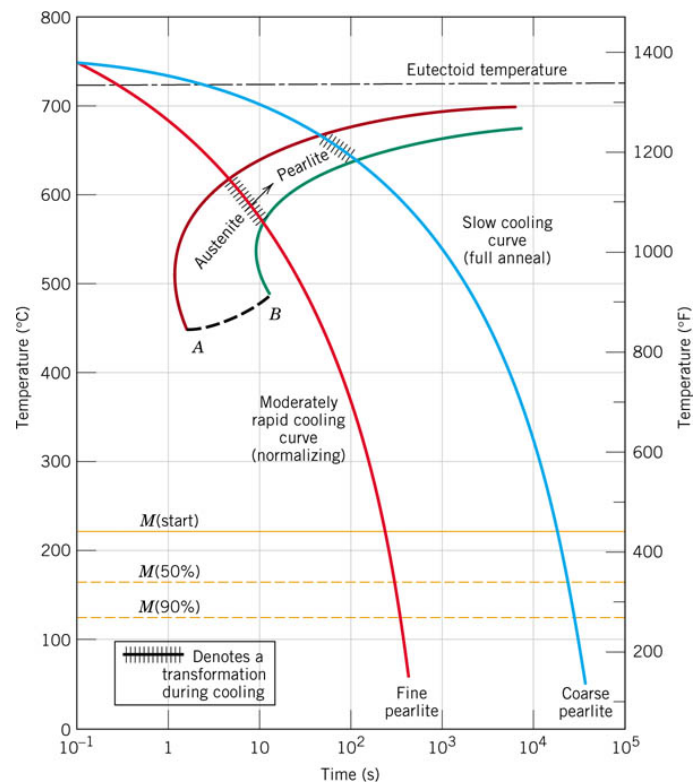
PRODUCT OF COOLING CURVE (E) : 50 % PEARLITE, 50 % MARTENSITE

10.6 Continuous Cooling Transformation Diagrams (CCT)

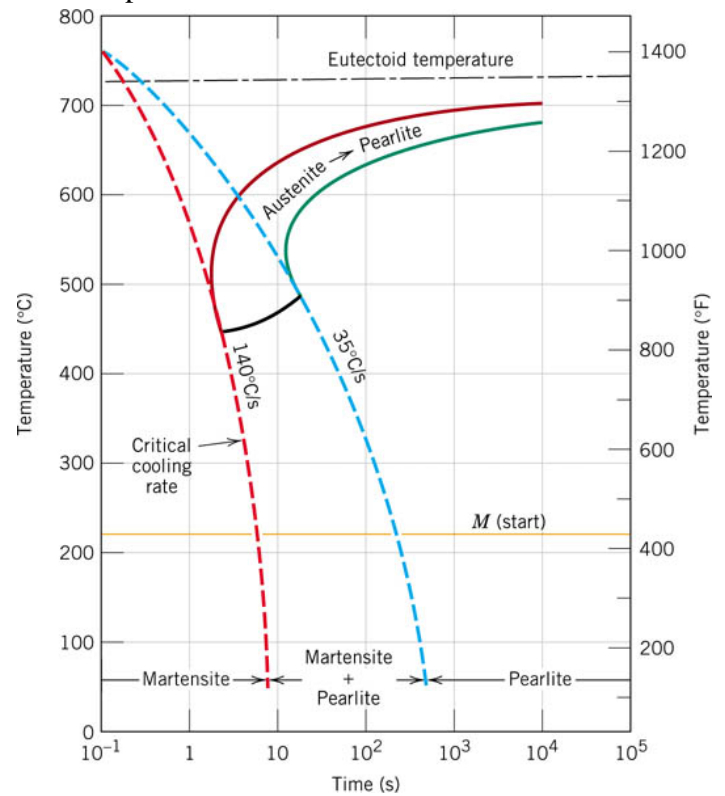
- ❖ Isothermal transformation diagram is valid only for constant temperature; it must be modified for continuous cooling.
- ❖ For continuous cooling, the time required for a reaction to begin and end is delayed. So IT curves are shifted to longer times and lower temperatures; as shown. (iron-carbon at eutectoid composition).



- ❖ Two cooling curves are superimposed and labeled in the next figure.
- ❖ Normally, bainite will not form when an alloy of eutectoid composition (or any plain carbon steel) is continuously cooled to room temperature. This is because all the austenite will have transformed to pearlite by the time the bainite transformation has become possible.
- ❖ Thus, the region representing the austenite-pearlite transformation terminates just below the nose (curve AB).



- ❖ For the continuous cooling of a steel alloy, there exists a critical quenching rate, which represents the minimum rate of quenching that will produce a totally martensite structure, see next figure.
- ❖ Note that only martensite will exist for quenching rates greater than the critical; in addition, there will be a range of rates over which both pearlite and martensite are produced. So, for any cooling curve passing through AB, the transformation ceases at the point of intersection. If we keep cooling, the unreacted austenite begins transforming to martensite upon crossing the $M(\text{start})$ line.
- ❖ For low cooling rates a totally pearlitic structure develops.



10.7 Mechanical Behavior of Iron-Carbon Alloys (Reading)

