Lecture 10

Phase Diagrams: Development of Microstructure and Alteration of Mechanical Properties

The Kinetics of Phase Transformations

- Process of phase transformation occurs in two stages:
  - Nucleation
    - The initial stage in a phase transformation. It is evidenced by the formation of small particles of the new phase that can grow.
  - Growth
    - During a phase transformation and after nucleation, the increase in size of a particle of a new phase.

The Kinetics of Phase Transformations

- Nucleation
  - Two types: Homogeneous and Heterogenous
    - Homogenous
      - Nuclei appear uniformly
    - Heterogeneous
      - Nuclei can appear in insoluble impurities, grain boundaries and dislocations.

The Kinetics of Phase Transformations

- Homogenous Nucleation
  - Free energy – defined in lecture 9.
    - We care about the change in Gibbs free energy ΔG. A negative value of ΔG means a transformation can occur.
  - Consider solidification of a pure material
    - Assume spherical shape to nuclei of radius r.
    - $\Delta G =$ volume free energy + surface free energy
    - $\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$
    - Critical radius $r^* = -\frac{2\gamma}{\Delta G_v}$
      - Corresponds to $G_v^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$, which is the activation energy to form a stable nuclei
    - $\Delta G_v = \Delta H_f \frac{(T_m - T)}{T_m}$, where ΔH_f is the latent heat of fusion and T_m is the equilibrium solidification temperature in Kelvin.
    - As temperature decreases, so does the critical radius and Gibbs energy becomes more negative.

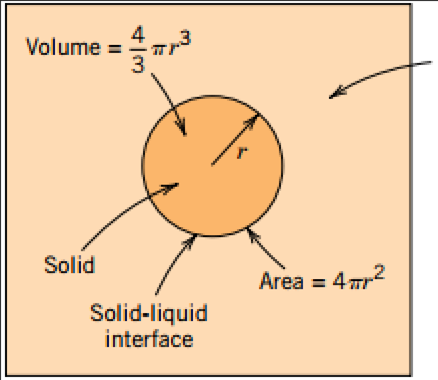
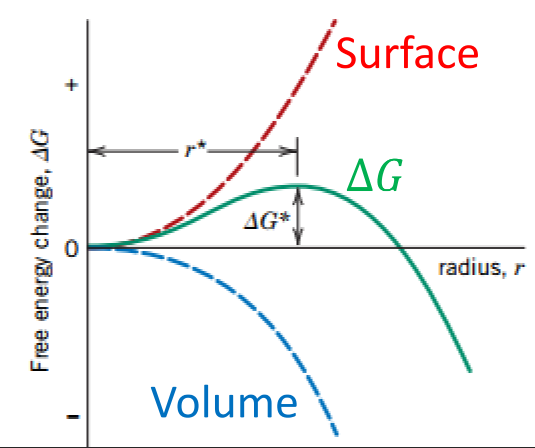


Figure 10.1 Schematic diagram showing the nucleation of a spherical solid particle in a liquid.



The Kinetics of Phase Transformations

- Homogenous Nucleation
  - Number of stable nuclei expressed by an Arrhenius equation

$$n^* = K_1 \cdot e^{-\frac{\Delta G^*}{k_b T}}$$

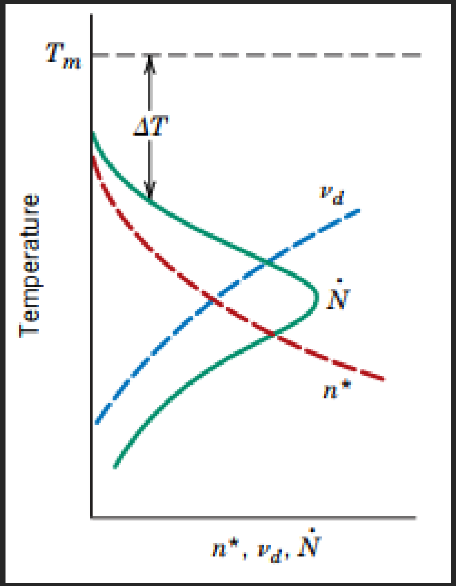
  - Diffusion also plays a role:

$$\nu_d = K_2 e^{-\frac{Q_d}{RT}}$$

    - Q_d activation energy for diffusion
    - K_2 is a constant
  - Nucleation rate expression for homogenous nucleation

$$\dot{N} = K_3 n^* \nu_d$$

    - K_3 is the number of atoms on a nucleus surface.



The Kinetics of Phase Transformations

- Heterogeneous Nucleation
    - Its easier for nucleation to occur preexisting surfaces and interfaces.
    - Consider nucleation on a flat surface
        - $\gamma_{IL} = \gamma_{SI} + \gamma_{SL}\cos(\theta)$
    - Critical radius and activation energy for heterogenous nucleation

$$r^* = -\frac{2\gamma_{SL}}{\Delta G_v}$$

$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2}\right)S(\theta)$$

- $\Delta G_{het}^* = \Delta G_{homo}^* S(\theta)$, where $S(\theta)$ ranges from 0 to 1.

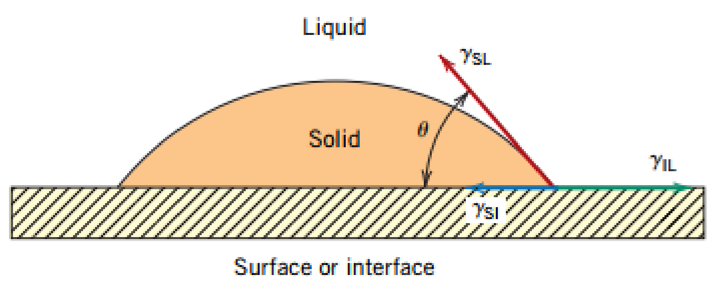


Figure 10.5 Heterogeneous nucleation of a solid from a liquid. The solid–surface (γ_{SI}), solid–liquid (γ_{SL}), and liquid–surface (γ_{IL}), interfacial energies are represented by vectors. The wetting angle (θ) is also shown.

The Kinetics of Phase Transformations

- Growth
  - This stage begins when $r_{embryo} > r^*$
  - Growth rate

$$\dot{G} = Ce^{-\frac{Q}{k_b T}}$$

- The overall rate of transformation is some product of the growth rate and nucleation rate.
  - Transformations happening at temperatures close to equilibrium temperature correspond to low nucleation and high growth rate, leading to few but large grains.
  - Inversely proportional to time required for some degree of completion.

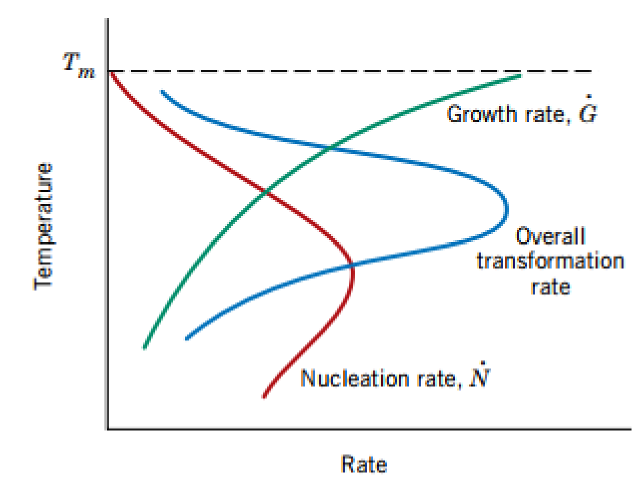


Figure 10.8 Schematic plot showing curves for nucleation rate ($\dot{N}$), growth rate ($\dot{G}$), and overall transformation rate versus temperature.

The Kinetics of Phase Transformations

- Kinetic Considerations of Solid-State Transformations
  - Kinetics
    - The study of reaction rates and the factors that affect them
  - Avrami Equation
    - Dependence of fraction of transformation on time.
    - $y = 1 - e^{-kt^n}$
      - k and n are constants for the reaction.
    - The rate of transformation is

$$rate = \frac{1}{t_{0.5}}$$

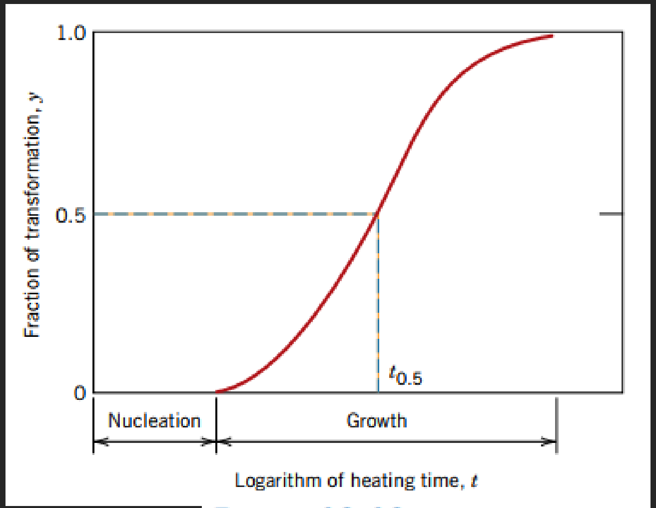


Figure 10.10 Plot of fraction reacted versus the logarithm of time typical of many solid-state transformations in which temperature is held constant.

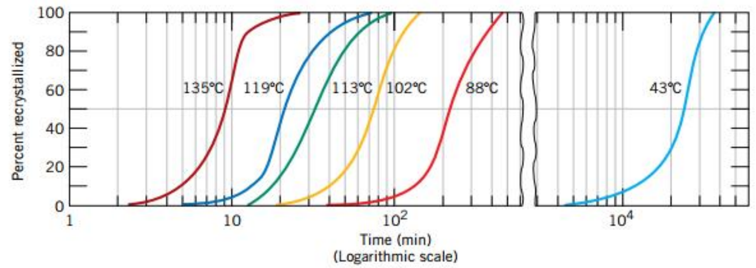


Figure 10.11 Percent recrystallization as a function of time and at constant temperature for pure copper. (Reprinted with permission from *Metallurgical Transactions*, Vol. 188, 1950, a publication of The Metallurgical Society of AIME, Warrendale, PA. Adapted from B. F. Decker and D. Harker, "Recrystallization in Rolled Copper," *Trans. AIME*, **188**, 1950, p. 888.)

Microstructural and Property changes in Iron-Carbon Alloys

- Isothermal Transformation Diagrams
  - Pearlite
    - Eutectoid reaction for the iron-iron carbide system fundamental to the development of microstructure in steel alloys.
      $\gamma(0.76\ wt\%C) \leftrightarrow \alpha(0.022\ wt\%C) + Fe_3C\ (6.70\ wt\%C)$
  - Isothermal Transformation diagrams (T-T-T plots)
    - A plot of temperature versus the logarithm of time for a steel alloy of definite composition. Used to determine when transformations begin and end of an isothermal heat treatment of a previously austenitzed alloy.
    - Different compositions will have different TTT plots.

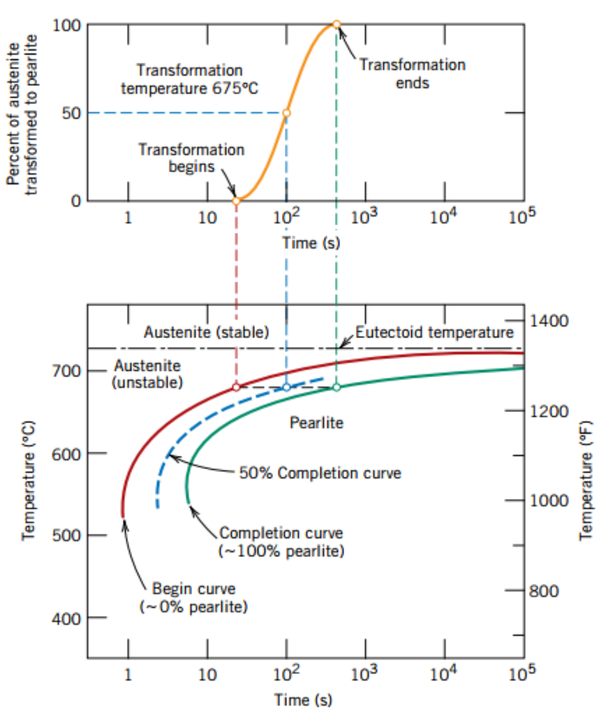


Figure 10.13 Demonstration of how an isothermal transformation diagram (bottom) is generated from percentage transformation-versus-logarithm of time measurements (top). [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Microstructural and Property changes in Iron-Carbon Alloys

- Isothermal Transformation Diagrams
  - Pearlite
  - Isothermal Transformation diagrams (T-T-T plots)
    - Line A-B: Rapid cooling
    - Isothermal treatment at line BCD
    - Coarse Pearlite
      - Pearlite for which the alternating ferrite and cementite layers are thick
    - Fine Pearlite
      - Pearlite I which the alternating ferrite and cementite layers are relatively thin.

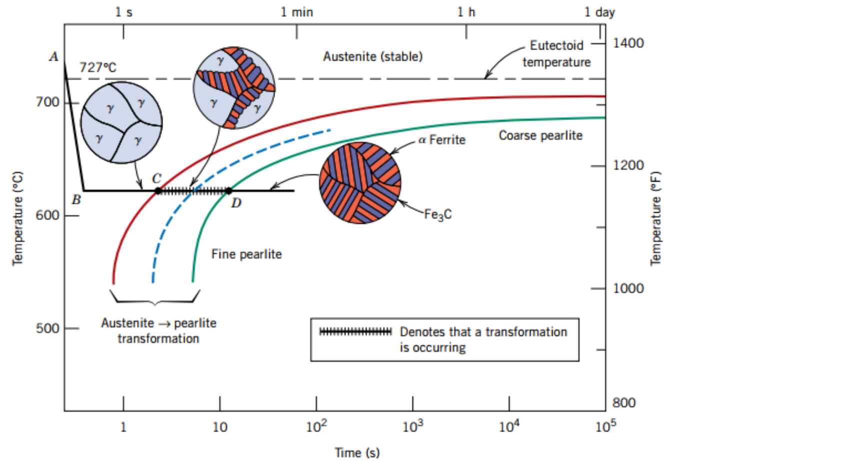


Figure 10.14 Isothermal transformation diagram for a eutectoid iron–carbon alloy, with superimposed isothermal heat treatment curve (*ABCD*). Microstructures before, during, and after the austenite-to-pearlite transformation are shown.
[Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Microstructural and Property changes in Iron-Carbon Alloys

- Bainite
  - An austenitic transformation product found in some steel and cast irons. It forms at temperatures between those at which pearlite and martensite transformations occur. The microstructure consists of a α-ferrite and a fine dispersion of cementite.
  - Cannot transform pearlite ↔ bainite without first heating back up to Austenite.

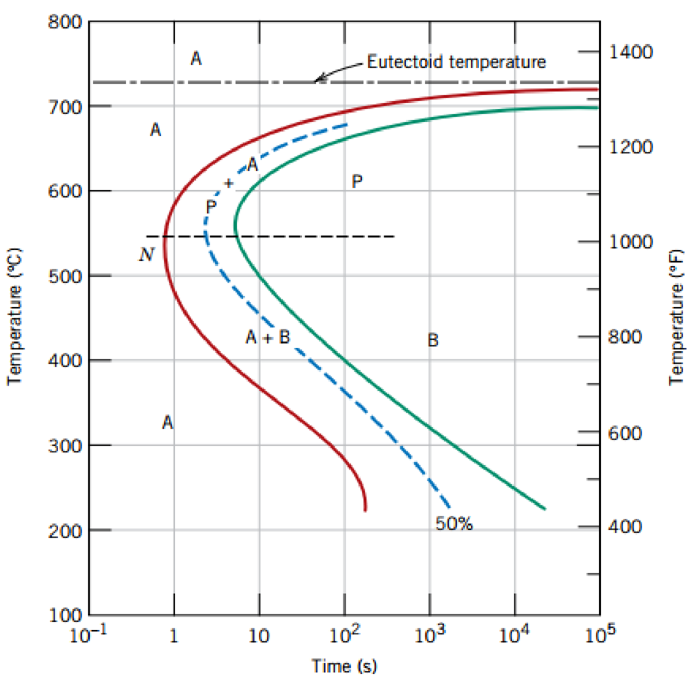


Figure 10.18 Isothermal transformation diagram for an iron–carbon alloy of eutectoid composition, including austenite-to-pearlite (A–P) and austenite-to-bainite (A–B) transformations.
[Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Microstructural and Property changes in Iron-Carbon Alloys

- Martensite
  - A metastable iron phase supersaturated in carbon that is the product of diffusionless (athermal) transformation.
  - Happens when rapidly cooled and prevents carbon diffusion.
  - FCC austenite transform to BCT martensite.
  - Time independent transformation- instantaneous
    - Non-equilibrium phase. Does not show up in iron-iron carbide phase diagram.

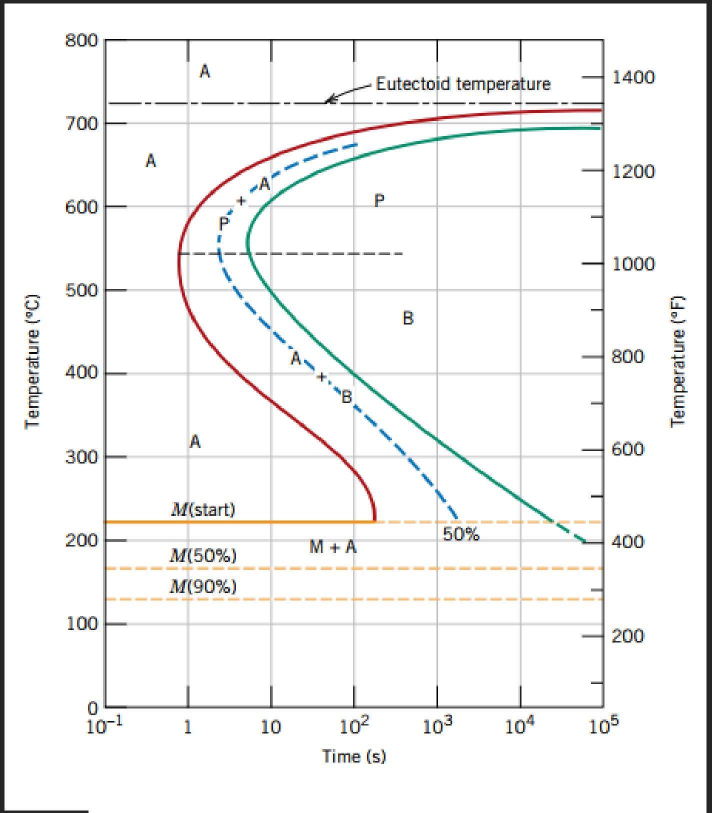


Figure 10.22 The complete isothermal transformation diagram for an iron–carbon alloy of eutectoid composition: A, austenite; B, bainite; M, martensite; P, pearlite.

Microstructural and Property changes in Iron-Carbon Alloys

- Continuous-Cooling Transformation Diagrams (CCT)
  - A plot of temperature versus the logarithm of time for a steel alloy. Used to indicate when transformations occur as the initially austenitized material is continuously cooled at a specified rate; in addition, the final microstructure and mechanical characteristics may be predicted.

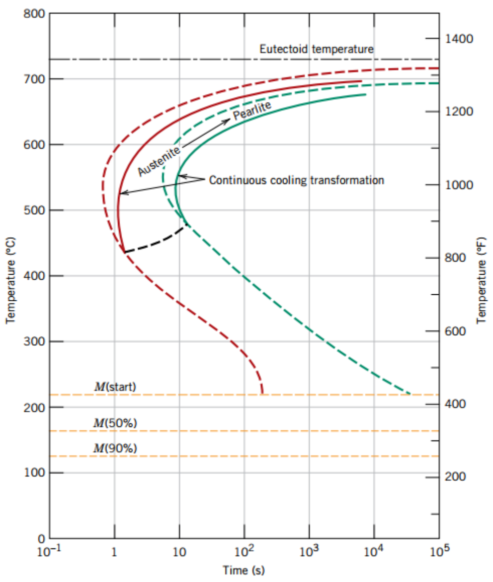


Figure 10.25 Superimposition of isothermal and continuous-cooling transformation diagrams for a eutectoid iron–carbon alloy.
[Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

Microstructural and Property changes in Iron-Carbon Alloys

- Continuous-Cooling Transformation Diagrams (CCT)
  - Most cases, all austenite transforms to pearlite before any bainite shows up when continuously cooling.
  - There are critical cooling rates that can help determine of the cooled product will be all martensite, pearlite or the combination of the two.
- CCTs and TTT plots can be seen as phase diagrams with a time component.

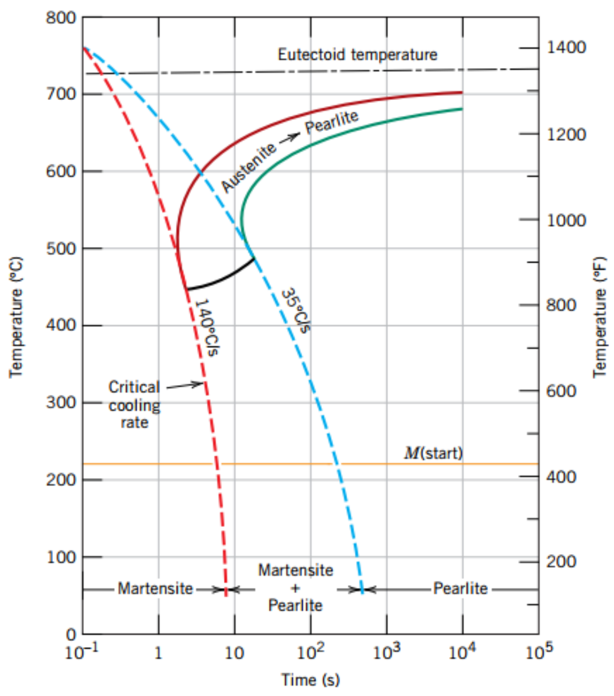


Figure 10.27 Continuous-cooling transformation diagram for a eutectoid iron–carbon alloy and superimposed cooling curves, demonstrating the dependence of the final microstructure on the transformations that occur during cooling.