Introduction to Engineering Materials
ENGR2000
Chapter 10: Phase Transformations in Metals
(10.1-2, 10.5-9)
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10.2 Basic Concepts

• Phase transformations involve alteration of the microstructure
  – Diffusion dependent transformations
    • No change in number or composition of phases present
    • Change in number of phases or composition
  – Diffusionless transformations
    • A metastable phase is produced

• Most phase transformations involve change in composition
  – redistribution of atoms via diffusion is required.
• The process of phase transformation involves:
  – **Nucleation** of the new phase - formation of stable small particles (nuclei) of the new phase. Nuclei are often formed at grain boundaries and other defects.
  – **Growth** – formation of new phase at the expense of the parent phase
  – Avrami equation: dependence of fraction of transformation on time,
    \[ y = 1 - \exp(-kt^n) \]
    – \( k, n \) : independent constants for particular reaction
Steels

• Plain carbon steels
  – Steels in which C is the primary alloying element

• Alloy steels
  – Contain significant concentrations of alloying elements such as Cr, Ni, Mo, W, etc.
α-ferrite
- low in C and for most cases, can be considered pure Fe
10.5 Isothermal Transformation Diagrams

• IT diagrams
  – Represent time & temperature dependence of transformations
• Besides temperature, what other parameters can be varied to induce a phase transformation?

• External pressure
• composition
Eutectoid reaction:

\[ \gamma(0.76\,\text{wt.}\%\ C) \rightleftharpoons \alpha(0.022\,\text{wt.}\%\ C) + Fe_3C(6.7\,\text{wt.}\%\ C) \]
Temperature dependence of an iron-carbon alloy of eutectoid composition

Date collected after rapidly cooling a specimen of 100% austenite to temperature indicated
Isothermal Transformation diagram for the eutectoid alloy (0.76 wt % C)
Points to note on using IT diagrams

- Diagrams are valid only for specific alloy compositions.
- Diagrams are accurate only for transformations in which the temperature of the alloy is held constant throughout the duration of the reaction.
Pearlite
- a two-phase mixture with layers of alternating ferrite & cementite

- Cooling 0.76 wt. % C alloy to just below the eutectoid temperature…single phase austenite transforms to pearlite
Figure 10.5 Isothermal transformation diagram for a eutectoid iron–carbon alloy, with superimposed isothermal heat treatment curve (ABCD).
• What phase exists at temperatures above eutectoid
  • Austenite only

• What phase is present to the left of the transformation start curve?
  • Austenite only

• What phase is present to the right of the transformation finish curve?
  • Pearlite only

• How does temperature affect transformation rate?
  • Transformation rate increases with decreasing temperature
Coarse pearlite and fine pearlite

- Coarse pearlite
  - At temperatures just below the eutectoid, relatively thick layers of both the $\alpha$-ferrite and cementite phases are produced. (high diffusion rates)

- Fine pearlite
  - With decreasing temperature ~ 540 C, the carbon diffusion rate decreases and the layers become thinner. (low diffusion rates)
Key points

• At low temperatures (Pearlite), the transformation occurs sooner due to
  o higher rate of nucleation (dominant)
  o slower grain growth (that is controlled by diffusion)

• Slow diffusion at low temperatures leads to fine-grained microstructure of pearlite (fine pearlite)

• At higher temperatures, high diffusion rates allow for larger grain growth and formation of thick layered structure of pearlite (coarse pearlite)
Figure 10.6 Photomicrographs of (a) coarse pearlite and (b) fine pearlite. 3000×. (From K. M. Ralls et al., An Introduction to Materials Science and Engineering, p. 361. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)
Microstructure of pearlite

Why should we care about lamellar thickness?

FIGURE 8.3–2  Microstructure of pearlite formed at different isothermal hold temperatures: (a) 655°C, (b) 600°C, (c) 534°C, and (d) 487°C. Notice that the morphologies of the two-phase structure are similar but their spacings decrease with decreasing isothermal hold temperature.
Bainite
-the ferrite phase is in the form of plates with cementite in-between

- Cooling 0.76 wt. % C alloy to further below the eutectoid temperature (below 550°C) … single phase austenite transforms to bainite (a two-phase mixture of ferrite & cementite)
No proeutectoid phase forms with bainite!
Where does maximum rate of transformation occur?
Coarse vs Fine Bainite

- In the bainite region, the transformation rate is controlled by microstructure growth (diffusion) rather than nucleation. Since diffusion is slow at low temperatures, this phase has a very fine (microscopic) microstructure at lower temperatures.
Microstructure of bainite

Pearlite and Bainite transformations

- Once a portion of an alloy has transformed to either pearlite or bainite, transformation to other microstructure is not possible without reheating to form austenite.
Martensite

- Quenching (cooling rapidly) 0.76 wt. % C alloy to ~200 C…
  - amount of transformed phase depends solely on temperature & not on time
  - same composition as the parent phase
  - Diffusionless transformation
  - A non-equilibrium phase, therefore does not appear on the iron-iron carbide phase diagram
Martensite

- The **FCC austenite** is transformed to BCT (BCC that has been elongated along one of its dimensions) martensite

*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
- a plate-like or needle-like microstructure

**Figure 10.12** Photomicrograph showing the lenticular or plate martensitic microstructure. The needle-shaped grains are the martensite phase, and the white regions are austenite that failed to transform during the rapid quench. 1220×. (Photomicrograph courtesy of United States Steel Corporation.)
Microstructure of martensite

**FIGURE 8.3–8** Progress of athermal martensitic transformation in an Fe–1.8 wt. % C alloy after cooling to (a) 24°C, (b) −60°C, and (c) −100°C. (Source: G. Kraus and A. R. Marder, The Morphology of Martensite in Iron Alloys. Metallurgical Transactions, Vol. 2, 1971, pp. 2343–57. Reprinted by permission of the publisher.)
10.8 Tempered Martensite

- Martensite (as-quenched)
  - Very hard & brittle
  - Cannot be used

- Tempered martensite
  - As hard & strong as before
  - Enhanced ductility & toughness
Tempering

- Heating to a temperature below the eutectoid for a specified time
- Time is allowed for diffusion

\[
\text{martensite (BCT, single phase)} \rightarrow \text{tempered martensite (}\alpha + \text{Fe}_3\text{C phases)}\]

more stable
Spheroidite

- If a steel alloy with either pearlitic, bainitic or tempered martensitic microstructures is heated to a temperature below the eutectoid and left at that temperature for a long period of time…
  - At 700 C for 18 to 24 hrs
  - Cementite phase appears as sphere-like particles embedded in a continuous \( \alpha \)-ferrite matrix.

- Transformation occurs by additional carbon diffusion with no change in compositions of relative amounts of ferrite and cementite phases!
• Which is more stable, the pearlite or spheroiditic microstructure?

Spheroiditic microstructures are more stable than pearlitic ones. Since pearlite transforms to spheroidite, the latter is more stable.
Figure 10.13 The complete isothermal transformation diagram for an iron–carbon alloy of eutectoid composition: A, austenite; B, bainite; M, martensite; P, pearlite.

Horizontal lines - transformation is independent of time.
Figure 10.13  The complete isothermal transformation diagram for an iron–carbon alloy of eutectoid composition: A, austenite; B, bainite; M, martensite; P, pearlite.
Consider an alloy of eutectoid composition rapidly cooled from a temperature above 727°C to 165°C... what% austenite immediately transforms to martensite?

50%

- Cite two major differences between martensitic and pearlitic transformations

1) atomic diffusion is necessary for the pearlitic transformation, whereas the martensitic transformation is diffusionless; and 2) relative to transformation rate, the martensitic transformation is virtually instantaneous, while the pearlitic transformation is time-dependent.
The effect of alloying

- Alloying elements other than C such as Cr, Ni, Mo, W, etc. cause significant changes in the shapes of the curves in the IT diagrams.
Figure 10.14
Isothermal transformation diagram for an alloy steel (type 4340): A, austenite; B, bainite; P, pearlite; M, martensite; F, proeutectoid ferrite.
Example 10.1

- Using the IT diagram for an Fe-C alloy of eutectoid composition, specify the nature of the final microstructure (in terms of the micro constituents present and approximate percentages) of a small specimen that has been subjected to the following time-temperature treatments. Assume that the specimen begins at 760 C and that it has been held at this temperature long enough to have achieved a complete and homogenous austenite structure.
(a) Rapidly cool to 350°C, hold for 10,000 s and quench to room temperature
(b) Rapidly cool to 250 C, hold for 100 s and quench to room temperature
(c) Rapidly cool to 650°C, hold for 20 s, rapidly cool to 400°C, hold for 1000 s, and quench to room temperature

Why this?
Suppose you need to analyze short holds in temperature eg. hold for 20 s, what would you do?

Also, where is the 1,020 seconds on the x-axis?

Note the composition at point P should be 50% P, 25%A and 25%B, but some time is needed for this to occur, say 20 s or so.
Some key points

• Diffusion rate
  – Diffusion rate responsible for thickness of lamellae
  – Diffusion rate is proportional to temperature

Not the same as

• Transformation rate
  – Rate at which one phase transforms to the other
Terminology for microstructures in Fe-C alloys

<table>
<thead>
<tr>
<th>Microstructure name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ-ferrite</td>
<td>An interstitial solid solution of carbon in δ iron (BCC).</td>
</tr>
<tr>
<td>Austenite</td>
<td>An interstitial solid solution of carbon in γ iron (FCC).</td>
</tr>
<tr>
<td>α-ferrite</td>
<td>An interstitial solid solution of carbon in α iron (BCC).</td>
</tr>
<tr>
<td>Pearlite</td>
<td>Eutectoid of α-ferrite and cementite with a lamellar microstructure of alternate α-Fe and cementite plates.</td>
</tr>
<tr>
<td>Bainite</td>
<td>Eutectoid of α-ferrite and cementite. The α-ferrite either has a feathery appearance or occurs as plates. Carbide particles lie between the α-ferrite regions.</td>
</tr>
<tr>
<td>Spheroidite</td>
<td>Spherical particles of cementite in a matrix of α-ferrite.</td>
</tr>
<tr>
<td>Martensite</td>
<td>An interstitial solid solution of carbon in a body-centered tetragonal (BTC) Fe crystal structure.</td>
</tr>
<tr>
<td>Hypoeutectoid steels</td>
<td>Alloys with compositions to the left of the eutectoid reaction.</td>
</tr>
<tr>
<td>Hypereutectoid steels</td>
<td>Alloys with compositions to the right of the eutectoid reaction.</td>
</tr>
<tr>
<td>Proeutectoid ferrite</td>
<td>Ferrite that forms prior to the eutectoid ferrite.</td>
</tr>
<tr>
<td>Proeutectoid cementite</td>
<td>Cementite that forms prior to the eutectoid cementite.</td>
</tr>
</tbody>
</table>
Example A

- The steel is rapidly quenched from above 727°C to 650°C, held at that temperature for 12s, then quenched to room temperature.

A 50-50 mixture of pearlite & martensite
Example B

- The steel is rapidly quenched from above 727°C to 600°C, held at that temperature for 3s, quenched to 350°C, held at that temperature for 1000s, then quenched to room temperature.

  a 50-50 mixture of pearlite & bainite
Example C

- When a eutectoid steel is heat-treated in the austenite phase field, quenched and isothermally held at temperatures below 727°C, different morphologies of ferrite and cementite are possible. Describe these microstructures and how they are produced.

Examples from reference:
- pearlite

- Quenching from above 727 °C and holding at temperatures below 727 °C, but above 550 °C results in pearlite.
  - layered structure of ferrite and cementite
  - lower the hold temperature, finer the layers.
- bainite

- Quenching from above 727°C and holding at temperatures below 550°C, but above ~200°C results in bainite.
  - cementite needles in a ferrite matrix
  - lower the hold temperature, finer the structure.
- spheroidite

- Tempering
  - spheroidite
Example D

- Prepare a sample of pearlite from a sample of eutectoid steel with a bainitic structure…
- Hint: The only way pearlite, bainite or martensite can be produced is through the decomposition of austenite.
• Transform the bainite to austenite
  – above 727°C

• Quench to a temperature below 727°C but above 550°C
  – at 600°C hold for 10s to transform the austenite to pearlite.
Example E

- Describe the microstructures that develop when a eutectoid steel is subjected to the following heat treatments...

(a) The steel is rapidly quenched from above 727°C to 650°C, held at that temperature for 12s, then quenched to room temperature.

(b) The steel is rapidly quenched from above 727°C to 600°C, held at that temperature for 3s, quenched to 350°C, held at that temperature for 1000s, then quenched to room temperature.
10.7 Mechanical Behavior of Iron-Carbon Alloys

- Cementite is much harder but more brittle than ferrite.
- Fine pearlite is harder & stronger than coarse pearlite.
- Spheroidite is extremely ductile & tough.
- Bainite is stronger & harder than pearlite.
- Martensite is the hardest & strongest & most brittle.
Figure 10.21  (a) Brinell and Rockwell hardness as a function of carbon concentration for plain carbon steels having fine and coarse pearlite as well as spheroidite microstructures. (b) Ductility (%RA) as a function of carbon concentration for plain carbon steels having fine and coarse pearlite as well as spheroidite microstructures. (Data taken from Metals Handbook: Heat Treating,
**Figure 10.22** Brinell hardness and tensile strength as a function of isothermal transformation temperature for an iron–carbon alloy of eutectoid composition, taken over the temperature range at which bainitic and pearlitic microstructures form. (Adapted from E. S. Davenport, “Isothermal Transformation in Steels,” *Trans. ASM, 27*, 1939, p. 847. Reprinted by permission of ASM International.)
Figure 10.23  Hardness as a function of carbon concentration for plain carbon martensitic, tempered martensitic [tempered at 371°C (700°F)], and pearlitic steels. (Adapted from Edgar C. Bain, Functions of the Alloying Elements in Steel, American Society for Metals, 1939, p. 36; and R. A. Grange, C. R. Hribal, and L. F. Porter, Metall. Trans. A, Vol. 8A, p. 1776.)
Microstructure of tempered martensite is similar to that of spheroidite but with smaller cementite particles.

**Figure 10.24** Electron micrograph of tempered martensite. Tempering was carried out at 594°C (1100°F). The small particles are the cementite phase; the matrix phase is α-ferrite. 9300×. (Copyright 1971 by United States Steel Corporation.)
10.9 Phase transformations for Fe-C alloys

**Figure 10.27** Possible transformations involving the decomposition of austenite. Solid arrows, transformations involving diffusion; dashed arrow, diffusionless transformation.
Problems 10.20 & 10.21

Figure 9.21 The iron–iron carbide phase diagram. [Adapted from Binary Alloy]
10.20 We are asked to determine which microconstituents are present in a 1.13 wt% C iron-carbon alloy that has been subjected to various isothermal heat treatments. These microconstituents are as follows:

(a) Martensite
(b) Proeutectoid cementite and martensite
(c) Bainite
(d) Spheroidite
(e) Cementite, medium pearlite, bainite, and marter
(f) Bainite and martensite
(g) Proeutectoid cementite, pearlite, and martensite
(h) Proeutectoid cementite and fine pearlite
10.21 This problem asks us to determine the approximate percentages of the microconstituents that form for five of the heat treatments described in Problem 10.20.

(a) 100% martensite
(b) 100% bainite
(c) 100% spheroidite
(d) 100% pearlite
(e) 60% bainite and 40% martensite

(h) After holding for 7 s at 600°C, the specimen has completely transformed to proeutectoid cementite and fine pearlite; no further reaction will occur at 450°C. Therefore, we can calculate the mass fractions using the appropriate lever rule expressions, Equations 9.22 and 9.23, as follows:

\[ W_{Fe_3C'} = \frac{C'_1 - 0.76}{5.94} = \frac{1.13 - 0.76}{5.94} = 0.062 \text{ or } 6.2\% \]

\[ W_p = \frac{6.70 - C'_1}{5.94} = \frac{6.70 - 1.13}{5.94} = 0.938 \text{ or } 93.8\% \]
Suggested Problems

- 10.14-10.21
- 10.D1, D2, D3, D7