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Chapter 10: Phase Transformations

10.1 Introduction: ISSUES TO ADDRESS...

- Transforming one phase into another takes time.
- How does the rate of transformation depend on time and \( T \)?
- How can we slow down the transformation so that we can engineer non-equilibrium structures?
- Are the mechanical properties of non-equilibrium structures better?
Learning Objectives

• Make a schematic fraction transformation-versus-logarithm of time plot for a typical solid-solid transformation; cite the equation that describes this behavior.

• Briefly describe the microstructure for each of the following microconstituents that are found in steel alloys: fine pearlite, coarse pearlite, spheroidite, bainite, martensite, and tempered martensite.
Learning Objectives

• Cite the general mechanical characteristics for each of the following microconstituents: fine pearlite, coarse pearlite, spheroidite, bainite, martensite, and tempered martensite. Now, in terms of microstructure (or crystal structure), briefly explain these behaviors.

• Given the isothermal transformation (or continuous cooling transformation) diagram for some iron-carbon alloy, design a heat treatment that will produce a specified microstructure.
Homework assignments

- Question and Problems 10.3
- Question and Problems 10.6
- Question and Problems 10.14
- Question and Problems 10.15
- Question and Problems 10.20
- Question and Problems 10.23
- Question and Problems 10.34
- Question and Problems 10.D4

Homework assignments will be discussed in Wednesday Class.

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Phase Transformations

10.2 Basic Concepts

Diffusion-dependent transformation 1 (no composition change): solidification...

Diffusion-dependent transformation 2 (composition change): eutectoid reaction...

Diffusionless transformation: martensitic transition

10.3 The Kinetics of Phase Transformations

Nucleation

– nuclei (seeds) act as template to grow crystals
– for nucleus to form rate of addition of atoms to nucleus must be faster than rate of loss
– once nucleated, grow until reach equilibrium
Solidification: Nucleation Processes

- **Homogeneous nucleation**
  - nuclei form in the bulk of liquid metal
  - requires supercooling (typically 80-300°C max)

\[
\Delta G_v = \frac{4}{3} \pi r^3 \Delta G_v
\]

\[
\Delta G_v = \text{volume free energy difference}
\]

\[
\Delta G_S = 4\pi r^2 \gamma
\]

\[
\gamma = \text{surface free energy}
\]

\[
V = \frac{3}{4}\pi r^3, \quad S = 3\pi r^2
\]
Homogeneous Nucleation & Energy Effects

Surface Free Energy destabilizes the nuclei (it takes energy to make an interface)

\[ \Delta G_S = 4\pi r^2 \gamma \]

\( \gamma \) = surface tension

Total Free Energy

\[ \Delta G_T = \Delta G_S + \Delta G_V \]

Volume (Bulk) Free Energy – stabilizes the nuclei (releases energy)

\[ \Delta G_V = 4 \pi r^3 \Delta G_{V_0} \]

\( \Delta G_{V_0} = \) volume free energy unit volume

\( r^* = \) critical nucleus: nuclei \( < r^* \) shrink; nuclei \( > r^* \) grow (to reduce energy)

Adapted from Fig.10.2(b), Callister 7e.
Solidification

\[ r^* = \frac{-2 \gamma T_m}{\Delta H_s \Delta T} \]

- \( r^* \) = critical radius
- \( \gamma \) = surface free energy
- \( T_m \) = melting temperature
- \( \Delta H_s \) = latent heat of solidification
- \( \Delta T = T_m - T \) = supercooling
- \( \Delta G_v = \Delta H_s (T_m - T)/T_m \)

Note: \( \Delta H_s \) = strong function of \( \Delta T \)
\( \gamma \) = weak function of \( \Delta T \)

\[ \therefore \quad r^* \text{ decreases as } \Delta T \text{ increases} \]

For typical \( \Delta T \) \( r^* \) ca. 100Å
Solidification

\[ \Delta G^* = -\frac{16\pi\gamma^3 T_m^2}{3\Delta H_s^2} \cdot \frac{1}{\Delta T^2} \]

\(\Delta G^*\) = critical free energy  
\(\gamma\) = surface free energy  
\(T_m\) = melting temperature  
\(\Delta H_s\) = latent heat of solidification  
\(\Delta T = T_m - T\) = supercooling

Note: \(\Delta H_s\) = strong function of \(\Delta T\)  
\(\gamma\) = weak function of \(\Delta T\)

\[\therefore \Delta G^* \text{ decreases as } \Delta T \text{ increases}\]
Solidification

\[ n^* = K_1 \exp\left( -\frac{\Delta G^*}{kT} \right) \]

\[ n^* = \text{number stable nuclei (r>r*)} \]
\[ K_1 = \text{constant} \]
\[ k = \text{Boltzmann’s constant} \]

\[ v_d = K_2 \exp\left( -\frac{Q_d}{kT} \right) \]

\[ v_d = \text{frequency of atom in liquid attached to the nucleus} \]
\[ K_2 = \text{constant} \]
\[ Q_d = \text{activation energy for diffusion, temperature independent} \]

Nucleation Rate

\[ \dot{N} = K_3 n^* v_d = K_1 K_2 K_3 \exp\left( -\frac{\Delta G^*}{kT} \right) \exp\left( -\frac{Q_d}{kT} \right) \]
Solidification: Nucleation Processes

- **Heterogeneous nucleation**
  - nuclei form on a flat surface of a solid particle

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

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

- \( \Delta G_v \) = volume free energy difference
- \( \gamma \) = interfacial energy
- \( 0 \leq S(\theta) \leq 1 \)

\[ \Delta G_{het}^* = \Delta G_{hom}^* S(\theta) \]
Solidification: Nucleation Processes

- Growth rate

\[ \dot{G} = C \exp\left(-\frac{Q}{kT}\right) \]

\( G = \text{activation energy} \)
\( C = \text{preexponential parameter independent to temperature} \)
Rate of Phase Transformations

**Kinetics** - measure approach to equilibrium vs. time

- Hold temperature constant & measure conversion vs. time
  - How is conversion measured?
    - X-ray diffraction – have to do many samples
    - electrical conductivity – follow one sample
    - sound waves – one sample
Rate of Phase Transformation

All out of material - done

maximum rate reached – now amount unconverted decreases so rate slows

rate increases as surface area increases & nuclei grow

Fraction transformed, y

Fixed T

log t

Avrami rate equation => $y = 1 - \exp\left(-kt^n\right)$

fraction transformed

time

– $k$ & $n$ fit for specific sample

By convention $rate = 1/t_{0.5}$

Adapted from Fig. 10.10, Callister 7e.
Rate of Phase Transformations

![Graph showing percent recrystallized vs time for different temperatures.](image)

- **In general, rate increases as** $T \uparrow$

\[ r = \frac{1}{t_{0.5}} = A \, e^{-Q/RT} \]

[Arrhenius expression]

- $R = \text{gas constant}$
- $T = \text{temperature (K)}$
- $A = \text{preexponential factor}$
- $Q = \text{activation energy}$

- $r$ often small: equilibrium not possible!

Adapted from Fig. 10.11, Callister 7e. (Fig. 10.11 adapted from B.F. Decker and D. Harker, "Recrystallization in Rolled Copper", Trans AIME, 188, 1950, p. 888.)
10.4 Metastable versus Equilibrium States

When the rate of approach to equilibrium of solid system is very slow, true equilibrium structures may be rarely achieved.

**Supercooling:** transformations are shifted to lower temperatures than indicated by the phase diagram

**Superheating:** transformations are shifted to higher temperatures than indicated by the phase diagram
10.5 Isothermal Transformation Diagrams

\[
\gamma(0.76\text{wt}\%\text{C}) \xrightarrow{\text{heating}} \alpha(0.022\text{wt}\%\text{C}) + \text{Fe}_3\text{C} (6.70\text{wt}\%\text{C})
\]

Austenite \hspace{2cm} Ferrite \hspace{2cm} Cementite

(Pearlite structure)
Eutectoid Transformation Rate

- Growth of pearlite from austenite:
  - Austenite (γ) grain boundary
  - Ferrite (α)
  - Cementite (Fe₃C)
  - pearlite growth direction

- Recrystallization rate increases with ΔT.

Course pearlite → formed at higher T - softer
Fine pearlite → formed at low T - harder
Nucleation and Growth

• Reaction rate is a result of nucleation and growth of crystals.

% Pearlite

Nucleation rate increases with $\Delta T$

Growth rate increases with $T$

log (time)

• Examples:

pearlite colony

$T$ just below $T_E$
Nucleation rate low
Growth rate high

$T$ moderately below $T_E$
Nucleation rate med.
Growth rate med.

$T$ way below $T_E$
Nucleation rate high
Growth rate low

Adapted from Fig. 10.10, Callister 7e.
Transformations & Undercooling

- **Eutectoid transf. (Fe-C System):**
  - Can make it occur at:
    - ...727°C (cool it slowly)
    - ...below 727°C (“undercool” it!)

  \[ \gamma \Rightarrow \alpha + \text{Fe}_3\text{C} \]
  
  - 0.76 wt% C
  - 6.7 wt% C
  - 0.022 wt% C

Adapted from Fig. 9.24, Callister 7e. (Fig. 9.24 adapted from Binary Alloy Phase Diagrams, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)
Isothermal Transformation Diagrams

- Fe-C system, $C_o = 0.76$ wt% C
- Transformation at $T = 675^\circ$C.

Adapted from Fig. 10.13, Callister 7e.
(Fig. 10.13 adapted from H. Boyer (Ed.) Atlas of Isothermal Transformation and Cooling Transformation Diagrams, American Society for Metals, 1977, p. 369.)
Effect of Cooling History in Fe-C System

- Eutectoid composition, $C_o = 0.76$ wt% C
- Begin at $T > 727^\circ$C
- Rapidly cool to 625°C and hold isothermally.

Adapted from Fig. 10.14, *Callister 7e*. (Fig. 10.14 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1997, p. 28.)
Transformations with Proeutectoid Materials

$C_o = 1.13 \text{ wt}\% \text{ C}$

Adapted from Fig. 10.16, Callister 7e.

Adapted from Fig. 9.24, Callister 7e.

Hyper-eutectoid composition – proeutectoid cementite
Non-Equilibrium Transformation Products: Fe-C

- Bainite:
  - $\alpha$ lathes (strips) with long rods of $\text{Fe}_3\text{C}$
  - diffusion controlled.
- Isothermal Transf. Diagram

![Isothermal Transformation Diagram](image)

(Adapted from Fig. 10.17, Callister, 7e. (Fig. 10.17 from Metals Handbook, 8th ed., Vol. 8, Metallography, Structures, and Phase Diagrams, American Society for Metals, Materials Park, OH, 1973.)

Adapted from Fig. 10.18, Callister 7e.
(Fig. 10.18 adapted from H. Boyer (Ed.) Atlas of Isothermal Transformation and Cooling Transformation Diagrams, American Society for Metals, 1997, p. 28.)
Spheroidite: Fe-C System

- **Spheroidite:**
  - $\alpha$ grains with spherical Fe$_3$C
  - Diffusion dependent.
  - Heat bainite or pearlite for long times
  - Reduces interfacial area (driving force)

Formation of spheroidite:
Pearlite or bainite is heated and left at $T$ just below the eutectoid for a sufficiently long period of time (e.g., 700$^\circ$C, 18-24hr)

(Adapted from Fig. 10.19, *Callister, 7e.* (Fig. 10.19 copyright United States Steel Corporation, 1971.)
Martensite: Fe-C System

- **Martensite:**
  - $\gamma$ (FCC) to Martensite (BCT)
    - (involves single atom jumps)
  - Fe atom sites
  - C atom sites

- **Isothermal Transf. Diagram**
  - $\gamma$ to M transformation...
    - is rapid!
    - % transf. depends on T only.

Adapted from Fig. 10.20, *Callister, 7e.*

Adapted from Fig. 10.21, *Callister, 7e.*
(Fig. 10.21 courtesy United States Steel Corporation.)
Martensite Formation

\[ \gamma \text{ (FCC)} \xrightarrow{\text{slow cooling}} \alpha \text{ (BCC)} + \text{Fe}_3\text{C} \]

\[ \gamma \text{ (FCC)} \xrightarrow{\text{quench}} \text{M (BCT)} \]

\[ \text{M (BCT)} \xrightarrow{\text{tempering}} \text{BCT if } C > 0.15 \text{ wt}\% \]

\[ \text{BCT} \rightarrow \text{few slip planes} \rightarrow \text{hard, brittle} \]

\textit{M = martensite} is body centered tetragonal (BCT)
Phase Transformations of Alloys

Effect of adding other elements
Change transition temp.

Cr, Ni, Mo, Si, Mn
retard $\gamma \rightarrow \alpha + Fe_3C$
transformation

Adapted from Fig. 10.23, Callister 7e.
10.6 Continuous Cooling Transformation Diagrams.

**Cooling Curve**

plot temp vs. time

Adapted from Fig. 10.25, *Callister 7e.*
Dynamic Phase Transformations

On the isothermal transformation diagram for 0.45 wt% C Fe-C alloy, sketch and label the time-temperature paths to produce the following microstructures:

a) 42% proeutectoid ferrite and 58% coarse pearlite
b) 50% fine pearlite and 50% bainite
c) 100% martensite
d) 50% martensite and 50% austenite
Adapted from Fig. 9.24, Callister 7e.
Example Problem for $C_o = 0.45$ wt% 

a) 42% proeutectoid ferrite and 58% coarse pearlite

first make ferrite then pearlite

course pearlite : higher $T$

Adapted from Fig. 10.29, Callister 5e.
Example Problem for $C_o = 0.45$ wt% 

b) 50% fine pearlite and 50% bainite

first make pearlite
then bainite

fine pearlite
∴ lower $T$

Adapted from Fig. 10.29, Callister 5e.
Example Problem for $C_o = 0.45$ wt%

c) 100 % martensite – quench = rapid cool

d) 50 % martensite and 50 % austenite

Adapted from Fig. 10.29, Callister 5e.
10.7 Mechanical Behavior of Iron–Carbon Alloys.

Mechanical Prop: Fe-C System (1)

• Effect of wt% C

Adapted from Fig. 9.30, *Callister 7e*. (Fig. 9.30 courtesy Republic Steel Corporation.)

Adapted from Fig. 9.33, *Callister 7e*. (Fig. 9.33 copyright 1971 by United States Steel Corporation.)

Adapted from Fig. 10.29, *Callister 7e*. (Fig. 10.29 based on data from *Metals Handbook: Heat Treating*, Vol. 4, 9th ed., V. Masseria (Managing Ed.), American Society for Metals, 1981, p. 9.)

Co < 0.76 wt% C

Hypoeutectoid

Co > 0.76 wt% C

Hypereutectoid

Hypo

Hyper

More wt% C: TS and YS increase, %EL decreases.
Mechanical Prop: Fe-C System (2)

- Fine vs coarse pearlite vs spheroidite

- Hardness: fine > coarse > spheroidite
- %RA: fine < coarse < spheroidite

Adapted from Fig. 10.30, Callister 7e. (Fig. 10.30 based on data from Metals Handbook: Heat Treating, Vol. 4, 9th ed., V. Masseria (Managing Ed.), American Society for Metals, 1981, pp. 9 and 17.)
Mechanical Prop: Fe-C System (3)

- Fine Pearlite vs Martensite:
  - Hardness: fine pearlite << martensite.

Adapted from Fig. 10.32, Callister 7e. (Fig. 10.32 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.)
10.8 Tempered Martensite.

**Tempering Martensite**

- reduces brittleness of martensite,
- reduces internal stress caused by quenching.

\[
\begin{array}{c|c|c}
\text{Tempering } T(°C) & \text{TS} \text{(MPa)} & \text{YS} \text{(MPa)} \\
\hline
200 & 1800 & 1600 \\
400 & 1600 & 1400 \\
600 & 1200 & 1000 \\
\end{array}
\]

- produces extremely small \( \text{Fe}_3\text{C} \) particles surrounded by \( \alpha \).
- decreases \( \text{TS} \), \( \text{YS} \) but increases \( \%\text{RA} \)

Adapted from Fig. 10.33, *Callister 7e*. (Fig. 10.34 adapted from Fig. furnished courtesy of Republic Steel Corporation.)

**Summary: Processing Options**

- **Austenite ($\gamma$)**
  - slow cool
  - Pearlite ($\alpha + Fe_3C$ layers + a proeutectoid phase)
  - Bainite ($\alpha + Fe_3C$ plates/needles)
  - Martensite (BCT phase diffusionless transformation)

- **Martensite**
  - rapid quench
  - reheat
  - Tempered Martensite ($\alpha +$ very fine $Fe_3C$ particles)

- **General Trends**
  - Strength
  - Martensite T Martensite bainite fine pearlite coarse pearlite spheroidite
  - Ductility
  - General Trends

Adapted from Fig. 10.36, *Callister 7e.*