Phase transformations

Fe₃C (cementite)

\[ \gamma \] (austenite)

\[ \gamma + L \]

\[ L + Fe₃C \]

\[ \gamma + Fe₃C \]

\[ \alpha + Fe₃C \]

\[ T(°C) \]

\[ C_o, \text{ wt}\% \text{ C} \]

1148°C

727°C
Eutectic, Eutectoid and Peritectic Reactions

Eutectic Reaction

\[ Liquid \Leftrightarrow Solid \ phrase(1) + Solid \ phrase \ (2) \]

Eutectoid reaction

\[ Solid \ phrase \ (1) \Leftrightarrow Solid \ phrase \ (2) + Solid \ phrase \ (3) \]

Peritectic Reaction

\[ Liquid \ phrase \ (1) + Solid \ phrase \ (2) \Leftrightarrow Solid \ phrase \ (3) \]
Phase Transformations

Nucleation

- nuclei act as seed points to grow crystals
- for nucleus to form
  - rate of addition of atoms > rate of loss
- once nucleated, growth $\rightarrow$ equilibrium

Driving force to nucleate increases as we increase $\Delta T$

- supercooling (eutectic, eutectoid)
- superheating (peritectic)

Small supercooling $\rightarrow$ few nuclei - large crystals
Large supercooling $\rightarrow$ rapid nucleation - many nuclei, small crystals
Solidification: Nucleation Processes

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

- Heterogeneous nucleation
  - much easier since stable “nucleus” is already present
    - Could be wall of mold or impurities in the liquid phase

Think of why you’d been asked never to put a used spoon back into a honey jar…

- allows solidification with only 0.1-10 °C supercooling
- concentration drive is also possible and often used!
Rate of Phase Transformation

Avrami (JMAK) rate equation:

\[ y = 1 - \exp(-kt^n) \]

- \( k \) & \( n \) are constants for specific system – \( n \) is roughly related to the growth front dimensionality + 1

The rate is:

\[ r = \frac{1}{t_{0.5}} \]

\( JMAK \) – Johnson, Mehl, Avrami, Kolmogorov
In general, rate increases as $T \uparrow$

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

- $R$ = gas constant
- $T$ = temperature (K)
- $A$ = pre-exponential factor
- $Q$ = activation energy

• $r$ often small: equilibrium not possible!
Eutectoid Transformation Rate

- Growth of pearlite from austenite:
  - Austenite ($\gamma$) grain boundary
  - Cementite ($Fe_3C$)
  - Ferrite ($\alpha$)
  - Pearlite growth direction

- Eutectoid transformation rate increases with $\Delta T$.

Course pearlite $\rightarrow$ formed at higher $T$ - softer
Fine pearlite $\rightarrow$ formed at low $T$ - harder
• Reaction rate is a result of nucleation and growth of crystals.

- Nucleation rate increases with $\Delta T$
- Growth rate increases with $T$

% Pearlite

<table>
<thead>
<tr>
<th>% Pearlite</th>
<th>Nucleation regime</th>
<th>Growth regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
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<td></td>
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<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\log (\text{time})$

- Examples:

  - $T$ 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

pearlite colony
Transformations & Supercooling

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

\[
\begin{align*}
\gamma &\Rightarrow \alpha + Fe_3C \\
0.76 \text{ wt\% C} &\quad 6.7 \text{ wt\% C} \\
0.022 \text{ wt\% C} &
\end{align*}
\]
Isothermal Transformation Diagrams

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

![Graph showing isothermal transformation at 675°C](image-url)
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.
Transformations with Proeutectoid Materials

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

Hypereutectoid composition – proeutectoid cementite
Non-Equilibrium Transformation

**Products: Fe-C**

- Bainite: (Davenport & Bain)
  - $\alpha$ strips with long needles of Fe$_3$C
  - diffusion controlled.
- Isothermal Transf. Diagram

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**Diagram**

- Fe$_3$C (cementite)
- $\alpha$ (ferrite)
- 100% pearlite
- 100% bainite
- pearlite/bainite boundary

**Axes**

- $T$ ($^\circ$C)
- time (s)

**Legend**

- A
- B
- 100% pearlite
- 100% bainite

**Comparisons**

- 5 $\mu$m
- 120 $\mu$m

**Note:** cf: Pearlite
Spheroidite: Fe-C System

- $\alpha$ + grains with spherical Fe$_3$C
- diffusion dependent.
- heat bainite or pearlite for long times (e.g. 18 h at 700°C)
- reduces interfacial area (driving force)
Martensite: Fe-C System

- Martensite: (Martens)
  - $\gamma$ (FCC) to Martensite (BCT)
    (involves single atom jumps)

- Isothermal Transf. Diagram

\[ T^\circ C \]

- $\gamma$ to M transformation..
  - is rapid!
  - % transf. depends on $T$ only.
  - can be stress-induced
Martensite Formation

\[ \gamma \text{ (FCC)} \xrightarrow{\text{quench}} M \text{ (BCT)} \xrightarrow{\text{slow cooling}} \alpha \text{ (BCC)} + Fe_3C \]

M = martensite is body centered tetragonal (BCT)

Diffusionless transformation

BCT if \( C > 0.15 \text{ wt}\% \)

BCT \( \rightarrow \) few slip planes \( \rightarrow \) hard, brittle
Phase Transformations of Alloys

Effect of adding other elements
Change transition temp.

Cr, Ni, Mo, Si, Mn
retard

γ → α + Fe₃C
transformation
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
Example Problem for $C_0 = 0.45$ wt%

a) 42 % proeutectoid ferrite and 58 % coarse pearlite (amounts determined by phase diagram)

first make ferrite

then pearlite

coarse pearlite $\therefore$ higher $T$
Example Problem for $C_o = 0.45$ wt%

a. the amount of pearlite and proeutectoid ferrite ($\alpha$)

note: amount of pearlite = amount of $\gamma$ just above $T_E$

$C_o = 0.45$ wt% C  
$C_\alpha = 0.022$ wt% C  
$C_{\text{pearlite}} = C_\gamma = 0.76$ wt% C

$$\frac{\gamma}{\gamma + \alpha} = \frac{C_o - C_\alpha}{C_\gamma - C_\alpha} \times 100 = 57.9\%$$

pearlite = 58 %  
proeutectoid $\alpha = 42 \%$
Example Problem for $C_o = 0.45$ wt%

b) 50% fine pearlite and 50% bainite

First make pearlite then bainite

Fine pearlite $\therefore$ lower $T$
Example Problem for $C_o = 0.45$ wt%

c) 100 % martensite – quench = rapid cool

d) 50 % martensite and 50 % austenite
Mechanical Prop: Fe-C System (1)

- Effect of wt% C
  - More wt% C: TS and YS increase, %EL decreases.

- Hypoeutectoid (C<sub>0</sub> < 0.76 wt% C)
  - Pearlite (med)
  - Ferrite (soft)

- Hypereutectoid (C<sub>0</sub> > 0.76 wt% C)
  - Pearlite (med)
  - Cementite (hard)

- Graphs showing:
  - YS, TS, hardness vs. wt% C
  - %EL, Impact energy (Izod, ft-lb) vs. wt% C

- 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
Mechanical Prop: Fe-C System (3)

- Fine Pearlite vs Martensite:

- Hardness: fine pearlite $\ll$ martensite.
Tempering Martensite

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

- produces extremely small Fe₃C particles surrounded by α.
- decreases TS, YS but increases %RA
Summary: Processing Options

Austenite ($\gamma$)

- slow cool
  - Pearlite ($\alpha + \text{Fe}_3\text{C}$ layers + a proeutectoid phase)
- moderate cool
  - Bainite ($\alpha + \text{Fe}_3\text{C}$ plates/needles)
- rapid quench
  - Martensite (BCT phase diffusionless transformation)

General Trends

- Strength
  - Martensite
  - Tempered Martensite
- Ductility
  - T Martensite
  - Bainite
  - Fine pearlite
  - Coarse pearlite
  - Spheroidite