Aalto University
School of Engineering

# COE-C2004 - Materials Science and Engineering

*Prof. Junhe Lian*
*Wenqi Liu (Primary teaching Assistant)*
*Rongfei Juan (Teaching Assistant)*

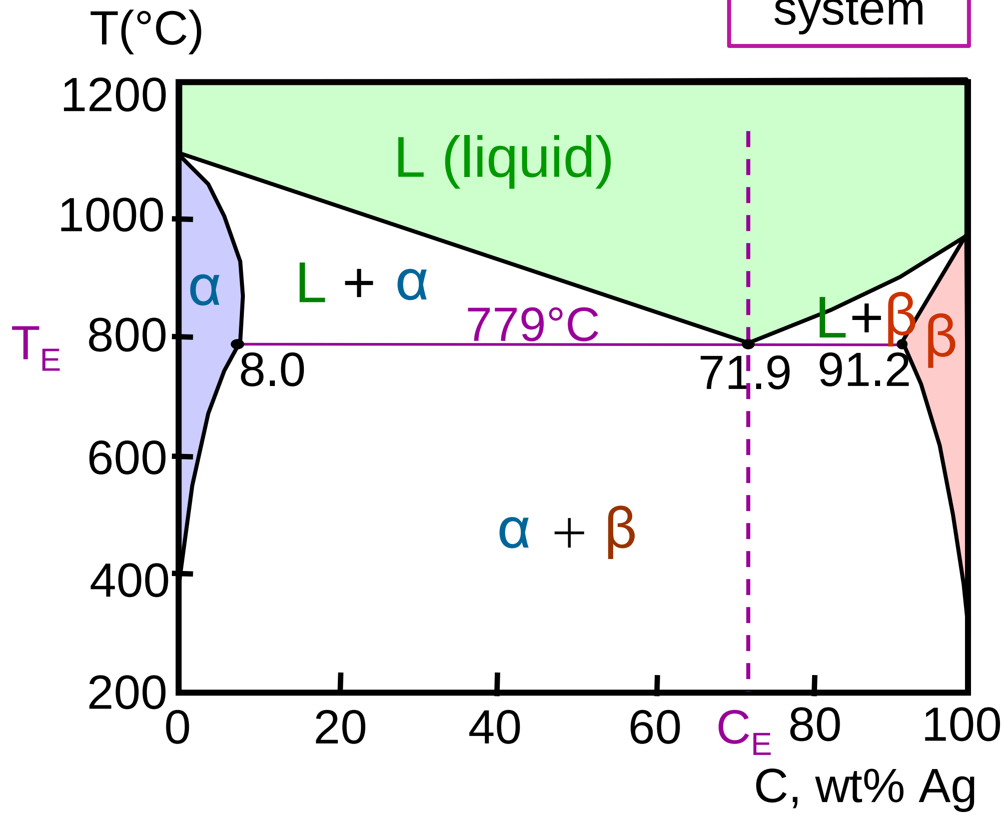
# Phase Diagram

# Binary – Eutectic Systems

2 components | has a special composition with a min. melting T. | Cu-Ag system

Ex.: Cu-Ag system

- 3 single phase regions (L, α, β)
- Limited solubility:
  - α: mostly Cu
  - β: mostly Ag
- $T_E$ : No liquid below $T_E$
- $C_E$ : Composition at temperature $T_E$
- **Eutectic reaction**



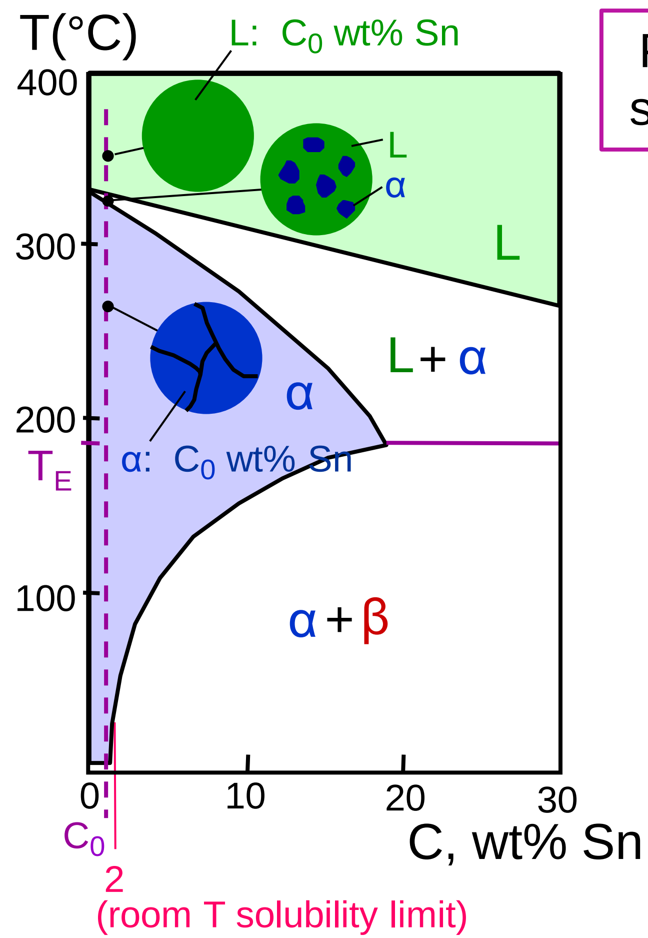

$$L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

Fig. 9.7, Callister & Rethwisch 10e [Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.].

$$L(71.9 \text{ wt\% Ag}) \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} a(8.0 \text{ wt\% Ag}) + b(91.2 \text{ wt\% Ag})$$

# Microstructural Developments in Eutectic Systems I

- For alloys for which
  $C_0$ < 2 wt% Sn
- Result: at room temperature
  -- polycrystalline with grains of
  α phase having
  composition $C_0$




Pb-Sn system

Fig. 9.11, Callister & Rethwisch 10e.

# Microstructural Developments in Eutectic Systems II

- For alloys for which
  2 wt% Sn < $C_0$ < 18.3 wt% Sn
- Result:
  at temperatures in α + β range
  -- polycrystalline with α grains
  and small β-phase particles

Pb-Sn system

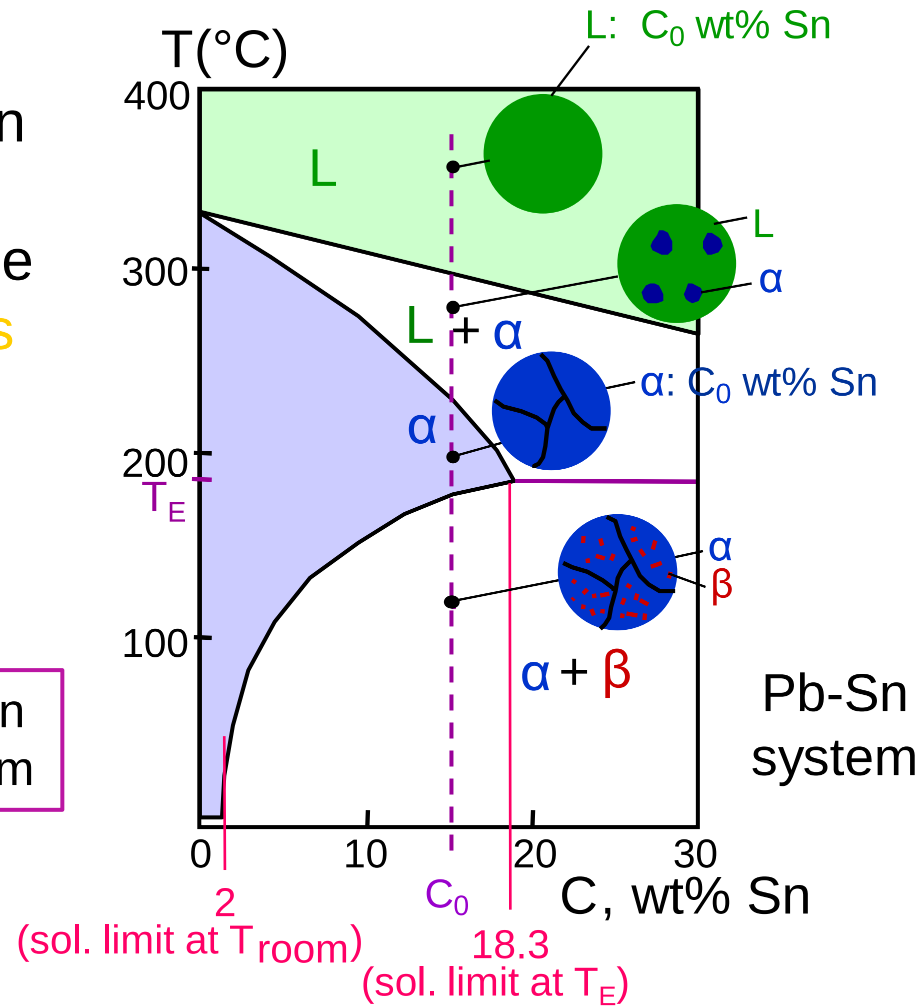
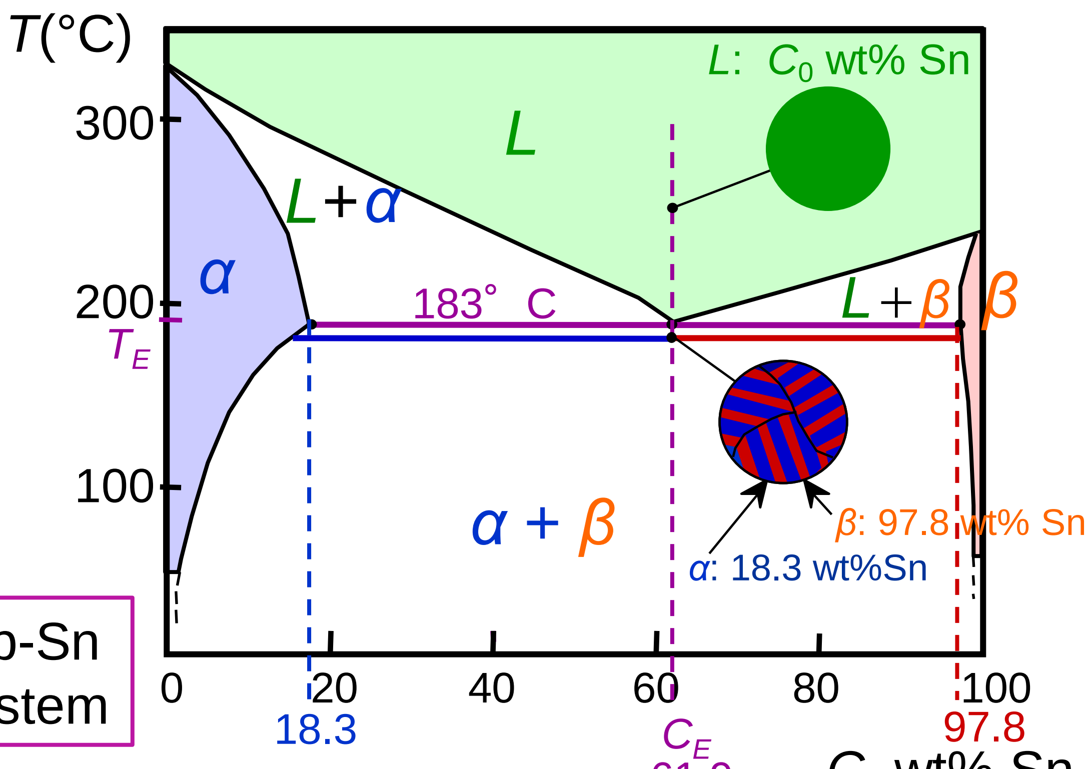



Fig. 9.12, Callister & Rethwisch 10e.

# Microstructural Developments in Eutectic Systems III

- For alloy of composition $C_0 = C_E$
- Result: Eutectic microstructure (lamellar structure)
  -- alternating layers (lamellae) of $\alpha$ and $\beta$ phases.




Pb-Sn system

Fig. 9.13, Callister & Rethwisch 10e.

Micrograph of Pb-Sn eutectic microstructure

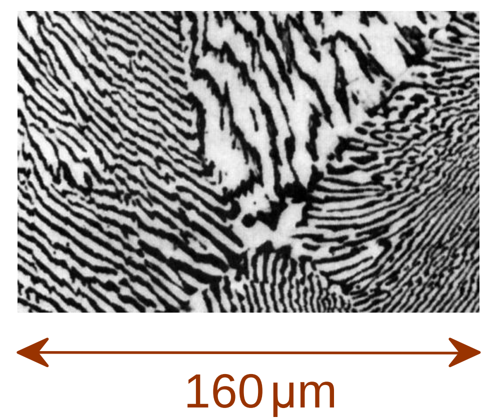
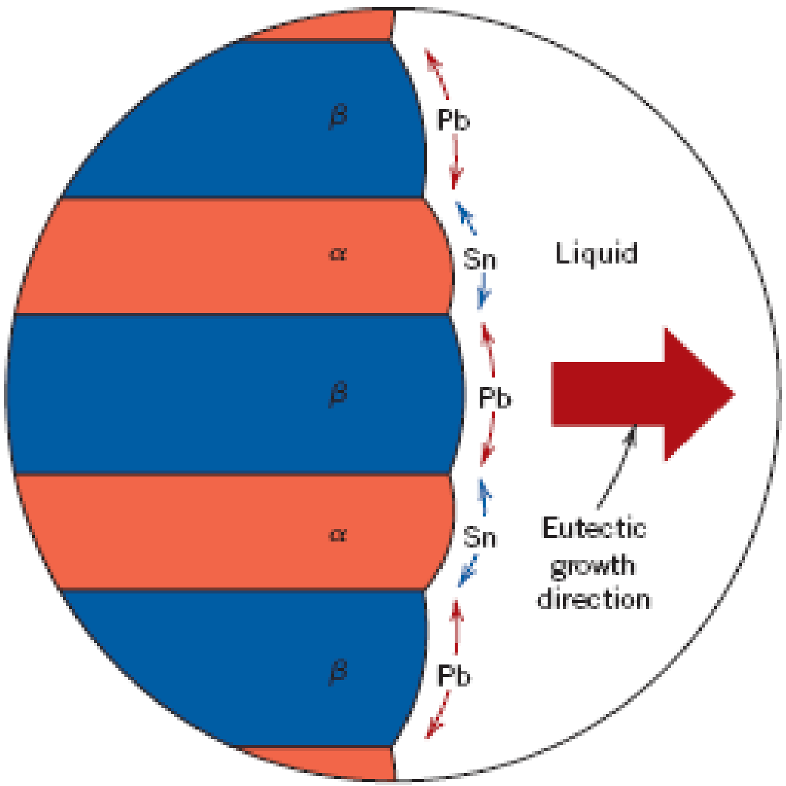
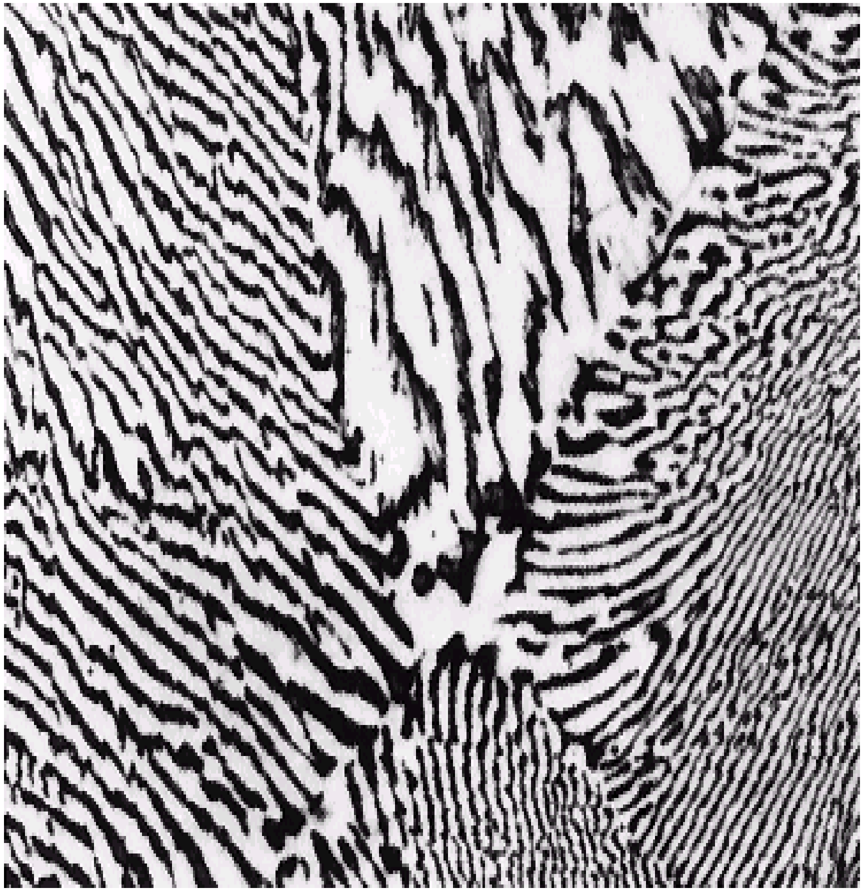



Fig. 9.14, *Callister & Rethwisch 10e.* (From *Metals Handbook*, 9th edition, Vol. 9, *Metallography and Microstructures*, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

# Lamellar Eutectic Structure



Figs. 9.14 & 9.15, Callister & Rethwisch 10e. (Fig. 9.14 from Metals Handbook, 9th edition, Vol. 9, Metallography and Microstructures, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

# Microstructural Developments in Eutectic Systems IV

- For alloys for which 18.3 wt% Sn < $C_0$ < 61.9 wt% Sn
- Result: α phase particles and a eutectic microconstituent

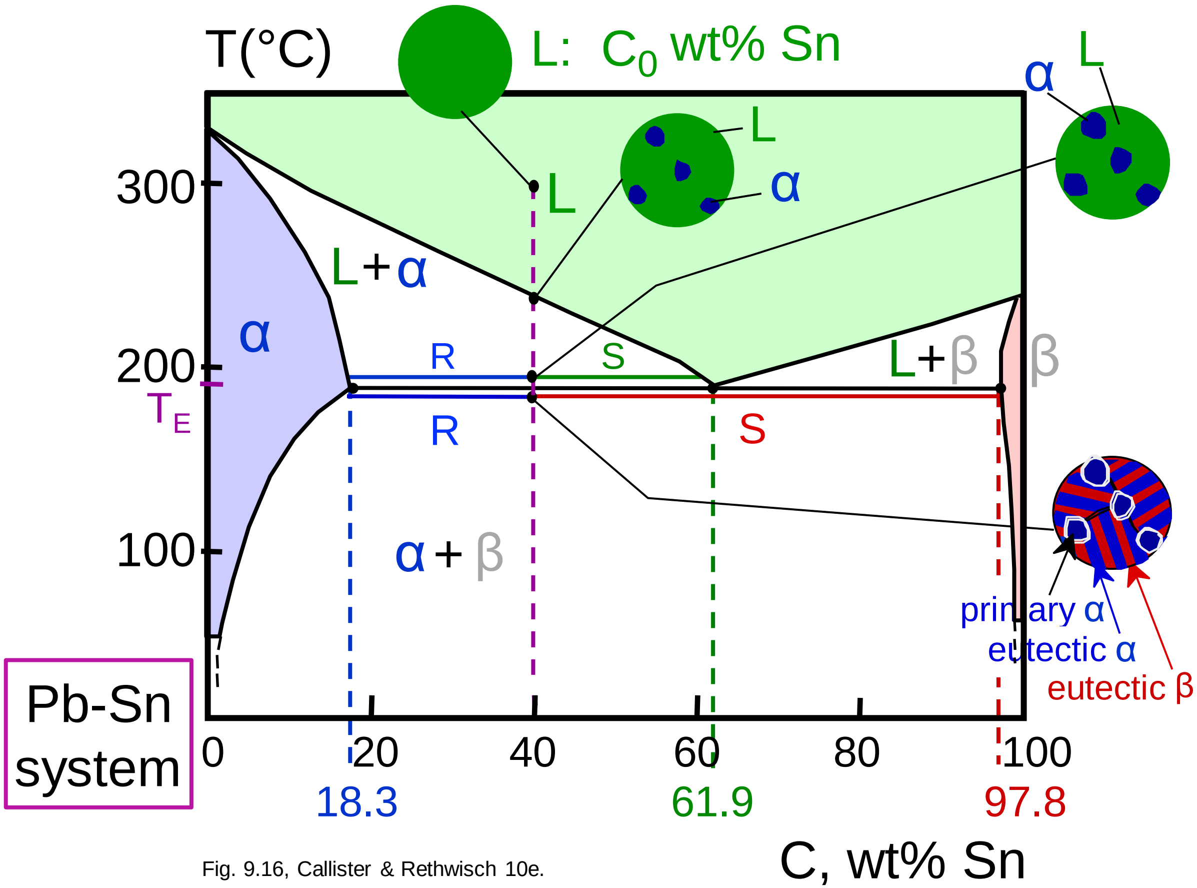



Fig. 9.16, Callister & Rethwisch 10e.

- Just above $T_E$ :

$C_\alpha$ = 18.3 wt% Sn

$C_L$ = 61.9 wt% Sn

$$W_\alpha = \frac{S}{R+S} = 0.50$$

$W_L$ = (1- $W_\alpha$) = 0.50

- Just below $T_E$ :

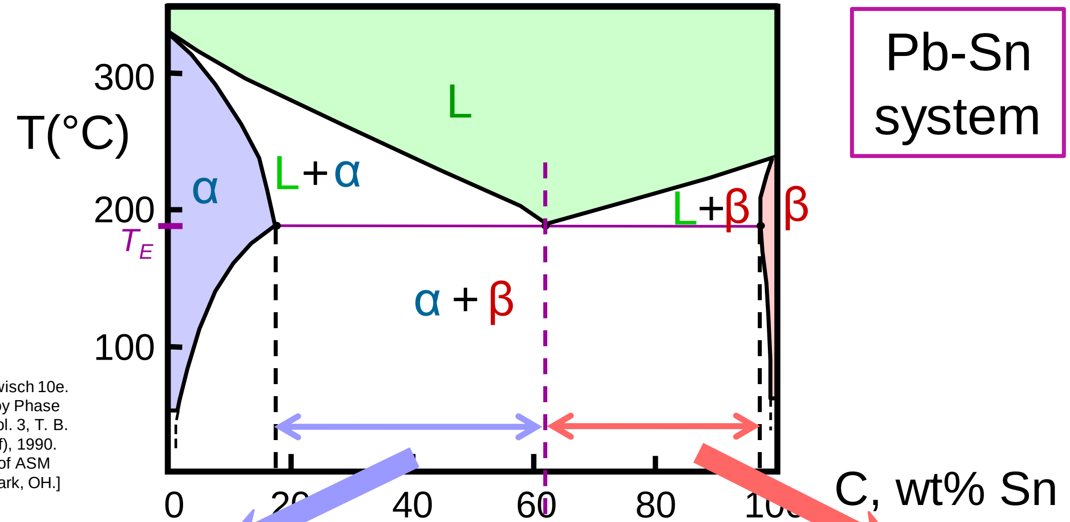
$C_\alpha$ = 18.3 wt% Sn

$C_\beta$ = 97.8 wt% Sn

$$W_\alpha = \frac{S}{R+S} = 0.73$$

$W_\beta$ = 0.27

# Hypoeutectic & Hypereutectic




Pb-Sn system

Fig. 9.8, Callister & Rethwisch 10e. [Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

hypoeutectic: $C_0$ = 50 wt% Sn

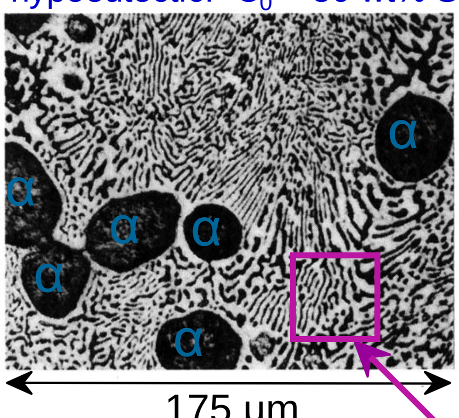



Fig. 9.17, Callister & Rethwisch 10e.

eutectic: $C_0$ = 61.9 wt% Sn

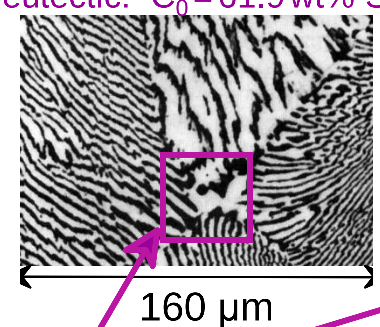
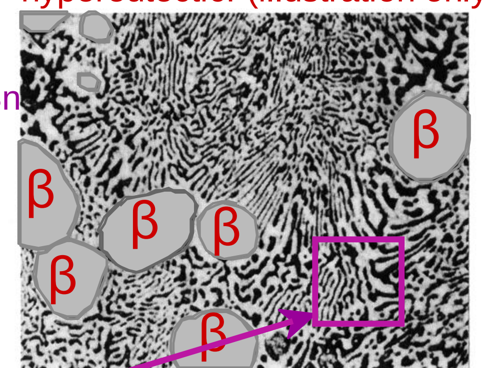



Fig. 9.14, Callister & Rethwisch 10e.

hypereutectic: (illustration only)




Adapted from Fig. 9.17, Callister & Rethwisch 10e. (Illustration only)

eutectic micro-constituent

# Terminal vs. Intermediate Solid Solutions

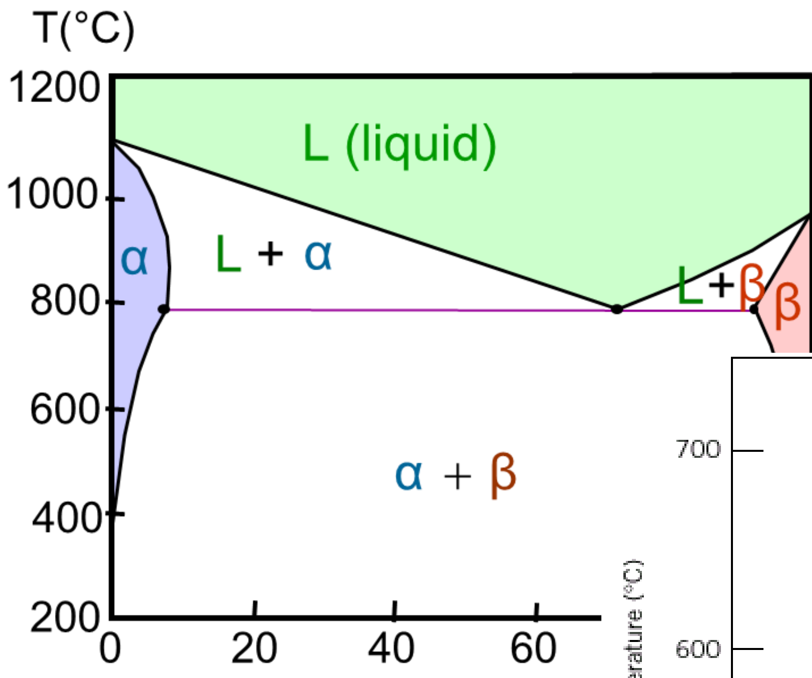



Fig. 9.7, Callister & Rethwisch 10e [Adapted from Binary Alloy Phase Diagram
Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM Internation

Cu-Ag system

Cu-Zn system

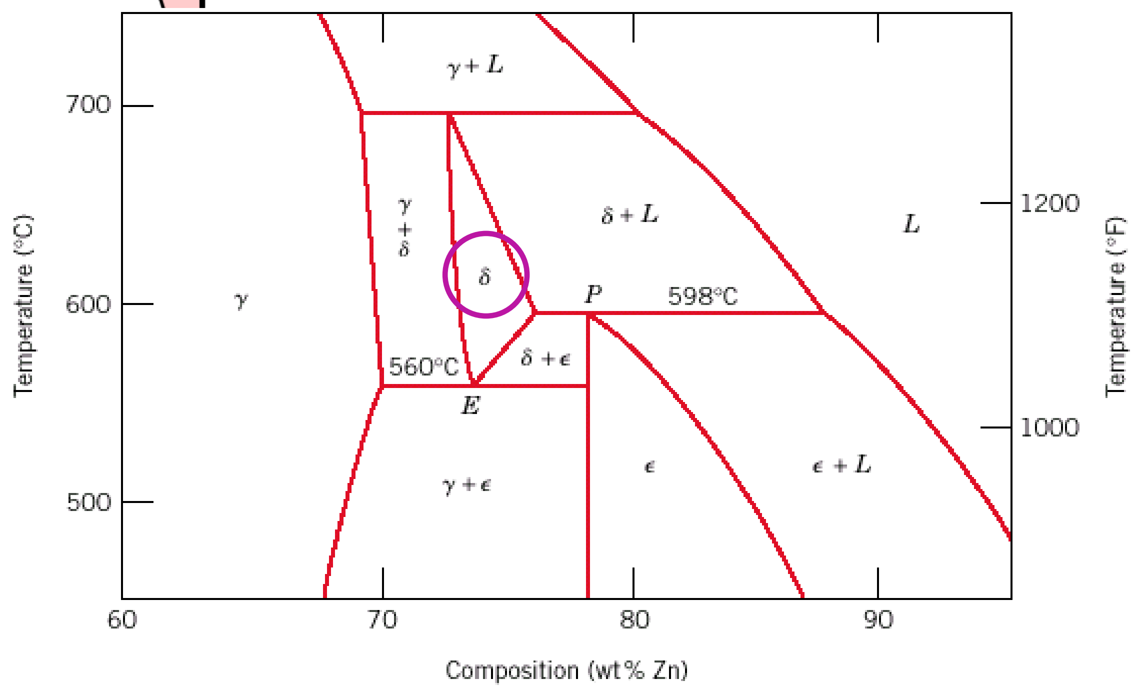
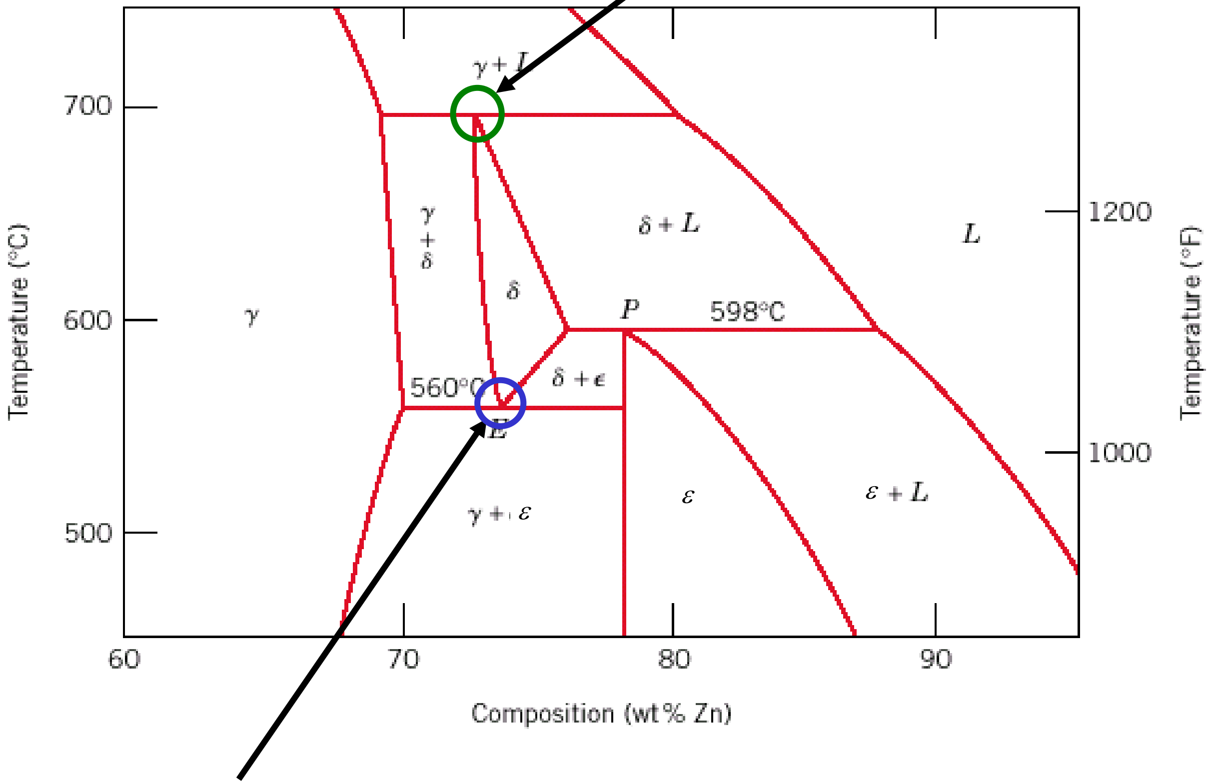



Fig. 9.21, *Callister & Rethwisch 10e.* [Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 2, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

# Eutectoid & Peritectic

Peritectic transformation $\gamma + L \rightleftharpoons \delta$

## Cu-Zn Phase diagram




Eutectoid transformation $\delta \rightleftharpoons \gamma + \varepsilon$

Fig. 9.21, *Callister & Rethwisch 10e.*
[Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 2, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

# Eutectic, Eutectoid, & Peritectic

- Eutectic - liquid transforms to two solid phases

$$L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + \beta \quad \text{(For Pb-Sn, 183°C, 61.9 wt\% Sn)}$$

- Eutectoid – one solid phase transforms to two other solid phases

$$S_2 \rightleftharpoons S_1 + S_3$$

intermetallic compound
- cementite

$$\gamma \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + Fe_3C \quad \text{(For Fe-C, 727°C, 0.76 wt\% C)}$$

- Peritectic - liquid and one solid phase transform to a second solid phase

$$S_1 + L \rightleftharpoons S_2$$

$$\delta + L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \gamma \qquad \text{(For Fe-C, 1493°C, 0.16 wt\% C)}$$

# Intermetallic Compounds

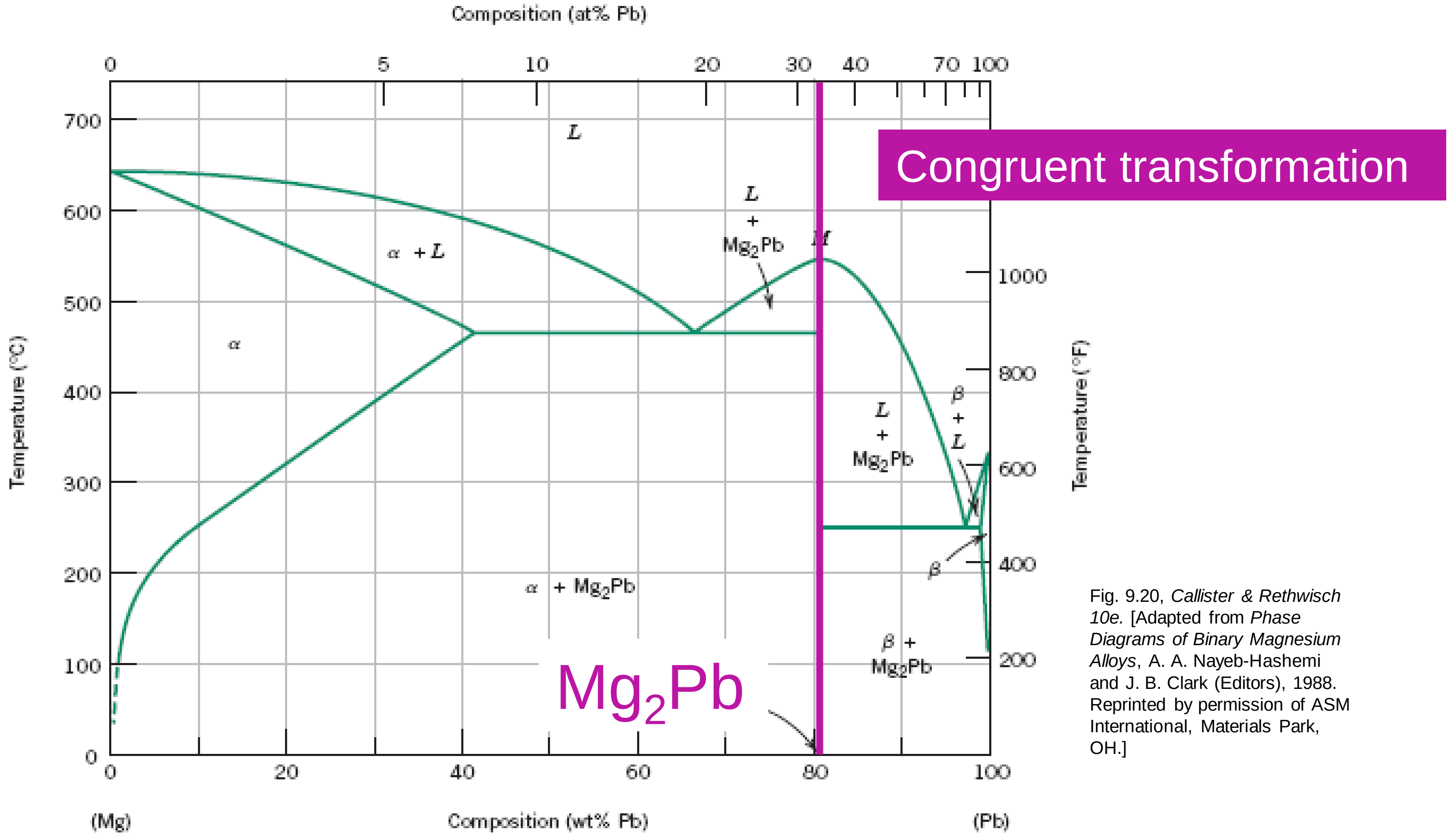



Fig. 9.20, *Callister & Rethwisch 10e.* [Adapted from *Phase Diagrams of Binary Magnesium Alloys*, A. A. Nayeb-Hashemi and J. B. Clark (Editors), 1988. Reprinted by permission of ASM International, Materials Park, OH.]

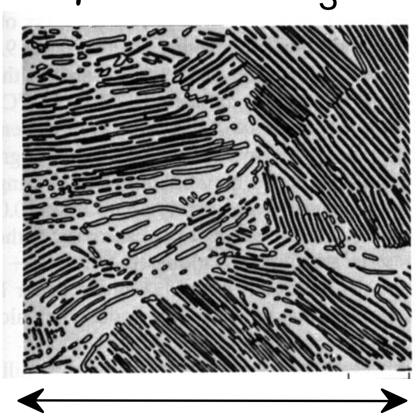
Note: intermetallic compound exists as a line on the diagram - not an area - because of stoichiometry (i.e. composition of a compound is a fixed value).

# Iron-Carbon (Fe-C) Phase Diagram

- 2 important points
  - Eutectic (A):

    $L \Rightarrow \gamma + Fe_3C$
  - Eutectoid (B):

    $\gamma \Rightarrow \alpha + Fe_3C$




Result: Pearlite = alternating layers of α and $Fe_3C$ phases

Fig. 9.27, Callister & Rethwisch 10e. (From Metals Handbook, Vol. 9, 9th ed., Metallography and Microstructures, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

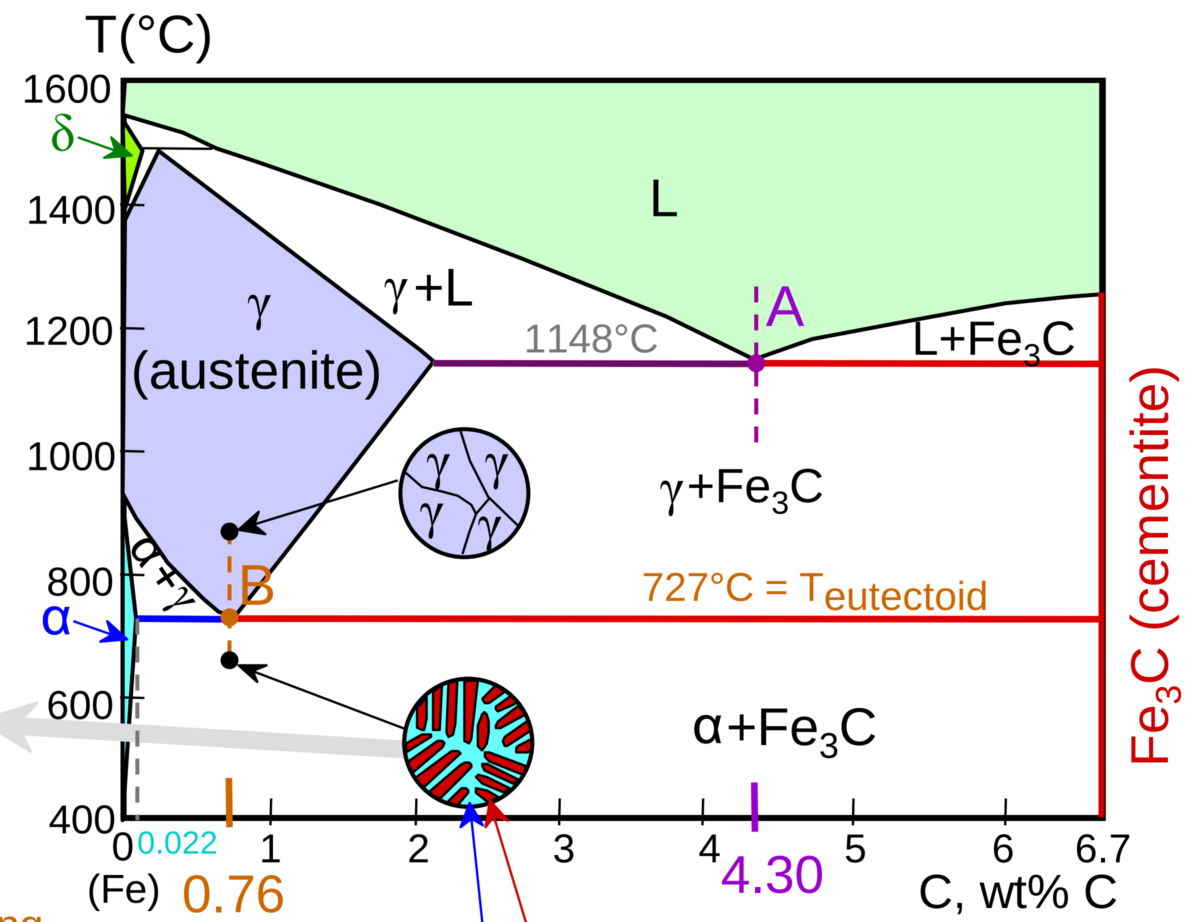
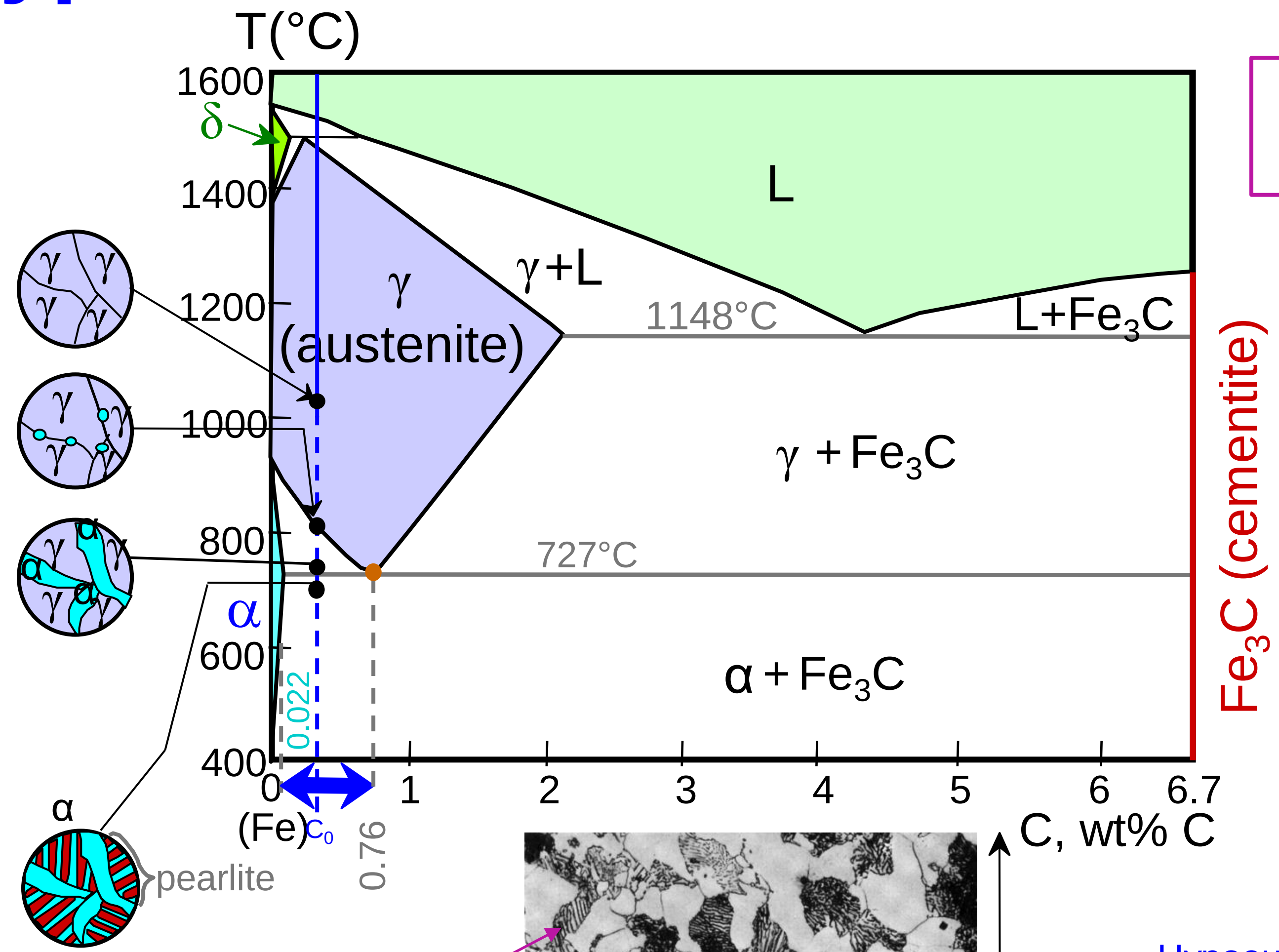


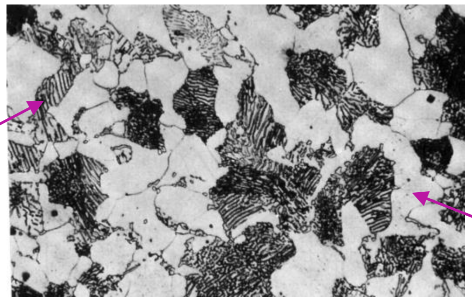

Fig. 9.24, Callister & Rethwisch 10e. [Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

# Hypoeutectoid Steel




Fe-C system

Adapted from Figs. 9.24 and 9.29, Callister & Rethwisch 10e. [Figure 9.24 adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]



pearlite

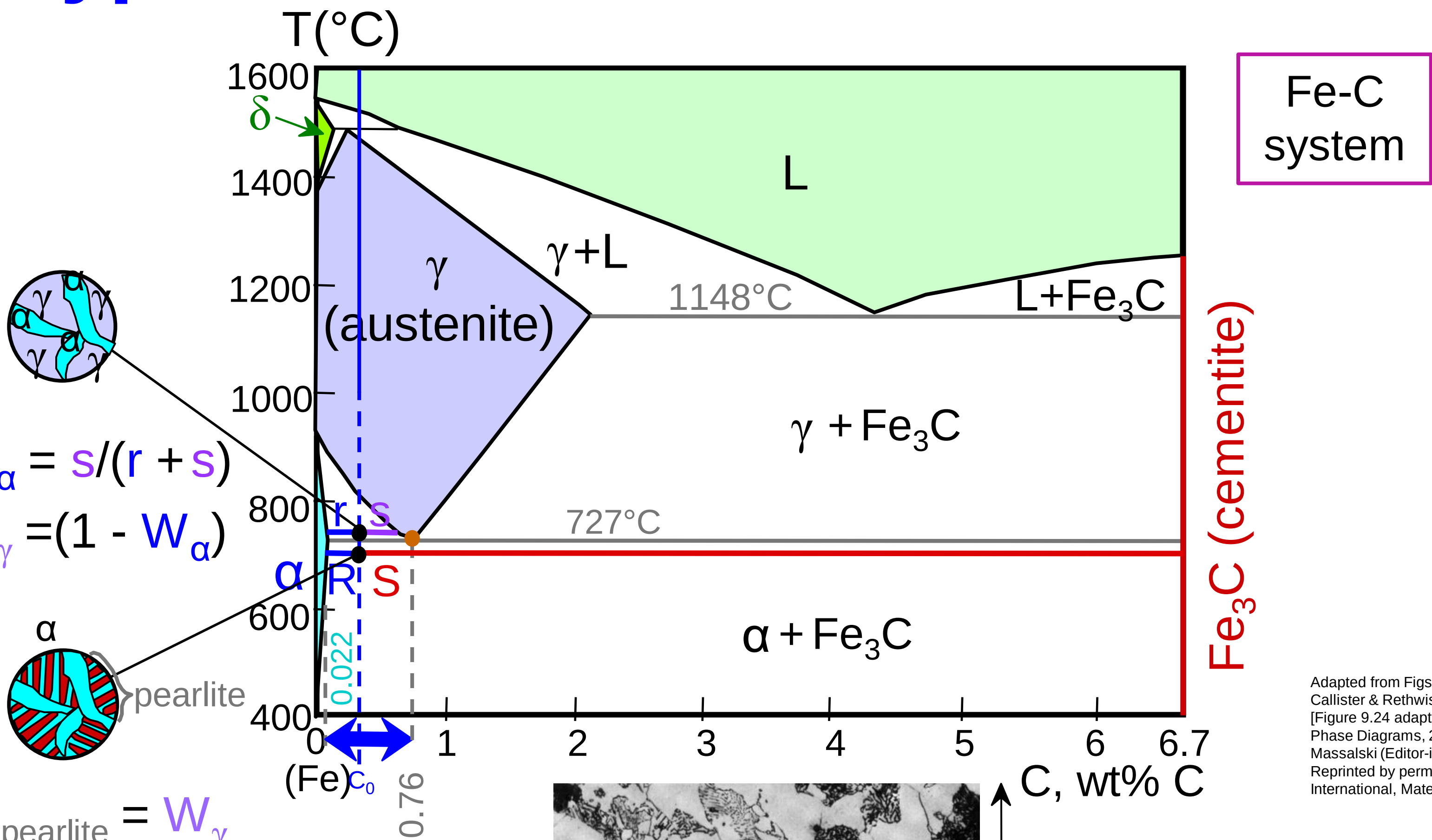
100 µm

Hypoeutectoid steel

proeutectoid ferrite

Adapted from Fig. 9.30, Callister & Rethwisch 10e. (Photomicrograph courtesy of Republic Steel Corporation.)

# Hypoeutectoid Steel




$W_\alpha = s/(r + s)$

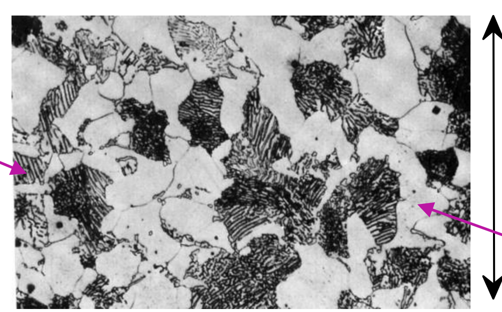
$W_\gamma = (1 - W_\alpha)$

$W_{pearlite} = W_\gamma$

$W_{\alpha'} = S/(R + S)$

$W_{Fe_3C} = (1 - W_{\alpha'})$

Adapted from Figs. 9.24 and 9.29, Callister & Rethwisch 10e. [Figure 9.24 adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]



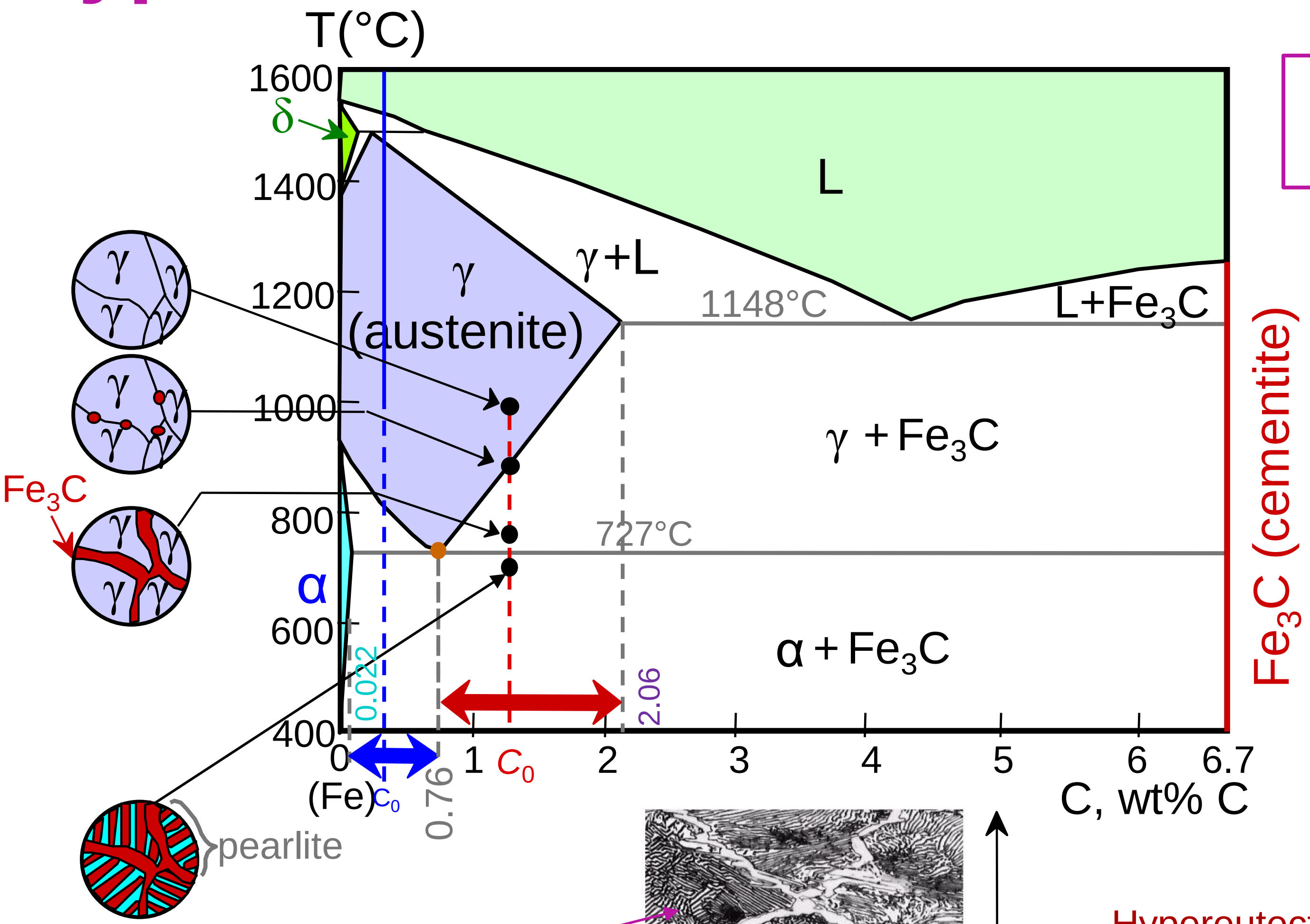

pearlite

proeutectoid ferrite

Hypoeutectoid steel

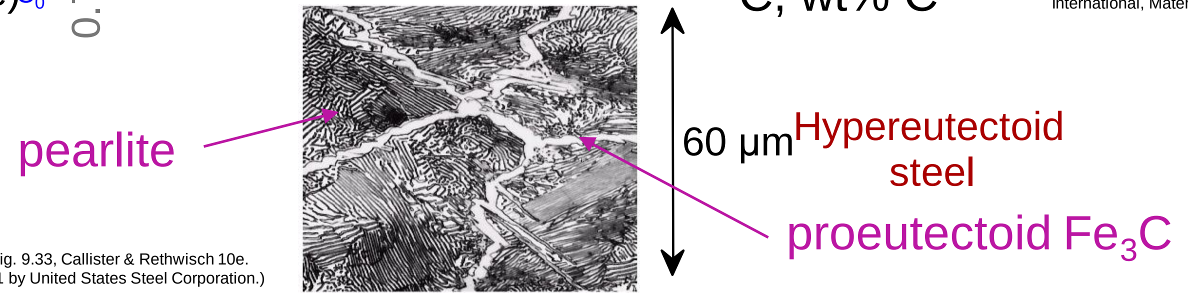
Adapted from Fig. 9.30, Callister & Rethwisch 10e. (Photomicrograph courtesy of Republic Steel Corporation.)

# Hypereutectoid Steel



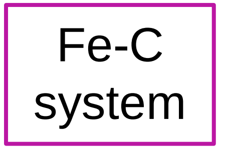

Fe-C system

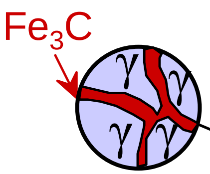
Adapted from Figs. 9.24 and 9.29, Callister & Rethwisch 10e.
[Figure 9.24 adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]




Adapted from Fig. 9.33, Callister & Rethwisch 10e.
(Copyright 1971 by United States Steel Corporation.)

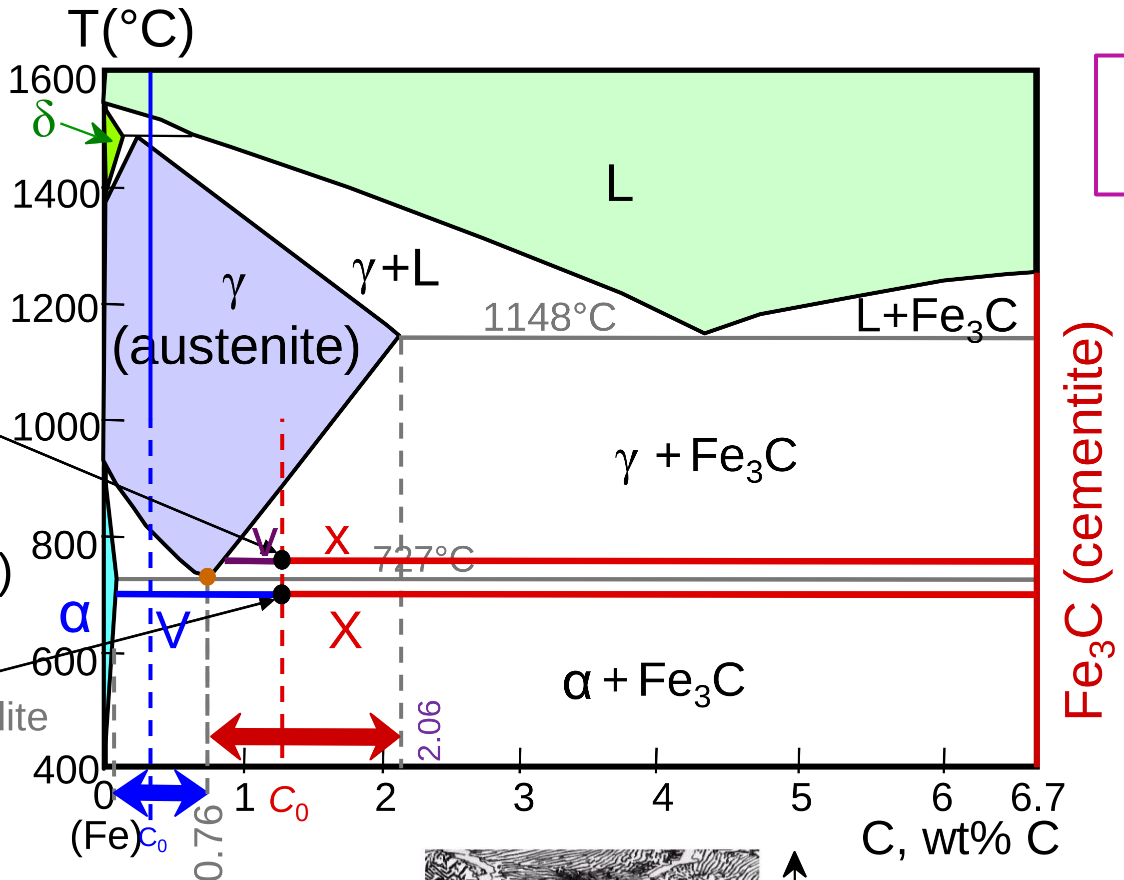
# Hypereutectoid Steel

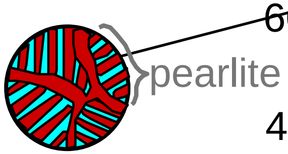



$W_\gamma$ =x/(v + x)

$W_{Fe_3C}$ =(1-$W_\gamma$)




Adapted from Figs. 9.24 and 9.29, Callister & Rethwisch 10e. [Figure 9.24 adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

$W_{pearlite} = W_\gamma$

$W_\alpha$ = X/(V + X)

$W_{Fe_3C'}$ =(1 - $W_\alpha$)


pearlite

Hypereutectoid steel

proeutectoid Fe$_3$C

Adapted from Fig. 9.33, Callister & Rethwisch 10e. (Copyright 1971 by United States Steel Corporation.)

# Alloying with Other Elements

- $T_{eutectoid}$ changes:

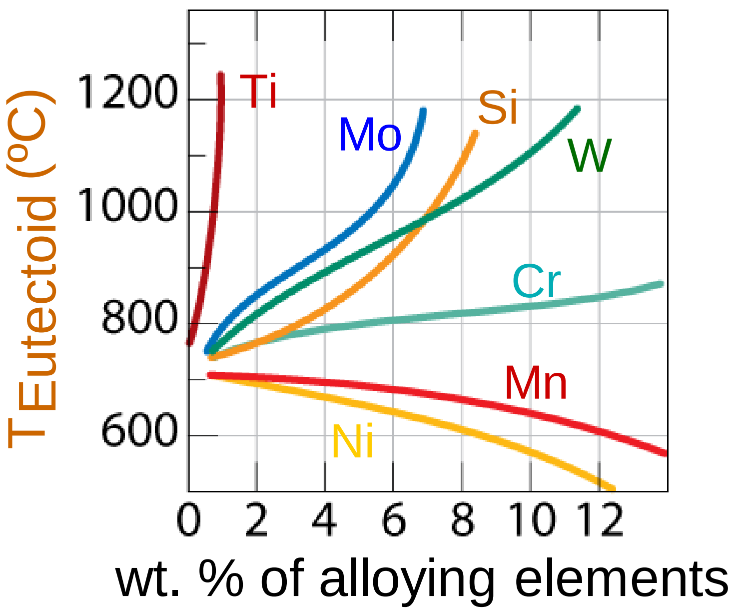



Fig. 9.34, Callister & Rethwisch 10e.
(From Edgar C. Bain, Functions of the Alloying Elements in Steel, 1939. Reproduced by permission of ASM International, Materials Park, OH.)

- $C_{eutectoid}$ changes:

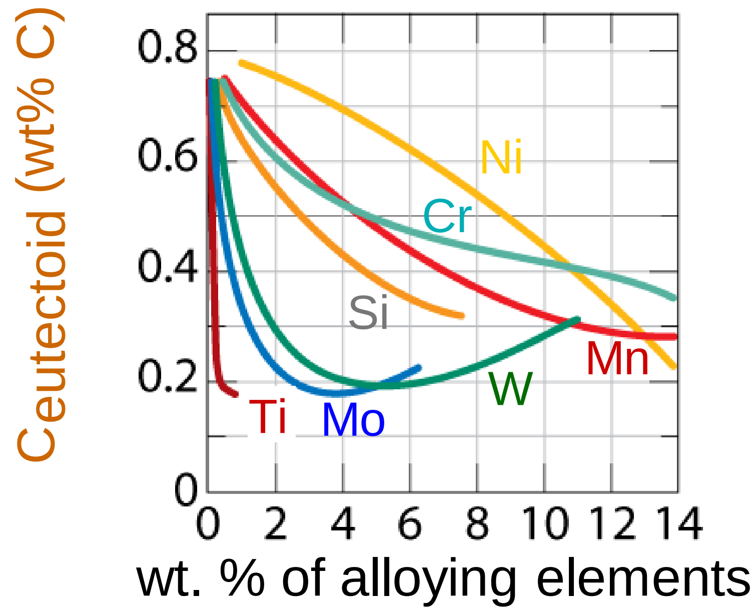



Fig. 9.35,Callister & Rethwisch 10e.
(From Edgar C. Bain, Functions of the Alloying Elements in Steel, 1939. Reproduced by permission of ASM International, Materials Park, OH.)

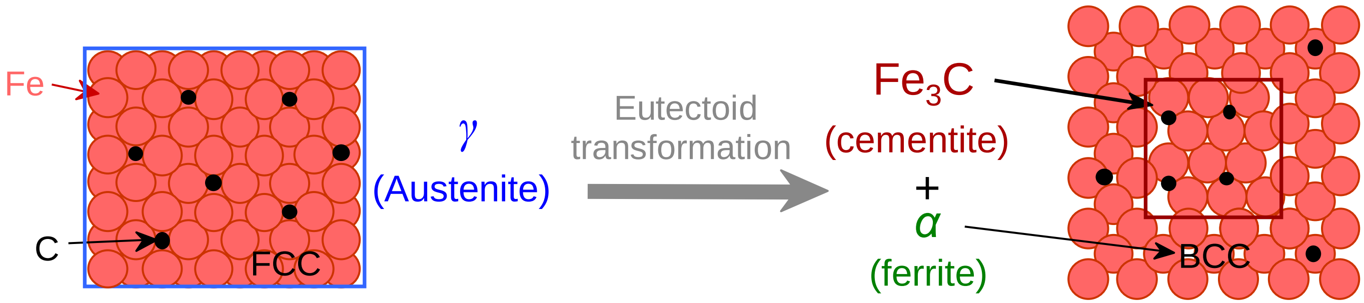
# Summary

- **Phase diagrams** are useful tools to determine: (given the temperature and composition of the system)
  - the number and types of phases present,
  - the composition of each phase,
  - and the weight fraction of each phase.
- Important phase diagram phase transformations include **eutectic**, **eutectoid**, and **peritectic**.
- The **microstructure** of an alloy strongly depends on:
  - its composition, and
  - whether or not cooling rate allows for maintenance of equilibrium.

# Phase Transformation

# Introduction

- Transforming one phase into another takes time to reach equilibrium.




- How does the rate of transformation depend on time and temperature ?
- What will form if a non-equilibrium phase transformation is conduced?
- What are the differences in microstructure and properties for the phase transformation in equilibrium and non-equilibrium?

# Learning Objectives

After this chapter you should be able to do the following:

- Make a schematic transformation vs. time plot and cite the equation that describes this behavior.
- Briefly describe the microstructure for the following microconstituents: fine pearlite, coarse pearlite, bainite, martensite, and tempered martensite.
- Cite the general mechanical characteristics for each of the following microconstituents: fine pearlite, coarse pearlite, bainite, martensite, and tempered martensite.
- Given the isothermal transformation (or continuous cooling transformation) diagram for some iron–carbon alloy, design a heat treatment that will produce a specified microstructure.

# Phase Transformations

## Nucleation and Growth

- nuclei (seeds) act as templates on which crystals grow
- for nucleus to form rate of addition of atoms to nucleus must be faster than rate of loss
- once nucleated, growth proceeds until equilibrium is attained

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

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

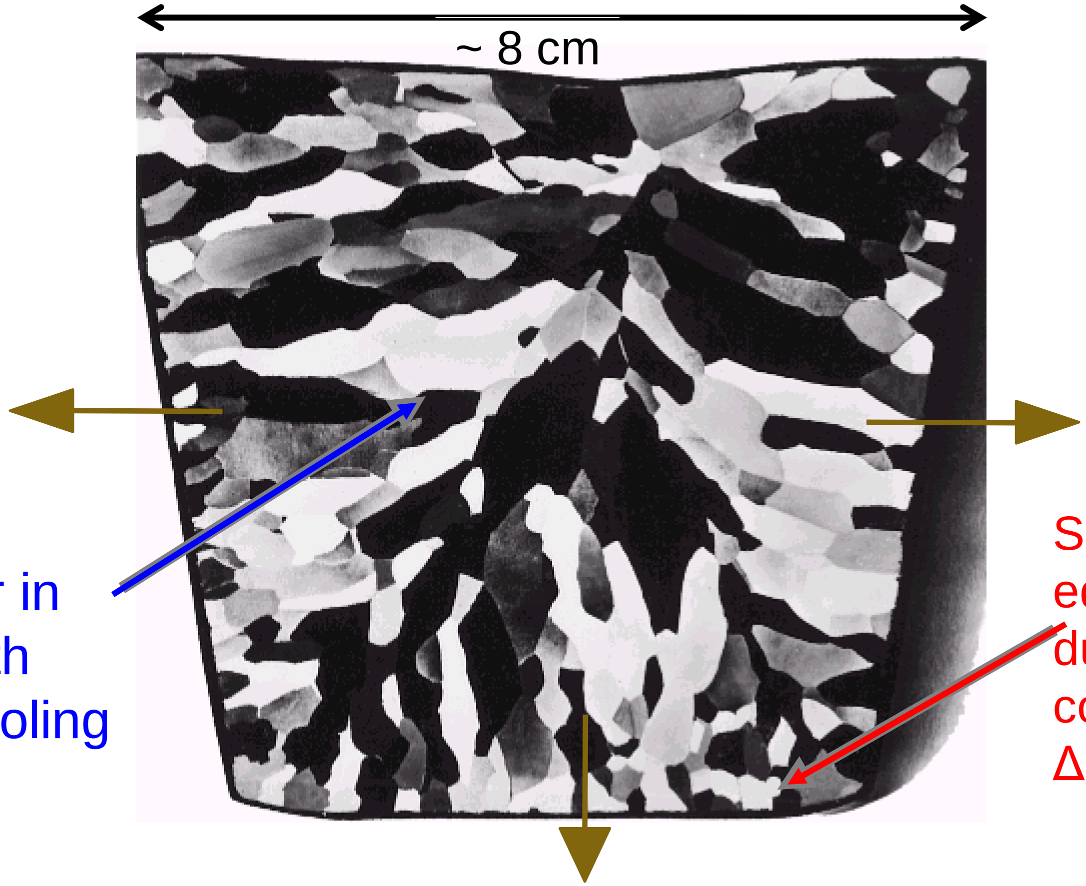
Small supercooling → slow nucleation rate - few nuclei - large crystals

Large supercooling → rapid nucleation rate - many nuclei - small crystals

# Solidification

Grains can be – equiaxed (roughly the same dimension in all directions)

- columnar (grains elongated in one direction)




Adapted from Fig. 5.17, *Callister & Rethwisch 3e.* (Reproduced with permission from Metals Handbook, Vol. 9, 9th edition, Metallography and Microstructures, ASM International, Materials Park, OH, 1985.)

Grain Refiner - added to make smaller, more uniform, equiaxed grains.

# Solidification: Nucleation Types

- Homogeneous nucleation
  - nuclei form in the bulk of liquid metal
  - requires considerable supercooling (typically 80-300°C)
- Heterogeneous nucleation
  - much easier since stable “nucleating surface” is already present — e.g., mold wall, impurities in liquid phase
  - only very slight supercooling (0.1-10°C)

# Rate of Phase Transformation

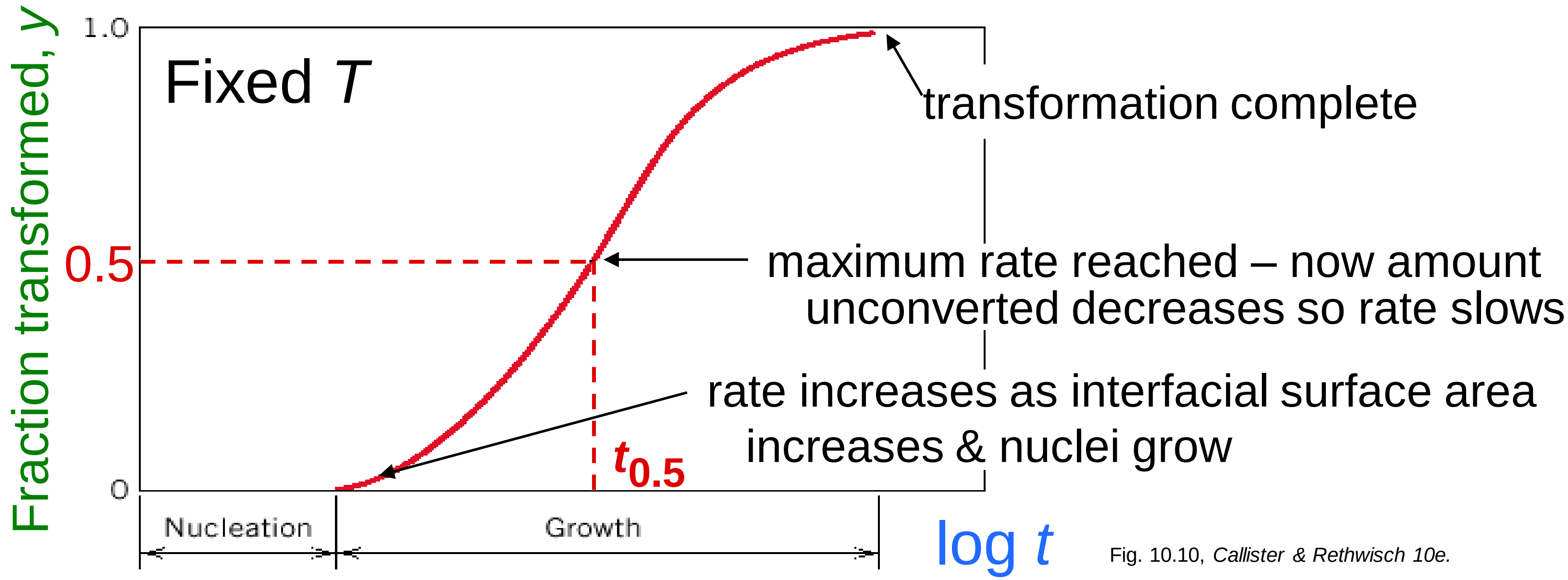



Fig. 10.10, *Callister & Rethwisch 10e.*

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

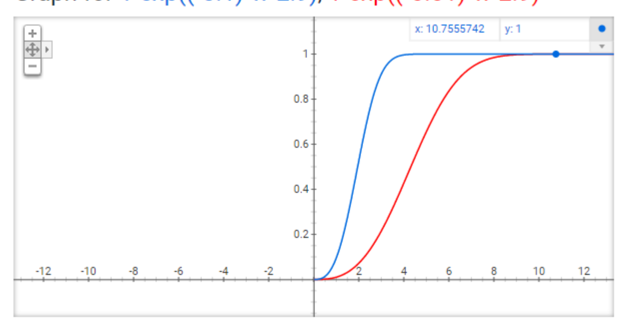
Also known as the JMAK EQUAITON

**fraction transformed** ($y$) **time** ($t$)

– $k$ & $n$ are parameters

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

Graph for 1-exp((-0.1)*x^2.9), 1-exp((-0.01)*x^2.9)



# Transformations & Undercooling

- Eutectoid transf. (Fe-$Fe_3C$ system): $\gamma \Rightarrow \alpha + Fe_3C$

0.76 wt% C
0.022 wt% C
6.7 wt% C

- For transf. to occur, must cool to below 727°C (i.e., must "undercool")

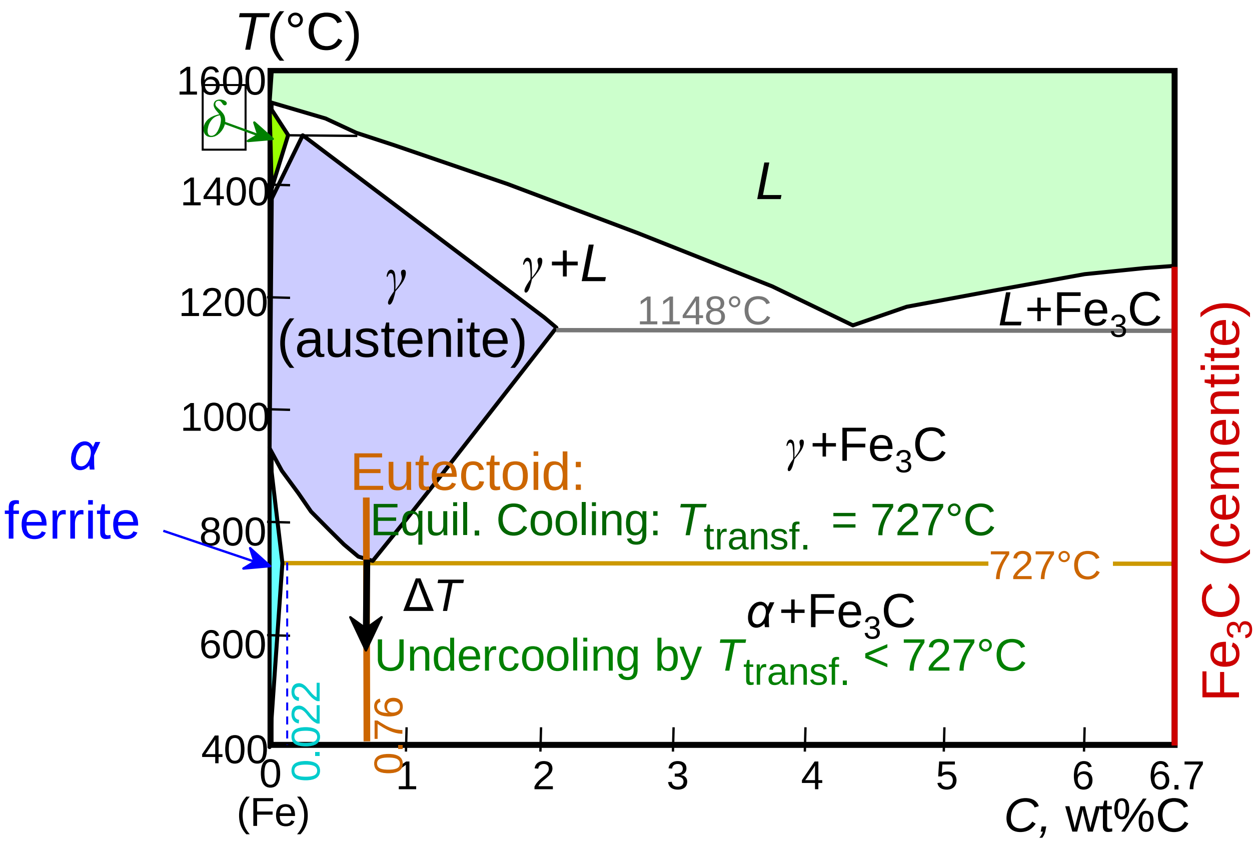
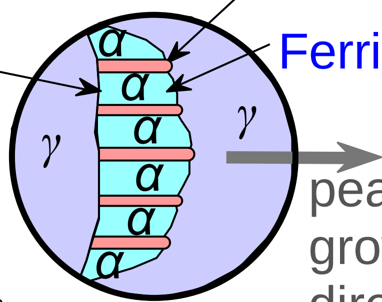



Fig. 9.24, Callister & Rethwisch 10e. [Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

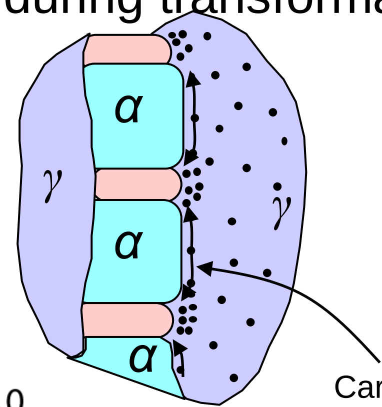
# The Fe-$Fe_3C$ Eutectoid Transformation

- Transformation of austenite to pearlite:

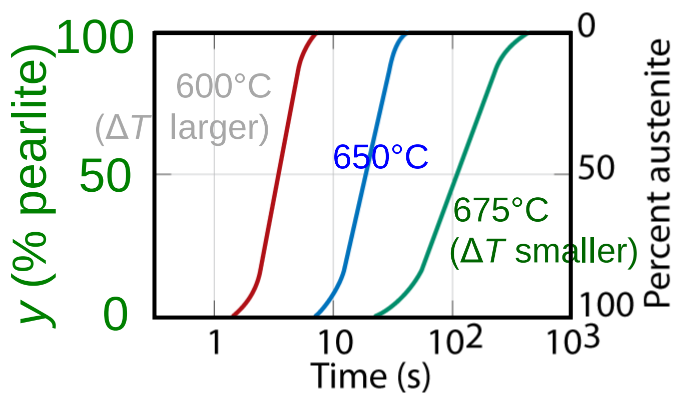



Adapted from Fig. 9.15, *Callister & Rethwisch 10e.*

Diffusion of C during transformation




- For this transformation, rate increases with $[T_{eutectoid} - T]$ (i.e., $\Delta T$).




Adapted from Fig. 10.12, *Callister & Rethwisch 10e.*

Coarse pearlite → formed at higher temperatures – relatively soft

Fine pearlite → formed at lower temperatures – relatively hard

# Generation of Isothermal Transformation Diagrams

Consider:

- The Fe-$Fe_3C$ system, for $C_0$ = 0.76 wt% C
- A transformation temperature of 675ºC.

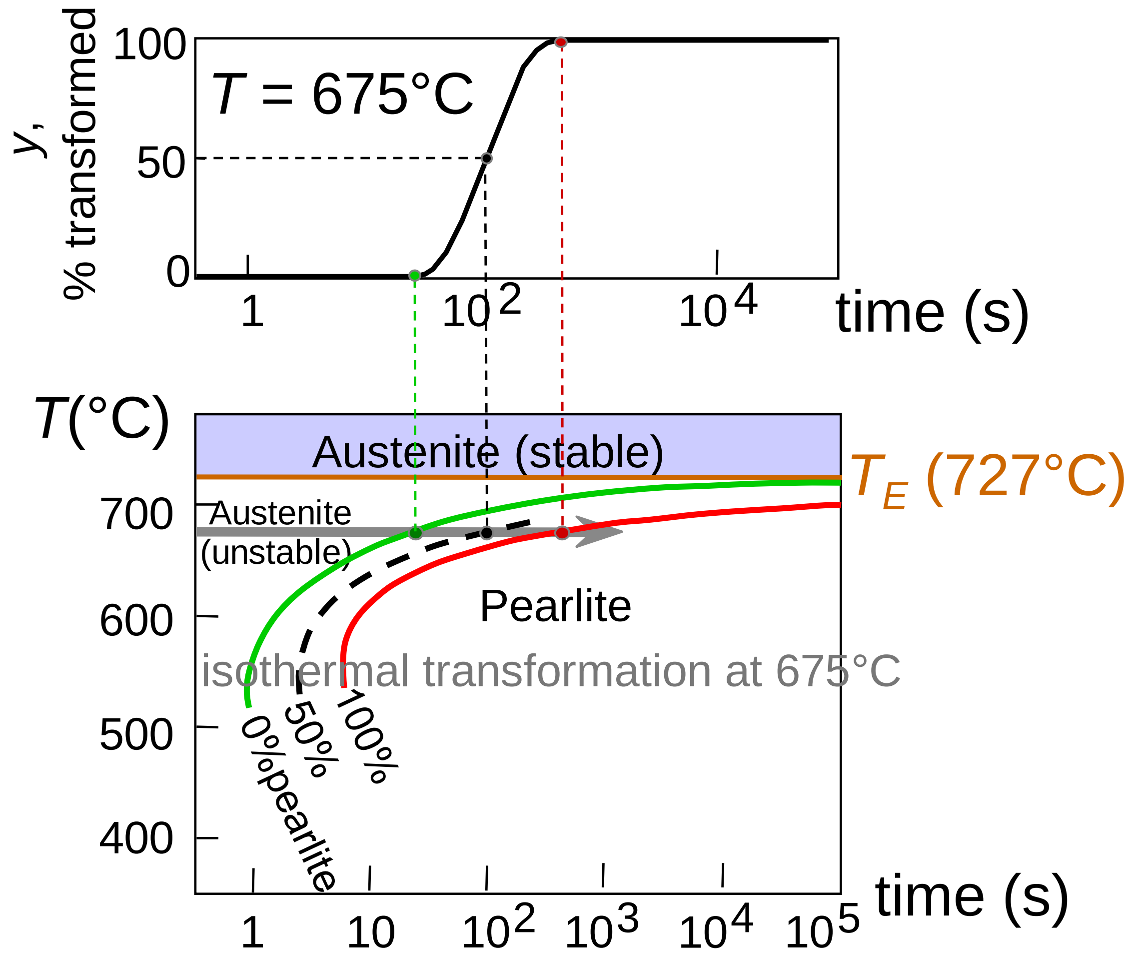



Fig. 10.13, *Callister & Rethwisch 10e.* [Adapted from H. Boyer (Editor), Atlas of Isothermal Transformation and Cooling Transformation Diagrams, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

# Austenite-to-Pearlite Isothermal Transformation

- Eutectoid composition, $C_0 = 0.76$ wt% C
- Begin at $T > 727°C$
- Rapidly cool to 625°C
- Hold $T$ (625°C) constant (isothermal treatment)

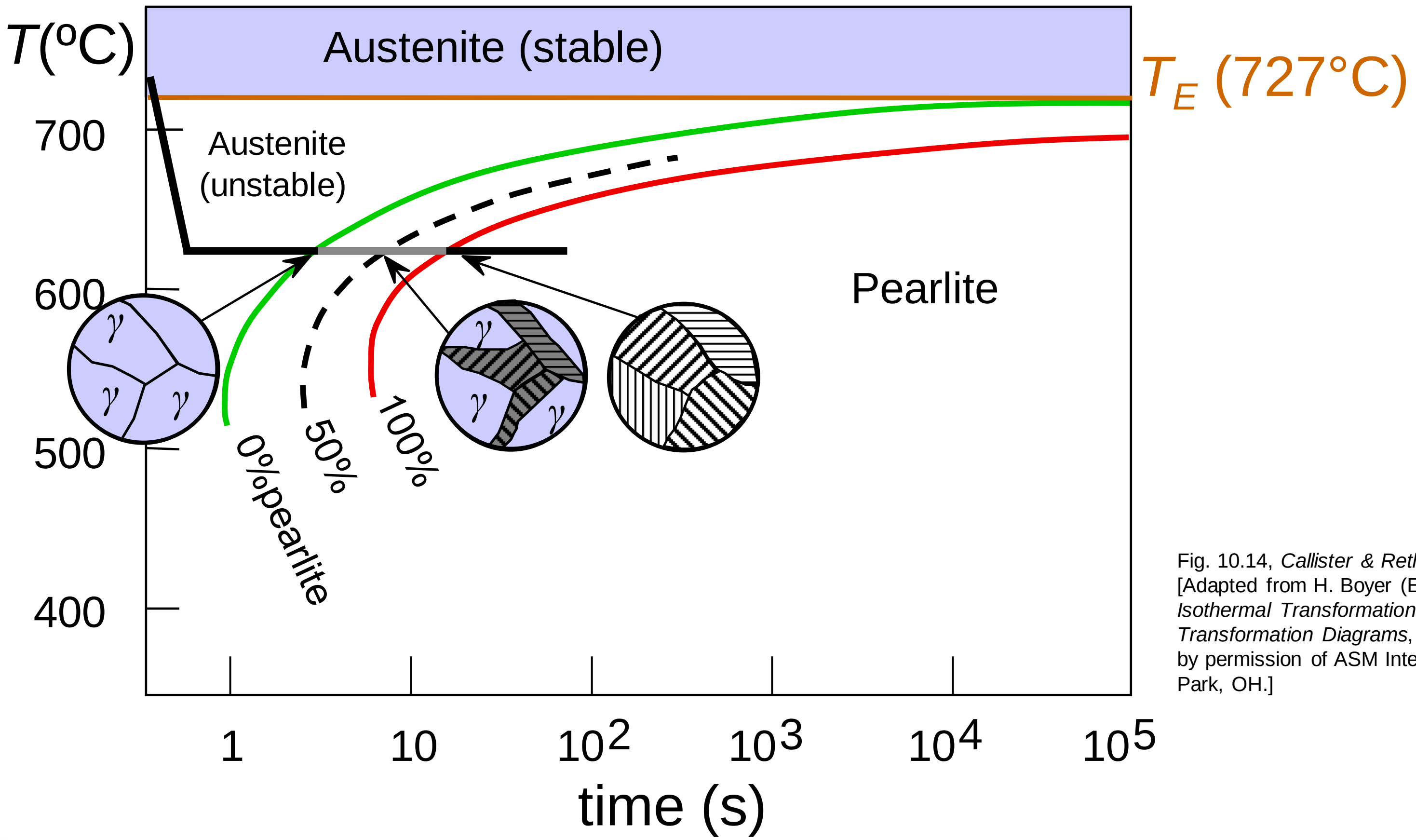



Fig. 10.14, *Callister & Rethwisch 10e.* [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

# Transformations Involving Noneutectoid Compositions

Consider $C_0$ = 1.13 wt% C

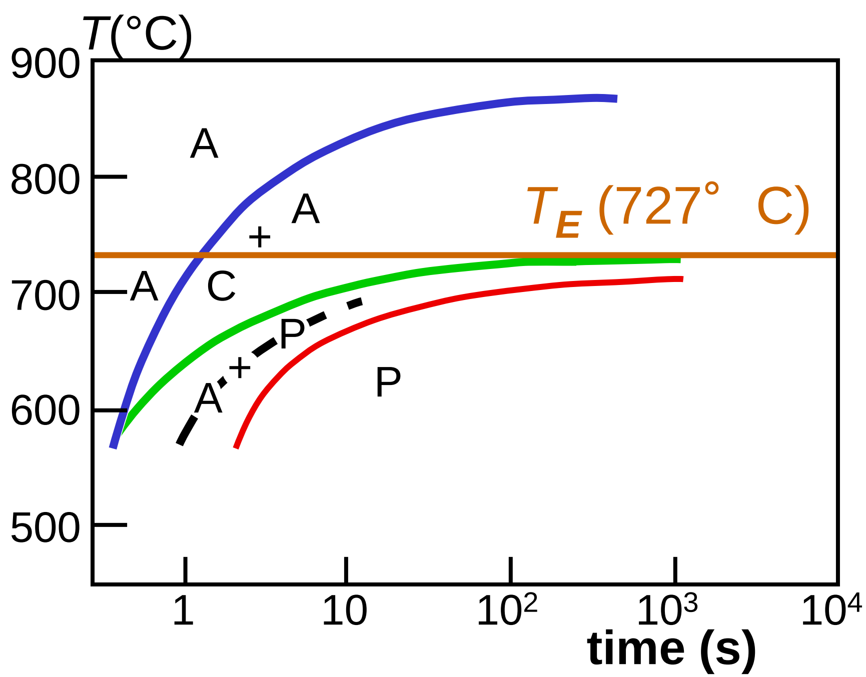



Fig. 10.16, *Callister & Rethwisch 10e.* [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

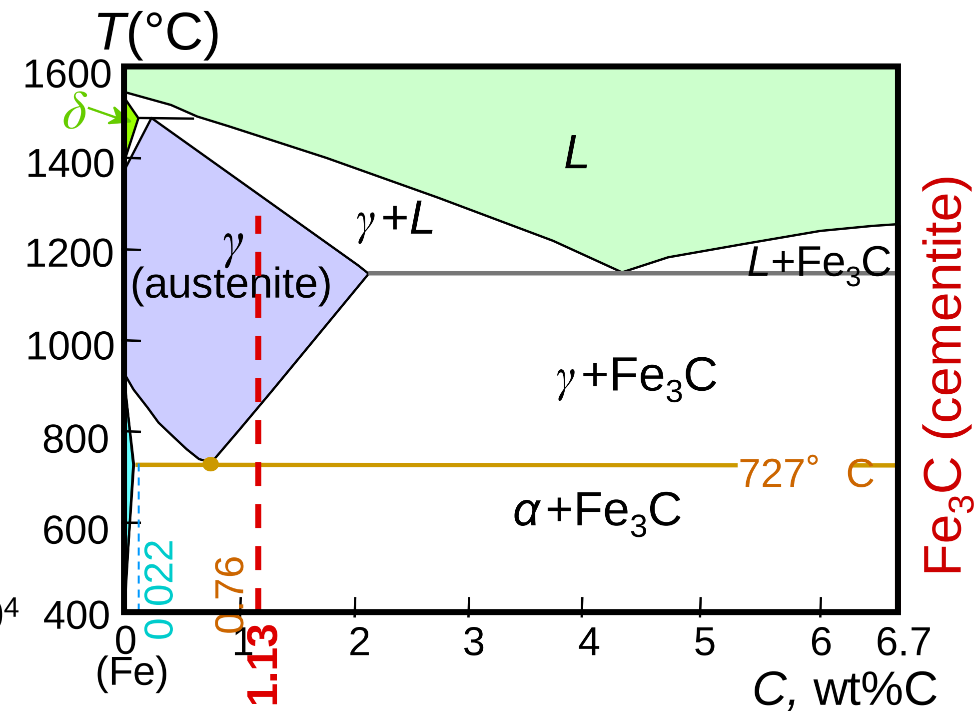
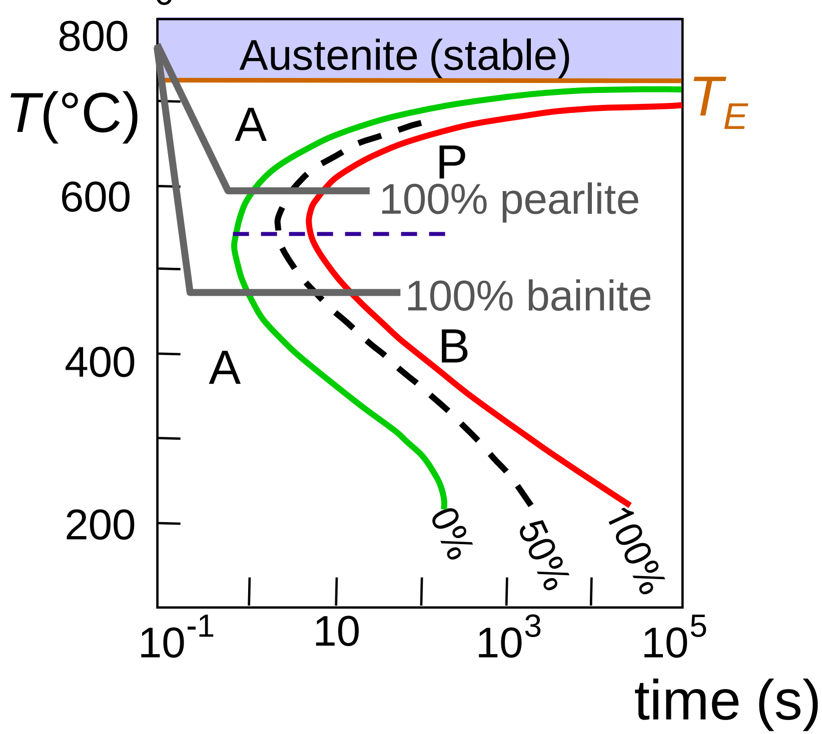



Fig. 9.24, *Callister & Rethwisch 10e*. [Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

## Hypereutectoid composition – proeutectoid cementite

# Bainite: Another Fe-$Fe_3C$ Transformation Product

- Bainite:
  - -- elongated $Fe_3C$ particles in $\alpha$-ferrite matrix
  - -- diffusion controlled
- Isothermal Transf. Diagram, $C_0$ = 0.76 wt% C



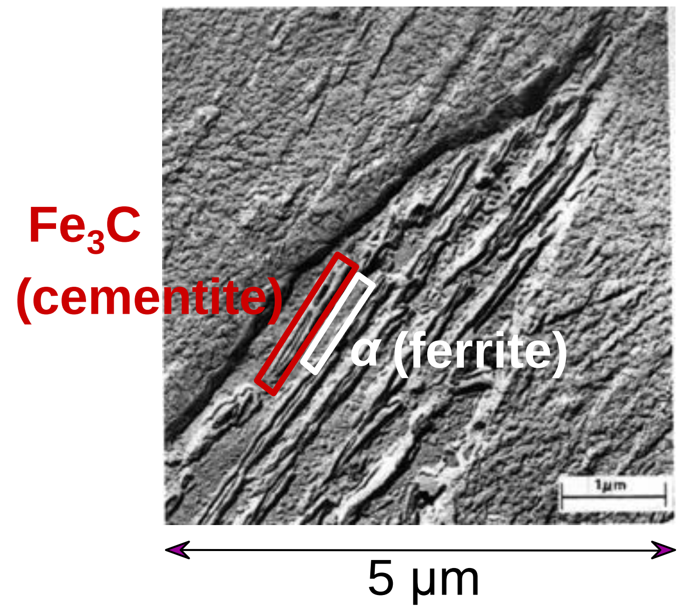



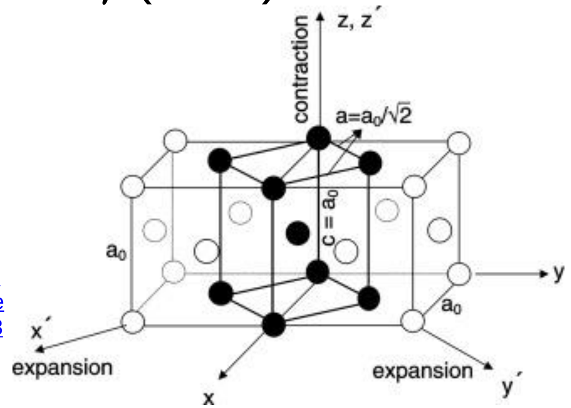

Fig. 10.17, *Callister & Rethwisch 10e.* (From *Metals Handbook*, Vol. 8, 8th edition, *Metallography, Structures and Phase Diagrams*, 1973. Reproduced by permission of ASM International, Materials Park, OH.)

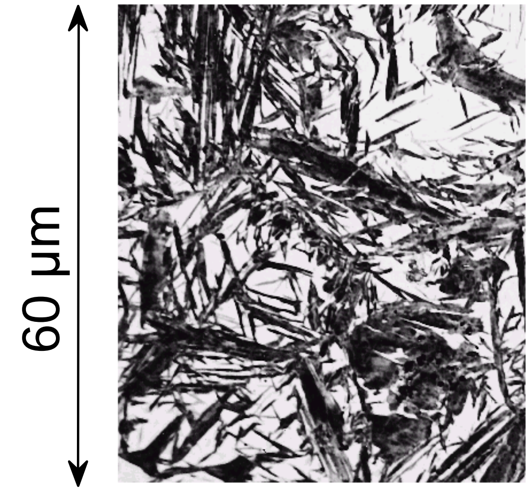
Fig. 10.18, *Callister & Rethwisch 10e.* [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

# Martensite: A Nonequilibrium Transformation Product

- Martensite: $\gamma$ (FCC) to Martensite (BCT)

https://www.sciencedirect.com/science/article/pii/S0039602801012390

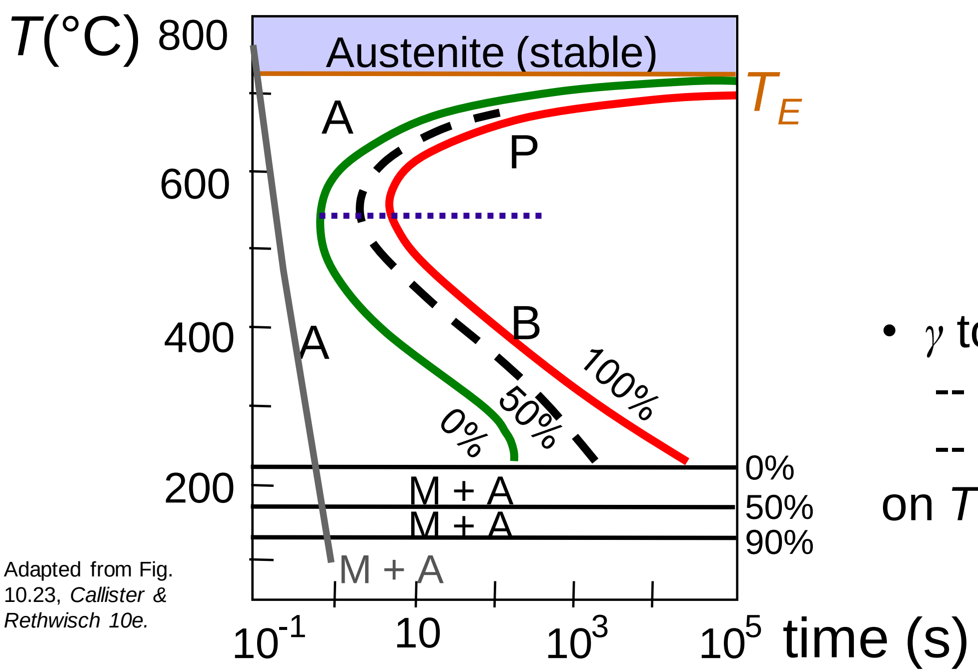



Martensite needles

Austenite

Fig. 10.21, *Callister & Rethwisch 10e.* (Courtesy United States Steel Corporation.)




Adapted from Fig. 10.23, *Callister & Rethwisch 10e.*

- $\gamma$ to martensite (M) transformation.
  - -- is rapid! (diffusionless)
  - -- % transformation depends only on $T$ to which rapidly cooled

# Martensite Formation

$$\begin{tikzcd} \gamma\ (\text{FCC}) \arrow[r, "\text{slow cooling}"] \arrow[d, "\text{quench}"] & \alpha\ (\text{BCC}) + Fe_3C \\ \boxed{\text{M (BCT)}} \arrow[ur, "\text{tempering}"'] & \end{tikzcd}$$

Martensite (M) -> High strength & Brittle

– single phase with body centered tetragonal (BCT) structure

– Diffusionless transformation by shearing

– Increased dislocation density and residual stresses

– Fine microstructure

– $Fe_3C$ during quenching

# Continuous Cooling Transformation Diagrams

Conversion of isothermal transformation diagram to continuous cooling transformation diagram

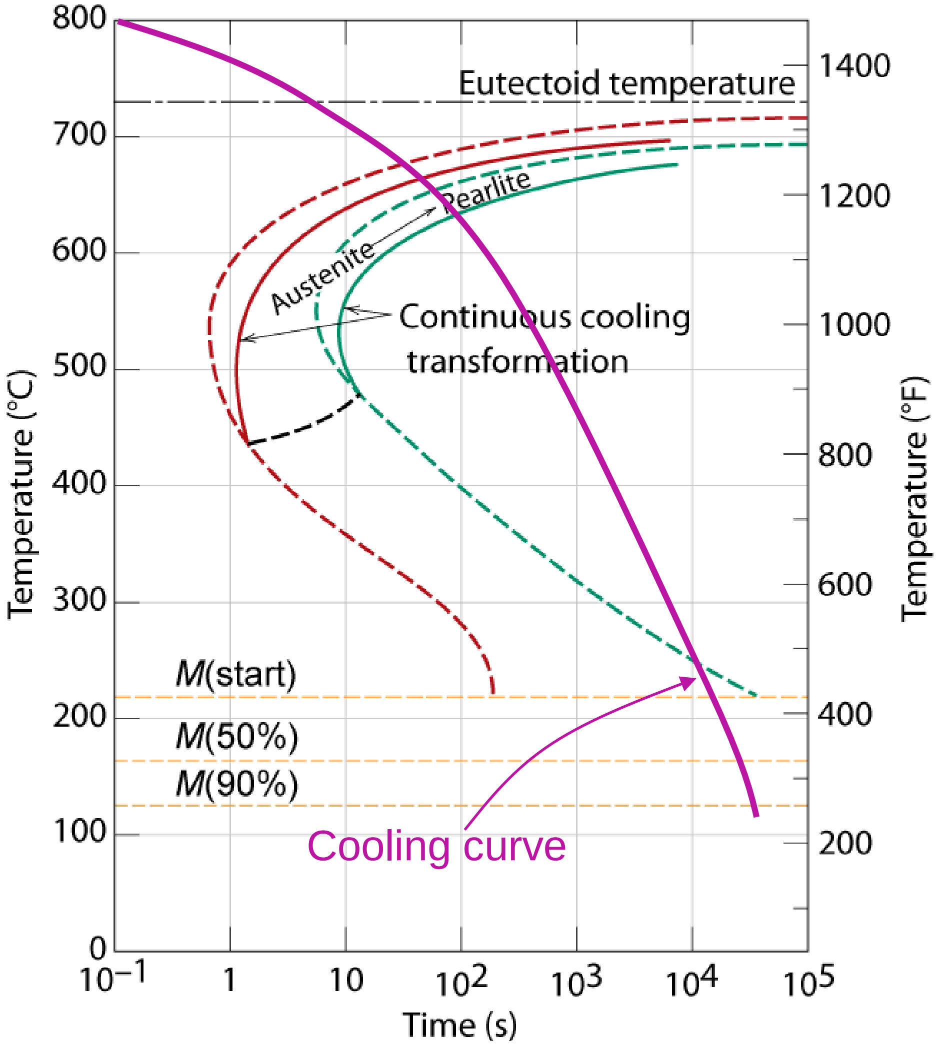
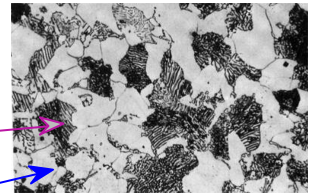



Fig. 10.26, *Callister & Rethwisch 10e.* [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, 1977. Reproduced by permission of ASM International, Materials Park, OH.]

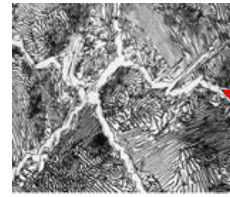
# Mechanical Props: Influence of C Content




$C_0$ < 0.76 wt% C

Hypoeutectoid

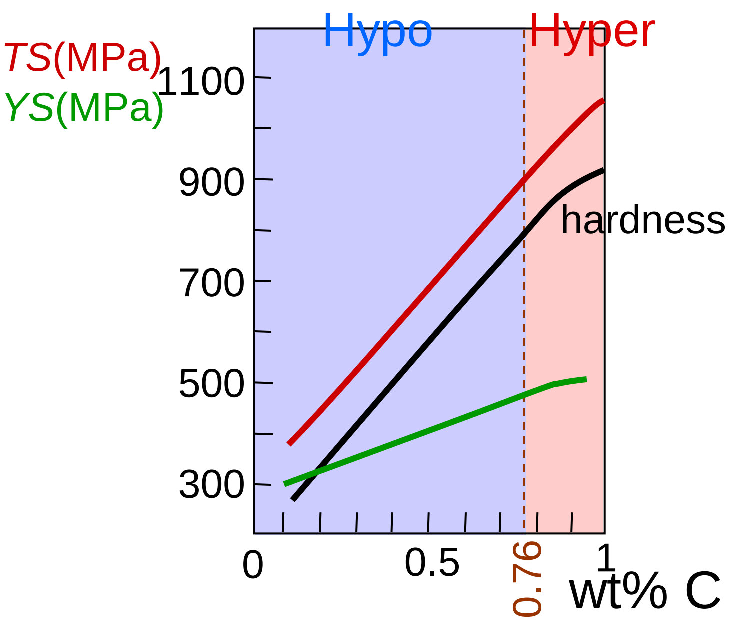
Fig. 9.30, *Callister & Rethwisch 10e.* (Courtesy of Republic Steel Corporation.)




$C_0$ > 0.76 wt% C

Hypereutectoid

Fig. 9.33, *Callister & Rethwisch 10e.* (Copyright 1971 by United States Steel Corporation.)



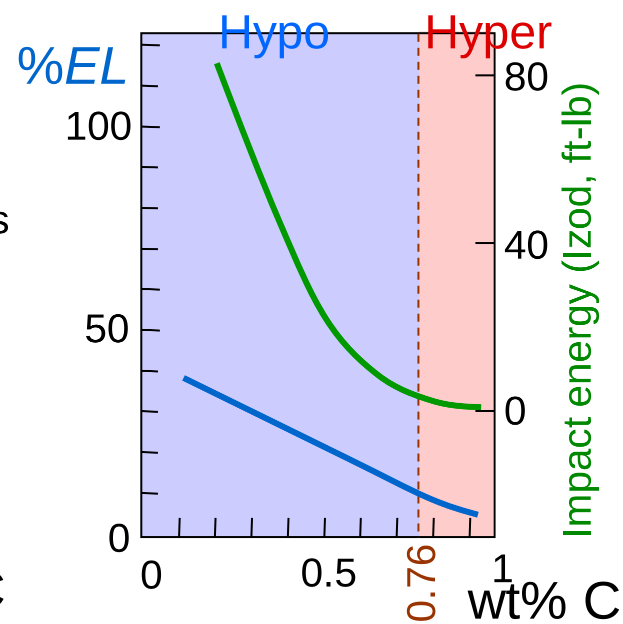
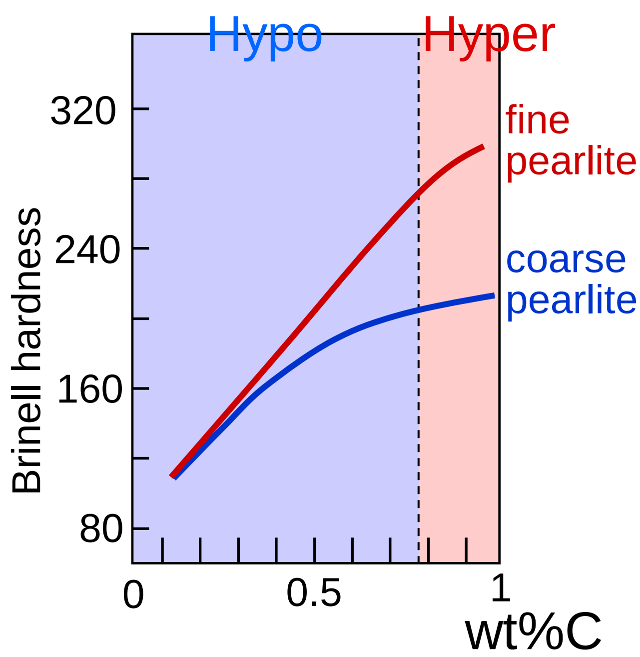
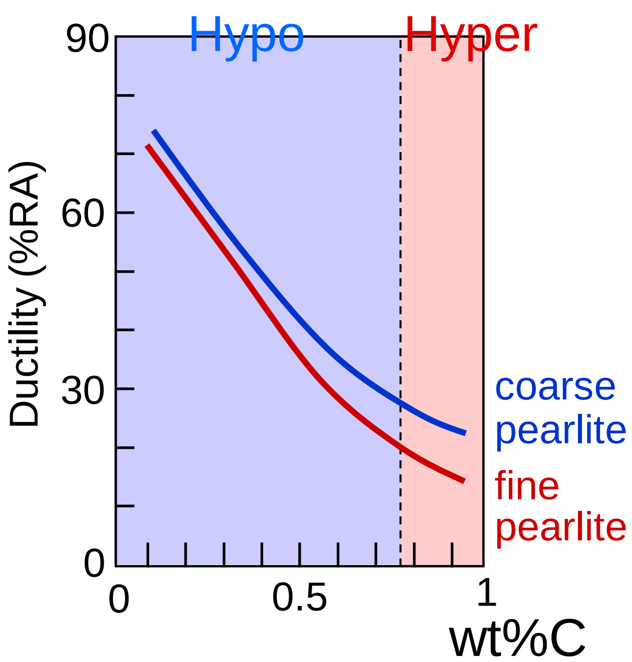




Fig. 10.30, *Callister & Rethwisch 10e.* [Data taken from *Metals Handbook: Heat Treating*, Vol. 4, 9th edition, V. Masseria (Managing Editor), 1981. Reproduced by permission of ASM International, Materials Park, OH.]

- Increase C content: *TS* and *YS* increase, %*EL* decreases

# Mechanical Props: Fine Pearlite vs. Coarse Pearlite




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

Fig. 10.31, *Callister & Rethwisch 10e.* [Data taken from *Metals Handbook: Heat Treating*, Vol. 4, 9th edition, V. Masseria (Managing Editor), 1981. Reproduced by permission of ASM International, Materials Park, OH.]

# Mechanical Props: Fine Pearlite vs. Martensite

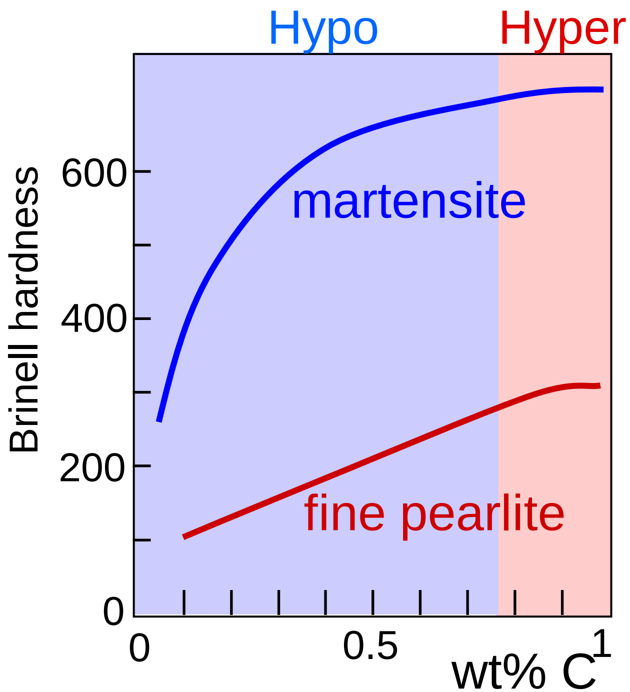



Fig. 10.33, *Callister & Rethwisch 10e.* (Adapted from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, 1939; and R. A. Grange, C. R. Hribal, and L. F. Porter, *Metall. Trans.* A, Vol. 8A. Reproduced by permission of ASM International, Materials Park, OH.)

- Hardness: fine pearlite << martensite.

# Tempered Martensite

Heat treat martensite to form tempered martensite

- tempered martensite less brittle than martensite
- tempering reduces internal stresses caused by quenching

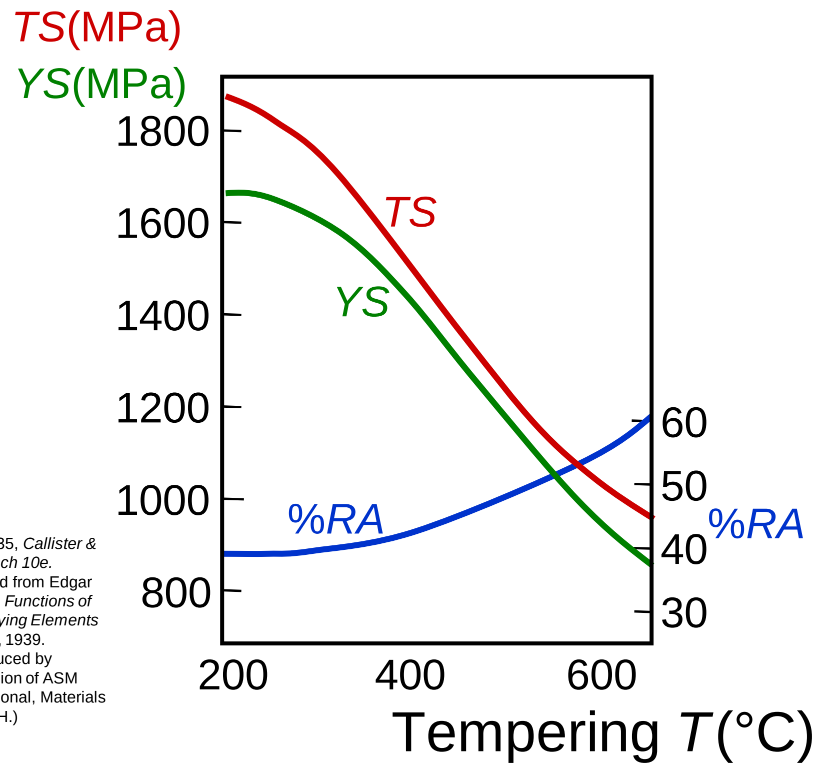



Fig. 10.35, *Callister & Rethwisch 10e.* (Adapted from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, 1939. Reproduced by permission of ASM International, Materials Park, OH.)

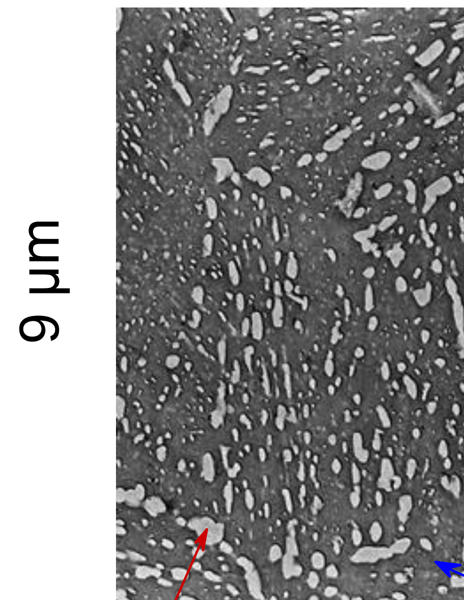
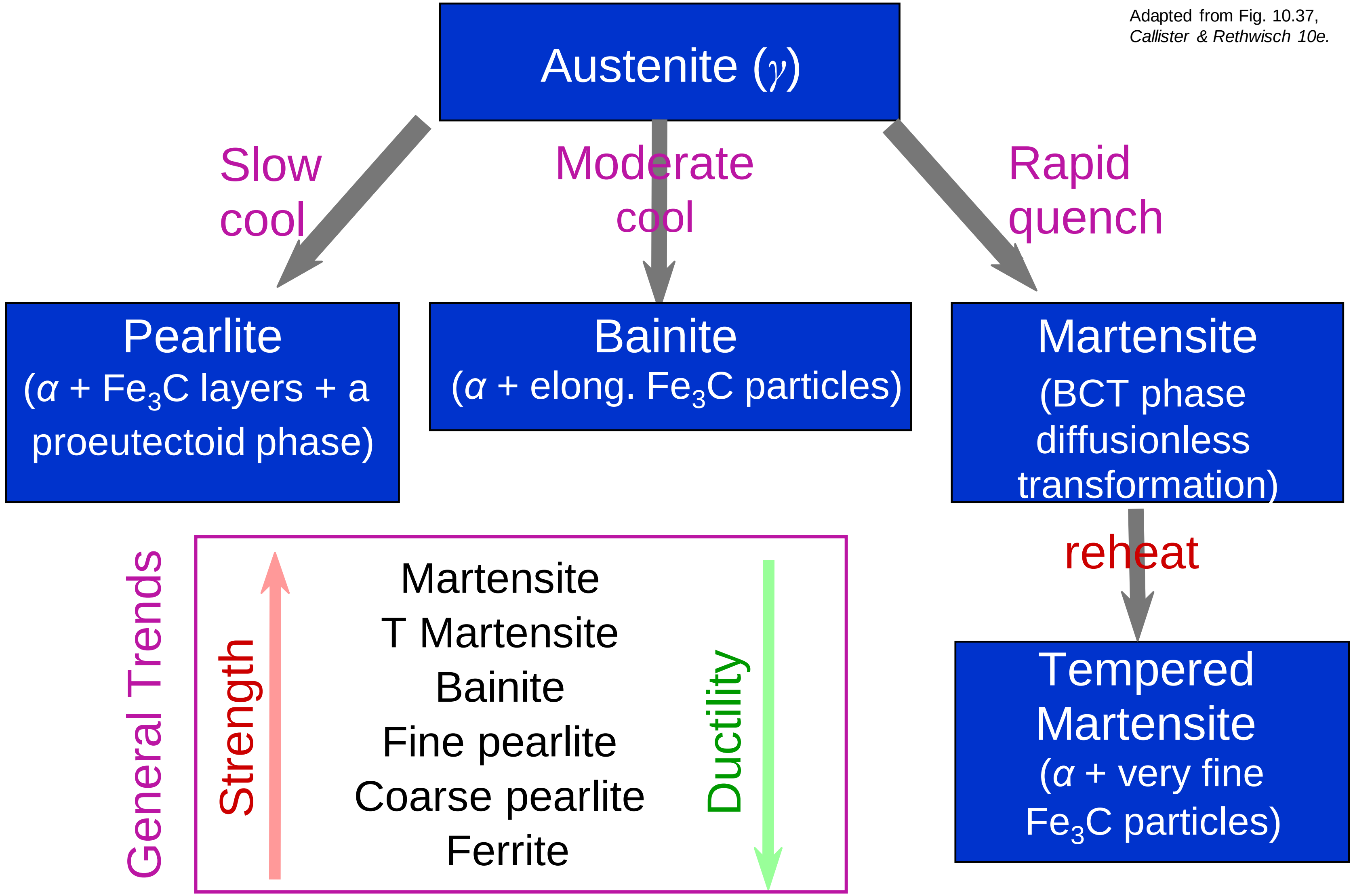



Figure 10.34, *Callister & Rethwisch 10e.* (Copyright 1971 by United States Steel Corporation.)

- tempering produces extremely small $Fe_3C$ particles surrounded by $\alpha$.
- tempering decreases *TS*, *YS* but increases %RA

# Summary of Possible Transformations




Adapted from Fig. 10.37, *Callister & Rethwisch 10e.*

# Summary

- Rate of Phase transformation given by **Avrami Equation**
- Two types of phase transformation diagrams:
  - **Isothermal transformation** diagrams
  - **Continuous cooling transformation** diagrams
- Heat treatments of Fe-C alloys produce microstructures including: **pearlite**, **bainite**, **martensite**, **tempered martensite**
- **Mechanical properties** of these heat-treated microstructures

# Announcements

Reading: Textbook **Ch. 5, 9, 10**

Assignment: Open; DL: **18:00 Sunday**

~~Q&A time:~~ ~~**Tuesday 16:30**~~ **(merged w/ Exercise)**

Exercise: **Thursday 10:15 – 12:00**

**Computational training (week 4-5)** will be optional and omitted from assignments. Slides and link will be provided later.

# Questions?