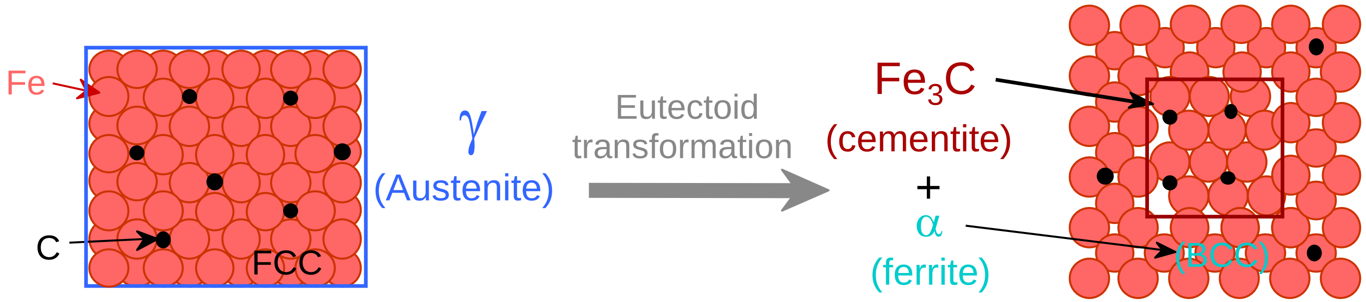
Chapter 10:
Phase Transformations

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 engineering non-equilibrium structures?
- Are the mechanical properties of non-equilibrium structures better?

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

Driving force to nucleate increases as we increase ΔT

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

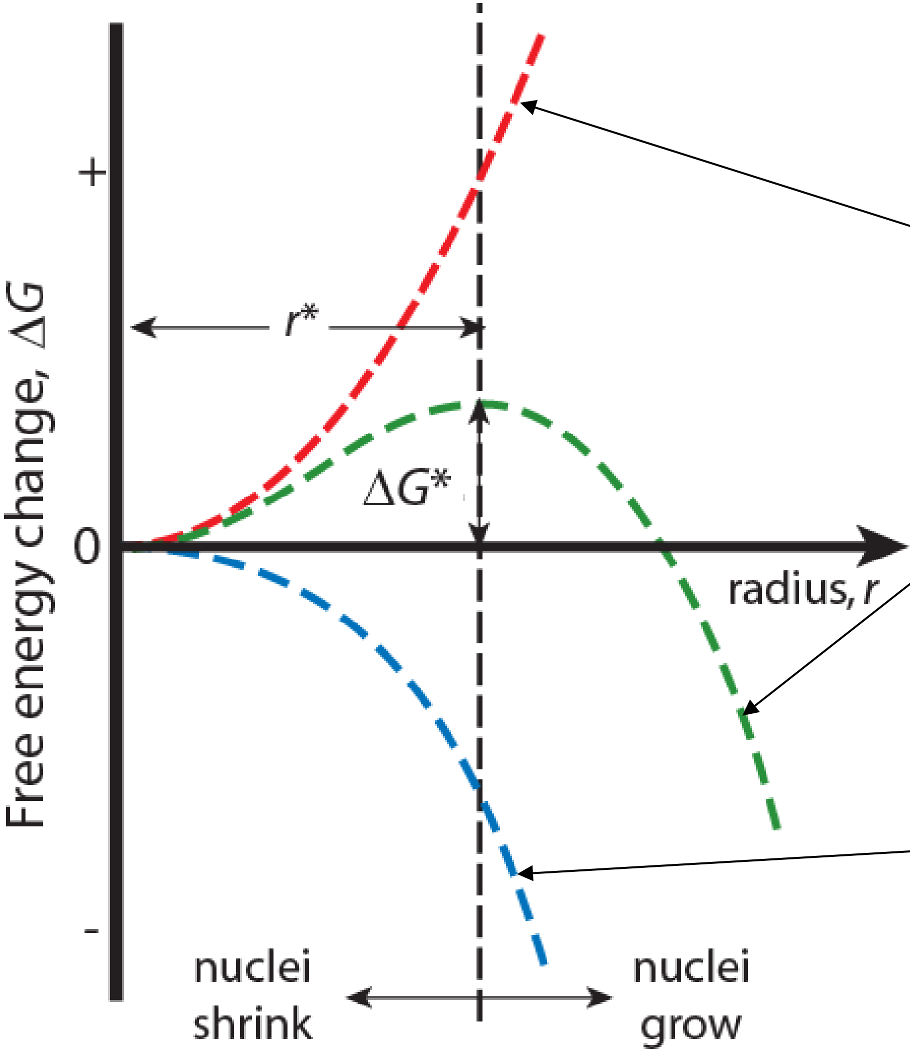
Small supercooling → few nuclei - large crystals

Large supercooling → 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
  – allows solidification with only 0.1-10ºC supercooling

Homogeneous Nucleation & Energy Effects



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

$$\Delta G_S = 4\pi r^2 \gamma$$

γ = surface tension

ΔG_T = Total Free Energy
$= \Delta G_S + \Delta G_V$

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

$$\Delta G_V = \frac{4}{3}\pi r^3 \Delta G_\upsilon$$

$$\Delta G_\upsilon = \frac{\text{volume free energy}}{\text{unit volume}}$$

*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

γ = surface free energy

T_m = melting temperature

ΔH_S = latent heat of solidification

$\Delta T = T_m - T$ = supercooling

Note: ΔH_S = strong function of ΔT

γ = weak function of ΔT

$\therefore$ r^* decreases as ΔT increases

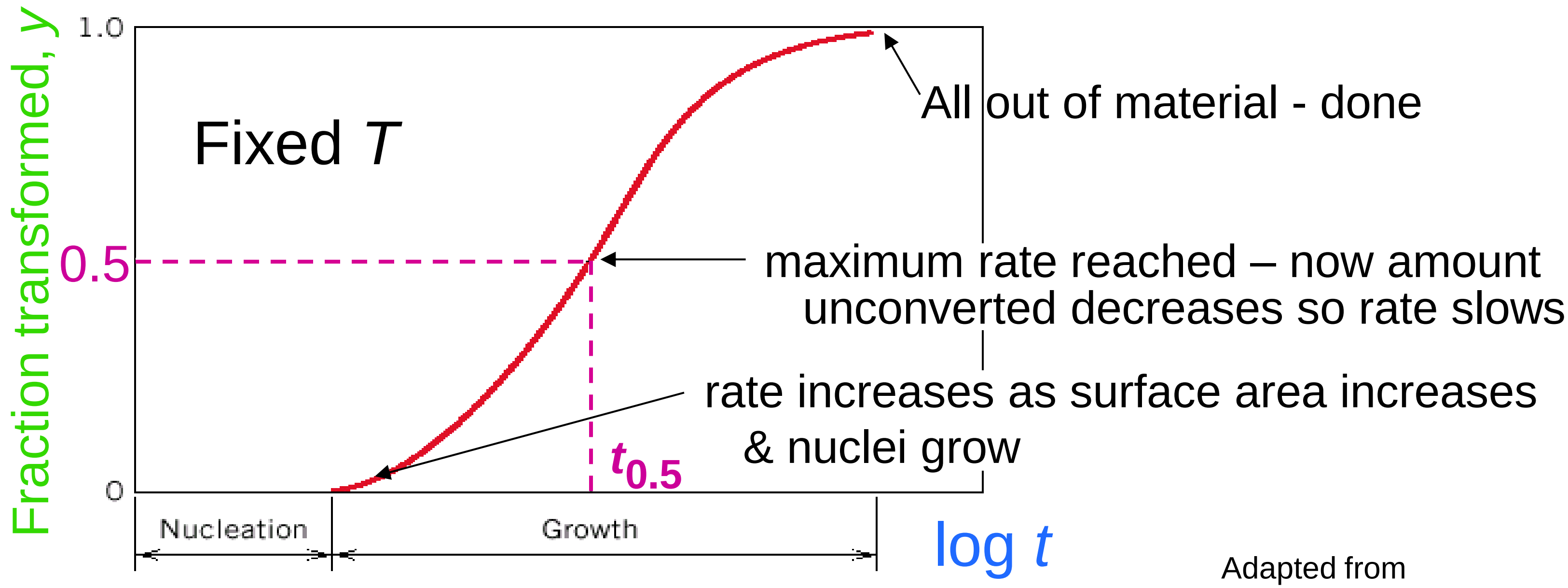
For typical ΔT r^* ca. 100Å

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



Adapted from Fig. 10.10, *Callister 7e.*

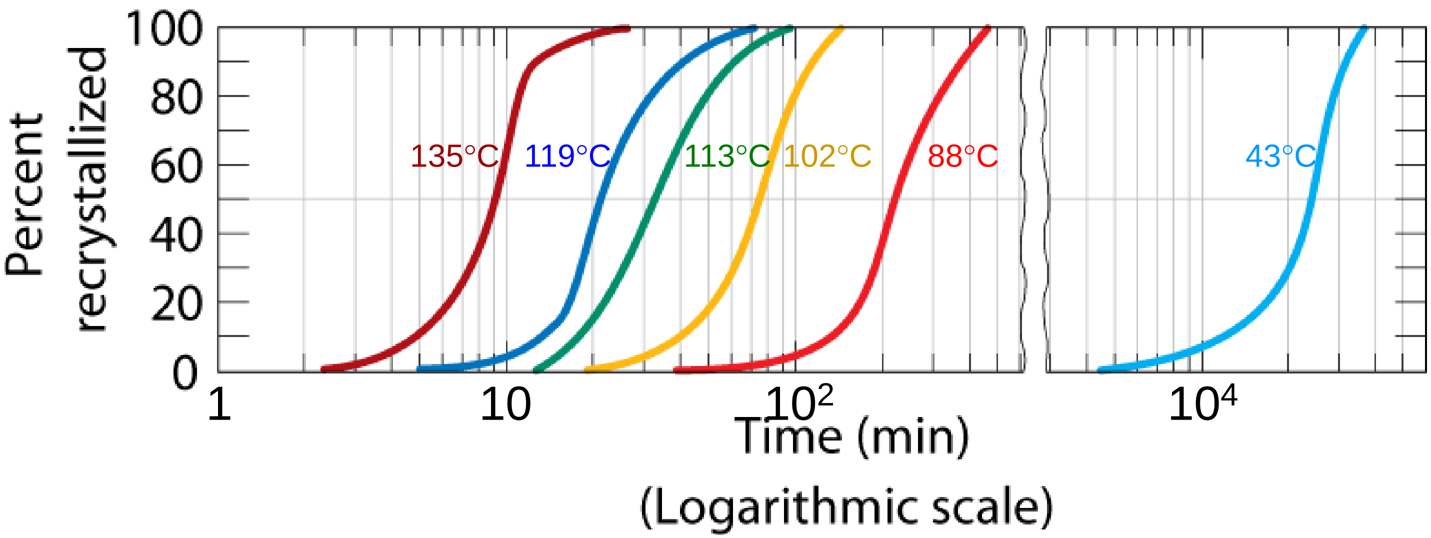
Avrami rate equation => $y = 1 - \exp(-kt^n)$

fraction transformed — time

– k & n fit for specific sample

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

Rate of Phase Transformations



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.)

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

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

  - R = gas constant
  - T = temperature (K)
  - A = preexponential factor
  - Q = activation energy

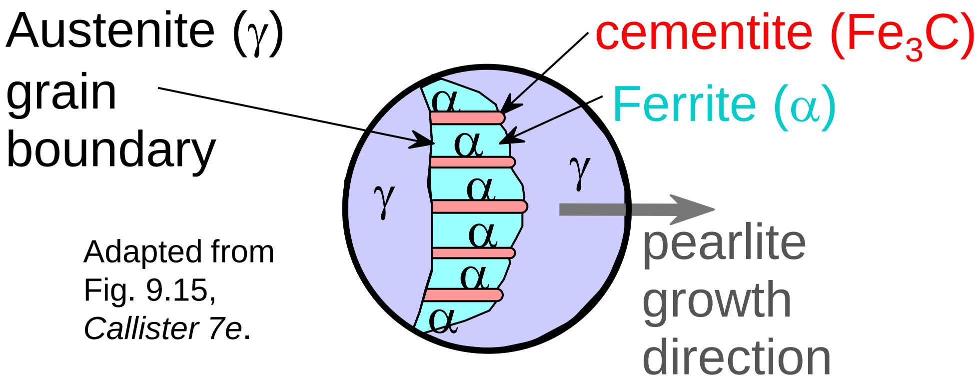
Arrhenius expression

- r often small: equilibrium not possible!

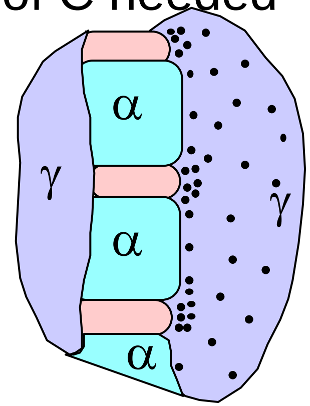
Eutectoid Transformation Rate

- Growth of pearlite from austenite:

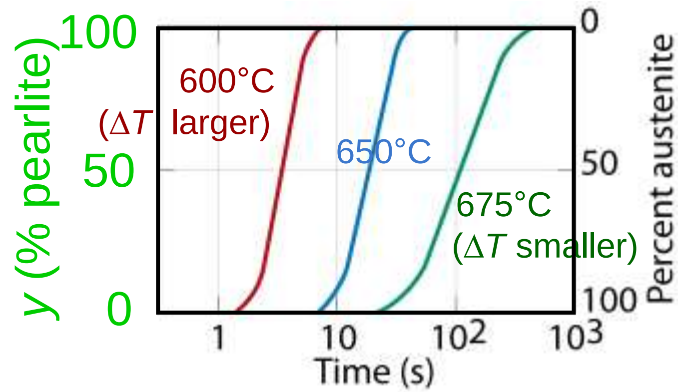
Diffusive flow of C needed



Adapted from Fig. 9.15, *Callister 7e*.



- Recrystallization rate increases with ΔT.



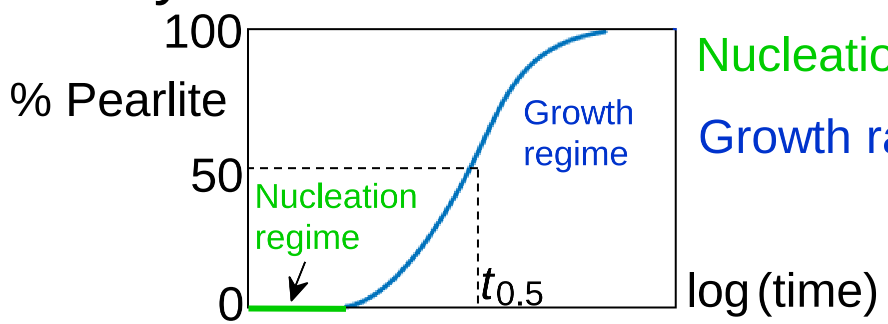
Adapted from Fig. 10.12, *Callister 7e*.

Course pearlite → formed at higher T - softer

Fine pearlite → formed at low T - harder

Nucleation and Growth

- Reaction rate is a result of nucleation <u>and</u> growth of crystals.

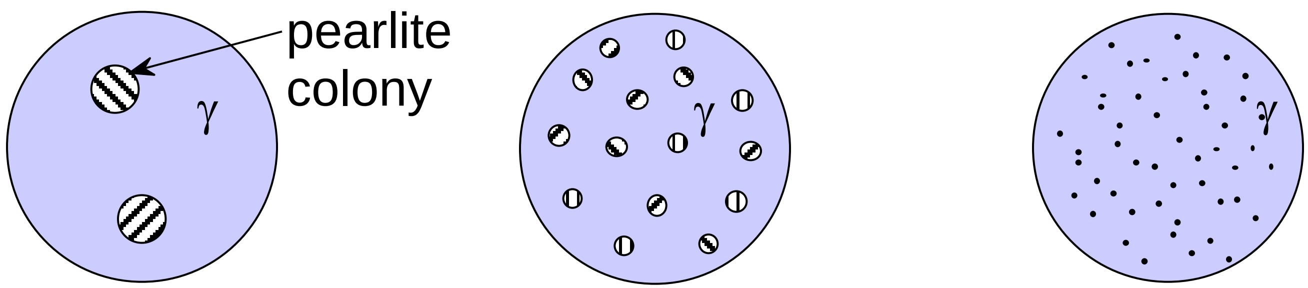


Nucleation rate increases with ΔT

Growth rate increases with T

Adapted from Fig. 10.10, *Callister 7e*.

- Examples:



T just below T_E	T moderately below T_E	T way below T_E
Nucleation rate low	Nucleation rate med .	Nucleation rate high
Growth rate high	Growth rate med.	Growth rate low

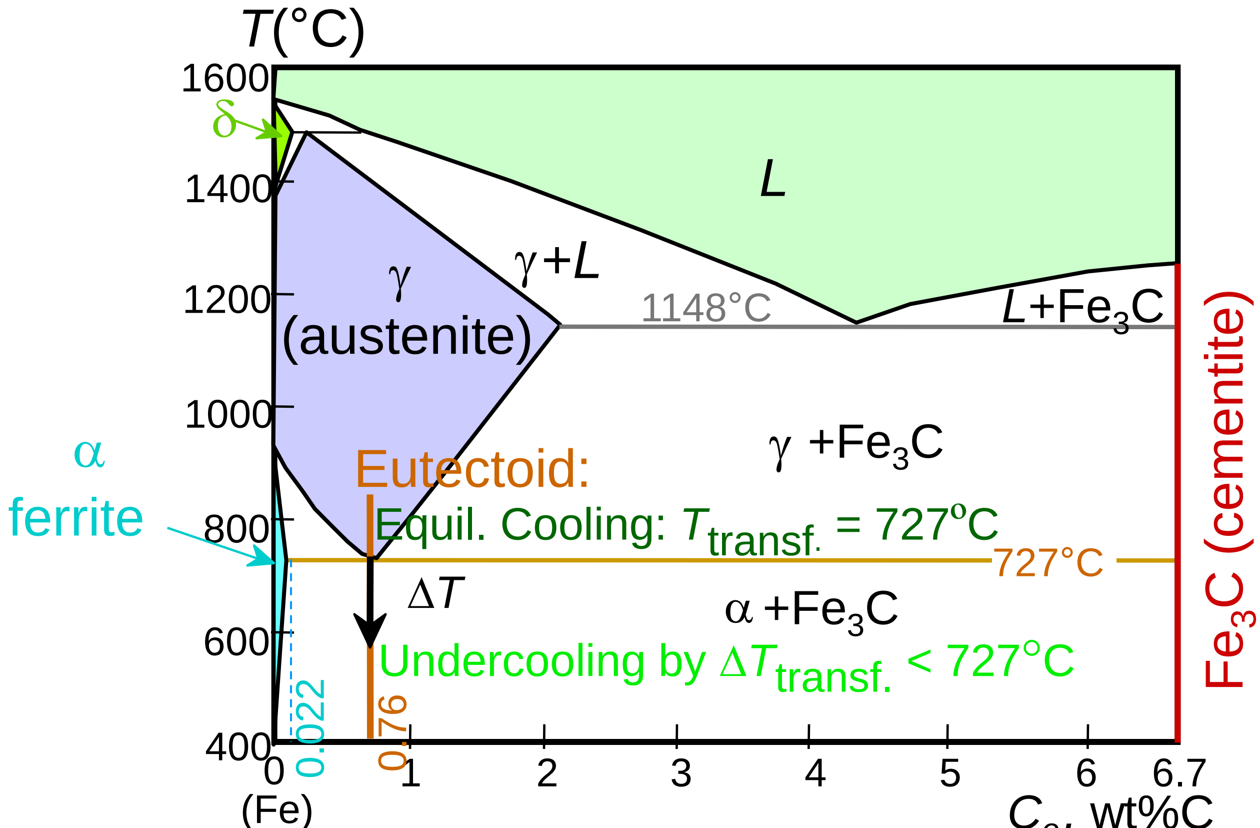
Transformations & Undercooling

- Eutectoid transf. (Fe-C System): $\gamma \Rightarrow \alpha + Fe_3C$
- Can make it occur at:
  - ...727°C (cool it slowly)
  - ...below 727°C ("undercool" it!)

0.76 wt% C

0.022 wt% C

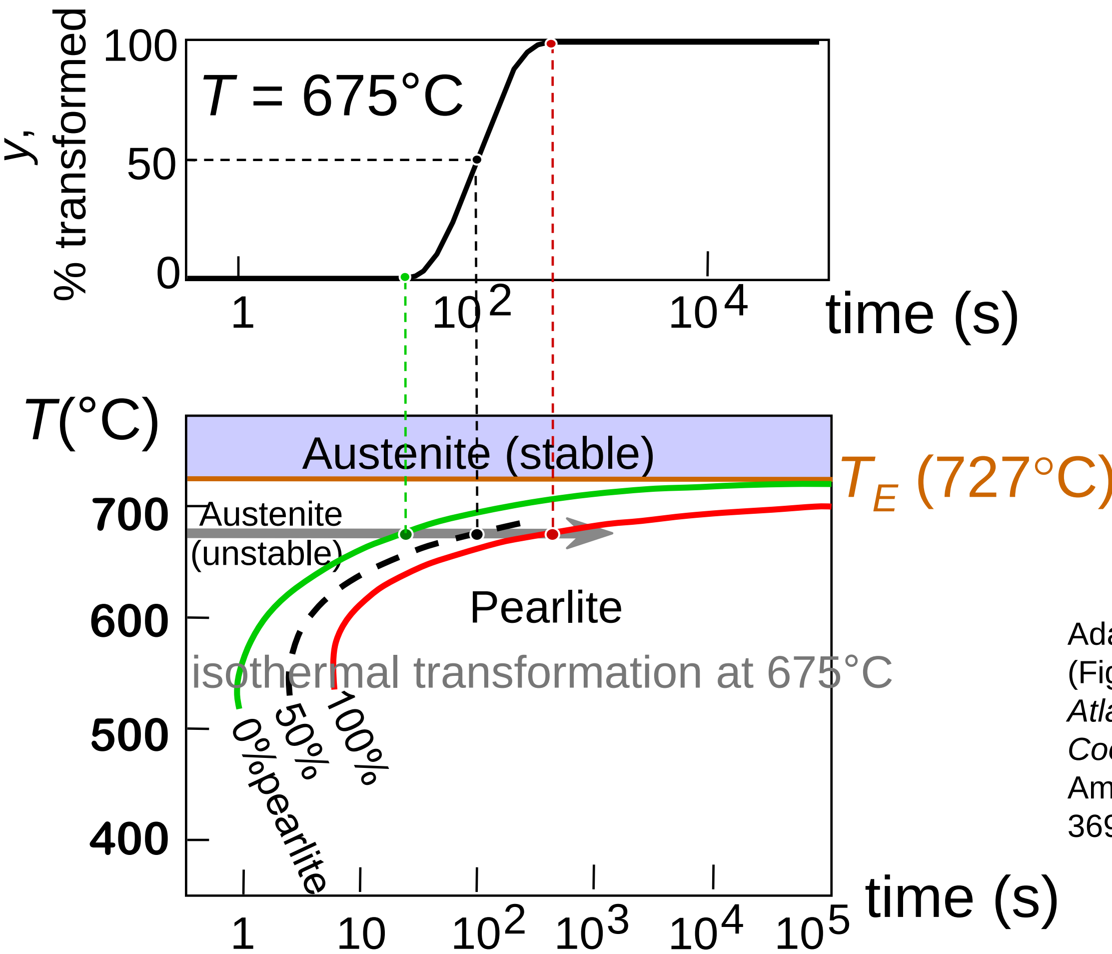
6.7 wt% C



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

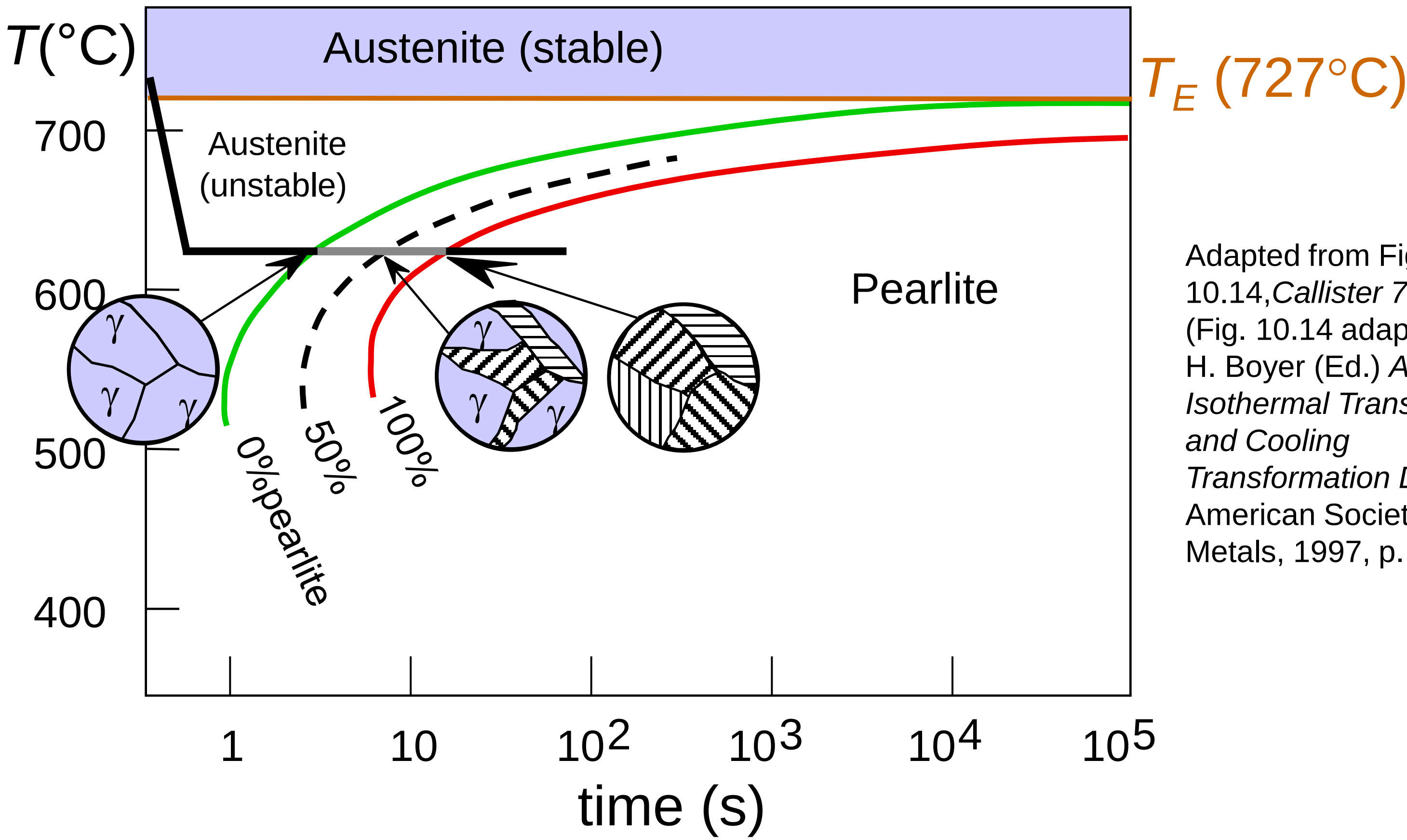
- Fe-C system, C_o = 0.76 wt% C
- Transformation at T = 675°C.



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

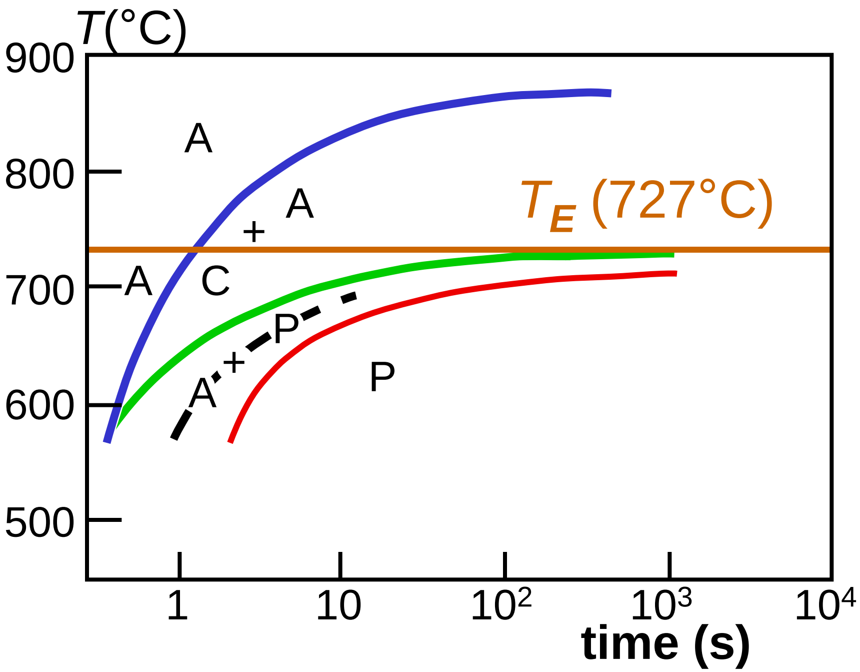
- Eutectoid composition, C_o = 0.76 wt% C
- Begin at T > 727°C
- Rapidly cool to 625°C and hold isothermally.



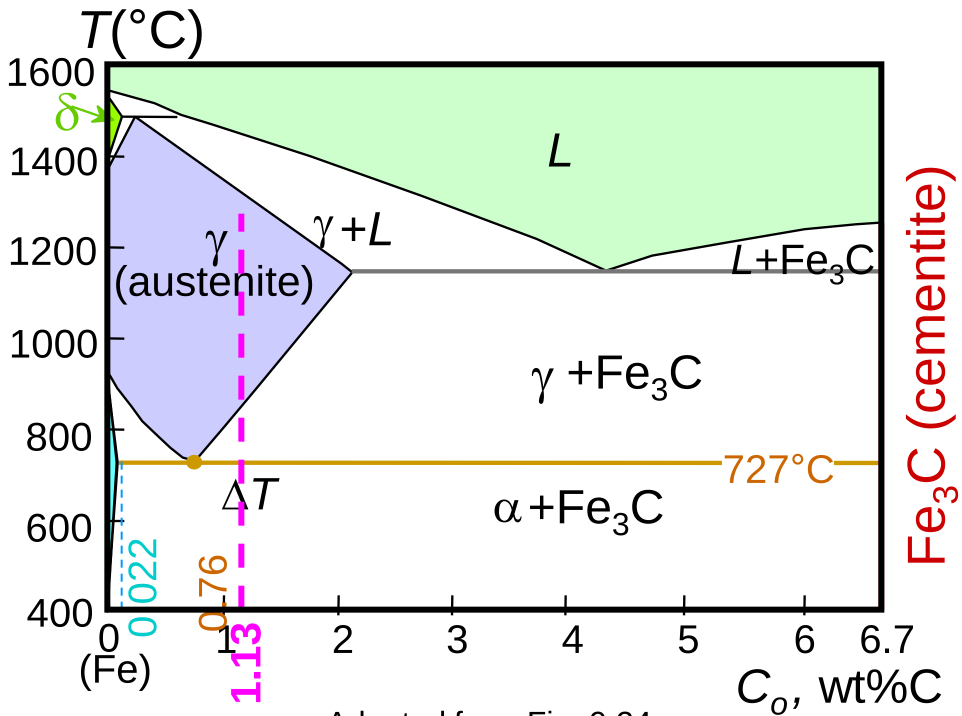
Adapted from Fig. 10.14,*Callister 7e*.
(Fig. 10.14 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1997, p. 28.)

Transformations with Proeutectoid Materials

C_o = 1.13 wt% C



Adapted from Fig. 10.16, *Callister 7e*.

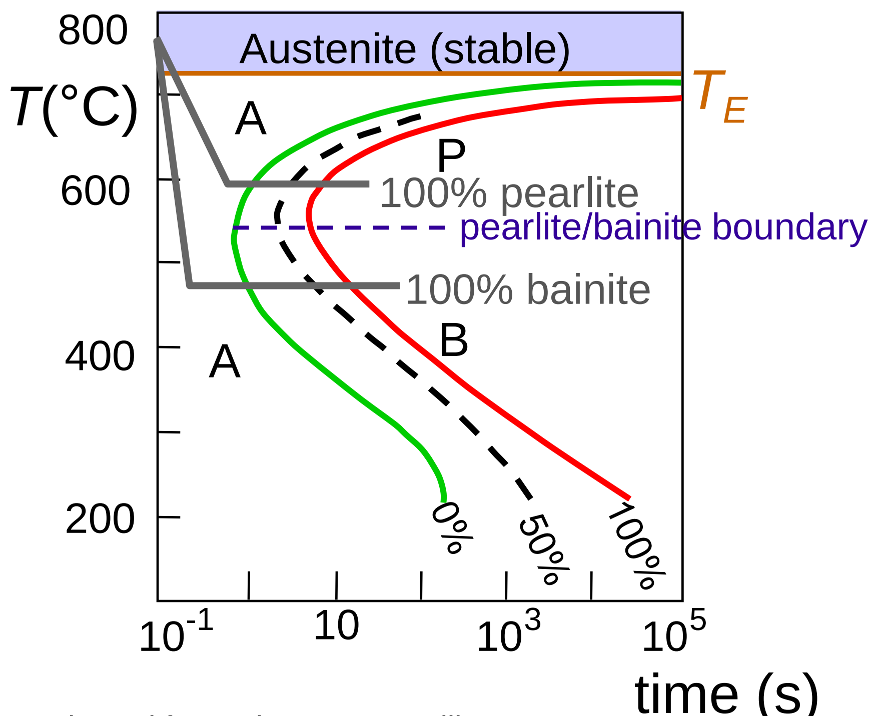


Adapted from Fig. 9.24, *Callister 7e*.

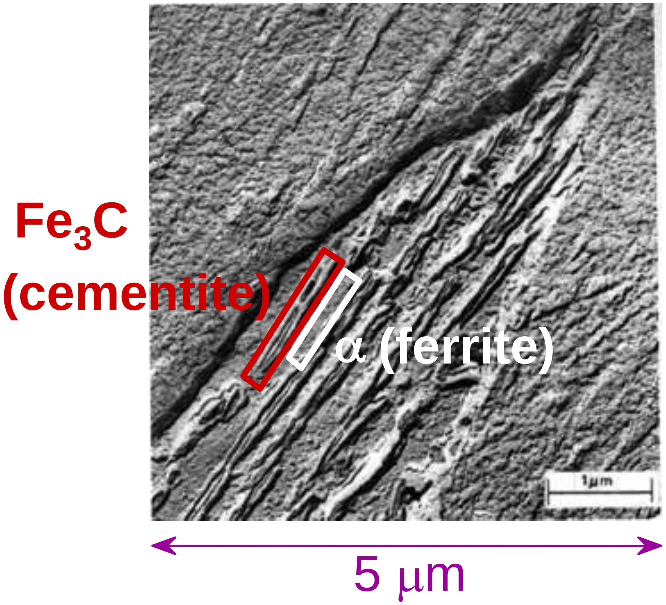
Hypereutectoid composition – proeutectoid cementite

Non-Equilibrium Transformation Products: Fe-C

- Bainite:
  --α lathes (strips) with long rods of Fe_3C
  --diffusion controlled.
- Isothermal Transf. Diagram



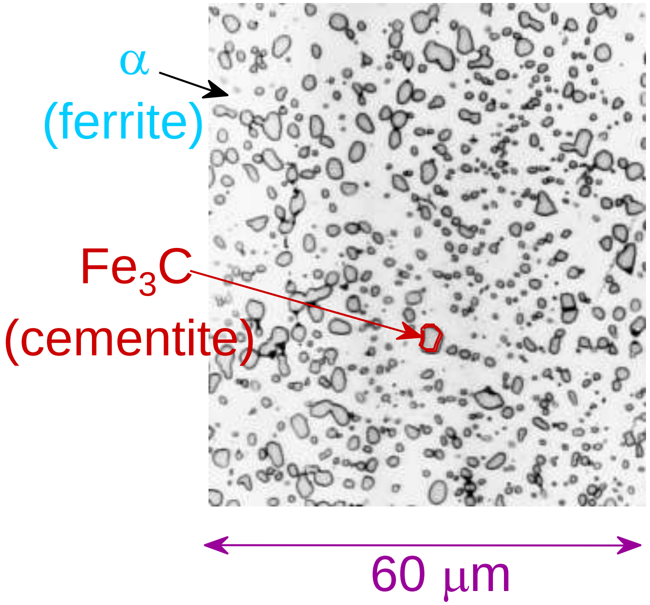
Adapted from Fig. 10.18, *Callister 7e*.
(Fig. 10.18 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1997, p. 28.)



(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.)

Spheroidite: Fe-C System

- Spheroidite:
  --α grains with spherical Fe_3C
  --diffusion dependent.
  --heat bainite or pearlite for long times
  --reduces interfacial area (driving force)

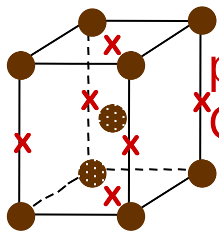


(Adapted from Fig. 10.19, *Callister, 7e*. (Fig. 10.19 copyright United States Steel Corporation, 1971.)

Martensite: Fe-C System

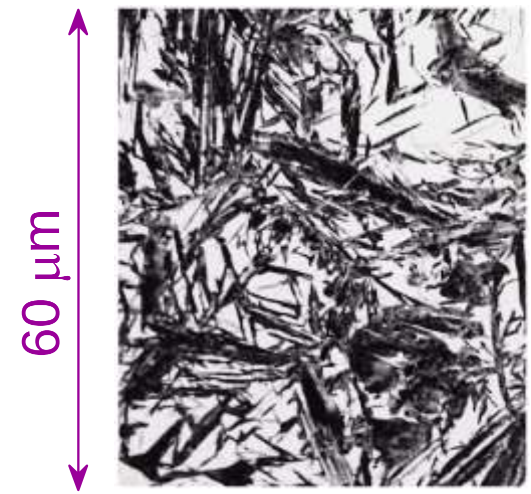
- Martensite:
  --γ(FCC) to Martensite (BCT)
  (involves single atom jumps)

Fe atom sites



potential C atom sites

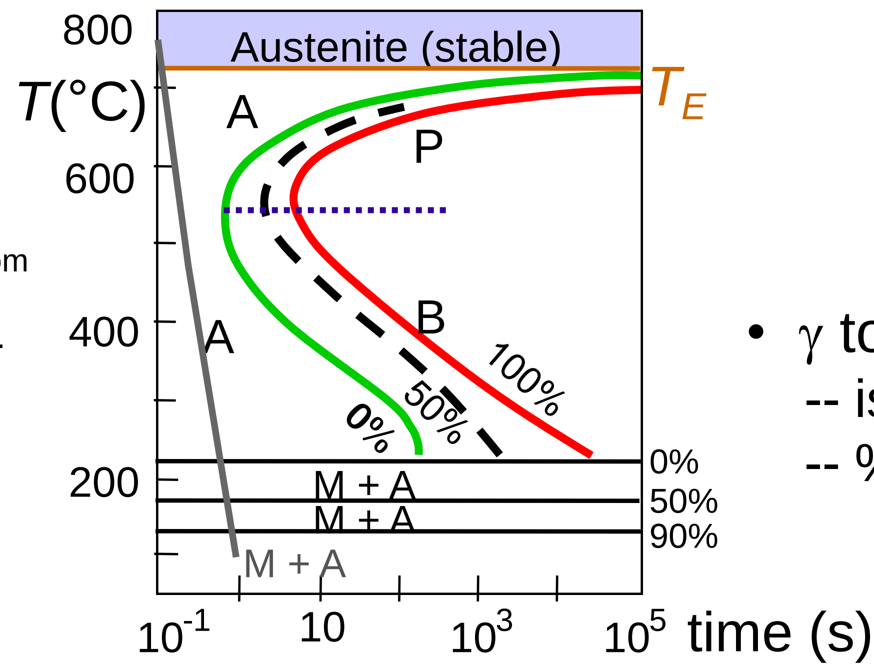
(Adapted from Fig. 10.20, *Callister, 7e*.



Martensite needles
Austenite

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

- Isothermal Transf. Diagram



Adapted from Fig. 10.22, *Callister 7e*.

- γ to M transformation..
  -- is rapid!
  -- % transf. depends on T only.

Martensite Formation

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

M = martensite is body centered tetragonal (BCT)

Diffusionless transformation   BCT if C > 0.15 wt%

BCT → few slip planes → hard, brittle

Phase Transformations of Alloys

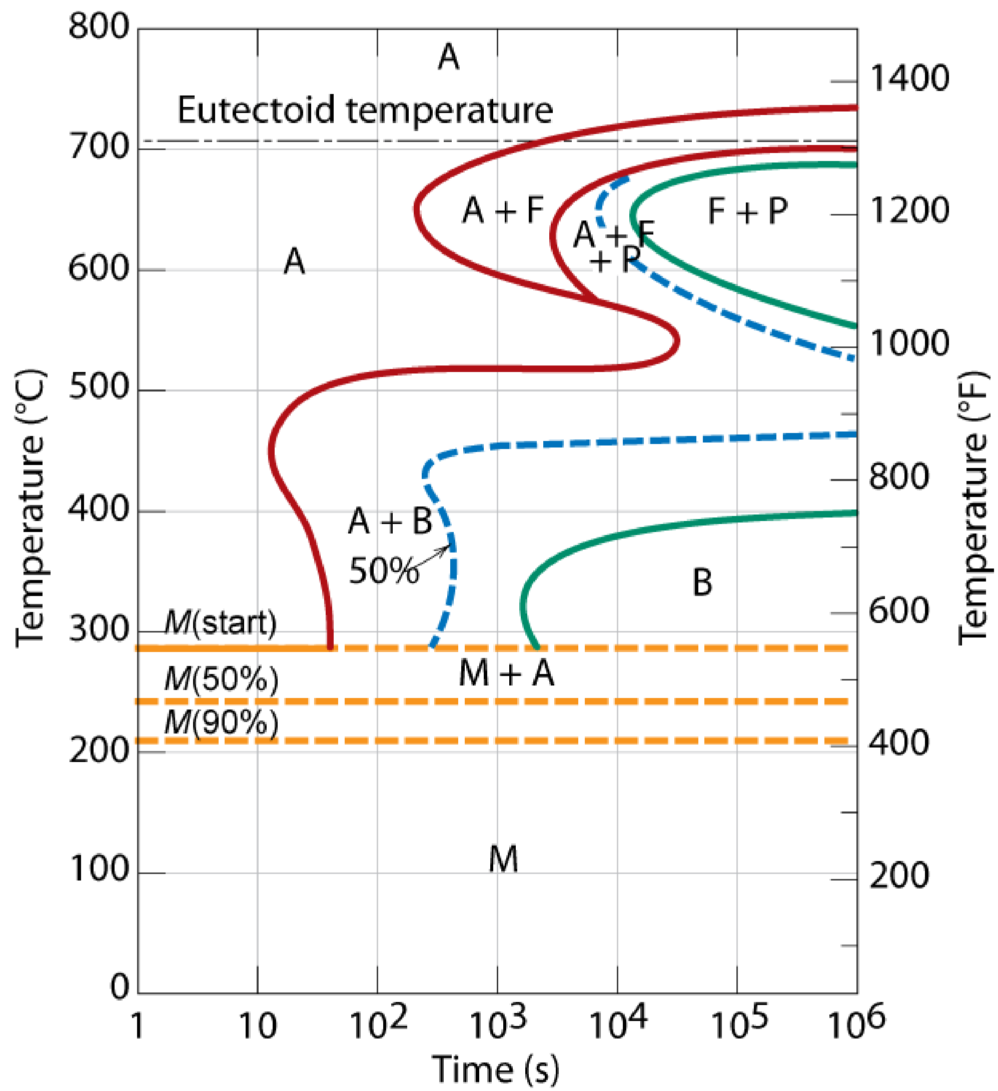
Effect of adding other elements

Change transition temp.

Cr, Ni, Mo, Si, Mn

retard $\gamma \rightarrow \alpha + Fe_3C$

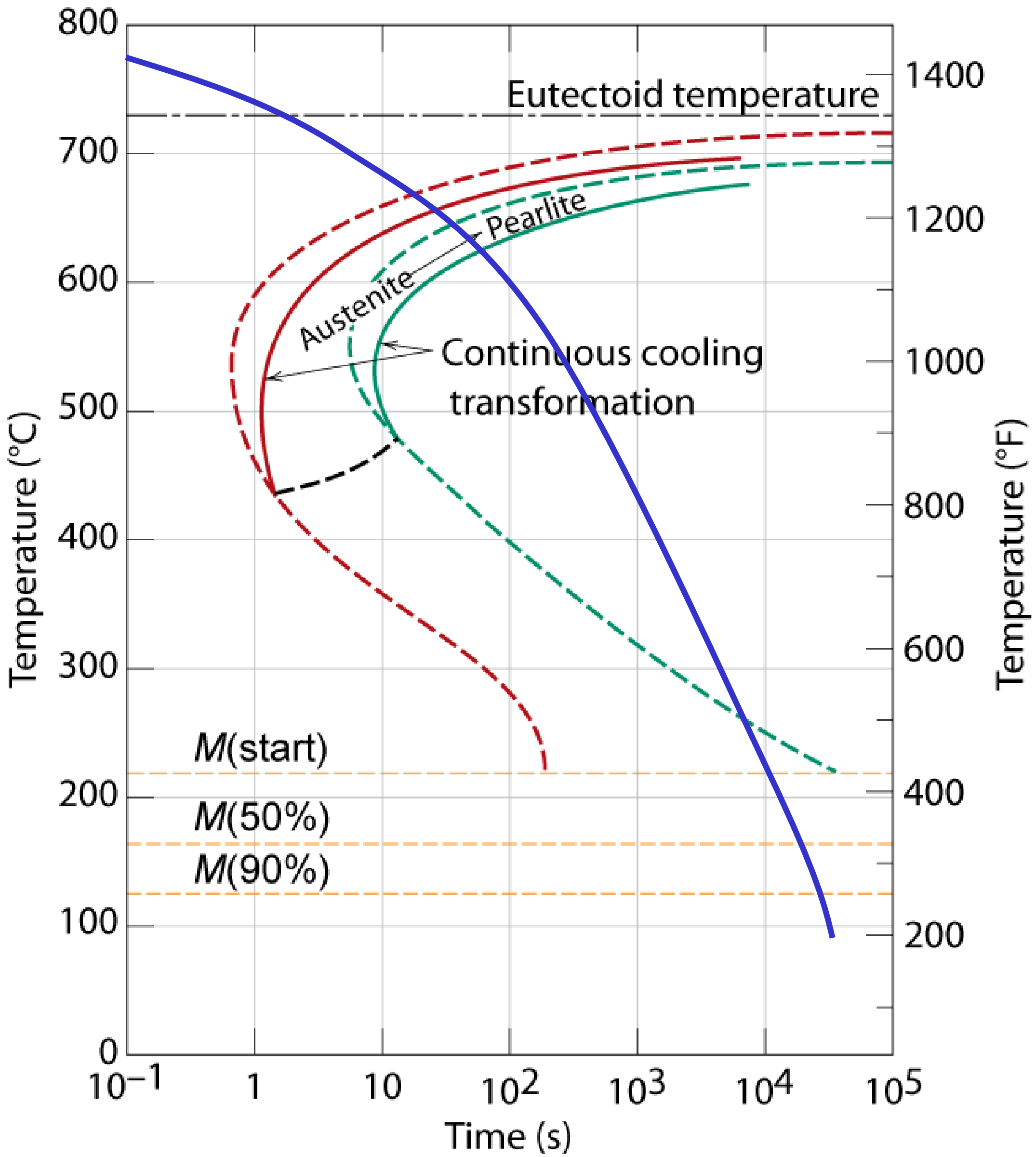
transformation



Adapted from Fig. 10.23, *Callister 7e*.

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

Example Problem for C_o = 0.45 wt%

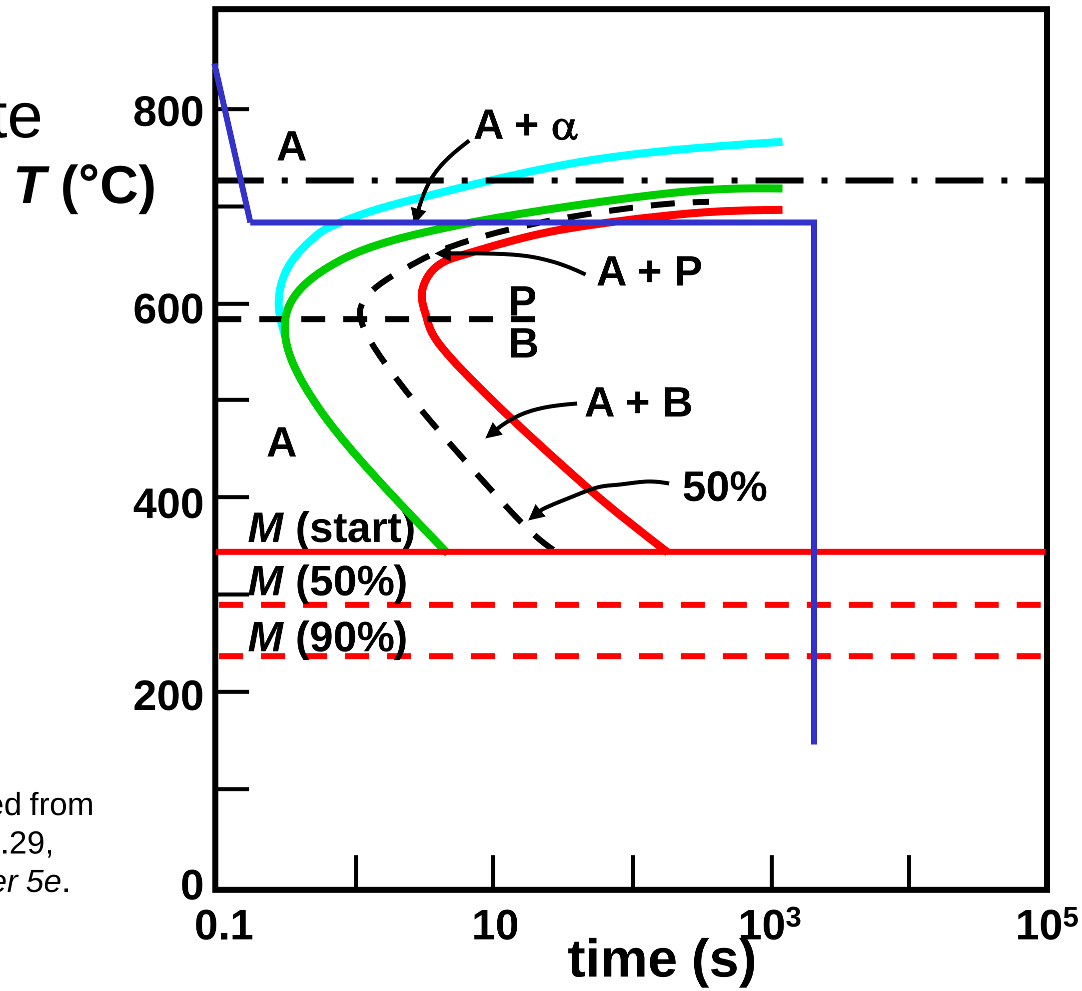
a) 42% proeutectoid ferrite and 58% coarse pearlite

first make ferrite

then pearlite

course pearlite

∴ higher *T*



Adapted from Fig. 10.29, *Callister 5e*.

Example Problem for C_o = 0.45 wt%

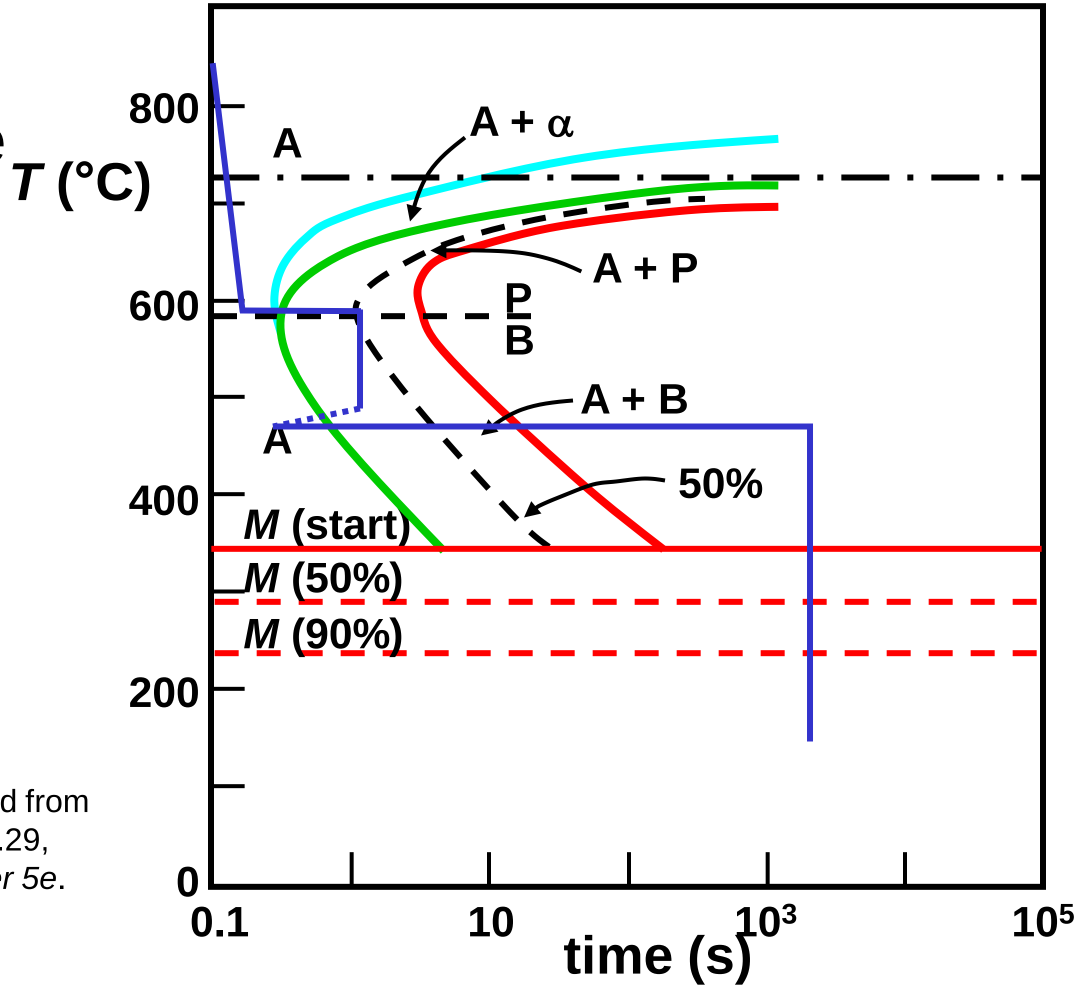
b) 50% fine pearlite and 50% bainite

first make pearlite

then bainite

fine pearlite

$\therefore$ lower T

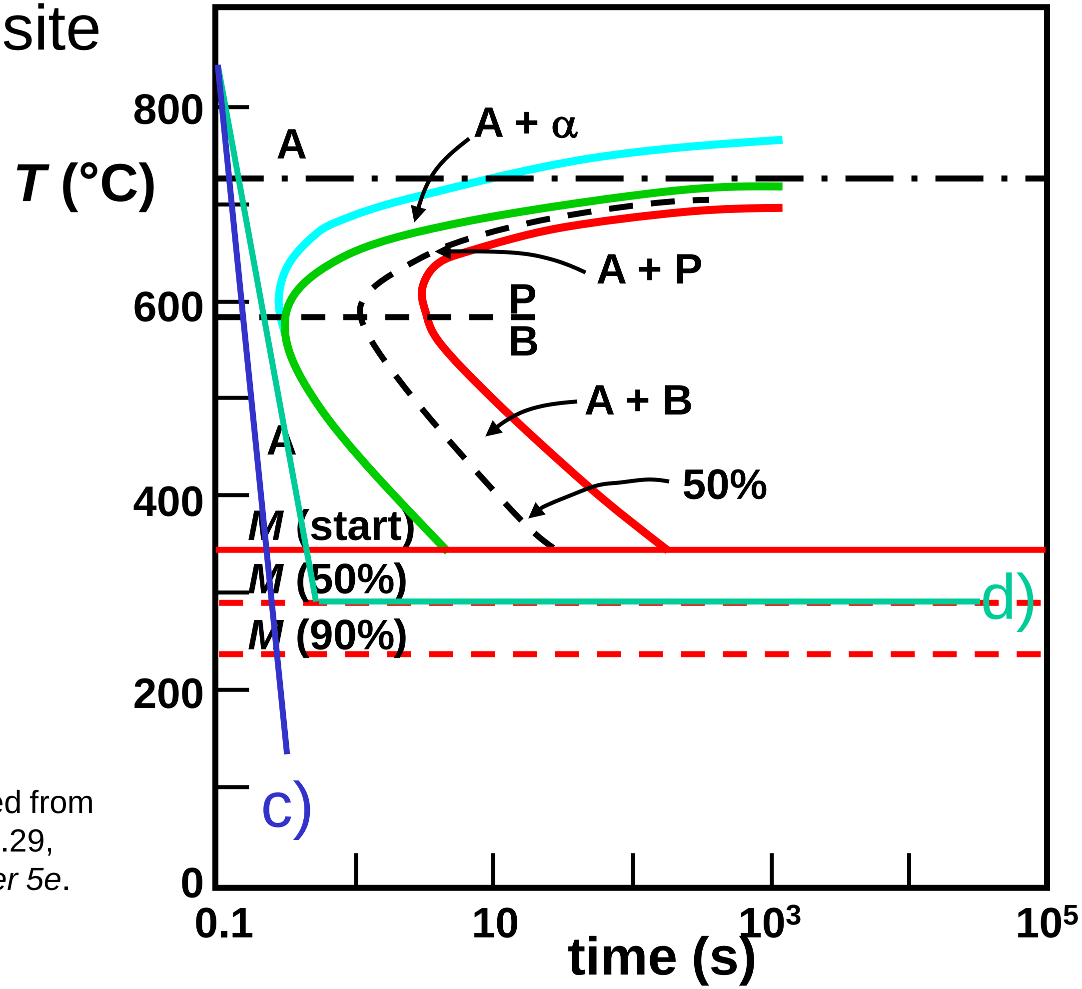


Adapted from Fig. 10.29, *Callister 5e*.

Example Problem for C_o = 0.45 wt%

c) 100 % martensite – quench = rapid cool

d) 50 % martensite and 50 % austenite

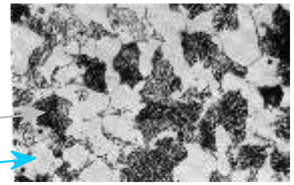


Adapted from Fig. 10.29, *Callister 5e*.

Mechanical Prop: Fe-C System (1)

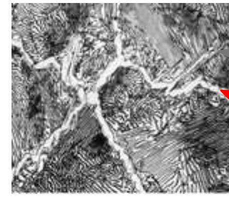
- Effect of wt% C

Pearlite (med)
ferrite (soft)



C_o < 0.76 wt% C
Hypoeutectoid

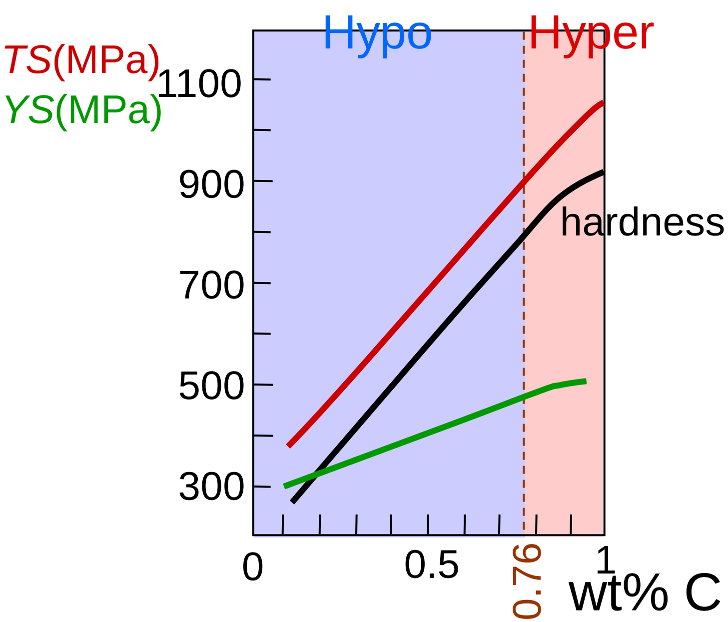
Adapted from Fig. 9.30, *Callister 7e*. (Fig. 9.30 courtesy Republic Steel Corporation.)

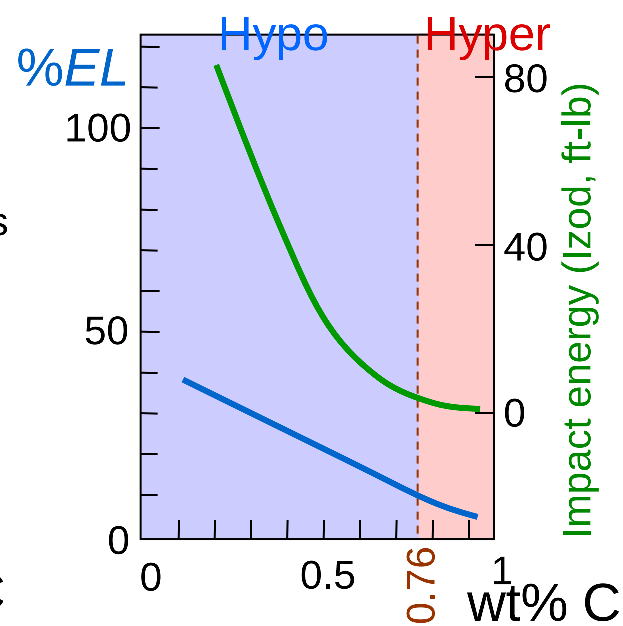


Pearlite (med)
Cementite (hard)

C_o > 0.76 wt% C
Hypereutectoid

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



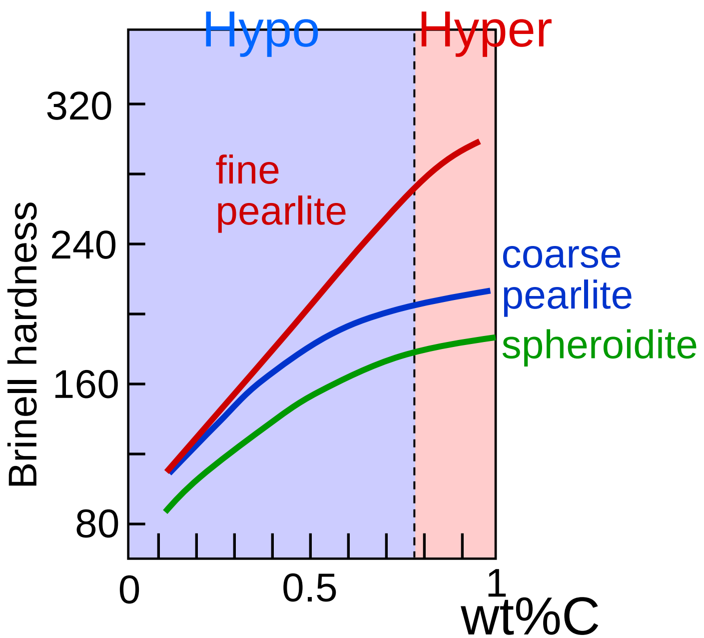


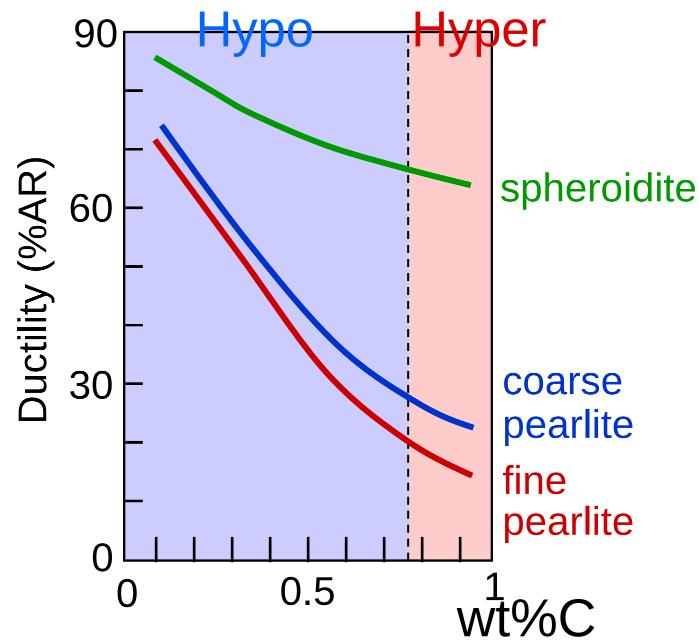
Adapted from Fig. 10.29, *Callister 7e*. (Fig. 10.29 based on data from *Metals Handbook: Heat Treating*, Vol. 4, 9th ed., V. Masseria (Managing Ed.), American Society for Metals, 1981, p. 9.)

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

Mechanical Prop: Fe-C System (2)

- Fine vs coarse pearlite vs spheroidite



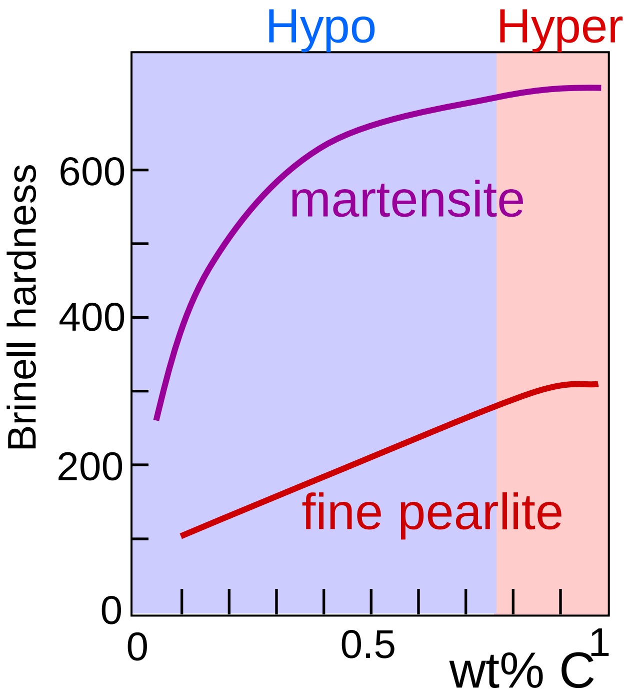


- Hardness: fine > coarse > spheroidite
- %RA: fine < coarse < spheroidite

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:



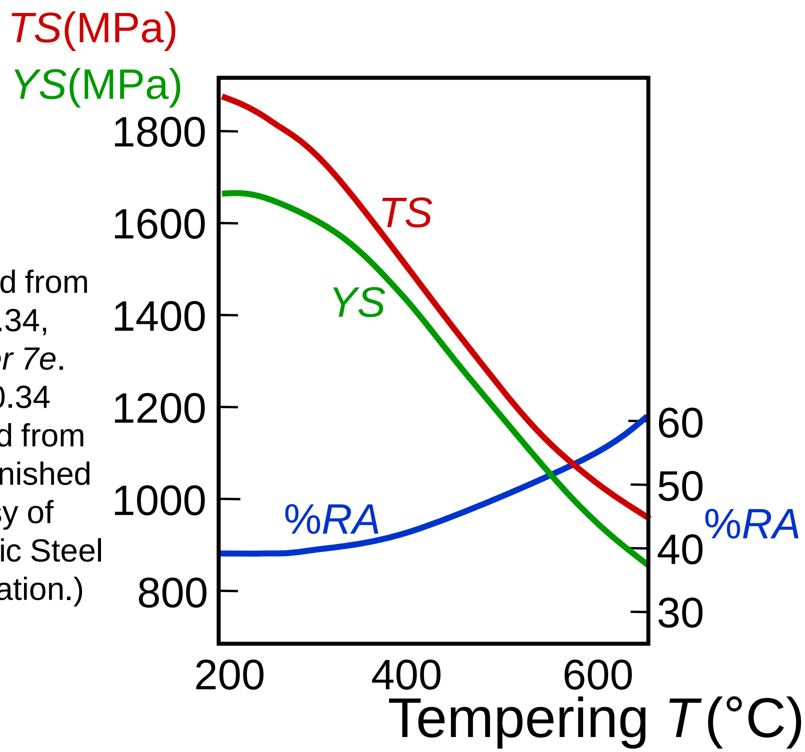
Adapted from Fig. 10.32, *Callister 7e*. (Fig. 10.32 adapted from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 36; and R.A. Grange, C.R. Hribal, and L.F. Porter, *Metall. Trans. A*, Vol. 8A, p. 1776.)

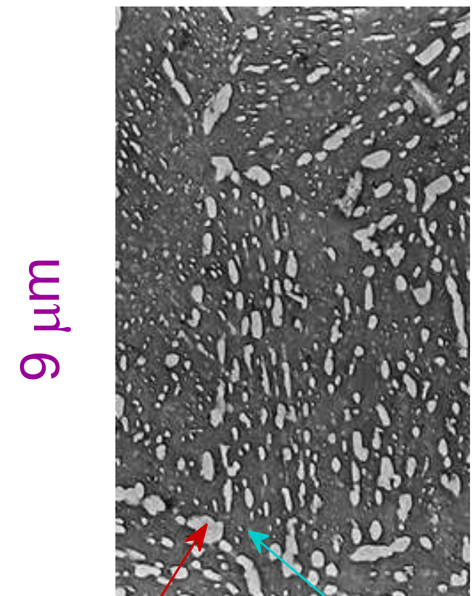
- Hardness: fine pearlite << martensite.

Tempering Martensite

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

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





Adapted from Fig. 10.33, *Callister 7e*. (Fig. 10.33 copyright by United States Steel Corporation, 1971.)

- produces extremely small Fe_3C particles surrounded by α.
- decreases *TS*, *YS* but increases %*RA*

Summary: Processing Options

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

Austenite (γ)

- slow cool → **Pearlite** (α + Fe_3C layers + a proeutectoid phase)
- moderate cool → **Bainite** (α + Fe_3C plates/needles)
- rapid quench → **Martensite** (BCT phase diffusionless transformation)
  - reheat → **Tempered Martensite** (α + very fine Fe_3C particles)

Strength ↑ | Ductility ↓

Martensite
T Martensite
bainite
fine pearlite
coarse pearlite
spheroidite

General Trends

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: