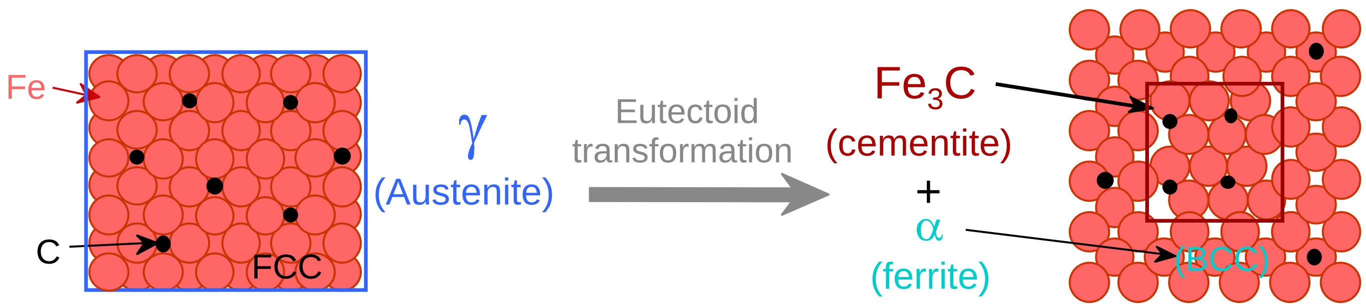
Chapter 10:
Phase Transformations

ISSUES TO ADDRESS...

- Transforming one phase into another takes time.



- How does the rate of transformation depend on time and temperature?
- Is it possible to slow down transformations so that non-equilibrium structures are formed?
- Are the mechanical properties of non-equilibrium structures more desirable than equilibrium ones?

Phase Transformations

Nucleation

- 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 ΔT

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

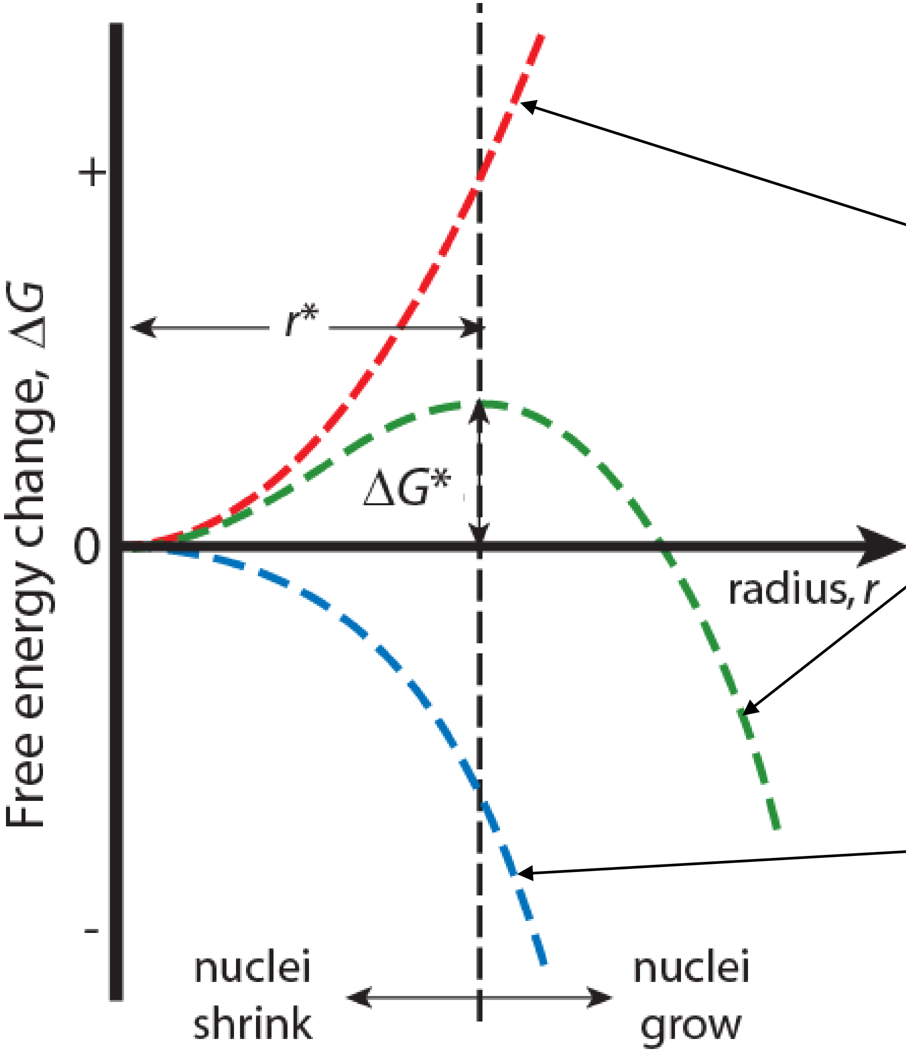
Small supercooling → slow nucleation rate - few nuclei - large crystals

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

Solidification: Nucleation Types

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

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: for *r* < *r** nuclei shrink; for *r* >*r** nuclei grow (to reduce energy)

Adapted from Fig.10.2(b), *Callister & Rethwisch 8e.*

Solidification

$$r^* = \frac{-2\gamma T_m}{\Delta H_f \Delta T}$$

r^* = critical radius

γ = surface free energy

T_m = melting temperature

ΔH_f = latent heat of solidification

$\Delta T = T_m - T$ = supercooling

Note: ΔH_f and γ are weakly dependent on ΔT

$\therefore$ r^* decreases as ΔT increases

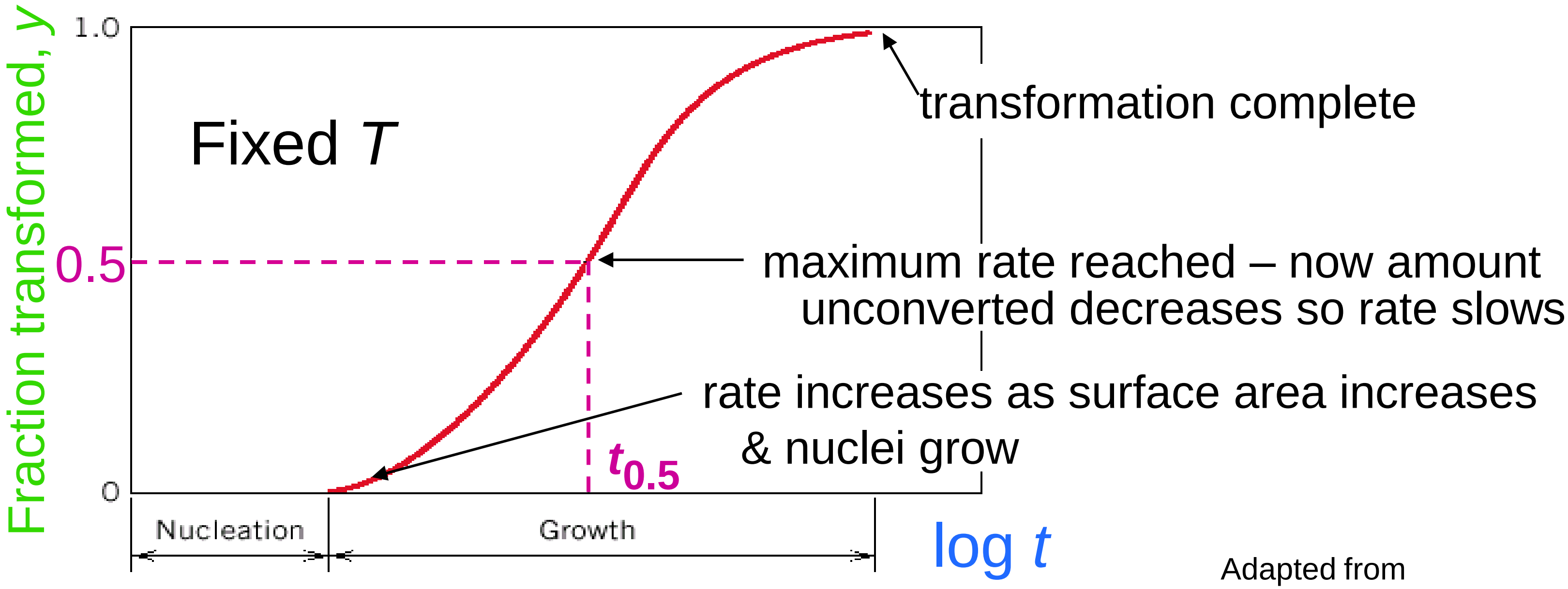
For typical ΔT $r^* \sim$ 10 nm

Rate of Phase Transformations

Kinetics - study of reaction rates of phase transformations

- To determine reaction rate – measure degree of transformation as function of time (while holding temp constant)
  - How is degree of transformation measured?
    - X-ray diffraction – many specimens required
    - electrical conductivity measurements – on single specimen
    - measure propagation of sound waves – on single specimen

Rate of Phase Transformation



Adapted from Fig. 10.10, *Callister & Rethwisch 8e.*

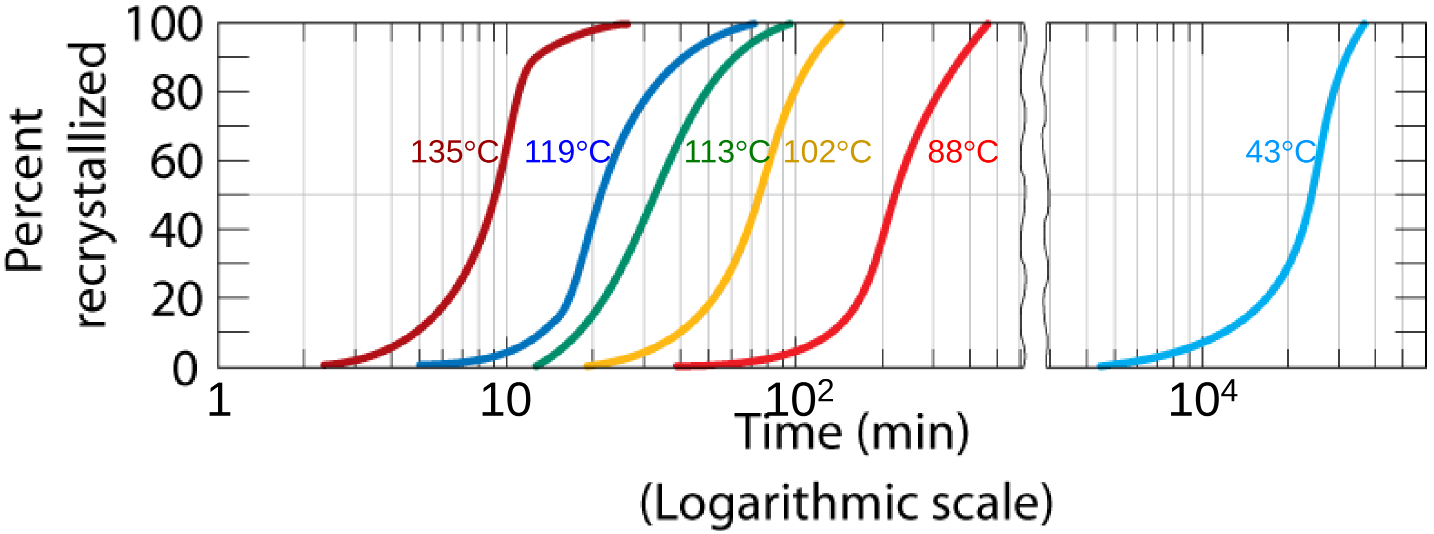
Avrami equation => $y = 1 - \exp(-kt^n)$

fraction transformed — y; time — t

– k & n are transformation specific parameters

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

Temperature Dependence of Transformation Rate



Adapted from Fig. 10.11, *Callister & Rethwisch 8e.* (Fig. 10.11 adapted from B.F. Decker and D. Harker, "Recrystallization in Rolled Copper", *Trans AIME*, **188**, 1950, p. 888.)

- For the recrystallization of Cu, since

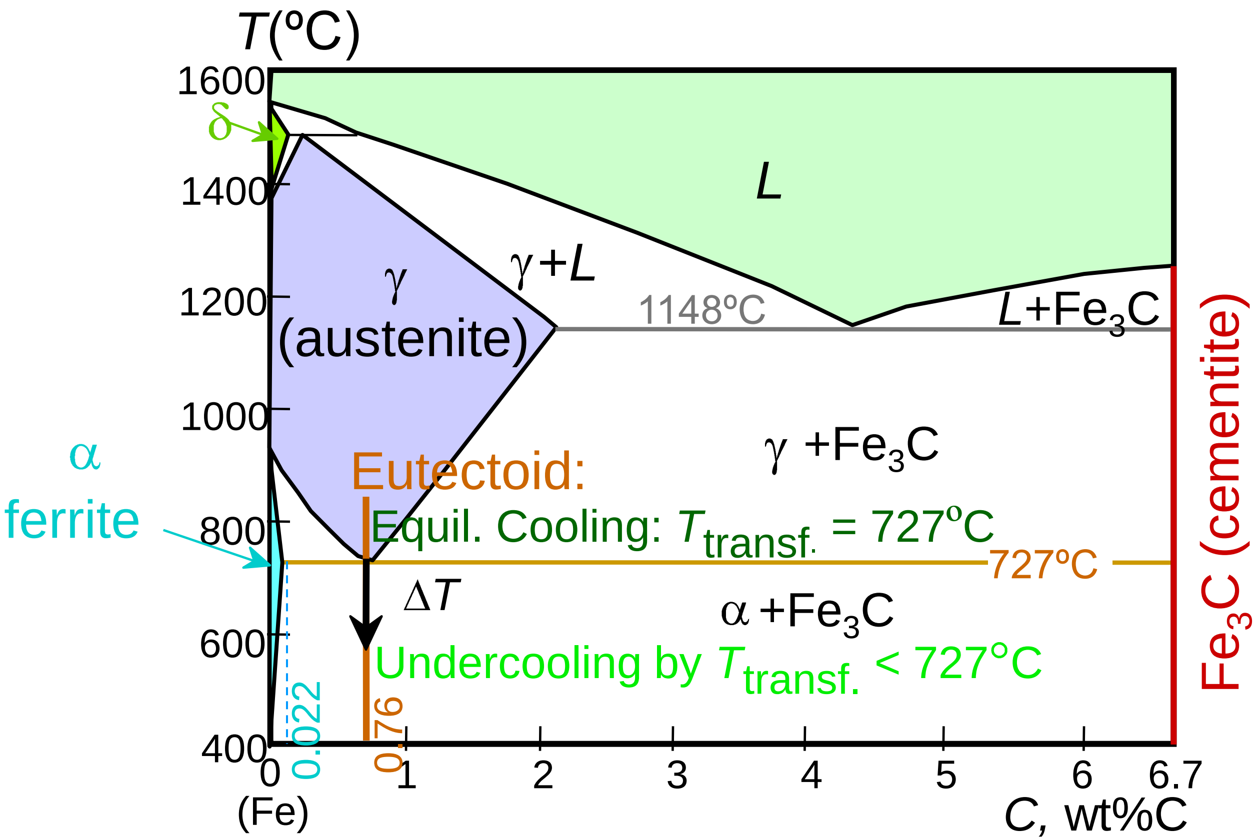
  $$rate = 1/t_{0.5}$$

  rate increases with increasing temperature

- Rate often so slow that attainment of equilibrium state not possible!

Transformations & Undercooling

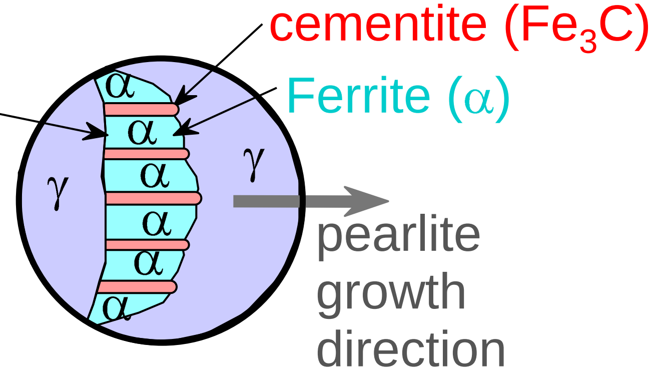
- Eutectoid transf. (Fe-Fe_3C system): $\gamma \Rightarrow \alpha + Fe_3C$
  - 0.76 wt% C (γ), 0.022 wt% C (α), 6.7 wt% C (Fe_3C)
- For transf. to occur, must cool to below 727ºC (i.e., must "undercool")



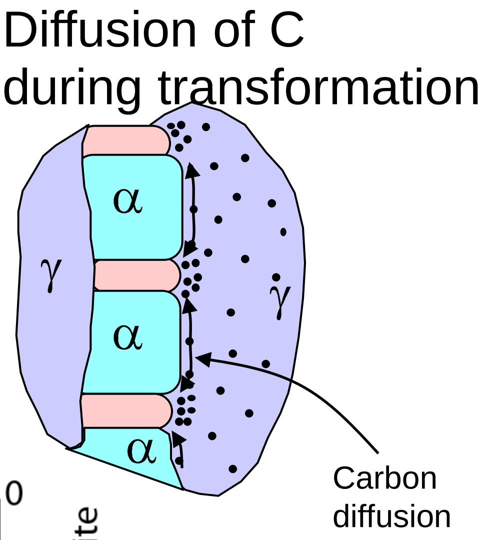
Adapted from Fig. 9.24, *Callister & Rethwisch 8e.* (Fig. 9.24 adapted from *Binary Alloy Phase Diagrams*, 2nd ed., Vol. 1, T.B. Massalski (Ed.-in-Chief), ASM International, Materials Park, OH, 1990.)

The Fe-Fe_3C Eutectoid Transformation

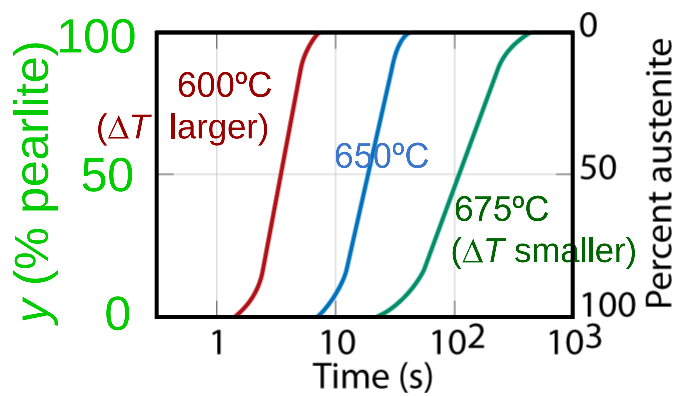
- Transformation of austenite to pearlite:



Adapted from Fig. 9.15, *Callister & Rethwisch 8e.*



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



Adapted from Fig. 10.12, *Callister & Rethwisch 8e.*

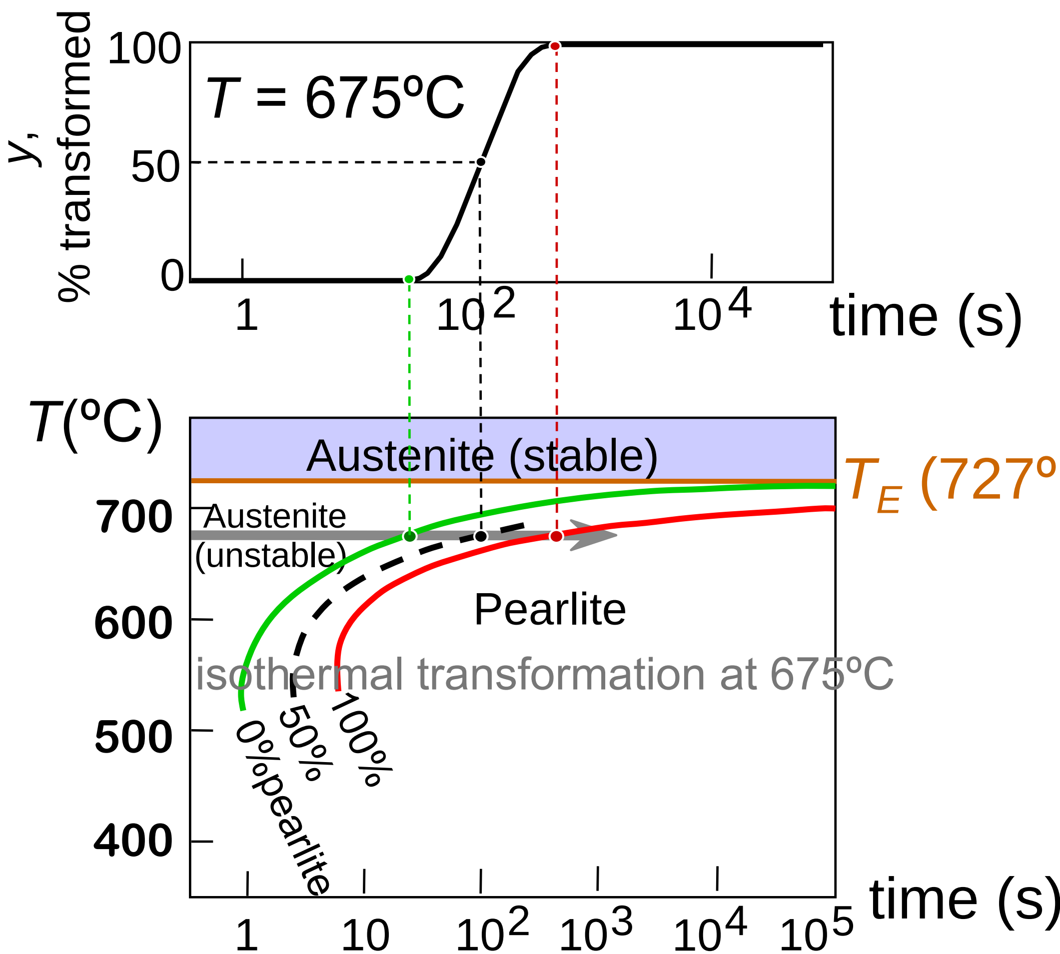
Coarse pearlite → formed at higher temperatures – relatively soft

Fine pearlite → formed at lower temperatures – relatively hard

Generation of Isothermal Transformation Diagrams

Consider:

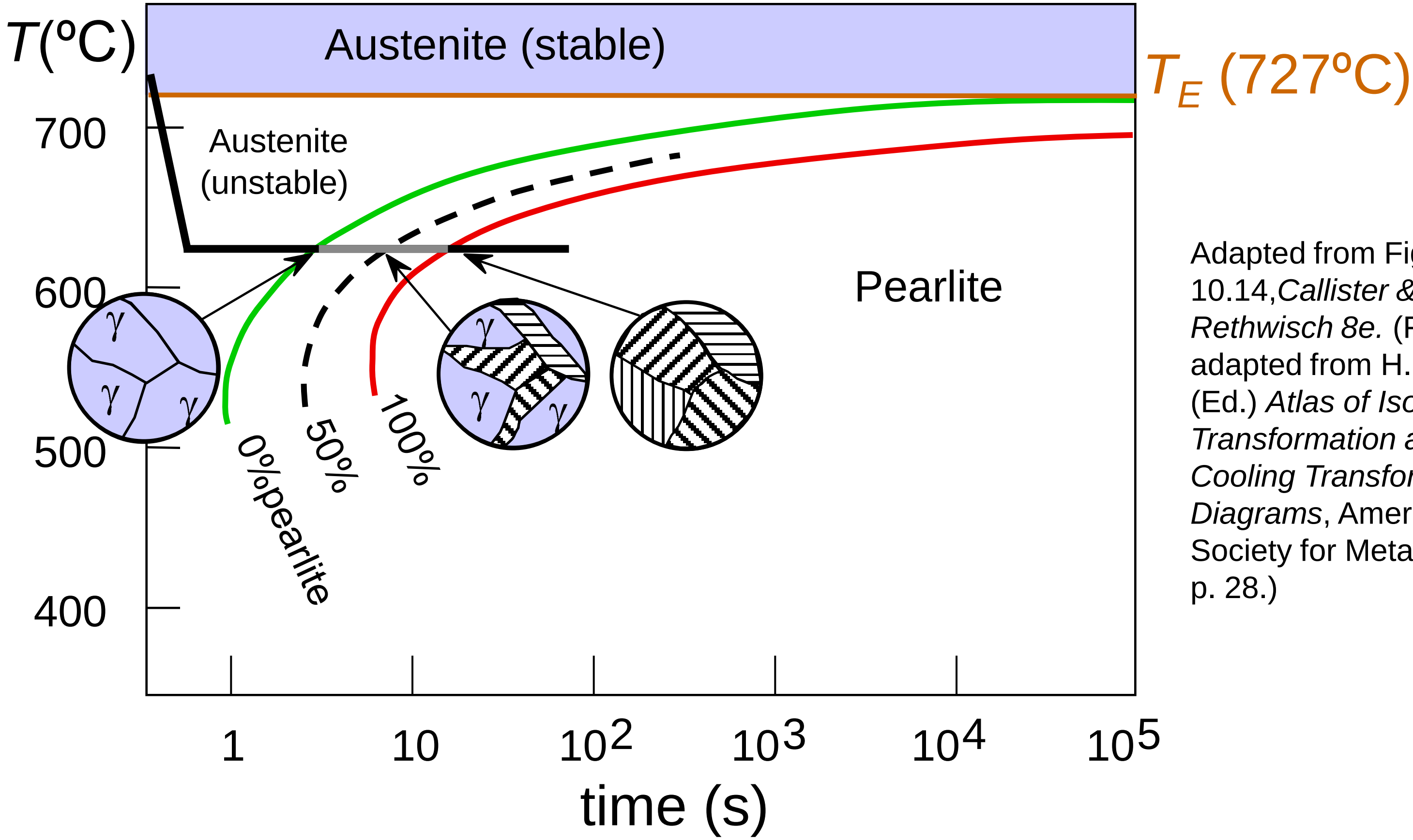
- The Fe-Fe_3C system, for C_0 = 0.76 wt% C
- A transformation temperature of 675ºC.



Adapted from Fig. 10.13,*Callister & Rethwisch 8e.* (Fig. 10.13 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 369.)

Austenite-to-Pearlite Isothermal Transformation

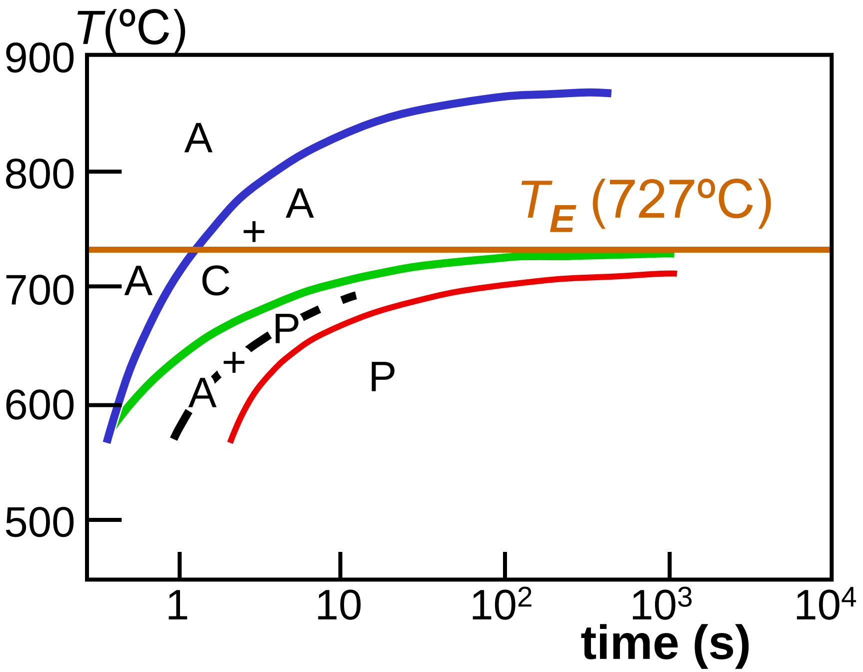
- Eutectoid composition, C_0 = 0.76 wt% C
- Begin at T > 727ºC
- Rapidly cool to 625ºC
- Hold T (625ºC) constant (isothermal treatment)



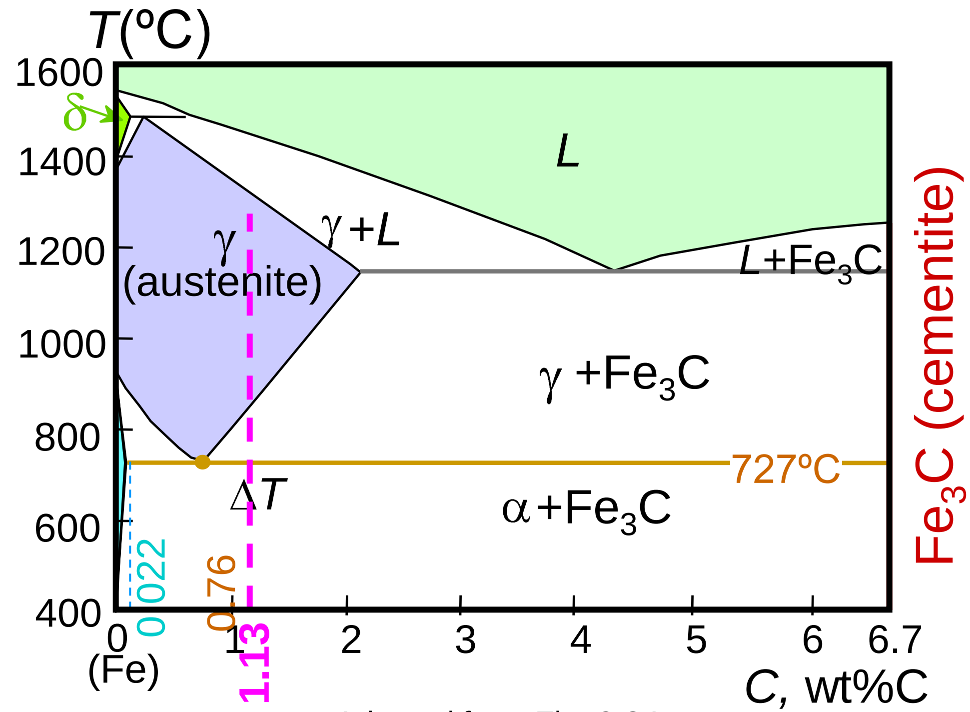
Adapted from Fig. 10.14,*Callister & Rethwisch 8e.* (Fig. 10.14 adapted from H. Boyer (Ed.) *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1997, p. 28.)

Transformations Involving Noneutectoid Compositions

Consider C_0 = 1.13 wt% C



Adapted from Fig. 10.16, *Callister & Rethwisch 8e.*

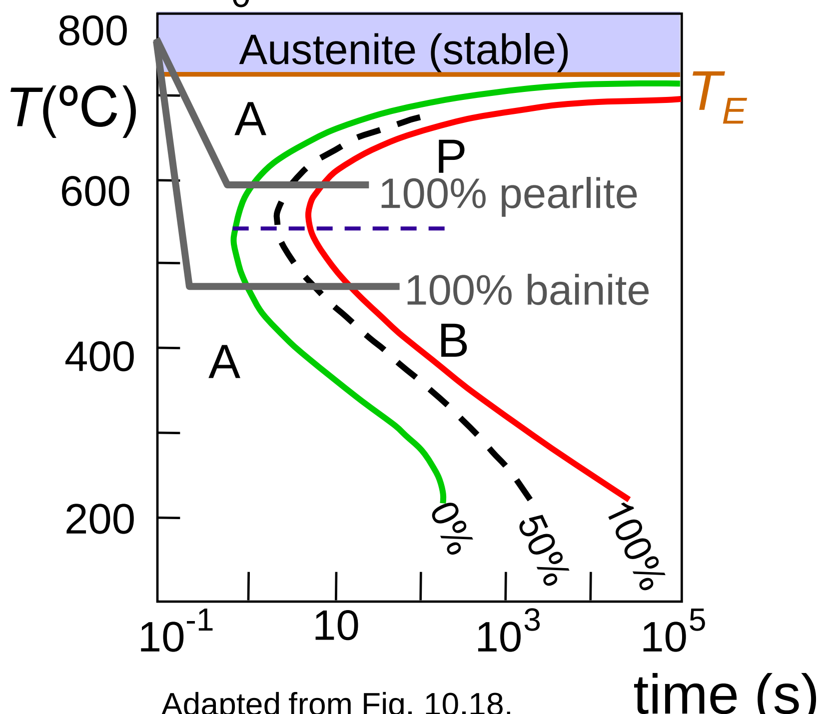


Adapted from Fig. 9.24, *Callister & Rethwisch 8e.*

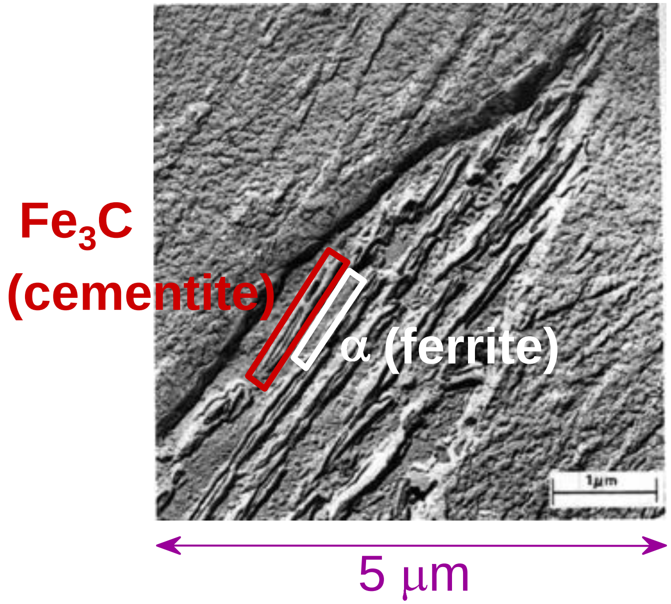
Hypereutectoid composition – proeutectoid cementite

Bainite: Another Fe-Fe_3C Transformation Product

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



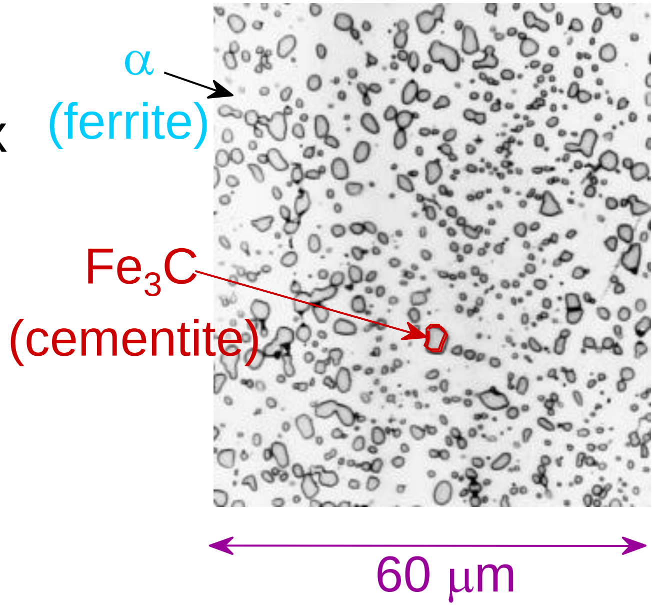
Adapted from Fig. 10.18, *Callister & Rethwisch 8e.*



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

Spheroidite: Another Microstructure for the Fe-Fe_3C System

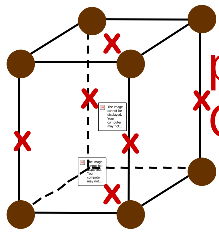
- Spheroidite:
  -- Fe_3C particles within an α-ferrite matrix
  -- formation requires diffusion
  -- heat bainite or pearlite at temperature just below eutectoid for long times
  -- driving force – reduction of α-ferrite/Fe_3C interfacial area



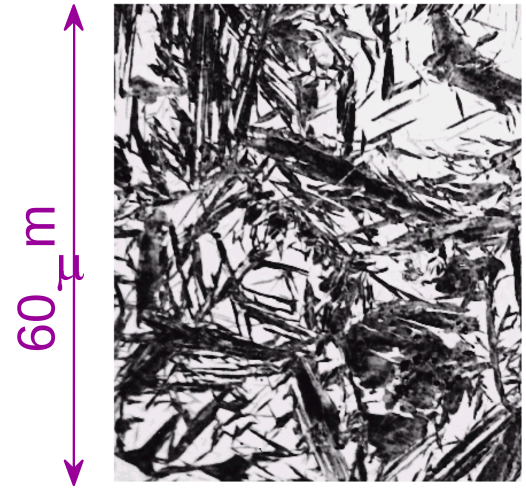
Adapted from Fig. 10.19, *Callister & Rethwisch 8e.* (Fig. 10.19 copyright United States Steel Corporation, 1971.)

Martensite: A Nonequilibrium Transformation Product

- Martensite:
  -- γ(FCC) to Martensite (BCT)



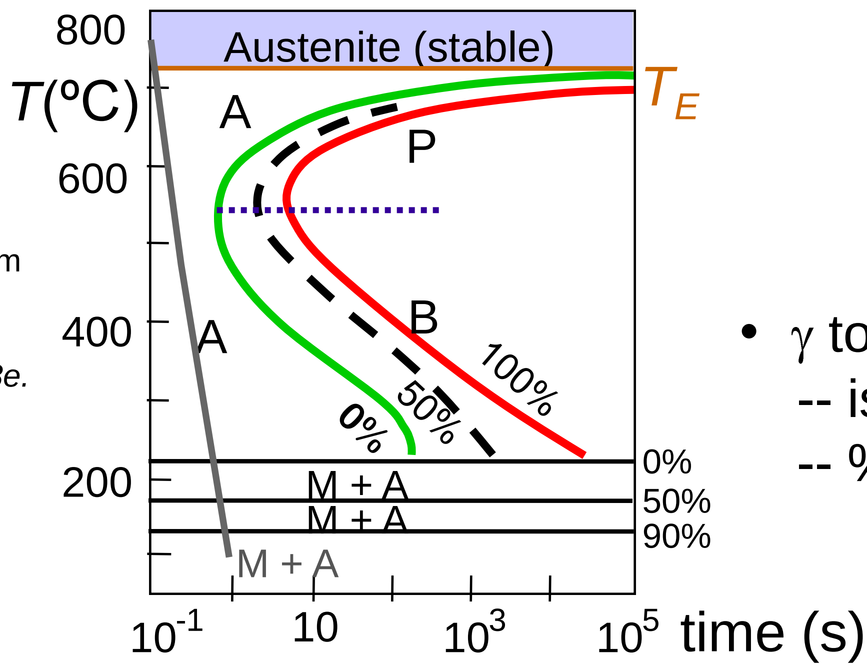
Adapted from Fig. 10.20, *Callister & Rethwisch 8e.*



Martensite needles
Austenite

Adapted from Fig. 10.21, *Callister & Rethwisch 8e.* (Fig. 10.21 courtesy United States Steel Corporation.)

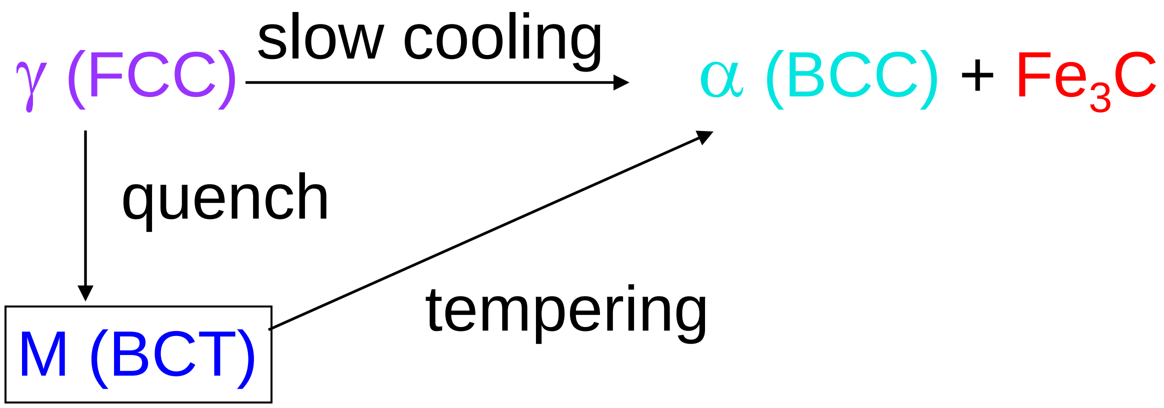
- Isothermal Transf. Diagram



Adapted from Fig. 10.22, *Callister & Rethwisch 8e.*

- γ to martensite (M) transformation..
  -- is rapid! (diffusionless)
  -- % transf. depends only on *T* to which rapidly cooled

Martensite Formation



Martensite (M) – single phase

– has body centered tetragonal (BCT) crystal structure

Diffusionless transformation   BCT if C_0 > 0.15 wt% C

BCT → few slip planes → hard, brittle

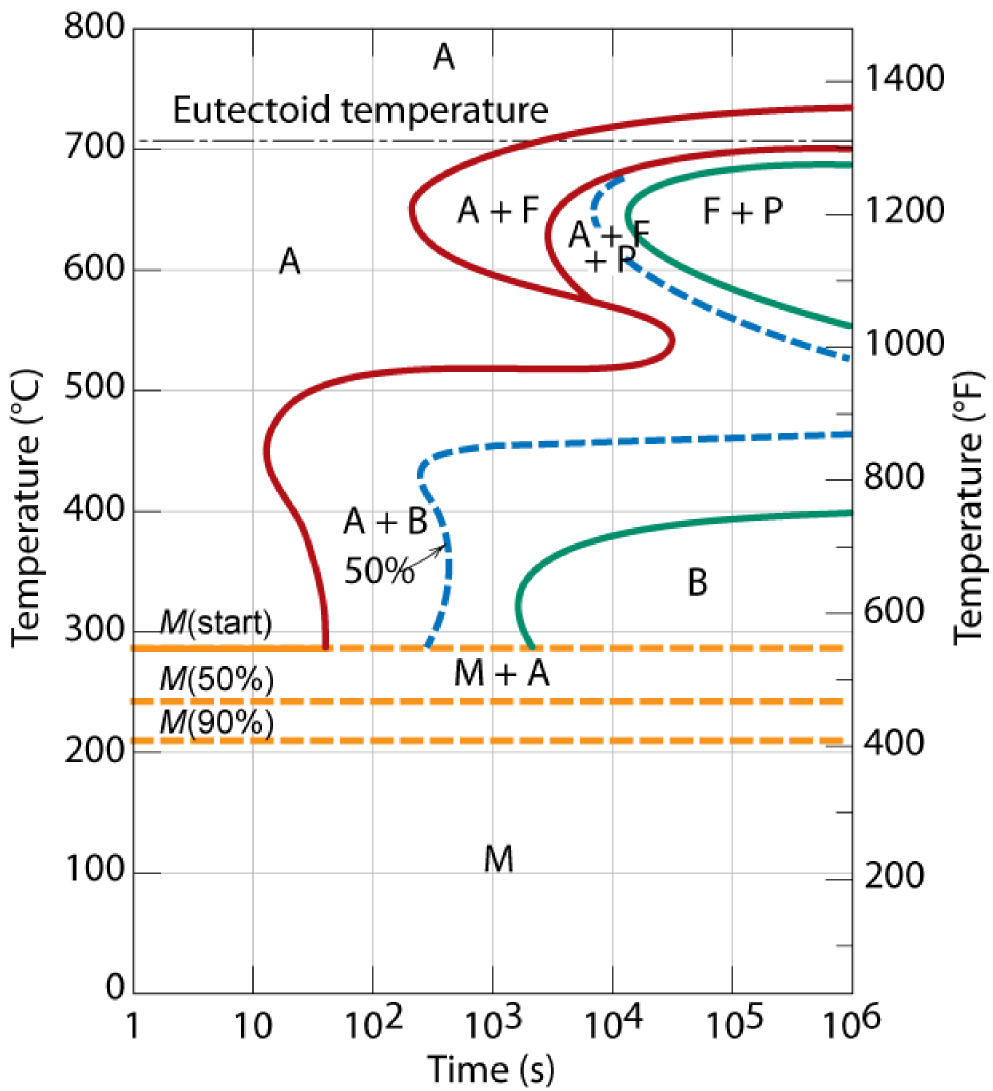
Phase Transformations of Alloys

Effect of adding other elements

Change transition temp.

Cr, Ni, Mo, Si, Mn

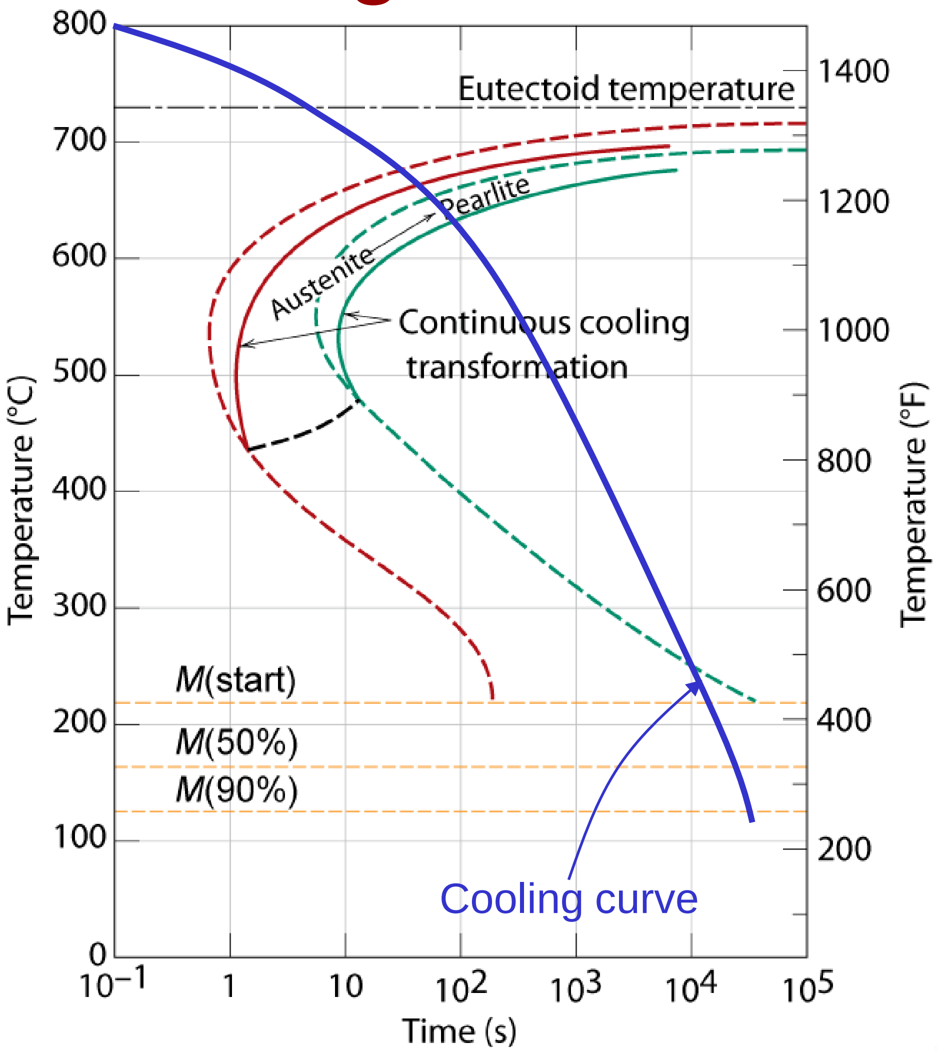
retard $\gamma \rightarrow \alpha + Fe_3C$ reaction (and formation of pearlite, bainite)



Adapted from Fig. 10.23, *Callister & Rethwisch 8e.*

Continuous Cooling Transformation Diagrams

Conversion of isothermal transformation diagram to continuous cooling transformation diagram



Adapted from Fig. 10.25, *Callister & Rethwisch 8e.*

Isothermal Heat Treatment Example Problems

On the isothermal transformation diagram for a 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

Solution to Part (a) of Example Problem

a) 42% proeutectoid ferrite and 58% coarse pearlite

Isothermally treat at ~ 680ºC

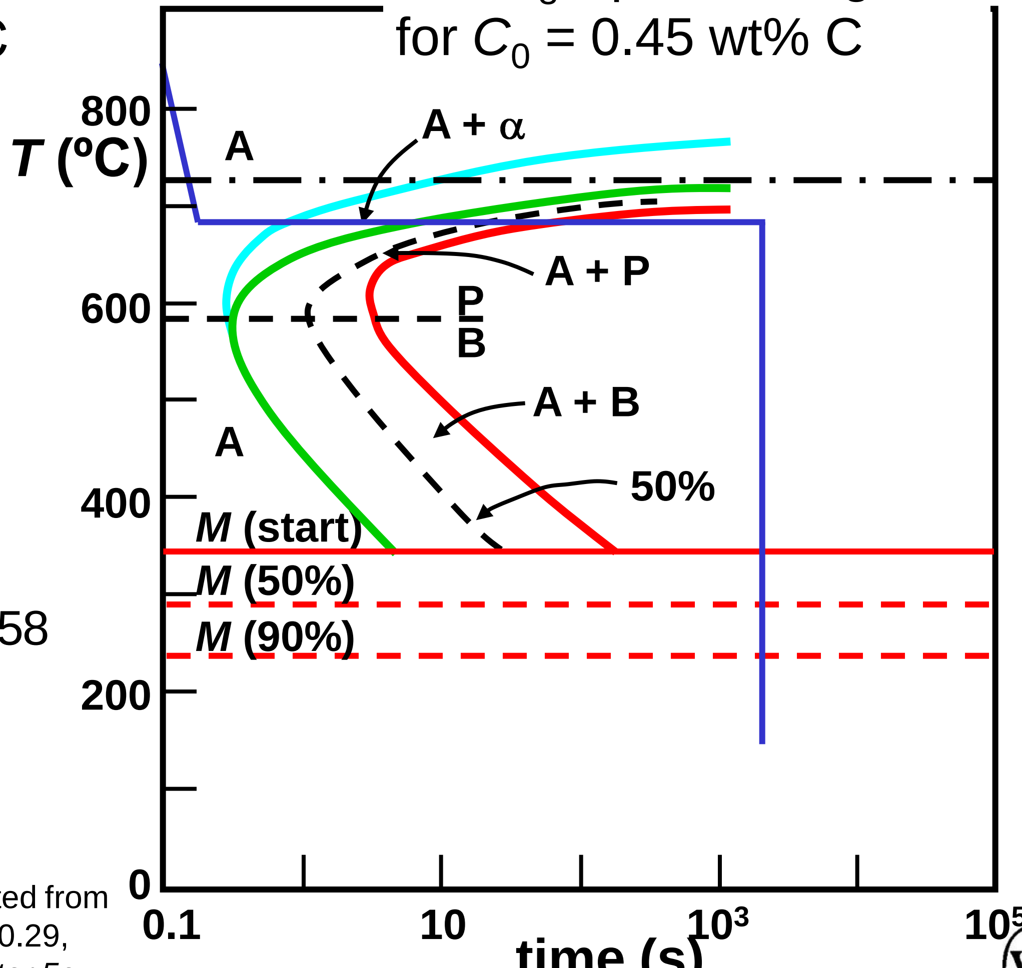
-- all austenite transforms to proeutectoid α and coarse pearlite.

$$W_{pearlite} = \frac{C_0 - 0.022}{0.76 - 0.022}$$

$$= \frac{0.45 - 0.022}{0.76 - 0.022} = 0.58$$

$$W_{\alpha'} = 1 - 0.58 = 0.42$$

Fe-Fe$_3$C phase diagram, for C_0 = 0.45 wt% C



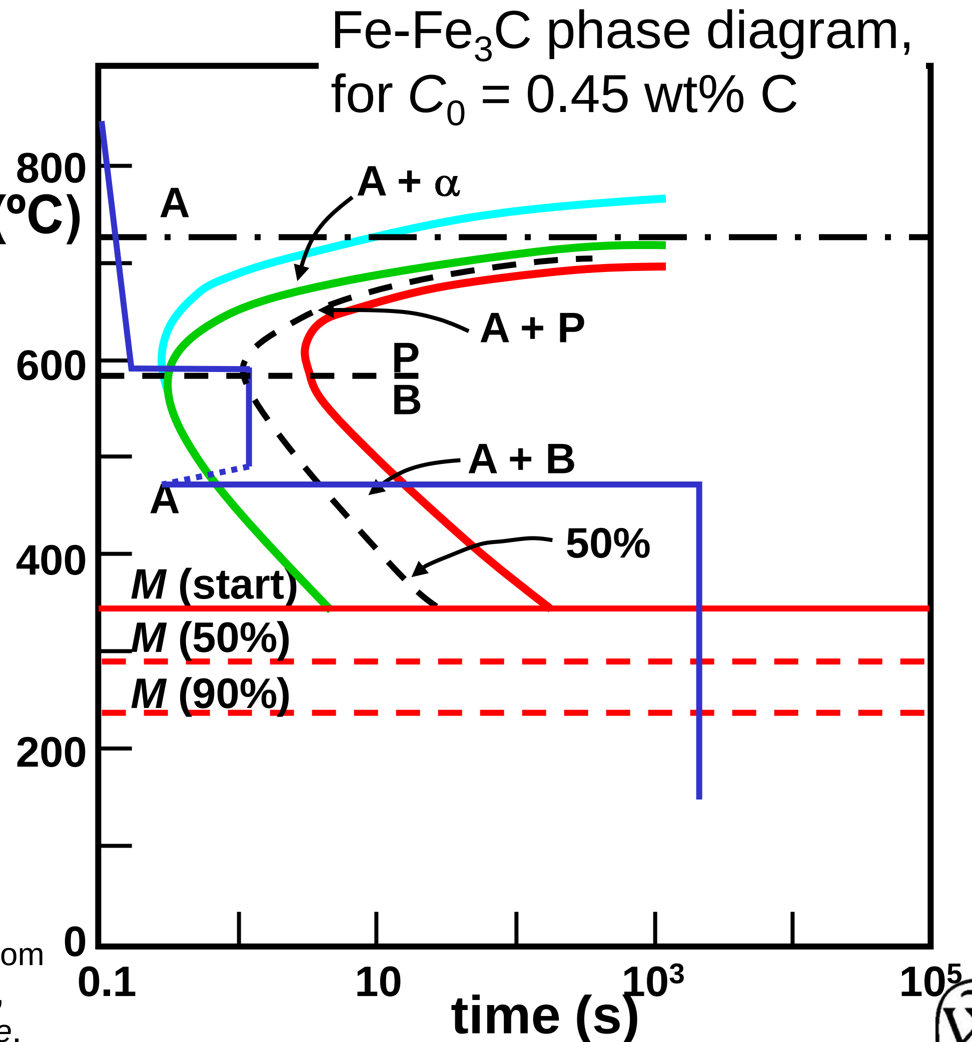
Adapted from Fig. 10.29, *Callister 5e*.

Solution to Part (b) of Example Problem

b) 50% fine pearlite and 50% bainite

Isothermally treat at ~ 590ºC
– 50% of austenite transforms
  to fine pearlite.

Then isothermally treat
  at ~ 470ºC
– all remaining austenite
  transforms to bainite.



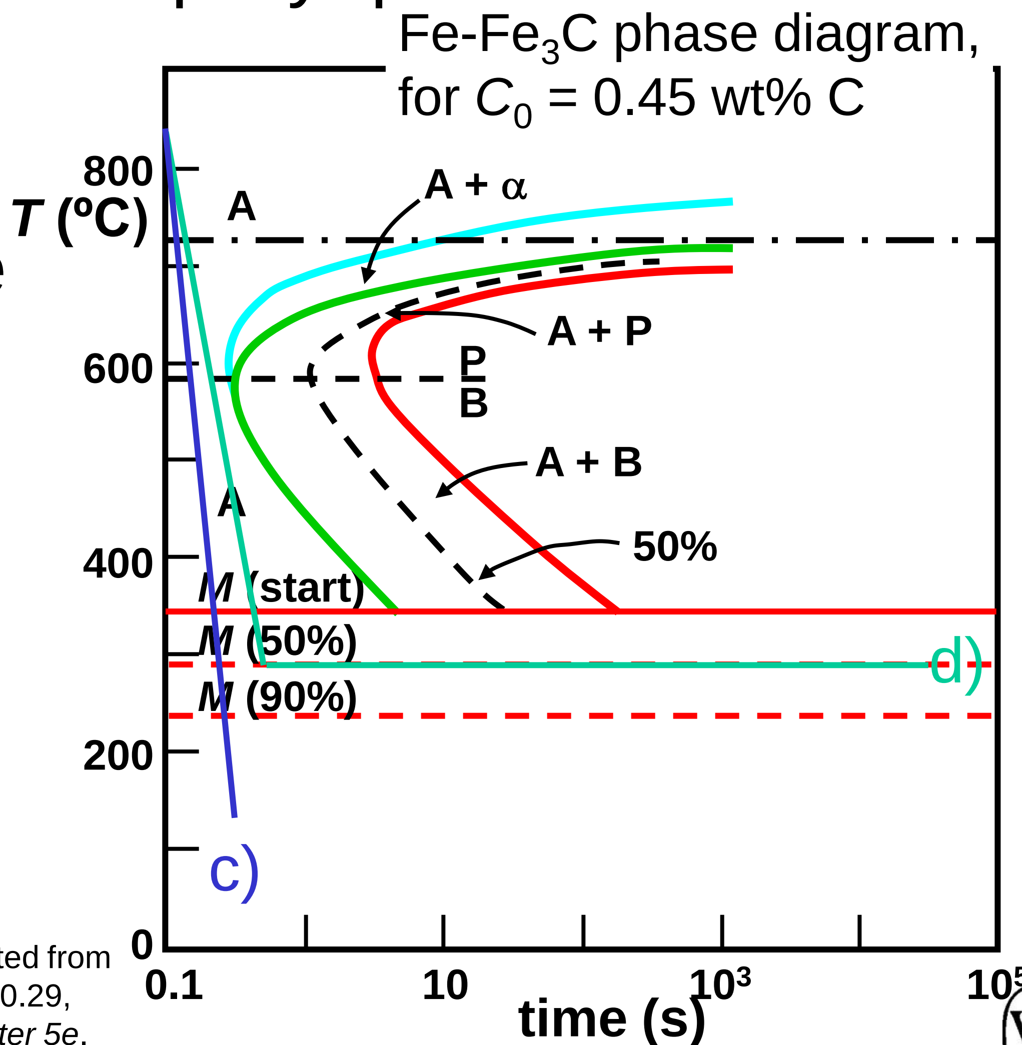
Adapted from Fig. 10.29, *Callister 5e*.

Solutions to Parts (c) & (d) of Example Problem

c) 100% martensite – rapidly quench to room temperature

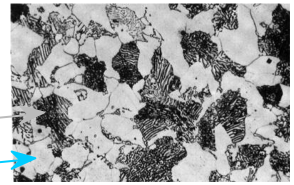
d) 50% martensite & 50% austenite

-- rapidly quench to ~ 290ºC, hold at this temperature



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

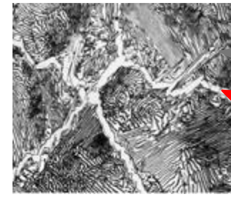
Mechanical Props: Influence of C Content



Adapted from Fig. 9.30, *Callister & Rethwisch 8e.*

$C_0 < 0.76$ wt% C

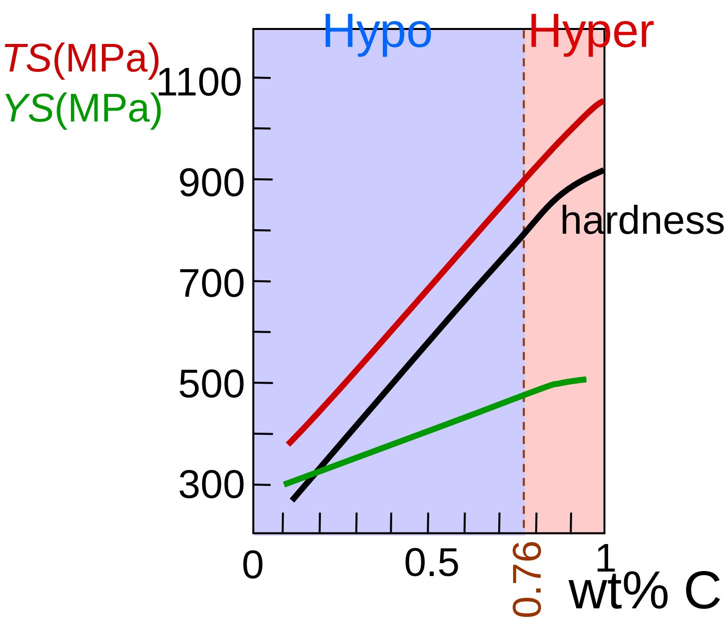
Hypoeutectoid

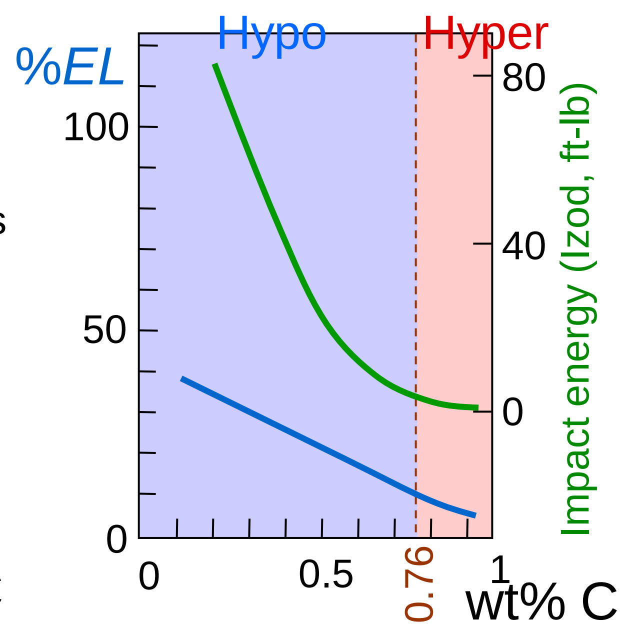


$C_0 > 0.76$ wt% C

Hypereutectoid

Adapted from Fig. 9.33, *Callister & Rethwisch 8e.*

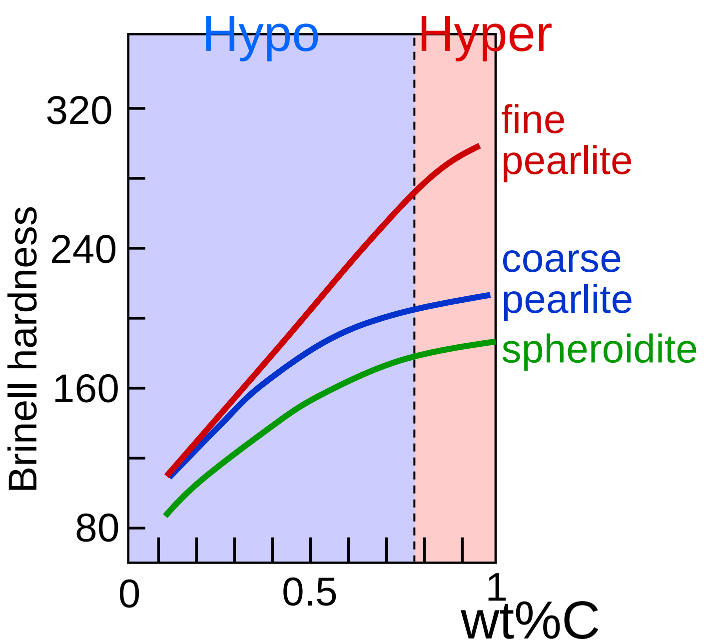


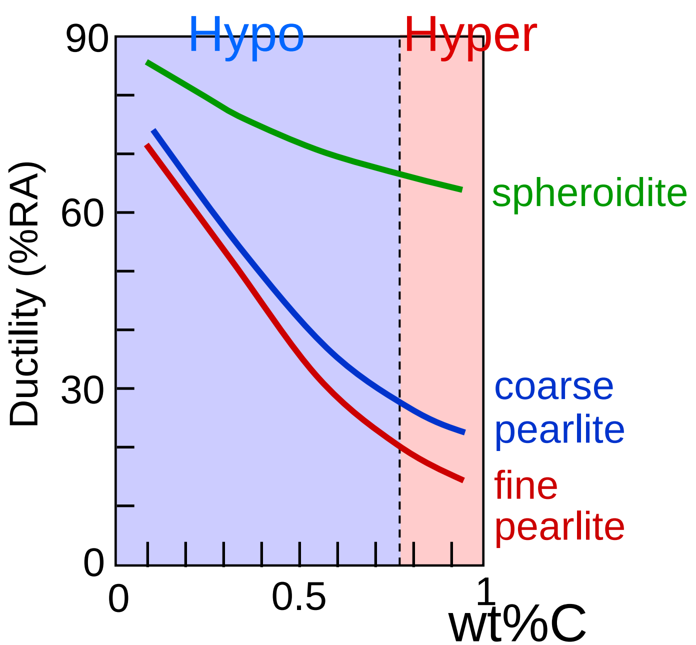


Adapted from Fig. 10.29, *Callister & Rethwisch 8e.* (Fig. 10.29 based on data from *Metals Handbook: Heat Treating*, Vol. 4, 9th ed., V. Masseria (Managing Ed.), American Society for Metals, 1981, p. 9.)

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

Mechanical Props: Fine Pearlite vs. Coarse Pearlite vs. Spheroidite

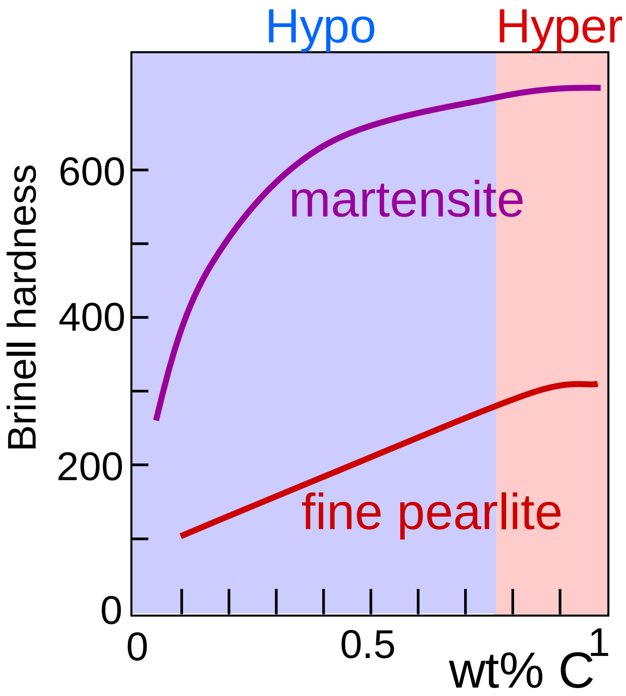




- Hardness: fine > coarse > spheroidite
- %RA: fine < coarse < spheroidite

Adapted from Fig. 10.30, *Callister & Rethwisch 8e.* (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 Props: Fine Pearlite vs. Martensite



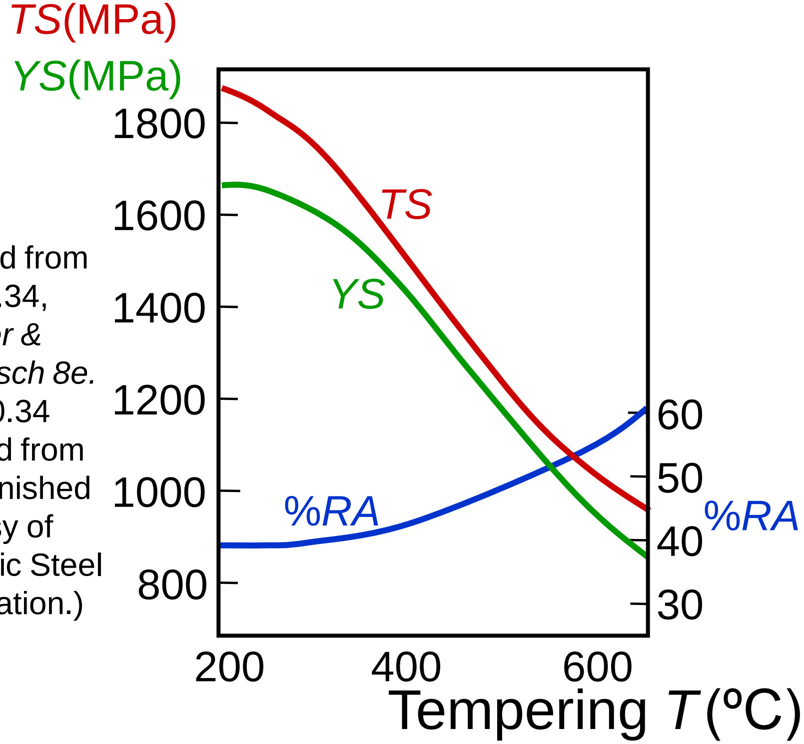
Adapted from Fig. 10.32, *Callister & Rethwisch 8e.* (Fig. 10.32 adapted from Edgar C. Bain, *Functions of the Alloying Elements in Steel*, American Society for Metals, 1939, p. 36; and R.A. Grange, C.R. Hribal, and L.F. Porter, *Metall. Trans. A*, Vol. 8A, p. 1776.)

- Hardness: fine pearlite << martensite.

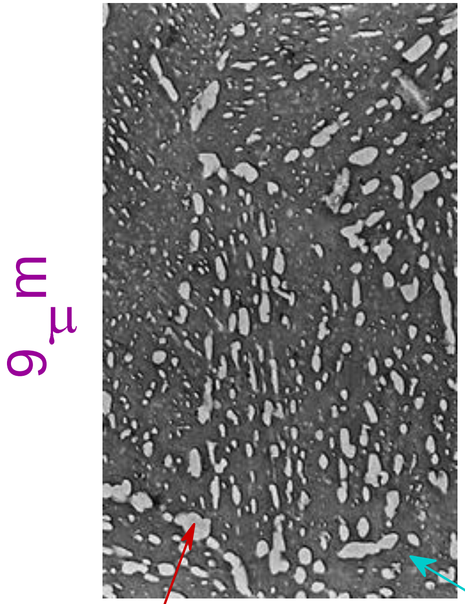
Tempered Martensite

Heat treat martensite to form tempered martensite

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



Adapted from Fig. 10.34, *Callister & Rethwisch 8e.* (Fig. 10.34 adapted from Fig. furnished courtesy of Republic Steel Corporation.)



Adapted from Fig. 10.33, *Callister & Rethwisch 8e.* (Fig. 10.33 copyright by United States Steel Corporation, 1971.)

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

Summary of Possible Transformations

Adapted from Fig. 10.36, *Callister & Rethwisch 8e.*

Austenite (γ)

slow cool → **Pearlite** (α + Fe_3C layers + a proeutectoid phase)

moderate cool → **Bainite** (α + elong. Fe_3C particles)

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: