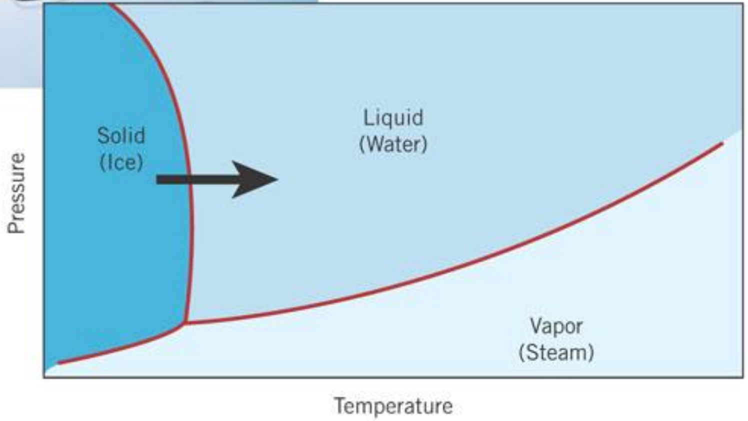
CHAPTER
12

Phase Transformations

- **Introduction**
- **Basic concepts**
- The kinetics of phase transformations
- Metastable versus equilibrium states
- Isothermal transformation diagrams
- Continuous cooling transformation diagrams
- Mechanical behavior of iron-carbon alloys
- Tempered martensite
- Review of phase transformations and mechanical properties for iron-carbon alloys

Phase Transformations

H_2O

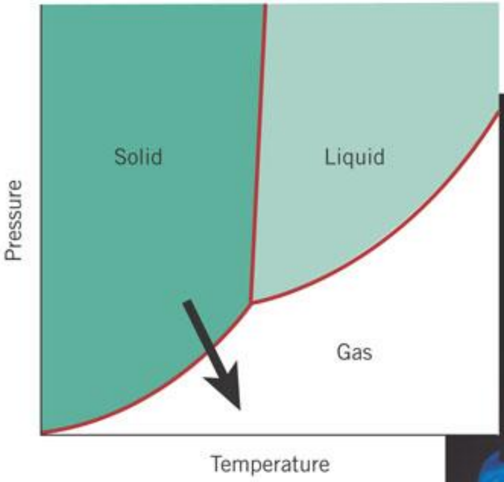


◆ Phase transformations occur, when phase boundaries (the red curves) on these plots are crossed as temp. and/or pressure is changed.

◆ Upon passing across the solid-gas phase boundary of the CO_2 phase diagram, dry ice (solid CO_2) sublimes (gaseous CO_2).

◆an arrow delineates this phase transformation

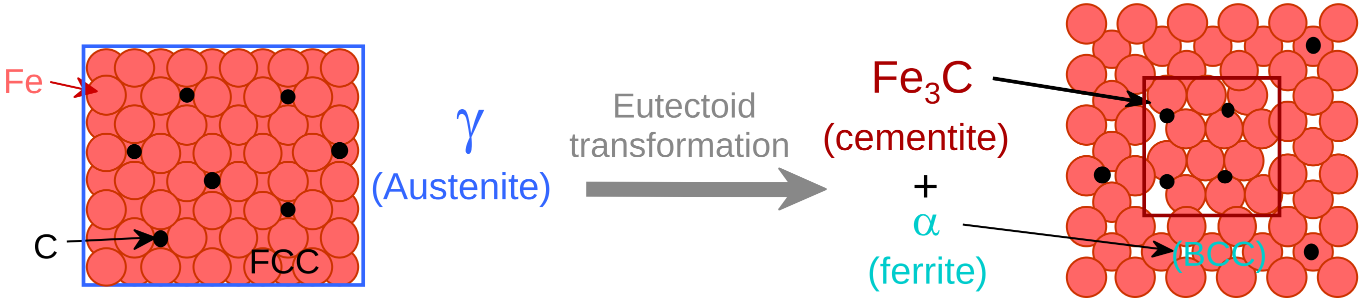
CO_2



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?

Three types of phase transformation

- Simple diffusion-dependent transformations -- no change in either the number or composition of the phase present.
  - solidification of a pure metal, allotropic transformations, recrystallization, grain growth.
- Diffusion-dependent transformations -- some alteration in phase compositions and often in the number of phases present; the final micro-structure ordinarily consists of two phases.
  - eutectoid reaction.
- Diffusionless, wherein a metastable phase is produced.
  - martensitic transformation.

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Kinetics of Phase Transformations I

- **Phase transformation**

  - At least one new phase is formed that has different physical/chemical characteristics and/or a different structure than the parent phase.

  - Begin by the formation of numerous small particles of the new phase(s), which increase in size until the transformation has reached completion.

- **Gibbs free energy**

  - Gibbs free energy is a function of the internal energy of the system (enthalpy, H) and a measurement of the randomness or disorder of the atoms or molecules (entropy, S). ($G = H - TS$)

  - A transformation will occur spontaneously only when the change in free energy ΔG has a negative value.

Kinetics of Phase Transformations II

Phase transformation may be broken down into two distinct stages:

- **Nucleation** (孕核，成核)
  - Nucleation involves the appearance of very small particles, or nuclei of the new phase, which are capable of growing.
  - For the homogeneous type, nuclei of the new phase form uniformly throughout the parent phase, whereas for the heterogeneous type, nuclei form preferentially at structural inhomogeneities, such as, container surfaces, insoluble impurities, grain boundaries, dislocations, and so on.

- **Growth**

  During the growth stage these nuclei increase in size, which results in the disappearance of some (or all) of the parent phase. The transformation reaches completion if the growth of these new phase particles is allowed to proceed until the equilibrium fraction is attained.

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

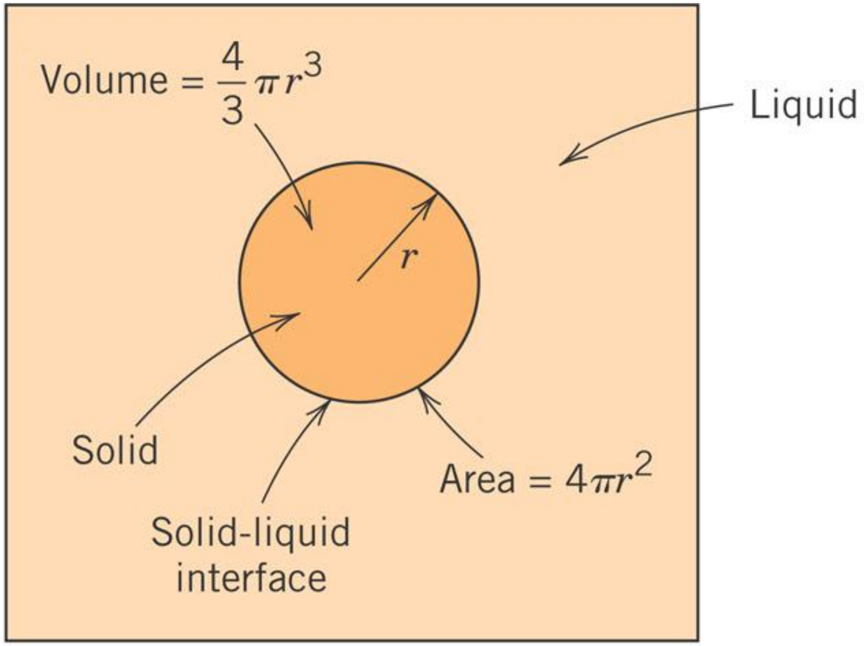
- supercooling (eutectic, eutectoid)
- superheating (peritectic)

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

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

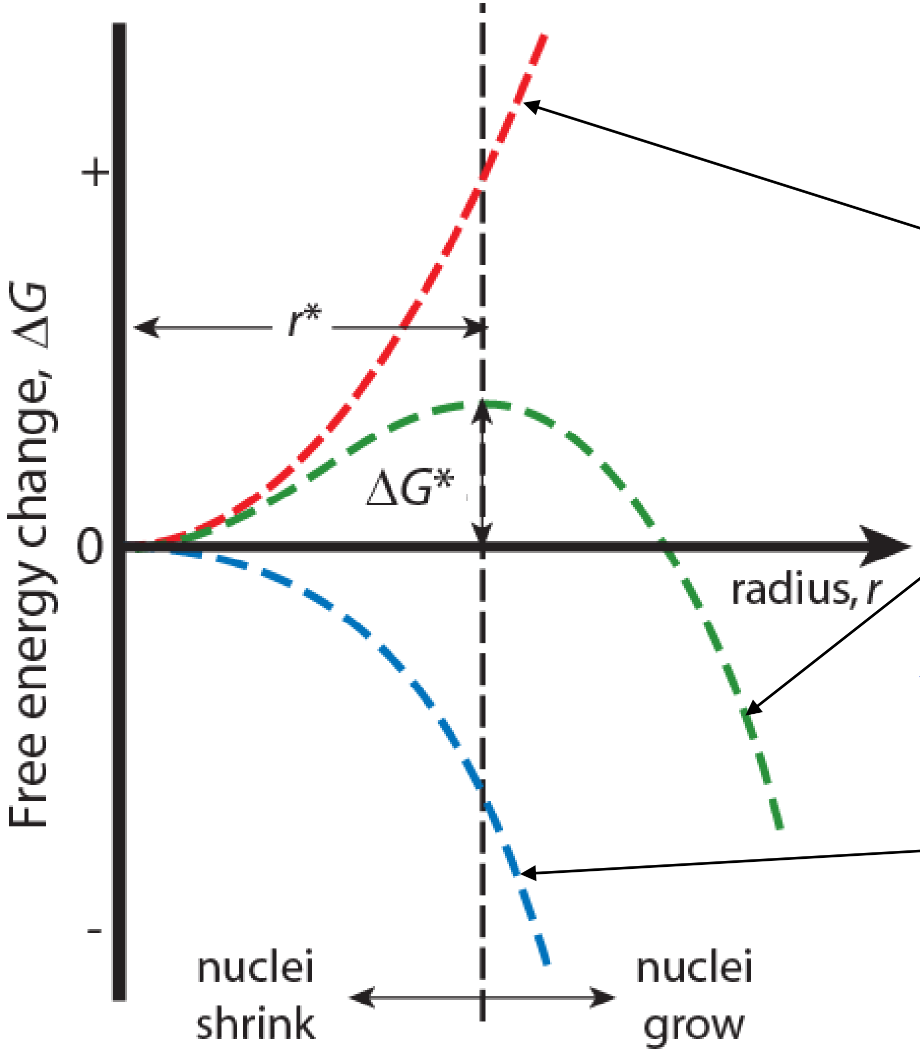
Solidification: Nucleation Types

- 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

$$\Delta G_T = \text{Total Free Energy} = \Delta G_S + \Delta G_V$$

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)

Kinetics of Phase Transformations

$$\Delta G = V\Delta G_v + A\gamma = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \qquad (10.1)$$

$$\frac{d(\Delta G)}{dr} = 4\pi r^2 \Delta G_v + 8\pi r \gamma = 0 \qquad (10.2)$$

When $r = r^*$ $\Rightarrow r^* = -\frac{2\gamma}{\Delta G_v}$ (10.3)

$$\Rightarrow \Delta G^* = \frac{4}{3}\pi\left(-\frac{2\gamma}{\Delta G_v}\right)^3 \Delta G_v + 4\pi\left(-\frac{2\gamma}{\Delta G_v}\right)^2 \gamma = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \qquad (10.4)$$

V: volume of spherical nucleus,
ΔG_v: volume free energy,
A: surface area of spherical nucleus,
γ: surface free energy,
r: radius of spherical nucleus,
r^*: critical radius of spherical nucleus,
ΔG^*: critical free energy, activation energy

Solidification

ΔG_v: volume free energy

$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$$

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

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

Kinetics of Phase Transformations

- The volume free energy change ΔG_v is the driving force for the solidification transformation, and its magnitude is a function of temperature. At the equilibrium solidification temperature T_m, the value of ΔG_v is zero, and with diminishing temperature its value becomes increasingly more negative. It can be shown that ΔG_v is a function of temperature as

$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m} \tag{10.5}$$

$$\Rightarrow r^* = -\frac{2\gamma}{\Delta G_v} = -\frac{2\gamma}{\dfrac{\Delta H_f (T_m - T)}{T_m}} = \left(-\frac{2\gamma T_m}{\Delta H_f}\right) \cdot \left(\frac{1}{T_m - T}\right) \tag{10.6}$$

$$\Rightarrow \Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} = \frac{16\pi\gamma^3}{3\left[\dfrac{\Delta H_f (T_m - T)}{T_m}\right]^2} = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right) \cdot \frac{1}{(T_m - T)^2} \tag{10.7}$$

ΔH_f: latent heat of fusion, T_m: equilibrium melting temperature (K),
T: real solidification temperature (K).

Kinetics of Phase Transformations

- Both the critical radius r^* and the activation free energy ΔG^* decrease as temperature T decreases. With a lowering of temperature at temperatures below the equilibrium solidification temperature (T_m), nucleation occurs more readily.

$$r^* = \left(-\frac{2\gamma T_m}{\Delta H_f}\right)\cdot\left(\frac{1}{T_m - T}\right) \qquad \Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\cdot\frac{1}{(T_m - T)^2}$$

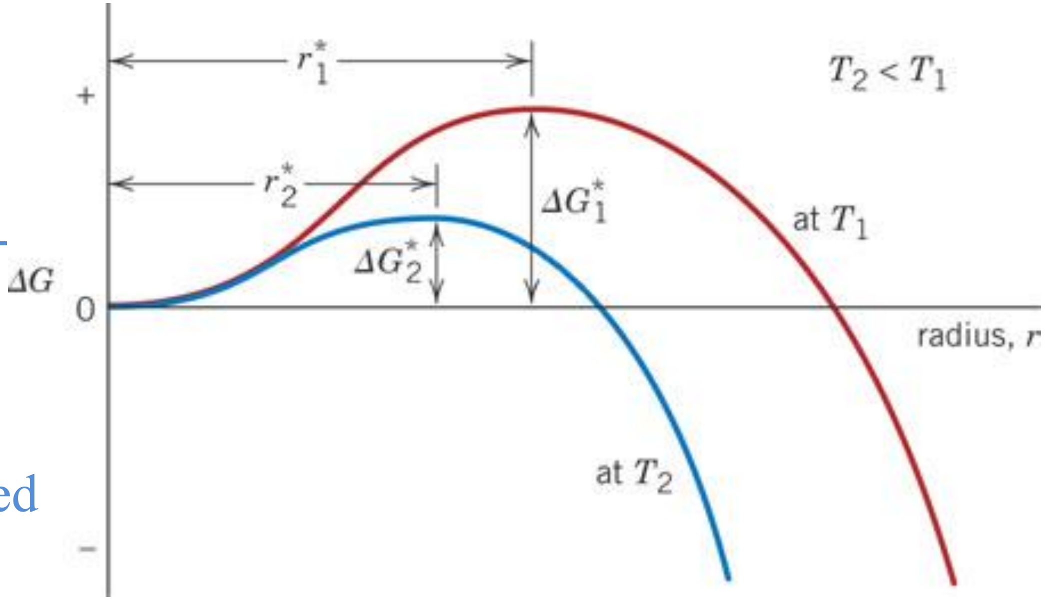
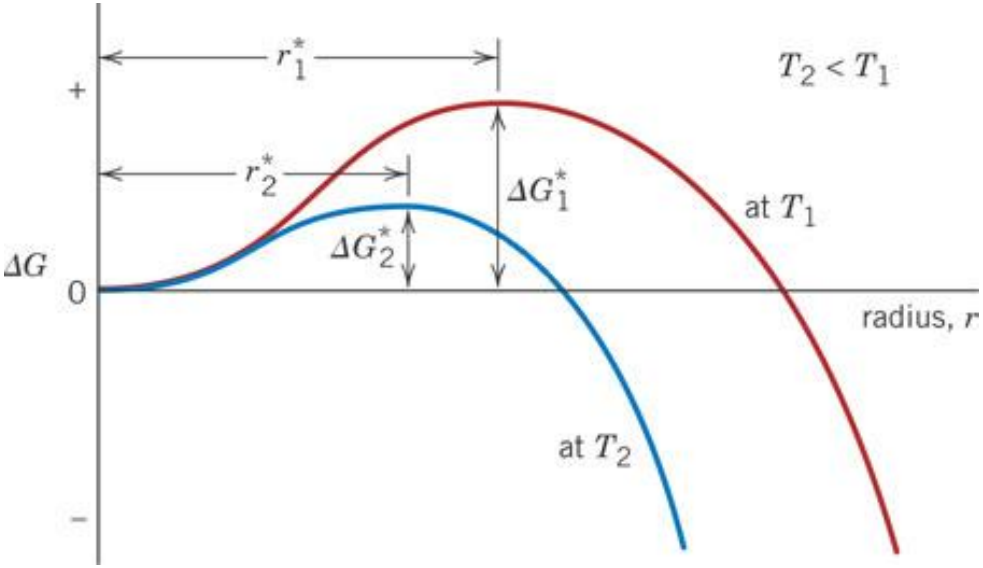
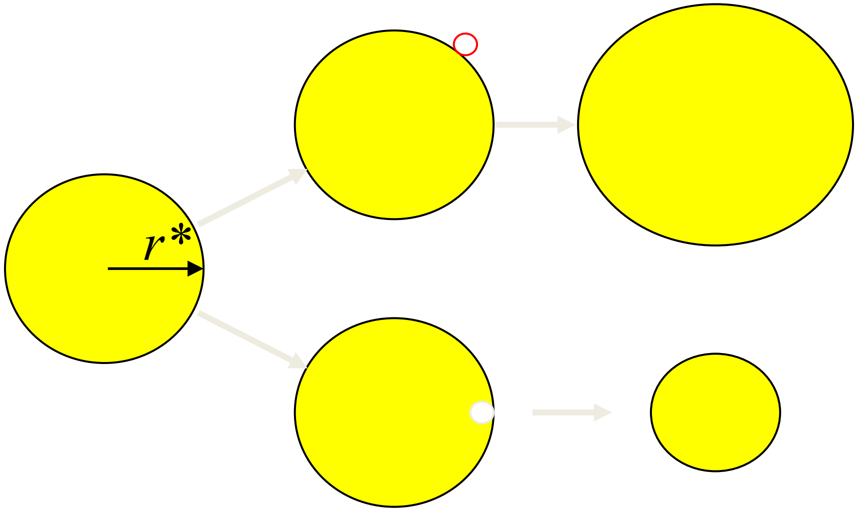


FIGURE 10.3 Schematic free energy-versus-embryo/nucleus radius curves for two different temperatures. The critical free energy change (ΔG^*) and critical nucleus radius (r^*) are indicated for each temperature.

Kinetics of Phase Transformations

- Supposed that there is a spherical embryo has a radius of r^*. If this embryo catches an atom, then it will become a stable nucleus, and it will grow up, since its Gibbs free energy gets smaller. If this embryo loses an atom, then it will disappear later because of the decrease of Gibbs free energy. Therefore, the computation of nucleation rate can be treated as two steps. The first is the probability of forming a embryo with a radius of r^*. The second is that the rate of this embryo getting an additional atom.





Kinetics of Phase Transformations

- The number of stable nuclei n^* (having radii greater than r^*) is a function of temperature as

$$n^* = K_1 \exp\left(-\frac{\Delta G^*}{kT}\right) \tag{10.8}$$

K_1: total number of nuclei of the solid phase.

- As the temperature is lowered below T_m, the exponential term in Equation 10.8 also decreases such that the magnitude of n^* increases.

$$T\downarrow \Rightarrow T_m\text{-}T\uparrow \Rightarrow \Delta G^*\downarrow \Rightarrow \exp(-\Delta G^*/kT)\uparrow \Rightarrow n^*\uparrow \qquad \Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\cdot\frac{1}{(T_m - T)^2}$$

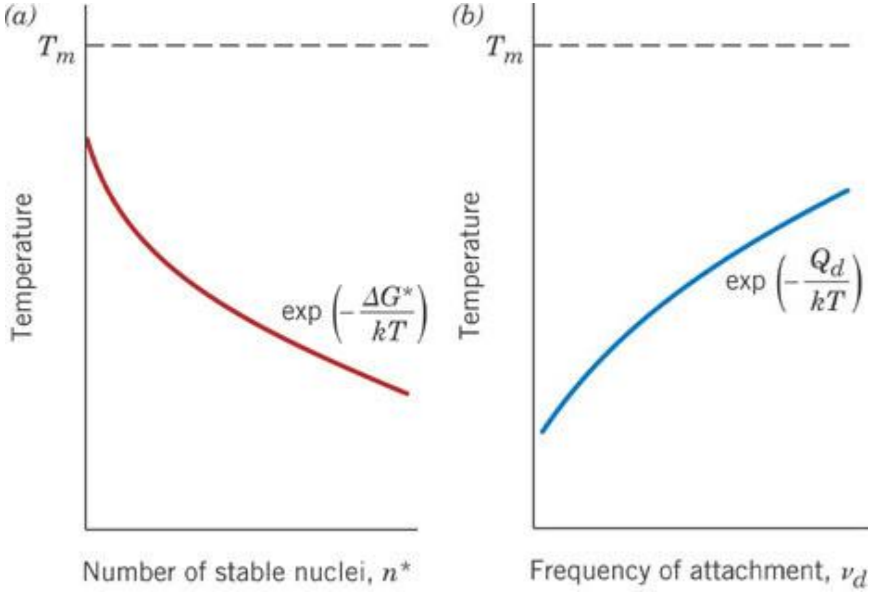


FIGURE 10.4 For solidification, schematic plots of (*a*) number of stable nuclei versus temperature, (*b*) frequency of atomic attachment versus temperature.

Kinetics of Phase Transformations

- The diffusion effect is related to the frequency at which atoms from the liquid attach themselves to the solid nucleus, v_d.

$$v_d = K_2 \exp(-\frac{Q_d}{kT}) \qquad (10.9)$$

Q_d: temperature-independent activation energy for diffusion,

K_2: temperature-independent constant.

- The nucleation rate is simply proportional to the product of n^* and v_d.

$$\dot{N} = K_1 K_2 K_3 \exp(-\frac{\Delta G^*}{kT}) \exp(-Q_d / kT) \qquad (10.10)$$

K_3: number of atoms on a nucleus surface.

- Note (Fig. 10.4c) that, with a lowering of temperature from below T_m, the nucleation rate first increases, achieves a maximum, and subsequently diminishes.

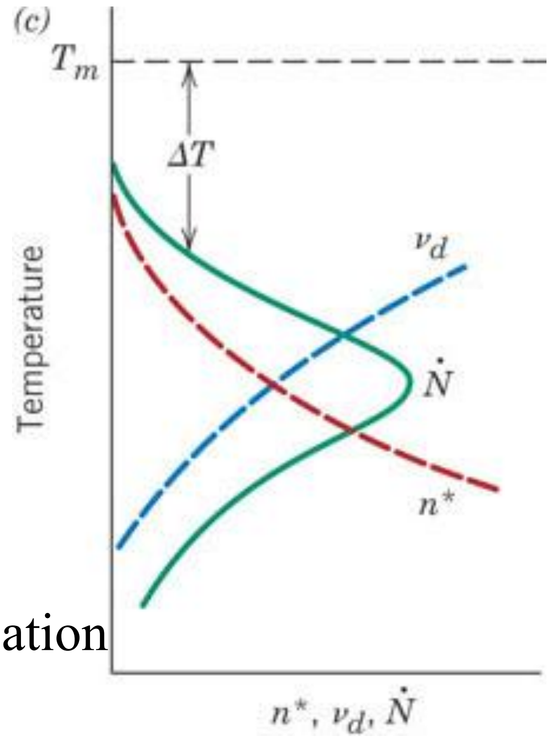


FIGURE 10.4 For solidification, schematic plots of (c) nucleation rate versus temperature.

Kinetics of Phase Transformations

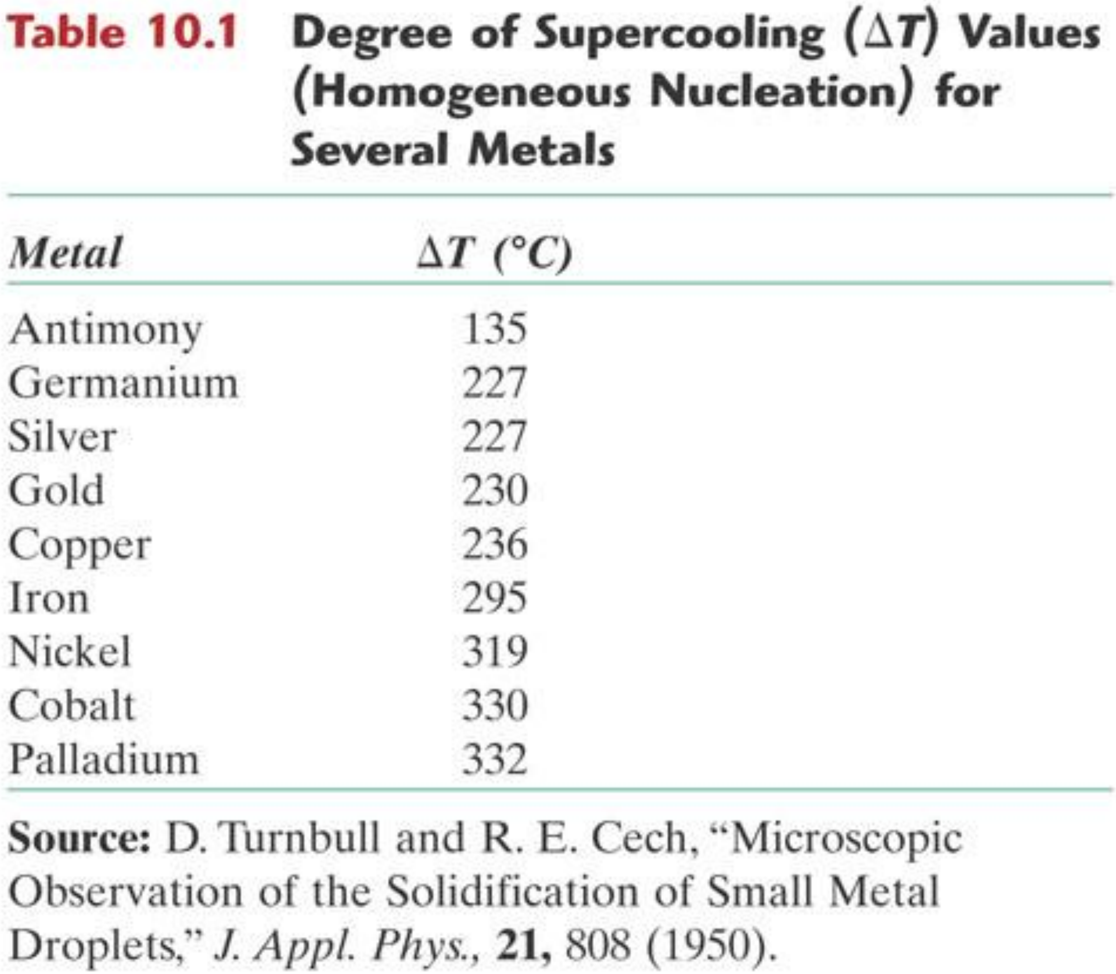


Table 10.1 **Degree of Supercooling (ΔT) Values (Homogeneous Nucleation) for Several Metals**

Metal	ΔT (°C)
Antimony	135
Germanium	227
Silver	227
Gold	230
Copper	236
Iron	295
Nickel	319
Cobalt	330
Palladium	332

Source: D. Turnbull and R. E. Cech, "Microscopic Observation of the Solidification of Small Metal Droplets," *J. Appl. Phys.*, **21,** 808 (1950).

Kinetics of Phase Transformations

- **Heterogeneous nucleation**
  - It is easier for nucleation to occur at surfaces and interfaces than at other sites. This type of nucleation is termed heterogeneous.
  - Let us consider the nucleation, on a flat surface, of a solid particle from a liquid phase. It is assumed that both the liquid and solid phases "wet" this flat surface. Taking a surface tension force balance in the plane of the flat surface (Fig. 10.5) leads to the following expression:

$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL}\cos\theta \qquad (10.12)$$

  - It is possible to derive equations for r^* and ΔG^*,

$$r^* = -2\gamma_{SL}/\Delta G_v \qquad (10.13)$$

$$\Delta G^* = S(\theta)\cdot\left(\frac{16\pi\gamma_{SL}^3}{3\Delta G_v^2}\right) \qquad (10.14)$$

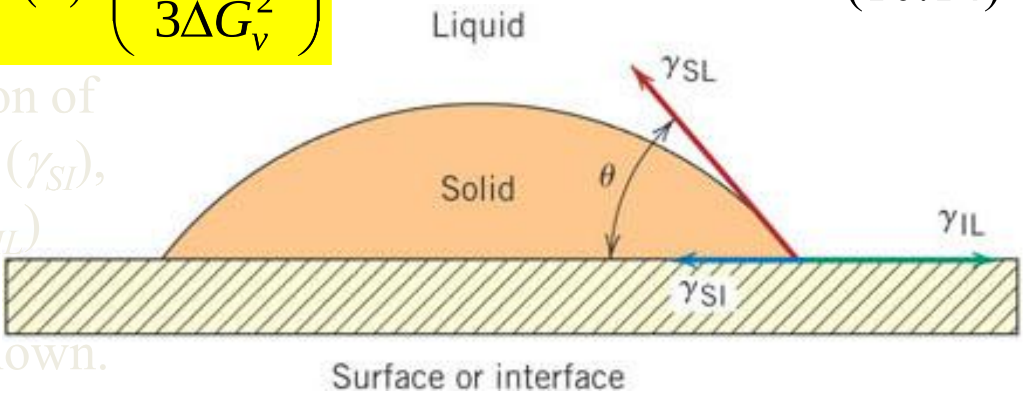
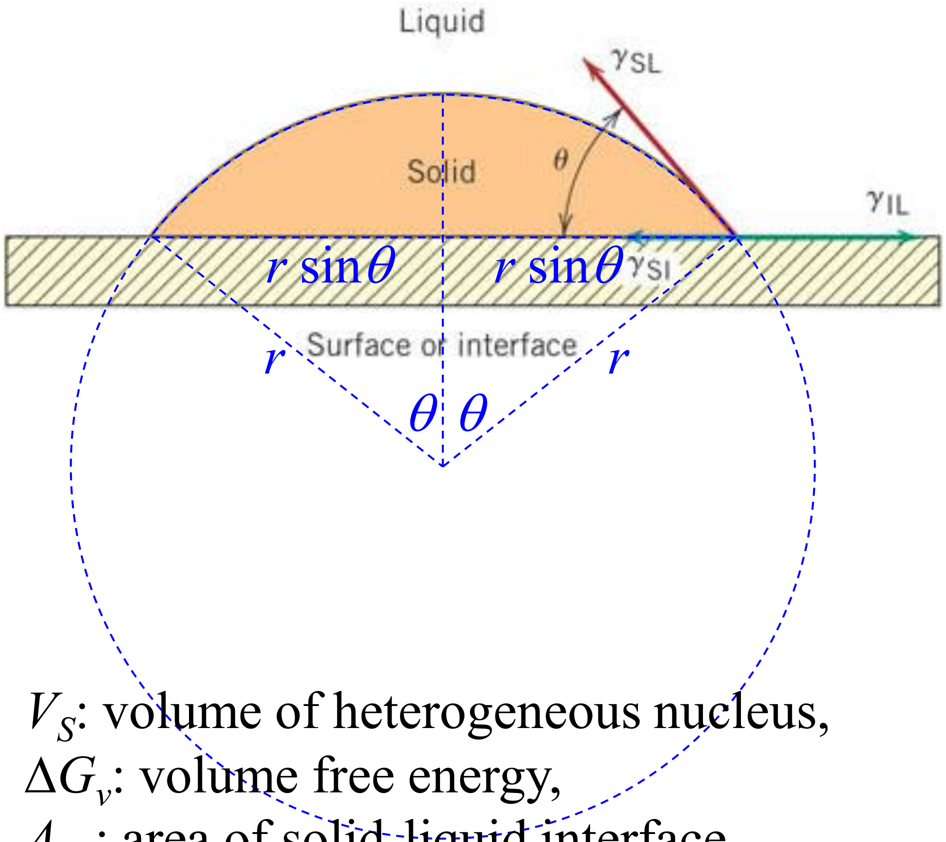


FIGURE 10.5 Heterogeneous nucleation of a solid from a liquid. The solid–surface (γ_{SI}), solid–liquid (γ_{SL}), and liquid–surface (γ_{IL}) interfacial energies are represented by vectors. The wetting angle (θ) is also shown.

Kinetics of Phase Transformations



V_S: volume of heterogeneous nucleus,
ΔG_v: volume free energy,
A_{SL}: area of solid-liquid interface,
A_{SI}: area of solid-surface interface,
γ_{SL}: surface free energy of solid-liquid interface,
γ_{SI}: surface free energy of solid-surface interface,
r: radius of spherical nucleus,
r^*: critical radius of spherical nucleus,
ΔG_{het}^*: critical free energy, activation energy

$$A_{SI} = \pi (r \sin\theta)^2$$

$$A_{SL} = 2\pi r^2 (1-\cos\theta)$$

$$V_S = \frac{\pi r^3}{3}(2 - 3\cos\theta + \cos^3\theta)$$

$$\gamma_{IL} = \gamma_{SI} + \gamma_{SL}\cos\theta$$

$$\Delta G_{het} = V_S \Delta G_v + A_{SL}\gamma_{SL} + A_{SI}\gamma_{SI} - A_{SI}\gamma_{IL}$$

$$\Rightarrow \Delta G_{het} = \Delta G \cdot S(\theta)$$

$$\Delta G = \frac{4\pi r^3}{3}\Delta G_v + 4\pi r^2 \gamma_{SL}$$

$$S(\theta) = \frac{(2+\cos\theta)(1-\cos\theta)^2}{4}$$

$$\Rightarrow r^* = -\frac{2\gamma_{SL}}{\Delta G_v}$$

$$\Rightarrow \Delta G_{het}^* = \frac{16\pi\gamma_{SL}^3}{3(\Delta G_v)^2} \cdot S(\theta)$$

$$\Rightarrow \Delta G_{het}^* = \Delta G_{\mathrm{hom}}^* \cdot S(\theta)$$

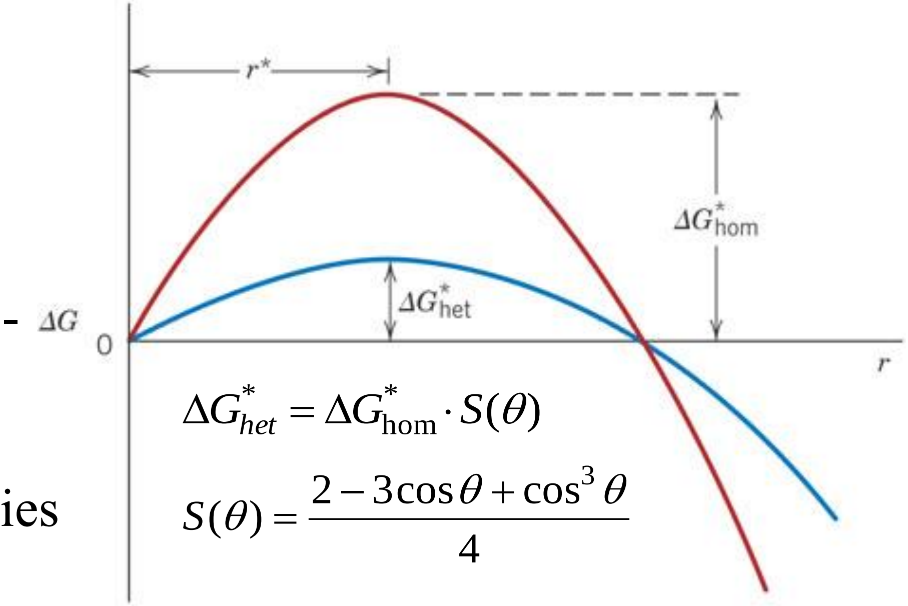
Kinetics of Phase Transformations

The $S(\theta)$ of this last equation is a function only of θ, which will have a numerical value between zero and unity.

- The critical radius r^* for heterogeneous nucleation is the same as for homogeneous, inasmuch as γ_{SL} is the same surface energy as γ in Equation 10.3 ($r^* = -2\gamma / \Delta G_v$).

$$\Delta G^*_{het} = S(\theta) \cdot \Delta G^*_{\mathrm{hom}} \tag{10.15}$$

- In Fig. 10.6, the lower ΔG^* for heterogeneous means that a smaller energy must be overcome during the nucleation process (than for homogeneous).



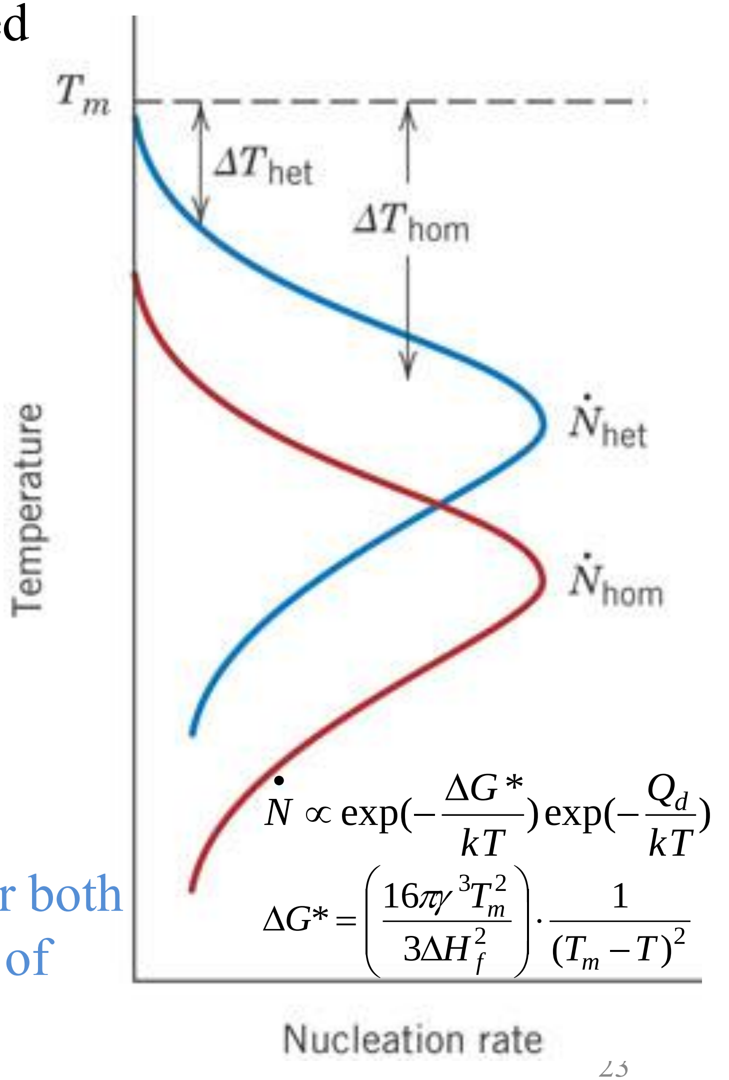
$$\Delta G^*_{het} = \Delta G^*_{\mathrm{hom}} \cdot S(\theta)$$

$$S(\theta) = \frac{2 - 3\cos\theta + \cos^3\theta}{4}$$

FIGURE 10.6 Schematic free energy-versus-embryo/nucleus radius plot on which is presented curves for both homogeneous and heterogeneous nucleation. Critical free energies and the critical radius are also shown.

Kinetics of Phase Transformations

- In terms of the nucleation rate, the $\dot{N}$-versus-T curve is shifted to higher temperatures for heterogeneous. This effect is represented in Fig. 10.7, which also shows that a much smaller degree of supercooling (ΔT) is required for heterogeneous nucleation.



$$\dot{N} \propto \exp\left(-\frac{\Delta G^*}{kT}\right)\exp\left(-\frac{Q_d}{kT}\right)$$

$$\Delta G^* = \left(\frac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\cdot\frac{1}{(T_m - T)^2}$$

FIGURE 10.7 Nucleation rate versus temperature for both homogeneous and heterogeneous nucleation. Degree of supercooling (ΔT) for each is also shown.

Kinetics of Phase Transformations

- **Growth**

  - The growth step in a phase transformation begins once an embryo has exceeded the critical size, r^*, and becomes a stable nucleus.

  - Particle growth occurs by long-range atomic diffusion, which normally involves several steps-for example, diffusion through the parent phase, across a phase boundary, and then into the nucleus. Consequently, the growth rate $\dot{G}$ is determined by the rate of diffusion, and its temperature dependence is the same as for the diffusion coefficient.

$$\dot{G} = C \cdot \exp\left(-\frac{Q}{kT}\right) \qquad (10.16)$$

Q: activation energy, independent of temperature;

C: constant, independent of temperature.

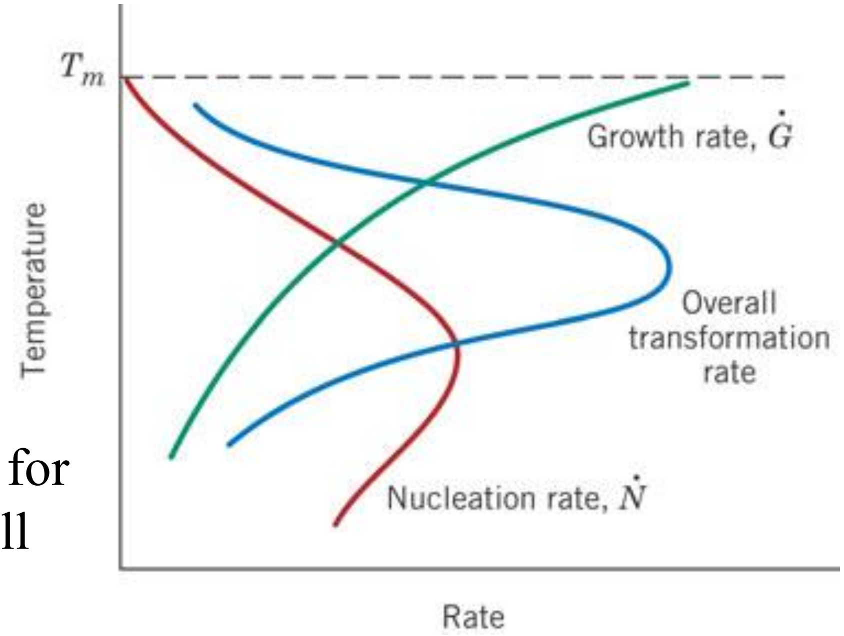
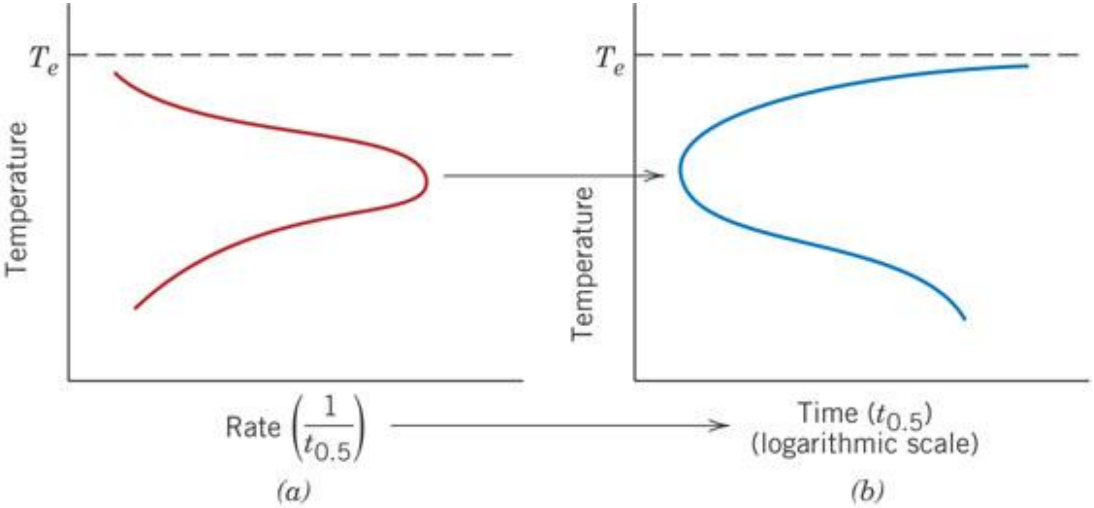


FIGURE 10.8 Schematic plot showing curves for nucleation rate ($\dot{N}$), growth rate ($\dot{G}$), and overall transformation versus temperature.

Kinetics of Phase Transformations

- At a specific temperature, the overall transformation rate is equal to some product of $\dot{N}$ and $\dot{G}$.
- Whereas the treatment on transformations has been developed for solidification, the same general principles also apply to solid-solid and solid-gas transformations.
- The rate of transformation and the time required for the transformation to proceed to some degree of completion are inversely proportional to one another.
- The kinetics of phase transformations are often represented using logarithm time-versus-temperature plots (Fig. 10.9).

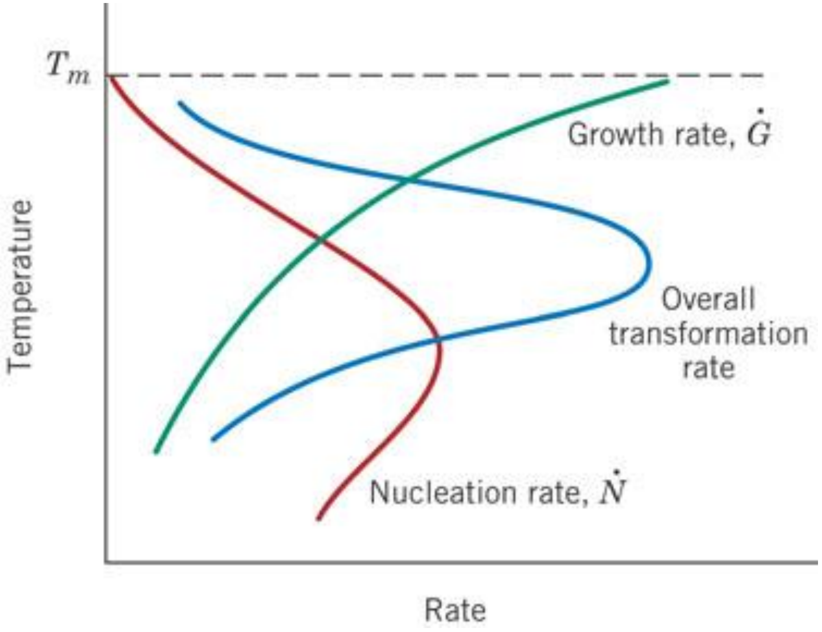
FIGURE 10.9 Schematic plots of (*a*) transformation rate versus temperature, and (*b*) logarithm time versus temperature. The curves in both (*a*) and (*b*) are generated from the same set of data-i.e., for horizontal axes, the time is just the reciprocal of the rate from plot (*a*).



Kinetics of Phase Transformations

- Transformation rate-versus-temperature curve

1. The size of the product phase particles will depend on transformation temperature. For example, for transformations that occur at temperature near T_m, corresponding to low nucleation and high growth rates, few nuclei form that grow rapidly. Thus, the resulting microstructure will consist of few and relatively large phase particles.
2. When a material is cooled very rapidly through the temperature range encompassed by the transformation rate curve to a relatively low temperature where the rate is extremely low, it is possible to produce nonequilibrium phase structures.

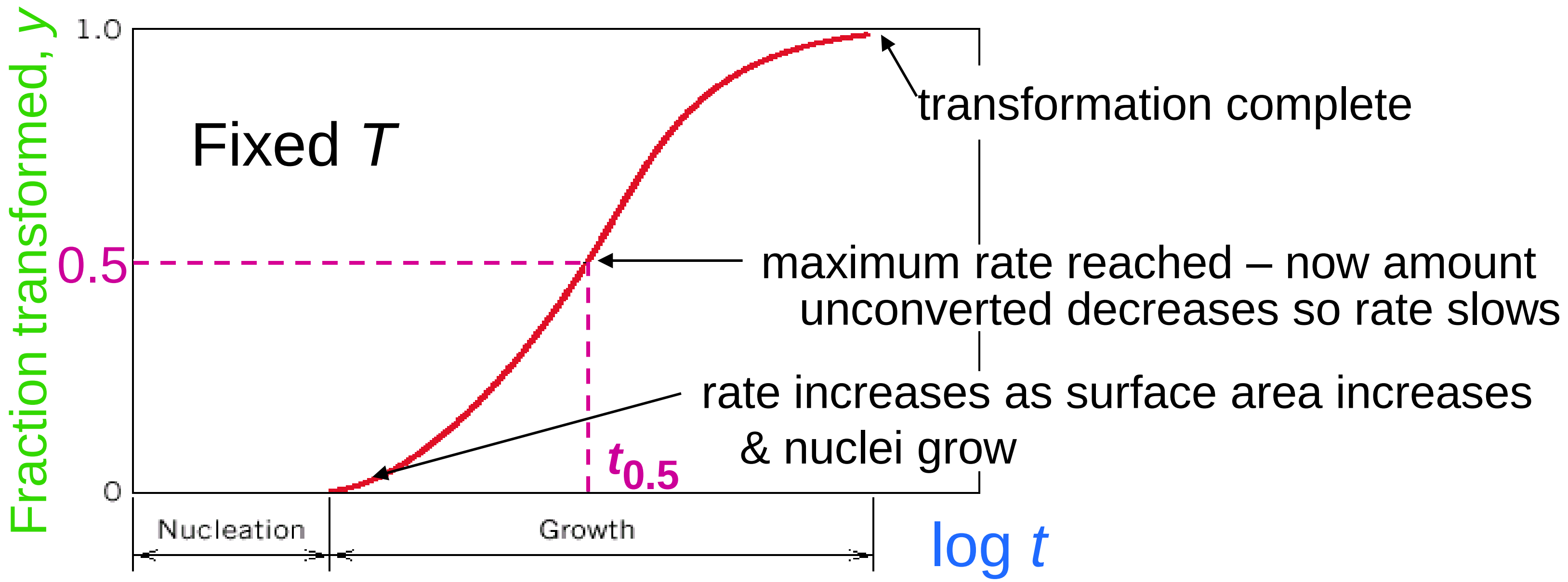


Rate of Phase Transformations

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



transformation complete

maximum rate reached – now amount unconverted decreases so rate slows

rate increases as surface area increases & nuclei grow

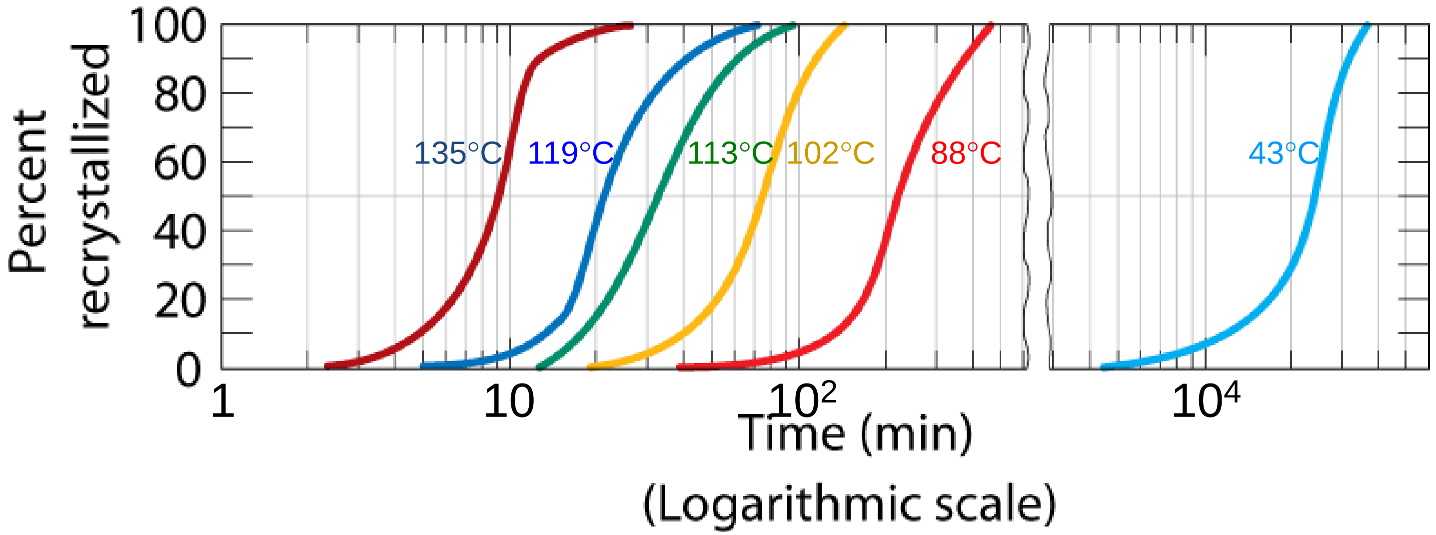
$$\boxed{\text{Avrami equation} \Rightarrow \quad y = 1 - \exp(-kt^{n})}$$

fraction transformed **time**

- k & n are transformation specific parameters

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

Temperature Dependence of Transformation Rate



- 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!

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Transformations & Undercooling

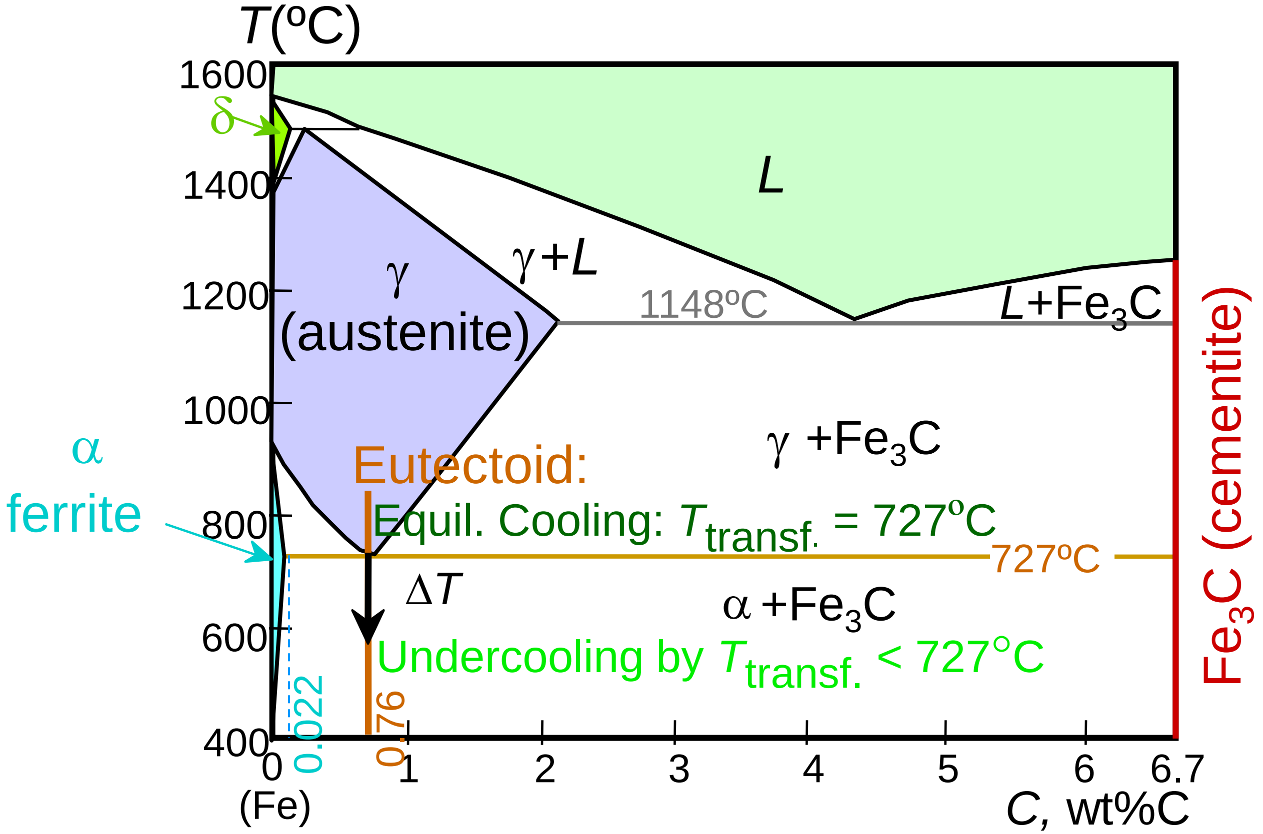
- Eutectoid transf. (Fe-Fe_3C system):
- For transf. to occur, must cool to below 727ºC (i.e., must "undercool")

$\gamma \Rightarrow \alpha + Fe_3C$

0.76 wt% C

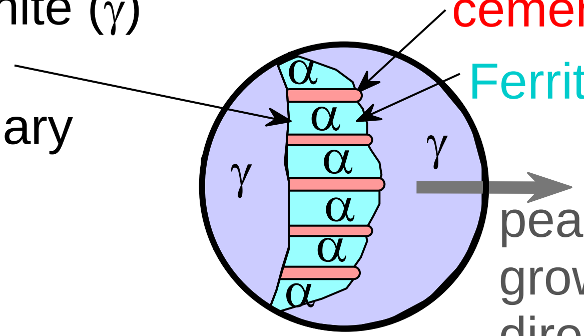
0.022 wt% C

6.7 wt% C



The Fe-Fe_3C Eutectoid Transformation

- Transformation of austenite to pearlite:



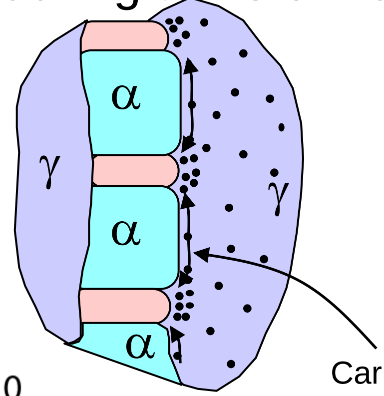
Austenite (γ) grain boundary

cementite (Fe_3C)

Ferrite (α)

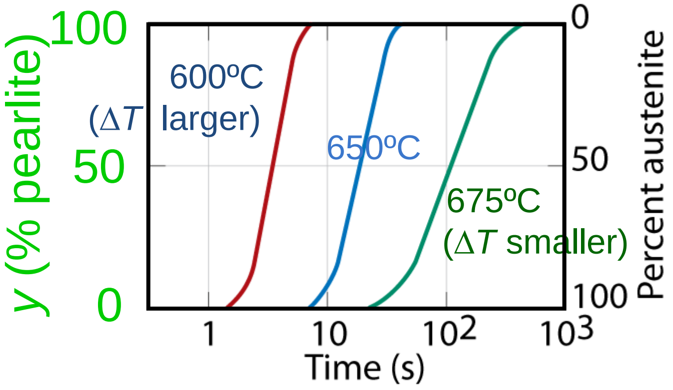
pearlite growth direction

Diffusion of C during transformation



Carbon diffusion

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



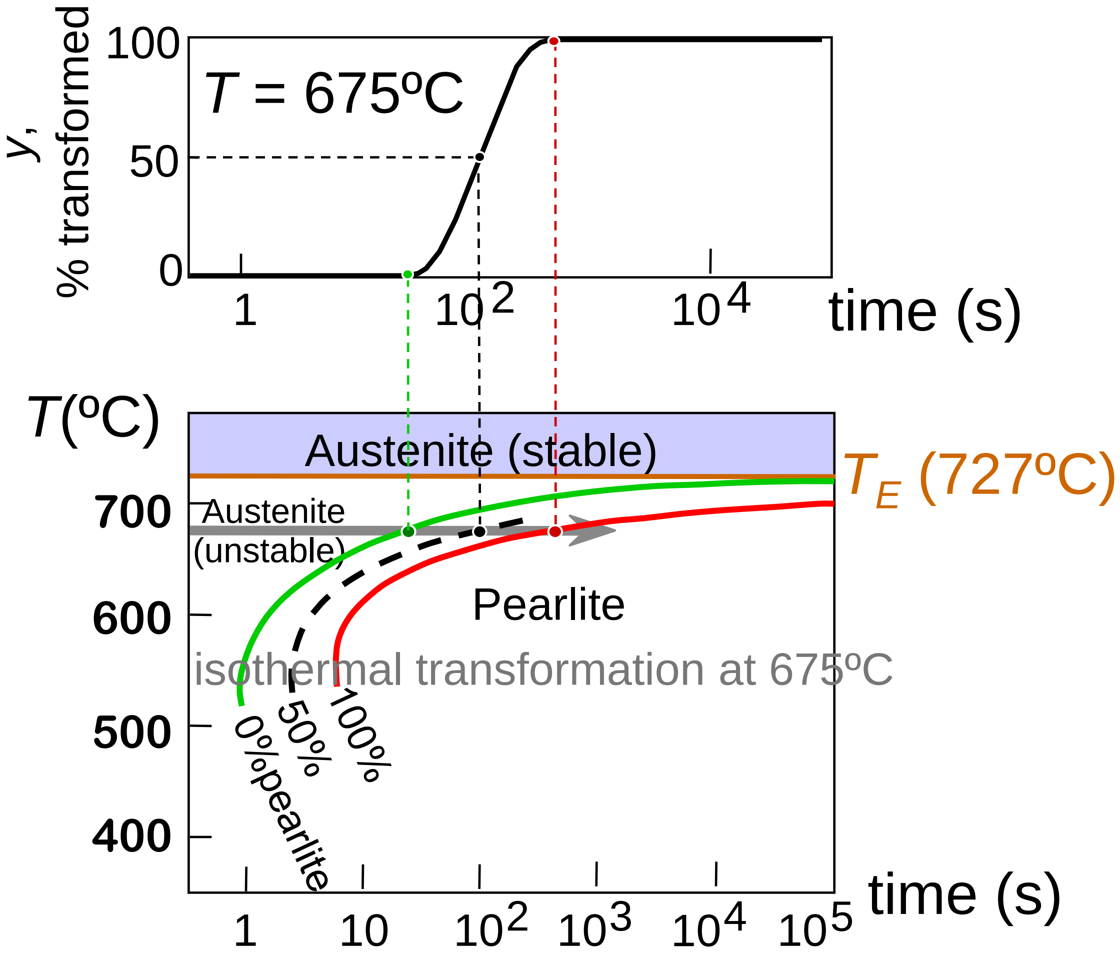
Coarse pearlite → formed at higher temperatures – relatively soft

Fine pearlite → formed at lower temperatures – relatively hard

Generation of Isothermal Transformation Diagrams

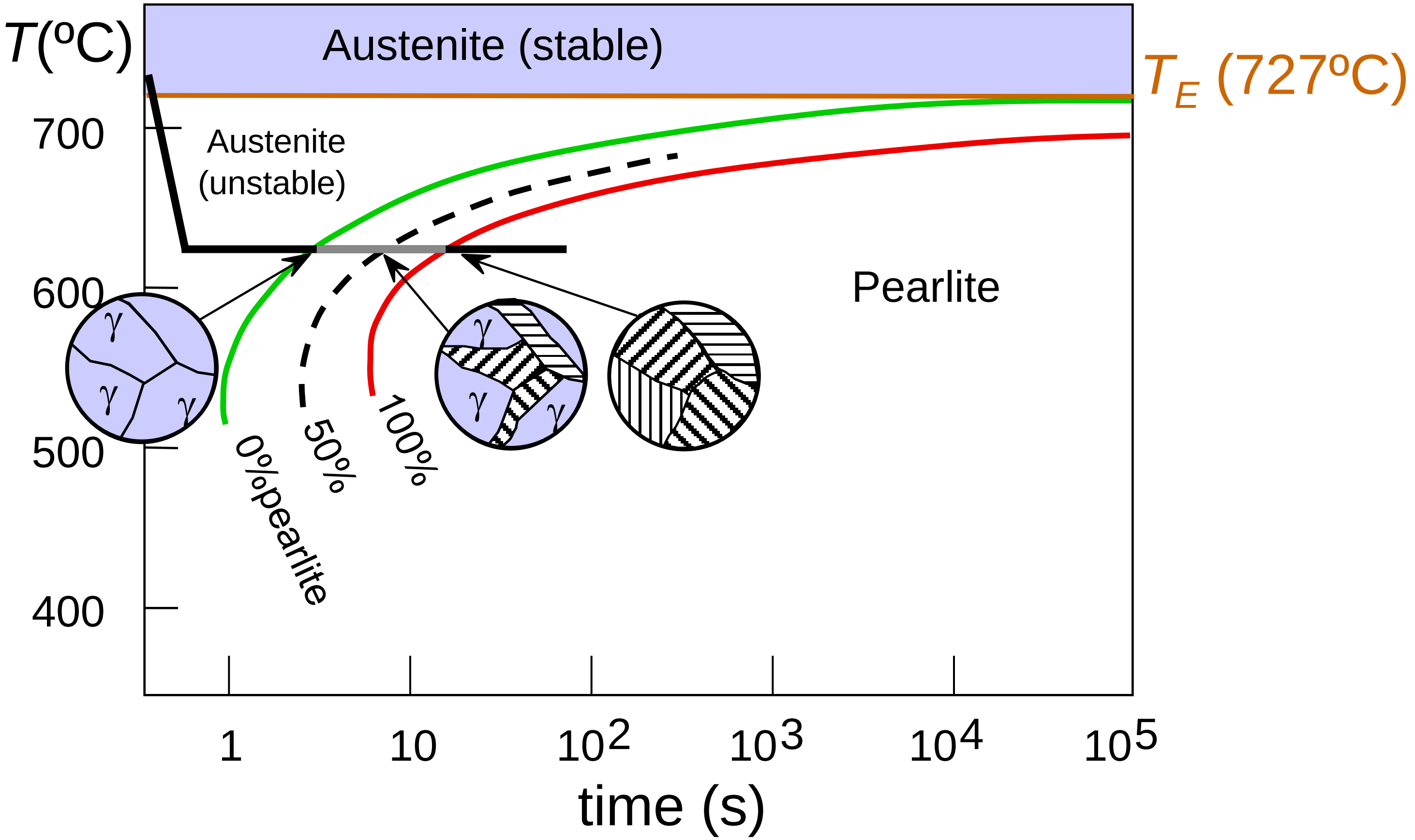
Consider:

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



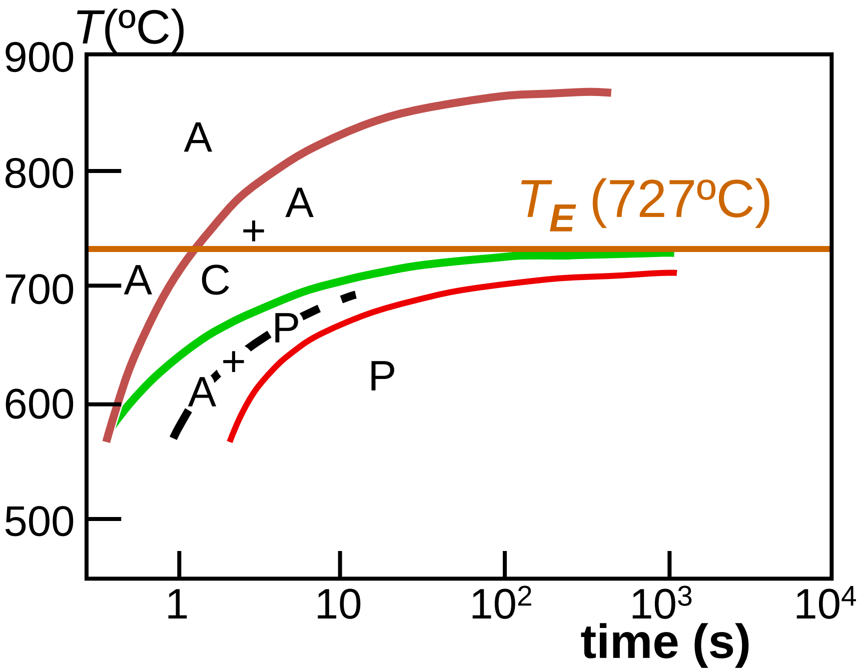
Austenite-to-Pearlite Isothermal Transformation

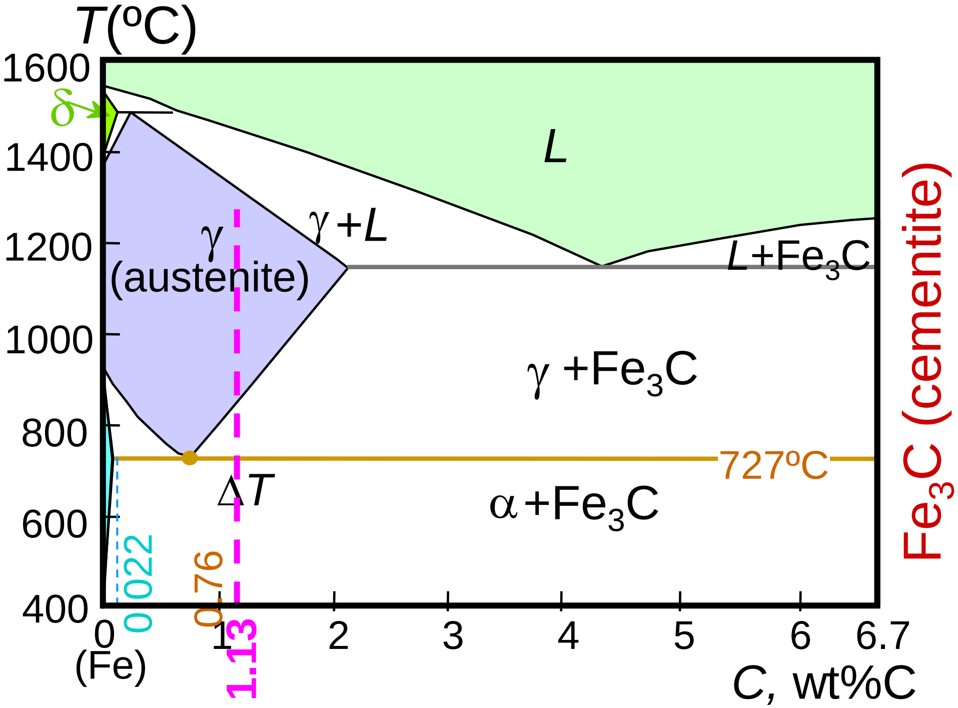
- Eutectoid composition, C_0 = 0.76 wt% C
- Begin at T > 727ºC
- Rapidly cool to 625ºC
- Hold T (625ºC) constant (isothermal treatment)



Transformations Involving Noneutectoid Compositions

Consider C_0 = 1.13 wt% C

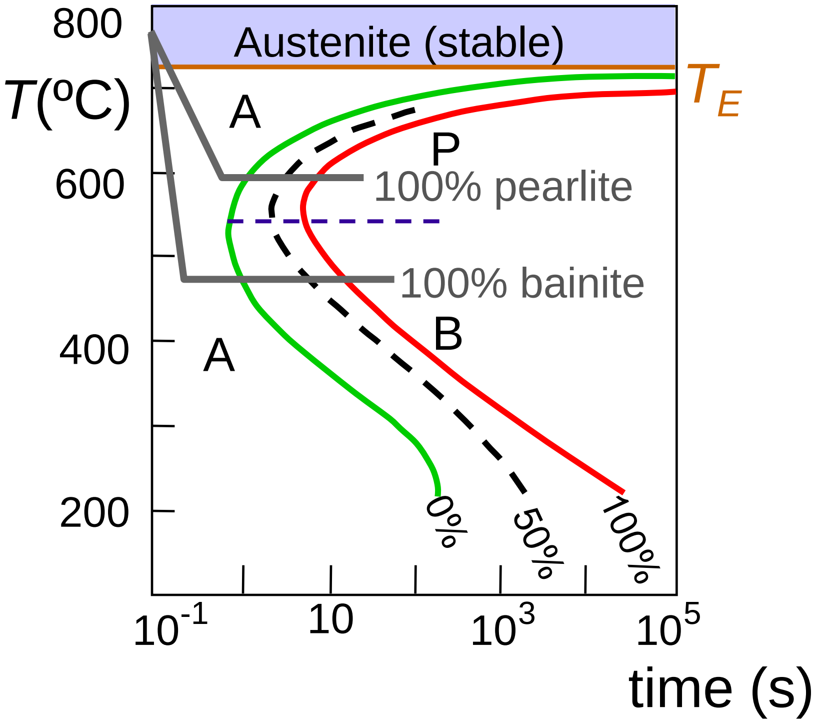


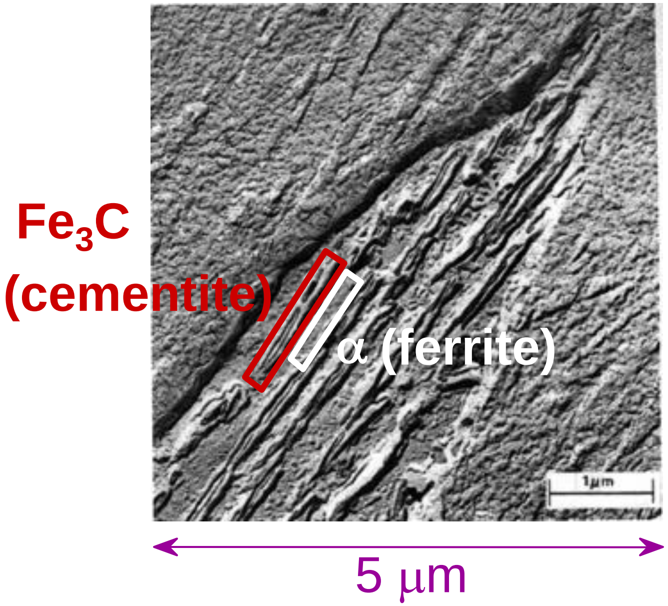


Hypereutectoid composition – proeutectoid cementite

Bainite: Another Fe-Fe_3C Transformation Product

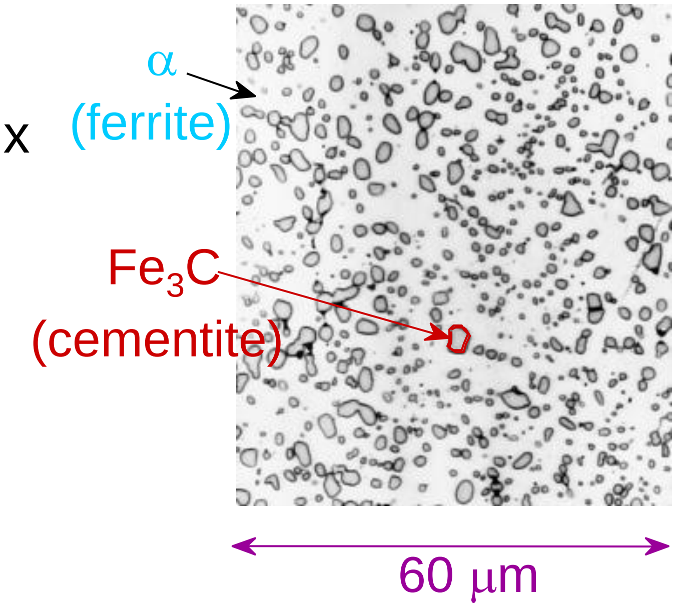
- Bainite:
  -- elongated Fe_3C particles in α-ferrite matrix
  -- diffusion controlled
- Isothermal Transf. Diagram, C_0 = 0.76 wt% C





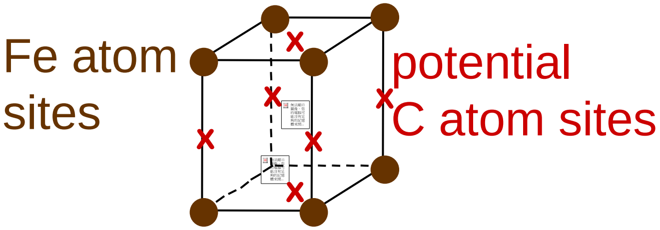
Spheroidite: Another Microstructure for the Fe-Fe_3C System

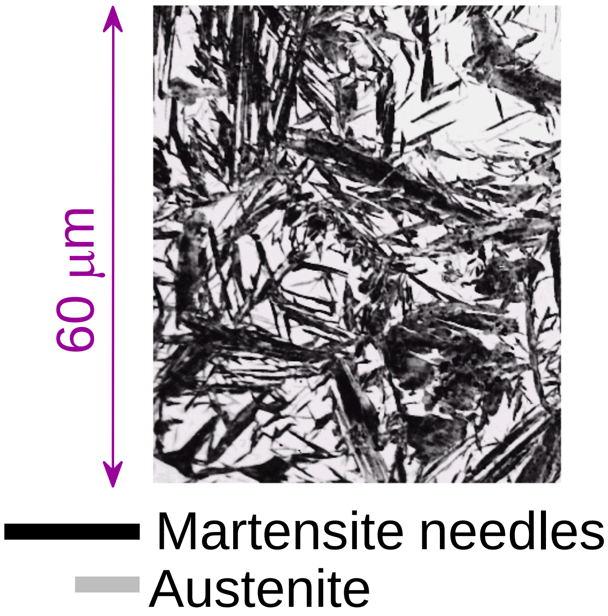
- Spheroidite:
  -- Fe_3C particles within an α-ferrite matrix
  -- formation requires diffusion
  -- heat bainite or pearlite at temperature just below eutectoid for long times
  -- driving force – reduction of α-ferrite/Fe_3C interfacial area



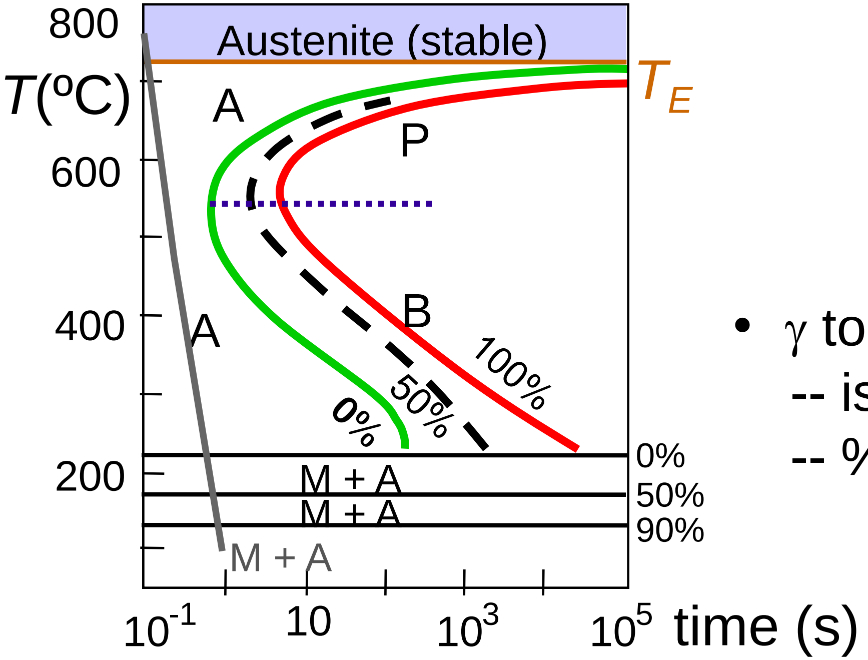
Martensite: A Nonequilibrium Transformation Product

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





- Isothermal Transf. Diagram



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

Martensite Formation

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

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

4340 Alloy Steel

Effect of adding other elements

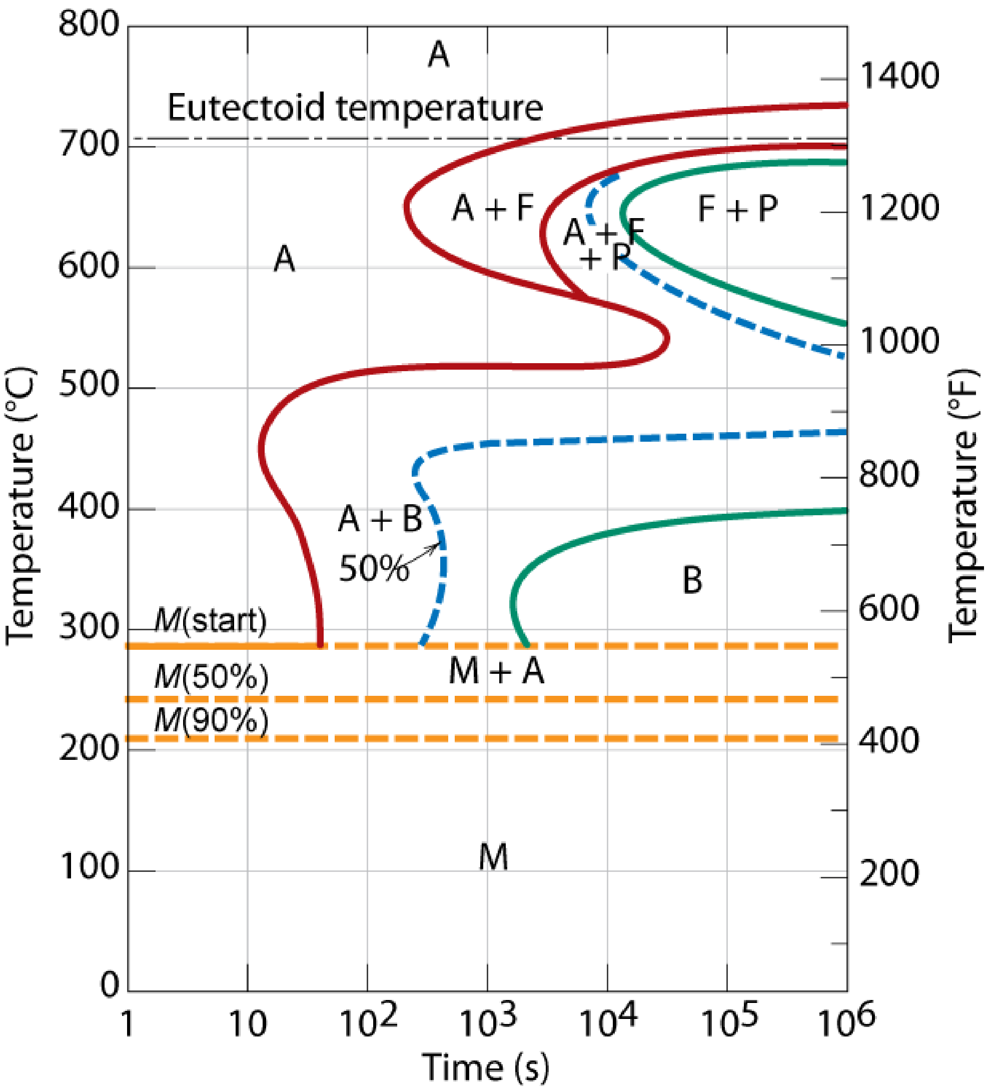
Change transition temp.

Cr, Ni, Mo, Si, Mn

retard $\gamma \rightarrow \alpha + Fe_3C$

reaction (and formation of

pearlite, bainite)



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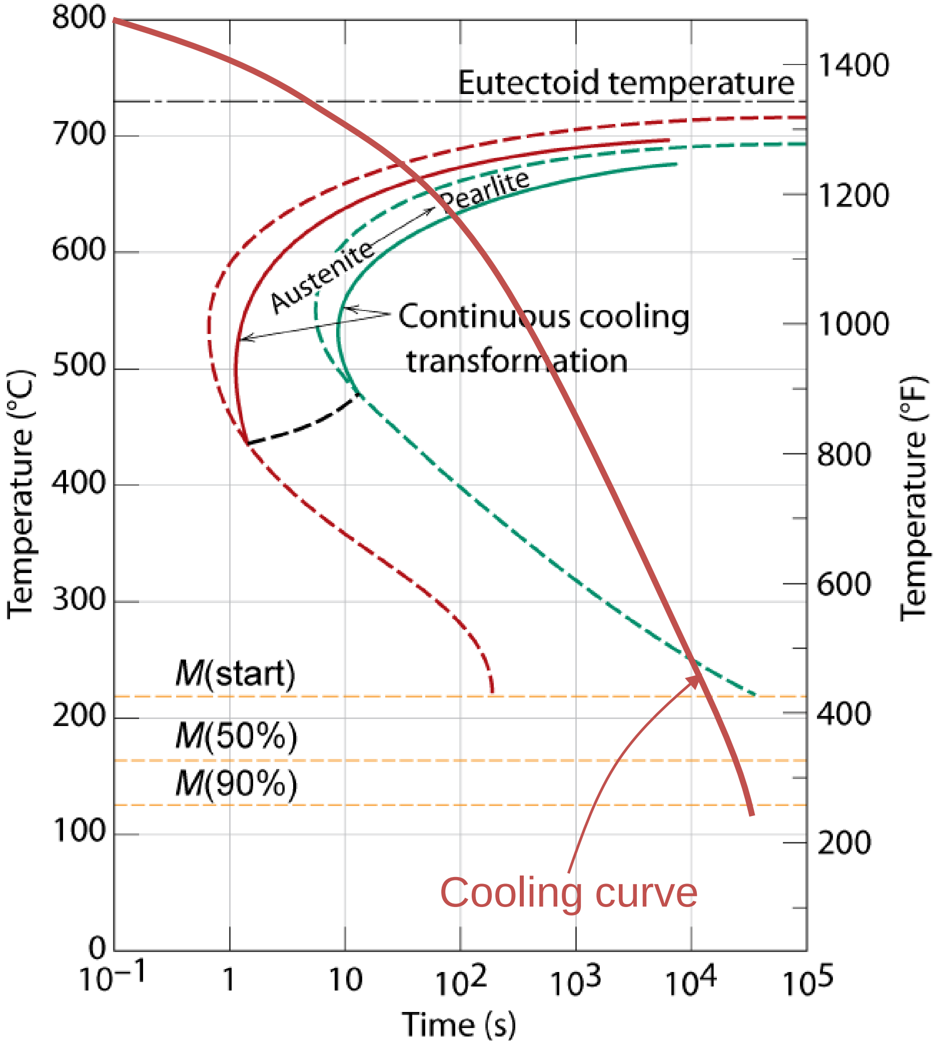
Continuous Cooling Transformation Diagrams

Conversion of isothermal transformation diagram to continuous cooling transformation diagram



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

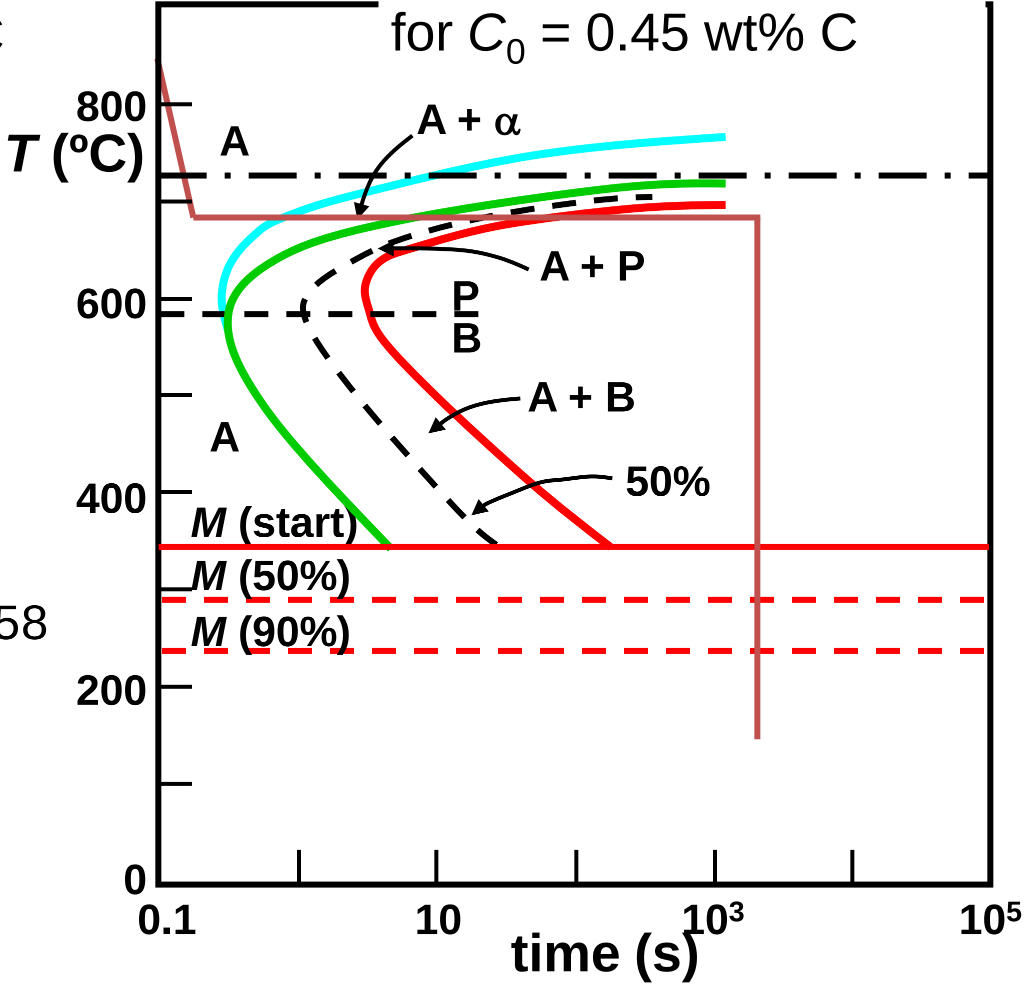
Isothermally treat at ~ 680ºC

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

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

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

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



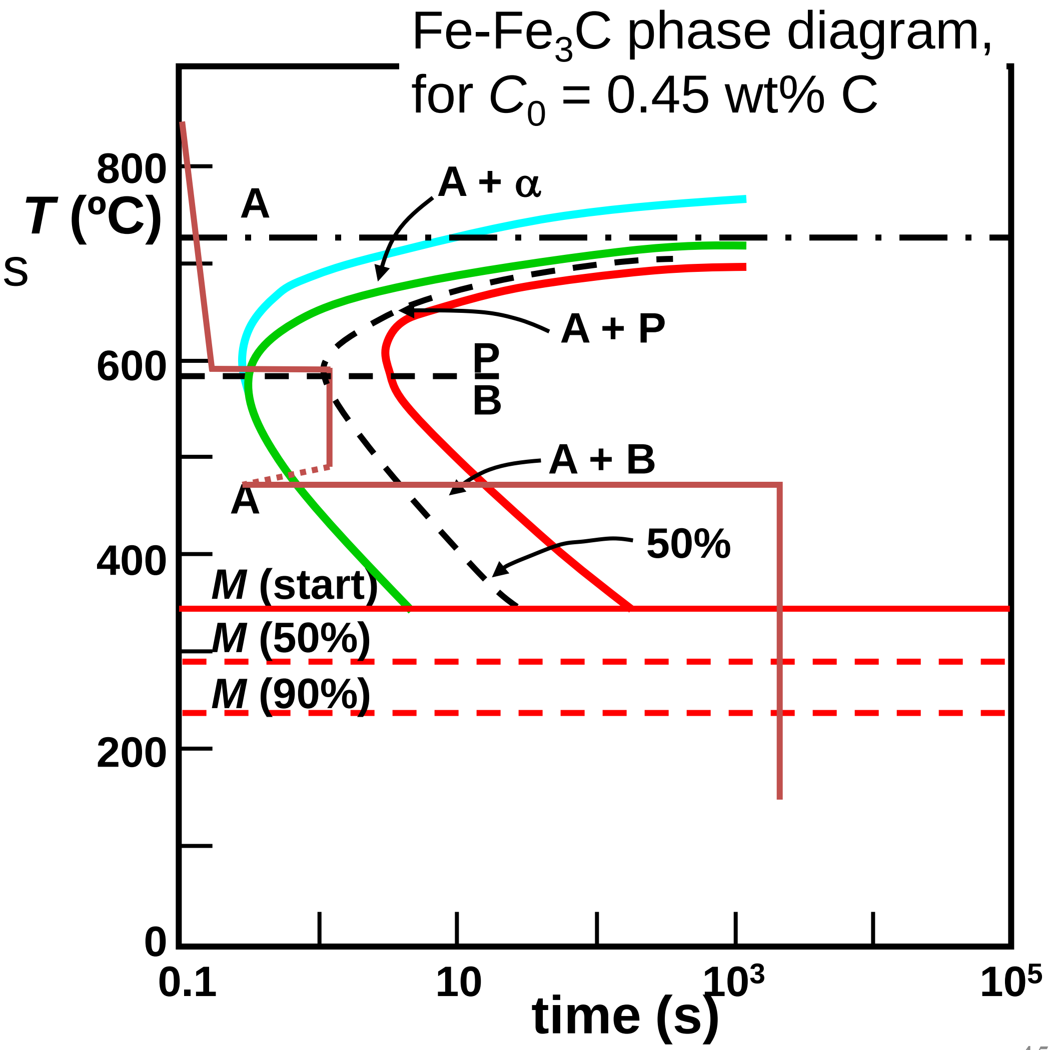
Fe-Fe$_3$C phase diagram, for C_0 = 0.45 wt% C

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.



Fe-Fe_3C phase diagram, for C_0 = 0.45 wt% C

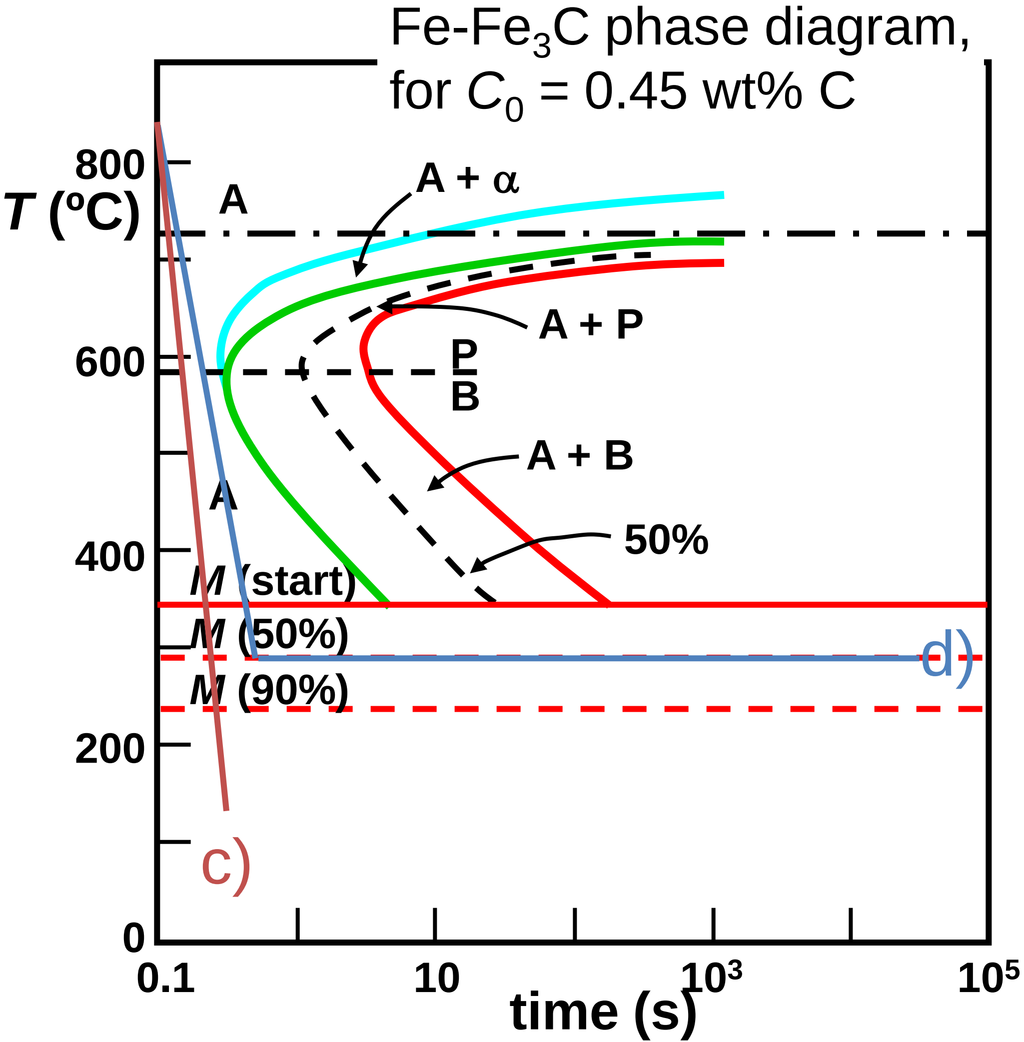
Solutions to Parts (c) & (d) of Example Problem

c) 100% martensite – rapidly quench to room temperature

d) 50% martensite

& 50% austenite

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



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

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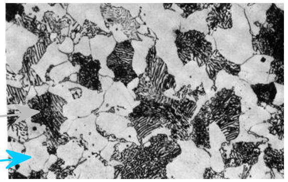
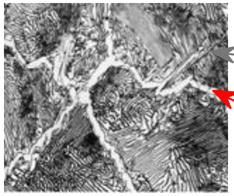
Mechanical Props: Influence of C Content

Pearlite (med)
ferrite (soft)



$C_0 < 0.76$ wt% C

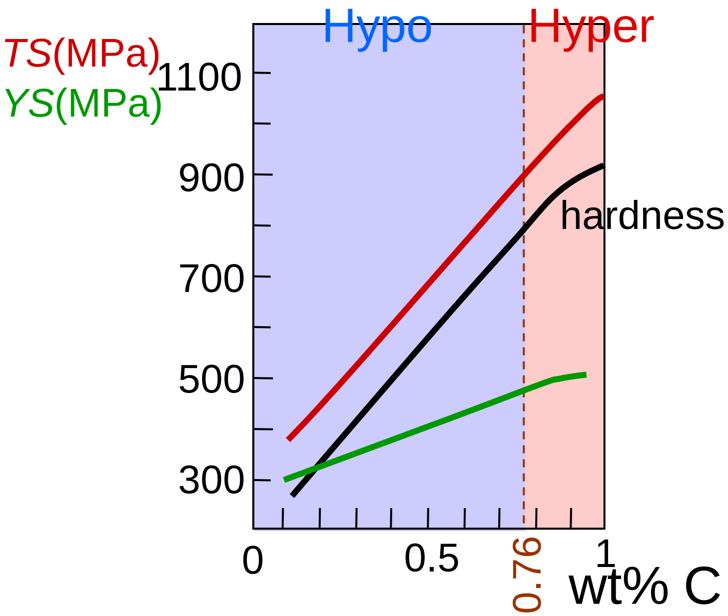
Hypoeutectoid

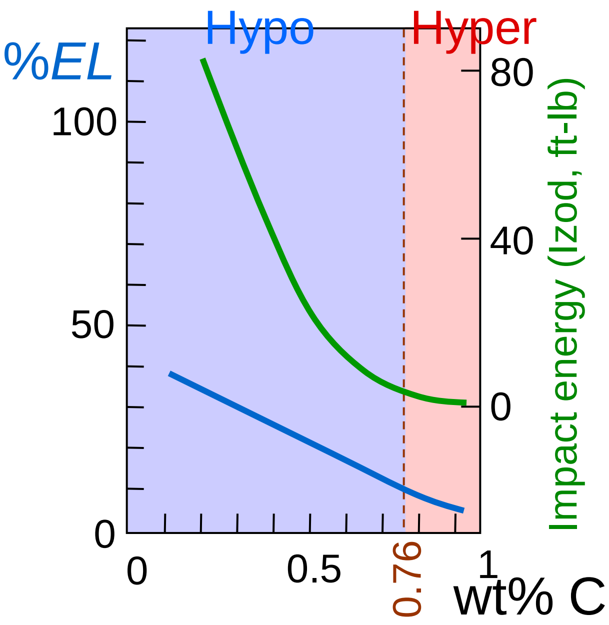


Pearlite (med)
Cementite (hard)

$C_0 > 0.76$ wt% C

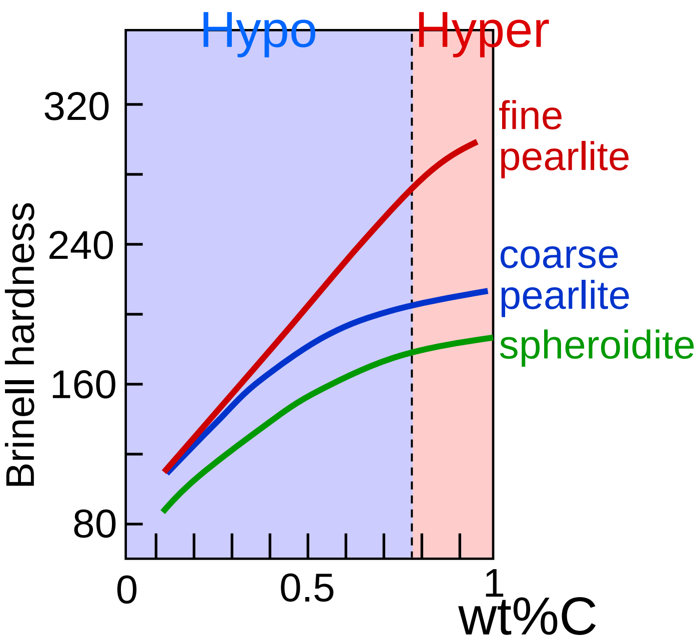
Hypereutectoid

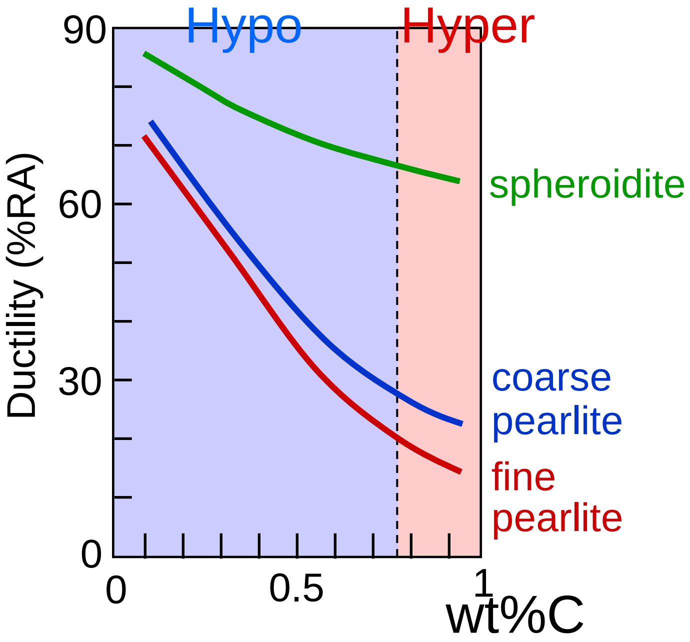




- Increase C content: *TS* and *YS* increase, %*EL* decreases

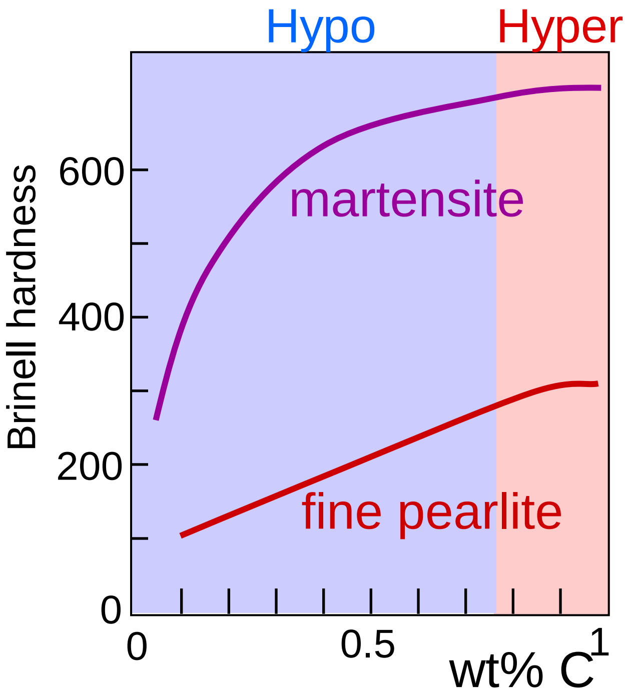
Mechanical Props: Fine Pearlite vs. Coarse Pearlite vs. Spheroidite





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

Mechanical Props: Fine Pearlite vs. Martensite



- Hardness: fine pearlite << martensite.

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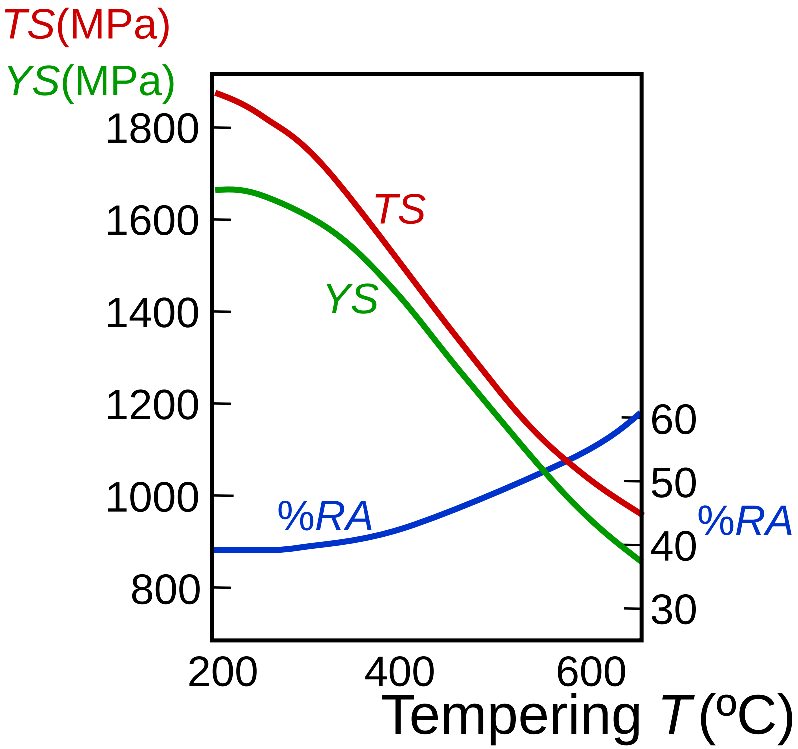
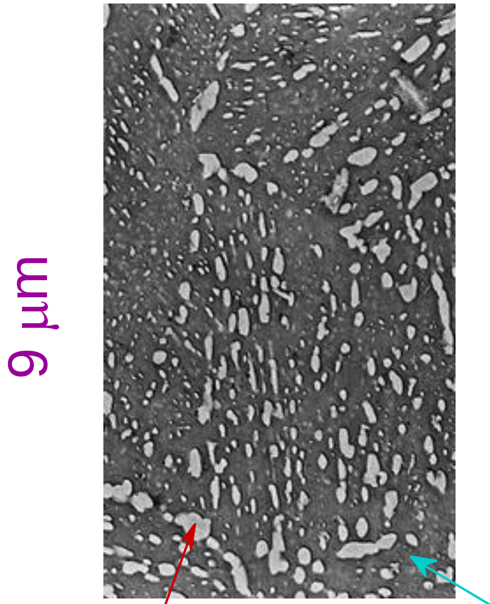
Tempered Martensite

Heat treat martensite to form tempered martensite

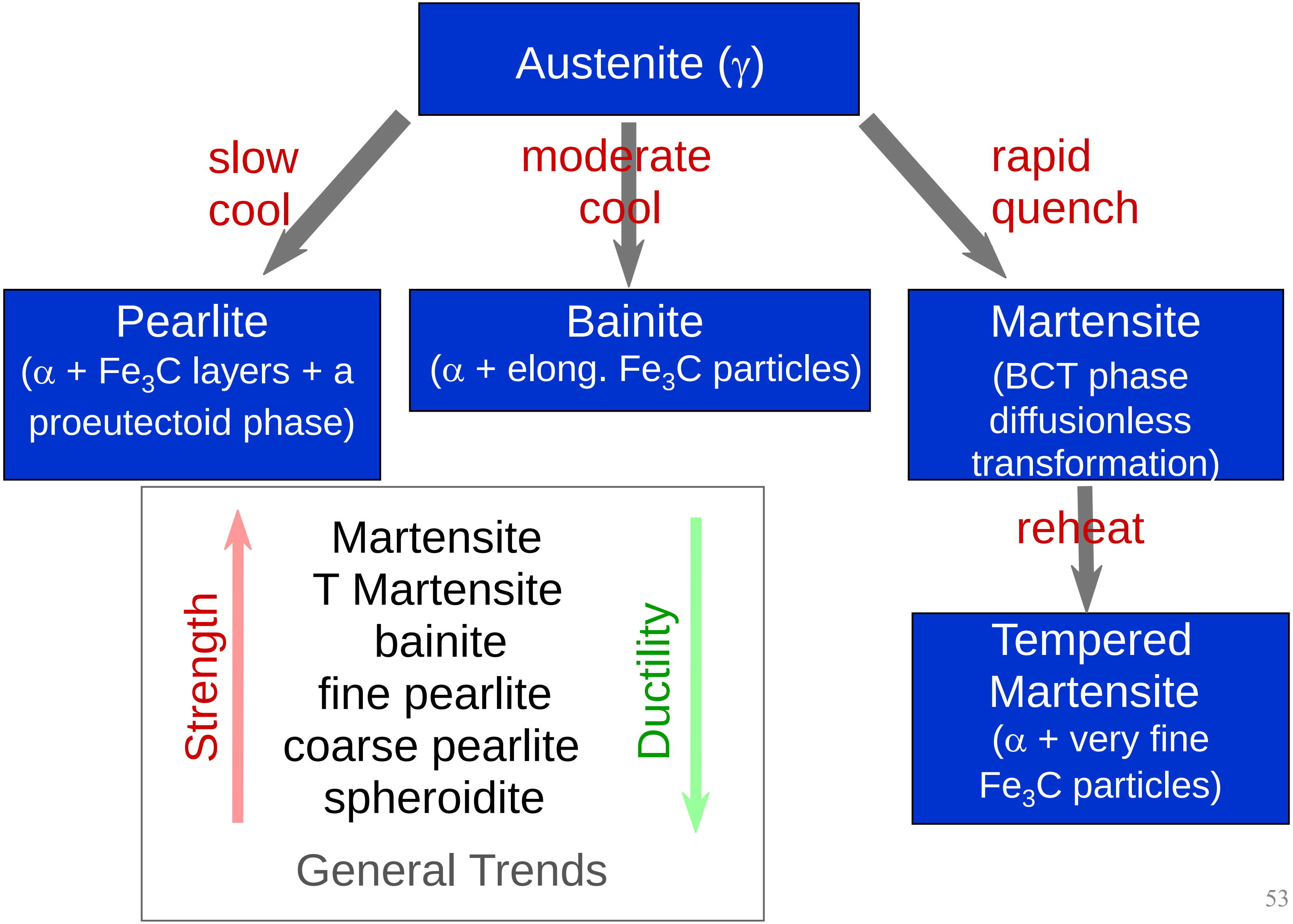
- tempered martensite less brittle than martensite
- tempering reduces internal stresses caused by quenching





- tempering produces extremely small Fe$_3$C particles surrounded by α.
- tempering decreases *TS*, *YS* but increases %RA

Summary of Possible Transformations



Austenite (γ)

slow cool

moderate cool

rapid quench

Pearlite
(α + Fe_3C layers + a proeutectoid phase)

Bainite
(α + elong. Fe_3C particles)

Martensite
(BCT phase diffusionless transformation)

reheat

Tempered Martensite
(α + very fine Fe_3C particles)

Strength

Martensite
T Martensite
bainite
fine pearlite
coarse pearlite
spheroidite

Ductility

General Trends

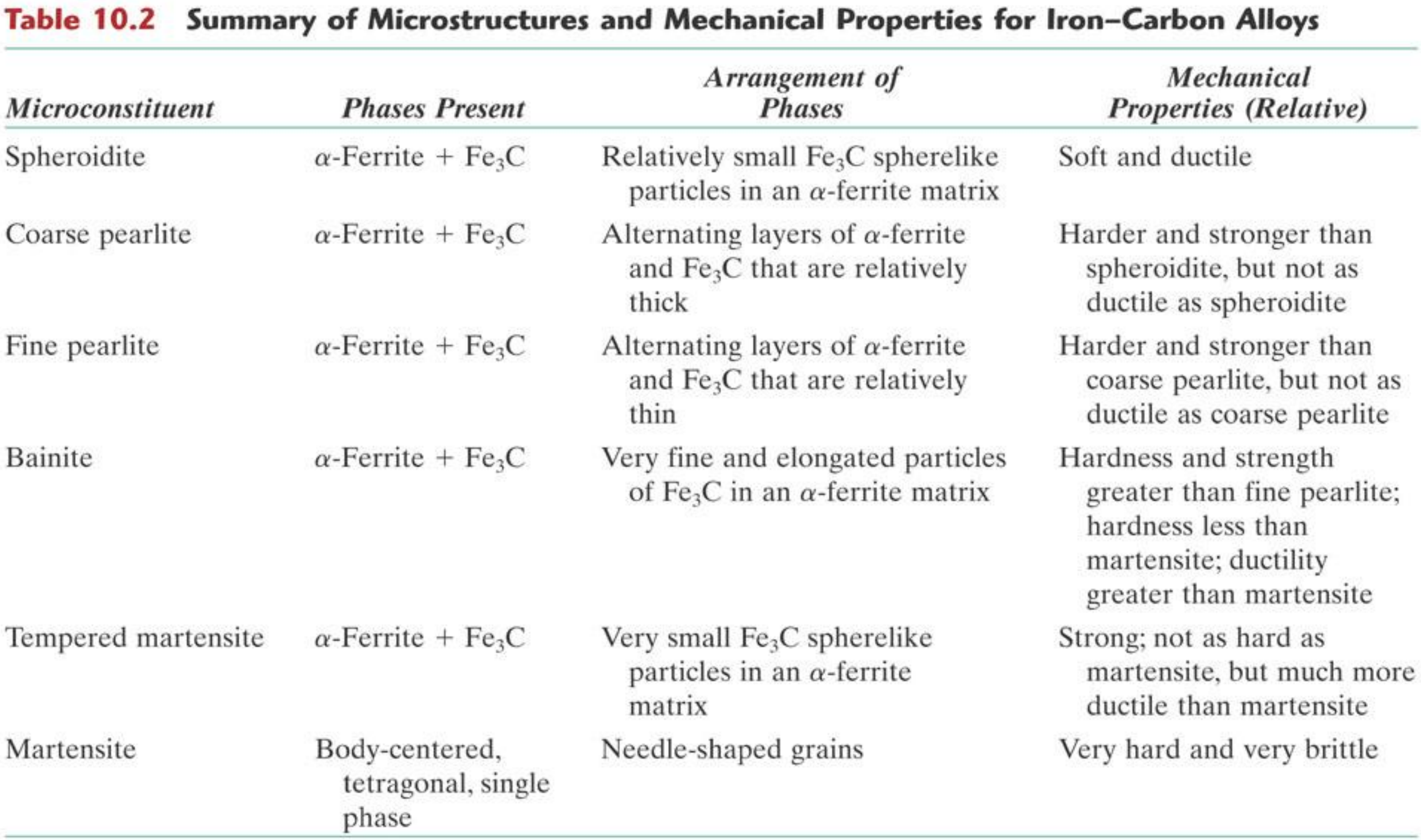
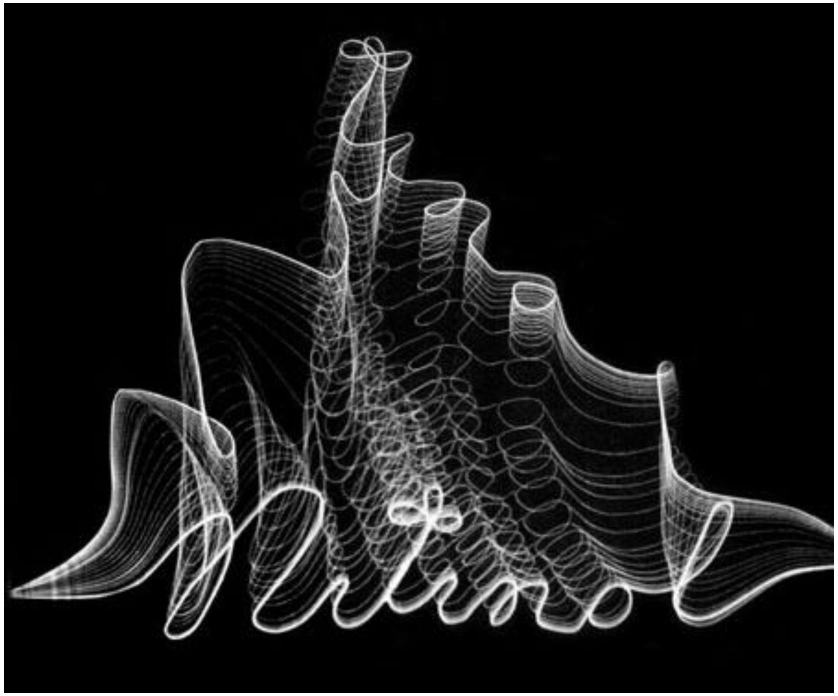


Table 10.2 Summary of Microstructures and Mechanical Properties for Iron–Carbon Alloys

Microconstituent	*Phases Present*	*Arrangement of Phases*	*Mechanical Properties (Relative)*
Spheroidite	α-Ferrite + Fe_3C	Relatively small Fe_3C spherelike particles in an α-ferrite matrix	Soft and ductile
Coarse pearlite	α-Ferrite + Fe_3C	Alternating layers of α-ferrite and Fe_3C that are relatively thick	Harder and stronger than spheroidite, but not as ductile as spheroidite
Fine pearlite	α-Ferrite + Fe_3C	Alternating layers of α-ferrite and Fe_3C that are relatively thin	Harder and stronger than coarse pearlite, but not as ductile as coarse pearlite
Bainite	α-Ferrite + Fe_3C	Very fine and elongated particles of Fe_3C in an α-ferrite matrix	Hardness and strength greater than fine pearlite; hardness less than martensite; ductility greater than martensite
Tempered martensite	α-Ferrite + Fe_3C	Very small Fe_3C spherelike particles in an α-ferrite matrix	Strong; not as hard as martensite, but much more ductile than martensite
Martensite	Body-centered, tetragonal, single phase	Needle-shaped grains	Very hard and very brittle

Shape-Memory Alloys

- **Shape-memory alloys** (形狀記憶合金)
  - One of the shape-memory alloys (SMAs), after being deformed, has the ability to return to its predeformed size and shape upon being subjected to an appropriate heat treatment-that is, the material "remembers" its previous size/shape.
  - Deformation normally is carried out at a relatively low temperature, whereas shape memory occurs upon heating.
  - A shape-memory alloy is polymorphic-that is, it may have two crystal structures (or phases), and the shape-memory effect involves phase transformations between them.



Time-lapse photograph that demonstrates the shape-memory effect. A wire of a shape-memory alloy (Nitinol) has been bent and treated such that its memory shape spells the word Nitinol. The wire is then deformed and, upon heating, springs back to its predeformed shape; this shape recovery process is recorded on the photograph.

Shape-Memory Alloys

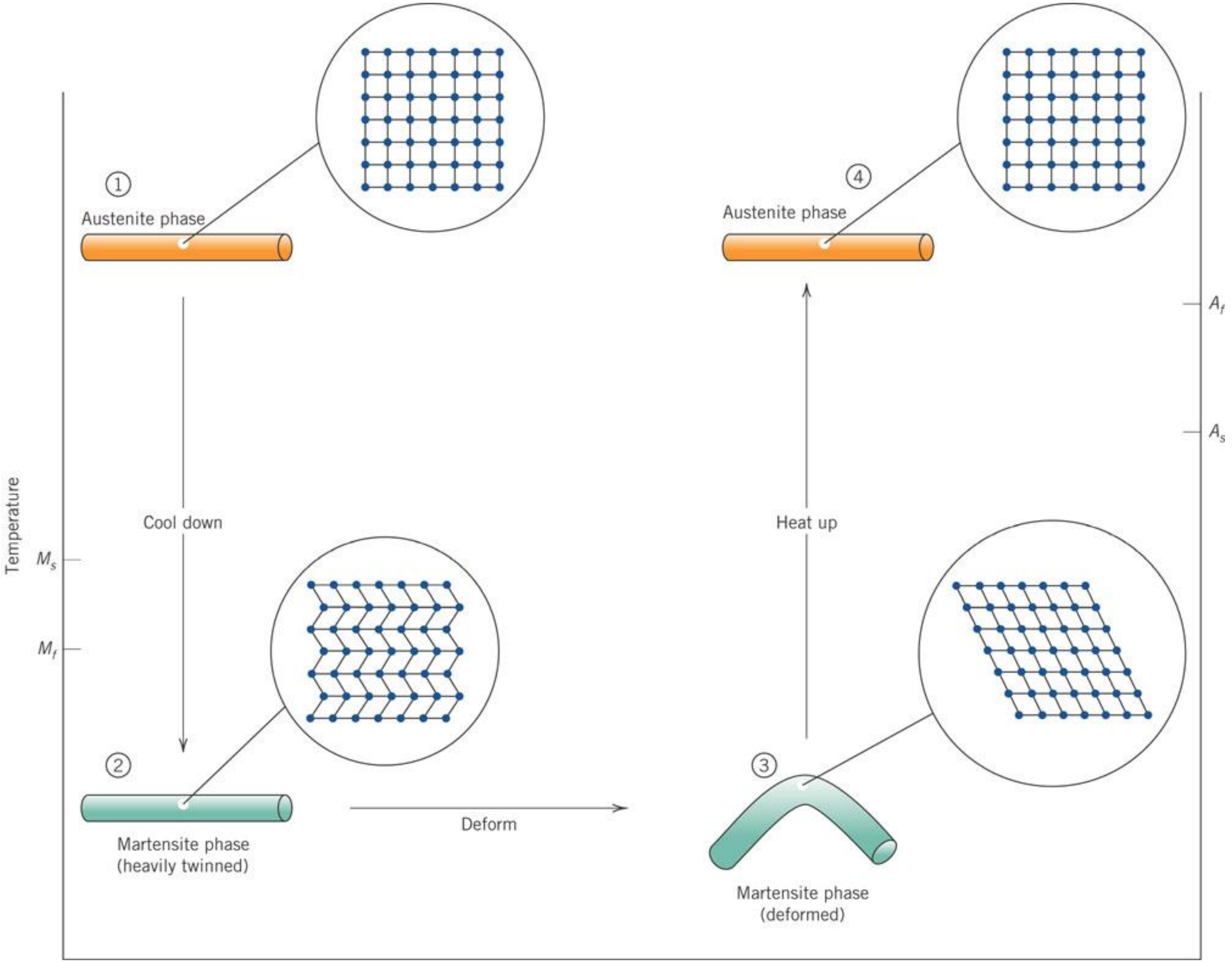


Fig. 10.37 Diagram illustrating the shape-memory effect. This insets are schematic representations of the crystal structure at the four stages. M_s and M_f denote temperatures at which the martensitic transformation begins and ends. Likewise for the austenite transformation, A_s and A_f represent beginning and end transformation temperatures.

Equation Summary

Equation Number	*Equation*	*Solving For*	*Page Number*
10.3	$r^* = -\dfrac{2\gamma}{\Delta G_v}$	Critical radius for stable solid particle (homogeneous nucleation)	346
10.4	$\Delta G^* = \dfrac{16\pi\gamma^3}{3(\Delta G_v)^2}$	Activation free energy for formation of stable solid particle (homogeneous nucleation)	346
10.6	$r^* = \left(-\dfrac{2\gamma T_m}{\Delta H_f}\right)\left(\dfrac{1}{T_m - T}\right)$	Critical radius—in terms of latent heat of fusion and melting temperature	347
10.7	$\Delta G^* = \left(\dfrac{16\pi\gamma^3 T_m^2}{3\Delta H_f^2}\right)\dfrac{1}{(T_m - T)^2}$	Activation free energy—in terms of latent heat of fusion and melting temperature	347
10.12	$\gamma_{\mathrm{IL}} = \gamma_{\mathrm{SI}} + \gamma_{\mathrm{SL}}\cos\theta$	Relationship among interfacial energies for heterogeneous nucleation	351
10.13	$r^* = -\dfrac{2\gamma_{\mathrm{SL}}}{\Delta G_v}$	Critical radius for stable solid particle (heterogeneous nucleation)	351
10.14	$\Delta G^* = \left(\dfrac{16\pi\gamma_{\mathrm{SL}}^3}{3\Delta G_v^2}\right)S(\theta)$	Activation free energy for formation of stable solid particle (heterogeneous nucleation)	351
10.17	$y = 1 - \exp(-kt^n)$	Fraction of transformation (Avrami equation)	355
10.18	$\text{rate} = \dfrac{1}{t_{0.5}}$	Transformation rate	355