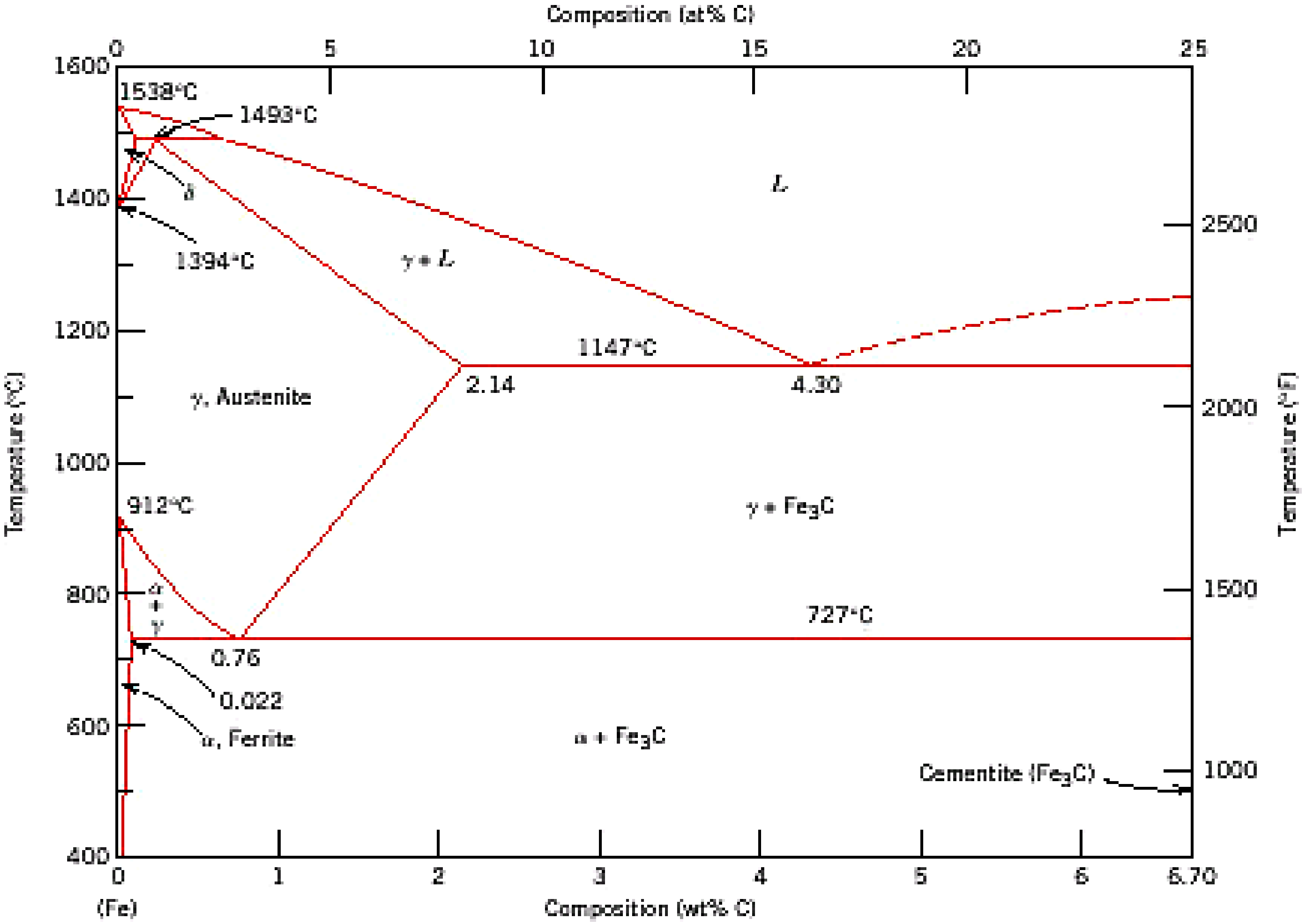
The Iron - Iron Carbide (Fe-Fe_3C) Phase Diagram



Reactions

Peritectic $L + \delta = \gamma$
at T=1493°C and 0.18wt%C

Eutectic $L = \gamma + Fe_3C$
at T=1147°C and 4.3wt%C

Eutectoid $\gamma = \alpha + Fe_3C$
at T=727°C and 0.77wt%C

Max. solubility of C
in ferrite=0.022%
in austenite=2.11%

Phases Present

L

δ ferrite delta
Bcc structure
Paramagnetic

γ austenite
Fcc structure
Non-magnetic
ductile

α ferrite
Bcc structure
Ferromagnetic
Fairly ductile

Fe_3C cementite
Orthorhombic
Hard, brittle

Phases in Fe–Fe_3C Phase Diagram

- **α-ferrite - solid solution of C in BCC Fe**
  - Stable form of iron at room temperature.
  - Transforms to FCC g-austenite at 912 °C
- **γ-austenite - solid solution of C in FCC Fe**
  - Transforms to BCC δ-ferrite at 1395 °C
  - Is not stable below the eutectic temperature (727 ° C) unless cooled rapidly.
- **δ-ferrite solid solution of C in BCC Fe**
  - It is stable only at T, >1394 °C. It melts at 1538 °C
- **Fe_3C (iron carbide or cementite)**
  - This intermetallic compound is metastable at room T. It decomposes (very slowly, within several years) into α-Fe and C (graphite) at 650 - 700 °C
- **Fe-C liquid solution**

Comments on Fe–Fe_3C system

C is an interstitial impurity in Fe. It forms a solid solution with α, γ, δ phases of iron

Maximum solubility in BCC α-ferrite is 0.022 wt% at 727 °C. BCC: relatively small interstitial positions

Maximum solubility in FCC austenite is 2.14 wt% at 1147 °C - FCC has larger interstitial positions

Mechanical properties: Cementite (Fe_3C is hard and brittle: strengthens steels). Mechanical properties also depend on microstructure: how ferrite and cementite are mixed.

Magnetic properties: α -ferrite is magnetic below 768 °C, austenite is non-magnetic

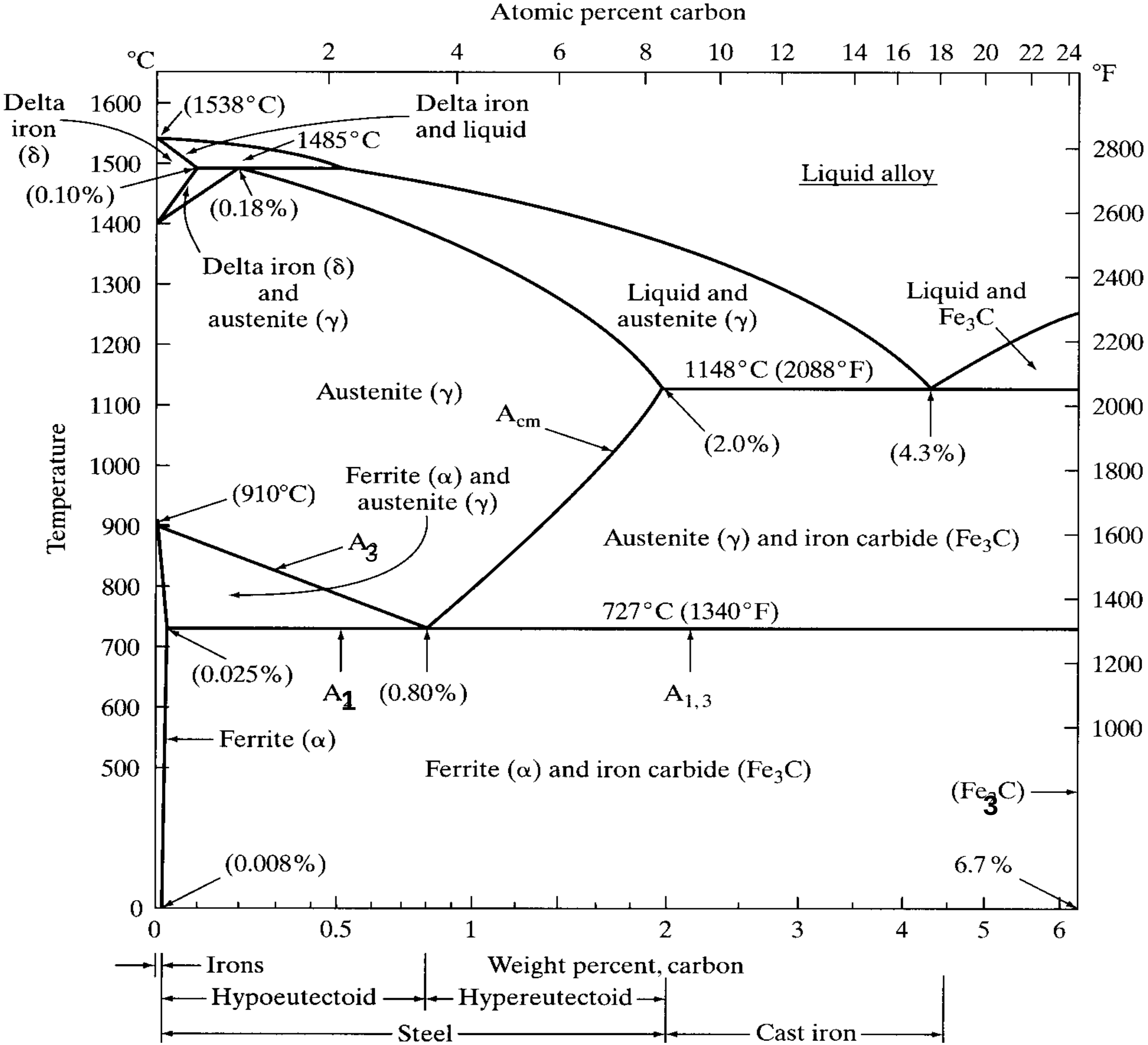
Classification.

Three types of ferrous alloys:

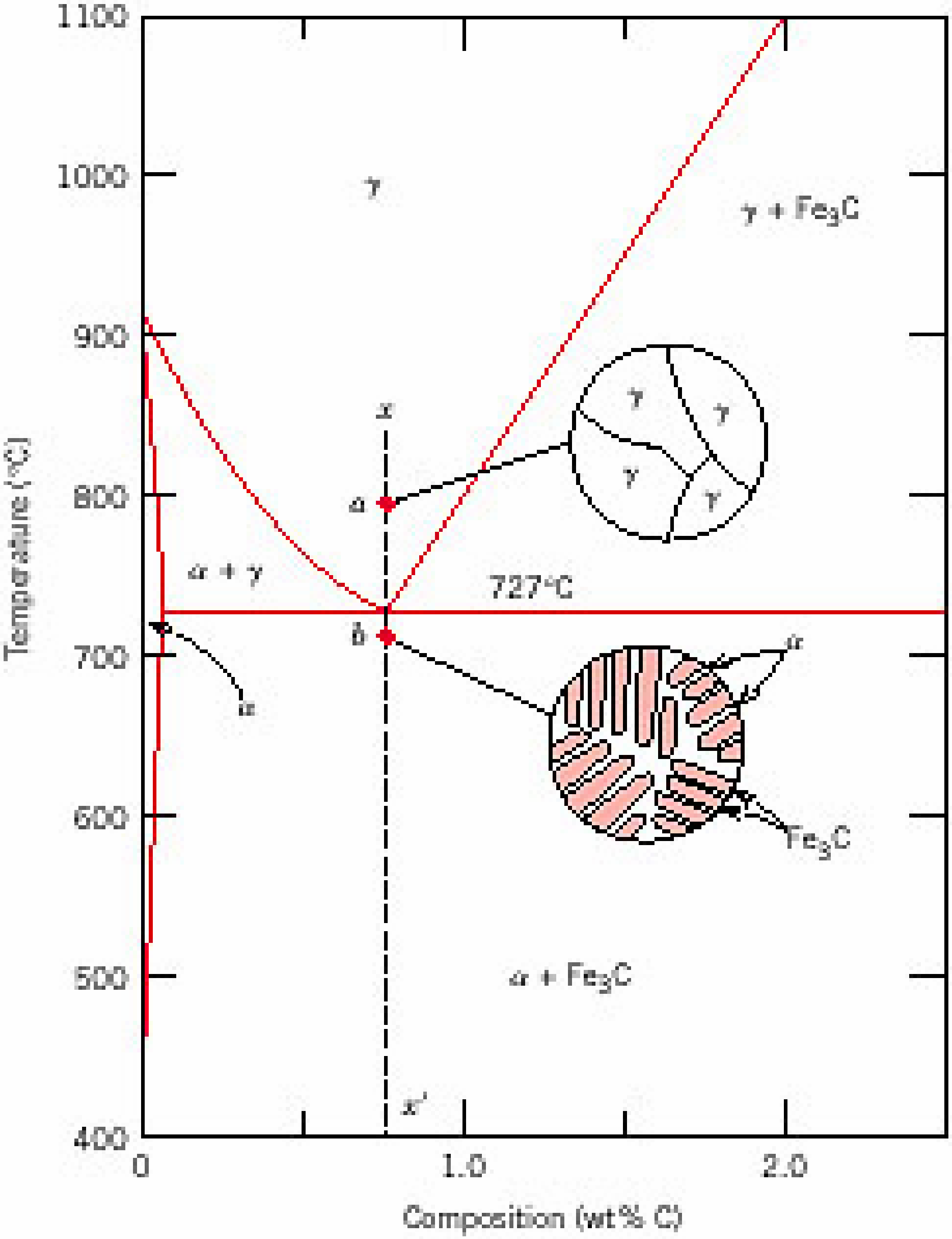
Iron: < 0.008 wt % C in α-ferrite at room T

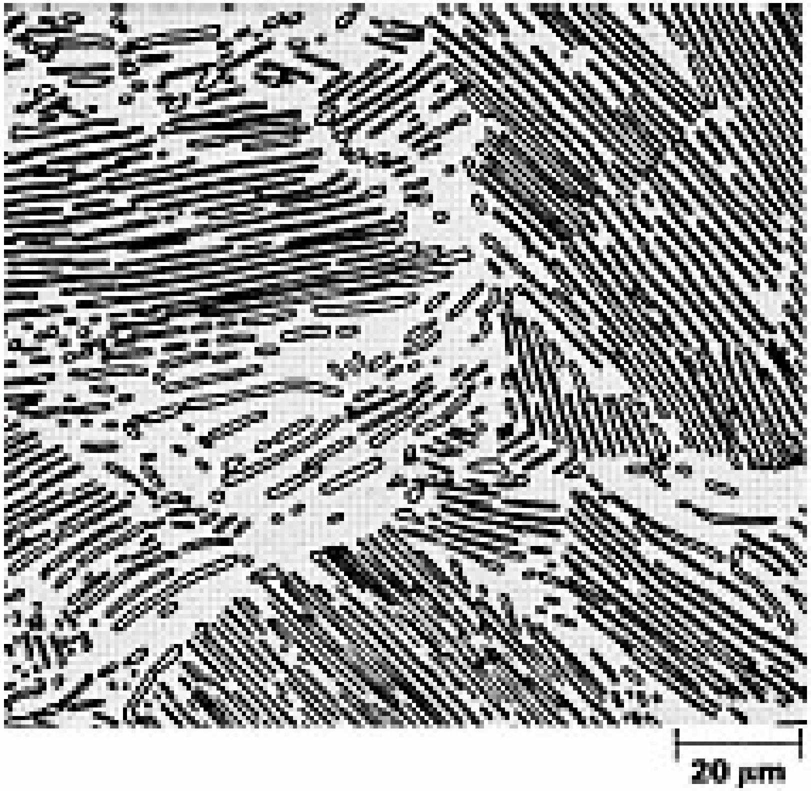
Steels: 0.008 - 2.14 wt % C (usually < 1 wt %)
α-ferrite + Fe_3C at room T

Cast iron: 2.14 - 6.7 wt % (usually < 4.5 wt %)


Atomic percent carbon
2
4
6
8
10
12
14
16
18
20
22
24
°C
°F
Delta iron (δ)
1600
(1538°C)
Delta iron and liquid
1485°C
1500
(0.10%)
(0.18%)
1400
Liquid alloy
2800
2600
Delta iron (δ) and austenite (γ)
1300
2400
Liquid and austenite (γ)
Liquid and Fe3C
1200
2200
1148°C (2088°F)
Austenite (γ)
1100
2000
Acm
(2.0%)
(4.3%)
1000
1800
Temperature
(910°C)
Ferrite (α) and austenite (γ)
900
1600
A3
Austenite (γ) and iron carbide (Fe3C)
800
1400
727°C (1340°F)
700
1200
(0.025%)
A1
(0.80%)
A1,3
600
1000
Ferrite (α)
500
Ferrite (α) and iron carbide (Fe3C)
(Fe3C)
(0.008%)
6.7%
0
0
0.5
1
2
3
4
5
6
Irons
Weight percent, carbon
Hypoeutectoid
Hypereutectoid
Steel
Cast iron

Eutectoid steel

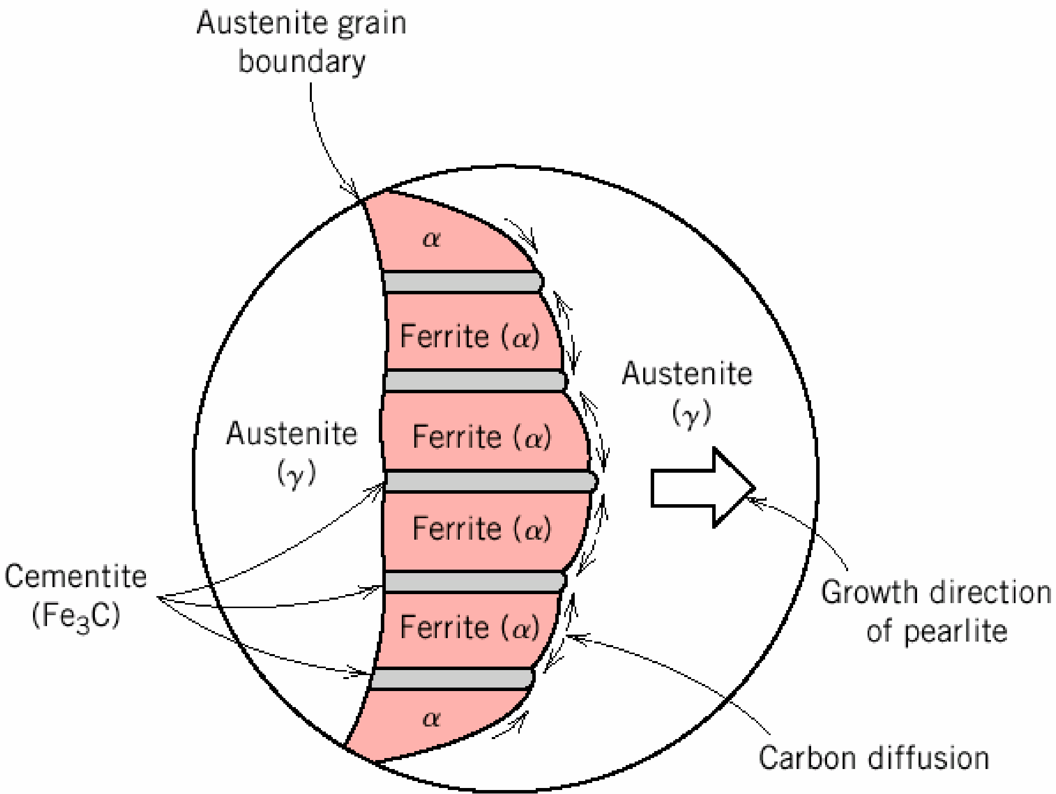


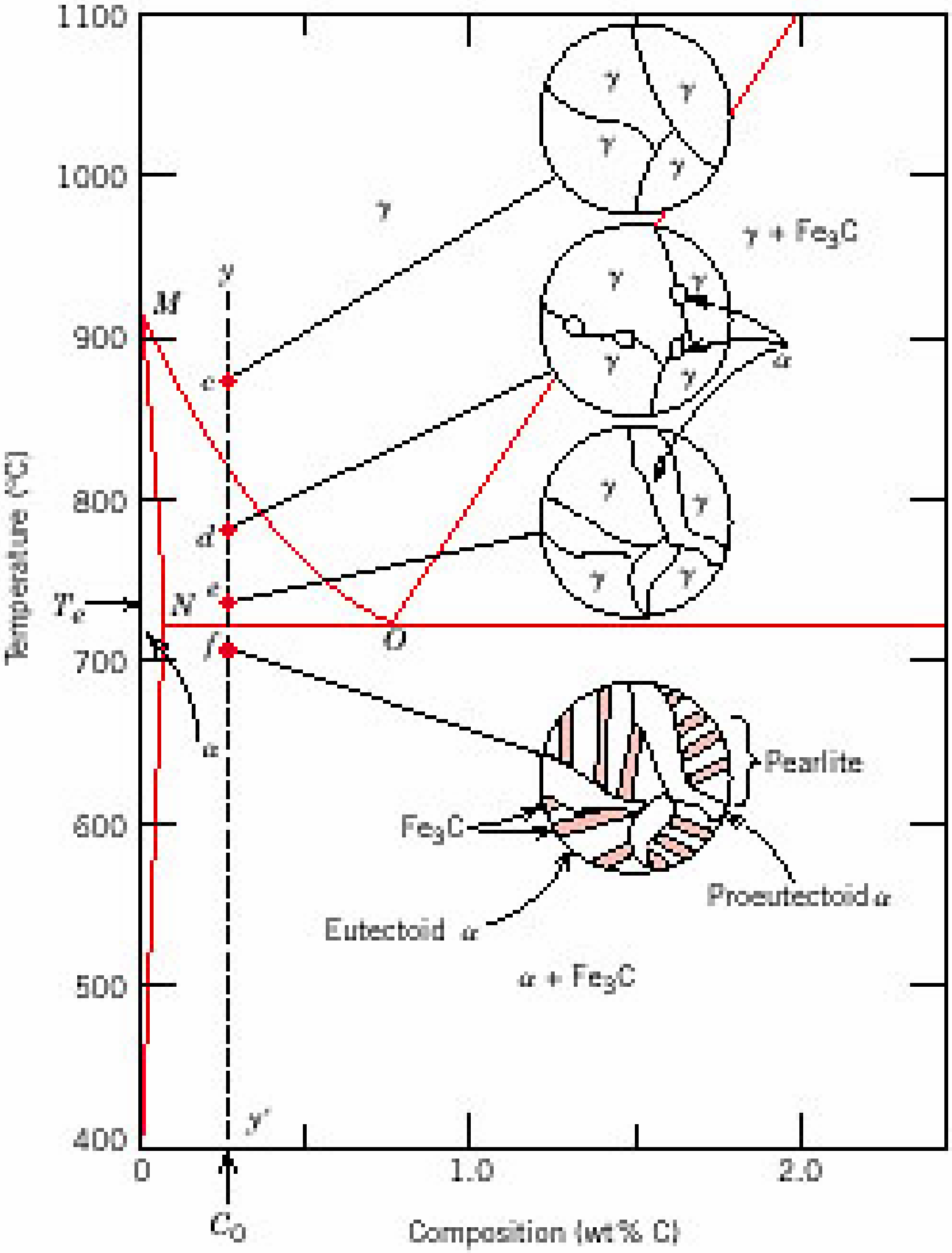


Microstructure of eutectoid steel

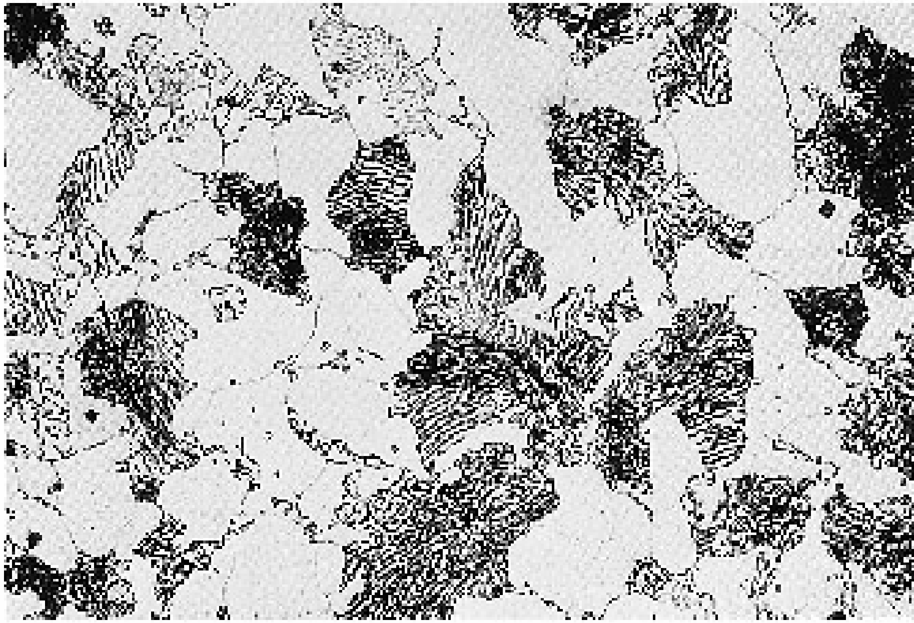
Alloy of eutectoid composition (0.76 wt % C) is cooled slowly: forms pearlite, layered structure of two phases: α-ferrite and cementite (Fe_3C)

Mechanically, pearlite has properties intermediate to soft, ductile ferrite and hard, brittle cementite.

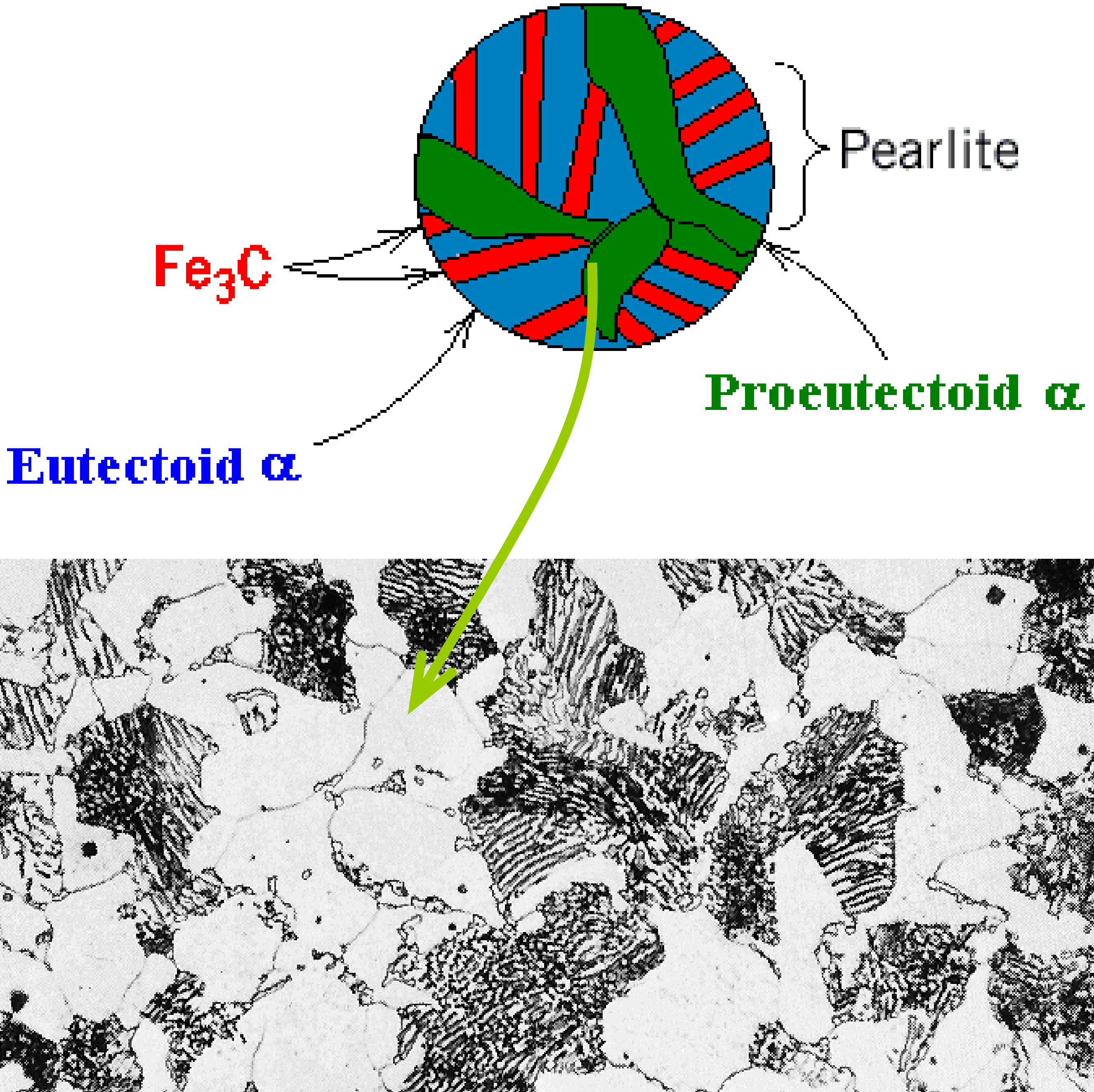




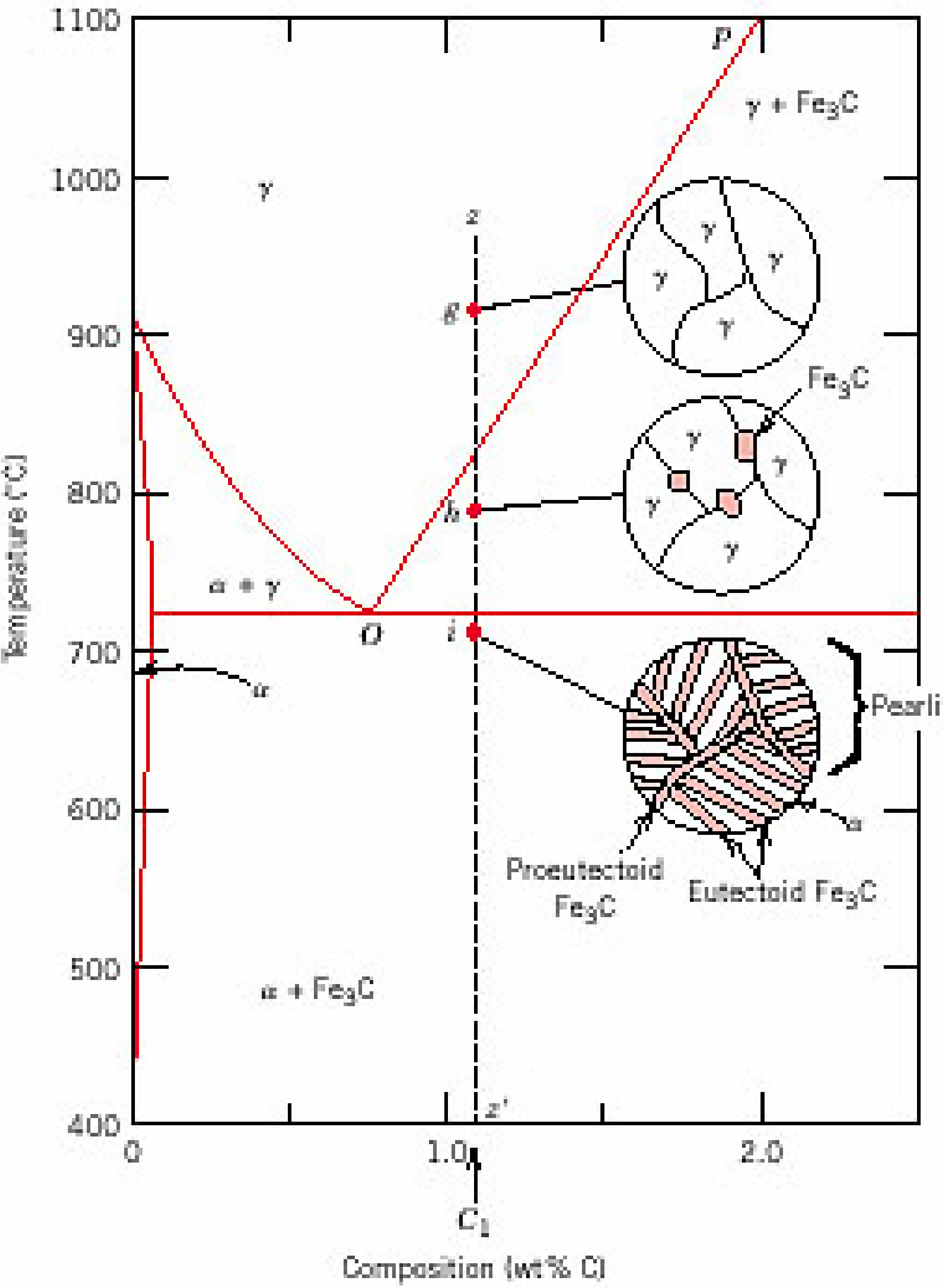
Hypoeutectoid steel



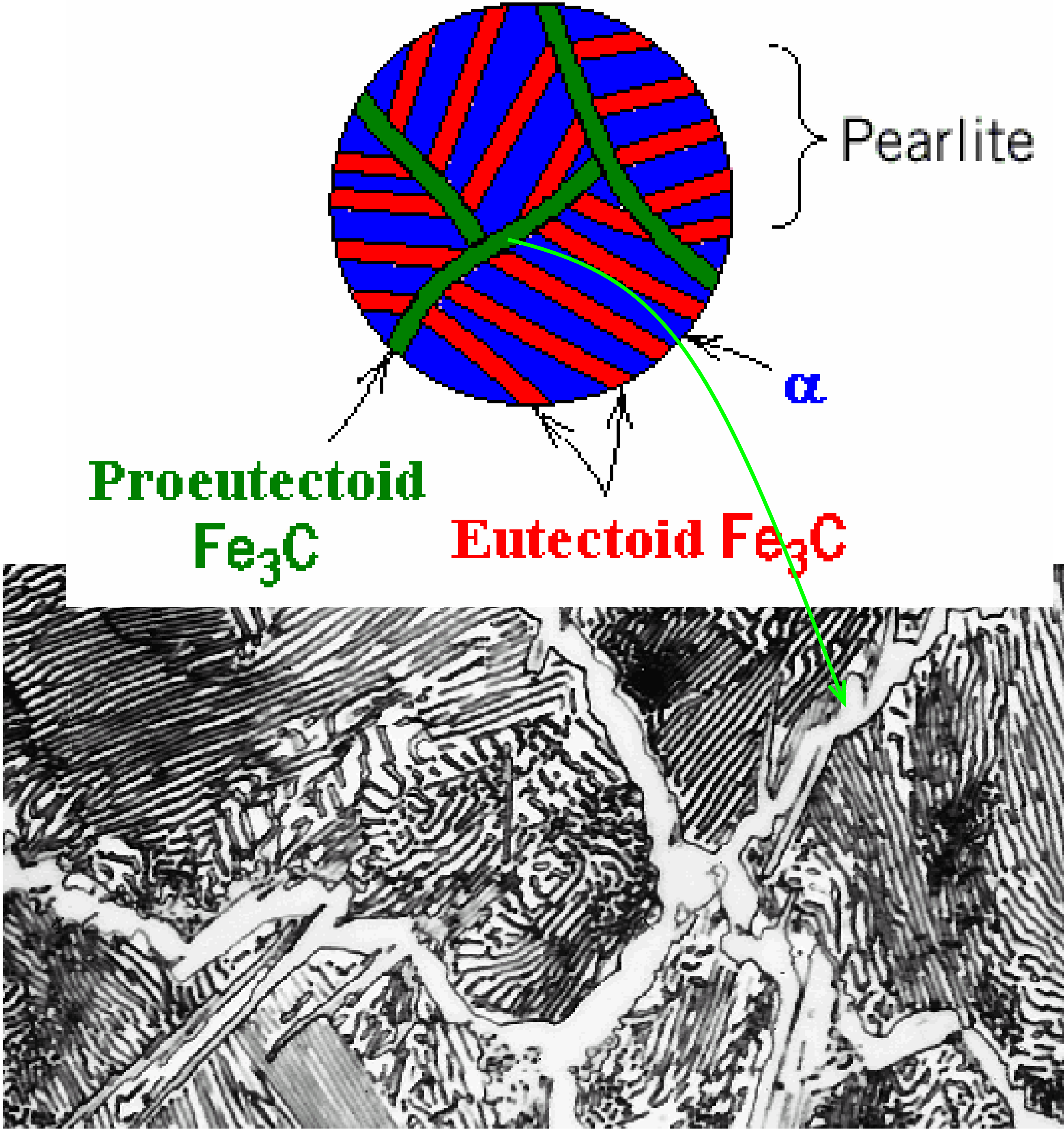
Hypoeutectoid alloys contain proeutectoid ferrite (formed above the eutectoid temperature) plus the eutectoid perlite that contain eutectoid ferrite and cementite.



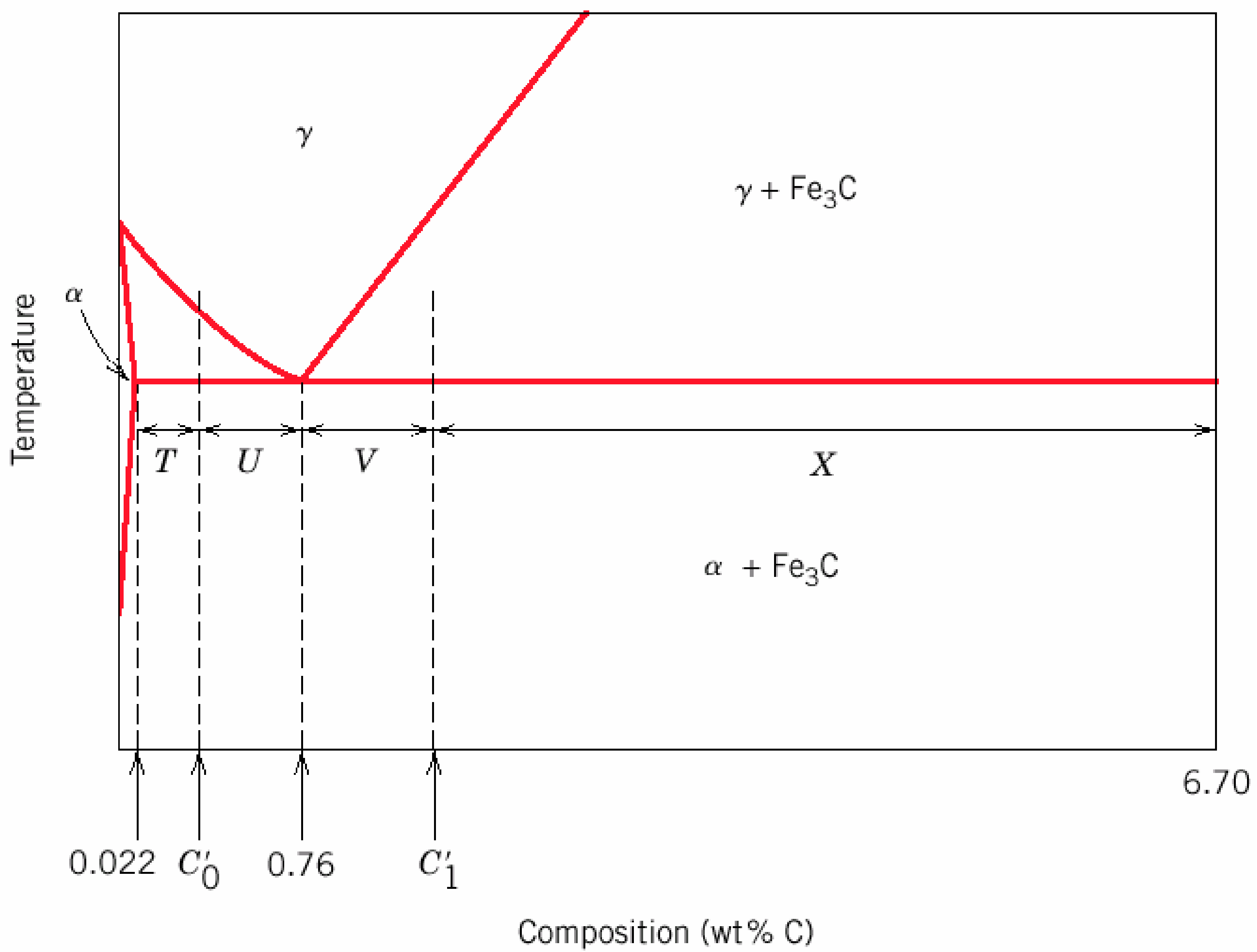
Hypereutectoid steel



Hypereutectoid alloys contain proeutectoid cementite (formed above the eutectoid temperature) plus perlite that contain eutectoid ferrite and cementite.



How to calculate the relative amounts of proeutectoid phase (α or Fe_3C) and pearlite?



Use the lever rule and a tie line that extends from the eutectoid composition (0.75 wt% C) to α (0.022 wt% C) for hypoeutectoid alloys and to Fe_3C (6.7 wt% C) for hypereutectoid alloys.

Example: hypereutectoid alloy, composition C_1

$$\text{Fraction of Pearlite} = W_P = \frac{X}{(V + X)} = \frac{(6.7 - C_1)}{(6.7 - 0.76)}$$

$$\text{Fraction of Proeutectoid Cementite} = W_{Fe3C} = \frac{V}{(V + X)} = \frac{(C_1 - 0.76)}{(6.7 - 0.76)}$$

Example

For alloys of two hypothetical metals ***A*** and ***B***, there exist an α, ***A***-rich phase and a β, ***B***-rich phase. From the mass fractions of both phases of two different alloys, which are at the same temperature, determine the composition of the phase boundary (or solubility limit) for both α and β at this temperature.

Alloy Composition	**Fraction of α phase**	**Fraction of β phase**
60wt%A – 40wt%B	0.57	0.43
30wt%A – 70wt%B	0.14	0.86

The problem is to solve for compositions at the phase boundaries for both α and β phases (i.e., $C\alpha$ and $C\beta$). We may set up two independent lever rule expressions, one for each composition, in terms of $C\alpha$ and $C\beta$ as follows:

$$W_{\alpha 1} = 0.57 = \frac{C_\beta - C_{o1}}{C_\beta - C_\alpha} = \frac{C_\beta - 60}{C_\beta - C_\alpha}$$

$$W_{\alpha 2} = 0.14 = \frac{C_\beta - C_{o2}}{C_\beta - C_\alpha} = \frac{C_\beta - 30}{C_\beta - C_\alpha}$$

In these expressions, compositions are given in weight percent ***A***. Solving for **Cα** and **Cβ** from these equations, yield

Cα = 90 (or 90 wt% A-10 wt% B)

Cβ = 20.2 (or 20.2 wt% A-79.8 wt% B)

Heat Treatment of Steels

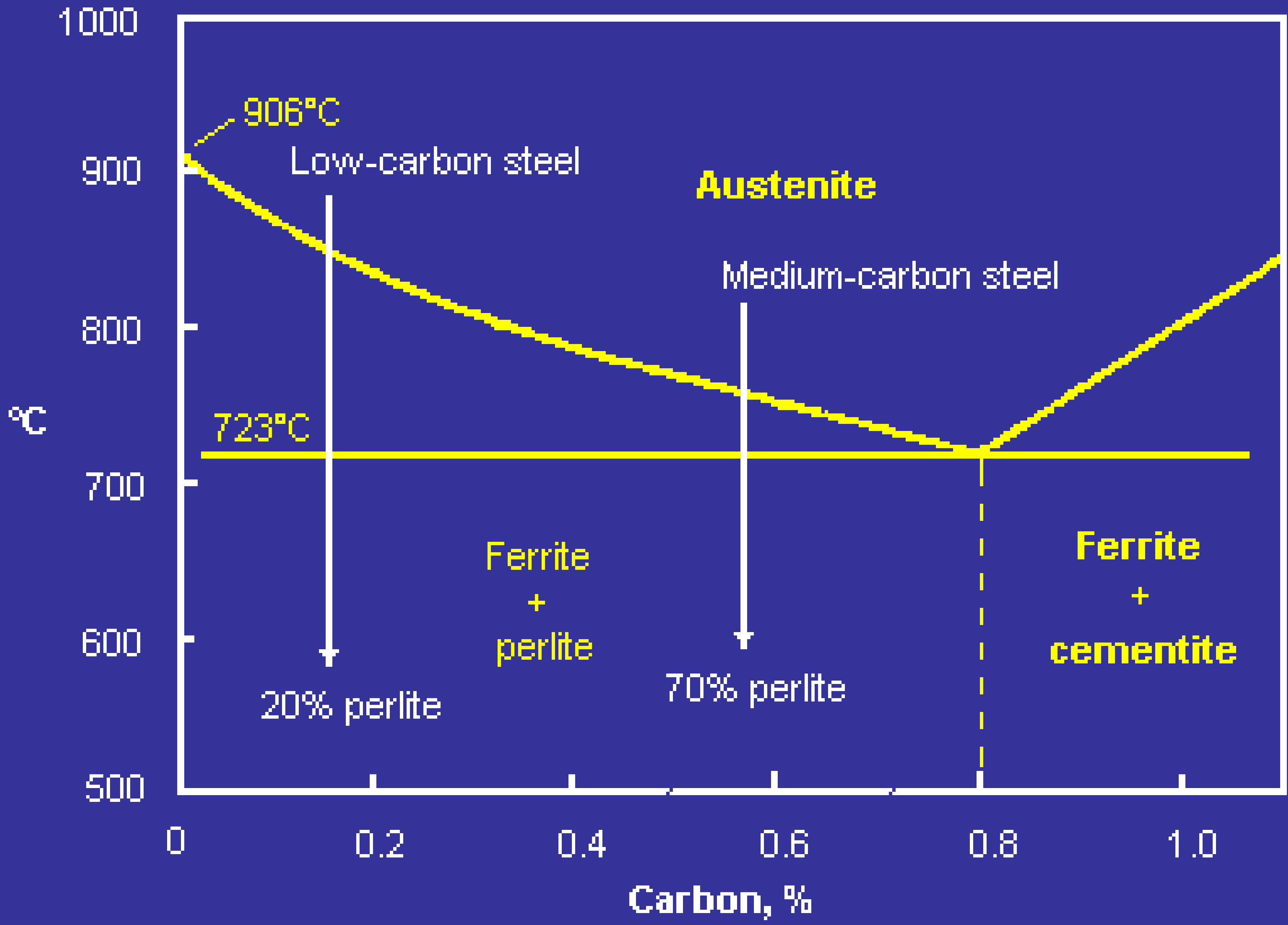
On slowly cooling the steels, the properties of the steel are dependent mainly on the percentage carbon.

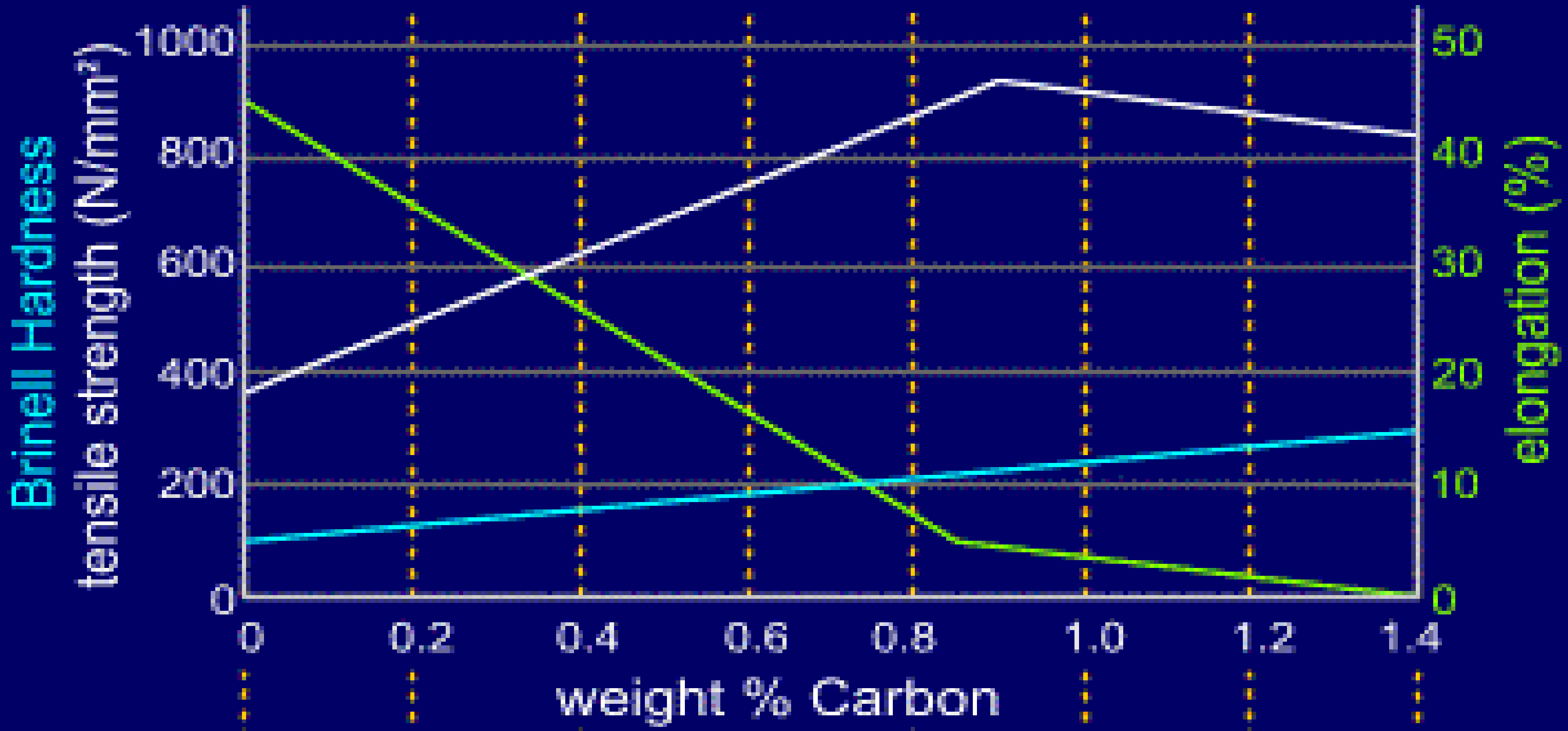
Different percentage carbon implies different percentage of microconstituents and phases

- pearlite and ferrite pro-eutectoid for the hypo-eutectoid steels
- pearlite and cementite pro-eutectoid for the hyper-eutectoid steels.

The temperature is high enough and the time at high temperature is long enough, for the atoms to diffuse and attain equilibrium conditions

PART OF THE IRON-CARBON PHASE DIAGRAM





chains
rivets
nails

screws
tinplate

axles
gears
shafts

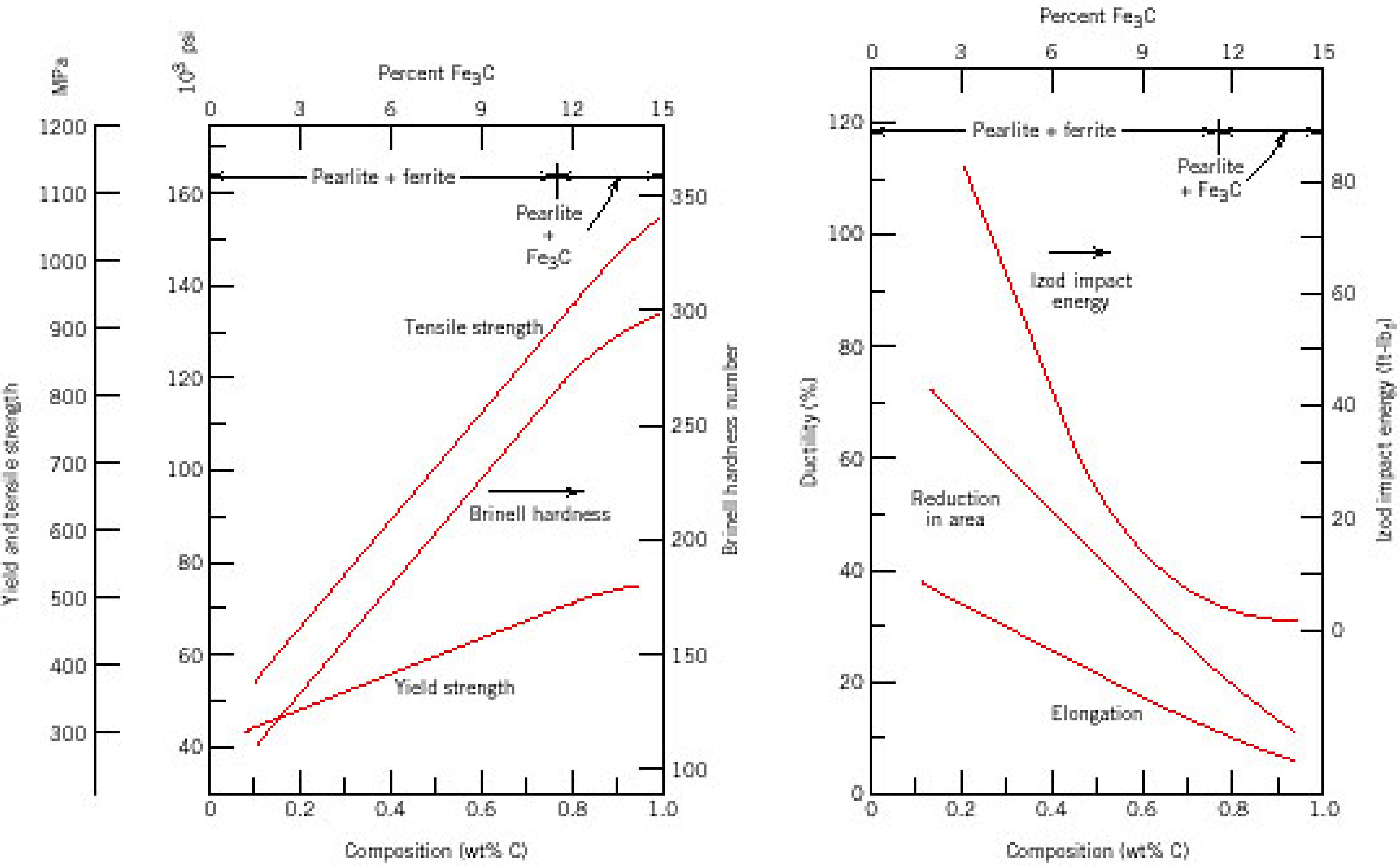
screwdrivers
wire ropes

cold chisels
shear blades
some hand tools

drills
taps
dies

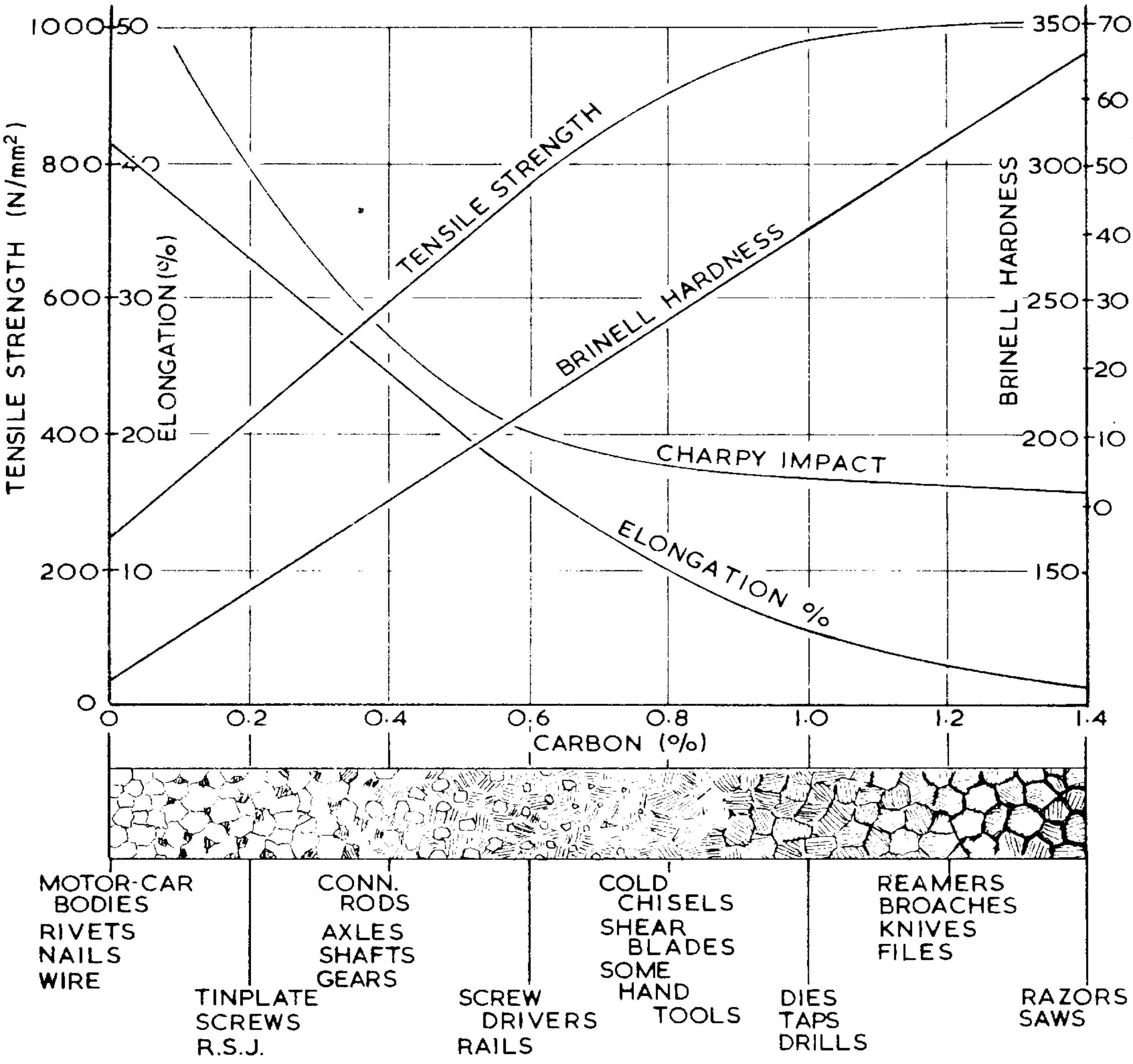
knives
reamers

saws
razors



(a) (b)

FIGURE 10.21 (*a*) Yield strength, tensile strength, and Brinell hardness versus carbon concentration for plain carbon steels having microstructures consisting of fine pearlite. (*b*) Ductility (%EL and %RA) and Izod impact energy versus carbon concentration for plain carbon steels having microstructures consisting of fine pearlite. (Data taken from *Metals Handbook: Heat Treating*, Vol. 4, 9th edition, V. Masseria, Managing Editor, American Society for Metals, 1981, p. 9.)


TENSILE STRENGTH (N/mm^2)
ELONGATION (%)
BRINELL HARDNESS
CHARPY IMPACT VALUE (J)
0
200
400
600
800
1000
10
20
30
40
50
150
200
250
300
350
0
10
20
30
40
50
60
70
TENSILE STRENGTH
BRINELL HARDNESS
CHARPY IMPACT
ELONGATION %
0
0·2
0·4
0·6
0·8
1·0
1·2
1·4
CARBON (%)
MOTOR-CAR BODIES
RIVETS
NAILS
WIRE
TINPLATE
SCREWS
R.S.J.
CONN. RODS
AXLES
SHAFTS
GEARS
SCREW DRIVERS
RAILS
COLD CHISELS
SHEAR BLADES
SOME HAND TOOLS
DIES
TAPS
DRILLS
REAMERS
BROACHES
KNIVES
FILES
RAZORS
SAWS

Why Heat Treatment?

By varying the manner in which plain-carbon are heated and cooled, different combinations of mechanical properties of the steel can be obtained.

The resulting mechanical properties are due to changes in the microstructure.

Properties can be tailored by changing the microstructure.

The development of the microstructure is not instantaneously and is ruled by the diffusion of atoms.

***Heat Treatment*: Heating and cooling procedure to manipulate structural changes (affect materials properties).**

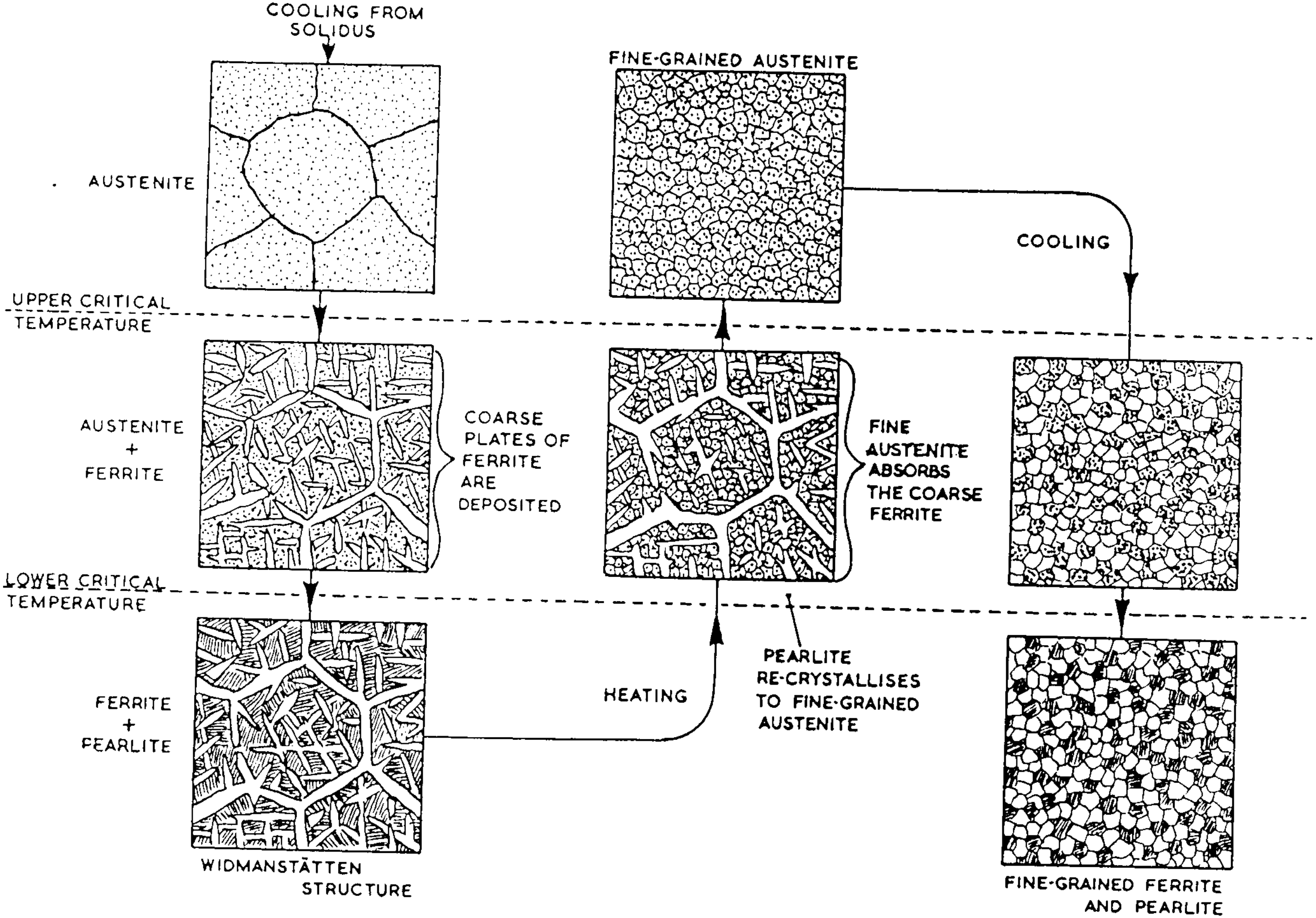


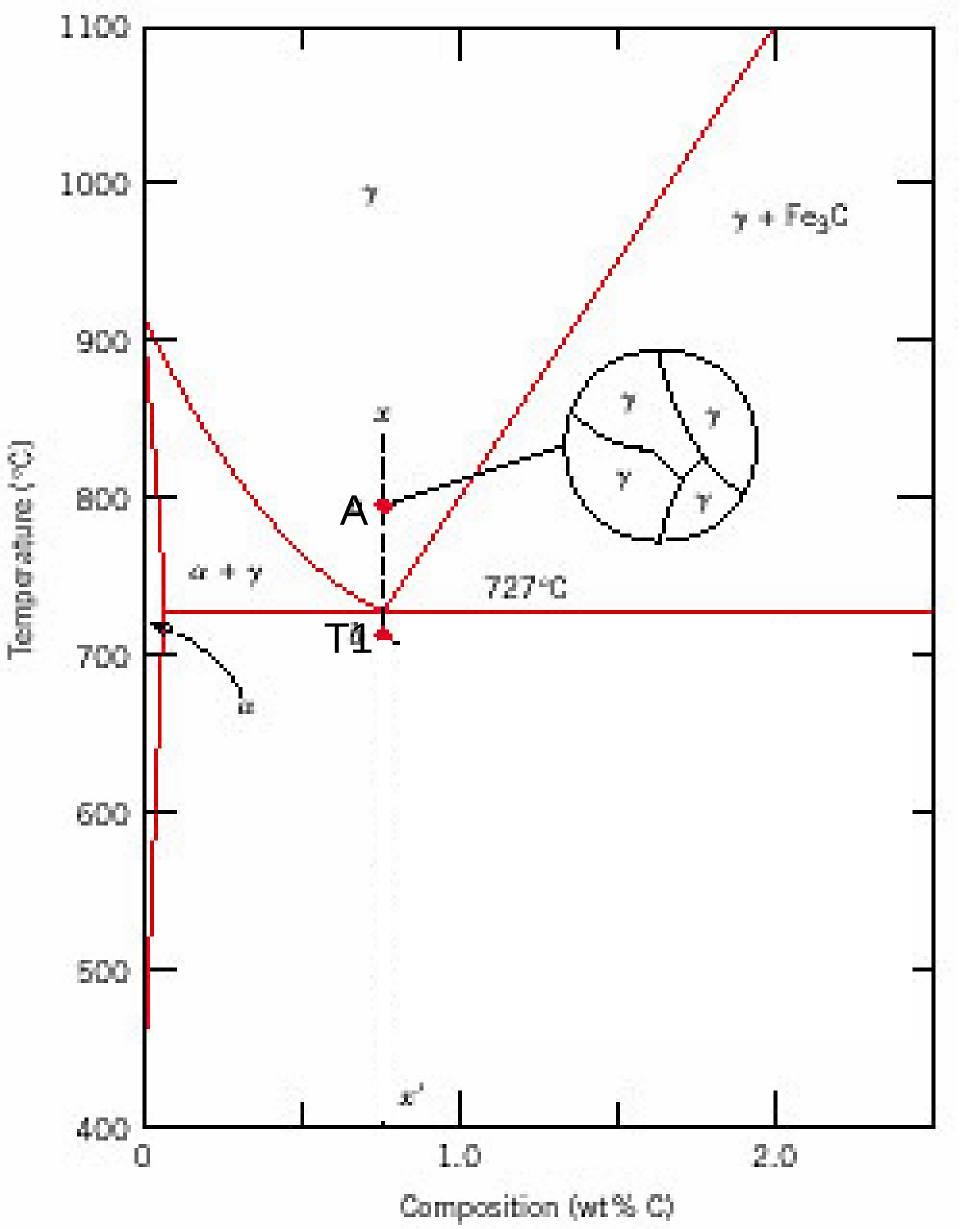
FIG. 11.9.—The Structural Effects of Heating a Steel Casting (Containing Approximately 0·35% Carbon) to a Temperature Just Above its Upper Critical, Followed by Cooling to Room Temperature.

Isothermal Transformation

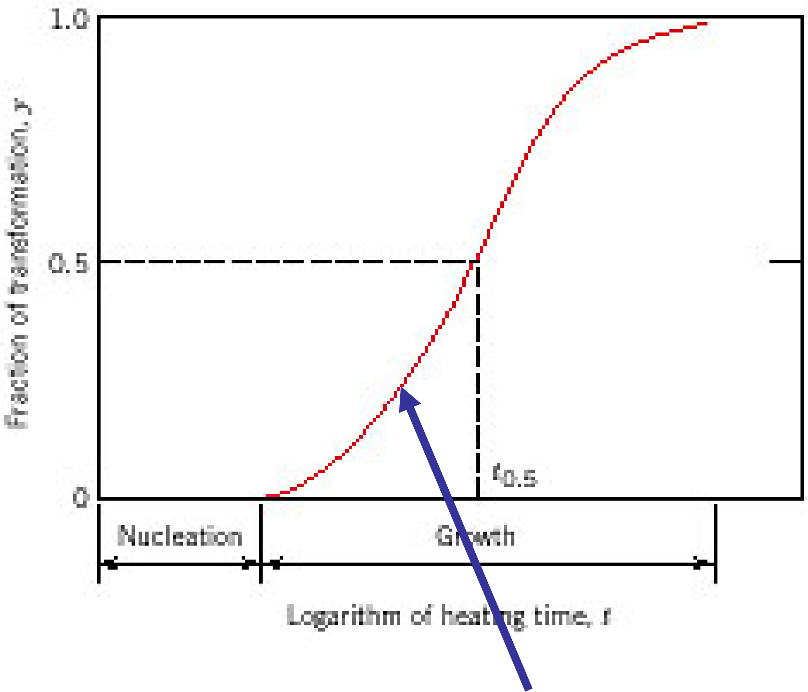
- Consider a rapid cooling from “A” to “T1” in the diagram for an eutectoid steel and keeping the steel at this temperature for the eutectoid reaction to occur.
- The eutectoid reaction will take place **isothermally**

$$\gamma(0.78\ \mathrm{wt\%C}) \rightarrow \alpha(0.02\%\mathrm{C}) + \mathrm{Fe_3C}(6.70\%\mathrm{C})$$

- Austenite, on time, will transform to ferrite and cementite.
- Carbon diffuses away from ferrite to cementite
- Temperature affects the rate of diffusion of carbon..



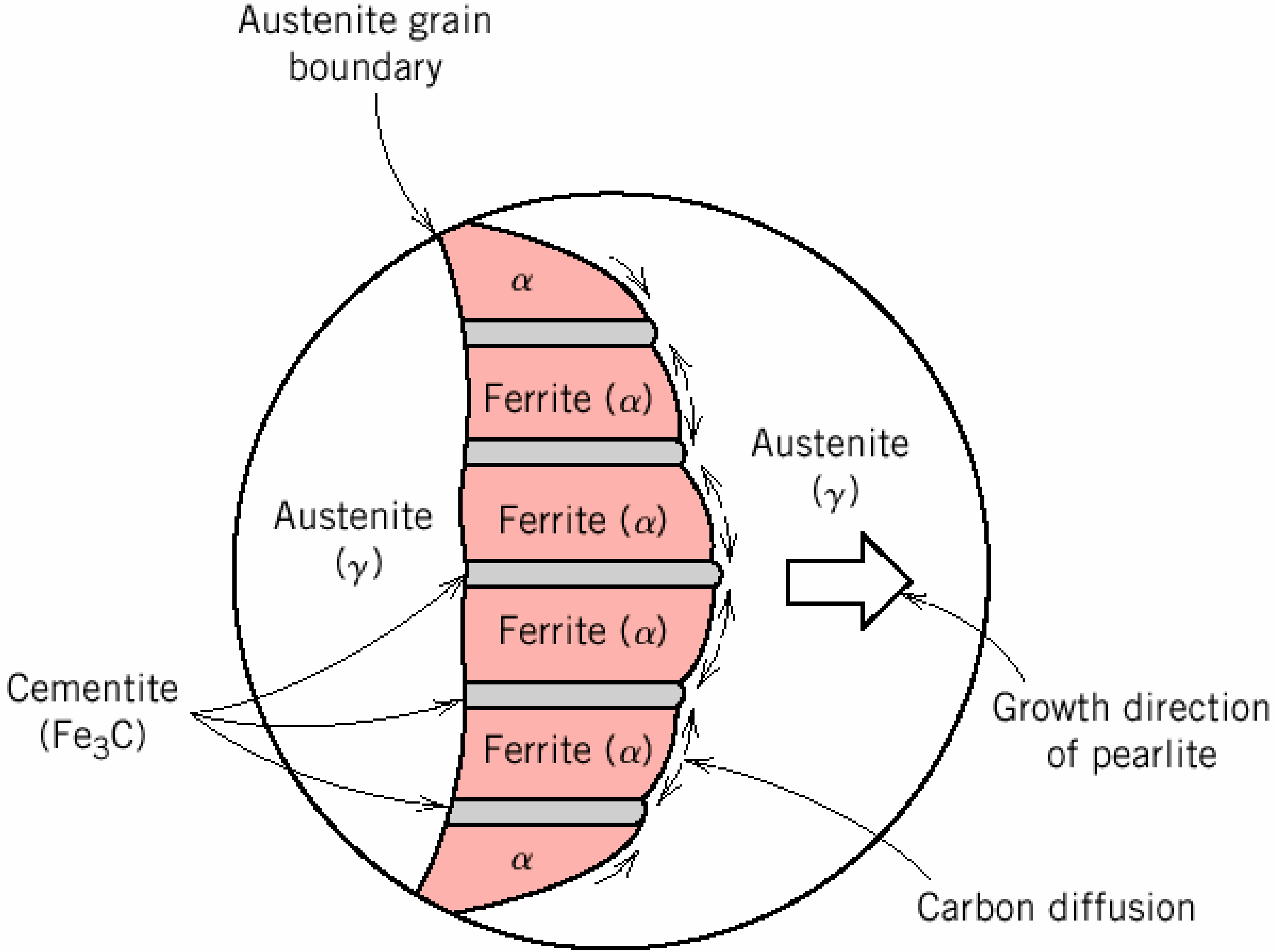
At temperature “T1” the transformation will occur gradually, following a “S” shape curve



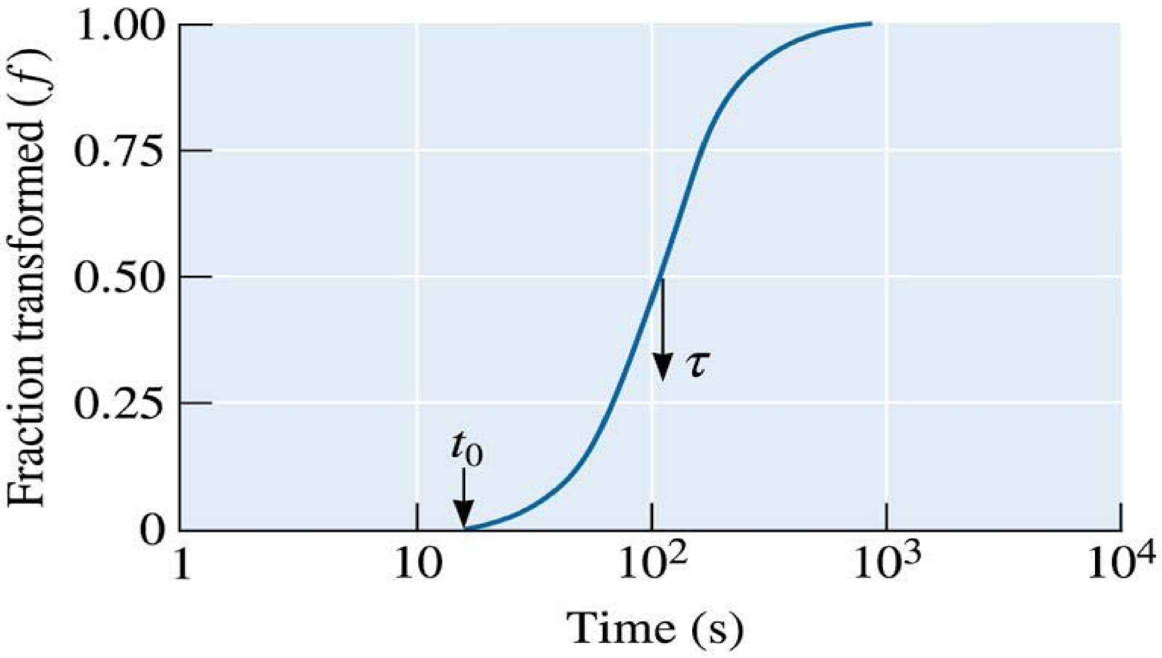
$$y = 1 - \exp(-kt^n)$$

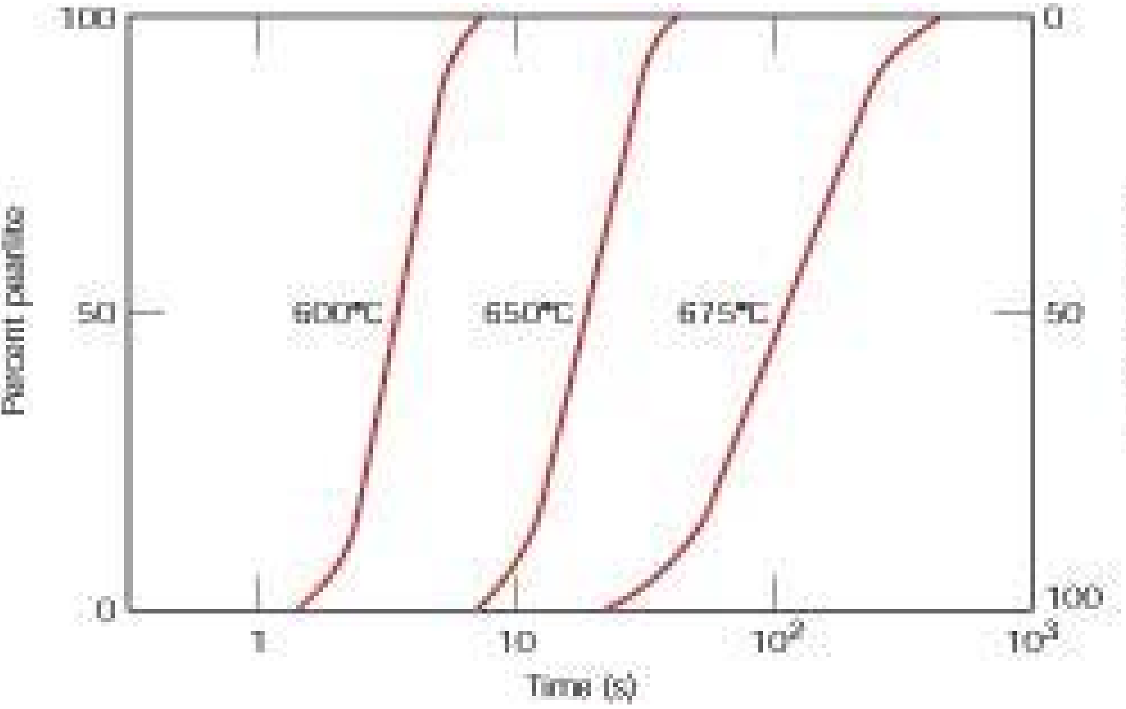
Avrami equation

Avrami relationship - Describes the fraction of a transformation that occurs as a function of time. This describes most solid-state transformations that involve diffusion, thus martensitic transformations are not described.



$$r = \frac{1}{t_{0.5}}$$

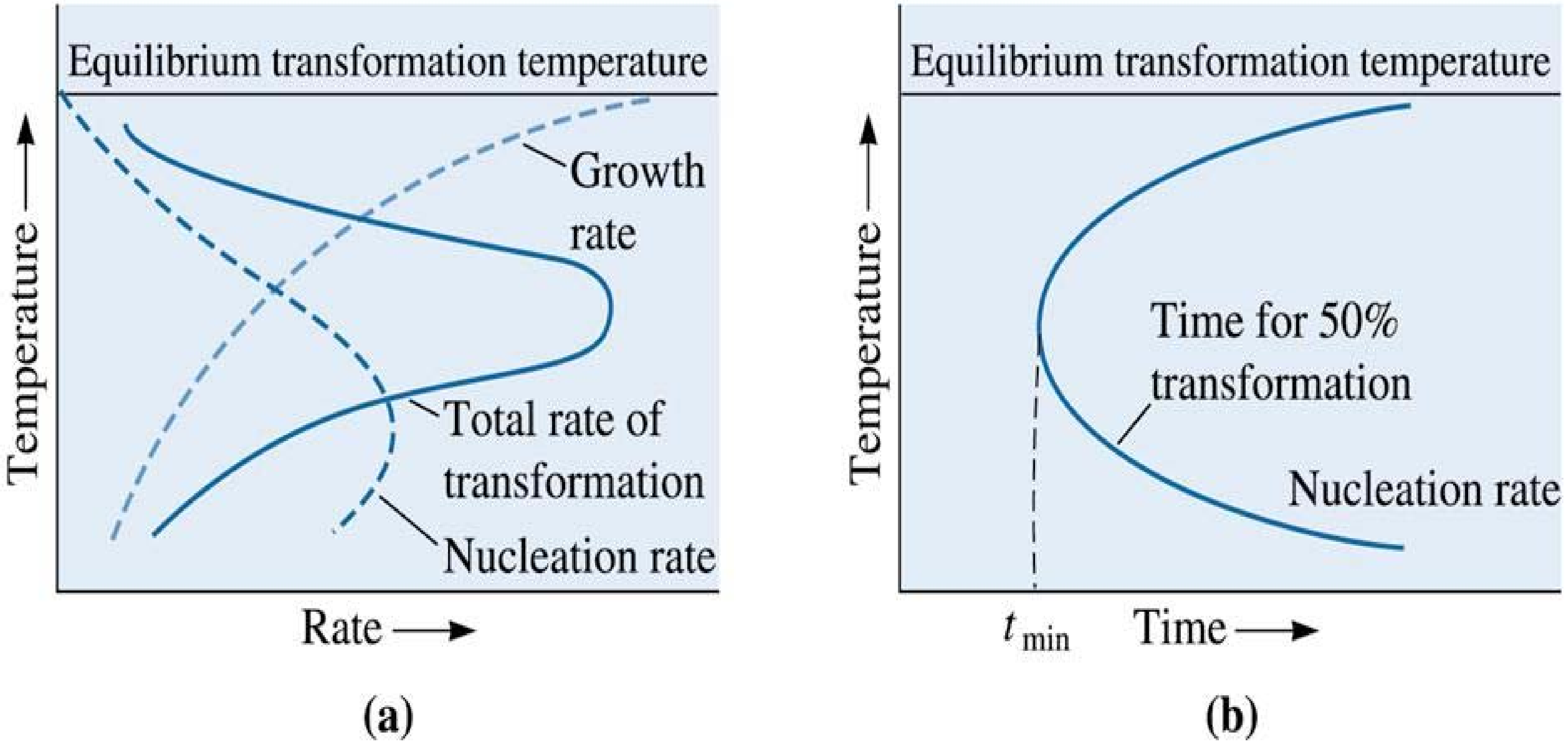




For most reactions rate increases with temperature:

Rate of transformation

$$r = Ae^{-Q/RT}$$



The rate of a phase transformation is the product of the growth rate and nucleation rate contributions, giving a maximum transformation rate at a critical temperature (a). Consequently, there is a minimum time (t_{min}) required for the transformation, given by the "*C*-curve".

Time-Temperature-Transformation Diagram

- TTT diagrams are **isothermal transformations** (constant T – the material is cooled quickly to a given temperature **THEN** the transformation occurs)

- The thickness of the ferrite and cementite layers in pearlite is ~ 8:1. The absolute layer thickness depends on temperature of transformation. The higher the temperature, the thicker the layers.

- At higher T. S-shaped curves shifted to longer times ⇒ transformation dominated by slow nucleation and high atomic diffusion. Grain growth is controlled by atomic diffusion.
- At higher temperatures, the high diffusion rates allow for larger grain growth and formation of thick layered structure of pearlite (**coarse pearlite**).

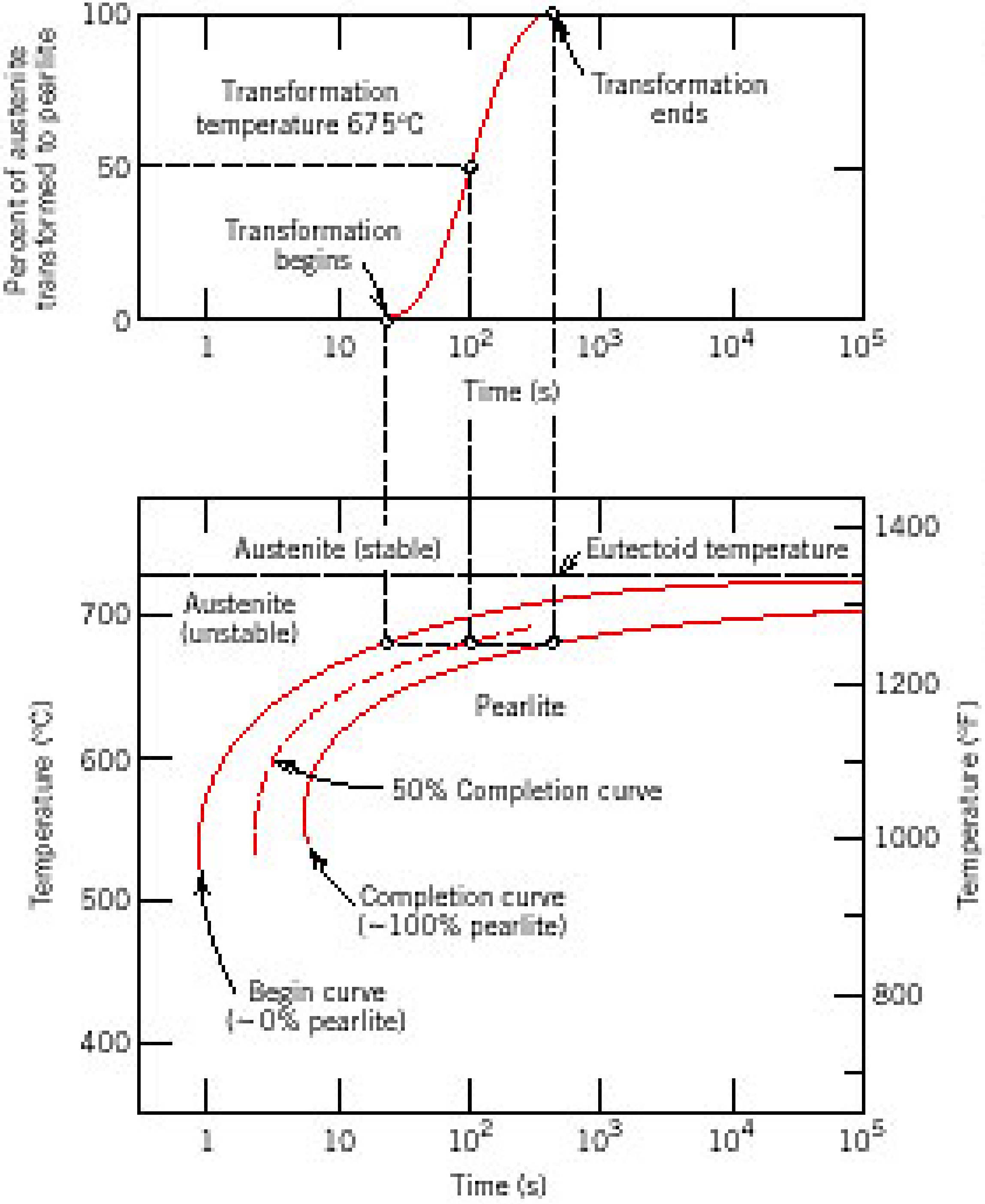
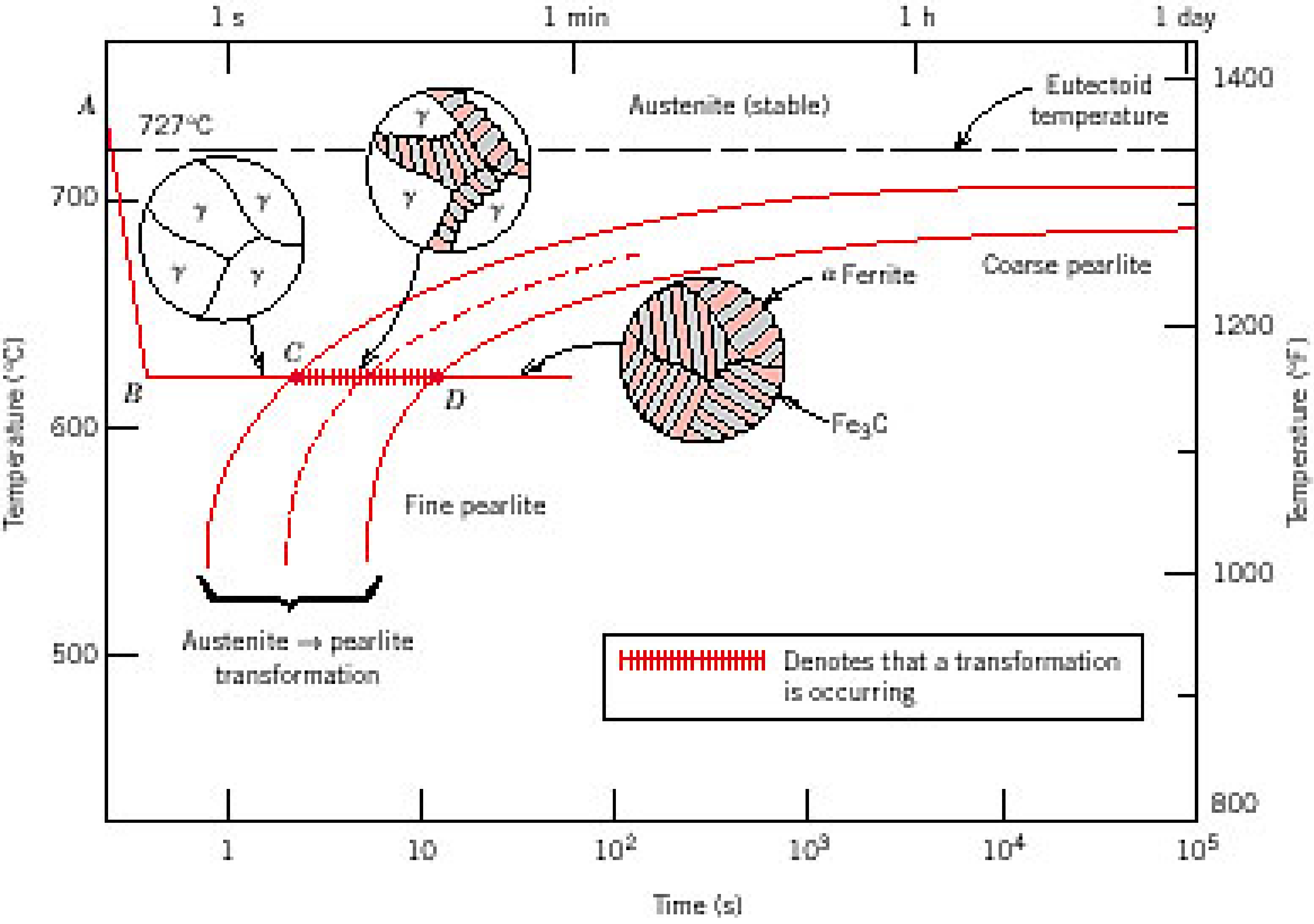


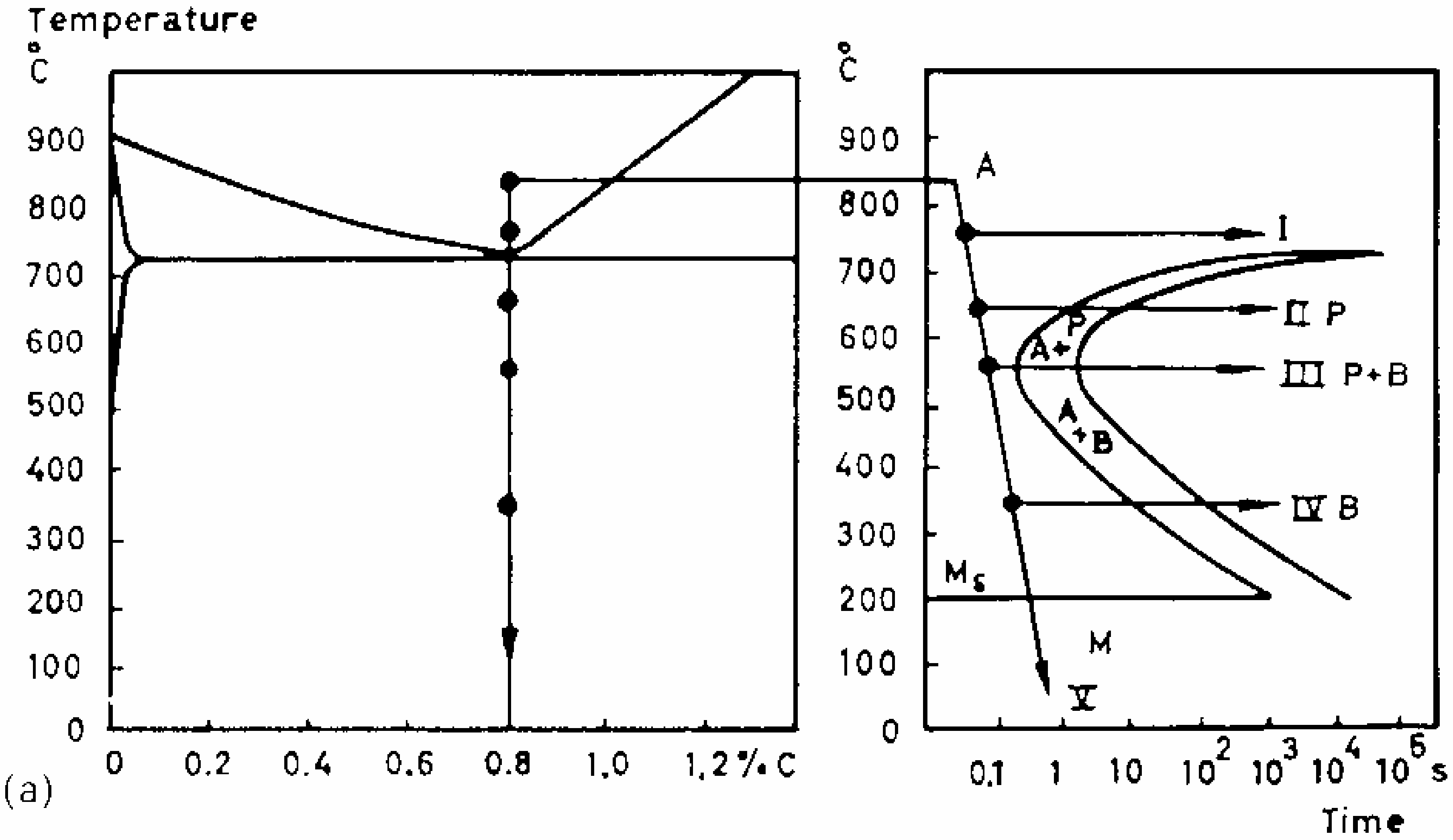
FIGURE 10.4
Demonstration of how an isothermal transformation diagram (bottom) is generated from percent transformation-versus-logarithm of time measurements (top).
(Adapted from H. Boyer, Editor, *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 369.)

- At low temperatures, the transformation is controlled by a rapid nucleation but slow atomic diffusion. Nucleation is controlled by supercooling.
- Slow diffusion at low temperatures leads to fine-grained microstructure with thin-layered structure of pearlite (**fine pearlite**).
- At compositions other than eutectoid, a proeutectoid phase (ferrite or cementite) coexists with pearlite.
- If transformation temperature is low enough (≤540°C) below the nose of the TTT curve the diffusion rates are greatly reduced
- Under such conditions is not possible to form pearlite and a different phase, bainite, is formed.

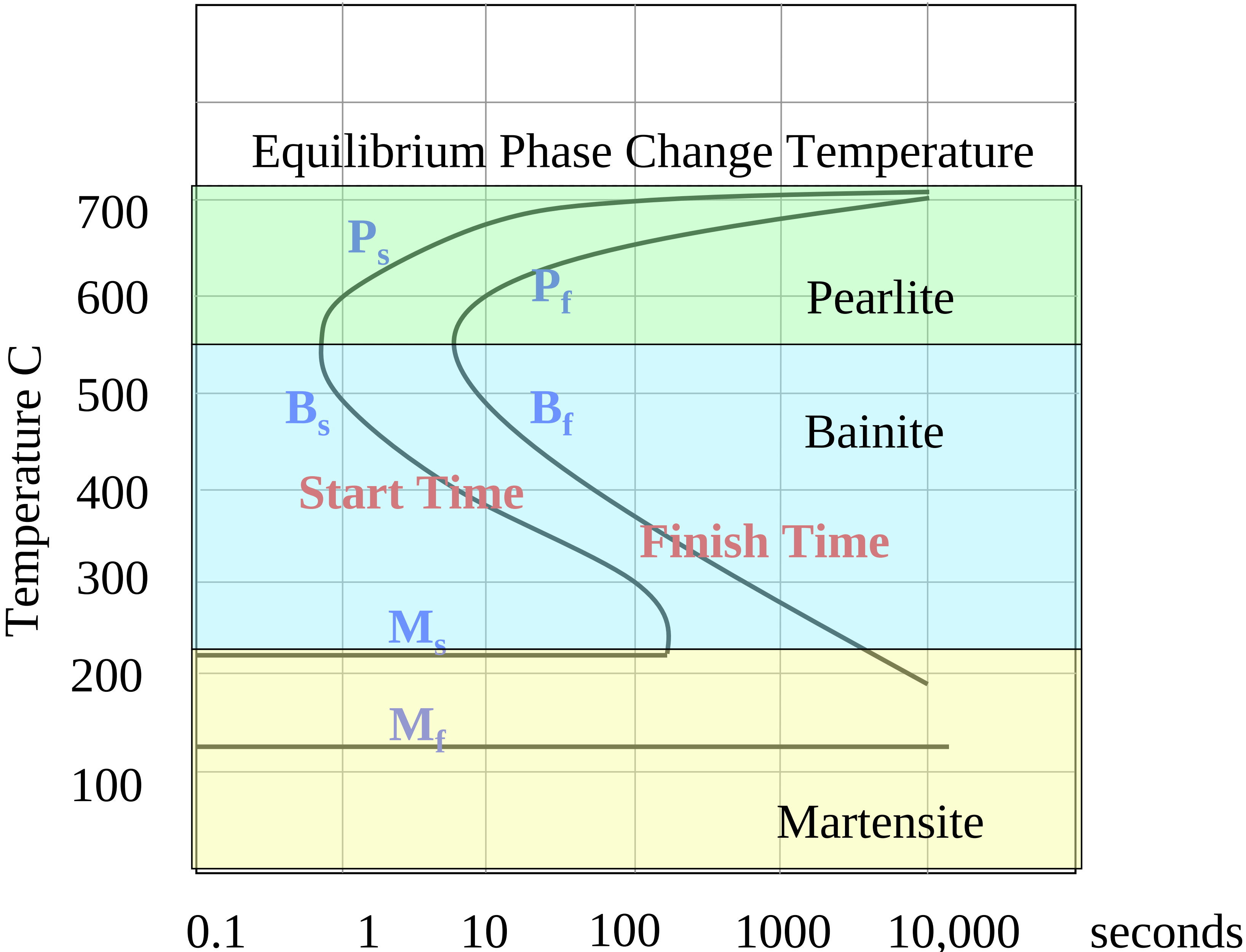

1 s
1 min
1 h
1 day
A
727°C
Austenite (stable)
Eutectoid temperature
1400
700
γ
α Ferrite
Coarse pearlite
1200
C
B
D
Fe$_3$C
600
Fine pearlite
1000
Austenite → pearlite transformation
500
Denotes that a transformation is occurring
800
1
10
10^2
10^3
10^4
10^5
Time (s)
Temperature (°C)
Temperature (°F)

Coarse pearlite

Fine pearlite

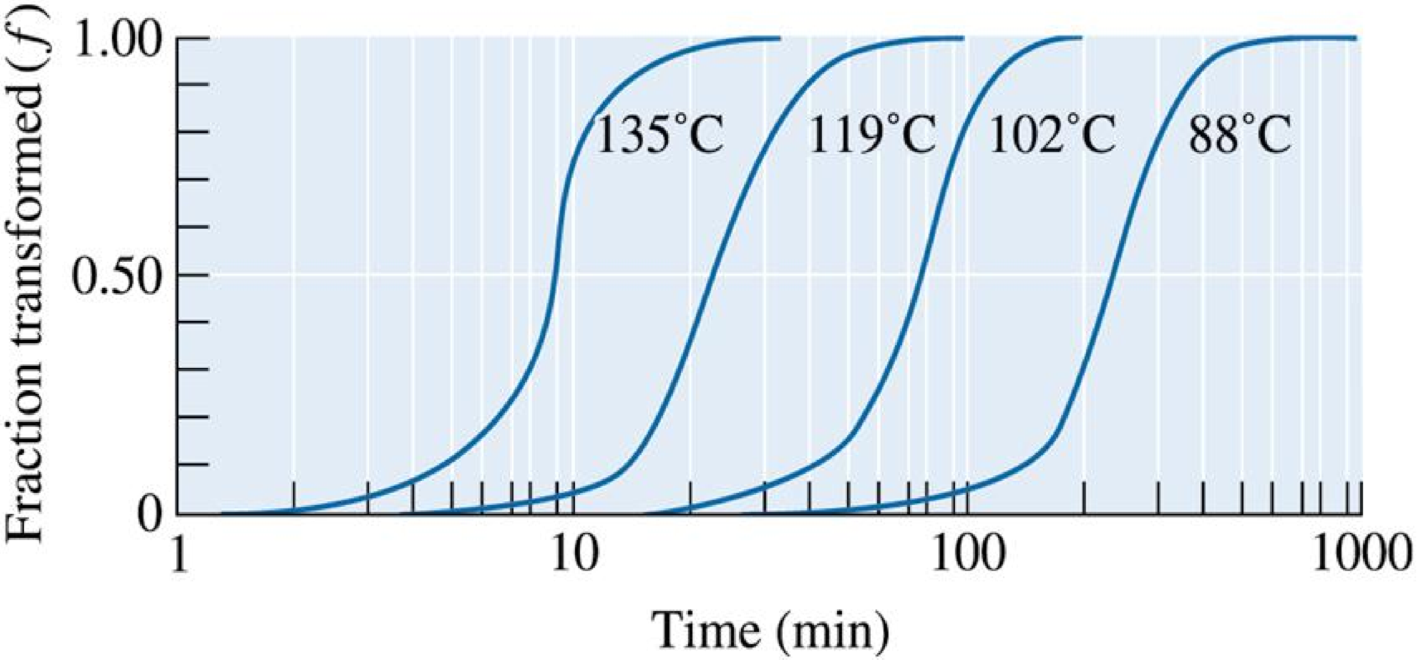

(a)
Temperature
°C
900
800
700
600
500
400
300
200
100
0
0
0.2
0.4
0.6
0.8
1.0
1,2 % C
°C
900
800
700
600
500
400
300
200
100
0
A
I
II P
A+P
III P+B
A+B
IV B
Ms
M
V
0.1
1
10
10²
10³
10⁴
10⁵ s
Time

TTT Curve - Eutectiod Steel



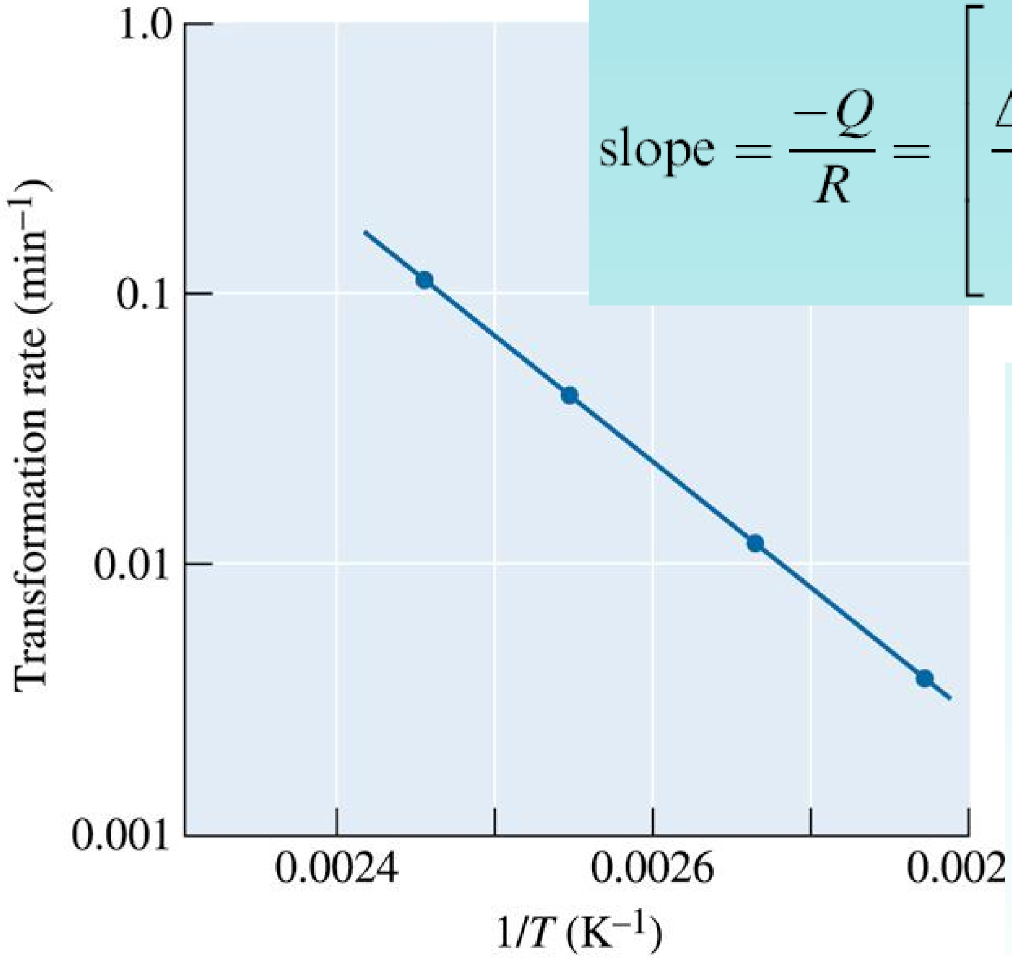
Problem:

Determine the activation energy for recrystallization of cold worked copper, given the fraction of recrystallization with time at different temperatures.



T(°C)	T (K)	τ (min)	Rate (min^{-1})
135	408	9	0.111
119	392	22	0.045
102	375	80	0.0125
88	361	250	0.0040

$$r = Ae^{-Q/RT}$$



$$\text{slope} = \frac{-Q}{R} = \left[\frac{\Delta \ln(\text{rate})}{\Delta\left(\frac{1}{T}\right)}\right] = \frac{[(\ln(0.111) - \ln(0.004))]}{\left[\frac{1}{408} - \frac{1}{361}\right]}$$

$$Q/R = 10{,}414$$

$$Q = 20{,}693\,\frac{\text{cal}}{\text{mol}}$$

$$\therefore 0.111 = A\,\exp\left(\frac{-20{,}693\ \text{cal/mol}}{\left(1.987\,\frac{\text{cal}}{\text{deg}-\text{mol}}\right) \times (408\ \text{deg})}\right)$$

$$A = 0.111/8.21 \times 10^{-12} = 1.351 \times 10^{10}\ \text{s}^{-1}$$

$$\therefore \text{rate} = 1.351 \times 10^{10}\ \exp\left(\frac{-20{,}693}{RT}\right)$$

Bainite – another product of austenite transformation

- Needles or plates – needles of ferrite separated by elongated particles of the Fe_3C phase
- Bainite forms as shown on the T-T-T diagram at temperatures below those where pearlite forms
- Pearlite forms – 540 to 727 ^0C
- Bainite forms – 215 to 540 ^0C

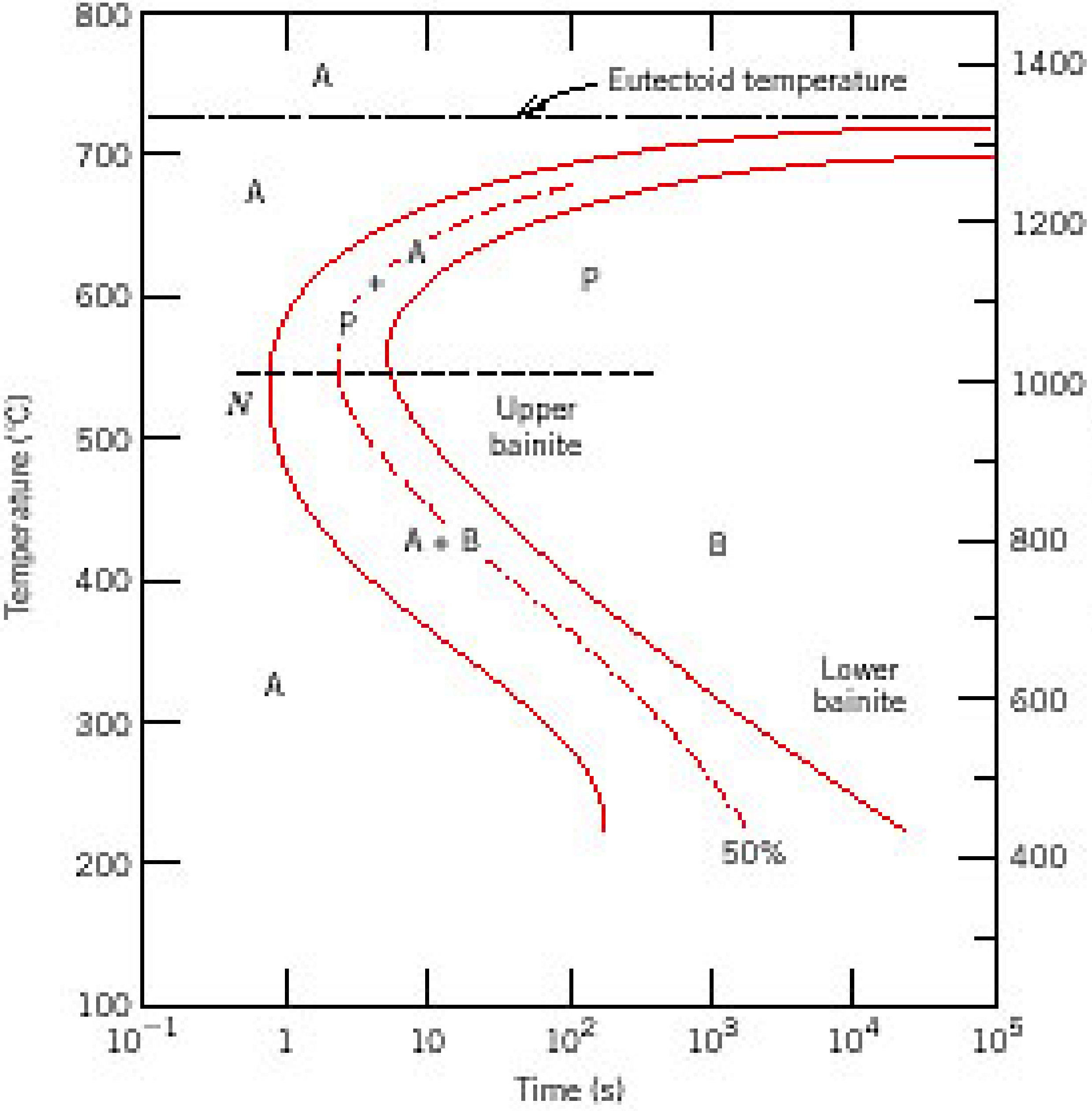
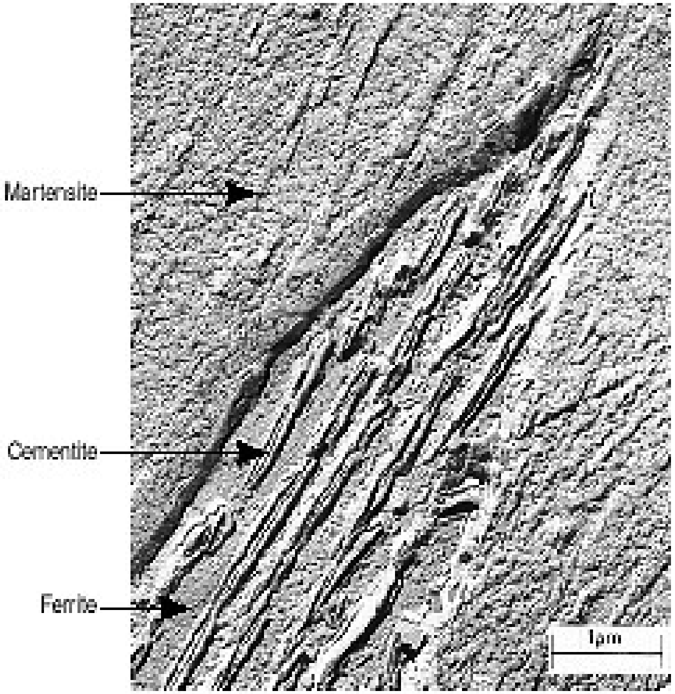
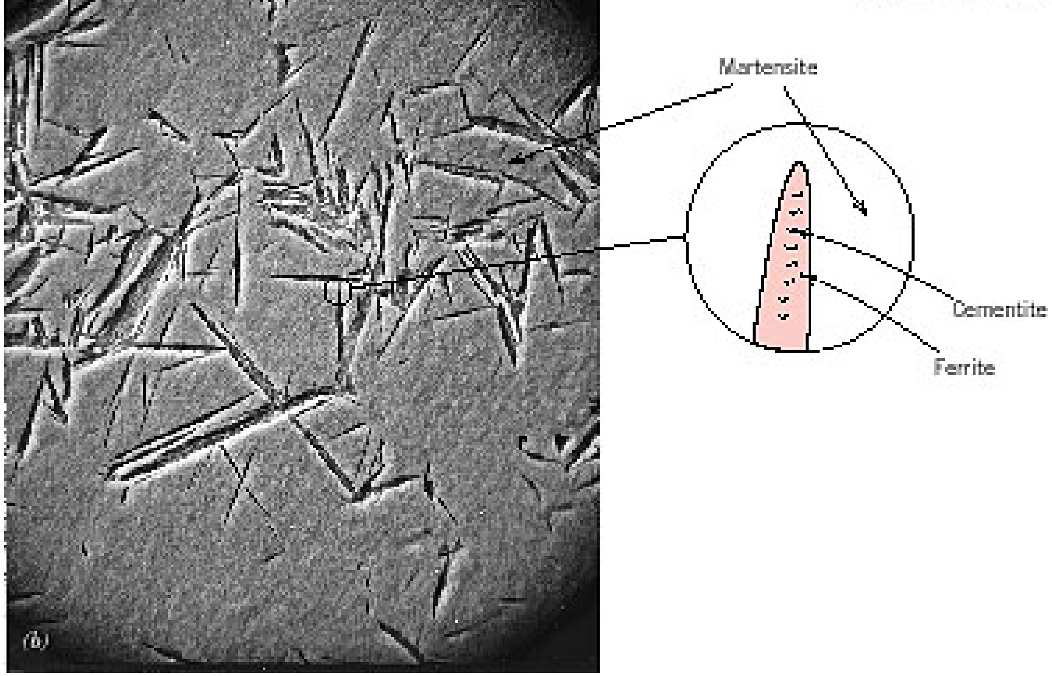


FIGURE 10.9 Isothermal transformation diagram for an iron–carbon alloy of eutectoid composition, including austenite-to-pearlite (A–P) and austenite-to-bainite (A–B) transformations. (Adapted from H. Boyer, Editor, *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 28.)

Figure 10.8 (*a*) Replica transmission electron micrograph showing the structure of upper bainite. A grain of bainite passes from lower left to upper right-hand corners, which consists of elongated and needle-shaped particles of Fe_3C within a ferrite matrix. The phase surrounding the bainite is martensite. (Reproduced with permission from *Metals Handbook*, Vol. 8, 8th edition, *Metallography, Structures and Phase Diagrams*, American Society for Metals, Materials Park, OH, 1973.) (*b*) Scanning electron micrograph showing lower bainite in a martensite matrix for an AISI steel that was transformed isothermally at 300°C. The inset shows the detail of a lower bainite grain. 2300×. (From John D. Verhoeven, *Fundamentals of Physical Metallurgy*, p. 502. Copyright © 1975 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

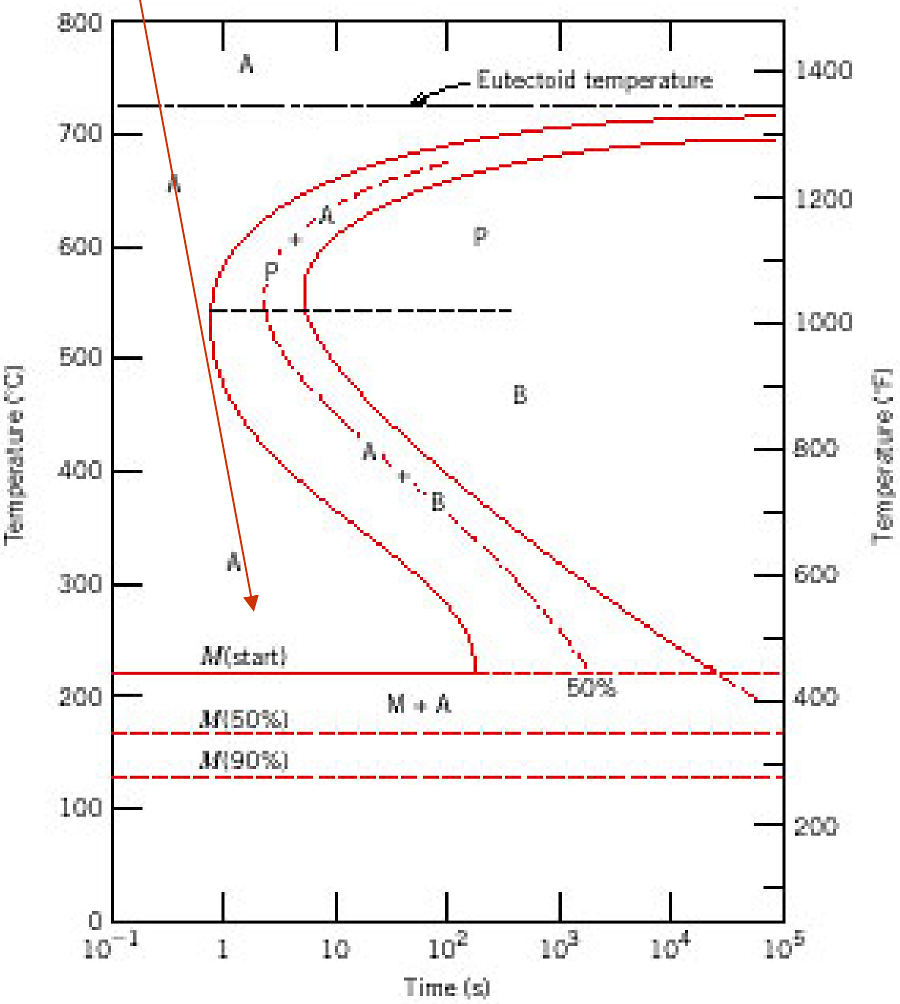


(a)



Martensite

Athermal transformation



Massive martensite

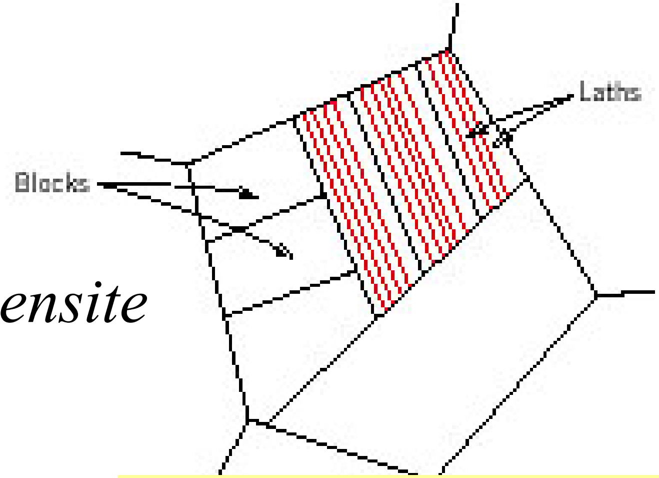
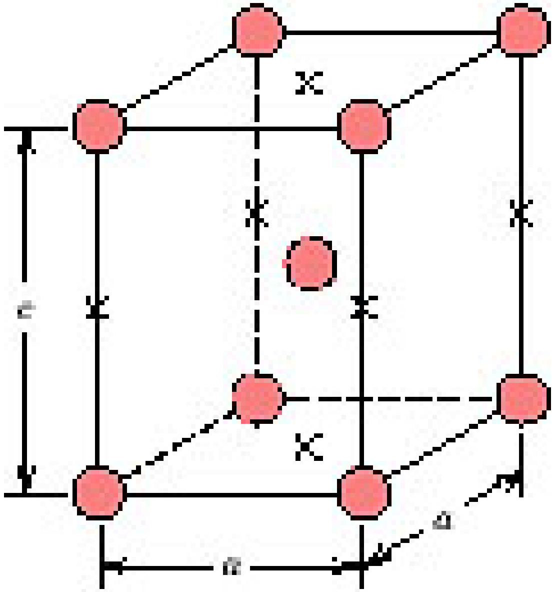


Plate martensite



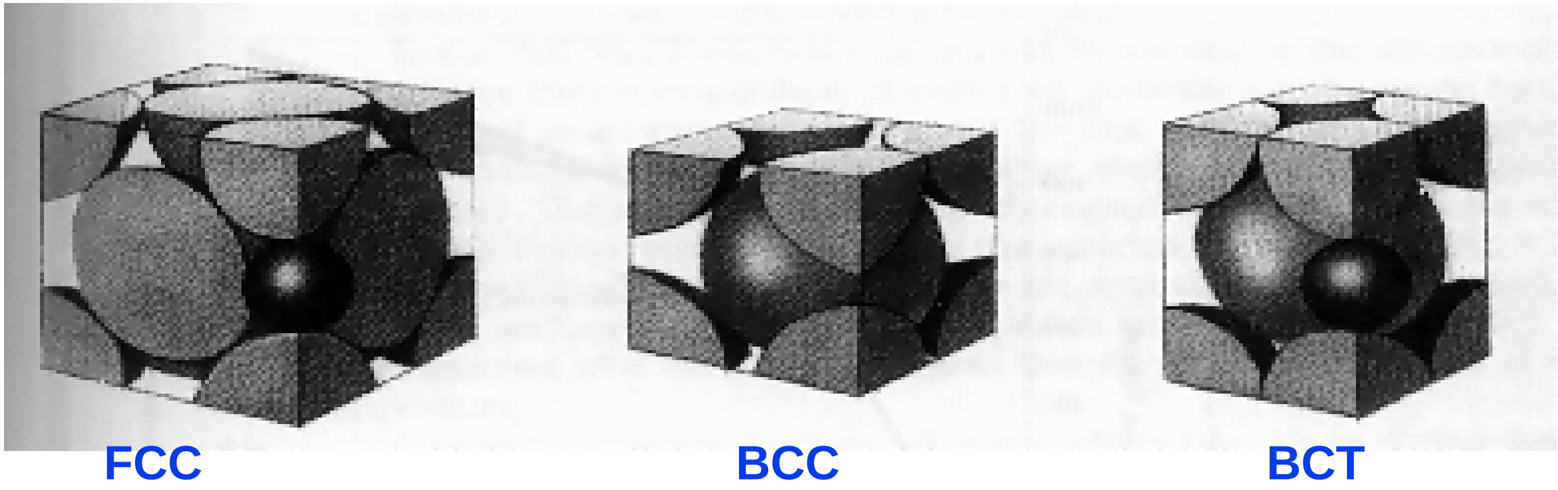
Body centered tetragonal (BCT) structure.

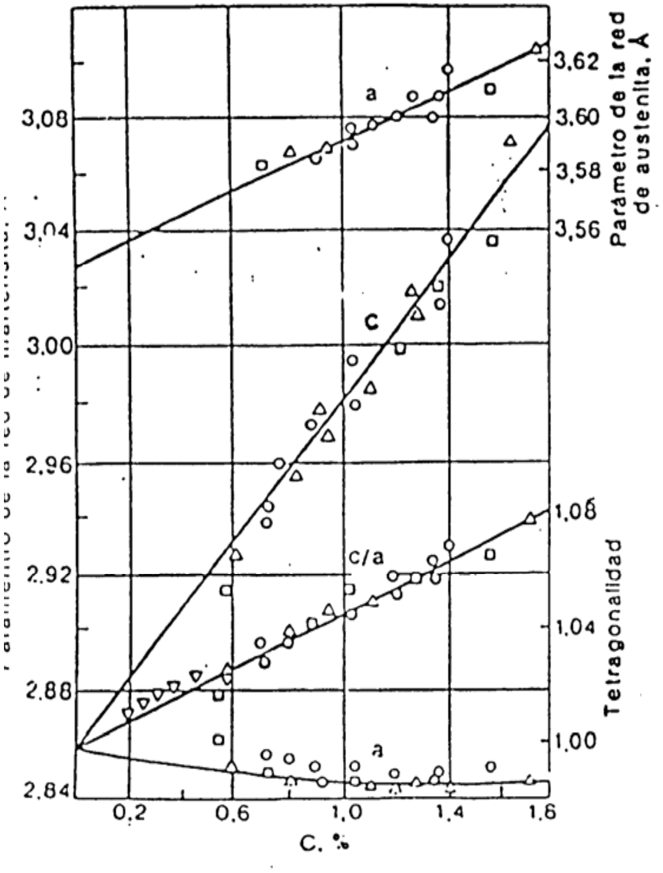
“M_s” stands for “*Martensite Start Temperature*” and

“M_f” stands for “*Martensite Finished Temperature*”.

Due to the fast cooling, diffusion of carbon is restricted. To make room for the carbon atoms, the lattice stretches along one crystal direction.

Martensite is a metastable phase.





Martensite is a supersaturated solution of carbon in iron.

Due to the high lattice distortion, martensite has high residual stresses.

The high lattice distortion induces high hardness and strength to the steel.

However, ductility is loss (martensite is too brittle) and a post heat treatment is necessary.

Heat treatment

Examples

(a) rapidly cool to 350^{o}C; hold 10^4s and then quench to room temp.

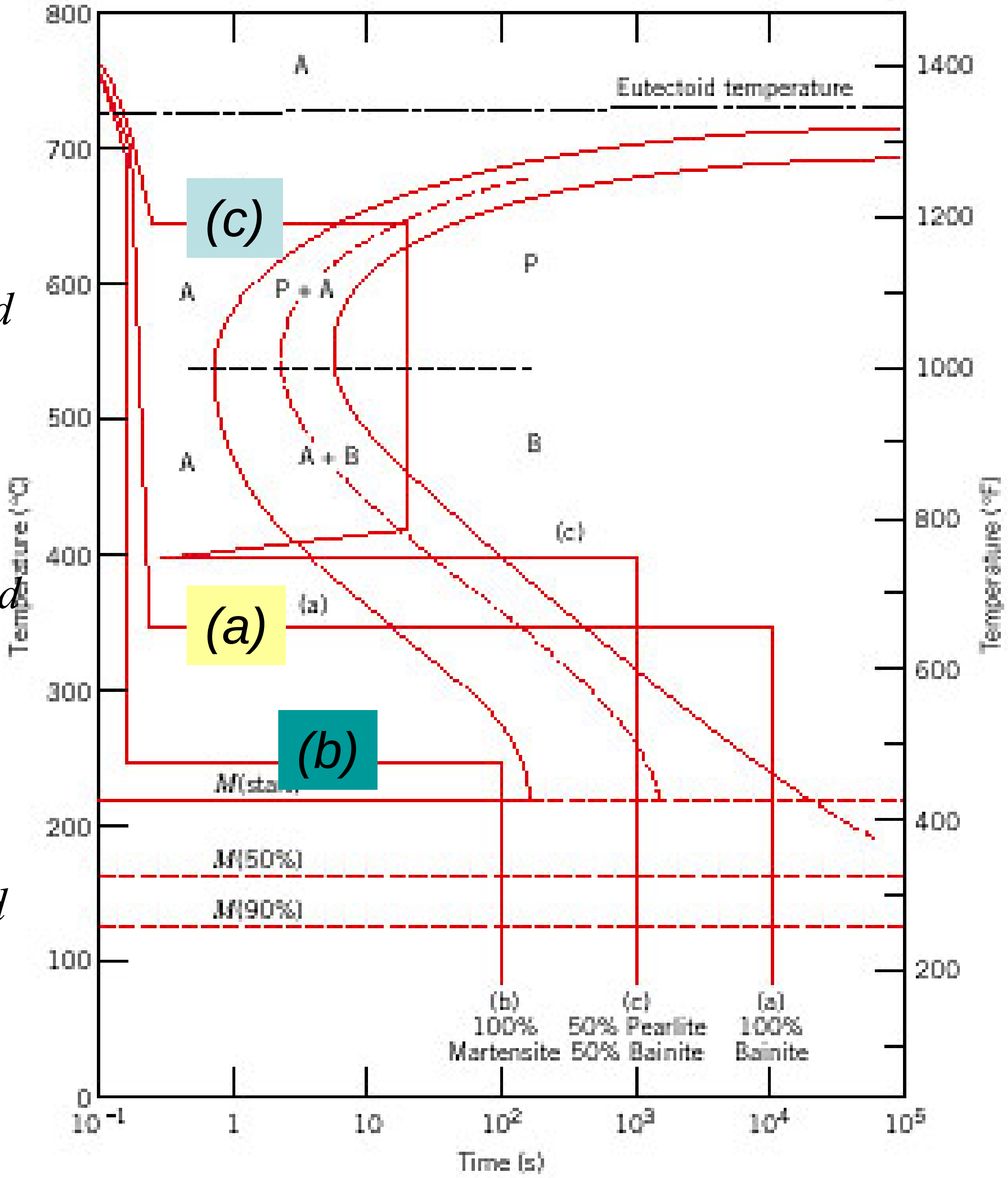
100% bainite

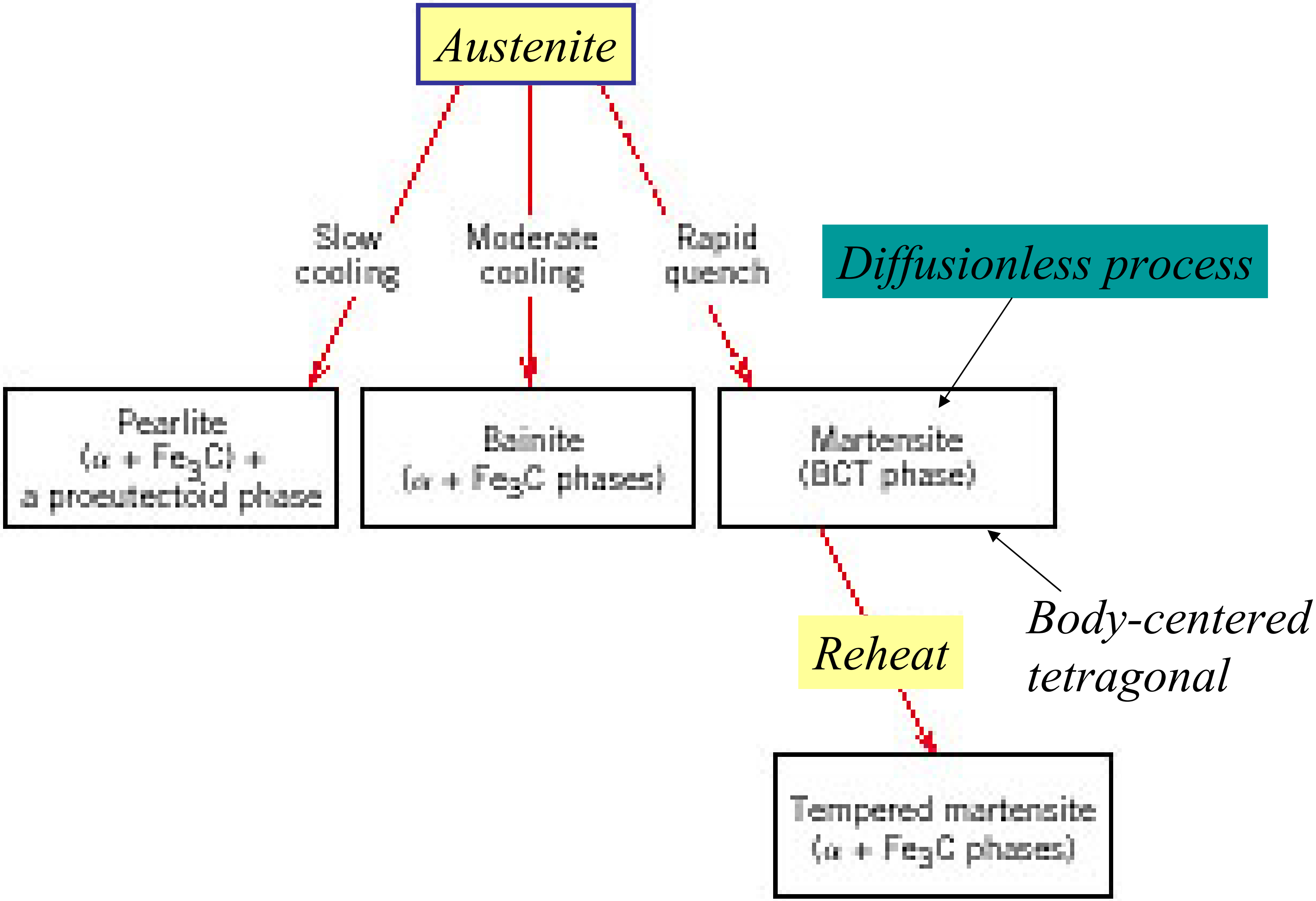
(b) rapidly cool to 250^{o}C; hold 100s and then quench to room temp.

100% martensite

(c) rapidly cool to 650^{o}C; hold 20s and rapidly cool to 400^{o}C, hold 103s, and and then quench to room temp.

50% pearlite + 50% bainite





Austenite

Slow cooling

Moderate cooling

Rapid quench

Diffusionless process

Pearlite
(α + Fe_3C) +
a proeutectoid phase

Bainite
(α + Fe_3C phases)

Martensite
(BCT phase)

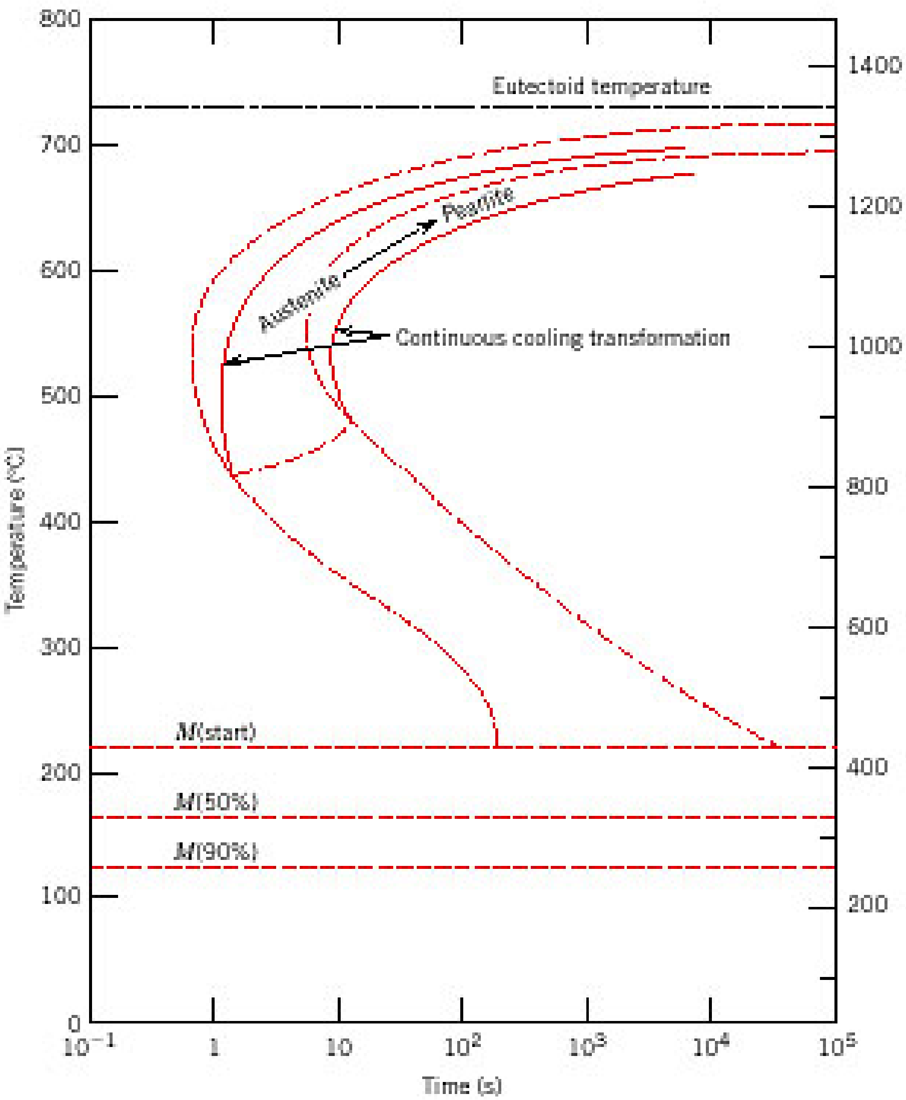
Body-centered tetragonal

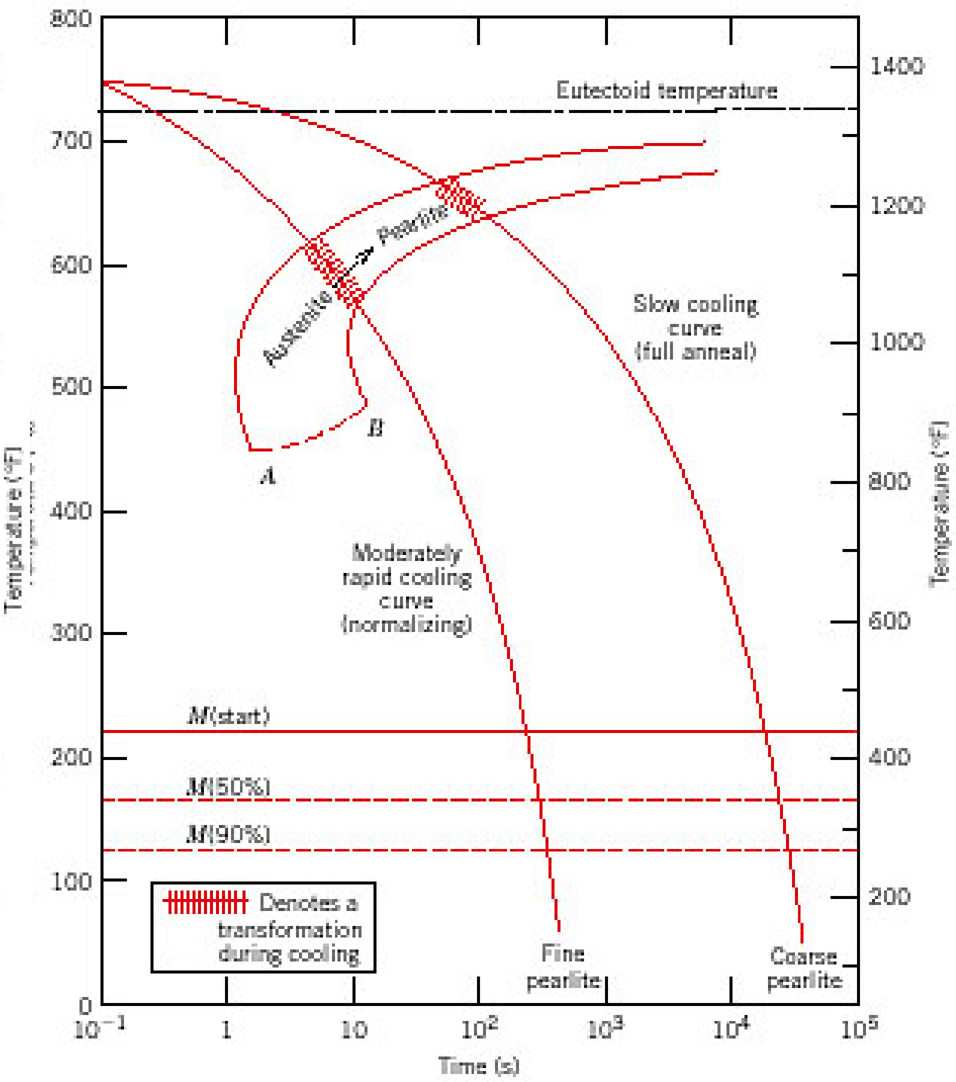
Reheat

Tempered martensite
(α + Fe_3C phases)

Temper embrittlement : reduction of toughness after tempering

Continuous Cooling Transformation *+ cooling curve*





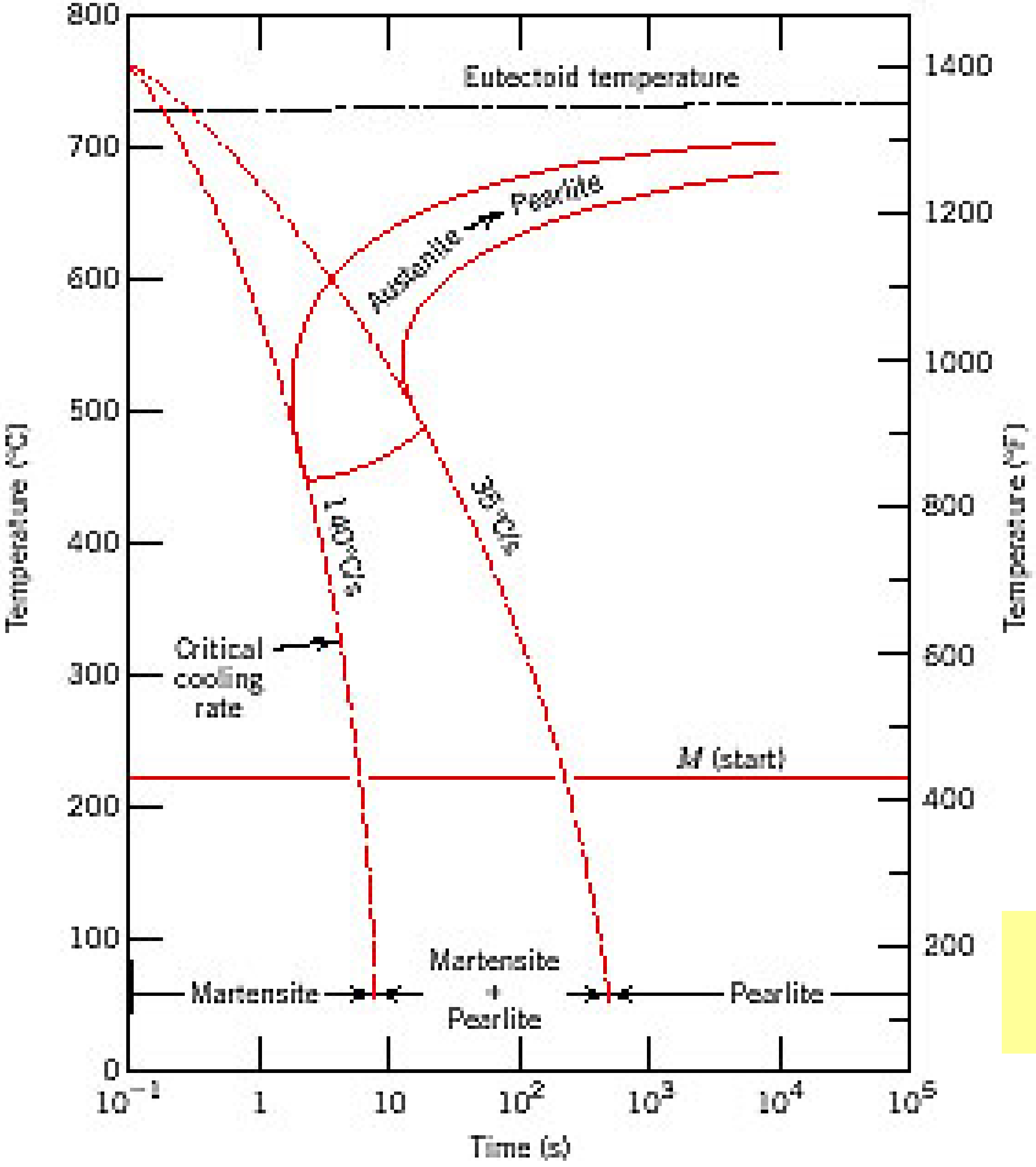


FIGURE 10.19 Continuous cooling transformation diagram for a eutectoid iron–carbon alloy and superimposed cooling curves, demonstrating the dependence of the final microstructure on the transformations that occur during cooling.

Control of final structures

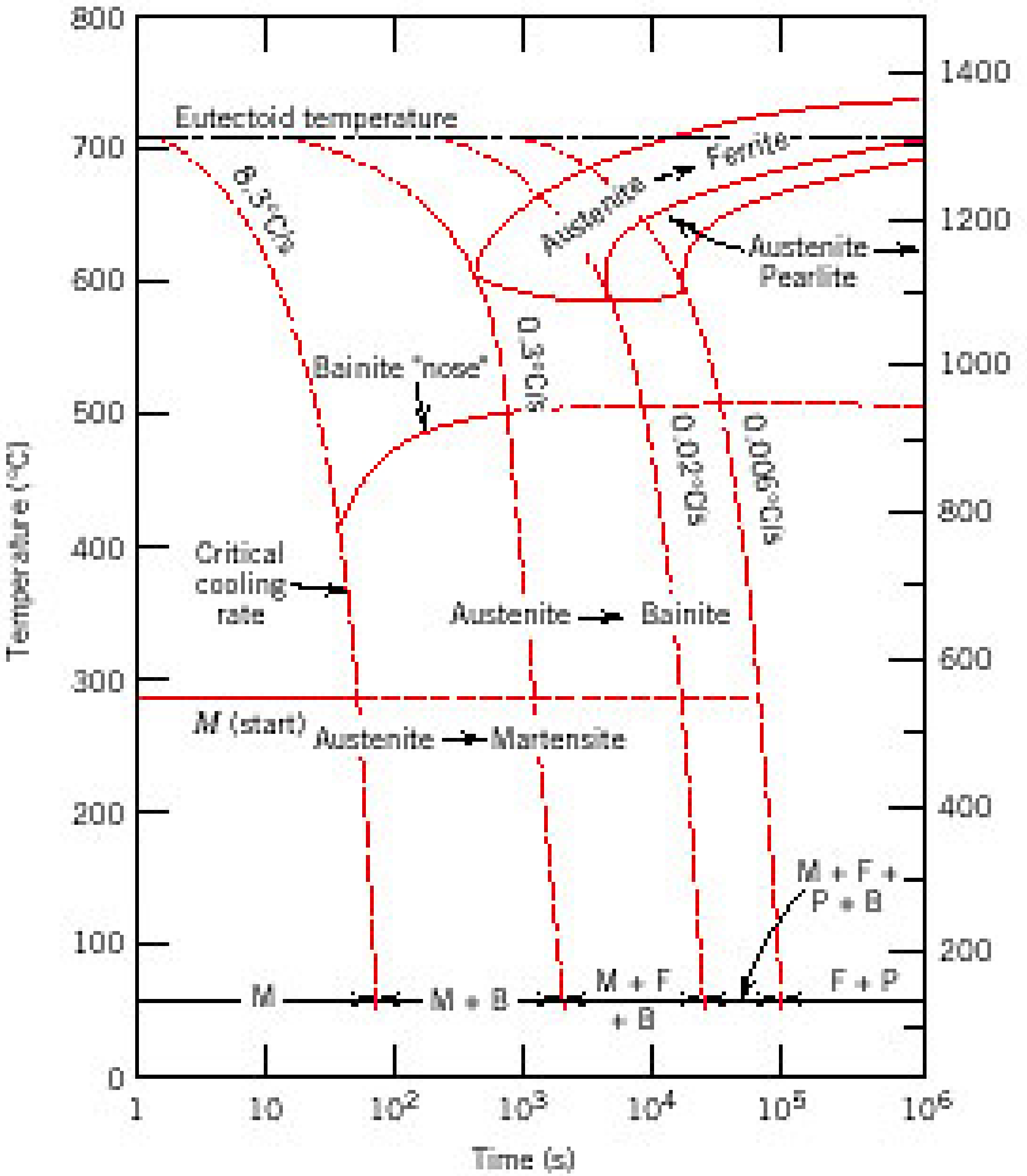


FIGURE 10.20 Continuous cooling transformation diagram for an alloy steel (type 4340) and several superimposed cooling curves demonstrating dependency of the final microstructure of this alloy on the transformations that occur during cooling. (Adapted from H. E. McGannon, Editor, *The Making, Shaping and Treating of Steel*, 9th edition, United States Steel Corporation, Pittsburgh, 1971, p. 1096.)

Common Industrial Heat Treatments

- **Annealing (slow cooling from austenitizing temperature. Product: coarse pearlite)**

- **Normalizing (air cooling from austenitizing temperature. Product: fine pearlite)**

- **Quench & Temper. Quench (fast – water or oil – cooling from austenitizing temperature. Product: martensite). Tempering (heating to $T < A_1$ to increase ductility of quenched steels)**

- **Martempering. (Quench to T above M_s and soak until all the steel section is at that temperature, then quench to ambient temperature. Product: Martensite)**

- **Austempering. (Quench to T above M_s and soak until phase transformation takes place. Product: Bainite**

Annealing

Stages of annealing:

- Heating to required temperature
- Holding (“soaking”) at constant temperature
- Cooling

The time at the high temperature (soaking time) is long enough to allow the desired transformation to occur.

Cooling is done slowly to avoid warping/cracking of due to the thermal gradients and thermo-elastic stresses within the or even cracking the metal piece.

Purposes of annealing:

- Relieve internal stresses
- Increase ductility, toughness, softness
- Produce specific microstructure

Examples of heat treatment

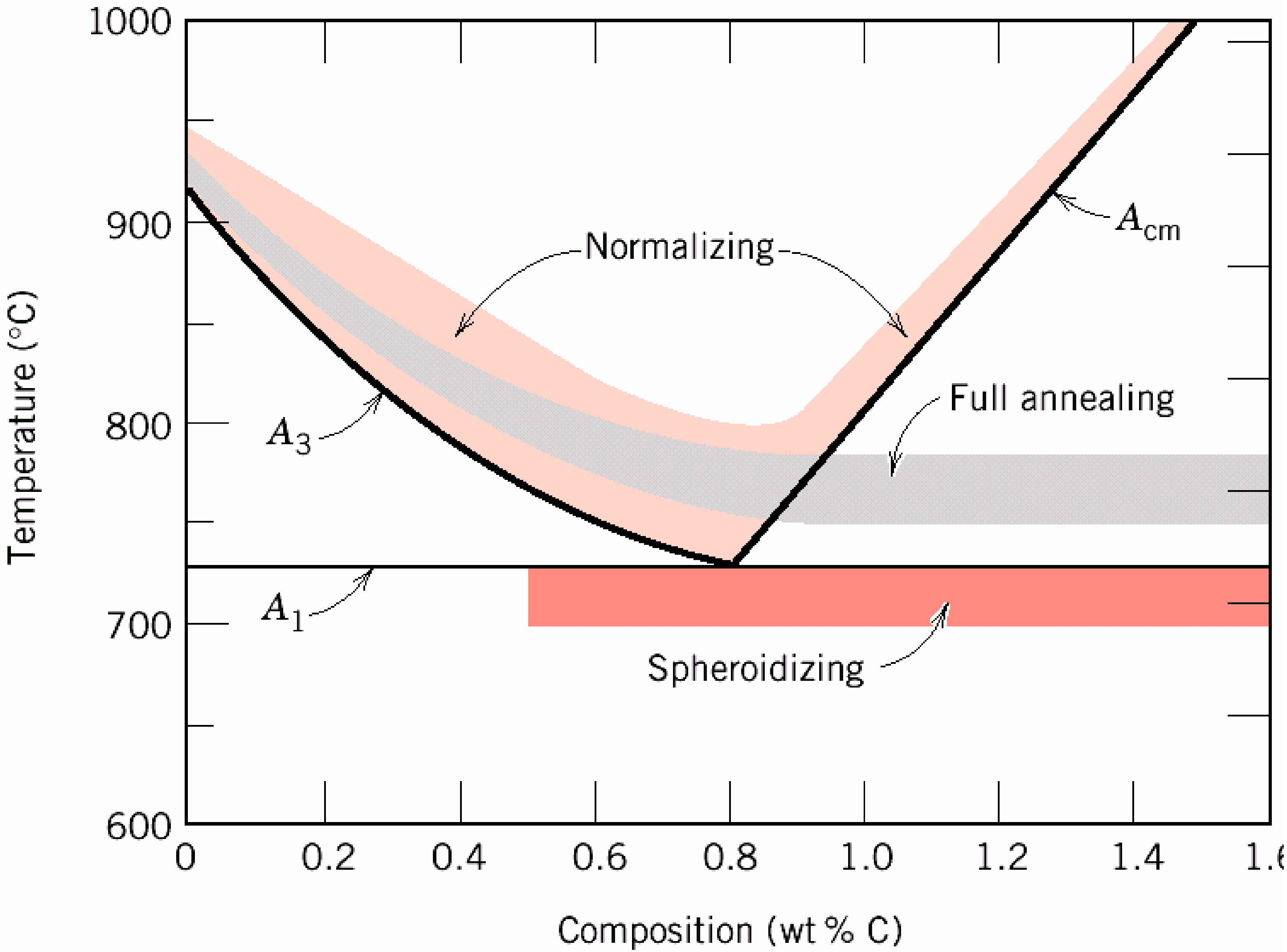
Process Annealing - effects of work-hardening (recovery and recrystallization) and increase ductility. Heating is limited to avoid excessive grain growth and oxidation.

Stress Relief Annealing – minimizes stresses due to

Plastic deformation during machining

- Nonuniform cooling
- Phase transformations between phases with different densities

Annealing temperatures are relatively low so that useful effects of cold working are not eliminated.


1000
900
800
700
600
Temperature (°C)
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Composition (wt % C)
Normalizing
A_{cm}
A_3
Full annealing
A_1
Spheroidizing

- **Lower critical temperature** A_1 below which austenite does not exist
- **Upper critical temperature** lines, A_3 and A_{cm} above which all material is austenite
- **Austenitizing** – complete transformation to austenite

Full annealing: austenizing and slow cooling (several hours). Produces coarse pearlite (and possible proeutectoid phase) that is relatively soft and ductile. It is used to soften pieces which have been hardened by plastic deformation, and which need to undergo subsequent machining/forming.

Temperatures for full annealing:

Hypoeutectoid steel : $A_3 + 50^oC$

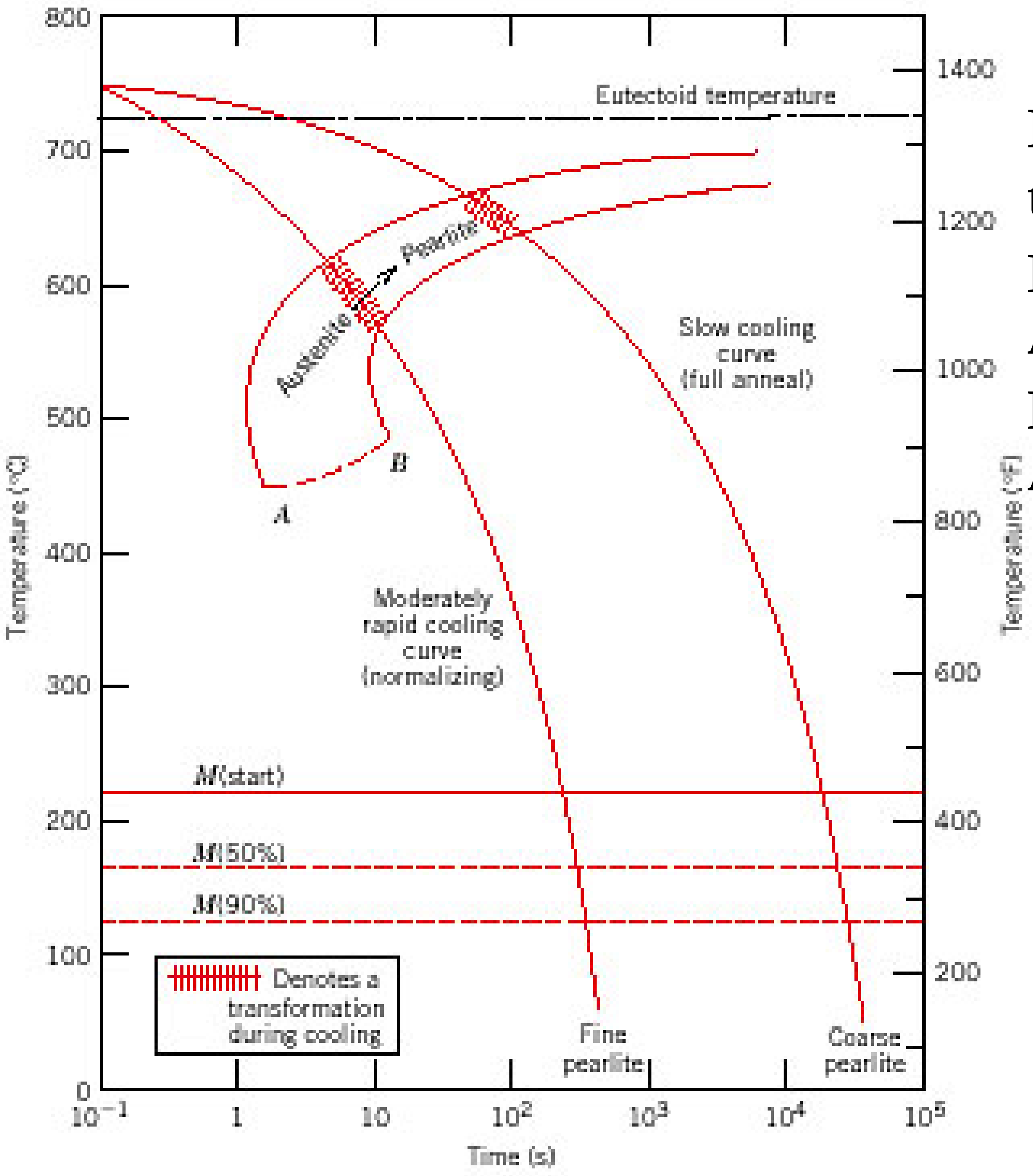
Hypereutectoid steel : $A_{1,3} + 50^oC$

Normalizing

Annealing heat treatment just above the upper critical temperature to reduce grain sizes (of pearlite and proeutectoid phase) and make more uniform size distributions.

The interlamellar distance of pearlite decreases as the cooling rate increases.

- Slow cooling (annealing – furnace cooling) – coarse pearlite – interlamellar spacing of 4.5μm – hardness of 200BHN
- Medium to slow cooling (normalizing – still air cooling) – normal pearlite – interlamellar spacing of 3.0μm – hardness of 220BHN
- Medium to Fast (normalizing – forced air cooling) – fine pearlite – interlamellar spacing of 2.0μm – hardness of 300BHN



Normalizing temperatures:

Hypoeutectoid steel :

$A_3 + 50^oC$

Hypereutectoid steel :

$A_{cm} + 50^oC$

Spheroidizing: **prolonged heating just below the eutectoid temperature, which results in the soft spheroidite structure. This achieves maximum softness needed in subsequent forming operations.**

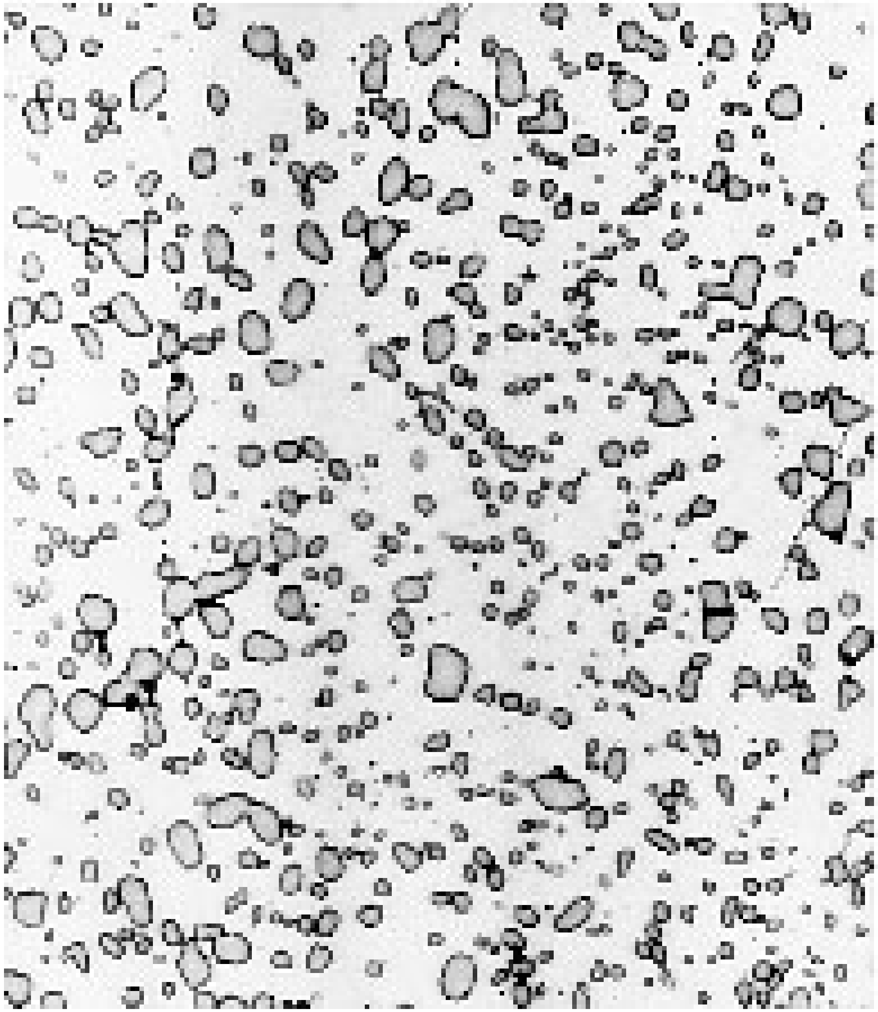


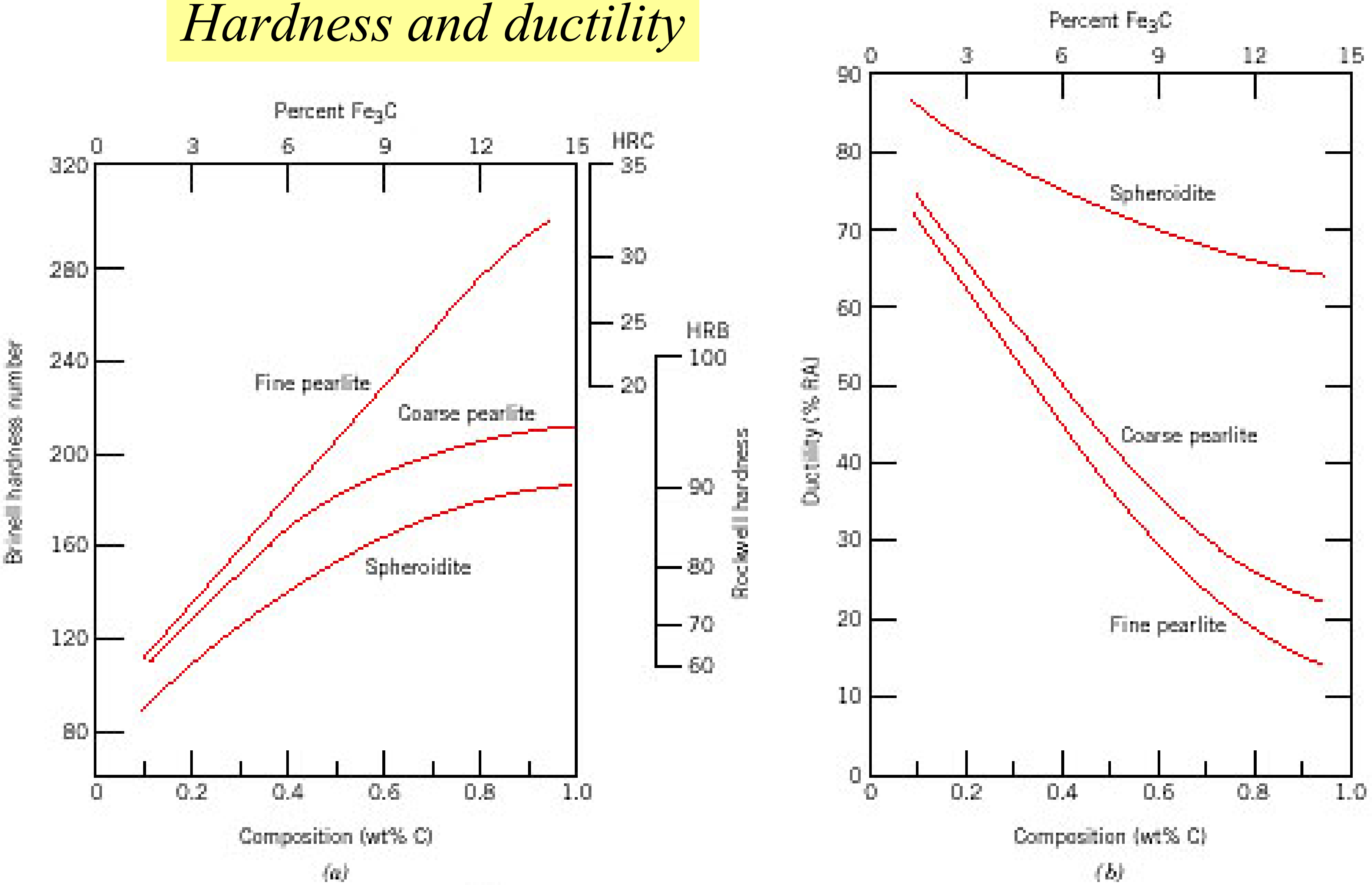
FIGURE 10.10 Photomicrograph of a steel having a spheroidite microstructure. The small particles are cementite; the continuous phase is α ferrite. 1000×. (Copyright 1971 by United States Steel Corporation.)

$$\textit{Pearlite or bainite} \xrightarrow[\textit{18\sim24h}]{\textit{Heating}} \textit{Spheroidite}$$

below the eutectoid temp.

Reduction of α /Fe_3C GB area

Hardness and ductility



Quenching

The most common method to harden a steel.

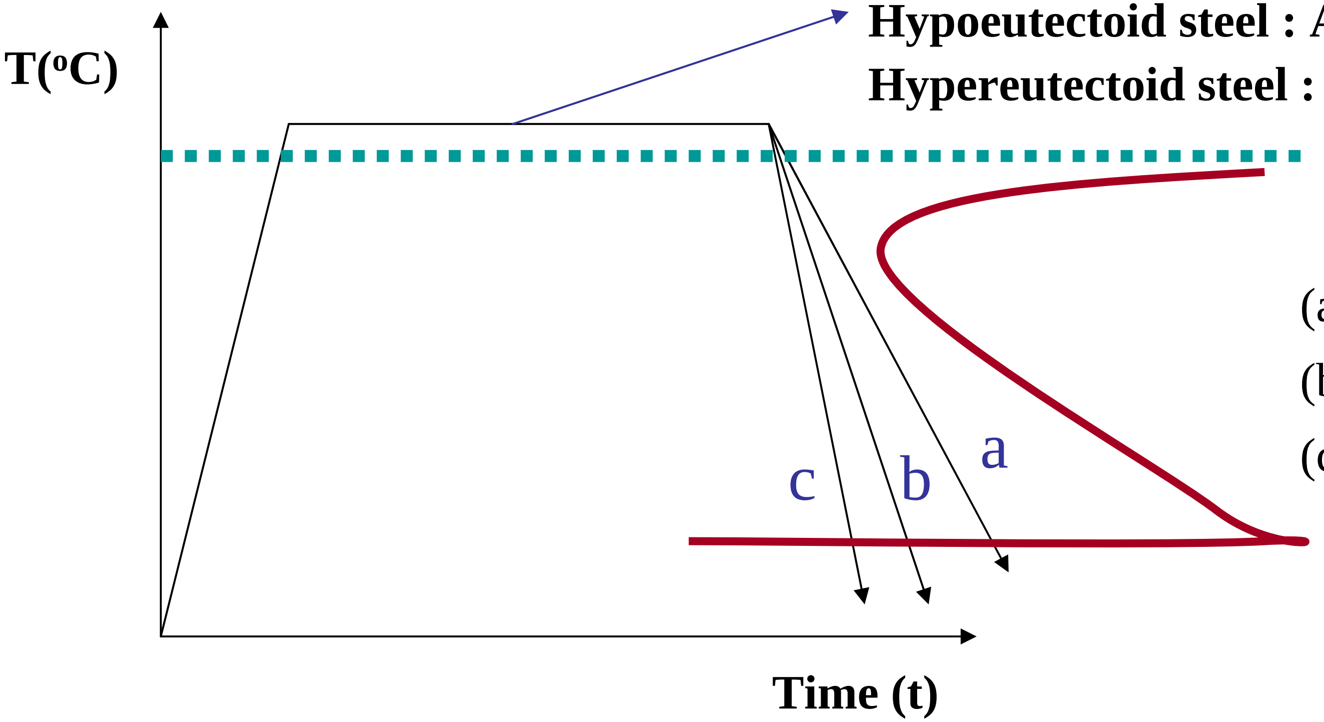
It consists of heating to the austenizing temperature (hypoeutectoid steel) and cooling fast enough to avoid the formation of ferrite, pearlite or bainite, to obtain pure martensite.

Martensite (α’) has a distorted BCT structure. It is the hardest of the structures studied. The higher hardness is obtained at 100% martensite.

Martensite hardness depends solely of the carbon content of the steel. The higher the carbon content, the higher the hardness.

Martensite is very brittle and can not be used directly after quench for any application.

Martensite brittleness can be reduced by applying a post-heat treatment known as - *tempering*.



Austenizing temperature:

Hypoeutectoid steel : $A_3 + 50^{\circ}$C

Hypereutectoid steel : $A_{1,3} + 50^{\circ}$C

(a) Cooling in oil

(b) Cooling in water

(c) Cooling in brine

Cooling depends on the geometry and mass of the component.

External surfaces are cooled faster than the inner core of the component.

Tempering of Martensitic Steels

- Martensite is too brittle to serve engineering purpose
- Tempering is necessary to increase ductility and toughness of martensite. Some hardness and strength is lost.
- Tempering consist on reheating martensitic steels (solution supersaturated of carbon) to temperatures between 150-500º C to force some carbide precipitation.

1st stage 80-160º C

$$\alpha' \longrightarrow \alpha''(\text{low C martensite}) + \varepsilon_{\text{carbide}}\ (Fe_{2.3}C)$$

2nd stage 230-280º C

$$\gamma_{\text{retained}} \longrightarrow \text{bainite}$$

3rd stage 160-400º C

$$\alpha'' + \varepsilon_{\text{carbide}} \longrightarrow \alpha + Fe_3C(\text{tempered martensite})$$

3rd stage (cont) 400-700ºC

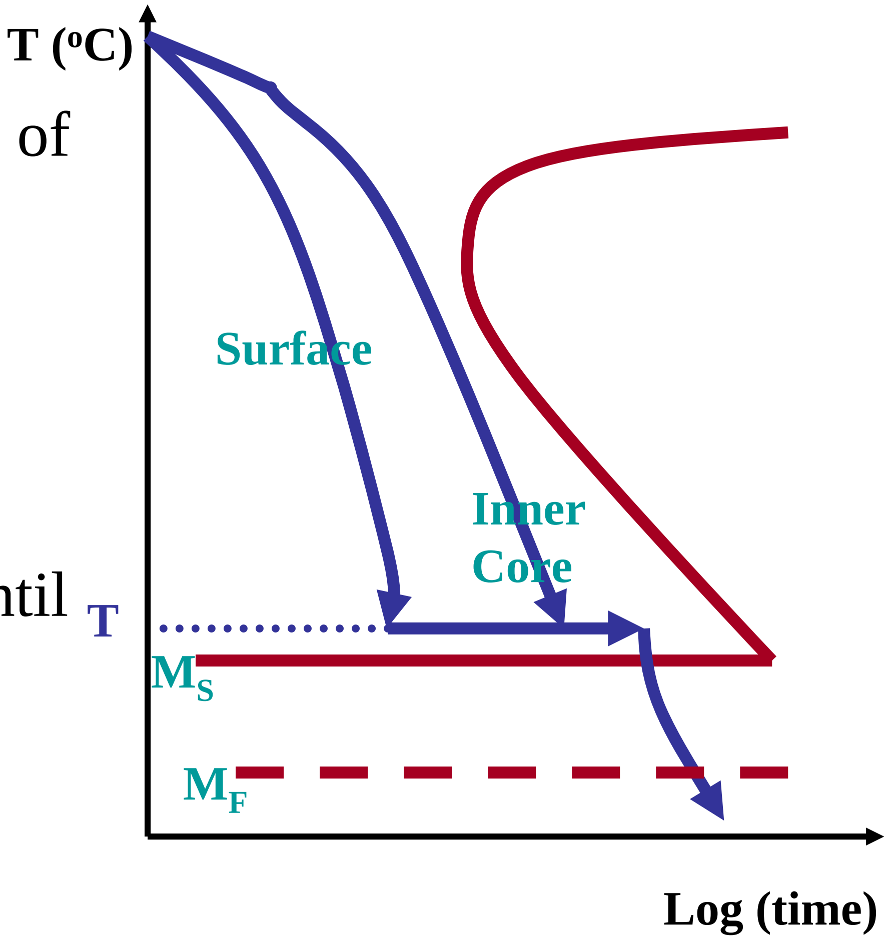
Growth and spherodization of cementite and other carbides

Martempering

A process to prevent the formation of quench cracks in the steel.

Cooling is carried out, as fast as possible, to a temperature over the M_S of the steel.

The steel is maintained at $T > M_S$ until the inner core and outer surface of the steel component is at the same temperature.



The steel is then cooled below the M_F to obtain 100% martensite. There is a need to increase the ductility of this steel by tempering.

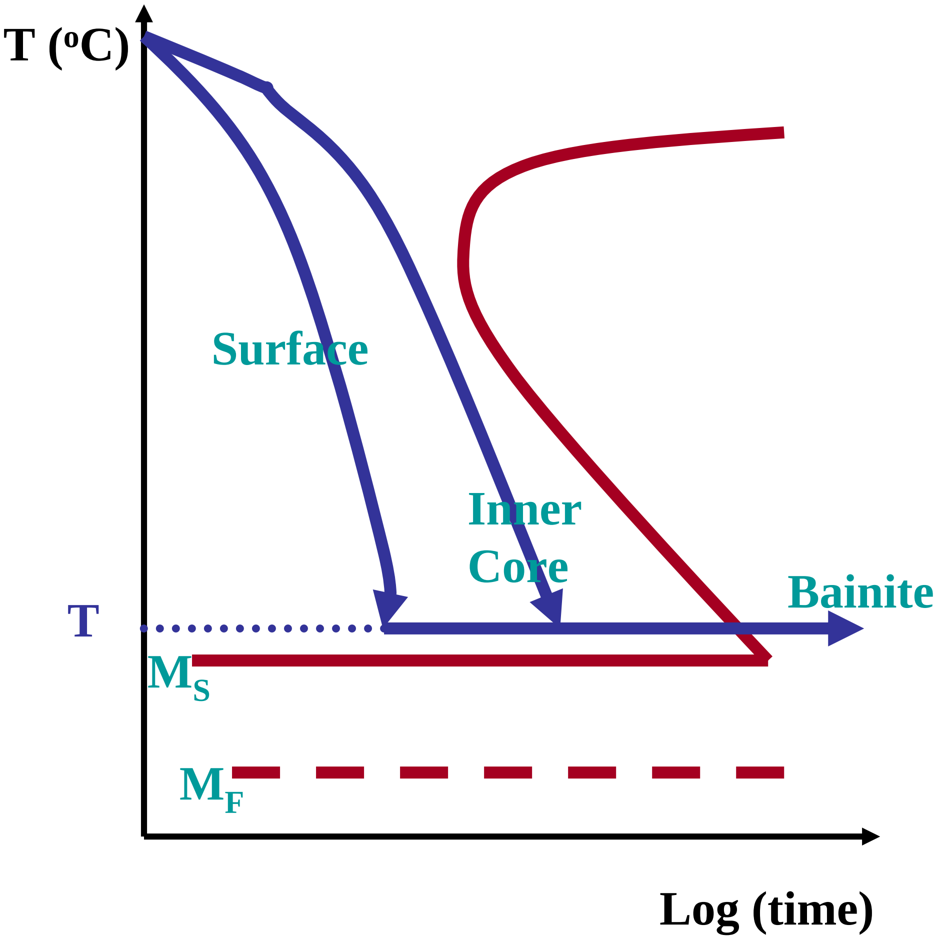
Austempering

A process to prevent the formation of quench cracks in the steel.

Cooling is carried out, as fast as possible, to a temperature over the M_S of the steel.

The steel is maintained at $T>M_S$ until the austenite transforms to 100% bainite.

There is no need of tempering post treatment.



Hardenability

Hardenability is the ability of the Fe-C alloy to transform to martensite during cooling. It depends on alloy composition and quenching media.

Hardenability should not be confused with “hardness”. A qualitative measure of the rate at which hardness decreases with distance from the surface because of decreased martensite content.

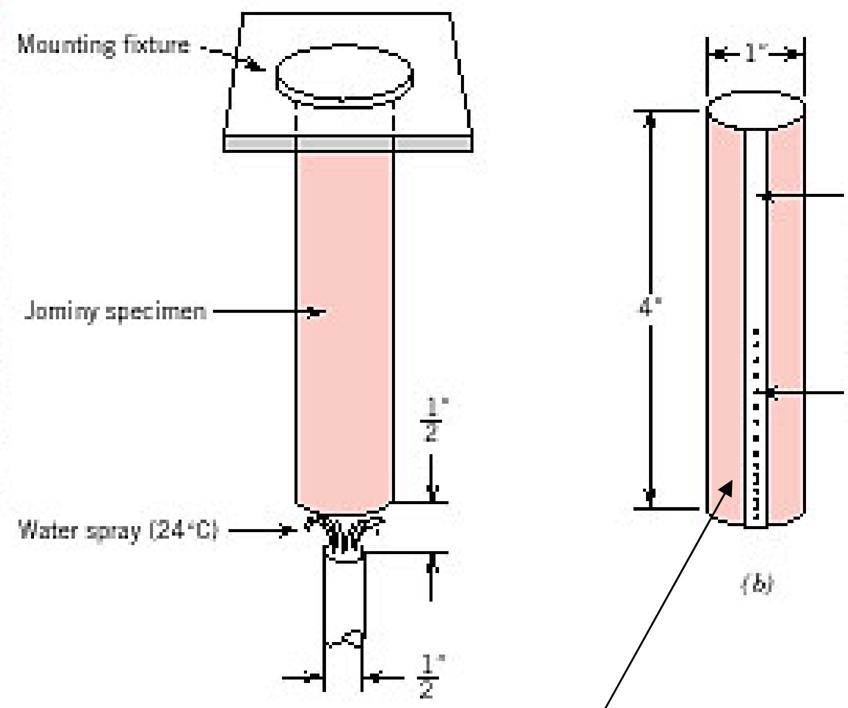
High hardenability means the ability of the alloy to produce a high martensite content throughout the volume of specimen.

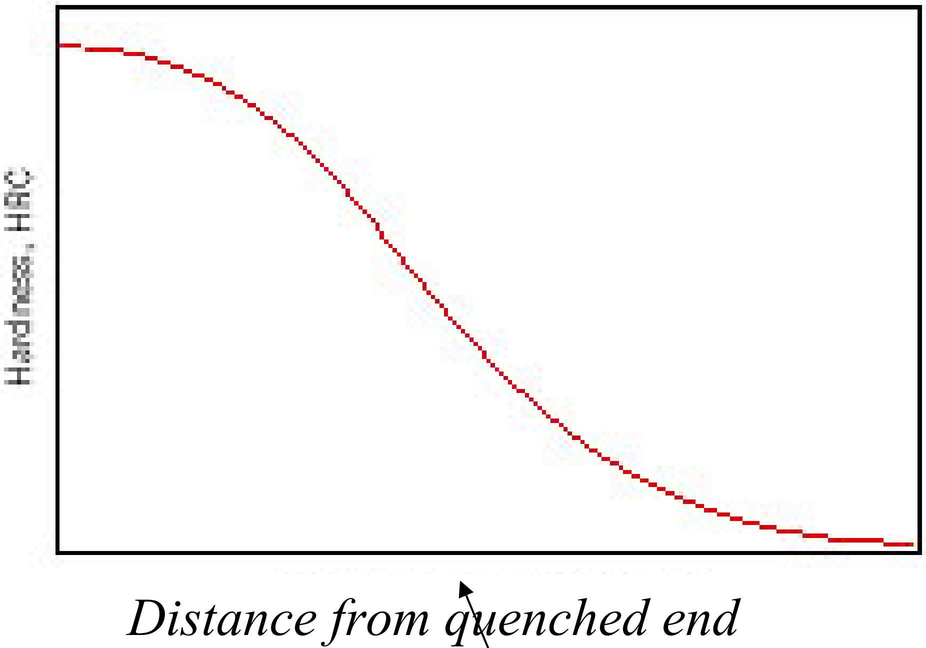
Hardenability is measured by the Jominy end-quench test performed in a standard procedure (cylindrical specimen, austenitization conditions, quenching conditions - jet of water at specific flow rate and temperature).

Hardenability

Ability to be hardened by the formation of martensite as a result of heat treatment

Jominy End-Quench Test

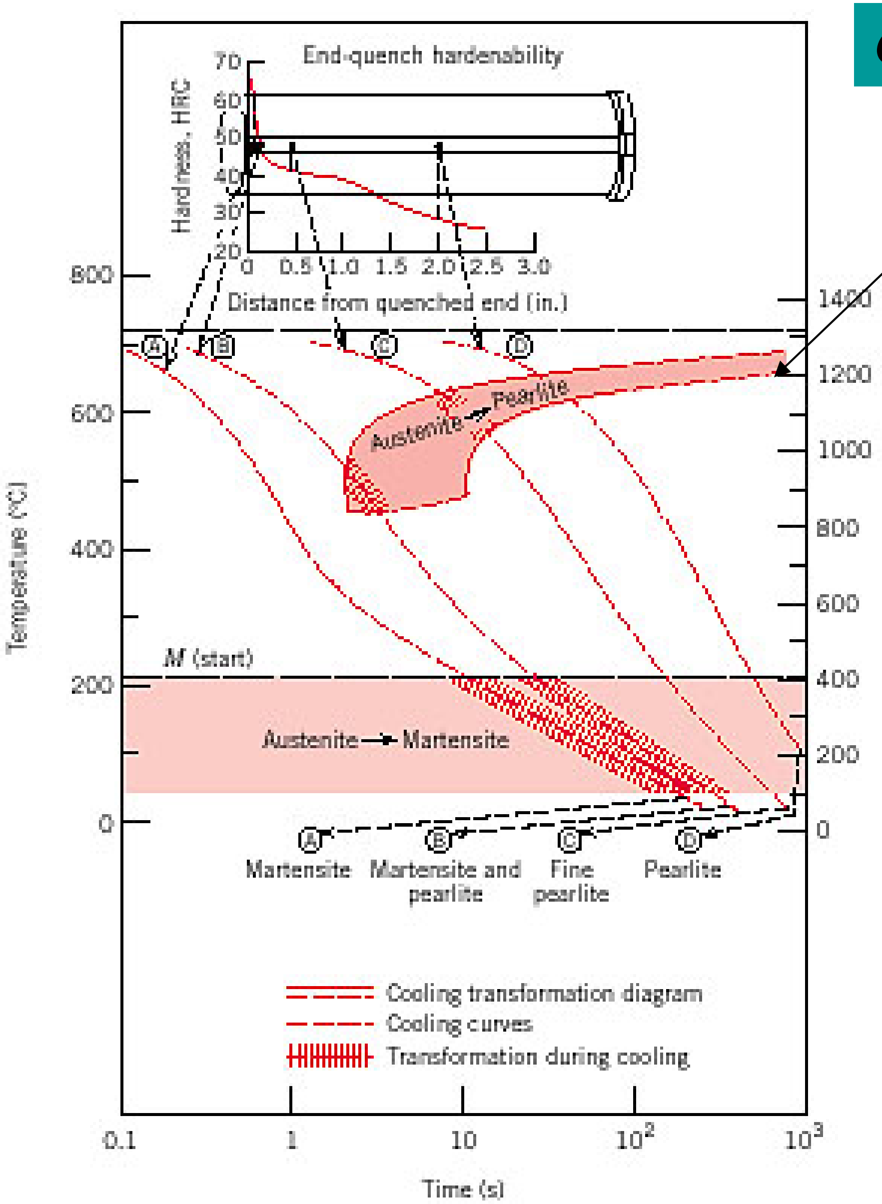




Rockwell Hardness

Different Cooling rate !!

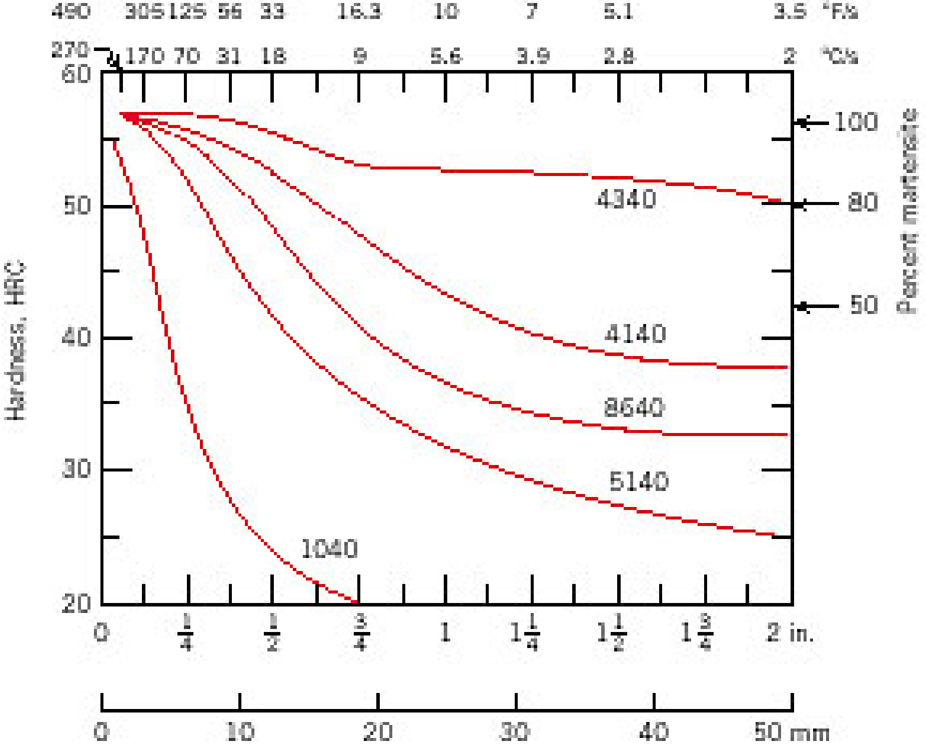
Hardness versus Cooling Rate



Continuous Cooling Transformation

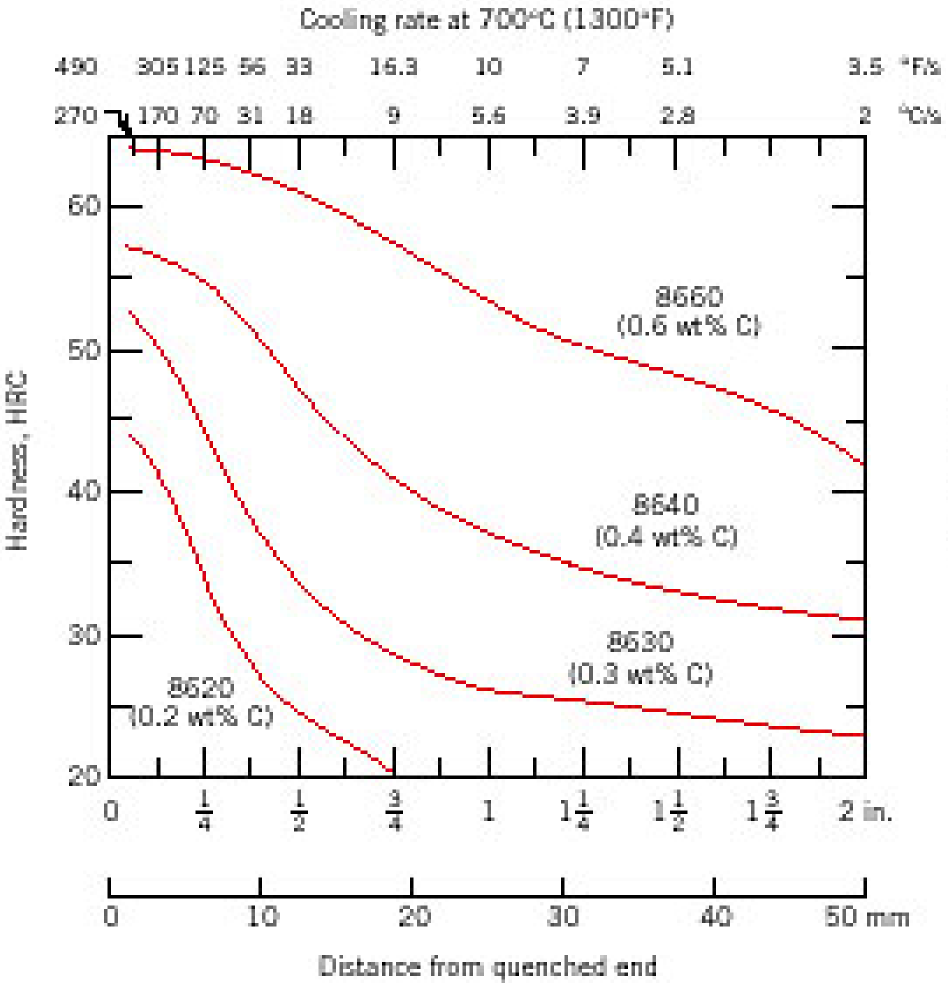
Hardenability Curve

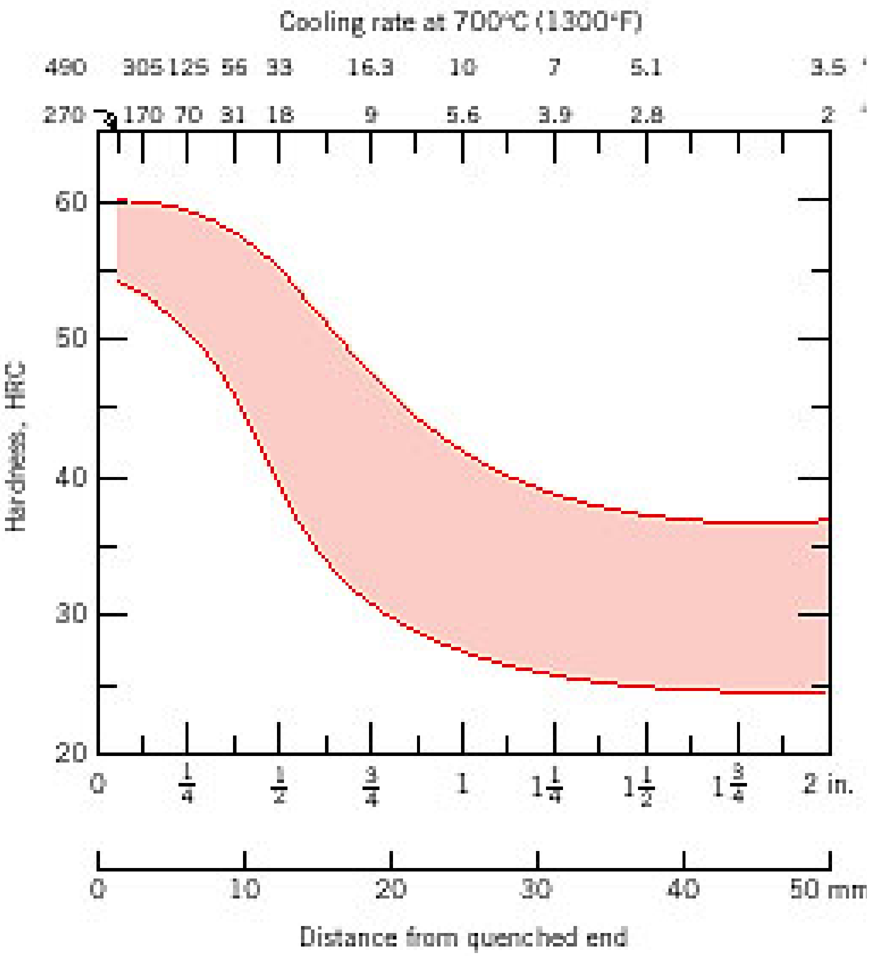
Cooling rate



Distance from quench end

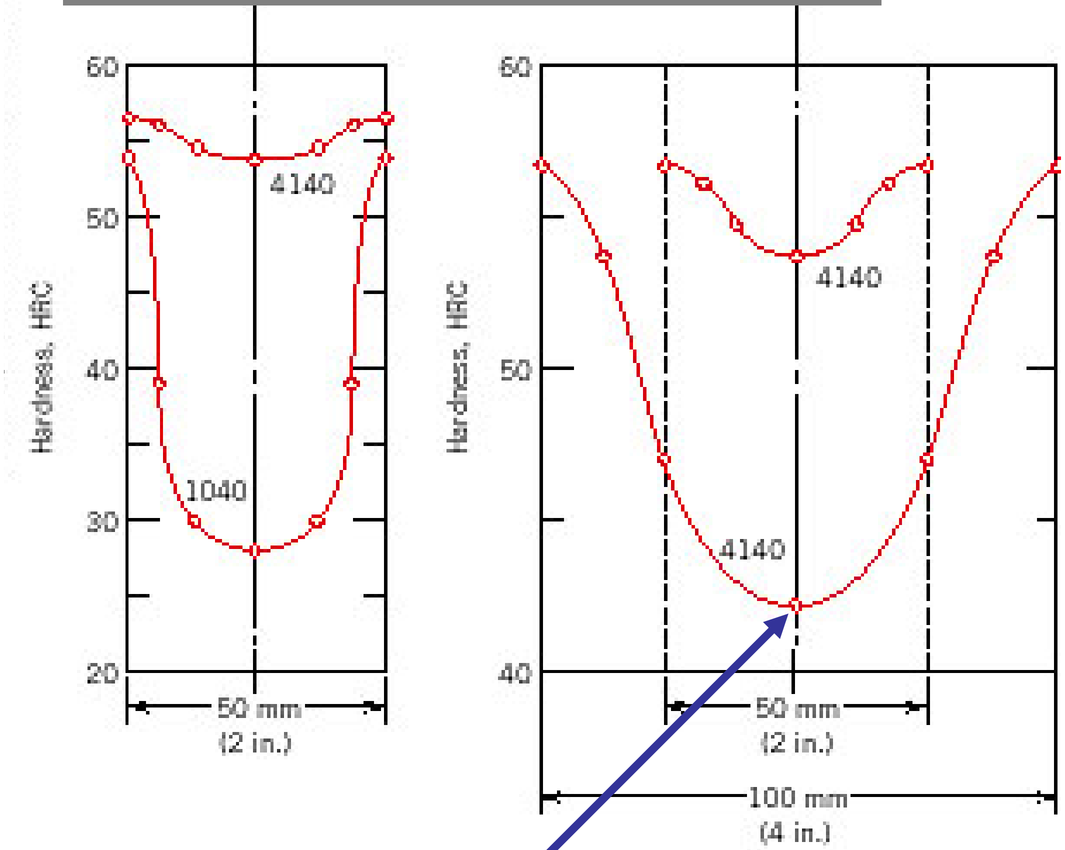
High carbon content, better hardenability



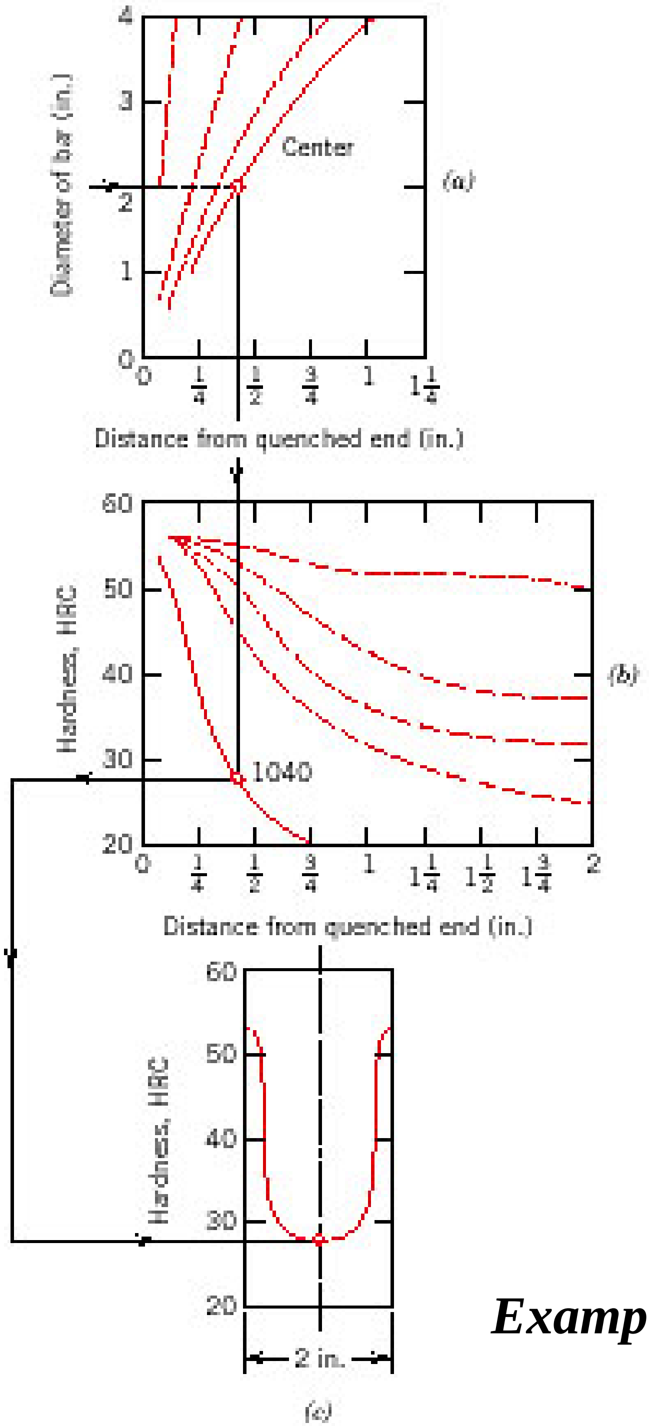


Use the hardenability data in the generation of hardness profile

Larger specimen, lower cooling rate



Closer to the center, lower the cooling rate



Example