Introduction to Engineering Materials

Phase Transformations

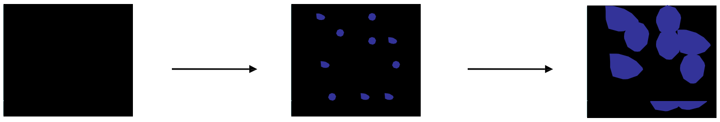
- Time and temperature dependence of phase transformations.
- Engineering non-equilibrium structures.
- Differences in mechanical properties between equilibrium and non-equilibrium structures (steel).
- Phase transformations in polymers.

Phase transformation

- Takes time (transformation rates: <u>kinetics</u>).
- Involves movement/rearrangement of atoms.
- Usually involves changes in microstructure.

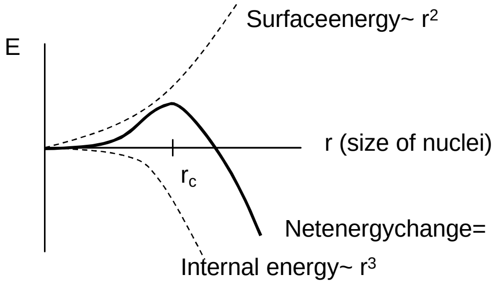
1. **“Simple” diffusion-dependent transformation**: no change in number or compositions of phases present (e.g. solidification of pure elemental metals, allotropic transformation, recrystallization, grain growth).
2. **Diffusion-dependent transformation:** transformation with alteration in phase composition and, often, with changes in number of phases present (e.g. eutectoid reaction).
3. **Diffusionless transformation:** e.g. rapid T quenching to “trap” metastable phases.

Kinetics of solid state reactions



Phase 1 (e.g. liquid) **Nucleation** of 2nd phase **Growth**

1. **Nucleation** (homogeneous): What hinders nucleation?



Net energy change = $\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$

Initially the surface energy dominates but eventually bulk energy takes over. **Need nuclei larger than critical radius before growth occurs!**

Kinetics of solid state reactions

Critical nucleus size (r_c) and the activation energy (ΔG^*)

Net energy = ΔG = $\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma$

Volume free energy change

surface free energy

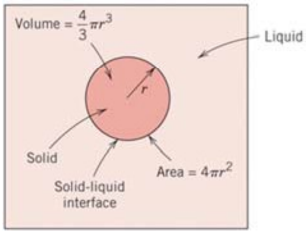
Take the derivative and set equal to zero to find max.

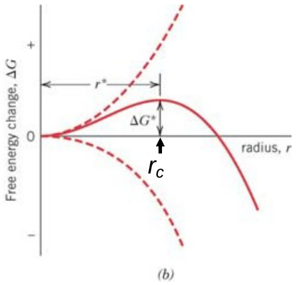
$$\frac{d(\Delta G)}{dr} = \frac{4}{3}\pi(\Delta G_v)(3r^2) + 4\pi\gamma(2r) = 0$$

$$r_c = -\frac{2}{\Delta G_v}$$

Sub-into overall ΔG equation

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2}$$





Kinetics of solid state reactions

In terms of heat of fusion ΔH_f (i.e. energy release upon solidification):

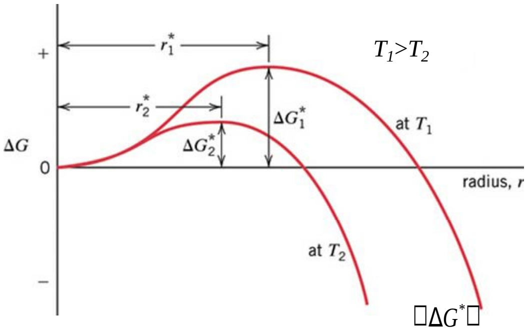
$$\Delta G_v = \frac{\Delta H_f (T_m - T)}{T_m}$$

Tells us how ΔG_v changes with temperature

With this definition, we then have:

$$r_c = -\frac{2\gamma}{\Delta H_f}\left(\frac{T_m}{T_m - T}\right)$$

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



As T decreases both r_c and ΔG^* becomes smaller

Number of stable nuclei: $n^* \propto \exp\left(-\frac{\Delta G^*}{kT}\right)$

→ **LIQUID INSTABILITY at LOWER TEMPERTURES**

Kinetics of solid state reactions

We also need to consider diffusion:

- Faster diffusion leads to more collisions between atoms.
- More collisions means higher probability of atoms sticking to each other.

Recall diffusion $$D = D_o \exp\left(-\frac{Q_d}{kT}\right)$$

Then, the frequency of atoms sticking together is directly related to diffusion:

Frequency of attachment: $$\nu_d \propto \exp\left(-\frac{Q_d}{kT}\right)$$

Kinetics of solid state reactions

Combining liquid instability and diffusion effects together:

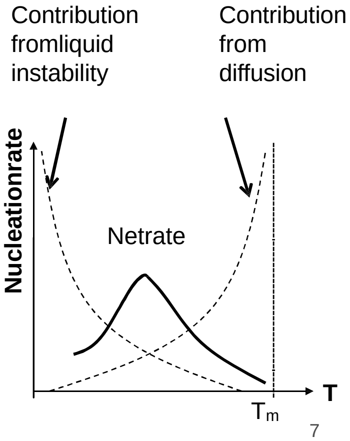
Rate of Nucleation

$$\frac{dN}{dt} = K n^{*} v_{d} = K' \exp\left(-\frac{\Delta G^{*}}{kT}\right)\exp\left(-\frac{Q_{d}}{kT}\right)$$

$$n^{*} \propto \exp\left(-\frac{\Delta G^{*}}{kT}\right) \qquad v_{d} \propto \exp\left(-\frac{Q_{d}}{kT}\right)$$

↑ Liquid instability

↑ Diffusion



Example problem: critical radius and activation energy for nucleation

A) If pure liquid gold is cooled to 230°C below its melting point, calculate the critical radius and the activation energy.

B) Calculate the number of atoms per nucleus of this critical size. Au is FCC with a = 0.413nm.

Kinetics of solid state reactions

2. Growth: nuclei increase in size

All solid

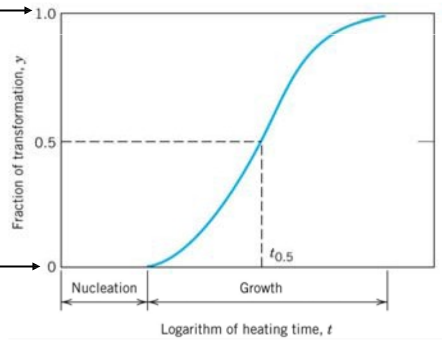


FIGURE 10.1 Plot of fraction reacted versus the logarithm of time typical of many solid-state transformations in which temperature is held constant.

All liquid

By convention:

$$rate \equiv \frac{1}{t_{1/2}}$$

This process can be described by:

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

Avrami eqn.

k and *n* are time independent constants

Kinetics of solid state reactions

Temperature dependence

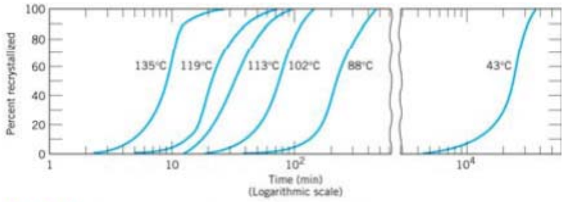
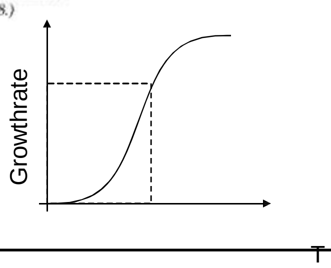


FIGURE 10.2 Percent recrystallization as a function of time and at constant temperature for pure copper. (Reprinted with permission from *Metallurgical Transactions*, Vol. 188, 1950, a publication of The Metallurgical Society of AIME, Warrendale, Pennsylvania. Adapted from B. F. Decker and D. Harker, "Recrystallization in Rolled Copper," *Trans. AIME*, **188**, 1950, p. 888.)

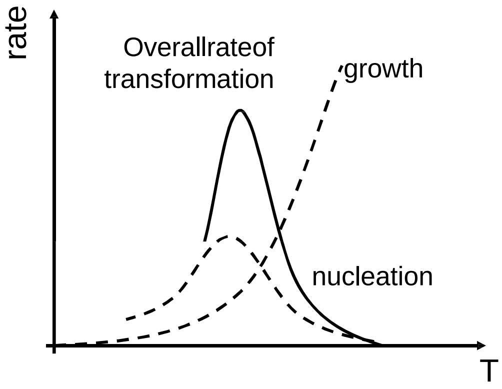
Arrhenius behavior!

$$rate = A\exp\left(-\frac{Q}{RT}\right)$$



Kineticsofsolidstate reactions

Combinednucleationand growth rate



Isothermaltransformation

Initial rapidTchangethen allowtransformationto occuratconstantT

Eutectoidreaction

$$\gamma(0.76wt\%C) \xrightleftharpoons[heat]{cool} \alpha(0.022wt\%C)+Fe_3C(6.70wt\%C)$$

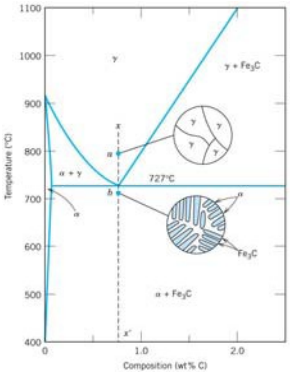
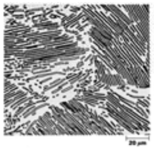


Figure 9.23 Schematic representations of the microstructures for an iron–carbon alloy of eutectoid composition (0.76 wt% C) above and below the eutectoid temperature.



Pearlite

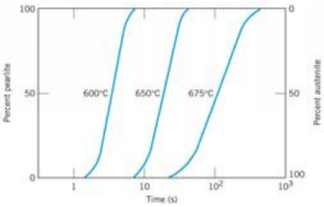


Figure 10.3 For an iron–carbon alloy of eutectoid composition (0.76 wt% C), isothermal fraction reacted versus the logarithm of time for the austenite-to-pearlit transformation.

Pearlite

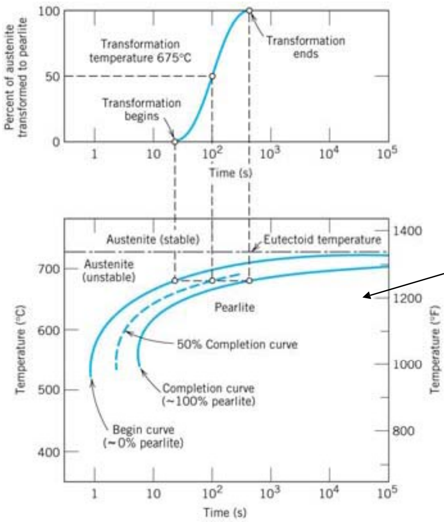


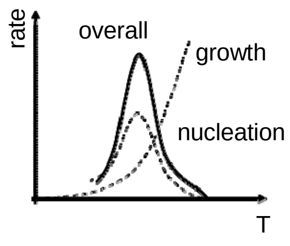
Figure 10.4 Demonstration of how an isothermal transformation diagram (bottom) is generated from percentage transformation-versus-logarithm of time measurements (top). [Adapted from H. Boyer, (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams,* American Society for Metals,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

T vs. **t** **t**ransformation plot (**TTT plot**)

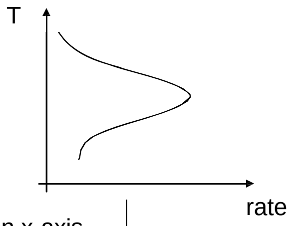
Where does the line shape (e.g. 50% completion curve) come from?

TTT plot and relation to rates

Recall rates as fxn of T…

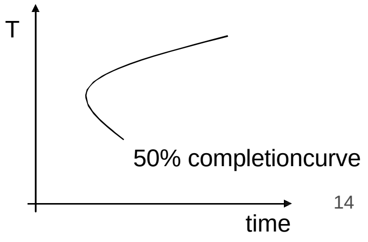


Flip x and y



Plot 1/rate on x-axis

Since rate is defined as: $rate \equiv \dfrac{1}{t_{1/2}}$



Pearlite

Initial rapid
Tquench

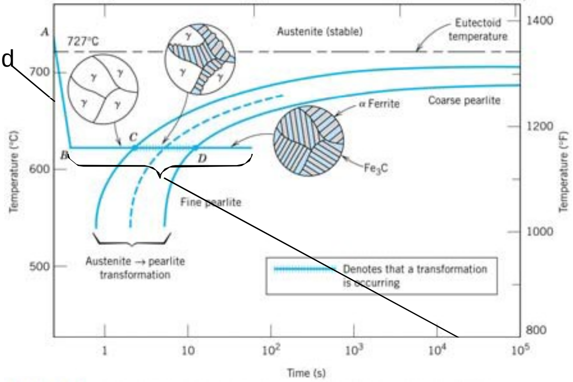


FIGURE 10.5 Isothermal transformation diagram for a eutectoid iron–carbon alloy, with superimposed isothermal heat treatment curve (*ABCD*). Microstructures before, during, and after the austenite-to-pearlite transformation are shown. [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 28.]

ConstantTduring transformation

DothemicrostructureschangewhenwequenchtodifferentT?

Pearlite

Recall limiteddiffusionin solidsleadingto layeredstructure…

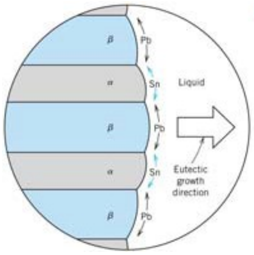
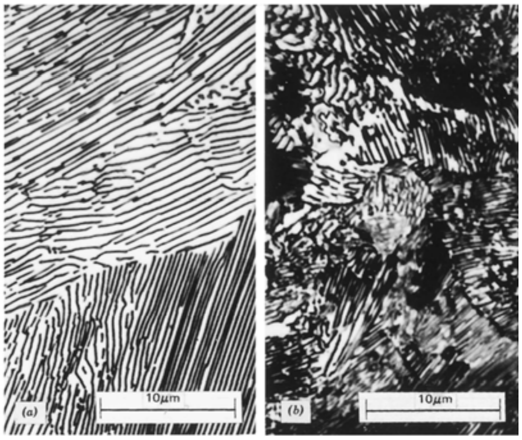


FIGURE 9.13 Sch
the formation of
the lead–tin syste
diffusion of tin ar
indicated by colo
respectively.



Fillinthe blank…
Initial rapidquenchto higherTwillleadto coarsepearlitestructure. Initial rapidquenchto lowerT willleadto__________fine___pearlitestructure.

Bainite&Martensite

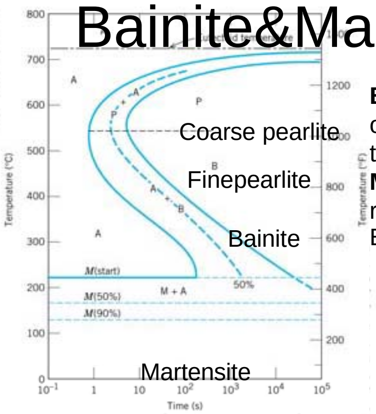


FIGURE 10.13 The complete isothermal transformation diagram for an iron–carbon alloy of eutectoid composition: A, austenite; B, bainite; M, martensite; P, pearlite.

Coarse pearlite

Finepearlite

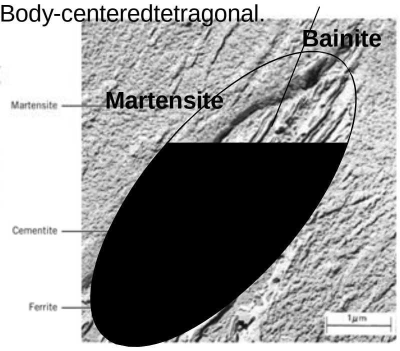
Bainite

Martensite

Materials Park, OH, 1973.)

Bainite:needlesor platesconsisting of cementite andferrite (much finer thanfinepearlite).

Martensite: Formedwhenquenched rapid enoughtopreventC diffusion. Body-centeredtetragonal.



Bainite

Martensite

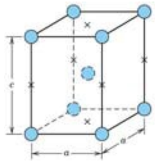
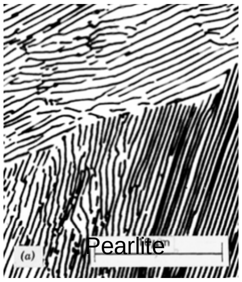


FIGURE 10.11 The body-centered tetragonal unit cell for martensitic steel showing iron atoms (circles) and sites that may be occupied by carbon atoms (crosses). For this tetragonal unit cell, $c > a$.

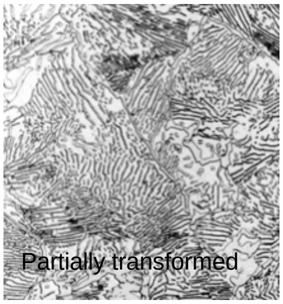
BCTstructure of martensite

Spheroidite

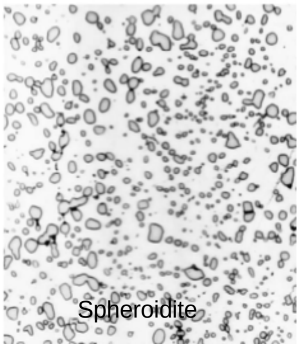
Formswhenpearliteorbainitestructuresareheated(below eutectoidT)foranextendedperiodoftime.



Pearlite



Partially transformed



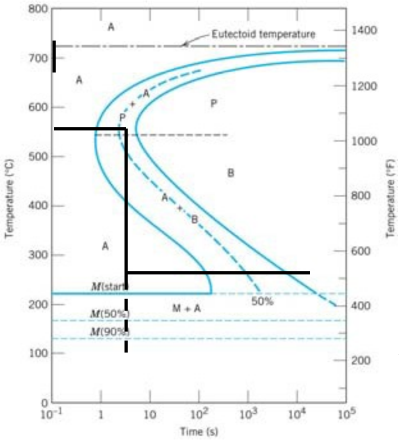
Spheroidite

Heating time →

Whydosphericalshapesdominateattheend?

Exampleproblem

FIGURE 10.13 The complete isothermal transformation diagram for an iron–carbon alloy of eutectoid composition: A, austenite; B, bainite; M, martensite; P, pearlite.



1. Whatisthemicrostructure ofsteelthathasbeen:
   - (i) instantaneously quenchedto560^oC
   - (ii) heldfor2sthen
   - (iii) Instantaneously quenchedto250^oC?
2. Whathappensifthe resultingstructureisheld at250^oCfor1day?
3. Whathappensifthe structurefrompart1is quencheddirectlytoRT?

Exampleproblem

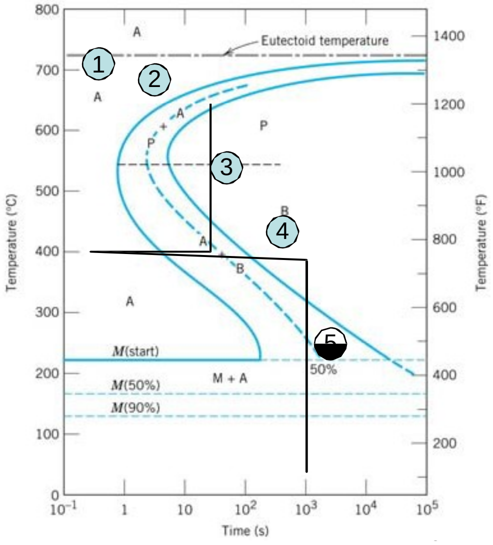
Specifyfinal microstructure(s) presentandapproximate percentageofeachfor followingprocessingcondition beginningat760^oC.

1. Rapidcoolto 650^oC.
2. Hold20s.
3. Rapidcoolto 400^oC.
4. Holdfor10^3s.
5. QuenchtoRT.

② -50%transformationtopearlite.

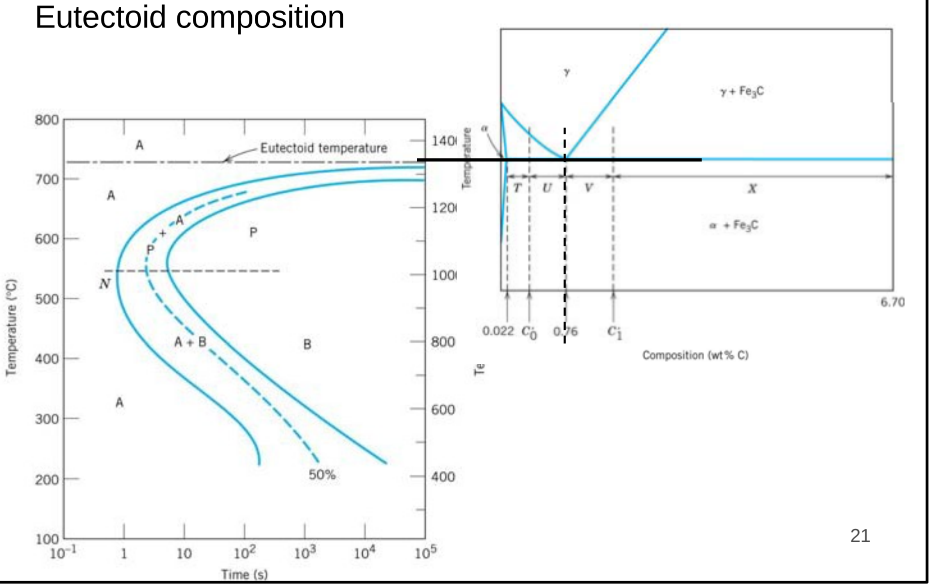
④ Essentiallyrestart transformationprocess(for theremaining50%).

⑤ Finalcomposition=50% pearlite,50%bainite



TTT diagrams at different compositions

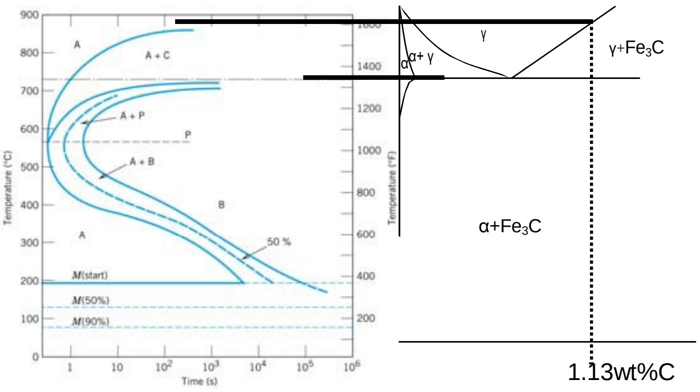
Eutectoid composition



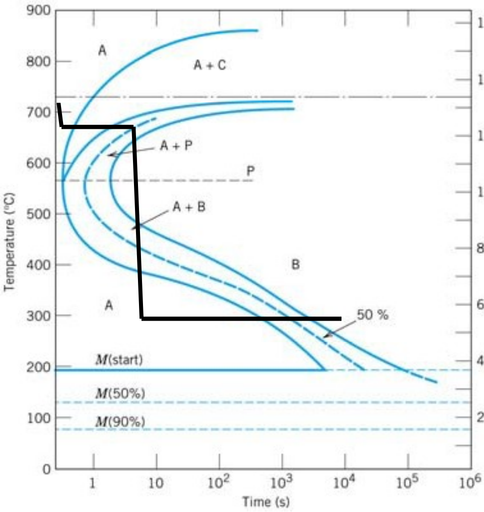
Hypereutectoid composition

e.g. 1.13wt%C

Figure 10.28 Isothermal transformation diagram for a 1.13 wt% C iron–carbon alloy: A, austenite; B, bainite; C, proeutectoid cementite; M, martensite; P, pearlite. [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 33.]

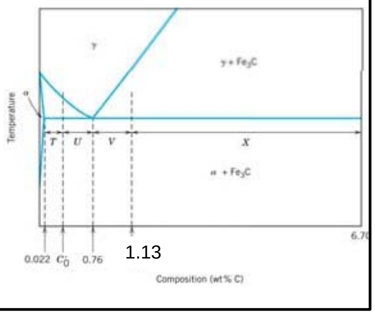


Example



TTTdiagramfor 1.13wt%CFe-C alloy

Startingwithaustenite having1.13wt%C in composition,whatcooling pathwill produce6.2% massfractionproeutectoid cementite,46.9%mass fractioncoarsepearlite, 46.9%massfraction Bainite?



ContinuousCoolingTransformation

Recall % transformedvs.time…

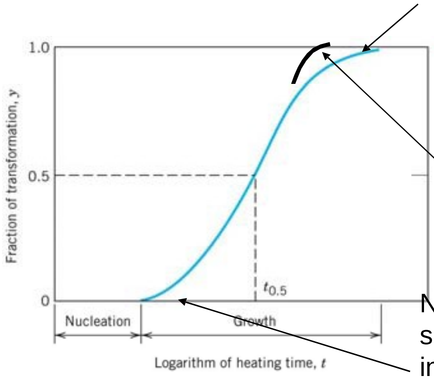


FIGURE 10.1 Plot of fraction reacted versus the logarithm of time typical of many solid-state transformations in which temperature is held constant.

TransformationatconstantT(T_1)

Completetransformation occursfasterduelowerfinal T.

Nucleationtogrowthtransitionis slowersinceitisnotcooled instantaneouslyinitially.

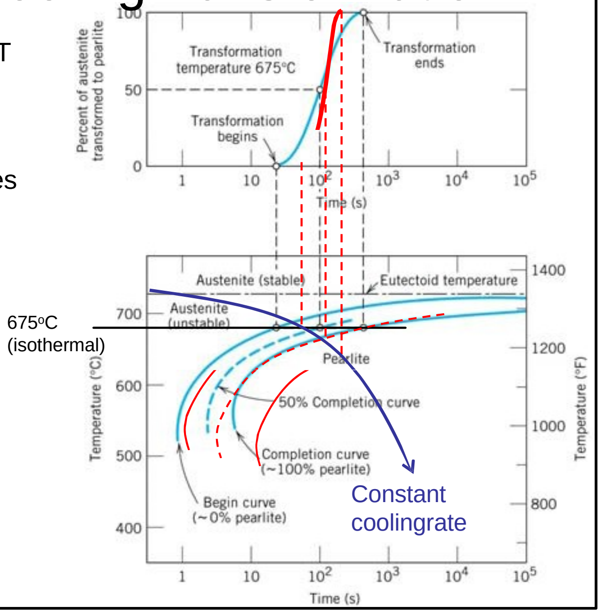
WhathappenswhenTisvariedastransformationoccurs? continuouslycoolfrom$T_o$toT_2ataconstantrate)

ContinuousCoolingTransformation

RecallhowwearrivedatTTT diagramforisothermal cooling…

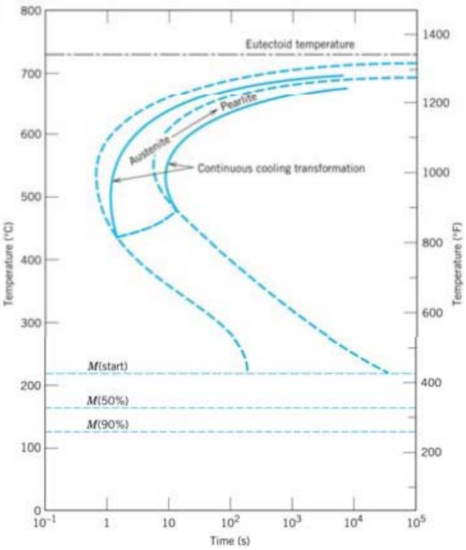
WhathappenswhenTvaries duringtransformation?

Lookslikethecurves areshifteddownand totheright.



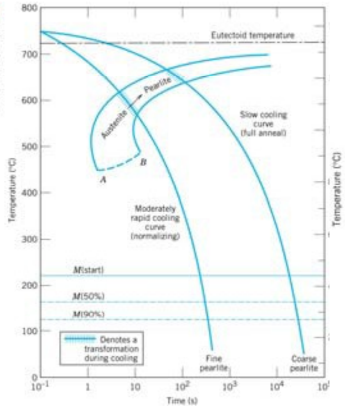
CCTdiagrams

FIGURE 10.16 Superimposition of isothermal and continuous cooling transformation diagrams for a eutectoid iron–carbon alloy. [Adapted from H. Boyer (Editor), *Atlas of Isothermal Transformation and Cooling Transformation Diagrams*, American Society for Metals, 1977, p. 376.]



Microstructures from continuous cooling

FIGURE 10.17 Moderately rapid and slow cooling curves superimposed on a continuous cooling transformation diagram for a eutectoid iron–carbon alloy.



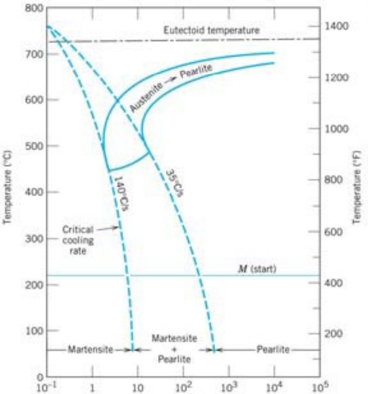


FIGURE 10.18 Continuous cooling transformation diagram for a eutectoid iron–carbon alloy and superimposed cooling curves, demonstrating the dependence of the final microstructure on the transformations that occur during cooling.

Note: usually no Bainite is formed in continuous cooling

Mechanical behavior of plain carbon steel

Fine pearlite

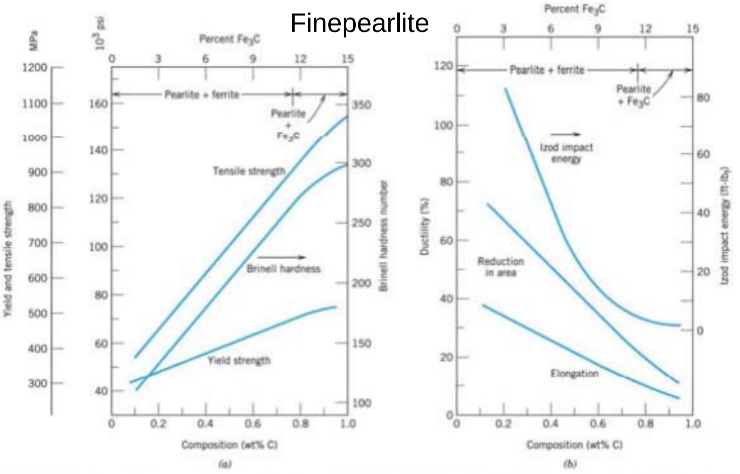


FIGURE 10.20 (*a*) Yield strength, tensile strength, and Brinell hardness versus carbon concentration for plain carbon steels having microstructures consisting of fine pearlite. (*b*) Ductility (%EL and %RA) and Izod impact energy versus carbon concentration for plain carbon steels having microstructures 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.]

Strength increases and ductility decreases with C content.

Howdo processingconditionschange mechanicalproperties?

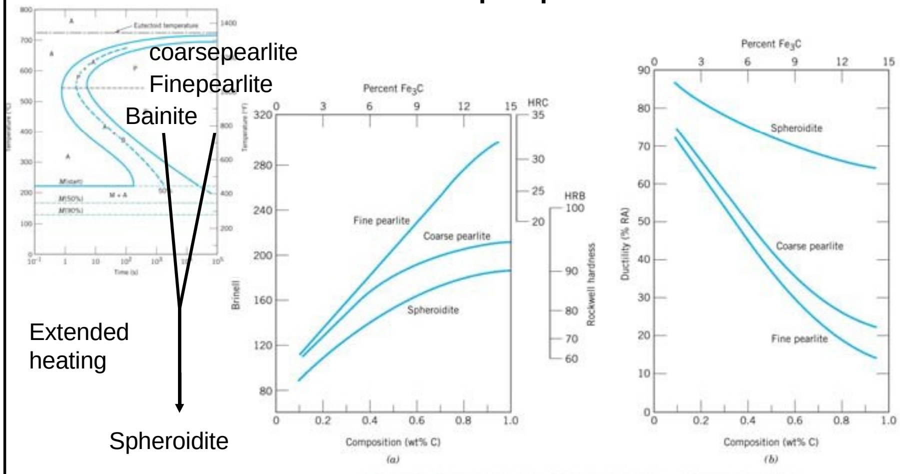
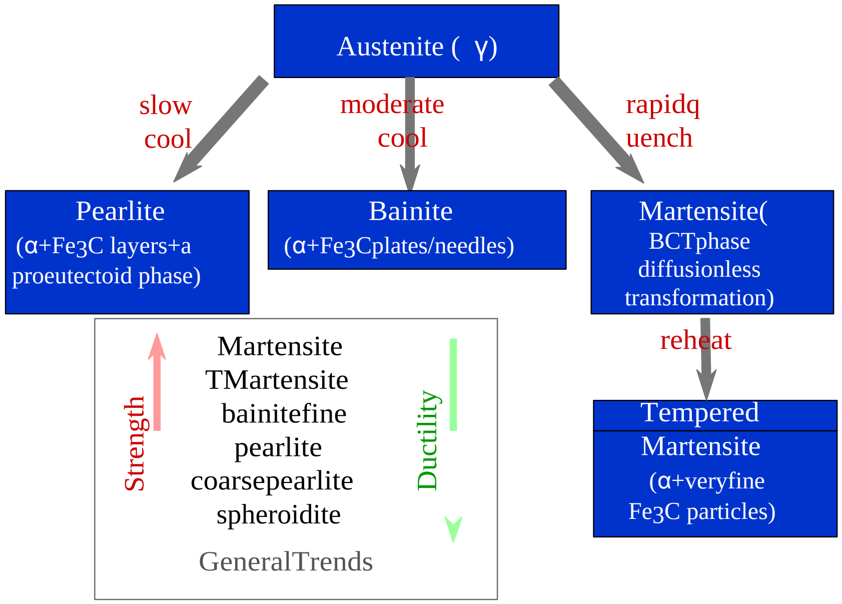


Figure 10.21 (a) Brinell and Rockwell hardness as a function of carbon …els having fine and coarse pearlite as well as …uctility (%RA) as a function of carbon …els having fine and coarse pearlite as well as … taken from *Metals Handbook: Heat Treating,* Vol. 4, 9th edition, V. Masseria, Managing Editor, American Society for Metals, 1981, pp. 9 and 17.)

Fastquench:higherstrength,lowerductility.
Slowquench:lowerstrength,higherductility.



Austenite (γ)

slow cool

moderate cool

rapidquench

Pearlite
(α+Fe3C layers+a proeutectoid phase)

Bainite
(α+Fe3Cplates/needles)

Martensite(
BCTphase
diffusionless
transformation)

reheat

Tempered
Martensite
(α+veryfine
Fe3C particles)

Strength

Martensite
TMartensite
bainitefine
pearlite
coarsepearlite
spheroidite

Ductility

GeneralTrends

Phasetransformationin polymers

- Crystallization.
- Melting.
- Glasstransition.

Crystallization

- Many polymercrystallizationprocessesare similar kinetics as discussed earlierin phase transformations (Avramiequation).
- Some differences:
  - Nucleationandgrowth
    - Randomentangledchainsbecomeorderedandaligned.
  - Usually100%crystallizationisnotachievable.
  - Crystallizationcanbeinducedbystrain.

Polypropylene

Normalized! →

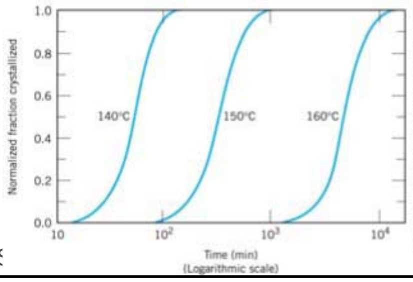
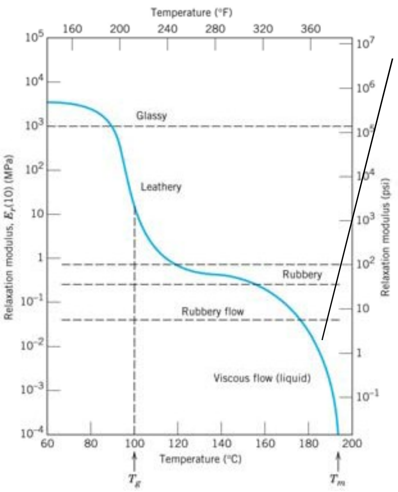


FIGURE 15.16 Plot of normalized fraction crystallized versus the logarithm of time for polypropylene at constant temperatures of 140°C, 150°C, and 160°C. (Adapted from P. Parrini and G. Corrieri, *Makromol. Chem.*, **62,** 83, 1963. Reprinted by permission of Hüthig & Wepf Publishers, Zug, Switzerland.)

Melting



Meltingoccursoverarangeoftemperature

Meltingtemperature(T_m)dependson:

1. **Historyofthespecimen**(e.g.how itwascrystallized).
2. **Heating rate**: faster heating rate leadstohigherT_m.
3. **Chemicalcomposition**
   - Bulkysidegroupsleadto higherT_m(hinderedrotation andflexibility).
   - Polarsidegroupsleadtohigher T_m(strongersecondary bonding).

Meltingcontinued…

Melting temperaturedependson:

4. **MolecularWeight**:at relatively low MW,$T_m$increaseswithMW.
5. **Degree ofbranching**:more branchingleadsto lower T_m.

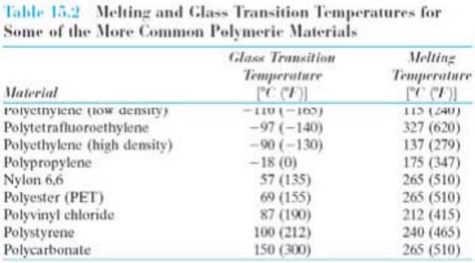


Table 15.2 Melting and Glass Transition Temperatures for Some of the More Common Polymeric Materials

Material	*Glass Transition Temperature* [°C (°F)]	*Melting Temperature* [°C (°F)]
Polyethylene (low density)	−110 (−165)	115 (240)
Polytetrafluoroethylene	−97 (−140)	327 (620)
Polyethylene (high density)	−90 (−130)	137 (279)
Polypropylene	−18 (0)	175 (347)
Nylon 6,6	57 (135)	265 (510)
Polyester (PET)	69 (155)	265 (510)
Polyvinyl chloride	87 (190)	212 (415)
Polystyrene	100 (212)	240 (465)
Polycarbonate	150 (300)	265 (510)

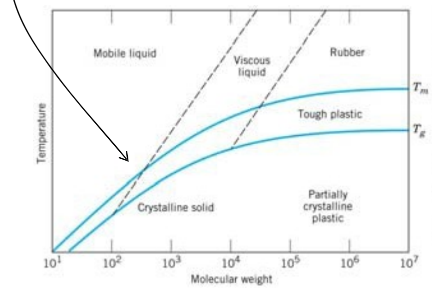


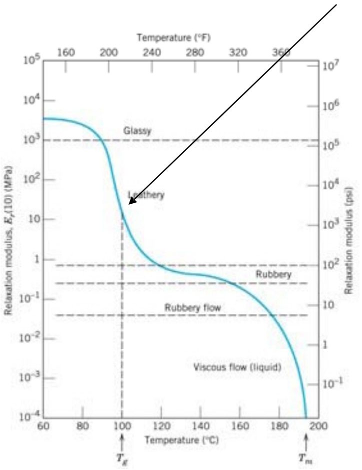
FIGURE 15.18 Dependence of polymer properties as well as melting and glass transition temperatures on molecular weight. (From F. W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd edition. Copyright © 1984 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

MeltingTemperature:exampleproblems

Foreach polymerpair, determinewhichwillhave **highermeltingtemperature**.

1. Branched polyethylene vs. Linear polyethylene
2. Polyethylene(n = 5000) vs. PMMA(n = 5000)
3. Polystyrene(Mn = 80,000g/mol) vs. Polystyrene(Mn = 800g/mol)
4. PE (Mn = 10^7g/mol) vs. PE (Mn = 10^6g/mol)

GlassTransition



- Transitionfromrubberytorigidstate.
  - Abruptchangesin:

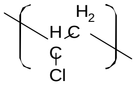
•Stiffness.
•Viscosity.
•Coefficientofthermalexpansion…

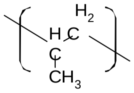
Glasstransitiontemperature(T_g)dependson:

1. **Chemicalcomposition**
   - BulkygroupsincreaseT_g.
   - PolargroupsincreaseT_g.
2. **Molecularweight**:higherMW–higherT_g.
3. **Degreeofbranching**:higherdensityof branching–higherT_g(entangledbranches restrictchainmotion).
4. **Crosslinking**increases$T_g$duetochain motionrestriction.

Glass transition: example problems

For each polymer pair, determine which will have **higher glass transition temperature**.





a) poly(vinylchloride) vs. polypropylene

b) polystyrene vs. polypropylene

Concepts to remember…

- Kinetics of solid state reaction:
  - nucleation (surface vs volume energies) and growth.
  - Avrami equation.
  - Rates.
- Isothermal transformation.
- TTT plots and relation to reaction rates.
- Microstructures of Fe-C systems at different cooling conditions:
  - Fine and coarse pearlite, bainite, spheroidite and martensite.
- CCT diagrams.
- Processing effects on mechanical properties.
- Phase transformation in polymers (consider similarities and differences with metals).