Announcements

- Tutorial quiz solutions are up.
- WebCT quiz example answers are up.
- This week’s Tuesday office hours are canceled. Replaced by Wednesday 9:30 – 11:00.
- Big news!

Non-steady State Diffusion

- **The concentration of diffusing species is a function of both time and position $C = C(x,t)$**
- **In this case Fick's Second Law is used**

Fick's Second Law

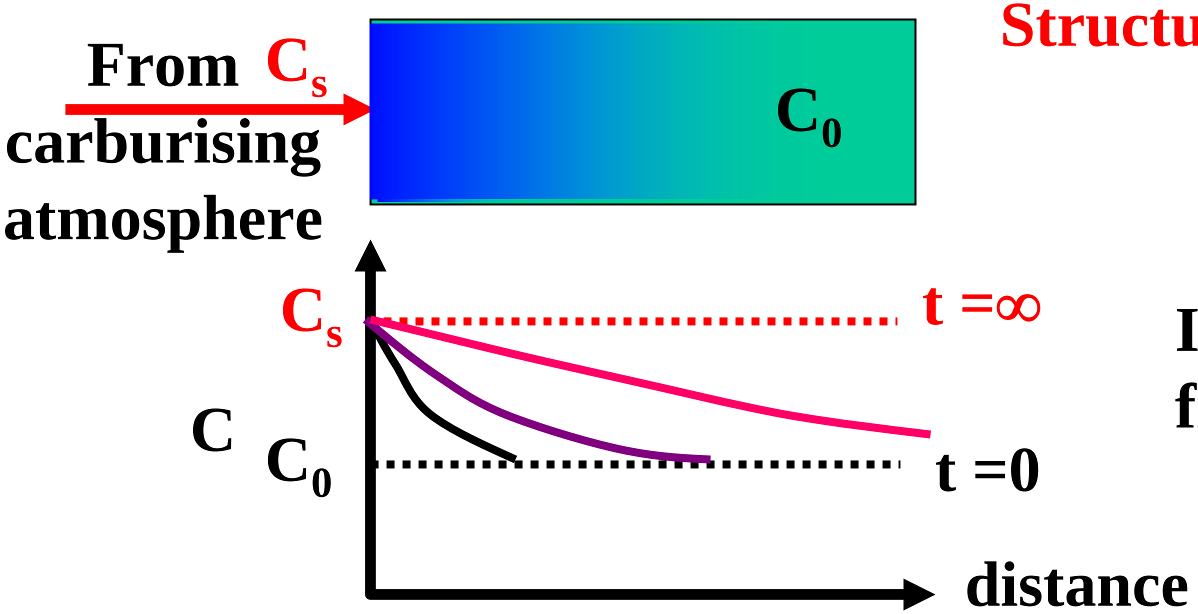
$$\boxed{\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}}$$

Applications of Ficks 2nd law

The Carburization of Steel

diffusion of dopant into Si

increase in C concn to increase surface hardness/wear resistance



Structure?

Increasing t
from t= 0

Require time to reach certain C concn to certain depth

solve Ficks 2nd law using following boundary conditions

at x=0, $C_B=C_s$

at x=∞ $C_B=C_0$

$$\frac{C(x,t)-C_o}{C_s-C_o} = 1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

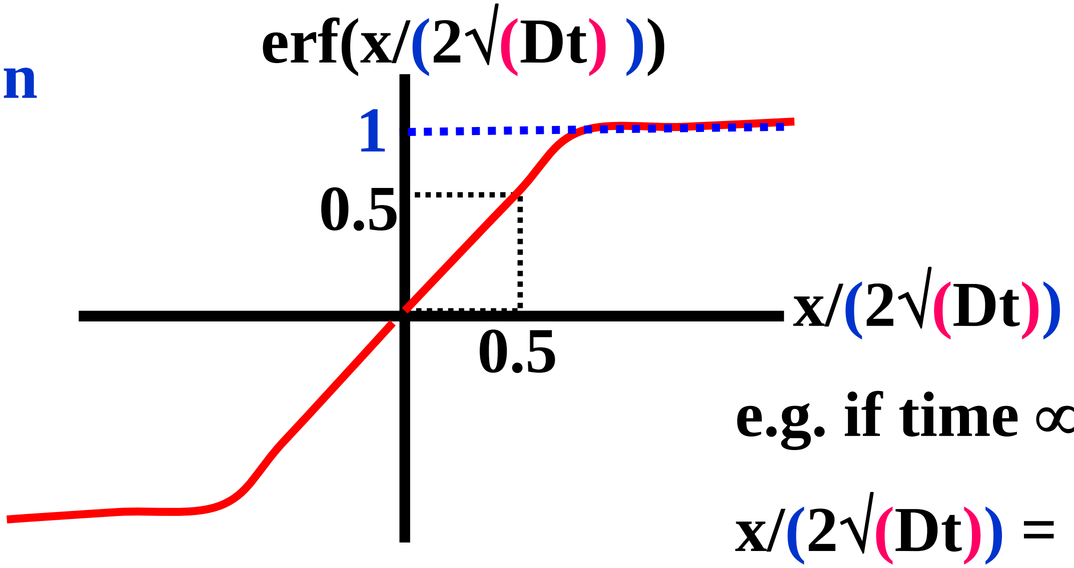
Solution

D varies with C%

Take avg value

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z \exp(-y^2)\,dy$$

Error function



e.g. if time ∞,

x/(2√(Dt)) = 0,

and C=C$_s$ throughout the specimen

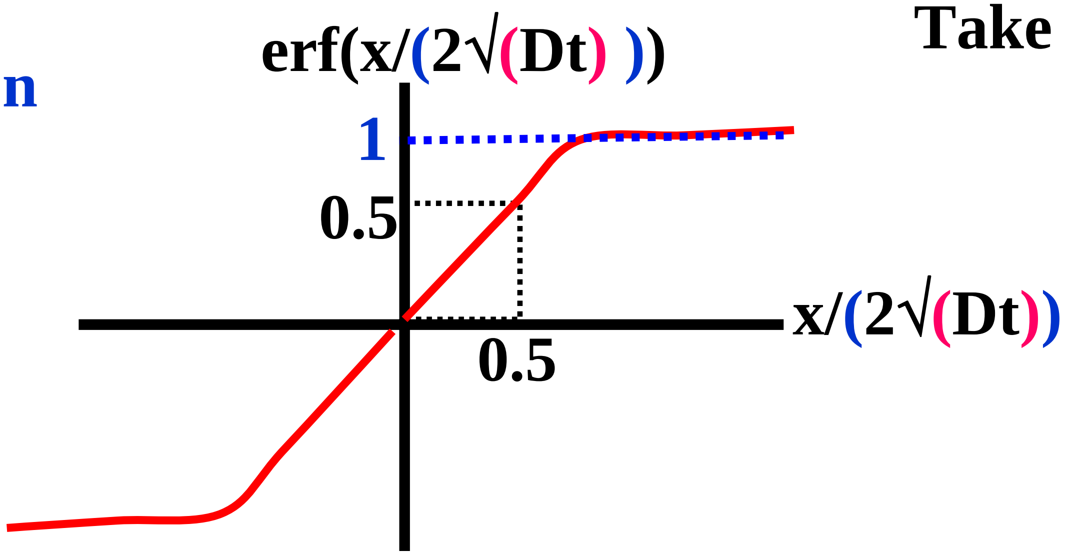
$$\frac{C(x,t)-C_o}{C_s-C_o}=1-erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

Solution

Varies with C%

Take avg value

Error function



erf (0.5) = 0.5

$$\frac{\mathrm{x}}{2\sqrt{\mathrm{Dt}}}=0.5,$$

therefore $$C=\frac{1}{2}(C_s+C_0)$$

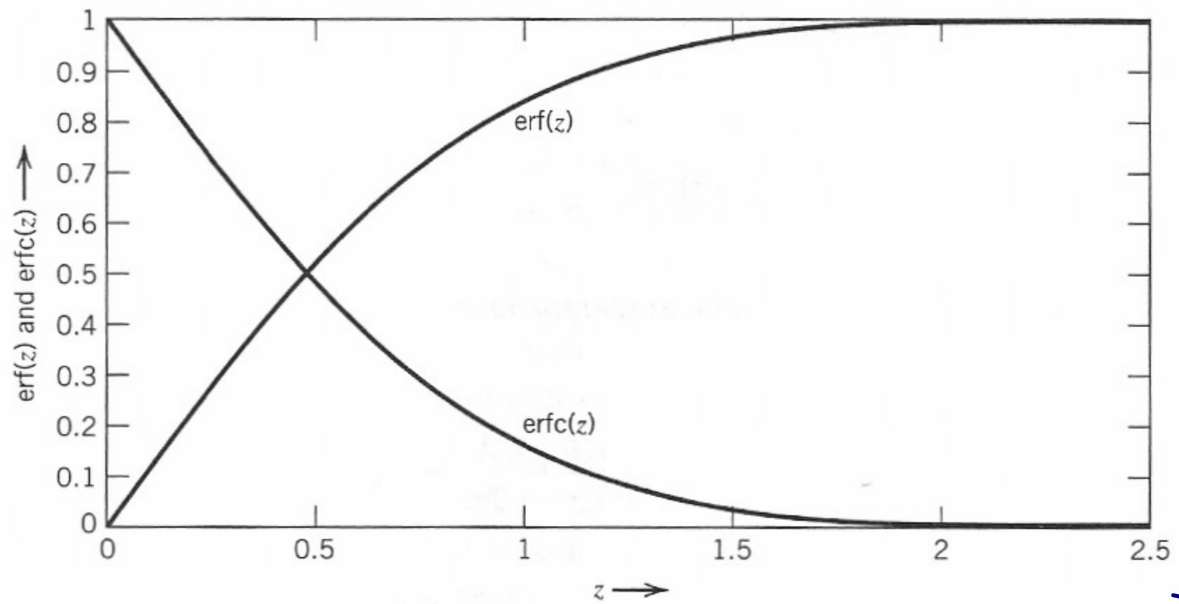


Figure 5A.1 Error function and complementary error function.

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z \exp(-y^2)\, dy$$

$$\mathrm{erfc}(z) = 1 - \mathrm{erf}(z)$$

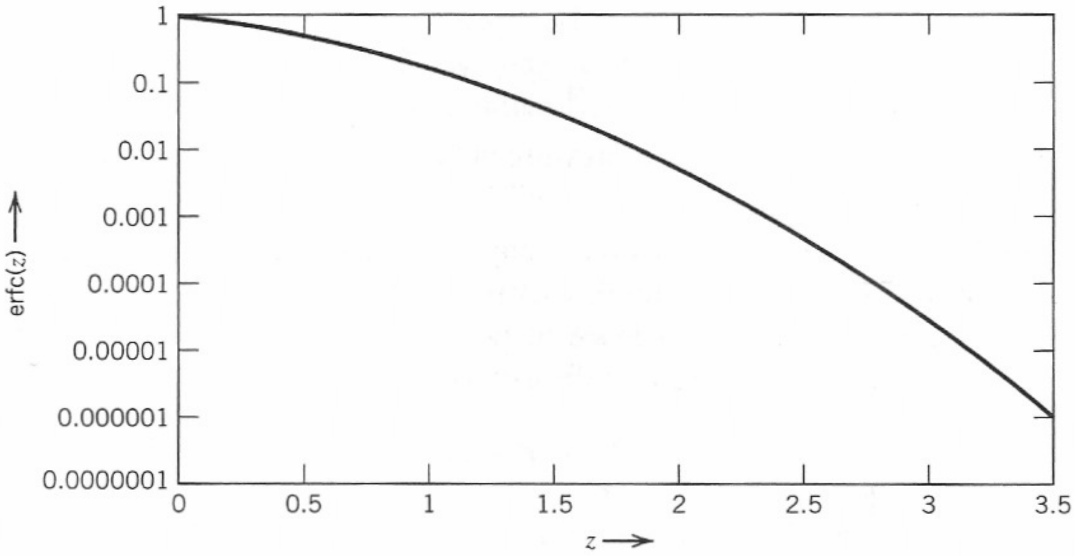


Figure 5A.2 Complementary error function (logarithmic scale).

$$\frac{\boxed{x}}{2\sqrt{Dt}} = 0.5,$$

erf (0.5) = 0.5

therefore $$C = \frac{1}{2}(C_s + C_0)$$

Re-stating:

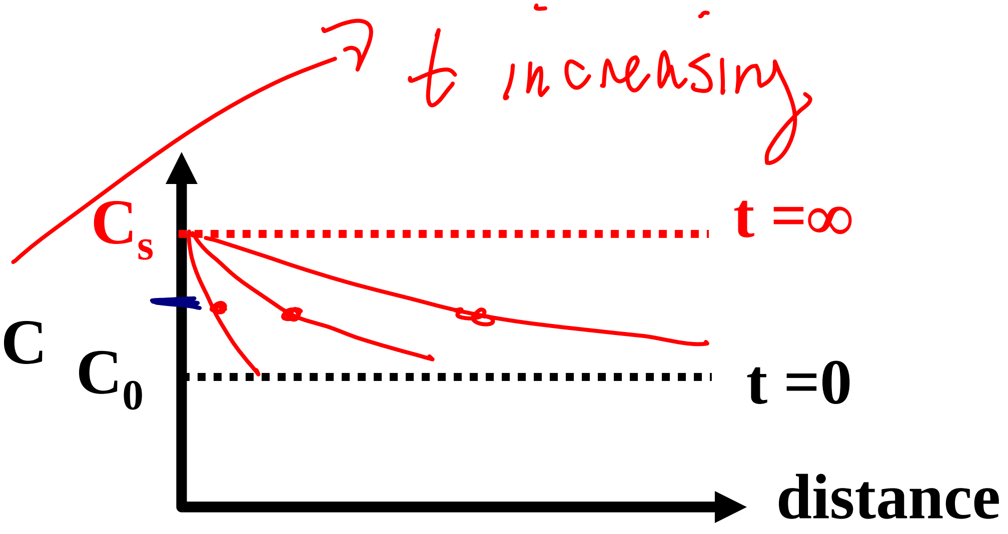
If carburisation is defined as $C=(C_s+C_0)/2$

then, after any time, t

carb depth, x = $\sqrt{(Dt)}$

in general, for any specific concn, C

depth is proportional to $\sqrt{(Dt)}$



Non-steady State Diffusion

- **Sample Problem: An FCC iron-carbon alloy initially containing 0.20 wt% C is carburized at an elevated temperature and in an atmosphere that gives a surface carbon concentration constant at 1.0 wt%. If after 49.5 h the concentration of carbon is 0.35 wt% at a position 4.0 mm below the surface, determine the temperature at which the treatment was carried out.**

$$\frac{C(x,t)-C_o}{C_s-C_o}=1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

- **Solution: use Eqn. 5.5**

Solution (cont.): $\frac{C(x,t)-C_o}{C_s-C_o}=1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$

- **t = 49.5 h**
- **C_x = 0.35 wt%**
- **C_o = 0.20 wt%**

x = 4 x 10^{-3} m

C_s = 1.0 wt%

$$\frac{C(x,t)-C_o}{C_s-C_o}=\frac{0.35-0.20}{1.0-0.20}=1-\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right)=1-\mathrm{erf}(z)$$

$\therefore$ 1 - erf(z) = 0.1875

Solution (cont.):

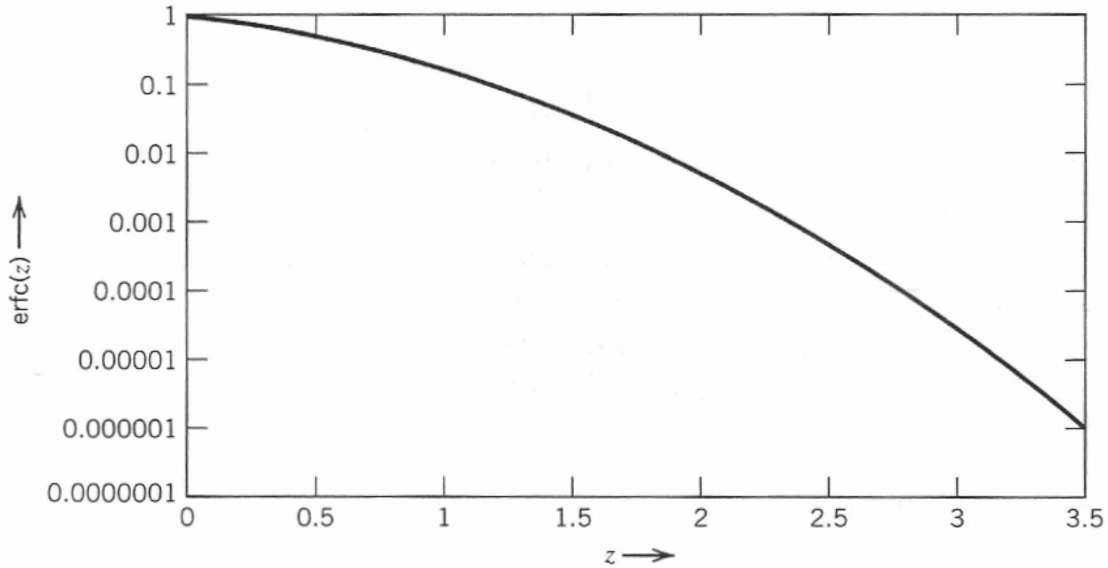


Figure 5A.2 Complementary error function (logarithmic scale).

Options:

1. **Erfc(z) calculator (online).**
2. **Extrapolate or interpolate from a table (given in Callister).**
3. **Measure using a graph.**

$z = 0.93$

Now solve for *D*

$$z = \frac{x}{2\sqrt{Dt}} \Rightarrow D = \frac{x^2}{4z^2 t}$$

$$\therefore D = \left(\frac{x^2}{4z^2 t}\right) = \frac{(4\,\mathrm{x}\,10^{-3}\,\mathrm{m})^2}{(4)(0.93)^2(49.5\,\mathrm{h})}\frac{1\,\mathrm{h}}{3600\,\mathrm{s}} = 2.6\,\mathrm{x}\,10^{-11}\,\mathrm{m^2/s}$$

$$D = D_o \exp\left(\frac{-Q_d}{RT}\right)$$

Solution (cont.):

- **To solve for the temperature at which *D* has above value, we use a rearranged form of Equation (5.9a);**

$$T = \frac{Q_d}{R(\ln D_o - \ln D)}$$

from Table 5.2, for diffusion of C in FCC Fe

$D_o = 2.3 \times 10^{-5}$ m^2/s $Q_d = 148{,}000$ J/mol

$$\therefore \quad T = \frac{148{,}000 \text{ J/mol}}{(8.314 \text{ J/mol-K})(\ln 2.3\text{x}10^{-5} \text{ m}^2\text{/s} - \ln 2.6\text{x}10^{-11} \text{ m}^2\text{/s})}$$

$$\boxed{T = 1300 \text{ K} = 1027°\text{C}}$$

Summary I

- Atoms diffuse in solids, without a driving force.
  - Atoms randomly acquire thermal energy and overcome Q.
  - To first order this is a random walk problem, and net diffusion distances are ‘small’
- Atoms diffuse in solids in response to a driving force.
  - Driving force is a concentration gradient $\propto$ other things
  - Fick’s first law
  - Steady state: Concentration profile does not change.
- Chemical diffusion will tend to ‘level off’ a concentration profile
  - Fick’s second law
  - Concentration profile evolves with time

Summary II

Diffusion FASTER for...

- open crystal structures
- smaller diffusing atoms
- lower density materials

Diffusion SLOWER for...

- close-packed structures
- larger diffusing atoms
- higher density materials

Diffusion Summary for EE

- Diffusion, even at room temperature, can affect a microelectronic or nanoelectronic device.

  Fe - C   3 mm   1100°C

- Electrical engineers take advantage of diffusion to fabricate microelectronics devices.
- It is an important design consideration for any electronics application.
  - Diffusion can change the dopant level/impurity levels in Si.
  - Diffusion can result in new phase formations.

Why is diffusion important…

- When we make a device? (i.e. processing stage)

- When we use a device? (i.e. reliability stage)

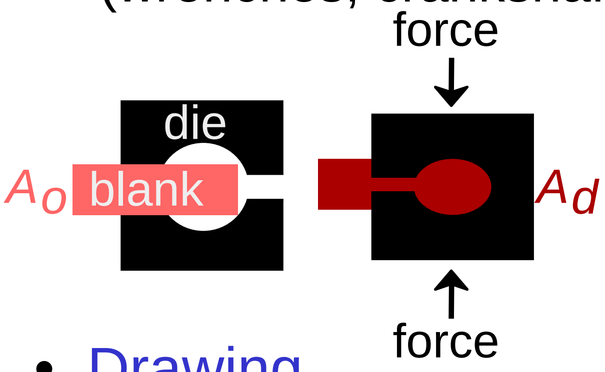
Next subject… (Ch. 11 and Jones, Ch. 4 and 9)

- Processing
  - How we make bulk engineering structures
  - How we make microelectronics devices

Metal Fabrication Methods - I

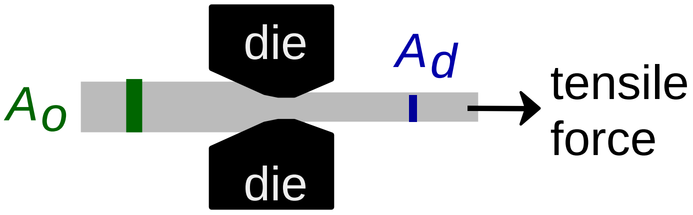
FORMING CASTING JOINING

- Forging (Hammering; Stamping)
  (wrenches, crankshafts)



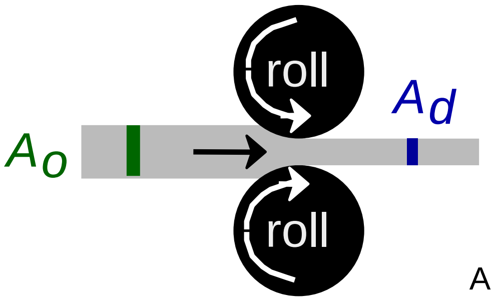
often at elev. T

- Drawing
  (rods, wire, tubing)



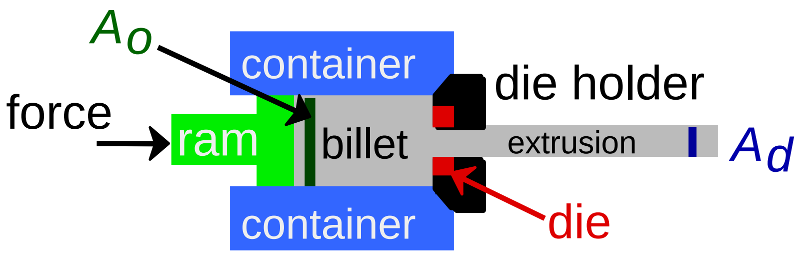
die must be well lubricated & clean

- Rolling (Hot or Cold Rolling)
  (I-beams, rails, sheet & plate)



Adapted from Fig. 11.8, *Callister 7e*.

- Extrusion
  (rods, tubing)



ductile metals, e.g. Cu, Al (hot)

Metal Fabrication Methods - II

FORMING CASTING JOINING

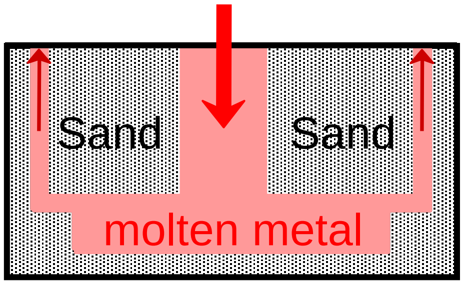
- Casting- mold is filled with metal
  - metal melted in furnace, perhaps alloying elements added. Then cast in a mold
  - most common, cheapest method
  - gives good production of shapes
  - weaker products, internal defects
  - good option for brittle materials

Metal Fabrication Methods - II

FORMING CASTING JOINING

- Sand Casting

  (large parts, e.g., auto engine blocks)



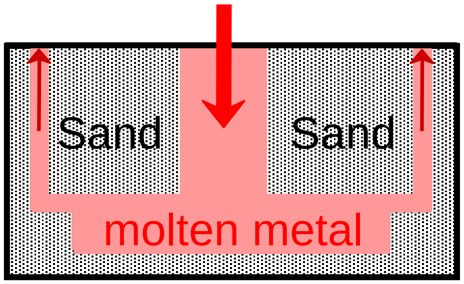
- trying to hold something that is hot
- what will withstand >1600ºC?
- cheap - easy to mold => sand!!!
- pack sand around form (pattern) of desired shape

Metal Fabrication Methods - II

FORMING CASTING JOINING

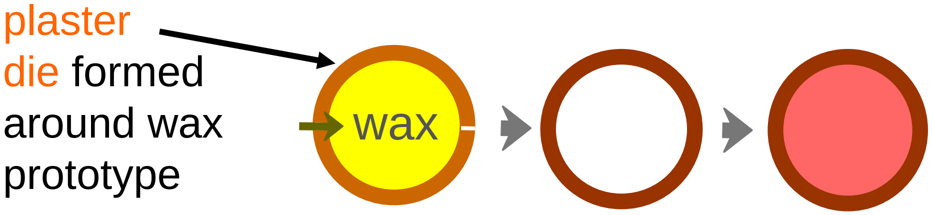
- Sand Casting

  (large parts, e.g.,
  auto engine blocks)



- Investment Casting

  (low volume, complex shapes
  e.g., jewelry, turbine blades)



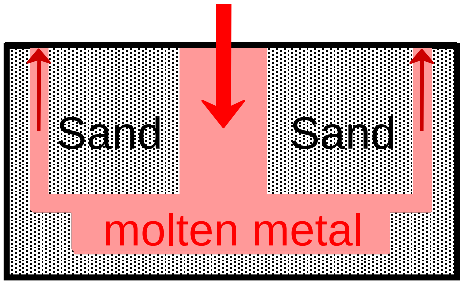
Investment Casting

- pattern is made from paraffin.
- mold made by encasing in plaster of paris
- melt the wax & the hollow mold is left
- pour in metal

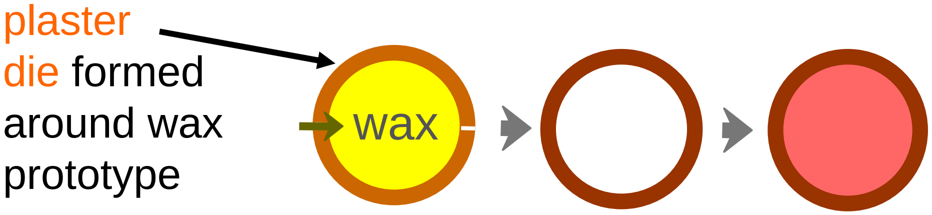
Metal Fabrication Methods - II

FORMING | CASTING | JOINING

- Sand Casting
  (large parts, e.g., auto engine blocks)

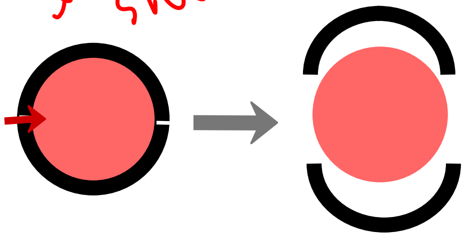


- Investment Casting
  (low volume, complex shapes e.g., jewelry, turbine blades)



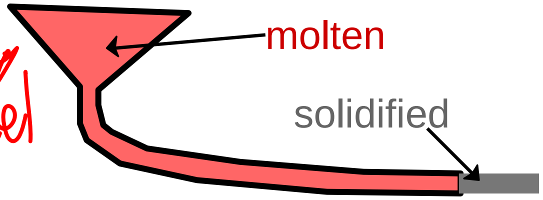
- Die Casting
  (high volume, low T alloys)

Sand → steel



- Continuous Casting
  (simple slab shapes)

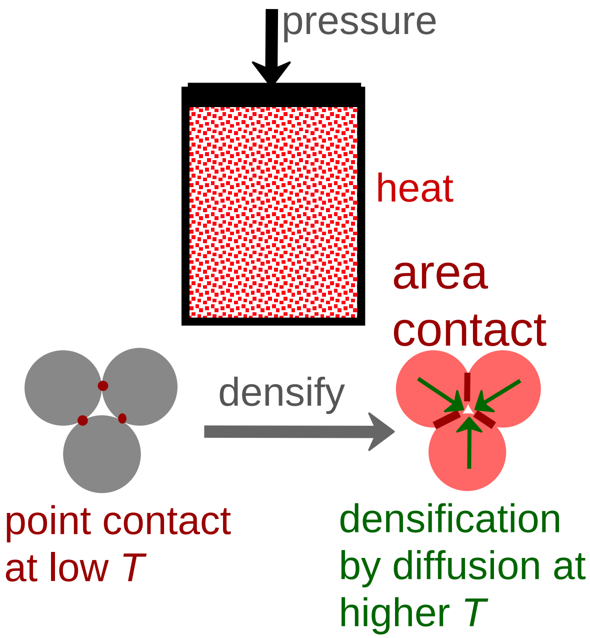
steel



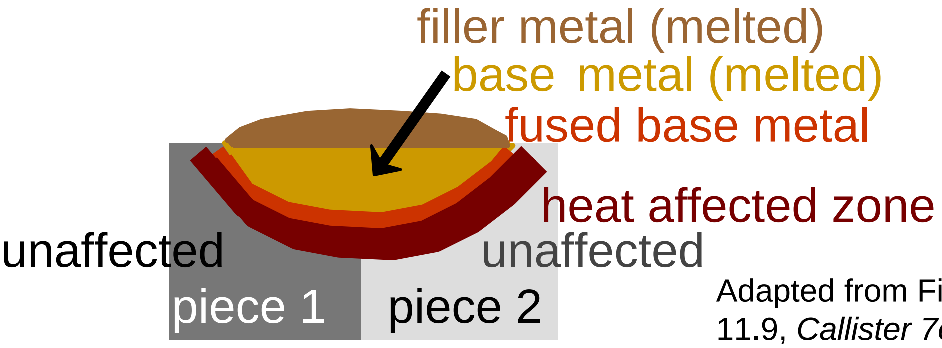
Metal Fabrication Methods - III

FORMING CASTING JOINING

- Powder Metallurgy
  (materials w/low ductility)



- Welding
  (when one large part is impractical)



Adapted from Fig. 11.9, *Callister 7e*. (Fig. 11.9 from *Iron Castings Handbook*, C.F. Walton and T.J. Opar (Ed.), 1981.)

- Heat affected zone:
  (region in which the microstructure has been changed).

Thermal Processing of Metals

Annealing: Heat to T_{anneal}, then cool slowly.

Types of Annealing

- **Stress Relief**: Reduce stress caused by:
  - -plastic deformation
  - -nonuniform cooling
  - -phase transform.

- **Spheroidize** (steels): Make very soft steels for good machining. Heat just below T_E & hold for 15-25 h.

- **Full Anneal** (steels): Make soft steels for good forming by heating to get γ, then cool in furnace to get coarse *P*.

- **Process Anneal**: Negate effect of cold working by (recovery/ recrystallization)

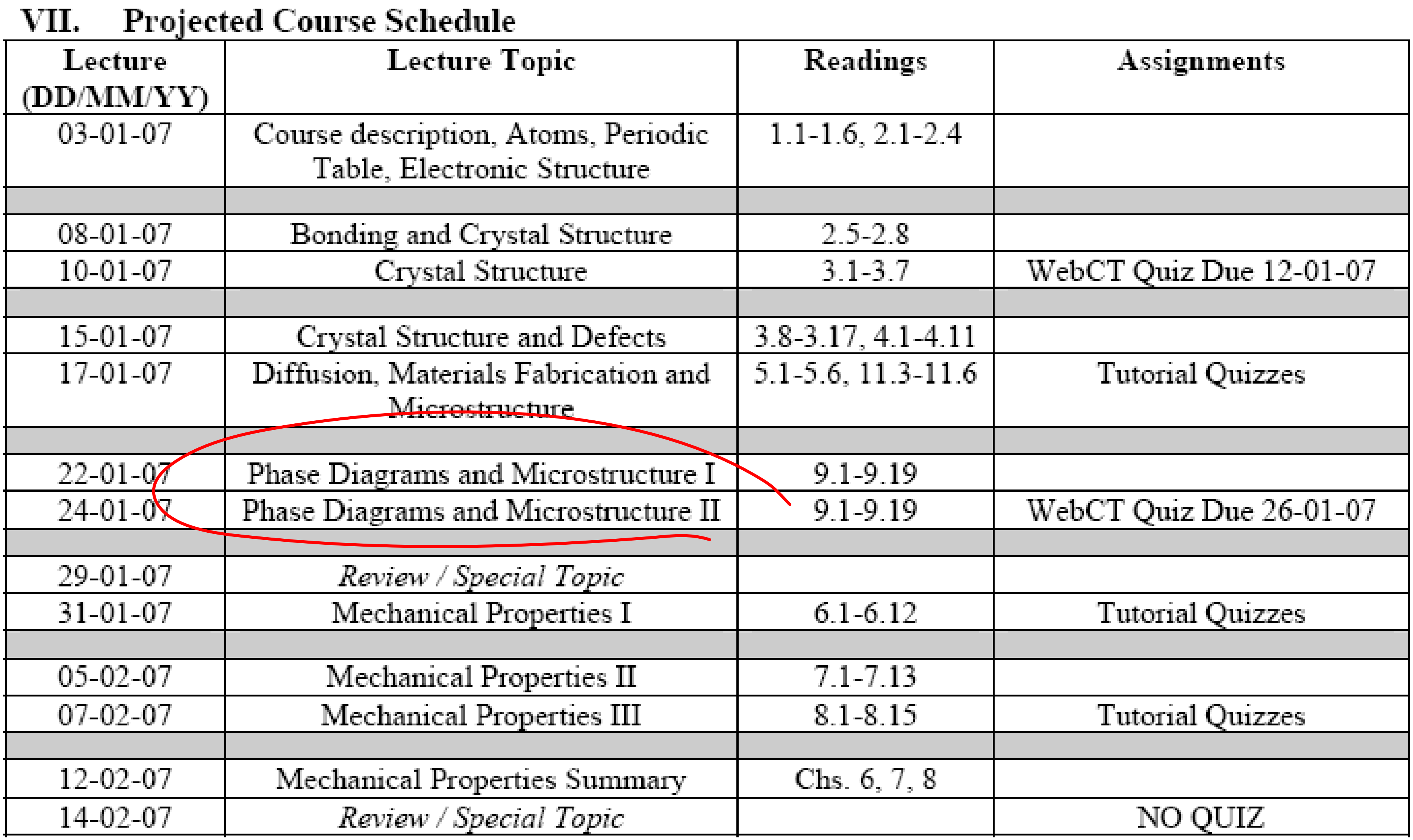
- **Normalize** (steels): Deform steel with large grains, then normalize to make grains small.

Based on discussion in Section 11.7, *Callister 7e*.

Great, those are all bulk materials!

- How are materials made for electrical and electronics applications?
- Are process and design considerations similar to a bulk application?
- What’s missing?

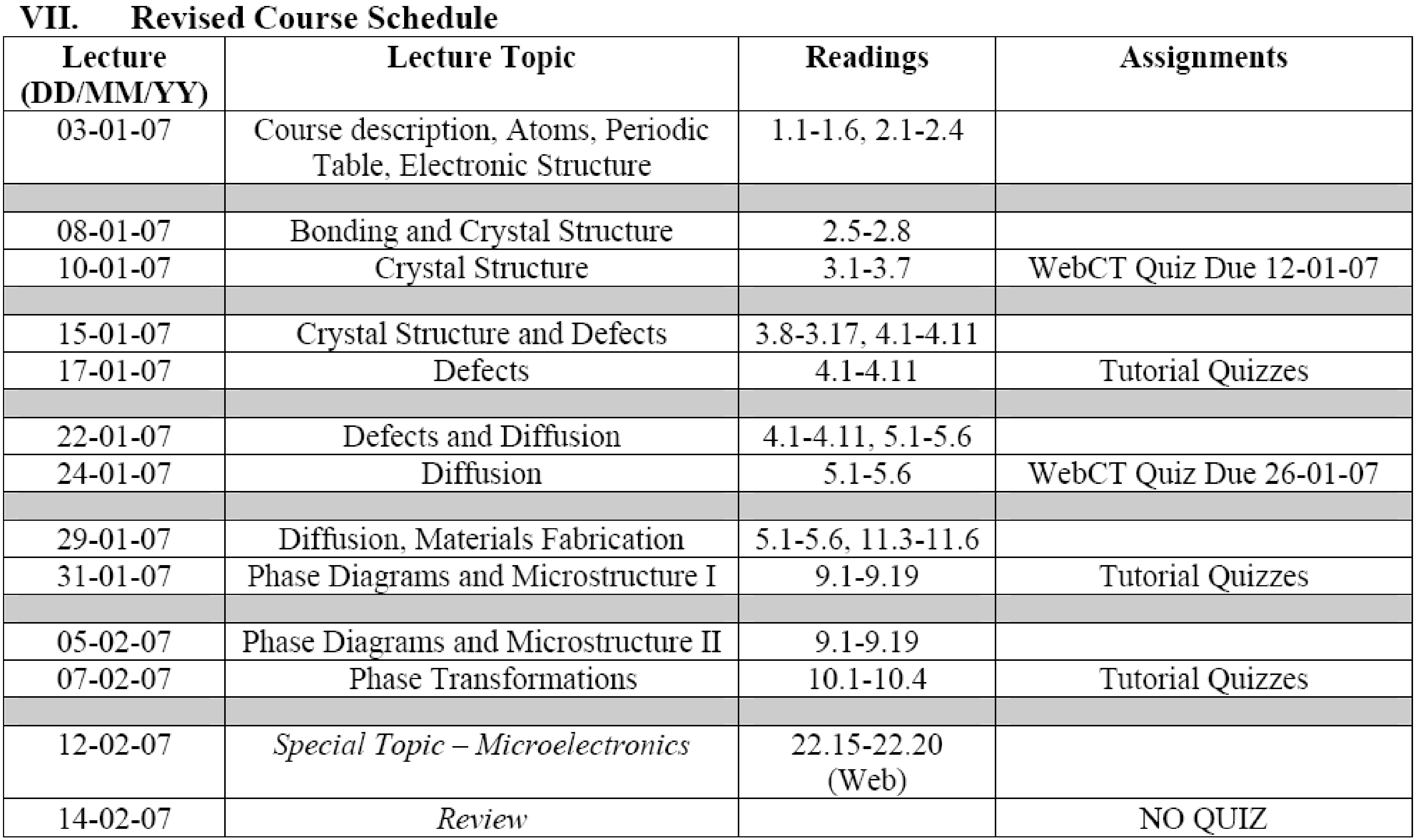
First thing missing – Phase Diagrams!



VII. Projected Course Schedule

Lecture (DD/MM/YY)	Lecture Topic	Readings	Assignments
03-01-07	Course description, Atoms, Periodic Table, Electronic Structure	1.1-1.6, 2.1-2.4	
08-01-07	Bonding and Crystal Structure	2.5-2.8	
10-01-07	Crystal Structure	3.1-3.7	WebCT Quiz Due 12-01-07
15-01-07	Crystal Structure and Defects	3.8-3.17, 4.1-4.11	
17-01-07	Diffusion, Materials Fabrication and Microstructure	5.1-5.6, 11.3-11.6	Tutorial Quizzes
22-01-07	Phase Diagrams and Microstructure I	9.1-9.19	
24-01-07	Phase Diagrams and Microstructure II	9.1-9.19	WebCT Quiz Due 26-01-07
29-01-07	*Review / Special Topic*		
31-01-07	Mechanical Properties I	6.1-6.12	Tutorial Quizzes
05-02-07	Mechanical Properties II	7.1-7.13	
07-02-07	Mechanical Properties III	8.1-8.15	Tutorial Quizzes
12-02-07	Mechanical Properties Summary	Chs. 6, 7, 8	
14-02-07	*Review / Special Topic*		NO QUIZ

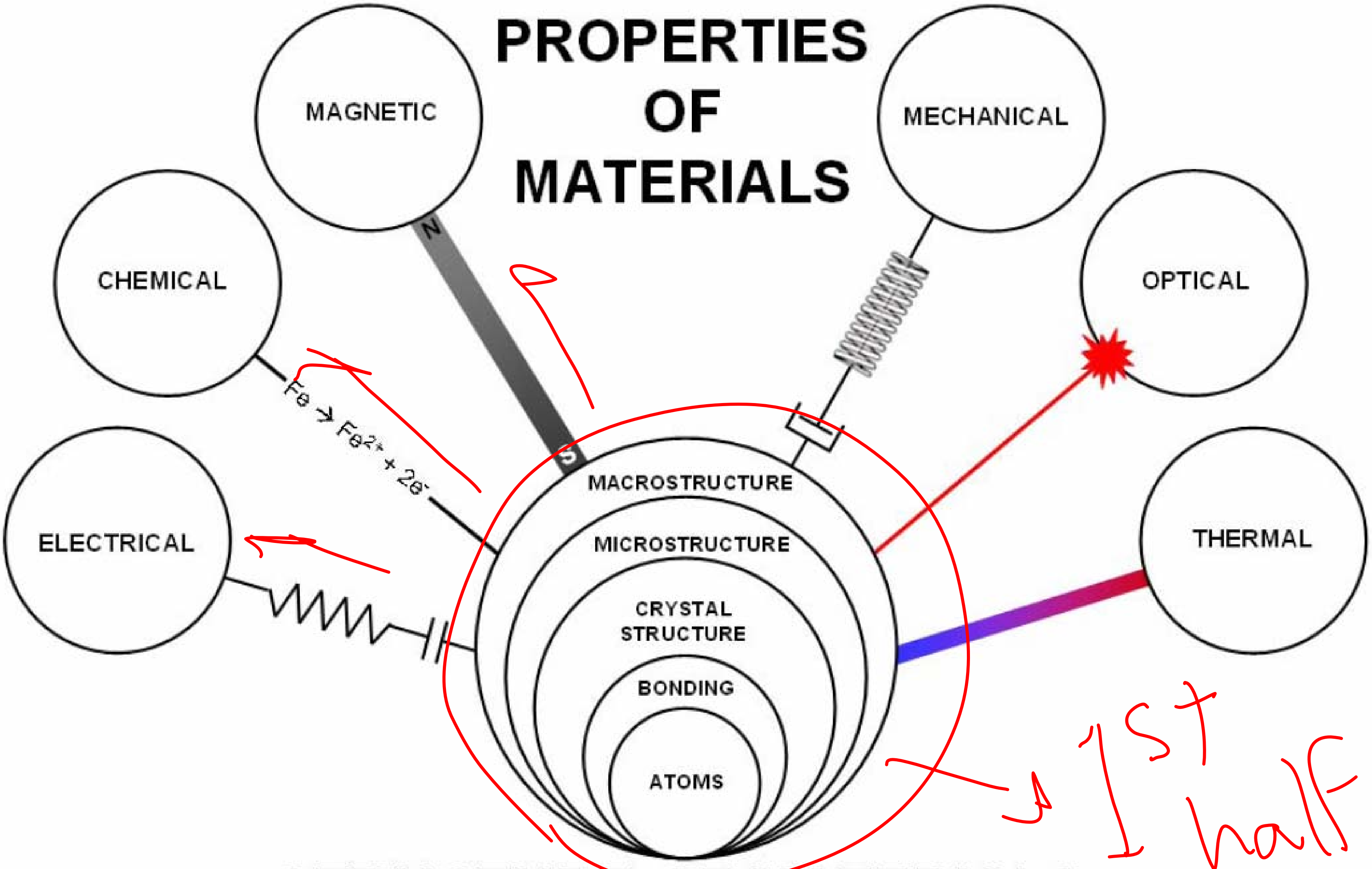
Revised Schedule



VII. Revised Course Schedule

Lecture (DD/MM/YY)	Lecture Topic	Readings	Assignments
03-01-07	Course description, Atoms, Periodic Table, Electronic Structure	1.1-1.6, 2.1-2.4	
08-01-07	Bonding and Crystal Structure	2.5-2.8	
10-01-07	Crystal Structure	3.1-3.7	WebCT Quiz Due 12-01-07
15-01-07	Crystal Structure and Defects	3.8-3.17, 4.1-4.11	
17-01-07	Defects	4.1-4.11	Tutorial Quizzes
22-01-07	Defects and Diffusion	4.1-4.11, 5.1-5.6	
24-01-07	Diffusion	5.1-5.6	WebCT Quiz Due 26-01-07
29-01-07	Diffusion, Materials Fabrication	5.1-5.6, 11.3-11.6	
31-01-07	Phase Diagrams and Microstructure I	9.1-9.19	Tutorial Quizzes
05-02-07	Phase Diagrams and Microstructure II	9.1-9.19	
07-02-07	Phase Transformations	10.1-10.4	Tutorial Quizzes
12-02-07	*Special Topic – Microelectronics*	22.15-22.20 (Web)	
14-02-07	*Review*		NO QUIZ

PROPERTIES OF MATERIALS



1st half

STRUCTURE OF MATERIALS

Phase diagrams

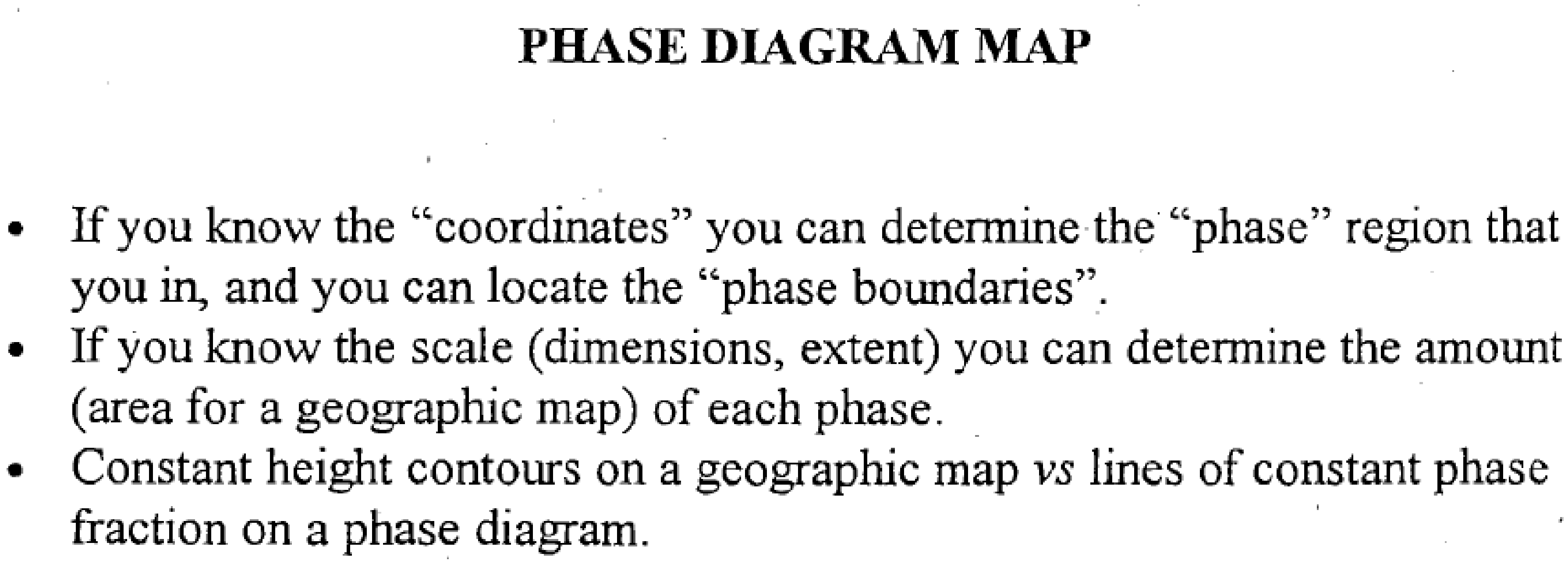
N

degrees

S

W Degrees E

Phase diagrams



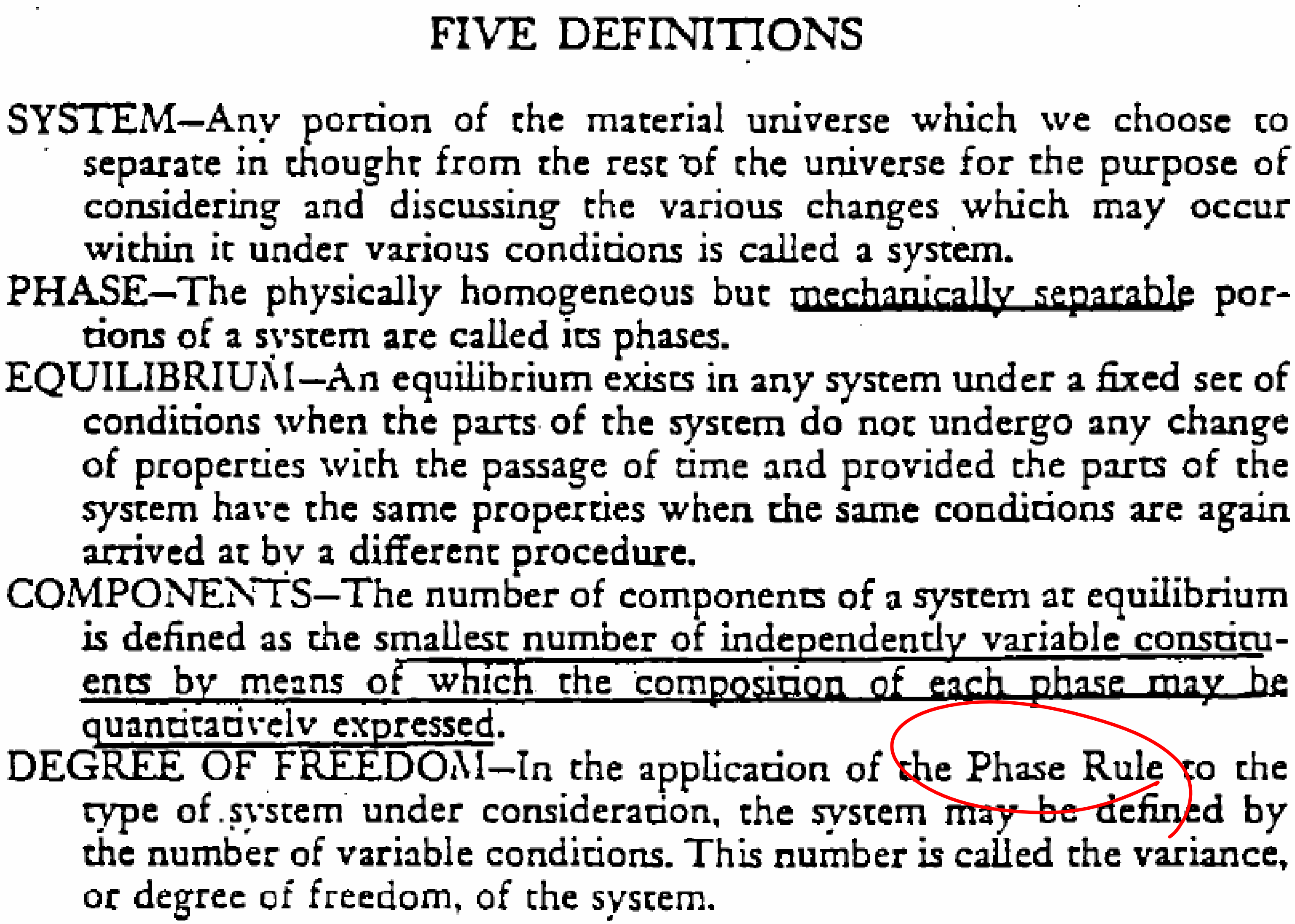
PHASE DIAGRAM MAP

- If you know the "coordinates" you can determine the "phase" region that you in, and you can locate the "phase boundaries".
- If you know the scale (dimensions, extent) you can determine the amount (area for a geographic map) of each phase.
- Constant height contours on a geographic map *vs* lines of constant phase fraction on a phase diagram.

Phase diagrams

PHASE DIAGRAMS

Phase diagrams



FIVE DEFINITIONS

SYSTEM—Any portion of the material universe which we choose to separate in thought from the rest of the universe for the purpose of considering and discussing the various changes which may occur within it under various conditions is called a system.

PHASE—The physically homogeneous but mechanically separable portions of a system are called its phases.

EQUILIBRIUM—An equilibrium exists in any system under a fixed set of conditions when the parts of the system do not undergo any change of properties with the passage of time and provided the parts of the system have the same properties when the same conditions are again arrived at by a different procedure.

COMPONENTS—The number of components of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase may be quantitatively expressed.

DEGREE OF FREEDOM—In the application of the Phase Rule to the type of system under consideration, the system may be defined by the number of variable conditions. This number is called the variance, or degree of freedom, of the system.

Components and Phases

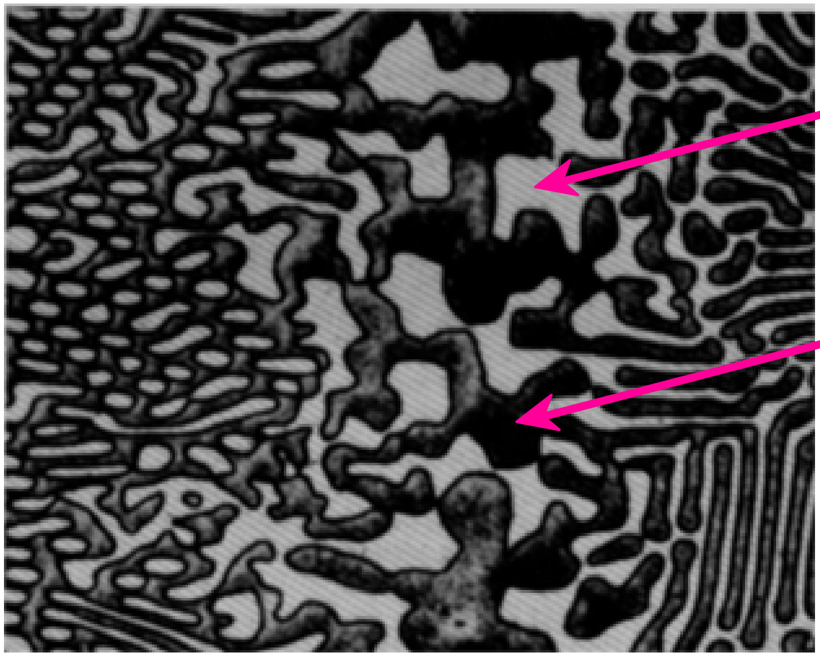
- Components:

  The elements or compounds which are present in the mixture (e.g., Al and Cu)

- Phases:

  The physically and chemically distinct material regions that result (e.g., α and β).

Aluminum-Copper Alloy

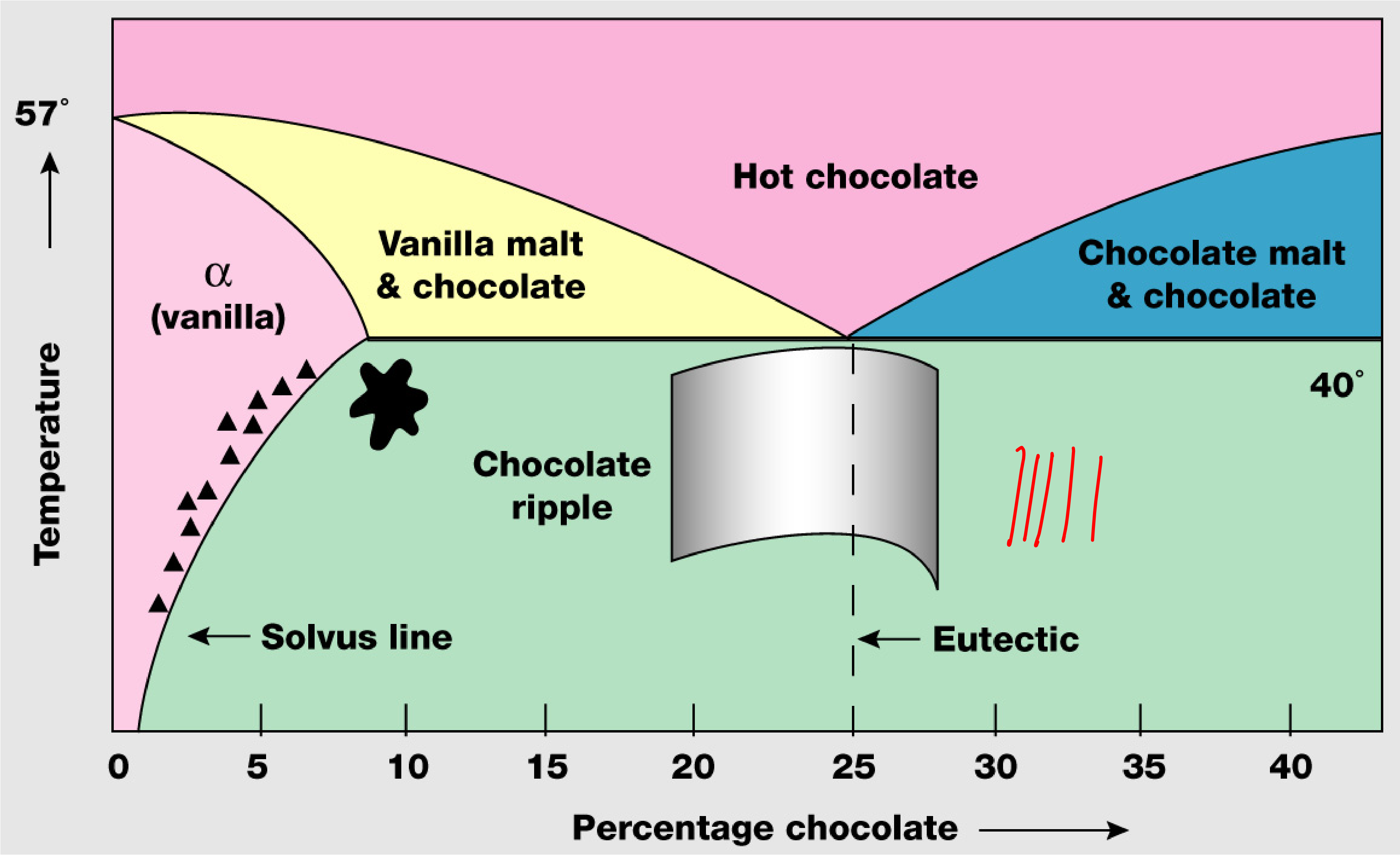


β (lighter phase)

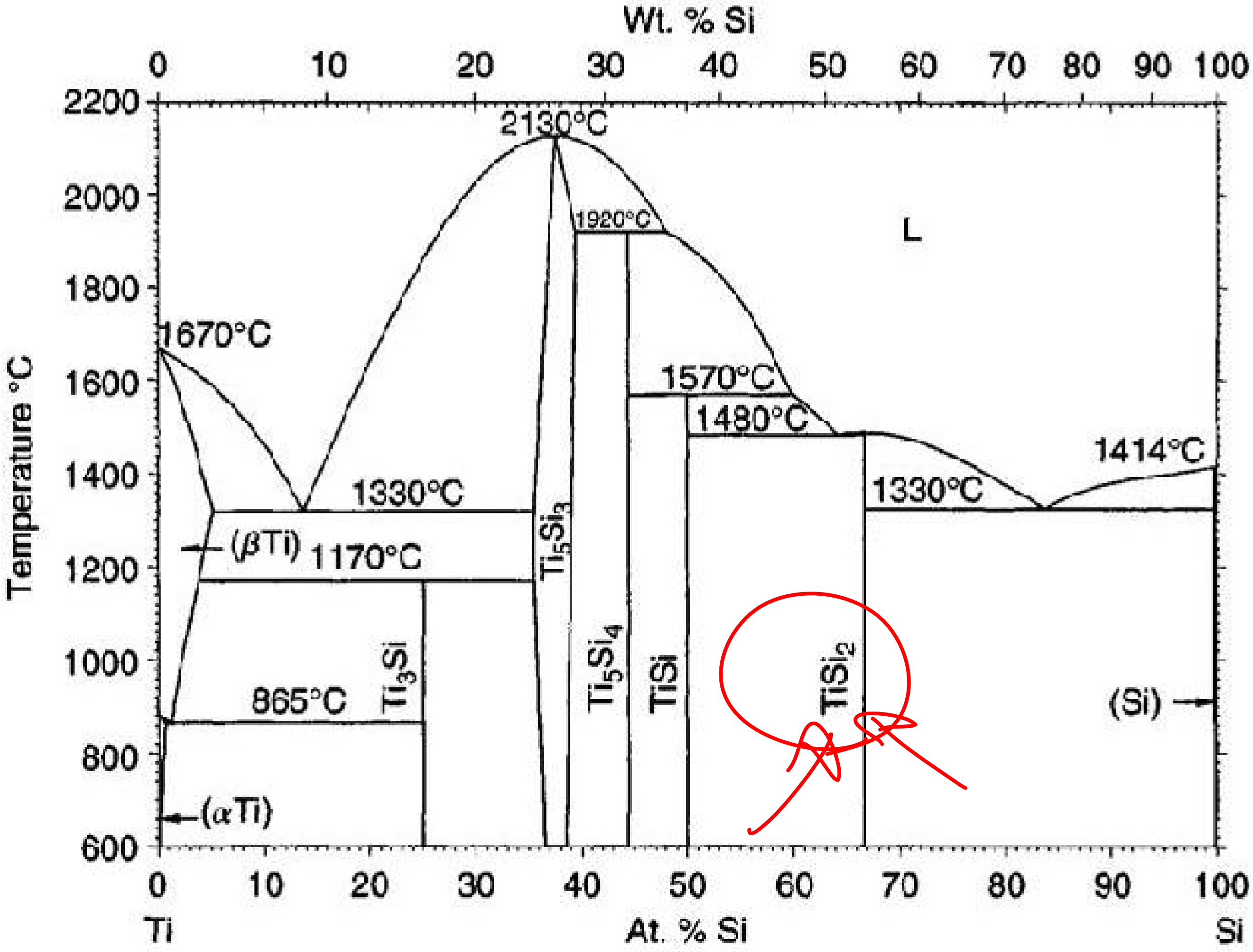
α (darker phase)

Adapted from chapter-opening photograph, Chapter 9, *Callister 3e.*

Left to right 1 → 2 - 1 → 2 NASA



Phase diagrams



Phase Equilibria: Solubility Limit

Introduction

- – Solutions – solid solutions, single phase
- – Mixtures – more than one phase

Adapted from Fig. 9.1, *Callister 7e.*

- Solubility Limit:

  Max concentration for which only a single phase solution occurs.

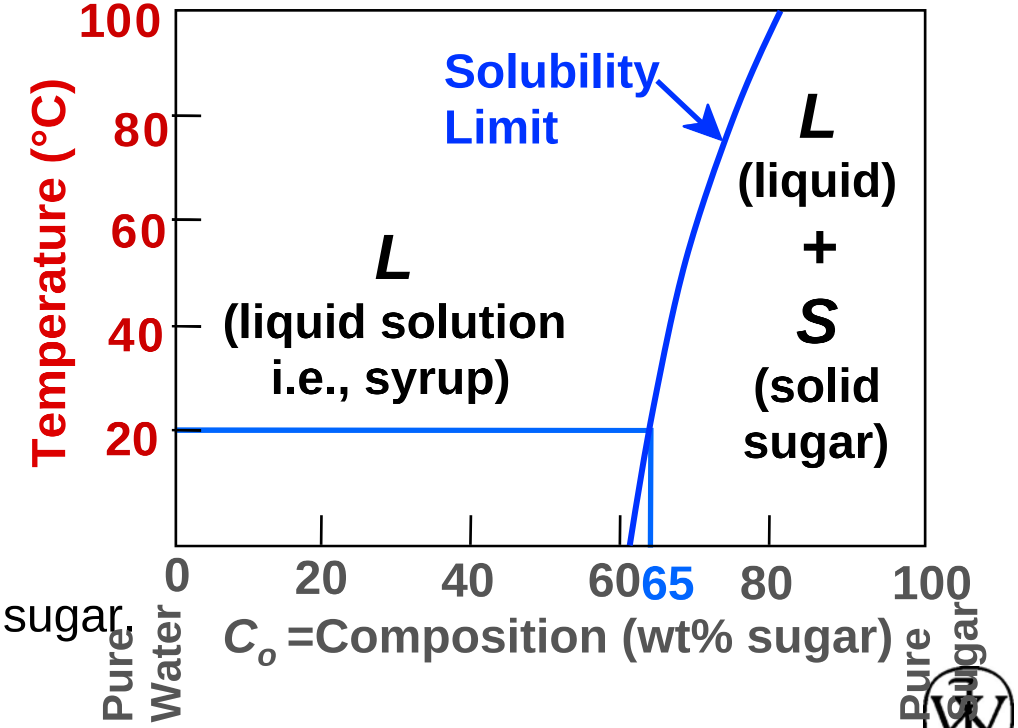
Question: What is the solubility limit at 20°C?

Answer: 65 wt% sugar.

If C_o < 65 wt% sugar: syrup

If C_o > 65 wt% sugar: syrup + sugar.

Sucrose/Water Phase Diagram



Phase Equilibria

Simple solution system (e.g., Ni-Cu solution)

	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- Both have the same crystal structure (FCC) and have similar electronegativities and atomic radii (W. Hume – Rothery rules) suggesting high mutual solubility.
- Ni and Cu are totally miscible in all proportions.

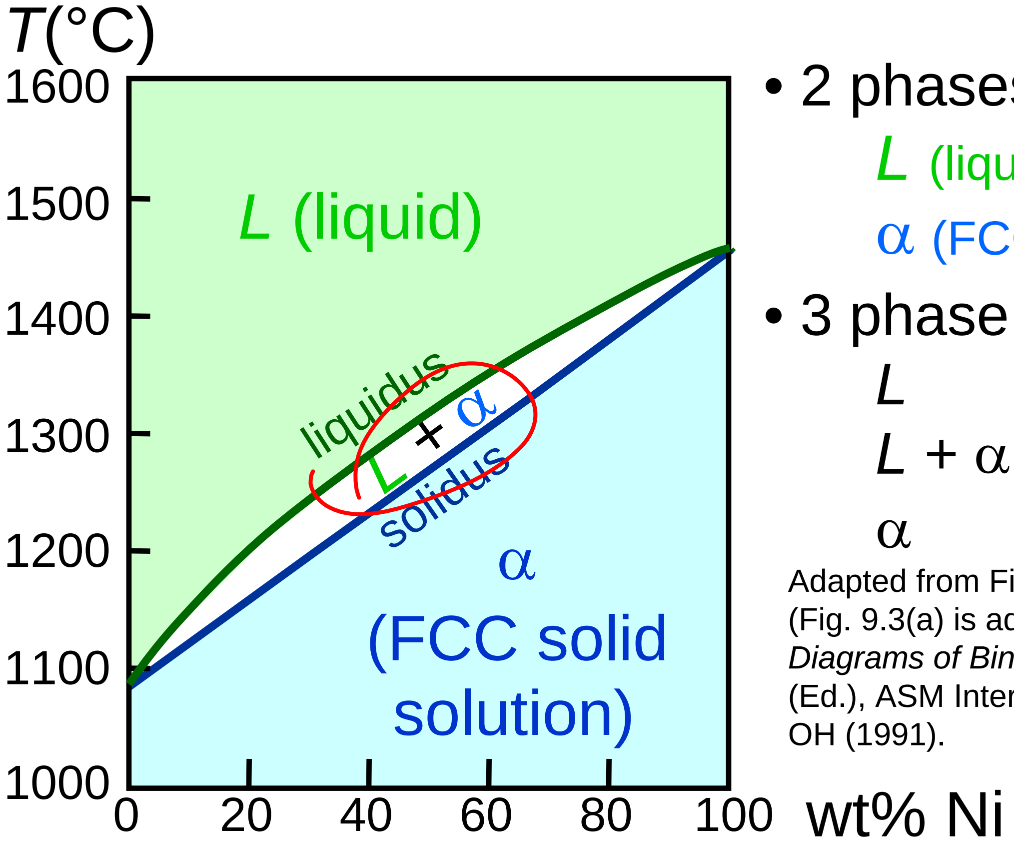
Phase Diagrams

- Indicate phases as function of T, C_o, and P.
- For this course:

  -binary systems: just 2 components.

  -independent variables: T and C_o (P = 1 atm is almost always used).

- Phase Diagram for Cu-Ni system



- 2 phases:
  - L (liquid)
  - α (FCC solid solution)
- 3 phase fields:
  - L
  - $L + \alpha$
  - α

Adapted from Fig. 9.3(a), *Callister 7e.* (Fig. 9.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH (1991).

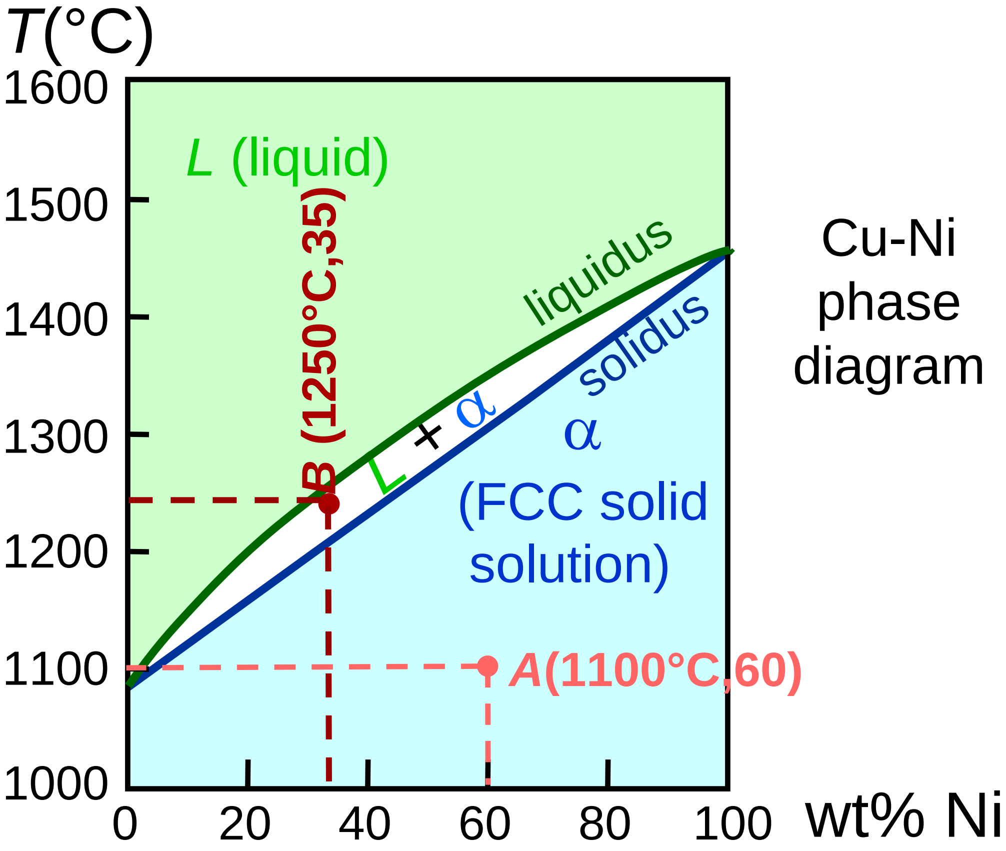
Phase Diagrams:
and types of phases

- Rule 1: If we know *T* and C_o, then we know:
  --the # and types of phases present.

- Examples:

A(1100°C, 60):
1 phase: α

B(1250°C, 35):
2 phases: *L* + α



Cu-Ni phase diagram

Adapted from Fig. 9.3(a), *Callister 7e.* (Fig. 9.3(a) is adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash (Ed.), ASM International, Materials Park, OH, 1991).