

## CME 300 Properties of Materials

### ANSWERS: Homework 4 October 12, 2011

1) The Scherrer equation can be obtained by taking the derivative of the Bragg Equation. Perform this derivative. Begin by multiplying  $\lambda$  and  $d$  by an integer  $m$  such that  $md = t$ , the Scherrer Size. Differentiate keeping in mind that  $m\lambda$  is a constant. The smallest increment in  $t$  is  $d$ , so “ $dt$ ” is equal to  $d$ . You must reuse Bragg’s law to simplify your final expression to obtain the Scherrer Equation using  $d\theta = B$ .

$$m\lambda = 2t \sin \theta$$

$$0 = 2 \sin \theta dt + 2t \cos \theta d\theta$$

$$0 = 2d \sin \theta + 2t \cos \theta B$$

$$0 = \lambda + t \cos \theta B$$

$$t = \frac{\lambda}{B \cos \theta} \sim \frac{0.9\lambda}{B \cos \theta}$$

2) Debye-Waller thermal broadening of diffraction peaks is modeled with a Gaussian function, that predicts a diffracted peak shape of  $I(q) = \exp\left(\frac{-q^2 \langle u^2 \rangle}{3}\right)$  where  $q$  is the scattering vector

$$q = \frac{2\pi}{d_{\text{Bragg}}} = \frac{4\pi}{\lambda} \sin(\theta) \text{ and } \langle u^2 \rangle \text{ is the mean square free path for the atoms about the lattice}$$

site. Compare the Debye-Waller function with the Gaussian Distribution function and give a value for the standard deviation about the peak (peak width) due to thermal broadening. Do you think it is logical to use the Gaussian Distribution to describe a diffraction peak (explain your answer, you need to explain what a Gaussian Distribution is normally used to describe).

The Gaussian distribution is  $P(x) = P(0) \exp\left(\frac{-(x - \langle x \rangle)^2}{2\sigma^2}\right)$  and describes a random

distribution about a mean value  $\langle x \rangle$  with the standard deviation of  $\sigma$ . This is the “bell shaped curve” for grade distribution; however, it is strictly inappropriate when there is a minimum or a maximum value (0 and 100 for grades). (A log-normal could be appropriate when there is a minimum value.) For the Debye-Waller Factor the mean is the atomic lattice position taken to be 0 and the angle converted to inverse distance or  $q$  replaces  $x$  in the Gaussian distribution so the variance is  $\sigma^2 = \frac{3}{2\langle u^2 \rangle}$ . The Debye-Waller Factor is used as

a prefactor to the intensity for a diffraction peak. The larger the atomic motion, the larger  $\langle u^2 \rangle$  and the smaller the peak intensity. If the diffraction peak were originally a Gaussian in

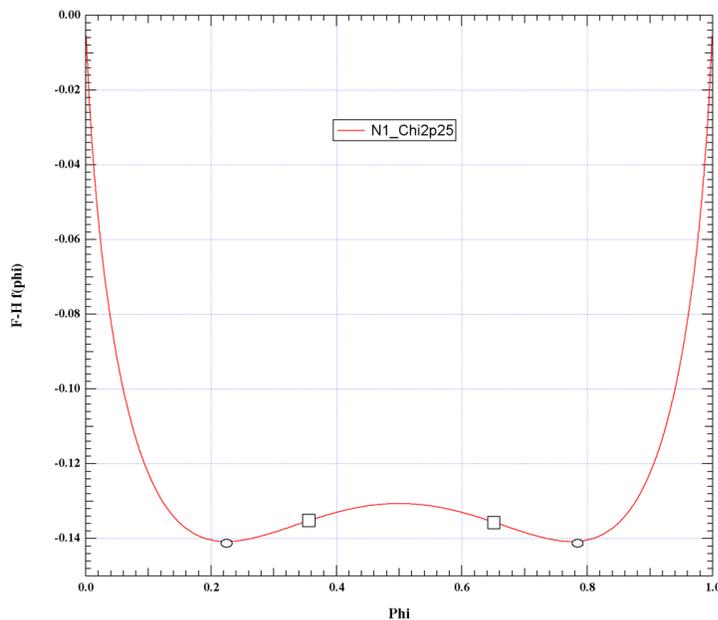
$q$ ,  $I(q) = I(0) \exp\left(\frac{-(q - q_{(hkl)})^2}{2\sigma_{(hkl)}^2}\right)$ , the Debye-Waller Factor is centered on  $q = 0$  not at  $q_{(hkl)}$  so

mostly effects the intensity of the peak, not the shape.

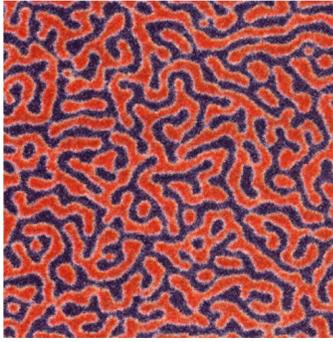
3) Why can't diffraction be used to make a picture of a crystal lattice? (Your answer should consider how a crystal would appear in inverse space).

Diffraction gives statistical information about the crystalline structure. An image has details about a specific small group of atoms. In inverse space, lattice points are given by Miller indices for planes. Each point includes all of the planes of a given type. So the lattice is not a picture of a few atoms in their lattice positions but an average of all of the Miller indices in the entire crystal. The spatial connection between the Miller indices, that is their arrangement in 3d space is lost in inverse space. So we know that certain repeat distances occur but we do not have the ability to reconstruct the 3d image directly from the diffraction pattern. This is called the loss of phase information.

4) In class we discussed the phase diagram for two polymers that display partial miscibility. Sketch a plot of the free energy change on mixing versus composition at a temperature where there is a miscibility gap. Show in this plot the origin of the spinodal and binodal regimes. Sketch the morphology that result from spinodal and binodal decomposition. Show the spinodal and binodal curves in a UCST system and indicate the points that are determined from your free energy versus composition plot.

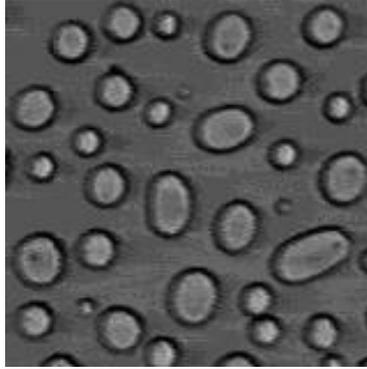


The binodal line is associated with the circles and spinodal line with the squares.

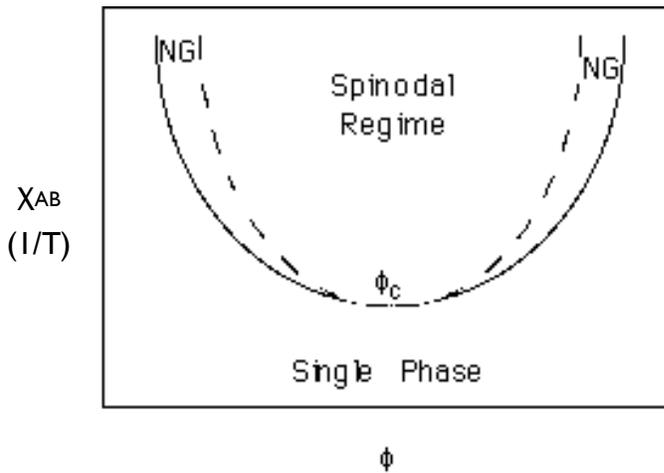


Simulation of pattern formed by spinodal decomposition in real space.

Spinodal

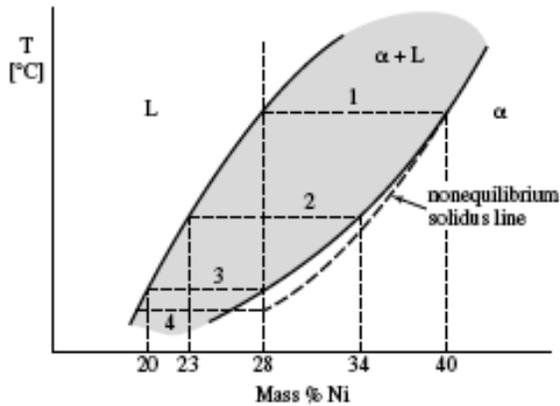


Binodal (Nucleation and Growth)



*Problems from Hummel (Chapter 5)*

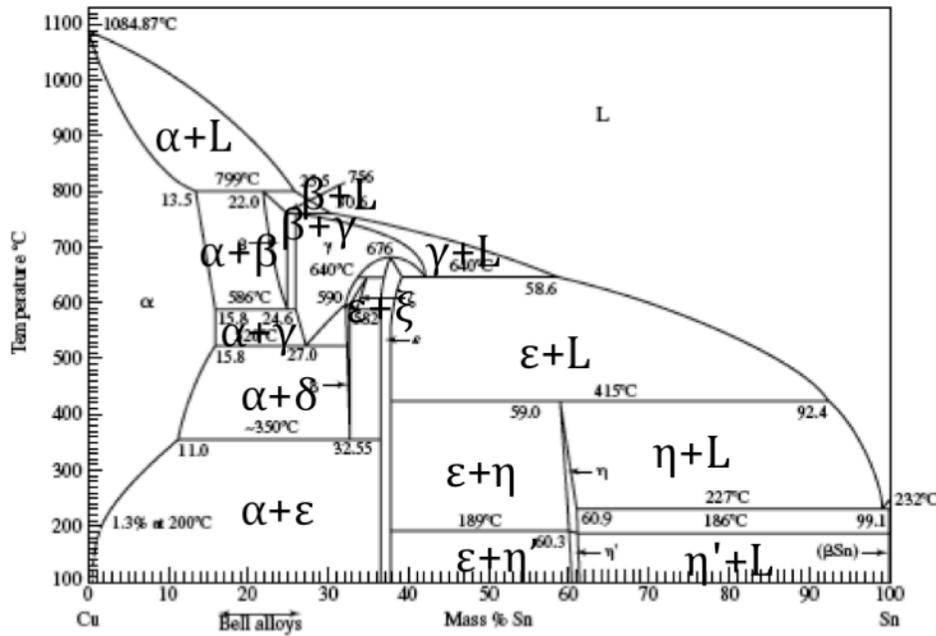
5.1. Give the amounts of the liquid and solid ( $\alpha$ ) phases (in percent) which are present when a Cu-28 mass % Ni alloy is very slowly cooled to a temperature corresponding to Tie Line #2 in Figure 5.5.



Amount of liquid =  $(34-28)/(34-23)=0.545$ ; Amount of solid =  $(28-23)/(34-23)=0.455$

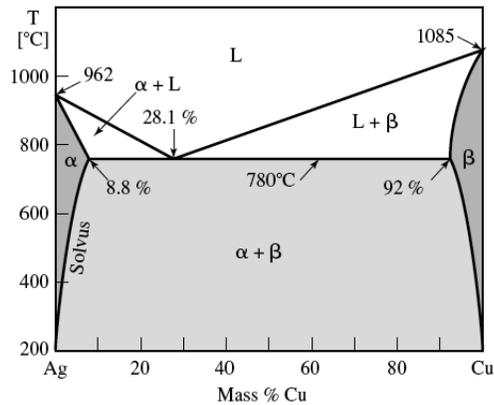
5.2. Figure 5.17 depicts the Cu–Sn phase diagram in which the single phase regions are labeled only.

- (a) Label the two-phase regions.
- (b) State the three-phase reactions that occur and give the temperatures at which they take place. Write the pertinent reaction equations.



799°C  $\alpha+L \Rightarrow \beta$ ; 586°C  $\beta \Rightarrow \alpha+\gamma$ ; 640°C  $\gamma+\epsilon \Rightarrow \xi$ ; 640°C  $\xi \Rightarrow \epsilon+L$ ; 526°C  $\gamma \Rightarrow \alpha+\delta$ ; 350°C  $\delta \Rightarrow \alpha+\epsilon$ ; 415°C  $\epsilon+L \Rightarrow \eta$ ; There are others but it gets confusing at the bottom right.

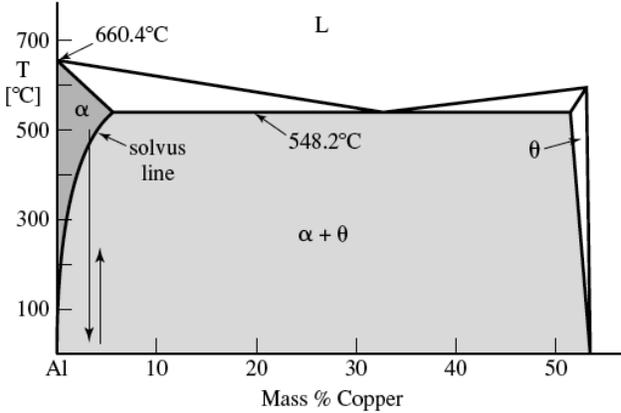
5.3. State the maximal solubility of (a) copper in silver and (b) silver in copper. At which temperatures do these maximal solubilities occur?



8.8% copper in silver and 8% silver in copper. Both occur at the eutectic temperature, 780°C.

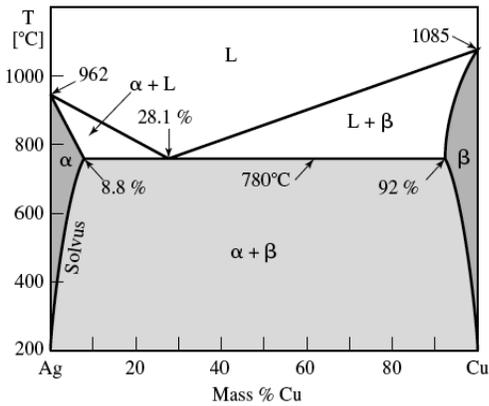
5.4. What is the approximate solubility of copper in silver at room temperature?  
 At 25°C there is almost no solubility of copper in silver.

5.5. Give the phases present and their compositions for an Al-5 mass % Cu alloy at 400°C.



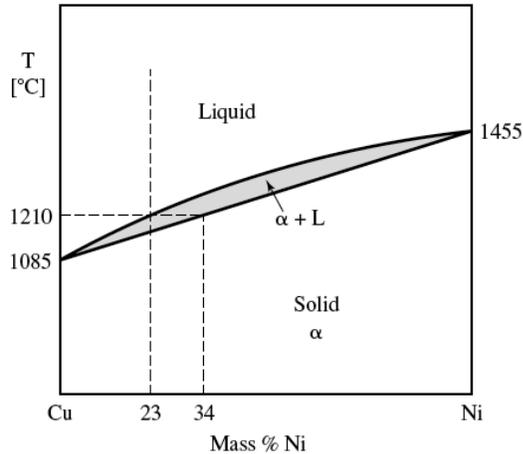
At 400°C and 5% Cu a mixture of  $\alpha$  and  $\theta$  phases are present. There will be about  $(5-3)/(52-3)=0.04$  fraction of the  $\theta$  phase and 96% of the  $\alpha$  phase.

5.6. Assume an Ag-10 mass % Cu alloy. To what temperature does this alloy have to be heated so that 50% of the sample is liquid?



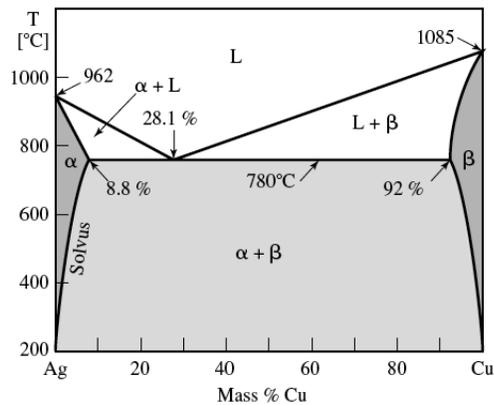
This occurs at about 820°C.

5.7. Does a copper–nickel binary alloy exist whose solid phase at equilibrium contains 36 mass % Ni and whose liquid phase contains 20 mass % Ni? Explain. Refer to Figure 5.3.



No it does not exist since both the solidus and liquidus slope upwards in the phase diagram so when the nickel content in the solid increases the nickel content in the liquid will also increase.

5.8. A silver–20 mass % copper alloy is slowly heated from room temperature.  
 (a) State the temperature at which a liquid phase starts to form.  
 (b) State the composition of this liquid phase.  
 (c) At which temperature is the alloy completely liquefied?  
 (d) Give the composition of the solid just before complete melting has occurred.



a) Eutectic temperature 780°C b) 28.1% Cu (Eutectic composition) c) about 812°C d)  $\alpha$  phase about 5% Cu.

**9.4** What thermodynamic condition must be met for a state of equilibrium to exist?

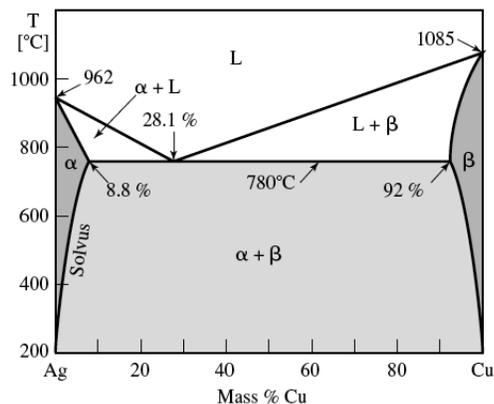
The chemical potential of two phases in equilibrium are the same. The chemical potential is the first derivative of free energy with respect to composition.

**9.8** Cite the phases that are present and the phase compositions for the following alloys:

- (a) 15 wt% Sn–85 wt% Pb at 100°C (212°F)
- (b) 25 wt% Pb–75 wt% Mg at 425°C (800°F)
- (c) 85 wt% Ag–15 wt% Cu at 800°C (1470°F)
- (d) 55 wt% Zn–45 wt% Cu at 600°C (1110°F)
- (e) 1.25 kg Sn and 14 kg Pb at 200°C (390°F)
- (f) 7.6 lb<sub>m</sub> Cu and 144.4 lb<sub>m</sub> Zn at 600°C (1110°F)
- (g) 21.7 mol Mg and 35.4 mol Pb at 350°C (660°F)
- (h) 4.2 mol Cu and 1.1 mol Ag at 900°C (1650°F)

- a)  $\epsilon + \eta$   $C_\epsilon = 87\%$  Zn  $C_\eta = 97\%$  Zn
- c) Liquid  $C_L = 55\%$  Ag
- e)  $\beta + \gamma$   $C_\beta = 49\%$  Zn  $C_\gamma = 58\%$  Zn
- g)  $\alpha$   $C_\alpha = 63.8\%$  Ni

**9.9** Is it possible to have a copper–silver alloy that, at equilibrium, consists of a  $\beta$  phase of composition 92 wt% Ag–8 wt% Cu, and also a liquid phase of composition 76 wt% Ag–24 wt% Cu? If so, what will be the approximate temperature of the alloy? If this is not possible, explain why.



Not possible. At 8% Cu the  $\beta$  phase does not exist.