Mat E 272
Fall 2001 – Lecture 15
Introduction to Phase Diagrams

Introduction:

Phase diagrams are valuable tools for any scientist or engineer involved in development, analysis, or specification of materials.

We will look at several different types of phase diagrams, beginning with the most simple involving two components – that of complete solubility in the solid state. Using the Cu-Ni (or Si-Ge) system as an example, we will learn how to determine what phases are present at any given temperature and composition. We will also develop a simple expression called the "lever law," which can be used to calculate the amounts of each phase of a binary system. Eutectic, peritectic, eutectoid, and peritectoid binary systems will be defined and discussed.

In previous lectures, we discussed how the properties of materials are determined by the arrangement of discrete phases, i.e., the microstructure. Once we have mastered the basic concepts of how to interpret phase diagrams, we will be able to predict the microstructure of an alloy given the overall composition and solidification rate. In addition, knowledge of the phase diagram allows us to determine the appropriate operating temperature range for a material.

Definitions:

Phase: **a chemically homogeneous portion of a microstructure; a region of uniform composition and crystal structure. Do not confuse "phase" with "grain." A single phase material may contain many grains, however, a single grain consists of only one phase.**

Component: **a distinct chemical substance (from which a phase is formed) Note that the substance need not be a pure element, such as Cu or Ni. A component can be a complex substance in its own right.**

Examples: Cu, Cu-30% Ni, Fe-0.001C, $TiAl_6V_4$, SiO_2, $C_{12}H_{22}O_{11}$

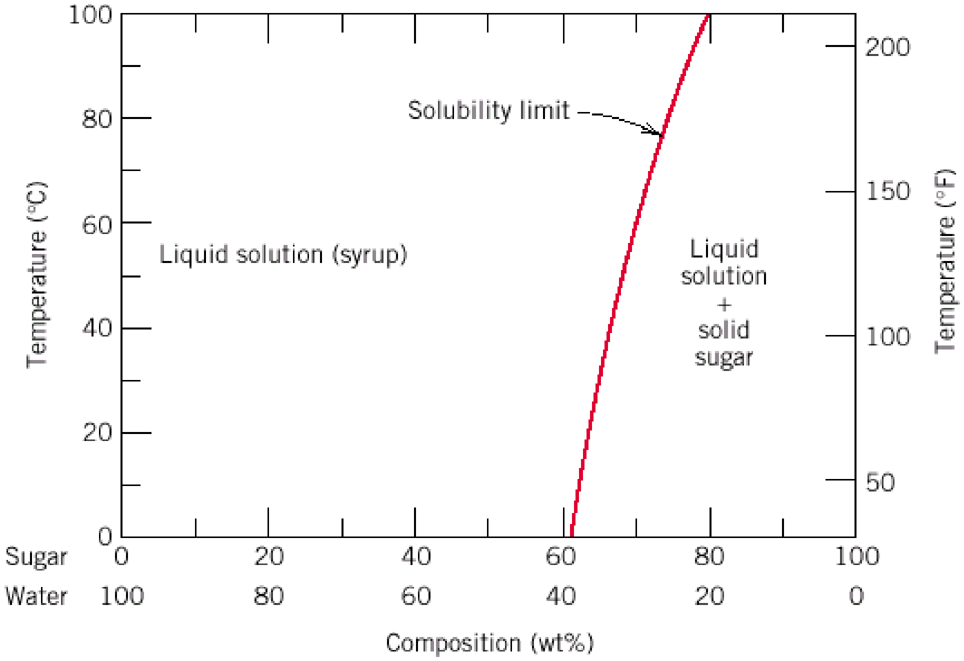
System: **a series of possible alloys, compounds, and mixtures resulting from the same components.**

Examples: the Fe-C system, the water-sugar system, the alumina-silica system.

Equilibrium: The "stable" configuration of a system, when a sufficient amount of time has elapsed that no further changes occur. Equilibrium may take place rapidly (on the order of microseconds), or may require a geological time frame. We will concern ourselves in this class with "equilibrium" phase diagrams, that is, the nature of a sytem at any given temperature after a "sufficiently" long period of time. (Extreme quench rates can sometimes shift phase boundaries relative to their equilibrium values)

Solubility Limit: The maximum amount of solute that can be added to a solvent without resulting in nucleation of a separate phase. In solids, this represents the maximum amount of interstitial or substitutional addition in which the original crystal structure of the host is maintained.

Example: sugar – water:



Important points:

- **Composition is plotted on the abscissa**
  - **Usually either weight % or atomic %**
- **Temperature is plotted on the ordinate**
- **The region to the left of the red line is a single phase region**
  - **= sugar completely dissolved in water**

- **The region to the right of the red line is a two phase region**
    - **= a mixture of syrup + undissolved sugar**

- **The red line represents the solubility limit**
    - **Note the temperature dependence!!**
        - **As T increases, so does the solubility**
    - **True for most solids (up to a point)**

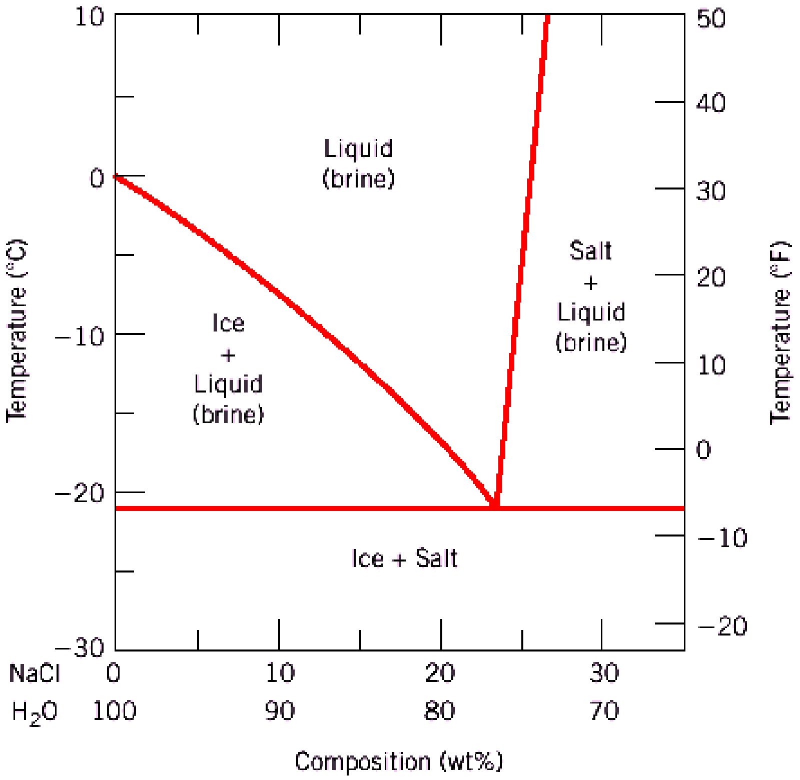
What is an "equilibrium phase diagram"?

Put the words together:

Equilibrium – stable over time
Phase – a chemically and structurally homogeneous region
Diagram – a map or drawing showing the general scheme of things

Another example of an equilibrium phase diagram:

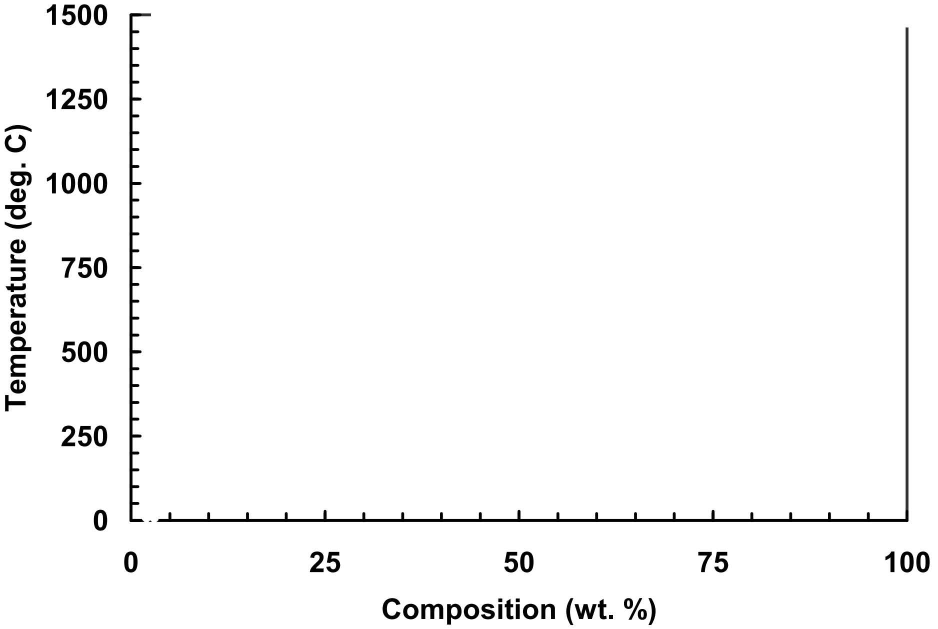
Note that the components do not need to be elements; they can themselves be alloys or chemical compounds, such as NaCl and H_2O. Sometimes we refer to such diagrams as "pseudo-binary" phase diagrams.



Note: this is only a portion of the entire NaCl-H_2O phase diagram.

In general, a complete phase diagram depicts the relationship between composition, temperature, and pressure for a particular system of components. Since most metallurgical work involves atmospheric pressure, we are usually most interested in composition – temperature diagrams.

At a minimum, a binary phase diagram must contain a composition axis and a temperature axis:



Boundary lines are constructed on the phase diagram to separate various phases

Determination of phase diagrams:

- **Phase diagrams are determined by preparing a series of compositions within the system of interest, heating each to various temperatures, and analyzing the phases present (usually by x-ray diffraction)**

- **Phase diagrams can also be calculated from fundamental thermodynamic principles.**

Information that can be obtained from phase diagrams:

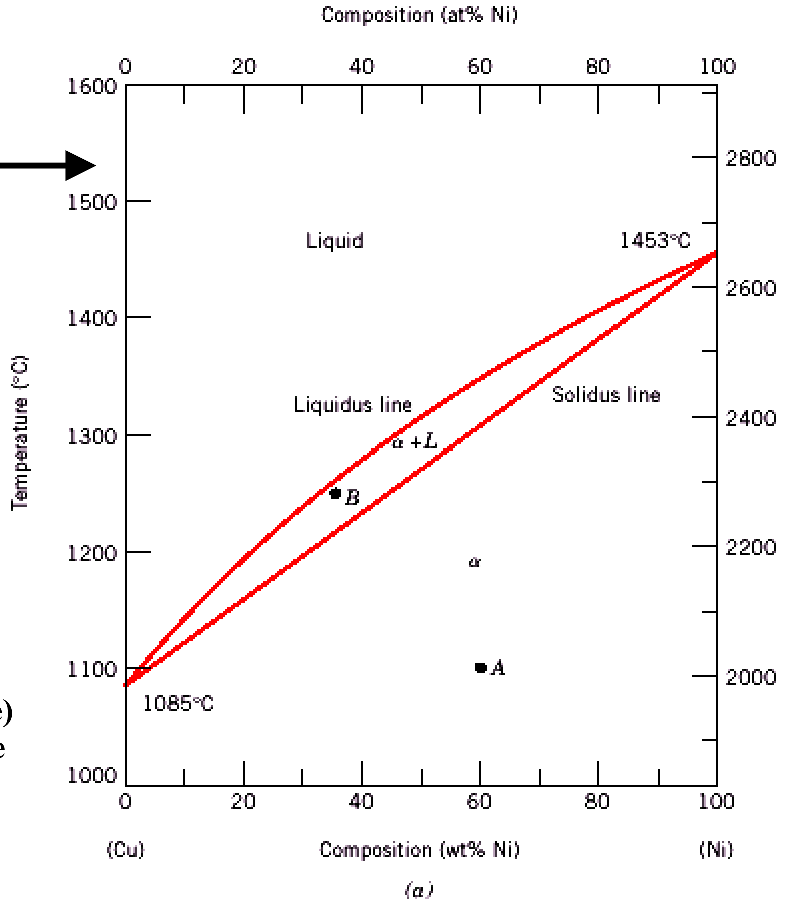
- **What phases exist at any given temperature – composition**
- **What the compositions of the phase(s) is(are)**
- **How much of each phase is present (phase amounts)**

- **Case I. Complete solubility in the solid state**

Example: Cu-Ni system

Pure copper along this vertical axis

Pure nickel along this vertical axis

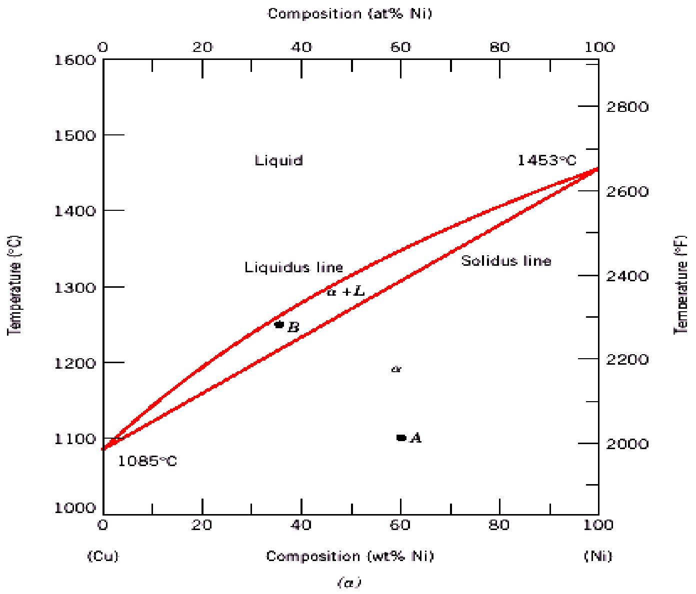


Above 1453 °C, Cu and Ni are completely soluble (miscible) in the liquid state

Below 1085 °C, Cu and Ni are completely soluble (miscible) in the solid state

I. Phases present:

- **Single phase liquid (at high temperatures) (denoted by the letter "L")**
- **Single phase solid (at low temperatures) (denoted by the Greek letter "α")**
- **Two-phase mixture of solid + liquid (at intermediate temperatures) (α + L)**



At any given point in this diagram, you should be able to identify what phase(s) is(are) present.

Can you identify what phase(s) is(are) present at point "A" in the Cu-Ni diagram? At point "B"?

Important point: in <u>every</u> binary equilibrium phase diagram, the phases present at any given temperature alternate in sequence from one terminal side to the other (e.g., single phase, two phase, single phase, two phase, … , single phase). There are no exceptions to this rule. This fact can be extremely helpful in interpreting complex phase diagrams. (Remember it!!!)

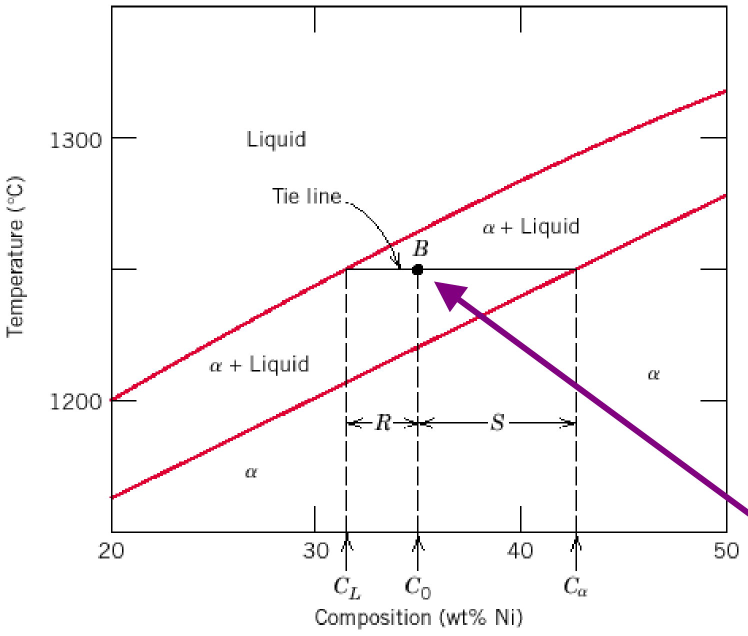
(When you see various phase diagrams in this and other sections, check out the validity of this rule at various temperatures. A handsome bounty will be offered for capture and delivery of any binary phase diagram found to be in violation of this rule.)

II. Composition of the phases:

- If in a single phase region, the composition is simply the overall composition of the alloy

  Example: the composition of point "A" in the Cu-Ni diagram is 60 wt. % Ni – 40 wt. % Cu.

- If in a two-phase region, the composition of each phase is obtained from the intersection of the composition's isotherm with the respective phase boundaries:
  - "Isotherm" refers to a line of constant temperature (i.e., a horizontal line on the phase diagram)
  - The particular isotherm connecting the point representing the alloy's overall composition with the nearest phase boundaries on either side is called a "tie line"



composition of each phase is obtained by dropping perpendiculars down to the composition axis from the intersection of the tie line with the phase boundaries boundary.

Example:

- overall alloy composition = Co (as shown above)
- temperature of interest = 1250°C
  - at the temperature of interest, this composition lies in a two-phase field (liquid in equilibrium with solid)
- composition of liquid = intersection of tie line with liquidus (= C_L)
- composition of solid = intersection of tie line with solidus (= C_s)

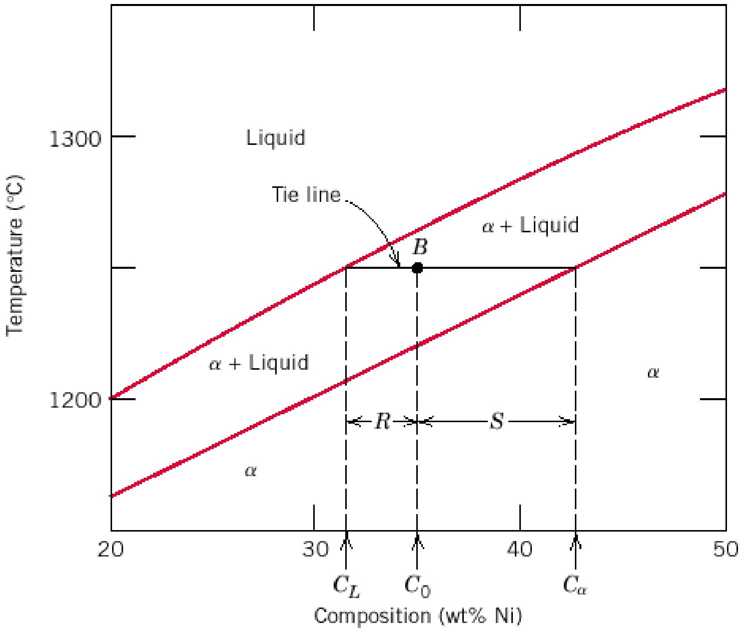
III. Amount (or mass fraction) of each phase:

- **If in a single phase region, the answer is trivial; the amount of phase is simply 100% (in other words, a phase fraction of 1.00) This is why we call it a "single phase" region!**

- **If in a two phase region, the amount of each phase is determined using a tool called the "lever law." (Actually, the proper description for this is an "inverse" lever law, as we shall soon see.)**

- **Recall the portion of the Cu-Ni phase diagram around composition "B":**

Since the overall composition of the alloy (Co) is closer to the liquidus than to the solidus, we expect more liquid phase than solid phase at this temperature.



Since there are only two components, the sum of the mass fraction of component 1 + component 2 must equal 1.0

For the composition "B" above, this statement can be written as $W_L + W_s = 1.0$ (1)

The mass of a particular component present in each phase (either Cu or Ni in the example above) must equal the total mass of that component in the alloy. (For example, if there are 112 pounds of Cu in the alloy, then the sum of the mass of Cu in the liquid and Cu in the solid must equal 112 pounds.)

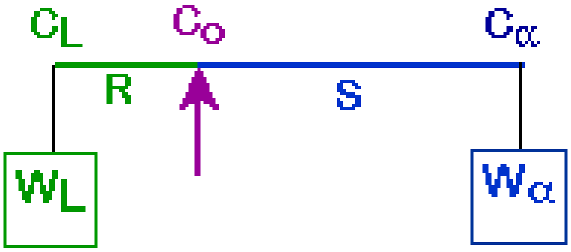
We can write this as $W_sC_s + W_lC_l = Co$ (2)

Equations 1 and 2 are two independent equations containing two unknowns (W_s and W_l). Consequently, we can solve for the two unknowns with the result:

$$W_l = \frac{C_s - C_o}{C_s - C_l} \quad \text{and} \quad W_s = \frac{C_o - C_l}{C_s - C_l} \qquad (3, 4)$$

giving the mass fraction of liquid and solid phases, respectively.

The validity of the lever-law in determining mass fraction of each component can be seen with the help of a mechanical lever analogy. Think of the overall composition of the alloy as the fulcrum, or balance point:



Example: **Again using the Cu-Ni phase diagram, suppose the overall composition of an alloy is 35 wt. % Ni and the alloy is at a temperature of 1250°C (i.e., point "B" in the figure). What are the mass fractions of solid and liquid phases at that temperature?**

Solution: **From the diagram, C_l = 31.5 wt. % Ni and C_s = 42.5 wt. % Ni. Since C_o = 35 wt. % Ni, we can directly substitute these values in equations 3 & 4, viz.,**

$$\text{Mass fraction of liquid} = \frac{42.5 - 35}{42.5 - 31.5} = 0.68$$

$$\text{Mass fraction of solid} = \frac{35 - 31.5}{42.5 - 31.5} = 0.32$$

so, at 1250°C, 68% of the alloy is liquid (with a composition 31.5 wt. % Ni) and 32% of the alloy is solid (with a composition of 42.5 wt. % Ni)

of course, since there are only two components, once you find either W_l or W_s, the remaining unknown can be determined by subtracting the known quantity from 1.0

Microstructural development:

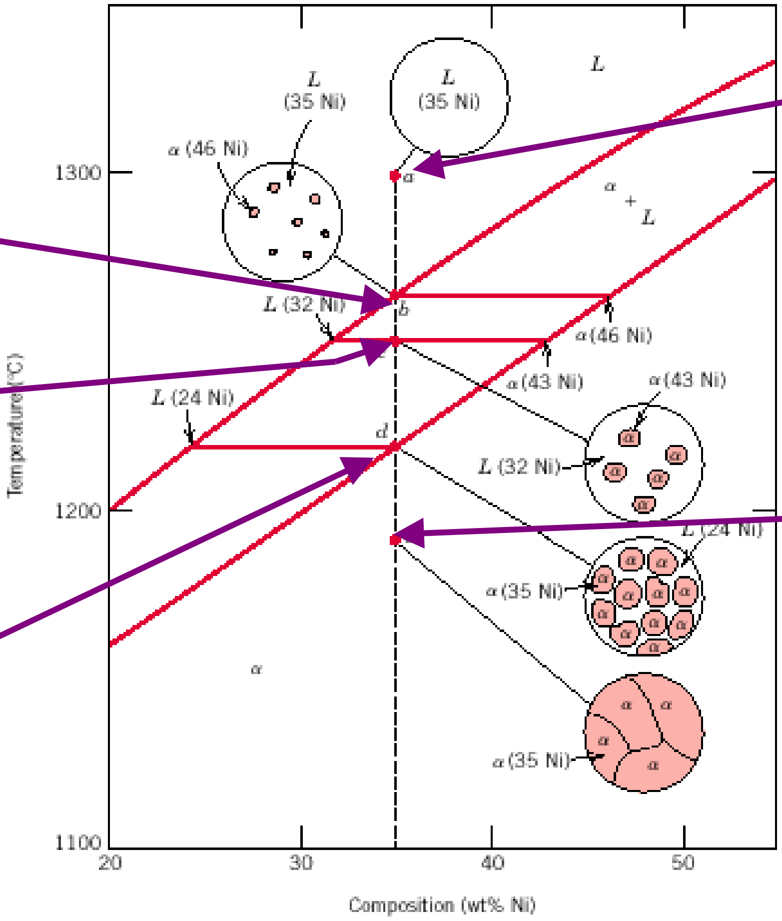
How does the microstructure of an alloy vary with position within the temperature-composition phase diagram?

In a binary alloy as shown above (exhibiting complete miscibility), it is impossible to solidify without passing through a two phase region.

Only in the case of the pure elements (i.e., the terminal end point compositions) will the melting temperature and freezing temperature coincide.

- **For all binary compositions, there exists a freezing (or mushy) zone, where solid and liquid are in equilibrium with each other. The resulting microstructure depends on how quickly freezing is allowed to occur.**

First, let's consider equilibrium solidification (wherein the rate of freezing is sufficiently low that at any time, equilibrium conditions exist). This simply means we cool the molten alloy very slowly.



1260°C; crossing liquidus boundary, first nucleation of solid phase (of composition 46 % Ni)

1250°C; within the two phase region, note composition of freezing solid phase is changing

1220°C; crossing solidus boundary, last liquid to freeze has composition 24 % Ni.

1300°C; single phase, uniform liquid composition

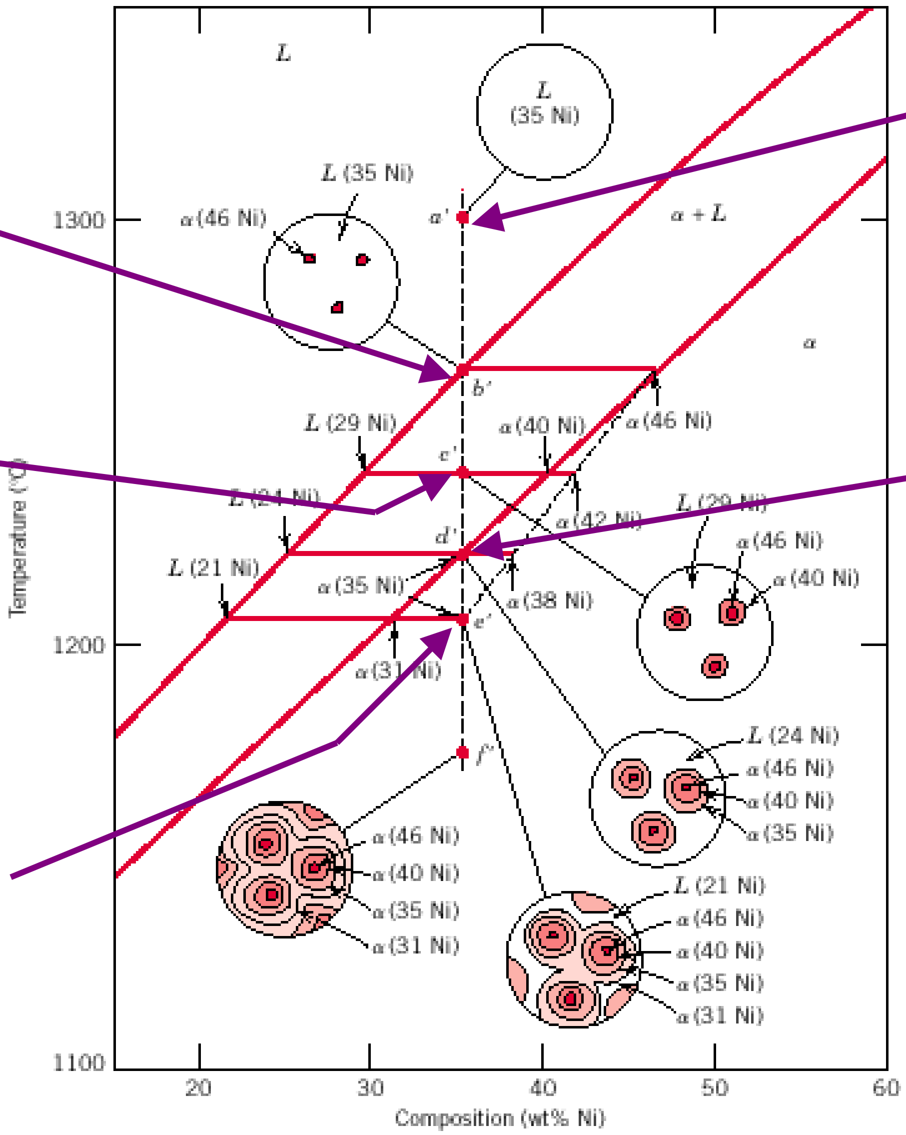
1190°C; single phase here, all solid. If cooled slowly enough, all grains of α have a uniform composition (35 % Ni). This is a single phase polycrystalline alloy

What we have just discussed is called equilibrium solidification.

- **Did you note that the composition of the first solid to freeze out of the liquid was different than the overall composition of the alloy?**
- **As freezing progresses, the composition of the liquid and solid phases at any given temperature follows the liquidus and solidus lines, respectively.**
- **By equilibrium solidification, we mean that the RATE of cooling is sufficiently slow that solid state diffusion will act to redistribute atoms within each particle, resulting in a uniform, homogeneous composition (= C_o).**
- **Since diffusion rates in the solid state are MUCH slower than diffusion rates in liquid (remember this??), the cooling rate must be EXTREMELY slow for this to happen.**

Now let's take our Cu-35 wt. % Ni alloy and heat it back up above the liquidus (say, to 1300°C). According to the phase diagram, the alloy is again 100% liquid.

Suppose we cool the alloy at a relatively fast rate. (This process is called NONEQUILIBRIUM SOLIDIFICATION) What differences might we see in the microstructure?



crossing liquidus boundary; nucleation of first solid phase (46 wt. % Ni)

1240°C; liquid composition = 29 % Ni; freezing α phase: 40 % Ni. <u>Average</u> composition of solid particle ~ 42%

1205°C; freezing complete, last liquid of composition 21 % Ni. Average α composition = 35 % Ni.

single phase liquid (of composition 35 wt. % Ni); same as before

1220°C; liquid composition = 24%, freezing α = 35%. Since diffusion in the particle is slow, the composition gradient results in an average composition of ~ 38% Ni.

- **Note the difference in microstructure; this time, a composition gradient exists within each grain. The composition at the center of the grains (the first solid to freeze out) is higher than the composition near the grain boundaries.**

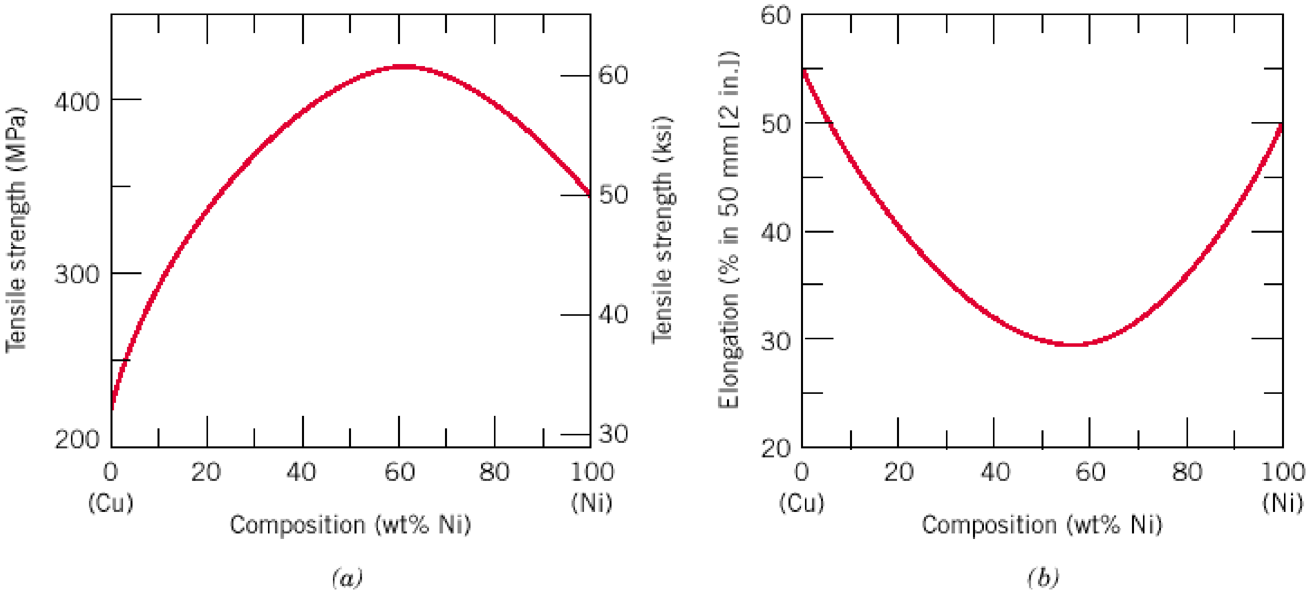
- **During freezing, the average composition of the solid phase exceeds the overall nominal composition of the alloy. Consequently, it is as if the solidus line is shifted to the right. As the cooling rate increases, the magnitude of this shift also increases.**

The solidified alloy is said to possess a "CORED" microstructure.

The last liquid to solidify ends up forming the grain boundaries. Since the composition of the resulting grain boundaries is Cu-rich (relative to the nominal composition of the alloy), and since the melting point of Cu is less than that of Ni, what do you think the implications of this would be for high temperature use of such a material?

What could you do to make the composition uniform throughout the alloy?

Before examining other types of phase diagrams, let's consider why we have an interest in alloys in the first place:



As you can see from the figures, the tensile strength of a Cu-Ni alloy is much greater than that of either component (with a corresponding decrease in ductility). By making appropriate choices of compositions and alloy elements, we can engineer materials to have specific properties needed for certain applications (mechanical, electrical, thermal, optical).