MIDTERM 2011 Solutions
Prof Morris E45

1.

(A) Materials that crystallize in the CsCl structure are ionic or metallic in their bonding, never covalent.

CsCl has a BCC structure. Due to its eight-fold coordination, these structures are either metallic or ionic because the configuration would be inconsistent with saturated covalent bonds. The atoms of a BCC structure do not have four nearest neighbors and cannot be covalent. Nearest neighbors of A-sites are B-sites, which is ideal for ionic boding to maintain charge neutrality. CsCl structure can be metallic because each atom has eight neighbors. When the valence electrons are fully shared with neighboring atoms, many valence states are left empty. The bonds are unsaturated and metallic.

(B) Materials that crystallize in the Cu_3Au structure are never ionic.

Atoms that occupy the Cu position in the structure would be nearest to one another. Their mutual repulsion would cause the structure to have a relatively high energy. For ionic structures, the positively and negatively charged atoms must be neighbors (not of the same kid due to high repulsion forces).

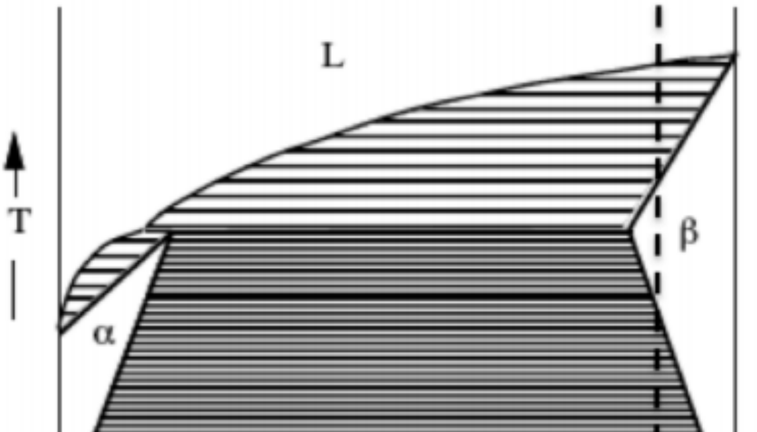
(C) Materials that crystallize in the ß-ZnS structure are covalent or ionic.

Each atom has four nearest neighbors in a tetrahedral coordination. The neighbors of FCC atoms are tetrahedral atoms so this is a natural structure for equivalent ionic compounds

Under what conditions might a metallic AB compound choose the β-ZnS structure?

If the sizes of A and B atoms vary to a great extent, they would choose the B-ZnS structure.

2.



Darker shaded part: A+B //Upper shaded part: B+L //Small shaded part: A+L

(A) Let a liquid with the composition indicated by the vertical line on the phase diagram be cooled from the liquid slowly enough to preserve equilibrium. Describe the evolution of the system as it is cooled.

The system remains liquid until it reaches the temperature of the shaded B+L two-phase field. As the temperature is cooled further, it becomes a homogenous solid solution in the B phase. It remains homogenous until the temperature is cooled into the A+B two-phase field. Here, small amount of B-rich beta phase precipitates out of alpha.

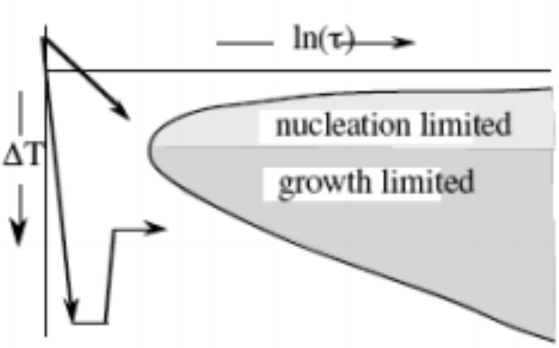
(B) Suppose that you are given the assignment of purifying a B-rich solution until it is almost pure B. How would you proceed?
A B-rich solution can be purified by first cooling it to B+L region. Let the boundaries of B melt because that contains the highest concentration of impurities. Isolate the B-rich areas from the liquid solution. Repeat the process for further extraction.

3. (A) Carbon diffuses through BCC iron much more rapidly than nickel does. Why?
Carbon is smaller than Ni so it diffuses more rapidly than nickel does. Carbon is an interstitial species whereas nickel is a substitutional species.

(B) At low to moderate temperature, nickel diffuses through polycrystalline iron more rapidly than through single crystal iron. Why?
At low temperatures, diffusivity is slower and it is generally more difficult for nickel (substitutional species) to diffuse. However, nickel diffuses through polycrystalline more rapidly than through a single crystal iron. A polycrystalline iron has higher defect density and already has many vacancies present at the dislocations. The nickel is able to diffuse along the grain boundaries of the polycrystalline iron. (Vacancies are plentiful at grain boundaries and the number of vacancies increases the rate of diffusion.) Substitutional species depends on the number of vacancies (present at grain boundaries) whereas interstitial species are independent of vacancies.

(C) If an iron-nickel alloy is quenched from high temperature, the diffusivity of nickel has an anomalously high value for a short time after the quench, but eventually decreases to its expected value. Why?
The high temperature vacancy concentration is preserved for some time; the excess vacancies must diffuse to boundaries, dislocations or other sinks before they can be eliminated. Thus, the diffusivity of substitutional species is high immediately after quench. But after some time, it decreases to its equilibrium value.

4.



Grain boundaries are the result of uneven growth when the solid is crystallizing
Grain boundaries are defects so they tend to decrease the electrical and thermal conductivity of the material.

The free energy associated with forming a nucleusa=volume*free energy (which is negative for transformation to happen) and surface area formation (which is always positive). Forming a surface always raises the energy.
$G=V*Gv+ sigma*A = r^3 + r^2$
When r is small ($r<1$), free energy is positive. When r is big($r>1$), free energy is negative. When the temperature difference from the transformation temperature is small, the driving force of nucleation is also small. Thus, the activation energy/barrier is bigger and the rate is nucleation limited. If the temperature difference is large, nucleation is easier due to a bigger driving force. Thus, the barrier is smaller and nucleation is easier, so the rate is growth limited (diffusivity-driven).

If the upper arrow cools material, the final microstructure contains nuclei of Beta almost exclusively in the grain boundaries of alpha.
It is easier to nucleate on grain boundaries. The barrier to nucleation is the formation of surface energy but at grain boundaries, it wipes out some of the interfacial energy of the already existing grains.
If the system is cooled slowly from the alpha phase, it allows enough time for the diffusion of beta particles. Thus, the beta diffuses to the boundaries of alpha particles.
Grain boundaries are common nucleation sites because the excess energy (due to the strain it exerts on the material due to disorder) is recovered by the nucleation of other grains.

If the material is cooled and then reheated, the final microstructure consists of a dense distribution of Beta precipitates in the interior of alpha grains.
If it is cooled too quickly, the precipitates are forced into the grain interiors by quenching the alloy to suppress nucleation on the grain boundaries and then reheating to induce precipitation at a low temp where nucleation happens predominantly in the interiors of the grains.
There is not enough time for diffusion so the beta phase particles are trapped in alpha phase so beta particles precipitate out of the alpha.