22.14: Nuclear Materials, Spring 2015

Problem Set 3

Topic: Free Energy and Phase Diagrams

Purpose

Now that we have explored how single substances are arranged on the atomic level, we turn to how binary systems of elements arrange themselves in different, crystallographically distinct *phases*. The concept of free energy can be used to explore whether two elements will mix for a given overall temperature and composition at equilibrium. Materials scientists use binary phase diagrams constantly to see which phases and how much of each will form, both for the prediction of long-term mechanical and chemical (corrosion) behavior. In particular, neutron radiation can cause transmutation and ion irradiation can inject ions into materials, both locally changing the microstructure and composition of a substance. Phase diagrams can tell us which phases will likely form where.

Assignment

1. (25 points) In class, we showed that the number of possible microstates of a system of two types of atoms A and B, with numbers N_A and N_B, is as follows:

$$\Omega = \frac{(N_A + N_B)!}{N_A! N_B!}$$

Using basic thermodynamic relations and the Boltzmann equation for entropy of a microstate:

$$S = k_B ln\Omega$$

show that the molar entropy of mixing is most easily expressed in terms of the mole fractions of each atom (X_A and X_B) as

$$T\Delta S = -RT \left(X_A ln X_A + X_B ln X_B \right)$$

where R is the ideal gas constant and T is the temperature. (Hint: look up how R and k_B are related). Can the entropy of mixing (ΔS) ever be negative? Why or why not?

2. (25 points) Reconstructing free energy diagrams from phase diagrams: For each of the following binary phase diagrams (source: http://products.asminternational.org/hbk/index.jsp), identify the number of unique phases present, and construct qualitative free energy diagrams for each phase at the following temperatures:

Ni-Cr (500°C, 1000°C, 1400°C, 1600°C)

Al-Ti (700°C, 1100°C, 1300°C, 1800°C)
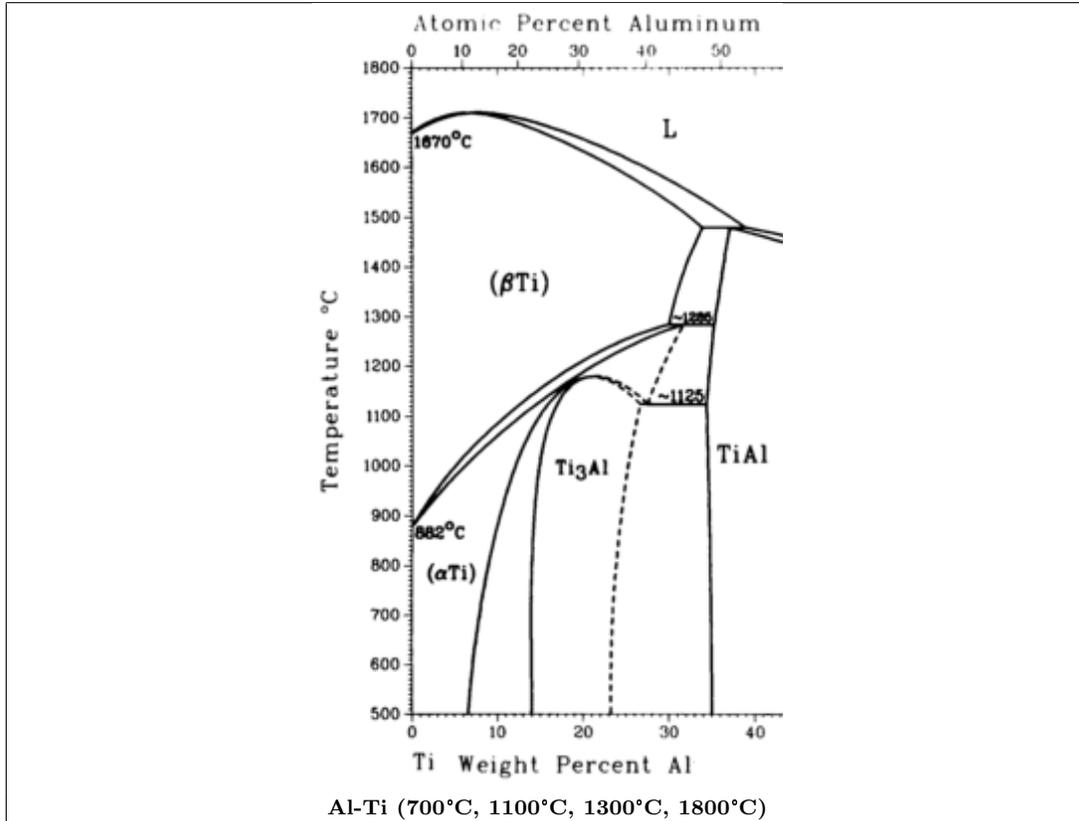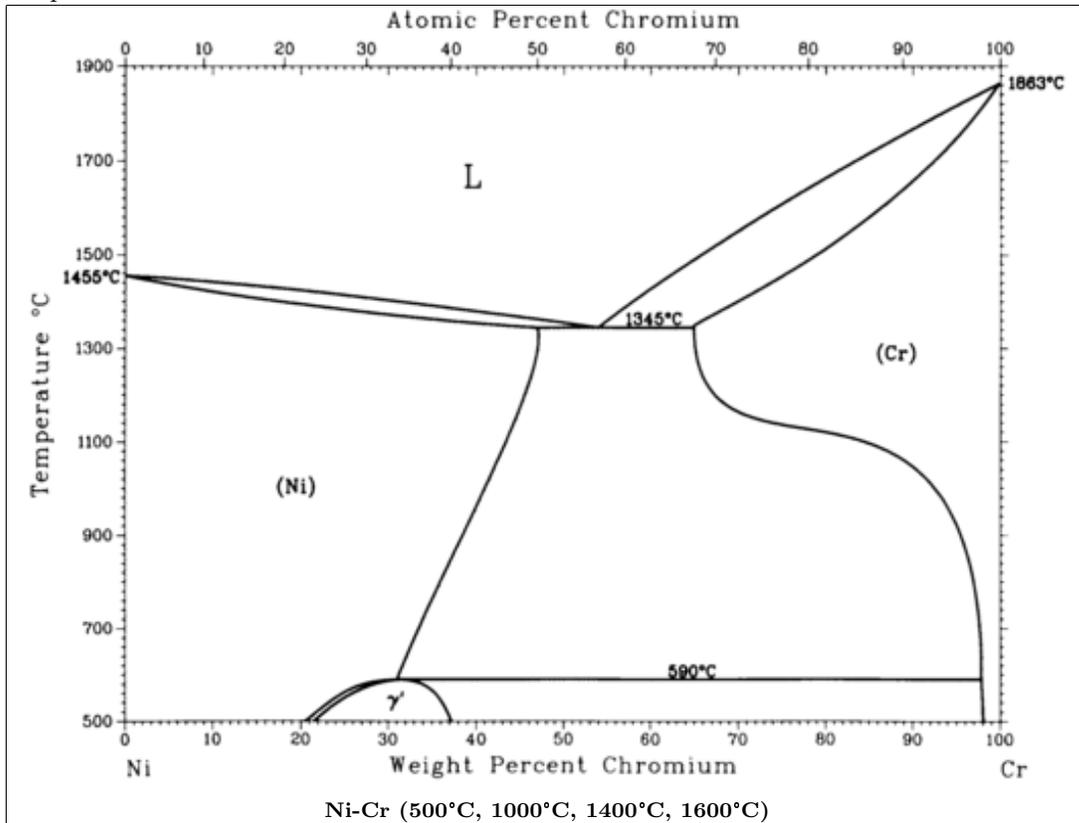
Source: ASM Handbook, Volume 3: Alloy Phase Diagrams.
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3. (25 points) Reading phase diagrams: For each composition (in weight percent) and temperature for the phase diagrams mentioned, use the lever rule to indicate the expected fractions, compositions, and crystal structures of each phase present. Next, answer the following questions to the best of your ability.

   (a) 30Ni-70Cr, 1000°C: What does this tell you about the microstructural stability and compositional variability of Ni-based superalloys?

   (b) Ti-10Al, 500°C: Look up the composition of Grade 6 titanium, commonly used in aircraft engines. Based on the Al-Ti phase diagram, why do you think the compositional limits for this alloy were chosen?

4. (25 points) Constructing phase diagrams from the following free energy diagrams at indicated, arbitrary temperatures, where $T_1 < T_2 < T_3 < T_4 < T_5 < T_6 < T_7$. Fill in what you expect the diagram to look like in between the specified temperatures.

(a)

(b)

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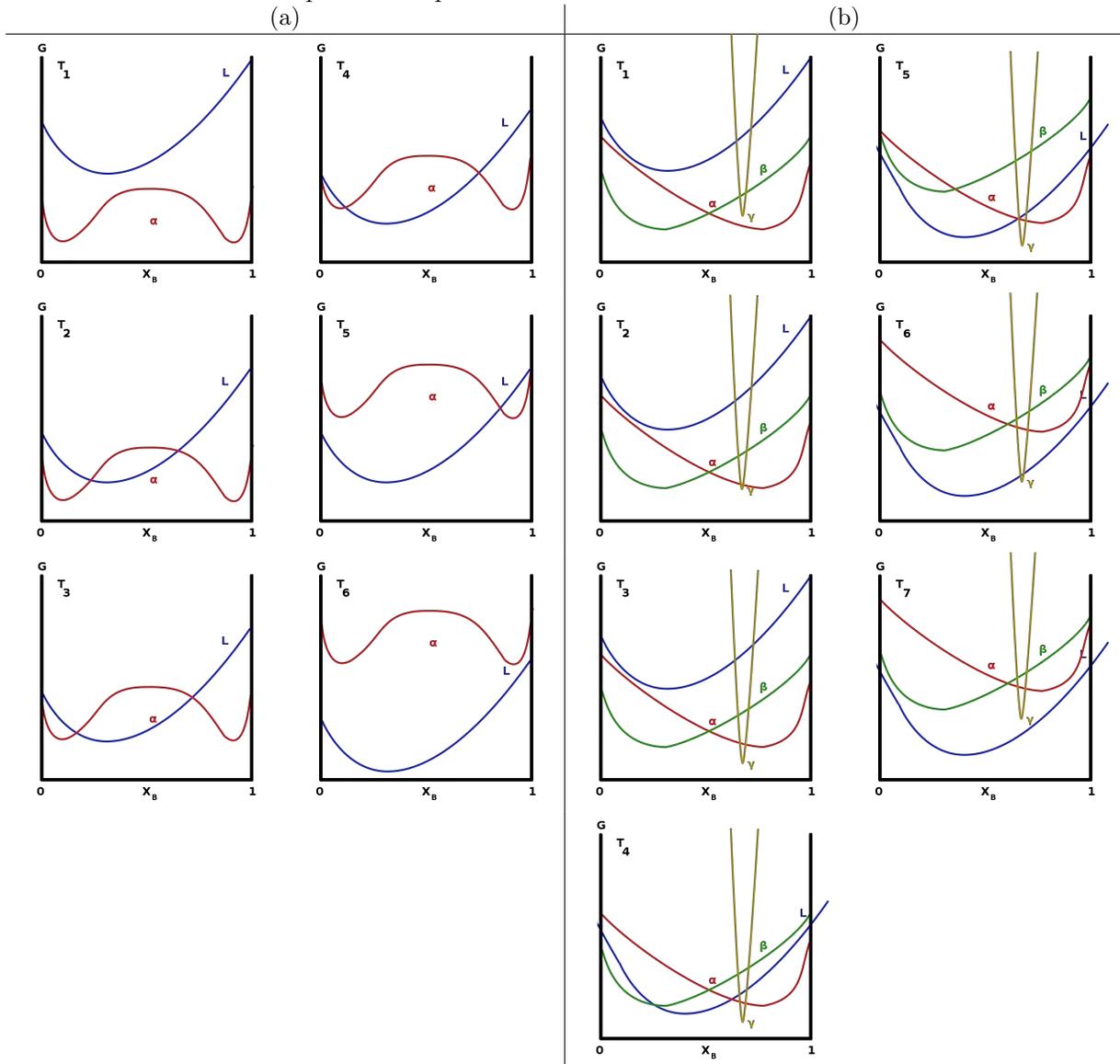
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