Mat Sci 103
Phase Transformations and Kinetics
First Midterm Exam
March 1, 2017

Name:

Instructions: Answer all questions and show your work. You will not receive partial credit unless you show your work. Good luck!

1a: 15 points	
1b: 10 points	
1c: 15 points	
1d: 15 points	
1e: 15 points	
2a: 15 points	
2b: 15 points	
Total: 100 points	

1. (70 points) Figure 1 on the next page shows the composition-temperature phase diagram for the Ni-Ru system, which features a peritectic invariant reaction, and three separate phases:

   FCC solid solution denoted (Ni)
   HCP solid solution denoted (Ru)
   Liquid denoted L

   Assume that (Ni) is an ideal solution, (Ru) is a regular solution with a Ω^{hcp} = 24 kJ mol^{-1}, and L is a regular solution with Ω^{L} = -10 kJ mol^{-1}.

   a. (15 points) Sketch molar Gibbs free energy curves for elemental, pure Ru in the fcc, hcp and L phases as a function of temperature from T = 2250°C to T = 2450°C. On your sketch label the equilibrium melting temperature of the hcp structure, as well as any other *metastable* transition temperatures present in your sketch.

   b. (10 points) On the phase diagram on the next page label all two-phase regions. List also the temperature of the peritectic reaction as well as the compositions (i.e., mole fraction of Ru) for each of the phases involved in this reaction.

   c. (15 points) Sketch molar Gibbs free energy curves at T = 1600°C for (Ni), (Ru) and L. In your sketch, use L as the reference states for both elemental Ni and Ru. (i.e., set $\bar{G}_{Ni}^{0,L} = 0$ and $\bar{G}_{Ru}^{0,L} = 0$). For this sketch:

      i. Label the free energies for pure Ru and Ni in each of the three phases and sketch each free energy curve over the entire composition range (i.e., for X_{Ru} ranging from 0 to 1).

      ii. Indicate the stable two-phase equilibrium with a common tangent line. *Note*: since this is intended to be a sketch, your common-tangent compositions do not need to quantitatively match the phase diagram.

   d. (15 points) For the temperature considered in part (c) compute the melting free energy ($\Delta\bar{G}_0^{s\to l}$) of elemental, pure Ru.

   e. (15 points) For a given application it is desired to design a Ni-rich solid Ni-Ru alloy that can operate at the highest temperature possible, without formation of the L phase. For this application it is required that the microstructure contain (Ni) and (Ru) phases with phase fractions of 0.9 and 0.1, respectively, at the highest possible operating temperature. What should be the composition (i.e., the mole fraction of Ru) for this alloy?

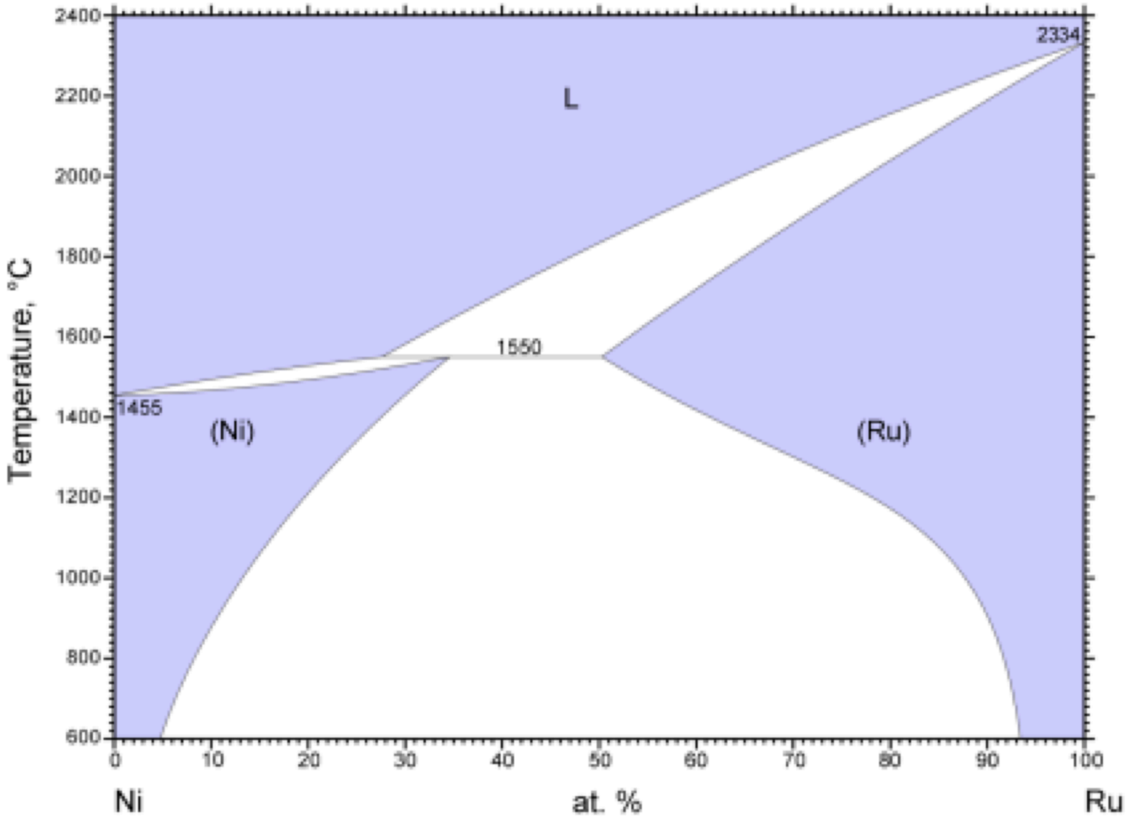


Figure 1: Composition-temperature phase diagram for Ni-Ru.

2. (30 points) Shown in Figure 2 is an isothermal section from the Cr-Fe-Mn phase diagram at at a temperature of $T = 900^{o}$C. The diagram contains single-phase regions for α (bcc solid solution), γ (fcc solid solution), σ (intermetallic phase) and δ (solid solution with the α-Mn structure) phases.

   a. (15 points) On Figure 2 label the two phase and three phase regions. Your labels should indicate the phases present in each of the regions (e.g., $\alpha+\gamma$). In the two-phase regions draw plausible tie lines (at least five for each region, roughly equally spaced).

   b. (15 points) For the point marked M in Fig. 2, determine:

      i. The composition (i.e., the mole fractions of Cr, Fe and Mn) of the mixture.

      ii. The phases present in equilibrium at this composition, and their phase fractions (using the lever rule).

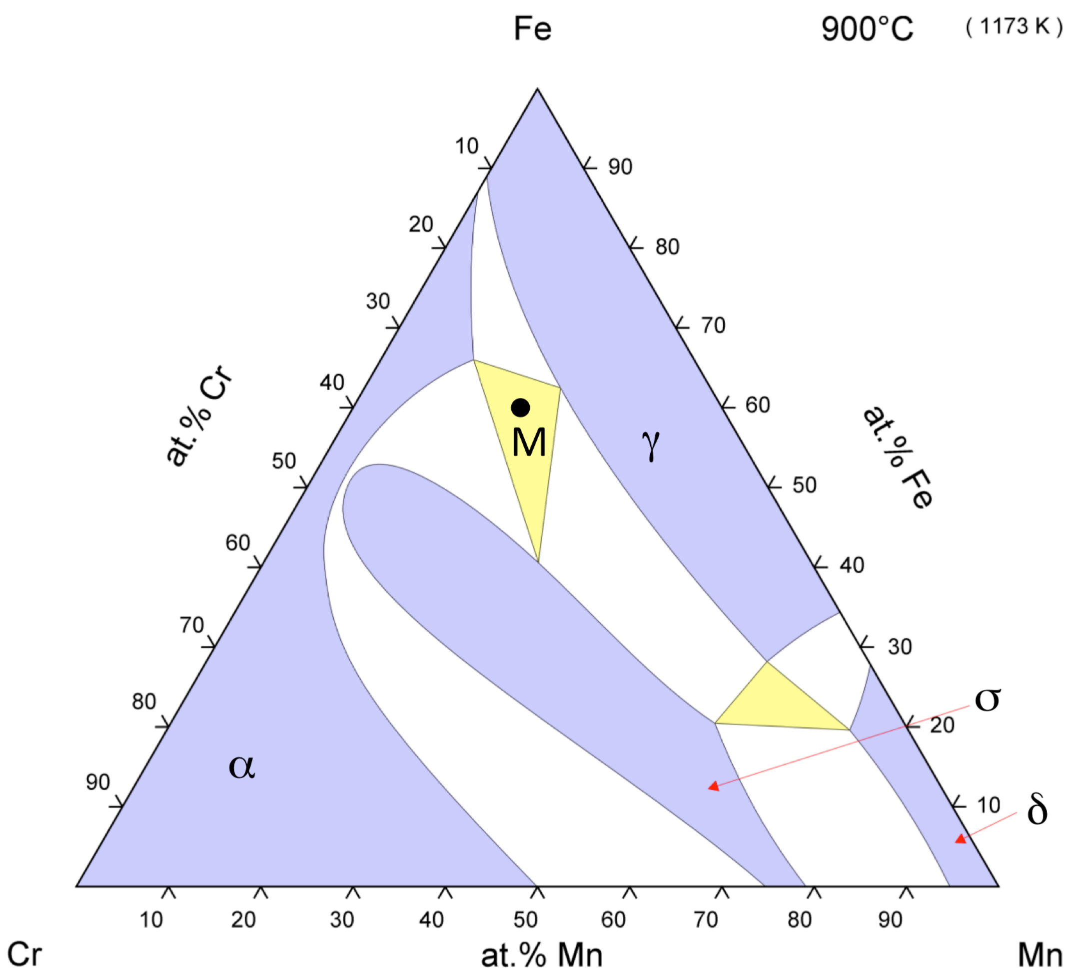


Figure 2: Isothermal section from the Cr-Fe-Mn phase diagram at T = 900°C.

Constants, Equations, Figures, Notation, Definitions

Ideal Gas Constant: R = 8.314 J mole^{-1} K^{-1}

Thermodynamic Relations:

$$G = H - TS$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P > 0$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T > 0$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P > 0$$

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial P^2}\right)_T > 0$$

Free Energy Difference Between Solid and Liquid Phases for Single-Component System:

$$\Delta \bar{G}_0^{s\to l}(T) \approx \frac{\Delta \bar{H}^{s\to l}}{T_m}[T_m - T] = \Delta \bar{S}^{s\to l}[T_m - T]$$

Chemical Potentials:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j\neq i}}$$

$$\mu_i^{\varphi} = \bar{G}_i^{0,\varphi} + RT \ln a_i^{\varphi}$$

$$a_i = \gamma_i x_i$$

Henry's Law: The activity coefficient for component i takes on a constant value (γ_i^{∞}) when i is dilute (i.e., $x_i \ll 1$)

Method of intercepts for a binary A-B mixture:

$$\mu_A(x_B) = \bar{G}(x_B) - \left(\frac{\partial \bar{G}}{\partial T}\right) x_B$$

$$\mu_B(x_B) = \bar{G}(x_B) + \left(\frac{\partial \bar{G}}{\partial T}\right)(1 - x_B)$$

Gibbs Free Energy for Mixture:

$$\bar{G}^{\phi} = \left[(1 - x_B)\bar{G}_A^{0,\phi} + x_B \bar{G}_B^{0,\phi}\right] + \Delta \bar{G}_M^{\phi}$$

Mixing free energy: $\Delta \bar{G}_M$

Ideal Solution Model for Binary A-B Mixture:

$\Delta\bar{G}_M \equiv \Delta\bar{G}_M^{id} = RT[x_B \ln(x_B) + (1 - x_B)\ln(1 - x_B)]$

$a_i = x_i$

Regular Solution Model:

$\Delta\bar{G}_M \equiv \Delta\bar{G}_M^{id} + \bar{G}^{xs}$

$\bar{G}^{xs} = \Omega x_B(1 - x_B)$

$a_i = \gamma_i x_i$

$$\gamma_A = \exp\left(\frac{\Omega x_B^2}{RT}\right)$$

$$\gamma_B = \exp\left(\frac{\Omega x_A^2}{RT}\right)$$

$$T_c = \frac{\Omega}{2R}$$

Lever Rule for two-phase equilibrium between phases α and β in a binary A-B system with overall composition x_B:

$$f^\alpha = \frac{\left(x_B - x_B^\beta\right)}{\left(x_B^\alpha - x_B^\beta\right)}$$

$$f^\beta = \frac{\left(x_B^\alpha - x_B\right)}{\left(x_B^\alpha - x_B^\beta\right)}$$

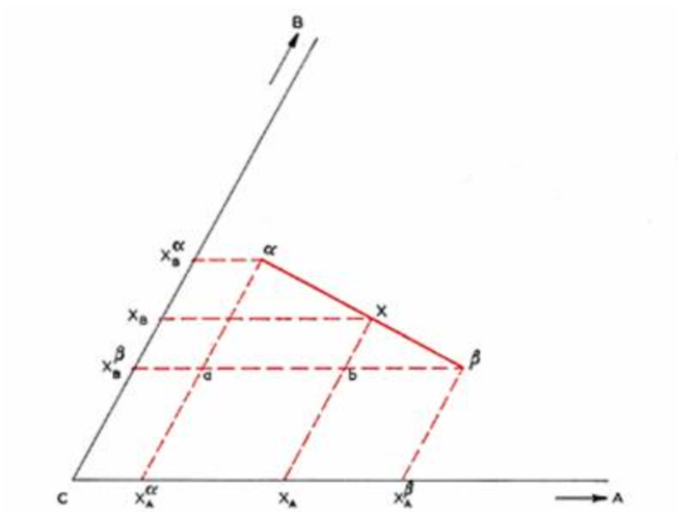
Gibbs Phase Rule at Fixed Pressure:

At fixed pressure: # degrees of freedom = # of components + 1 – # of phases

Invariant Equilibria in Binary Systems:

Euctectic: $L \Leftrightarrow \alpha + \beta$
Monotectic: $L_1 \Leftrightarrow L_2 + \alpha$
Peritectic: $L + \alpha \Leftrightarrow \beta$
Congruent: $L \Leftrightarrow \alpha$
Critical Point: $\alpha \Leftrightarrow \alpha_1 + \alpha_2$

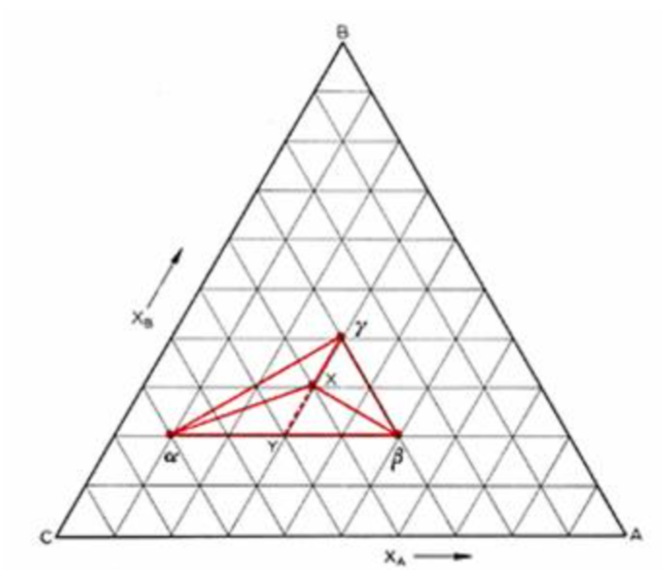
Two-Phase Lever Rule for Ternary Phase Diagram:



$$f^{\alpha} = \frac{x\alpha}{\beta\alpha} = \frac{x_i - x_i^{\beta}}{x_i^{\alpha} - x_i^{\beta}}$$

$$f^{\beta} = 1 - f^{\alpha}$$

Three-Phase Lever Rule for Ternary Phase Diagram:



$$f^{\gamma} = \frac{XY}{\gamma Y}$$