1st Test, 27-302, Monday Nov. 11th

1a. You are given an alloy and told that the solubility of the main solute element decreases by a factor of 10 between the temperature at which it is solutionized, 550°C, and the temperature at which it is age hardened, 220°C. Assuming that the solute content is equal to the solubility limit at the solutionizing temperature, estimate the (molar) driving force for nucleation of precipitation.

Here we can apply the formula, $\Delta G_m = -RT \ln(X_e/X)$

$$= -8.31 * (220+273) * \ln(10)$$
$$= 4{,}097 \text{ J/mole}$$

Can also apply the equation that assumes a regular solution model with X=Aexp-Q/RT, solve for Q and then apply $\Delta G = Q.\Delta T/T_e$. This gives a larger driving force, ~ 9400 J/mole.

1b. Sketch the free energy versus composition diagram that illustrates the difference between the overall driving force for precipitation and the driving force for nucleation of precipitation.

The expected answer shows the difference between the smaller ΔG_0 associated with the difference in intersections of the alloy composition with the two common tangent lines, and the larger ΔG_m associated with the difference between the chemical potential at the composition for the precipitate ("beta" in the diagram in Porter & Easterling).

2. Explain why the nucleation of precipitation is rarely observed to be homogeneous and why heterogeneous nucleation is generally observed.

The expected answer includes a discussion of homogeneous nucleation theory and the significant barrier to nucleation that exists for most precipitate phases. Contrast this with heterogeneous nucleation where the barrier is much reduced by the presence of a defect.

3. Explain what is meant by the concept of "extended volume" in the derivation of the KJMA equation. Hint: writing down the differential equation on which the derivation is based is a good place to start.

The differential equation is $df = df^* (1-f)$, where f is the actual fraction transformed and f^* is the extended fraction. The extended volume is the volume to which the new phase would grow if no impingement occurs. The increment in real fraction is equal to the increment in the extended volume, multiplied by the remaining *untransformed fraction*, which is equal to ($1-f$). In words, the less volume available for further transformation, the less contribution to the actual fraction transformed that the imaginary growth can make. At time zero with no contact between particles, however, the rate of growth of actual volume is exactly equal to the rate of growth of the extended volume.

3b. The precipitation and growth of ferrite on prior austenite grain boundaries often occurs as plates. If site-saturated nucleation conditions apply and the growth rate is constant (as happens for interface-limited growth), what is the exponent likely to be in a KJMA analysis?

The expected exponent is 1 because the plates grow along the normal to the surface of the plate and therefore the growth is 1-dimensional.

4. When a new crystalline phase precipitates inside another crystalline phase, the new phase typically has a different density from the parent phase. Explain how this affects driving force and nucleation barrier for precipitation. An equation that makes the explanation quantitative will help.

The consequence of a change in density is that there is an elastic strain developed on precipitation. The energy associated with this is volumetric and proportional to the modulus and the square of the strain. It subtracts from the driving force available for the precipitation reaction.

5. What is the relationship between the curves in a TTT diagram and those in a CCT diagram? A "curve" in one of these diagrams is a contour that corresponds to a certain fraction transformed. Explain the relationship between the two diagrams.

Comparing two curves in a TT and a CCT diagram for the same alloy and starting temperature, the CCT curve will below and to the right (longer times, lower temperatures) of the TTT curve. This is the case because the a point with the same time and temperature in the CCT diagram has been approached from above, whereas in the TTT diagram, it has been approached horizontally, i.e. at constant temperature. Therefore the integrated driving force over the history of a CCT curve is less than for a TTT curve going through the same point.

6. Explain the relationship between viscosity and nucleation rate in glasses.

The connection is through the diffusion coefficient (in a general sense). Lower viscosity means higher diffusion rates in a glass. Higher diffusion rates means faster nucleation.

7. What does "impingement" mean in the context of precipitate growth?

At first, the diffusion of solute to precipitates occurs independently around each precipitate. Impingement means that, after some diffusion and growth has occurred, the decrease in solute content around one precipitate affects the solute level around another precipitate. Eventually as precipitation proceeds to completion, the solute level everywhere drops to the equilibrium value. At this point coarsening has taken over.

8. (a) Explain the driving force for precipitate coarsening. (b) If the average particle size is 10 nm after a certain amount of annealing time (t=0) and is 20 nm after a further 20

minutes (t=20 minutes), what particle size do you expect to observe after one hour (t=60 minutes)?

(a) Through the Gibbs-Thomson effect, small particles have a higher solubility than large particles because of their higher curvature. This is equivalent to saying that the component in the small precipitates has a higher chemical potential than in the larger precipitates. Therefore solute will diffuse from the smaller to the larger precipitates. (b) Using the relationship $\langle R^3 \rangle - \langle R^3(t=0) \rangle = kt$, we obtain *k* by setting

$$k = \langle R^3 \rangle - \langle R^3(t=0) \rangle / t = (20^3 - 10^3)/20 = (8000-1000)/20 = 350.$$

Then we use the *k* values so obtained to find the radius at the longer time:

$$\langle R^3 \rangle = \langle R^3(t=0) \rangle + kt = 1000 + 350*60 = 22{,}000.$$
$$R(t=60 \text{ minutes}) = \sqrt[3]{22000} = 28.0 \text{ nm}.$$