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3.21 Kinetics Processes in Materials—Spring 2006

Examination #2

April 10, 2006

9:30–10:55 A.M.

This is a *closed book* examination. Calculators may be used when necessary.

Please answer the questions directly on the exam pages. If you require more room, use the backs of the facing pages.

There are four questions on this examination, and each is worth 25 points. Apportion your time accordingly.

Keep your answers short and to the point. When appropriate, include sufficient information to indicate your reasoning. This will enable us to award appropriate credit even if you do not answer the question completely.

Good luck!

Please write your name here

1. Consider an oxygen-deficient oxide MO_{3-x} that contains a low concentration of solute arising from the addition of the soluble oxide AO_2. Assume that oxygen diffusion occurs by a vacancy mechanism.

   (a) Write the reduction reaction for reducing MO_{3-x} and a corresponding equation for its equilibrium constant K^{eq}.

   (b) Write a defect reaction for the incorporation of the solute A into MO_3.

   (c) Write the charge neutrality condition for the impure, nonstoichiometric oxide.

Problem 1, continued:

(d) Explain under what conditions it might be possible to use MO_3 as the active component in an oxygen sensor.

2. Harrison's "B regime" of short-circuit grain-boundary diffusion is illustrated in Fig. 1.

Consider a volume element in the boundary of dimensions $\delta \times dy \times dz$ as shown in Fig. 2b. By relating the accumulation in the volume element to the fluxes into each of the six faces of the volume element, show that the differential equation governing this regime has the general form

$$\frac{\partial c^B}{\partial t} = A \frac{\partial^2 c^B}{\partial y^2} + B \frac{\partial c^{XL}}{\partial x} \tag{1}$$

You do not have to evaluate the constants A and B in your derivation.

See *Kinetics of Materials,* Figure 9.4*b*, p. 215

Figure 1: "B regime" of Short-Circuit Grain-Boundary Diffusion.

(a) See *Kinetics of Materials* Figure 9.8*a*, p. 218
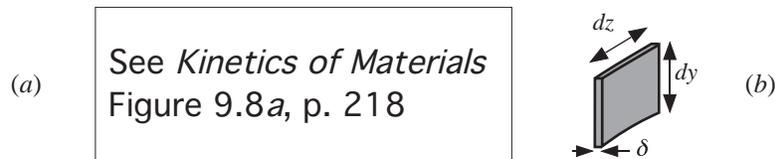
dz *dy* (b) δ

Figure 2: (a) Model Geometry for Diffusion Along a Grain Boundary. (b) Volume Element for Description of Short-Circuit Grain-Boundary Diffusion.

3. The *Gibbs–Thomson* equation can be written in the form

$$\mu_B^\beta(P^\beta) - \mu_B^\beta(P^\alpha) = \frac{2\Omega_B\gamma}{r} \tag{2}$$

(a) Explain the meaning of each quantity in this equation and give SI units for each quantity.

(b) Explain the relevance of the Gibbs–Thomson equation to the phenomenon of particle coarsening (Ostwald ripening).

Problem 3, continued:

(c) The accompanying figure shows coarsening data from Hardy and Voorhees' experiments on semi-solid Pb–Sn alloys. In what way are the data *consistent* with a prediction of the mean-field theory of particle coarsening? In what way are the data *inconsistent* with the mean-field theory?

See *Kinetics of Materials,* Figure 15.9, p. 372

Figure 3: Coarsening Data on Semi-Solid Pb–Sn Alloys (Hardy and Voorhees 1988).

4. Please identify which of the following statements is true or false. Give a brief justification for each answer. *Full credit requires concise, correct reasoning.*

(a) In KCl containing $MgCl_2$, there will be an intrinsic regime of cation diffusion in which the cation vacancy concentration is independent of temperature.

(b) The activation volume for self-diffusion in metallic glasses is near zero, indicating that self-diffusion likely takes by a cooperative many-body process.

(c) The theory of random walks can be used to model self-diffusion in a polymer melt.

(d) Single-phase interfaces tend to migrate toward their center of curvature.