Department of

MATERIALS SCIENCE AND ENGINEERING

Doctoral Written Exam

Day 2

Core Areas:

ADVANCED THERMODYNAMICS OF MATERIALS
KINETICS AND PHASE TRANSFORMATIONS
STRUCTURE OF MATERIALS

Friday, May 14, 2004

Department of Materials Science and Engineering

DOCTORAL WRITTEN EXAM – Day 2
May 14, 2004

Your exam packet for day 2 contains a total of nine (9) questions from three (3) core areas, ADVANCED THERMODYNAMICS OF MATERIALS, KINETICS AND PHASE TRANSFORMATIONS, and STRUCTURE OF MATERIALS, plus 10 answer sheets. Each question is on a separate page. A copy of the Table of Constants is included for your reference. **You must submit 6 questions, 2 from each core area for grading**. You will have 6 hours to complete the questions. You can obtain extra answer sheets from the proctor, if needed. Please use the following procedure:

Write a four (4) digit code of your choice, and your name on the 3 X 5 card provided. Use this code in place of your name to identify all answer sheets you submit for both days of the exam. Renee will keep the code information, sealed in an envelope, until after the exams are graded.

For each answer, use the question sheet as the first page of your answer. If additional pages are required, use the blank answer sheets provided. At the end of the examination, staple each question sheet and corresponding answer sheets for each question separately, put this instruction sheet on top of the questions you are turning in, and place them in one side of your exam folder. Place all other exam pages in the other side of your folder, and return everything to the proctor, or Renee if you finish before 2:30 P.M.

Please be sure to complete the information required on each page.

GOOD LUCK!

CODE NUMBER ________________

CHECK THE 6 QUESTIONS YOU WISH TO HAVE GRADED.

ADVANCED THERMODYNAMICS OF MATERIALS:	KINETICS AND PHASE TRANSFORMATIONS:	STRUCTURE OF MATERIALS:
1. ____	4.____	7.____
2. ____	5.____	8.____
3. ____	6.____	9.____

Day 2 – ADVANCED THERMODYNAMICS OF MATERIALS **CODE #________**

1.

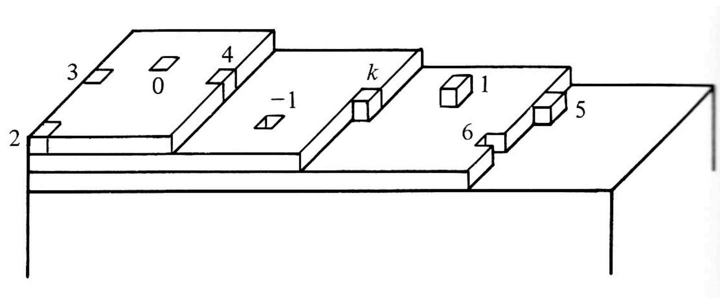
(a) A gas mixture of the following composition (in volume percent) - 30% CO, 10% CO_2, 10% H_2, and 50% N_2 - is introduced into a heat-treating furnace at 950ºC. Calculate the equilibrium composition of the gas mixture if the total pressure in the furnace is one atmosphere. (b) After the gas mixture has equilibrated, iron is placed into the furnace. Determine whether or not the iron will oxidize upon exposure to this atmosphere. (c) How will the answer to Part (b) change if both iron and titanium are introduced into the furnace?

2.

(a) Write down the Clausius-Clapeyron equation as it usually applies to two-phase equilibrium in pressure-temperature space for a single-component system. Draw a typical pressure versus temperature diagram for a one-component system. Derive the analogous differential equation that describes the same two-phase coexistence in chemical potential - temperature space and draw a similar diagram. (b) Define mathematically the material property known as the isothermal compressibility. It is sometimes important to define an **adiabatic** compressibility. Define this parameter mathematically and show how it is related to the isothermal compressibility and various specific heat quantities.

3.

The figure below shows a (100) surface of an FCC crystal. The heat of vaporization is 420 kJ/mole. Calculate the excess energy for each of the atomic configurations depicted in the figure, assuming a first nearest neighbor only bond model. What is the probability of finding the states (-1,1) relative to state 0, and states (5,6) relative to state 4.



Day 2 – KINETICS AND PHASE TRANSFORMATIONS **CODE #______**

4.

Consider a void of radius *R* in Cu at a temperature *T*. Due to its curvature, the vacancy concentration at the void surface is $c_{vR} = c_v^0 \exp(\frac{2\gamma\Omega}{k_B TR})$, where c_v^0 is the thermal equilibrium concentration, γ, the surface free energy, k_B, Boltzmann's constant. The resulting vacancy concentration gradient leads to shrinkage of the void.

a) Solve the vacancy diffusion equation and determine the vacancy flux as a function of void radius.

b) Asuming the exponent in the expression for c_{vR} can be linearized, calculate how long it would take for a void of radius 25 nm to disappear at 300 and 500 °C.

For Cu, use γ = 1.73 J/m^2, a vacancy formation energy of 1.3 eV and migration energy of 0.7 eV.

5.

The oxidation of Zn to form ZnO occurs via transport of Zn towards the oxide/gas interface. Zn diffuses as interstitial species.

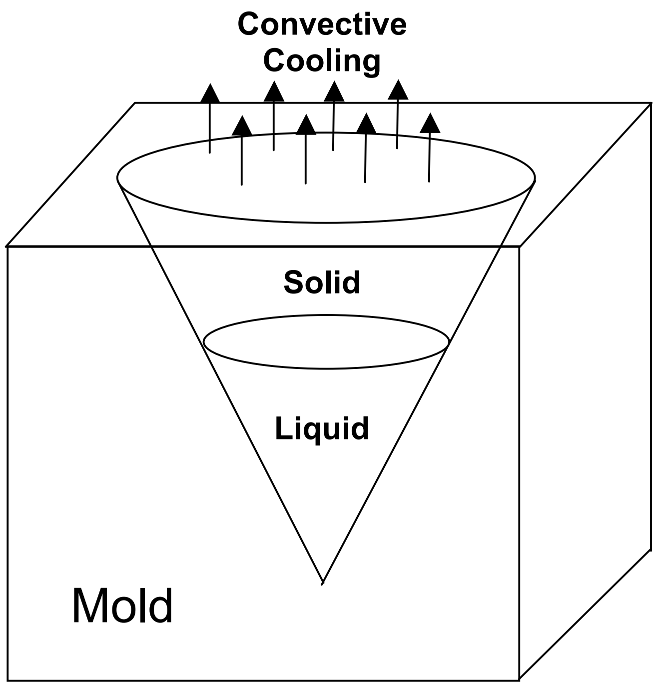
1) Derive the rate law, which gives the thickness of the oxide layer as a function of time. Be certain to identify the diffusion coefficient of Zn in ZnO as part of the rate coefficient.

2) What is the dependence of the rate coefficient on the oxygen partial pressure?

6.

A liquid metal with high thermal conductivity is poured into a perfectly insulating cone shaped mold. Heat leaves the metal through convective cooling of the top surface. The heat transfer coefficient at the top surface is h and the temperature of the air above the mold is T_a. The diameter of the top of the cone is D and the height of the cone is L. Assuming the solidification front always remains parallel to the top surface, derive an expression for the time it will take for the mold to solidify. Denote the density r, the melting temperature T_m and the heat of fusion H_f. Assume negligible undercooling.

Note: For a cone d = D[1-(z/L)] where d is the cross-sectional diameter at a distance z from the base.



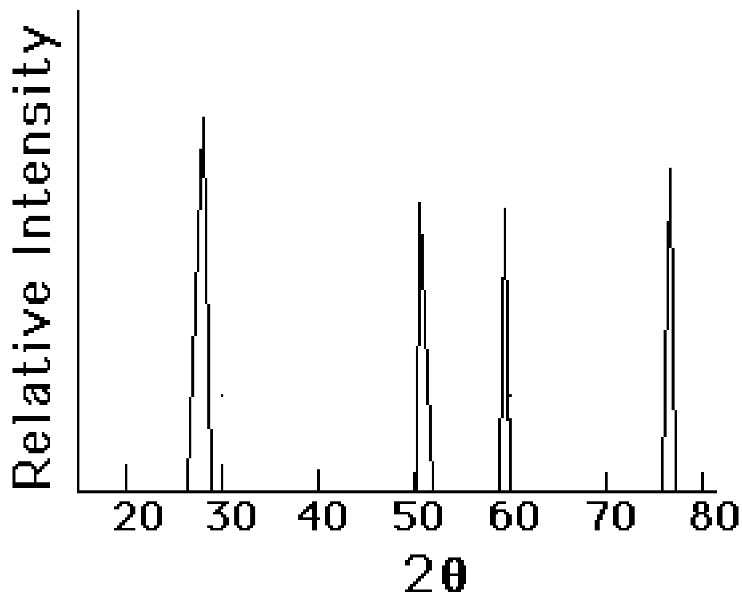
7.

Your research group has synthesized a new rigid polymer that can be readily drawn into highly crystalline, elongated fibers with the molecules oriented parallel to the fiber axis (the [001] direction). The molecules have a characteristic lateral size of a=0.5 nm in one direction and b=0.35 nm in the other. You have found that the packing symmetry in the crystalline state is nominally orthogonal. The repeat distance along the backbone of the molecule is 2.0 nm. In the solid state the molecules are close packed laterally, but the interactions between chains in the [100] direction is much stronger than those in the [010] direction. Because of this the effective crystallite size for the (100) reflection is about 50 nm, whereas for the (010) reflection it is only about 5 nm.

Draw as accurately as possible a schematic fiber diffraction pattern from this polymer in a Laue transmission geometry obtained at a camera length of 5 cm using Cu K_α radiation. Assume the fiber axis is vertical, as is conventional.

8.

A powder pattern is taken from an unknown sample which displays diffraction peaks at 2θ = 28.8, 50.8, 59.6 and 76.1 degrees as shown below for incident radiation from a Cu(K_α) target:



a) What is the crystal structure of the unknown? (Hint: it is always best to start with the simplest assumption.) (4)

b) What is the lattice parameter? (4)

c) You retake this diffraction pattern at 600°C. Draw the diffraction pattern you obtain on roughly the same scale as drawn above and compare the new positions of the diffraction peaks and the new intensities. Explain briefly. (2)

9.

Use a structure factor calculation to demonstrate that for a crystal in space group $P4_2/mnm$ (No. 136), the following conditions exist on diffraction patterns:

for *0kl*, $k+l=2n$

for *00l*, $l=2n$

for *h00*, $h=2n$