Department of

MATERIALS SCIENCE AND ENGINEERING

Doctoral Written Exam

Day 2

Core Areas covered:

ADVANCED THERMODYNAMICS OF MATERIALS
KINETICS ND PHASE TRANSFORMATIONS
STRUCTURE OF MATERIALS

Friday, May 25, 2007

Department of Materials Science and Engineering

DOCTORAL WRITTEN EXAM – Day 2
May 25, 2007

Your exam packet for day 2 contains a total of nine (9) questions from three (3) core areas, ADVANCED THERMODYNAMICS OF MATERIALS, KINETICS ND PHASE TRANSFORMATIONS, STRUCTURE OF MATERIALS, plus 15 answer sheets. Each question is on a separate page. A copy of the Table of Constants is included for your reference. **You must submit 2 questions 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 3:30 P.M.

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

GOOD LUCK!

CODE NUMBER _________________

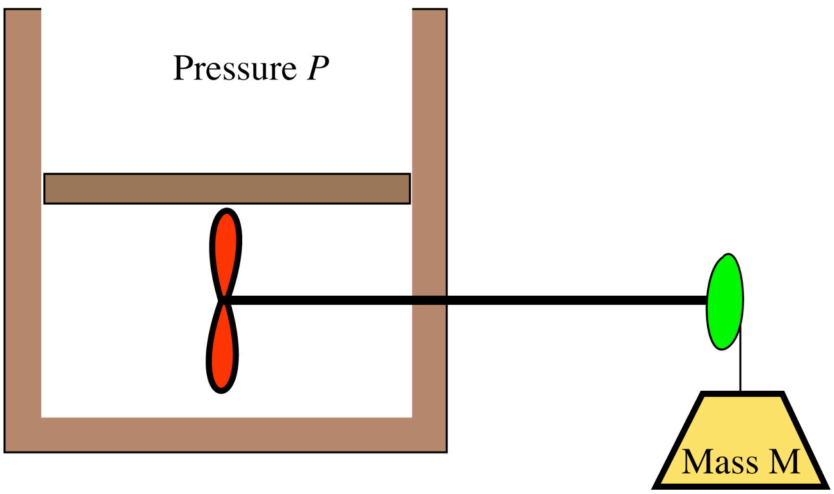
CHECK THE 6 QUESTIONS YOU WISH TO HAVE GRADED:

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 fluid is held in a container that is covered with a frictionless piston. The container and piston are thermally insulated (no heat exchange with the environment) and the environment is at constant pressure *P*. A paddle is placed within the container, which is rotated by dropping a weight of mass *M* attached to a frictionless pulley contraption (see figure). Assume that the mass *M* drops by a distance *h*.



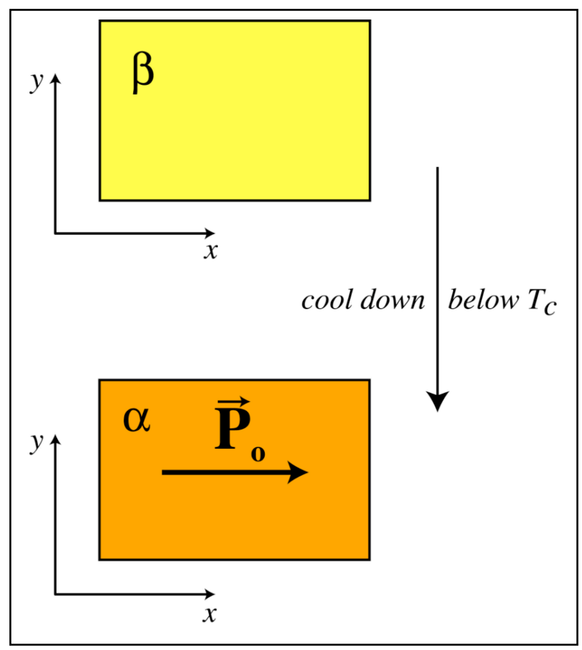
You are lucky in that the response functions for this fluid, C_p, C_V, β (thermal expansion coefficient at constant *P*) and κ (compressibility at constant *T*) happen to have been measured and are tabulated. It also turns out that they are constant within a large temperature interval.

a) Does the fluid undergo a reversible or irreversible change of state?
b) Derive an expression for the change in temperature ΔT between the final equilibrated state after *M* has been dropped and the initial state before *M* is dropped. Write your answer in terms of *M*, *h* and response functions of the fluid.
c) Derive a similar expression for the change in volume ΔV.

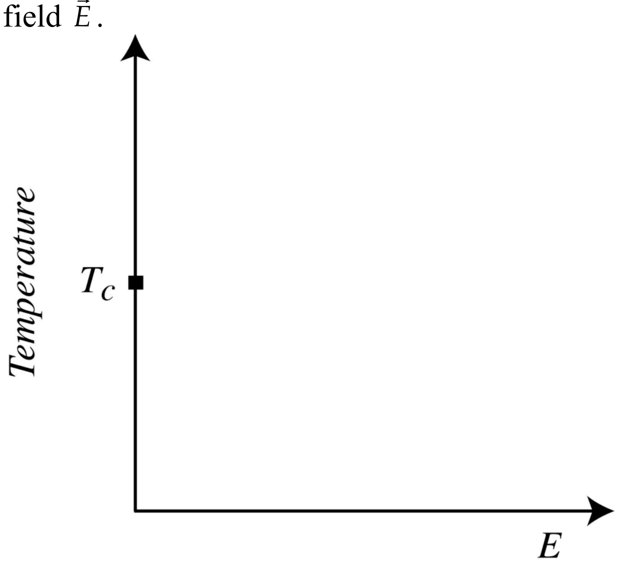
Day 2 – ADVANCED THERMODYNAMICS OF MATERIALS CODE #________

2.

A ferroelectric crystal undergoes a phase transformation from β to α upon cooling through a transition temperature T_c. The high-temperature β phase has no dipole moment in the absence of an electric field, while the low-temperature α-phase is characterized by a dipole moment $\vec{P}_o$. Assume that a single crystal of this ferroelectric is oriented such that the spontaneous dipole moment $\vec{P}_o$ in the α phase is parallel to the x-axis. How will the transition temperature change if an electric field parallel to the x-axis (directed in the positive x-direction) is imposed on the crystal? Schematically draw the variation of the transition temperature as a function of $\vec{E}$ and explain your answer (use appropriate thermodynamic relations to justify your answer).



- The transformation from α to β upon heating through T_c is accompanied by the absorption of a latent heat Q at constant pressure P and zero electric field $\vec{E} = 0$.
- You can assume that the dipole moment of the β phase depends on $\vec{E}$ according to $\vec{P}^{\beta} = \chi \cdot \vec{E}$.
- The dipole moment of the α phase depends on $\vec{E}$ according to $\vec{P}^{\alpha} = \vec{P}_o + \chi \cdot \vec{E}$, where $\vec{P}_o$ is a constant (independent of T and $\vec{E}$).
- In both the α and β phases, χ has the same value and has the same dependence on temperature. You can assume that χ is independent of the electric field $\vec{E}$.



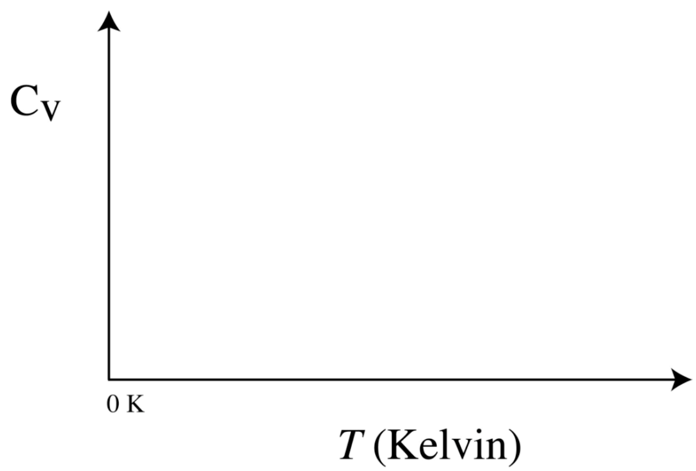
Day 2 – ADVANCED THERMODYNAMICS OF MATERIALS CODE #________

3.

a) Consider a binary system in a two-phase state at constant T and p. A famous scientist stated in a recent paper that when the concentration is changed to increase the amount of one of the phases present (but remaining in the two-phase state) the entropy of the system does not change. Is this correct or not?

_______S does not change _____S changes.

b) Schematically sketch the heat capacity C_v of a crystalline solid as a function of temperature.



c) Briefly explain the second law of thermodynamics as applied to an isolated system at constant volume.

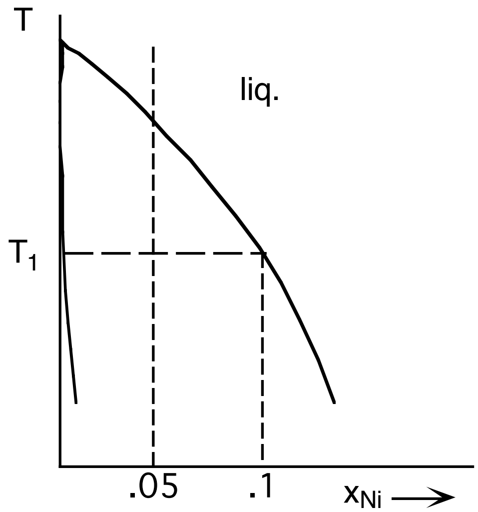
Day 2 – KINETICS AND PHASE TRANSFORMATIONS CODE #________

4.

The rate determining step in the catalyzed reaction, A + B = products, is the combination of the two species when they are adsorbed on a surface. Assume there is no site selectivity for either species on the surface. The Gibbs free energies for the adsorption-desorption reactions at ambient pressure are –12.1 and –8.7 kJ/mol for A and B respectively. What total fraction of the surface is covered if the partial pressures of A and B are 0.35 and 0.65, respectively. Assume the Langmuir model.

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

5.



Consider the solidification of a binary material. A liquid Ni-Ti alloy containing 5 mol% Ni is rapidly cooled and then held at T_1 = 1300 ˚C, as indicated in the adjacent (schematic) phase diagram. At this temperature the solubility of Ni in Ti is negligible, whereas the melt is saturated with 90 mol% Ti. Assume that the solidification front is planar, and progresses strictly perpendicular to the interface. Assume furthermore that the solidification process is entirely controlled by the diffusion of Ni into the melt. Derive a formalism that describes the amount of solidified Ti at early times of the solidification process. (Hint: Begin by establishing the boundary conditions for the diffusion process. You may verify your result by finding that the amount of Ti growth approximately as the square root of time.)

6.

Liquid droplets of Al are quenched upon dropping them into an oil bath. The droplets have a diameter of 1 mm. Assume that their shape is spherical throughout the process, and that upon hitting the surface of the oil bath they reach their terminal sinking velocity immediately. The droplets start out at a temperature of 1073 K and the melting point of Al is 933 K. Assume that both the oil bath and the Al melt are in thermal equilibrium due to turbulent mixing and high thermal conductivity, respectively. The principal barrier to heat transfer is the convective boundary layer of oil surrounding the metal droplet. The heat transfer coefficient in this boundary layer can be evaluated using the expression

$$\mathrm{Nu} = 2.0 + 0.6\left(\frac{D\upsilon\rho_L}{\eta}\right)^{1/2}\left(\frac{c_{p(L)}\eta}{k_L}\right)^{1/3},$$

Where $\eta = 9\cdot10^{-4}$ Pa·s is the viscosity of the oil, D is the diameter of the Al droplets, υ is the terminal velocity of the droplets, $\rho_L = 890$ kg/m^3 is the density of the oil, $c_{p(L)} = 750$ J/kgK is the specific heat of the oil, and $k_L = 0.15$ W/mK is the thermal conductivity of the oil. The Nusselt number is defined as $\mathrm{Nu} = \frac{hD}{k_L}$. Furthermore given are the density of Al (2600 kg/m^3) and the specific heat of Al (1100 J/kgK).

Calculate the depth the oil bath must have for the Al droplets to cool down to the melting temperature of Al before they hit the bottom of the container.

7.

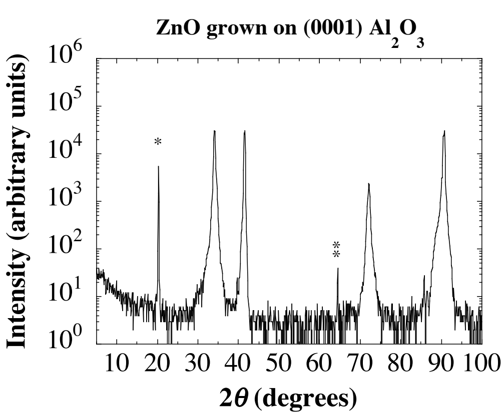
An epitaxial ZnO thin film is grown on the (0001) surface of sapphire. Figure A shows the x-ray diffraction pattern (ϑ-2ϑ scan) of the sample. Figure B is the ϕ-scan of the sample film using the $10\bar{1}1$ reflection of ZnO.

a) Index all (six) peaks appearing in Figure A. (**4 pts**)
b) Explain the possible origin of the two peaks marked by * and **. (**2 pts**)
c) Find the orientation relationship between the ZnO film and the sapphire substrate. (**4 pts**)

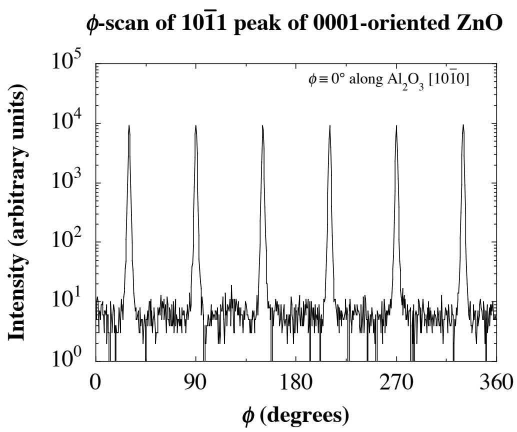
ZnO: hexagonal (*wurtzite*), a = 3.2495 Å, c = 5.2069 Å

Al_2O_3: hexagonal (*corundum*), a = 4.7628 Å, c=13.0032 Å

The wavelength of x-ray was 1.5406Å.



(A)



(B)

8.

a) In a cubic system, what is the zone axis of $(\bar{1}10)$, $(\bar{3}12)$, $(1\bar{3}2)$ planes? (**4 pts**)

b) Find the indices of any two other planes that also belong to this zone. (**3 pts**)

c) In a primitive orthorhombic system, does the $[2\bar{2}1]$ direction lie in the (110) plane? (**3 pts**)

Day 2 – STRUCTURE OF MATERIALS **CODE #________**

9.

Figure 1 is a phase diagram of two metals A and B, which are partially soluble. Draw schematics and show the characteristics of powder x-ray diffraction patterns (ϑ–2ϑ) of the solid solutions at H, K, L, and M, respectively. Assuming the α phase has an f.c.c. structure with a=0.4 nm, while the β phase has a b.c.c structure with a=0.3nm. (**10 points**)