Department of

MATERIALS SCIENCE AND ENGINEERING

Doctoral Written Exam

Core Areas:

Materials Physics And Chemistry
Advanced Mechanical Behavior
Advanced Thermodynamics Of Materials
Kinetics and Phase Transformations
Structure Of Materials

Thursday, May 19, 2011

Department of Materials Science and Engineering

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Your exam packet contains 3 questions from each core area for which you signed up, along with several answer sheets. A copy of the Table of Constants is included for your reference. **You must submit 2 questions from each core area you are taking for grading**. You will have 1 1/2 hours to complete each section. 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 Renee if you finish before your time is up.

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

CODE NUMBER ________________

CHECK THE QUESTIONS YOU WISH TO HAVE GRADED:

Materials Physics And Chemistry:

1. _____
2. _____
3. _____

Advanced Mechanical Behavior:

4. _____
5. _____
6. _____

Advanced Thermodynamics Of Materials

7. _____
8. _____
9. _____

Kinetics and Phase Transformations

10. ______
11. ______
12. ______

Structure of Materials

13. ______
14. ______
15. ______

4.

Using a pure aluminum polycrystalline material as a baseline, calculate estimates of the individual increases in shear strength that arise from the various strengthening mechanisms that occur in an engineering aluminum alloy. The pure aluminum has a grain size of 100μm and a dislocation density of $10^{11}/m^2$. The engineered alloy has been processed to have a grain size of 10μm and a dislocation density of $10^{13}/m^2$. It has been heat treated to contain a maximum of 0.5 atomic percent of Mg in substitutional solid solution and 5 volume percent of non-deformable Mg_2Si precipitates with an average radius of 10nm. For the purposes of this problem, you may assume all strengthening mechanisms are independent.

The following may be helpful for your analysis
k_y'=0.038MN/m$^{3/2}$.
Young's Modulus = 70 GPa
Shear Modulus = 26.1 GPa
Poisson's ratio = 0.345
Burger's Vector = 0.286 nm
Solute hardening parameter of Mg atoms in Al = 0.5

5.

A gas turbine aircraft engine has a metallic component subjected to a sustained stress of 100MPa at a temperature of 600°C that induces a steady state creep strain rate of $3x10^{-8}$/sec. The material has been processed to provide a grain size of 10μm. The creep mechanism at this temperature is Coble creep with an activation energy of 75kJ/mole.

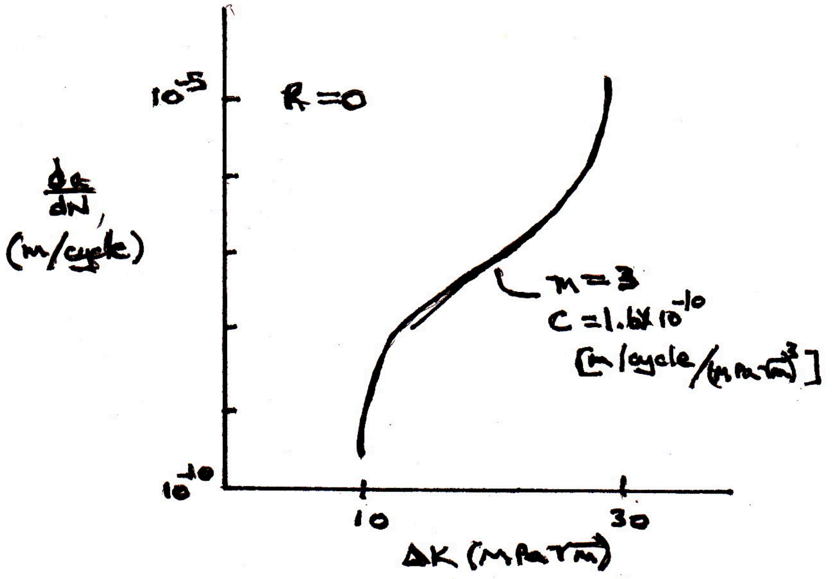
If the stress is increased to 150MPa and the temperature to 700°C calculate the expected creep rate?

At a stress of 100MPa and temperature of 600°C, the designer requires a steady state creep strain rate of $1x10^{-9}$/sec. It has been proposed that the component be processed to change the grain size to achieve this steady state creep rate. Determine if this would be an effective strategy and, if so, what grain size would be required. Show calculations to support your conclusion.

6.

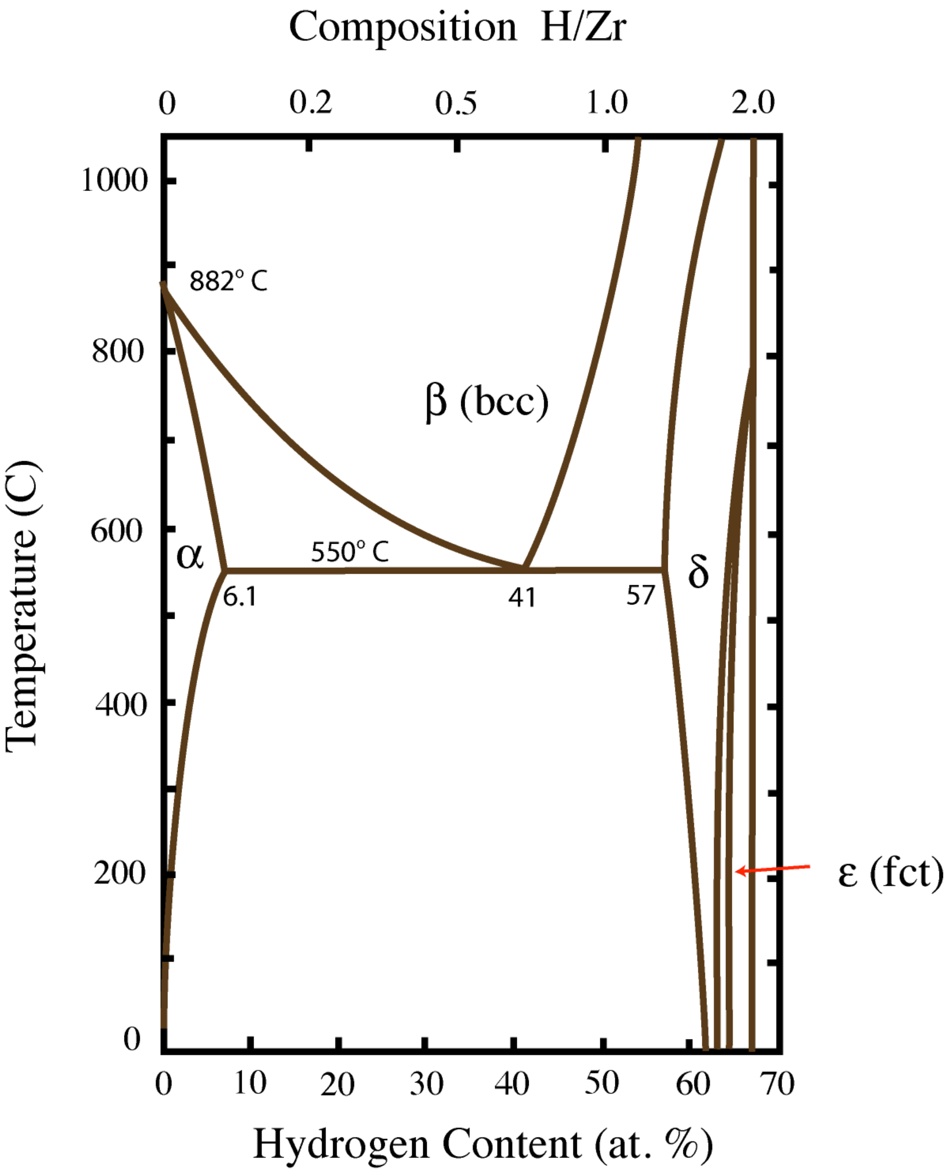
a) Assuming a cracked structure is subjected to a constant cyclic stress, $\Delta\sigma$, derive an analytical (closed form) expression for the number of cycles to propagate an initial crack, of length a_o, to final fracture at crack length, a_f. Please provide a rationale for all assumptions used.

b) Using the expression in part a) and information in the figure provided below, estimate the number of cycles to propagate a crack, a_o, of length 0.02m to fracture when subjected to a cyclic stress range of 80 MPa at R=0. The K_{IC} of this material is 30MPa-√m.

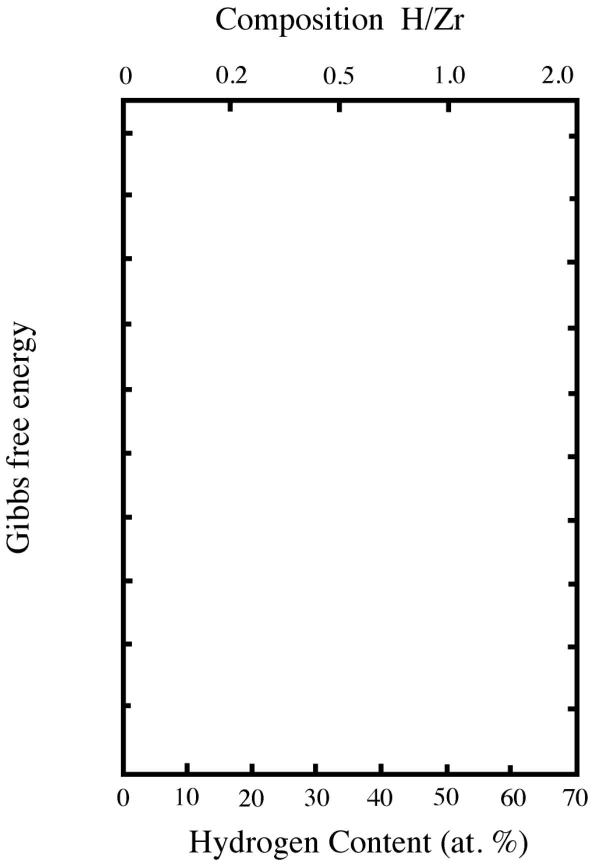


7.

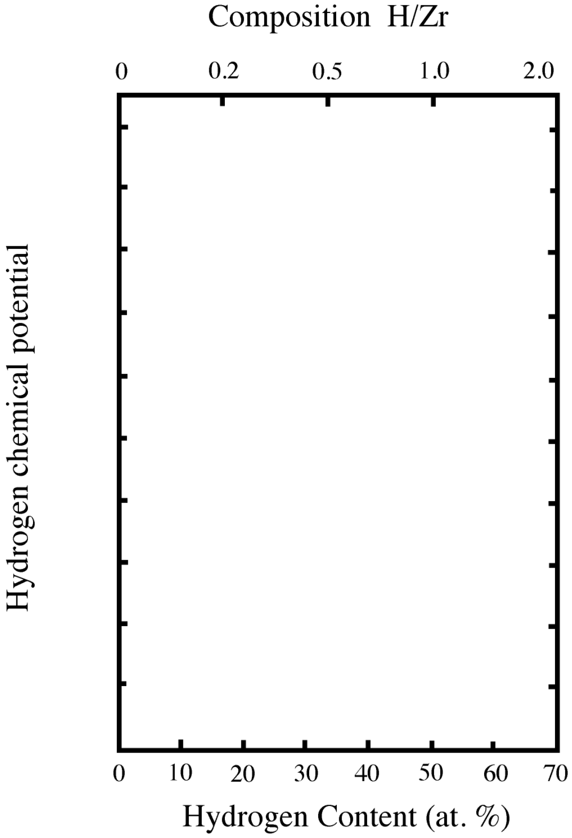
Below is the Zr-H phase diagram. The maximum hydrogen content in Zr is 66% corresponding to the ZrH_2 stoichiometry. Above that there is a two-phase mixture between H_2 gas and ZrH_2.



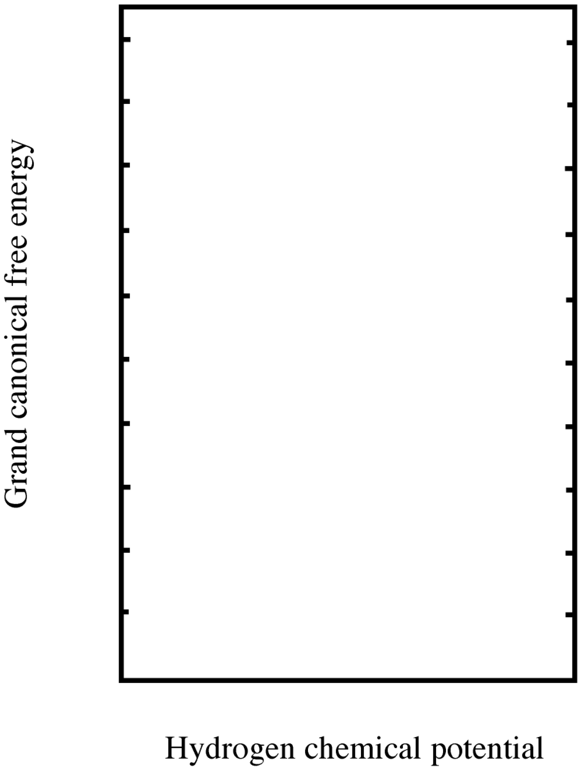
(a) At 600 C, plot the Gibbs free energy as a function of composition (draw common tangents where necessary).



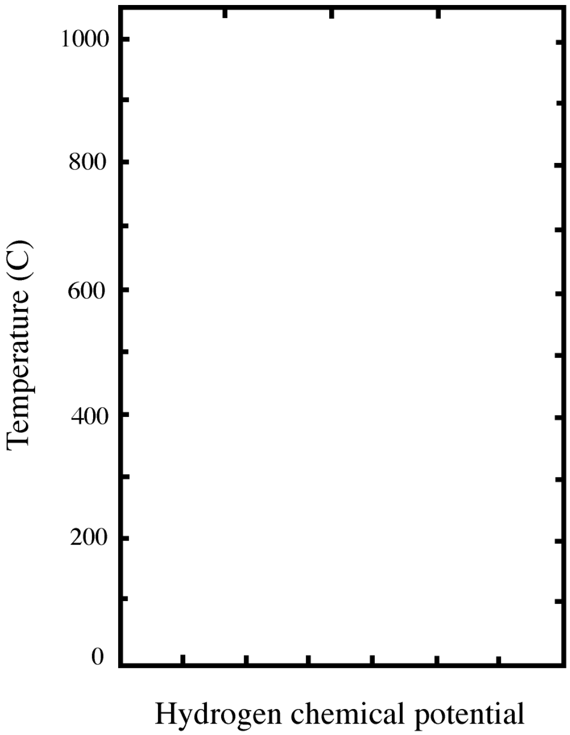
(b) Schematically plot the hydrogen chemical potential as a function of hydrogen concentration at 600 C.



c) At 600 C, plot the grand canonical free energy defined as $\Phi=G-\mu_H \cdot N_H$ as a function of the hydrogen chemical potential μ_H (make sure to justify the shape of your plotted grand canonical free energies as a function of μ_H).



d) Schematically plot a phase diagram for this system as a function of temperature and hydrogen chemical potential.



8.

A Li-intercalation compound (Li_xCoO_2) is used as a cathode in a Li-battery (consisting of a metallic reference Li anode). Rewrite the following expression in terms of thermodynamic state variables and response functions.

$$\left(\frac{\partial G}{\partial S}\right)_{P,N_{CoO_2},\mu_{Li}} = ?$$

9.

A new intercalation compound MPO_4F has been discovered that can accommodate Li ions within its interstitial sites. The interstitial sites are large and far apart such that Li ions occupying the interstitial sites do not interact with each other. The energy of taking a Li atom from a pure metallic Li foil and inserting it into the intercalation compound is ε. The energy of the intercalation compound (having M interstitial sites) without any Li ions is E_o. The volume of the intercalation compound (having M interstitial sites) is V_o *and increases by an amount v for every Li added to the host*.

The Li ions within their interstitial sites vibrate within a parabolic potential well having a curvature *f*. The atoms of the host (MPO_4F) can be assumed to be very tightly bound to each other such that their vibrational degrees of freedom can be neglected.

The new intercalation compound is used as a cathode in a Li battery with a metallic Li reference anode (a metallic Li foil). The battery is at constant temperature, T, and pressure, P, and is held at a constant voltage $\Phi\left(=-\left(\mu_{Li}^{cathode}-\mu_{Li}^{anode}\right)\right)$.

a) Explicitly sum the partition function for the intercalation compound and obtain a closed form analytical expression for it (make sure to account for all relevant degrees of freedom).
b) Relate the average number of Li ions within the intercalation compound to the externally imposed voltage (or equivalently, the Li chemical potential), temperature and pressure.

10.

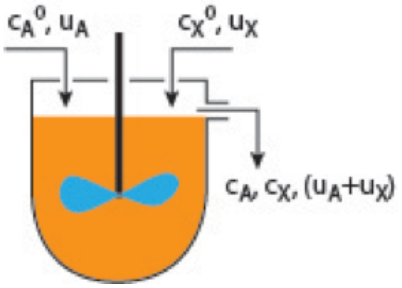
Consider the following catalytic reaction:

$A + X \xrightarrow{k} P + X$,

where *A* is the reactant, *P* the product, and *X* the catalyst. The reaction rate depends on the concentration of catalyst, i.e., $r = -kc_A c_X$, but the catalyst is **not** consumed in the reaction. The process is designed to take place in a continuously stirred tank reactor (CSTR) with a capacity of 150 liters. Reactant and catalyst enter the CSTR in separate streams, each at a volume flow rate of 1 l/s. The concentration of *A* in the incoming stream is 20 mol/l and that of *X* is 0.5 mol/l, respectively. Derive the expression for

a) the yield, *Y*, of this process, and
b) the production rate, *P*, of the process.

Calculate the numerical values of these two quantities with the above parameters. Also given is the reaction rate coefficient, which is 0.04 s^{-1}l/mol.



11.

a.) Derive an expression for an adsorption isotherm for a two-component gas. Assume a single layer maximum coverage, and that the adsorption energy for each component is different.

b.) Consider Ar gas at 100K. Upon physisorption on solid carbon, its Gibbs free energy is lowered by 3.6 kJ/mol. Condensation of Ar, however, would release 0.8 kJ/mol less at that temperature. Assuming that multi-layer adsorption can occur, calculate the partial pressure (with respect to the saturation pressure) of Ar, at which the equivalent of two layers have been adsorbed on the carbon.

c.) Calculate the number of layers that it takes in reality to accommodate 95% of this amount.

12.

The oxidation of Zn to form ZnO occurs via interstitial diffusion of Zn in ZnO towards the oxide/gas interface. The defect equilibrium is described by

$$Zn_i^{\bullet} + e^- + \frac{1}{2}O_2 \longleftrightarrow ZnO \qquad \text{with } \Delta G^\circ = -380900 + 34.8T \text{ (J/mol)}$$

At 800K the fraction of occupied interstitial sites in ZnO at the metal/oxide interface is $2 \cdot 10^{-5}$. ZnO has a density of 5.58 g/cc at this temperature and crystallizes in the zincblende structure shown in the adjacent graph. The Debye temperature of the compound of $\theta_D = 416$ K, and an activation energy of migration for interstitial Zn of 400 kJ/mol, calculate the time it takes for the oxide layer on Zn to reach a thickness of 1 μm. Ignore correlation effects in the Zn diffusion process. The molecular weight of ZnO is 81.4 g/mol.