

PRELIM PART 1 TOPICS & EXAM QUESTIONS – 06/08

THE WEAR OF ULTRAHIGH MOLECULAR WEIGHT POLYETHYLENE ACETABULAR COMPONENTS FOR ARTIFICIAL HIP IMPLANTS

Question 1

1. Why do polymers crystallize? Show a free energy versus temperature plot for polyethylene above and below its melting temperature as a starting point for discussion.
2. When a polymer crystallizes, there is an increase in the order of the polymer. If a polymer is trying to maximize disorder to lower its free energy, what must be true about the forming of crystalline arrays? Write the overall free energy equation governing the reaction at a starting point.
3. Discuss the reasons why the enthalpy is lowered via crystallization of the polymer. Use PE as the polymer of interest.
4. What limits crystallization in UHMWPE?
5. Within the main chain of PE there are 2 H atoms bonded to each C atom. In polytetrafluoroethane, there are 2 F atoms bonded to each C atom. How might the difference in the sizes of each atom (C with a radius of 0.12 nm and F with a radius of 0.135 nm) affect the conformation of the main chain in each polymer type as it assumes a low energy conformation?

Question 2

Describe the thermal history of a ceramic droplet in the plasma spray process, from injection into the plasma stream to the end of the coating process. Divide the process into 2 parts: flight and impact. Define important dimensionless parameters and propose a simple, back-of-the-envelope model for each of the two parts. Assume you have all the thermophysical property data and describe the kinds of experimental data you might need to complete the models.

Question 3

- 1) In many cases, UHMWPE is processed atypically by either powder sintering (compression molding with low shear) or gel-spinning (in the case of Spectra fiber).
 - A) Why is UHMWPE not simply injection molded for extremely large MW?
 - B) Describe the sintering process and the energetics involved.
- 2) During molding, UHMWPE is brought above its melting temperature and then cooled to bring about crystallinity.
 - A) Describe the crystallization process of UHMWPE and the energetics associated with it.
 - B) Low molecular weight PE (15,000 g/mol) is typically lower crystallinity than high molecular weight PE (150,000 g/mol). However, UHMWPE (2,000,000 g/mol) is in between. Explain these observations.

Question 4

1. Please describe how strain hardening occurs in semicrystalline polymers.
2. Does strain hardening depend on molecular weight?

Question 5

1. How is the fatigue of polymers affected by the loading frequency? Do polymers show a fatigue limit? What is a typical fatigue curve for UHMWPE? Does it have a fatigue limit? How do the stress levels that occur in service compare to the fatigue curves?
2. How are the particle sizes measured? What other techniques could be used? What would the issues be in measuring particle sizes in polymers as compared to metals or ceramics?
3. What are the diffusion mechanisms in polymers? What are typical diffusion rates? Given these rates, would chain rotation be expected?
4. What techniques would be useful to characterizing the nature of the wear surfaces? What features could be measured?
5. How could you measure the crystalline fraction in a polymer sample? What corrections would be necessary as compared to a metal or ceramic sample? What other techniques could be used to measure crystalline fraction? How do you measure the molecular weight of a polymer?

GIANT ELECTROSTRICTION OF ELECTRON IRRADIATED FERROELECTRIC POLY(VINYDILENE FLUORIDE TRIFLUOROETHYLENE) RELAXOR

Question 1

- 1) Consider the direct piezoelectric effect between electric polarization and an applied external stress. For an electron-irradiated P(VDF-TrFE) copolymer film, is a direct piezoelectric effect measurable? Please explain.
- 2) From problem 1, would the application of an external dc electric field in the through-thickness direction change the results? Please explain. Are the same results expected for the converse piezoelectric effect?
- 3) How are amorphous polymers processed to be piezoelectric? What are some of the differences with semicrystalline polymers?

Question 2

- 1.) Describe the differences and similarities among ferroelectric, paraelectric, piezoelectric and electrostrictive behavior as a function of electric field, stress and strain and any other relevant variables.
- 2.) Are the phases of PVDF-TrFE equilibrium phases? Draw / sketch the regions of stability of the different phases as a function of composition and temperature and stress and irradiation and any other variables that you think might be important.
- 3.) Describe in detail the Conventional Phenomenological Theory outlined in Appendix I. Specifically describe all the terms in equation 13 and point out how they are related to the electrostrictive, piezoelectric, ferroelectric and Maxwell strains. Does the existence of ferroelectric switching in these materials cause strain?

Question 3

1. Sketch a powder x-ray diffraction pattern for lead titanate above its Curie temperature.
2. Show how this pattern changes when lead titanate is cooled below its Curie temperature.
3. If you doped lead titanate with 1-2 atomic percent of barium titanate or strontium titanate how would the diffraction pattern change? Assume $r(\text{Pb}^{2+})=0.119 \text{ nm}$, $r(\text{Ba}^{2+})=0.135 \text{ nm}$ and $r(\text{Sr}^{2+})=0.118 \text{ nm}$.

4. What characterization method(s) might you use to measure the dopant concentration quantitatively?

Question 4

What is the "loss tangent"?

Sketch the real and imaginary parts of the complex ac permittivity as a function of temperature for a ferroelectric material. Explain.

How would these properties change for a relaxor material?

Question 5

1. Consider the data from a paper by Adem and coworkers published in the Mexican Review of Physics showing irradiation effects on PVDF. Describe the effects that the irradiation has on the diffraction peaks. Why does it affect some diffraction peaks more or less than others?

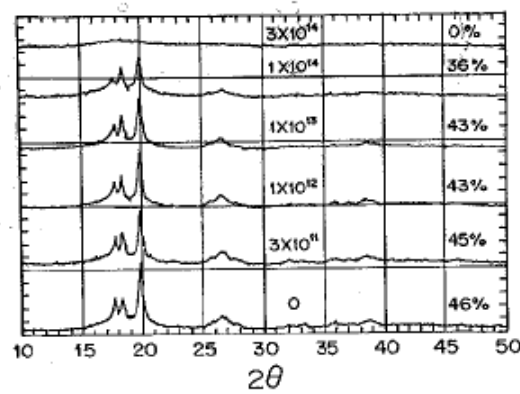


FIGURE 5. X-ray diffractograms for different values of fluence (in cm^{-2}). The percent amount indicates the crystalline content in each sample as a function of fluence.

2. Can you predict the effects of the irradiation on Differential Scanning Calorimetry?

3. Sketch a plot of Specific Volume versus Temperature for this material before and after irradiation.

THERMAL TRANSPORT IN SUPERLATTICE STRUCTURES AND ITS INFLUENCE ON THERMAL CONDUCTIVITY

Question 1

Describe the behavior of an epitaxial thin film as it grows on a monocrystalline substrate with a different bulk lattice parameter. Consider first the case of a (100) oriented film with the FCC structure growing on an FCC substrate, where the bulk relaxed lattice parameter of the substrate is a few percent smaller than that of the film.

How is the lattice mismatch accommodated initially?

How does the stored strain energy per unit area of interface vary with film thickness?

What mechanisms are available for the relaxation of the strain energy?

Question 2

In your presentation, you indicated that the interfacial roughness of the superlattices played a strong role in phonon scattering.

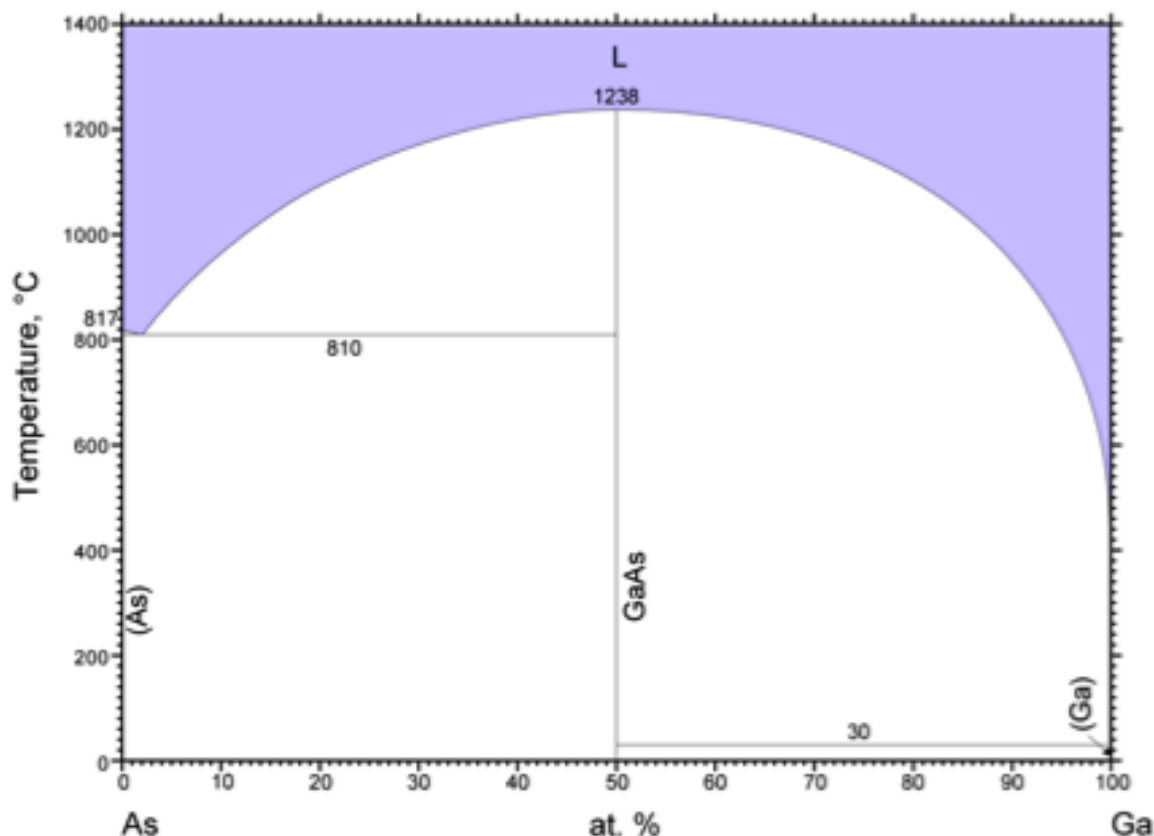
- Indicate at least three characterization techniques that might be useful in quantifying interfacial roughness, either during or after film growth.
- What is the structure factor for scattering of either electrons or x-rays from AlAs and GaAs
- How might you exploit differences in the structure factor for these two materials to characterize interfacial roughness?
- When might point defects contribute strongly to phonon scattering? What techniques are available for characterizing point defect distributions in these systems?

Question 3

Surface and interfacial roughness is known to promote diffuse interface scattering of energy carriers that reduces thermal conductivity. However, those working on superlattice thermoelectrics often seek atomically smooth interfaces to reduce thermal conductivity. Why?

Question 4

An arsenic-gallium phase diagram (Okamoto, 1990) is shown below.



- Sketch the phase diagram and label the phase fields.
- Trace and label the liquidus over the entire range of compositions.

- c. Indicate the eutectic point and write the eutectic transformation as a chemical reaction, including the phases and their compositions.
- d. Does GaAs melt congruently? Explain.
- e. The diagram shows another invariant on the Ga side at 30°C but the details of this transformation are unknown. Expand the scale and qualitatively complete (sketch) the diagram near the Ga border for the case that the unknown transformation is an eutectic and (another sketch) for the case it is a peritectic.

Question 5

1. Consider a laminated material of total thickness L divided into N bilayers of thickness $l=L/N$. Each bilayer is composed of different materials A and B of equal thickness. Assuming that the phonon mean free path is small compared to the thickness of each layer and atomistically sharp interfaces, write an expression for the thermal conductivity of the composite material as a function of the bilayer thickness (l) in terms of the bulk thermal conductivity of materials A and B (k_A and k_B) and the conductivity of the interfaces.
 - i) Do you expect the interfacial conductivity to be the same when energy flows from A to B or B to A?
 - ii) Explain how your expression will break down as the L/N decreases and becomes comparable with the phonon mean free path? Will it overestimate or underestimate the thermal conductivity?
2. (Time permitting) In the document it is correctly stated that umklapp processes is dominant at high temperatures where phonons near the boundary of the BZ are excited. Would you expect results from molecular dynamics simulations (where the classical equations of motion of all the atoms are solved) to capture the temperature dependence of the probability of umklapp processes accurately? Hint: Think about classical vs. quantum statistical mechanics.

THE MERIT OF SPARK PLASMA SINTERING AS A POST DENSIFICATION TREATMENT FOR THIN PLASMA-SPRAYED YTTRIA-STABILIZED ZIRCONIA ELECTROLYTES IN SOFC'S

Question 1

Your graduate research involves stress relaxation experiments on thin-walled coatings. The relaxation behavior observed in the YSZ fits Maxwell-type models for viscoelasticity. The following questions deal with this topic.

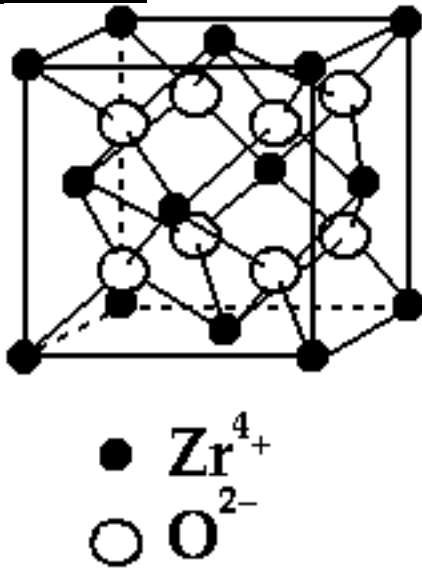
- (a) Derive the Maxwell Model (see schematic below). Begin by stating the assumptions regarding stress and strain in the system. Put your answer in terms of $d\gamma/dt =$.



- (b) On the axis provided draw a plot of the expected $\sigma(t)$ and $\gamma(t)$ behavior as a function of time for a Maxwell model where a strain of γ_0 is applied and maintained. What is the maximum amount of stress expected in the $\sigma(t)$ plot (answer symbolically)? On the $\gamma(t)$ plot, draw the response of the stress in the spring and dashpot as a function of time.

(c) How does the solution change if we add multiple Maxwell elements in parallel? Is there a limit to how many we can add in parallel? Schematically illustrate a model with two Maxwell elements in parallel. What are the contributions to the stress response of model?

Question 2



1. Shown above is the unit cell for zirconia with a cubic lattice. How does yttria play a role in the existence of this unit cell?
2. Define the likely Burgers vector and slip system you would expect for this structure for dislocations to be mobile.
3. If the zirconia is not fully stabilized the unit cell above becomes face-centered-tetragonal, which is not one of the allowed Bravais lattices. Which Bravais lattice is it?
4. Most researchers working on SPS are focused on producing nanoscale grain sizes by suppressing grain growth. Would that produce ideal properties for SOFC applications?

Question 3

- 1) Explain how edge and screw dislocations are defined and describe their movement by glide.
- 2) Give the Burgers vector, slip plane, and line direction of an edge dislocation for $\langle 01\bar{1} \rangle \{011\}$ slip in an ionic crystal with the rock salt structure.
- 3) Sketch the above structure with the edge dislocation.
- 4) Discuss how edge dislocations may be affected by the application of an electric field (p.16).

Question 4

- a. Discuss the coarsening behavior of nanopowders versus micron sized powders.
- b. How is the heating rate during sintering related to the grain growth behavior of materials? What are the restrictions/limitations/disadvantages of the application of a high heating rate during sintering?
- c. Discuss the relationship between electrical current application and heating rate.

Question 5

1. Discuss the anisotropy of the effects of the applied pressure and applied field during SPS. Would you expect more grain growth in one direction? Do the samples processed by SPS show any anisotropy in grain shape, crystallographic texture, location of porosity or pore shape?
2. During grain growth, while there is a reduction in the overall grain boundary area and a resultant decrease in the Gibbs free energy, the motion of the grain boundaries is driven by the curvature of the grain boundary. In which direction do curved grain boundaries move? What causes this motion?
3. As ZrO_2 contains both Zr and O ions which have opposite charges, how does the application of an electric field lead to enhanced densification? What are the mechanisms and paths for diffusion during sintering for the different ions?

ROOM TEMPERATURE FERROMAGNETISM IN Mn DOPED III-V SEMICONDUCTORS

Question 1

In your presentation, you mentioned “Guenther's Law”. What is the physical basis for Guenther's law? In other words, why must this law be satisfied in order to grow stoichiometric III-V semiconductors by physical vapor deposition (i.e., molecular beam epitaxy)?

Question 2

Sketch a magnetic hysteresis curve that might be desirable for a ferromagnetic material intended for use in a spin-valve, and explain why that shape of curve is the most appropriate.

Explain the microstructural changes that occur in the material as we go around the hysteresis loop.

What is the structure when the material has zero magnetization, and what determines the magnetic domain size at that point?

What can be done to control the domain size for technological applications?

Question 3

In your document you presented an isothermal section of ternary phase diagram for Ga-As-Mn at 400 degree C.

1. What are the equilibrium phases that you might expect in Mn-doped GaAs?
2. How could you estimate the solubility of Mn in GaAs?
3. What are possible effects of precipitate size and shape on boundaries on the phase diagram, including solvus lines?
4. How would the composite nature of GaAs or GaN with precipitates manifest itself in magnetic measurements, including measurements of Curie temperature?

Question 4

In heterogeneous and homogeneous nanostructures, spatial confinement can reduce phonon thermal conductivity in two primary ways that are related to the dual wave-particle nature of phonons. Describe these mechanisms and the length scales at which they commonly occur, including how they change with temperature.

Question 5

1. During the course of your presentation, you described in detail the large discrepancies between the Curie temperatures in a GaMnN alloys. Growth method and annealing were implicated, as was precipitation phenomena.

One aspect you did not discuss in detail was potential differences in vacancy concentrations, and defect-vacancy interactions. Please describe how you might experimentally & theoretically investigate differences in vacancy effects in these different materials systematically, both in terms of concentration and electronic activity.

In a similar vein, GaMnN alloys always have relatively high dislocation densities. How might these affect the observed magnetic behavior? Would you expect Mn to segregate to these cores, and how might you determine if it does?

BETA SILICON NITRIDE MICROSTRUCTURE EFFECTS ON FRACTURE TOUGHNESS

Question 1

- 1) Show a synthesis of Silicon Nitride from organic starting materials progressing through a polymer all the way to ceramic.
- 2) In your document, Silicon Nitride is modeled as a composite material of rods dispersed in a matrix.
 - a) If the model is correct, then interface bonding between the matrix and fibers is extremely important. Going from weak to strong interface bonding, discuss what happens to the composite as a crack propagates through it and what does this mean for the properties.
 - b) It is mentioned that grain diameter and orientation information is described as being “not accurate”. As the system is modeled as rods in a matrix, propose and discuss an alternate characterization method.

Question 2

1. How are elastic constants of anisotropic solids determined experimentally?
2. When the diameter of a fiber reduces to nano scale, what needs to be considered in evaluating its Young's modulus?

Question 3

- 1) Describe what the term "plane strain" means when reporting the plane strain fracture toughness, K_{Ic} , of a material. Discuss and explain what testing conditions must be met when testing materials with high K_{Ic} values, such as metals.
- 2) Discuss the transport mechanisms needed to maintain a concave shape for the end of the \square -Si₃N₄ crystal shown in Figure 4 (page 7). What conditions favor this case? What is the value of the shape parameter (S)?

Question 4

In the Vapor-Liquid-Solid mechanism for whisker growth, it was experimentally observed in the 1970s that larger diameter whiskers grow at a greater velocity than smaller diameter whiskers. There is also a minimum diameter, below which no growth is observed. What is the origin of the growth rate dependence on diameter?

This year, a group at IBM observed that during VLS growth of Si nanowires using Au catalyst nanoparticles, smaller diameter nanowires tapered as they grew, whereas larger diameter nanowires tended to widen. What phenomenon is likely responsible for this observation?

Question 5

1. Construct a Wulff plot in the $(\bar{1}0)$ plane for the following relative relationship between solid-vapor interfacial energies: $\gamma_{001} < \gamma_{111} \ll \gamma_{110}$
2. Sketch a \square - Si_3N_4 crystal unit cell, labeling the (0002) and $(\bar{1}10)$ planes.
3. Based on the shape of the \square -grain, what can be said about the relative interfacial energies of the dominant faces?

REVIEW ON THE ACTUATION BEHAVIOR OF IONIC POLYMER-METAL COMPOSITES

Question 1

The strength of ceramics is normally measured by bend testing instead of tensile testing.

- A. Explain the main reason or reasons why this is the case.
- B. Compare and contrast the two main types of bend testing and describe the stress that serves as the measure of "strength." What type of stress is it and what is its orientation and distribution in the specimens.
- C. Describe the main analytical approach used to predict or model the strength of ceramics in terms of independently measurable characteristics.

Question 2

- a) Propose a better geometrical model than the triangle?
- b) Which of the 3 modifications to the Nemat-Nasser/Li model that you performed is most important and why?
- c) For the Young's modulus increase modification, a calibration constant of 1/3 is used. Where does this value come from and how accurate is it? Can we develop a calibration constant directly from the membrane structure?

NOTE: On page 28 graph b is data obtained from ref. 15 and maximizes at 6 plating cycles. Page 40 shows ostensibly the same data from ref. 15 yet maximizes at 4 plating cycles while graph a looks remarkably similar to the graph on page 28. You might consider that there may be a mislabeled figure in the document.

Question 3

- 1) In your review, you estimated a correction factor of $M=0.34$ (page 37) to explain the difference in the experimentally determined and the calculated Young's modulus of the composite. Would you expect the value of M to remain constant for each plating cycle? Explain.
- 2) Discuss other methods for estimating the elastic modulus of the composite (e.g. can one obtain a better estimate without using a "correction factor"?).
- 3) List and discuss the factors that may affect Young's modulus of the polymer itself.

Question 4

- 1) Is this a fractal model since it seems like you are just modifying the topography in some pre-determined way to catch the reaction surface area increase?

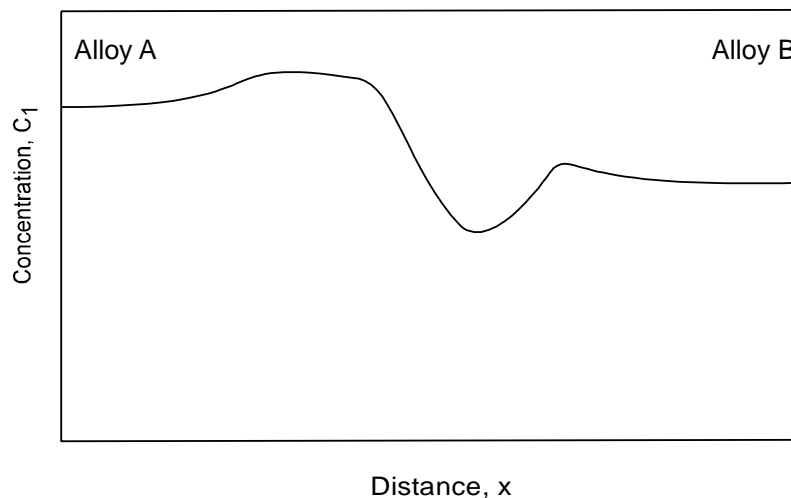
Have you looked at fractal modeling of surfaces in EC deposition, dendritic growth etc. which have some relations derived for surface area changes?

- 2) What evidence exists to support cluster sizes of 4-5 nm? How have these been estimated or measured?
- 3) Why does the tip displacement decay with time as you show in one of your figures? What is the operative mechanism?
- 4) Because of the plating the thickness of film varies as you have seen? Can this thickness change have a more dominant effect on the displacement rather than the Modulus?
- 5) Any critical experiments you would recommend to refine, validate your model assumptions?
- 6) If the IPC film is in a dry environment, would its actuation capabilities degrade quickly with time?

Question 5

Two ternary alloys A and B of different compositions were bonded together and diffusion annealed at temperature T for time t . Shown below is a schematic concentration profile of one of the components, identified as component 1, obtained in the diffusion zone after diffusion annealing.

1. How would you locate the Matano plane for the concentration profile?
2. Draw a schematic profile of interdiffusion flux of component 1 as a function of x .
3. Any comments on the interdiffusion behavior of component 1?



Schematic concentration profile for component 1 after diffusion annealing

PREDICTING COMPOSITE ARCHITECTURE IN MICROFABRICATION BY COEXTRUSION

Question 1

1. Describe the factors that determine the force required to perform extrusion.
2. How is the angle of the die related to this required force?
3. Describe one approach for estimating the force required to perform extrusion.

4. Describe how strain rate sensitivity can influence the force required to perform extrusion.

Question 2

1. Can you give any examples of products that are currently produced by co-extrusion? Is there any particular characteristic of the materials used in these applications?
2. Consider a three-layer slab of material made up of layers of two different, plastically deformable materials A and B, as shown below.

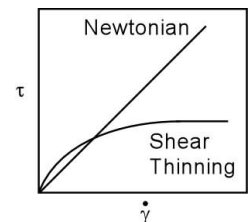


It is desired to roll this slab to a smaller thickness, and end the process with the outer layers making up one half of the total thickness. Considering that the flow properties of the two materials are different, what would you need to know in order to determine the starting thicknesses of the layers of material that are necessary, to produce the desired final configuration?

Question 3

Draw the shear stress profile for a polymer flowing through a capillary. Next, draw the velocity profile of a polymer exhibiting Newtonian flow through a capillary. On the same drawing, draw the velocity profile of the shear thinning polymer indicated in the schematic below.

In relation to the velocity profile for the Newtonian flow, why did you draw the velocity profile this way *near the wall*? In relation to the velocity profile for the Newtonian flow, why did you draw the velocity profile this way *near the center of the capillary*?



How would a) increasing the extrusion rate and b) increasing the process temperature affect the die swell in an extruded polymer? Explain.

Question 4

Rather than extrusion, imagine a process where, after heating to the desired temperature, a feedrod was simply stretched without the use of a mold at all much less an extruder. How would the stress state of the polymer be different compared to extrusion, and what are the relevant rheological characteristics of the polymer determining whether it is possible to obtain a uniform section as the feedrod is stretched?

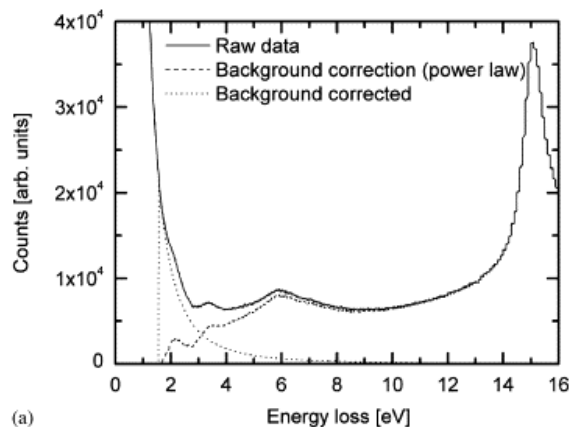
Question 5

- (1) On p. 11 of the document, you state that “At shear rates approaching 1 s^{-1} , polymer fluid flow can approach Newtonian fluid flow.” Why does this behavior depend on the units used (i.e., why wouldn’t it be true for 1 min^{-1})? What feature must the flow have for a power-law fluid to have the same velocity profile as a Newtonian fluid?
- (2) Consider your discussion of the dependence of die swell on Re . What are useful definitions of Re for Newtonian and non-Newtonian flows in a die? How do they depend on average fluid velocity? shear stress? pressure in the die upstream of the exit?

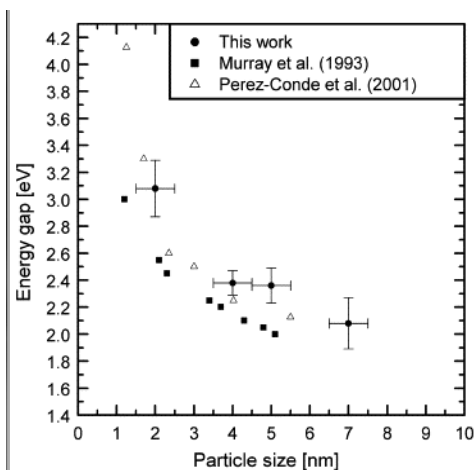
NUCLEATION AND GROWTH OF CdSe SEMICONDUCTOR NANOCRYSTALS IN COLLOIDAL SYNTHESIS

Question 1

1. Throughout your presentation, PL was used as a way to characterize nanocrystal size. This multi-part question examines a potential concern with using PL.
 - a.) Draw on the board a simple band structure (energy vs. wavevector) for a semiconductor material such as CdSe. Describe the “direct” transition that defines the “optical bandgap”.
 - b.) Describe how the technique of photoluminescence is performed.
 - c.) There is an equivalent technique called “valence electron energy loss spectroscopy” (VEELS) that allows measurements of band gap. How this technique work? An example spectrum¹ from CdSe is shown to the
 - d.) A series of measurements were made different nanoparticles using VEELS in same paper^{Error! Bookmark not defined.} and shown below. Can you offer an explanation for the observed discrepancy?



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¹ “Quantification of the size-dependent energy gap of individual CdSe quantum dots by valence electron energy-loss spectroscopy”; Rolf Erni and Nigel D. Browning, Ultramicroscopy, **107**(2-3), 267-273, 2007.

Question 2

- A. In the graph of data on particle size, concentration, and number of particles, you indicated a region that corresponds to where Ostwald ripening begins to dominate. Why did you choose the particular regions as corresponding to Ostwald ripening? How does Ostwald ripening kinetics change with particle size?
- B. In the hot injection method, are there any experiments you could use to distinguish between diffusion-limited growth and reaction-limited growth? What about in the experiments that LaMer did on sulfur?

Question 3

1. ZrO_2 is a widely used ceramic material. It has uses as an electrolyte in fuel cells and oxygen sensors, as a toughened structural material and as a thermal barrier coating.
2. What properties of ZrO_2 make it good for each application?
3. In use ZrO_2 is stabilized to remain in the cubic phase. What is the crystal structure of the cubic phase? Why is the cubic phase used? What are the polytypes that occur when it is not stabilized? What is the role of particle size in stabilization?
4. Many ceramic materials are faceted. What is the faceting due to? Are ZrO_2 materials faceted? Would the size of the particle matter for faceting? What other terms need to be included in the description of ZrO_2 to be able to include size dependent faceting?
5. Describe the transformation between the different polytypes. What is different when comparing the transition between the ZrO_2 polytypes and the transition from a zincblende structure to a wurtzite structure?
6. What is the difference between toughness and strength?

Question 4

1. Let's discuss how confinement (size and dimensionality) affects the electronic properties of materials. You may want to start with the Schrödinger equation and describe solutions for a particle in a box (infinite potential well) and wire with square cross sections.
2. (If time permits) Consider a case of diffusion-limited growth where the initial size of the particles is the same but they are not homogeneously distributed in space. Compare the growth of a particle with nearby neighbors and one without any other in close proximity to it.

THE EVALUATION OF STRESS IN PZT THIN FILM MULTILAYERS USING WAFER CURVATURE AND THE STONEY EQUATION

Question 1

1. Assume the substrate for a thin film application process is a single crystal of aluminum. Is it possible for the application of a thin film to result in plastic deformation?
2. Describe how the stresses for film deposition might result in a different yield stress than we would expect for uniaxial deformation.
3. How would the stresses differ if the substrate was a polycrystal?

Question 2

- For the most anisotropic elastic solids, how many independent elastic constants are there? How do you arrive at this number?

Question 3

- 1) For the equations listed in your document for stress relaxation, μ is listed as the modulus. What modulus is it?
- 2) Consider the deformation mechanisms that may operate in bulk polycrystalline and thin film specimens as a function of temperature. List and discuss what differences (in their formulation, description, or operation) that should be considered between the thin film and bulk polycrystalline forms.

Question 4

In your document you mention that Pt_3Pb is a metastable phase that forms during the crystallization process but disappears over the course of a few minutes when held at temperatures of 500°C .

1. How does the Pt_3Pb form, and what is the proposed role of Pt_3Pb in thin film PZT texture development?
2. Is the Pt_3Pb film necessarily continuous? How does this affect the stress analysis?
3. If you wanted to prevent the formation of Pt_3Pb , or at least minimize or even eliminate its influence on texture development in PZT thin films, how could you go about it?

Question 5

Briefly discuss the main steps of the PZT film deposition by the sol-gel method.

Question 6

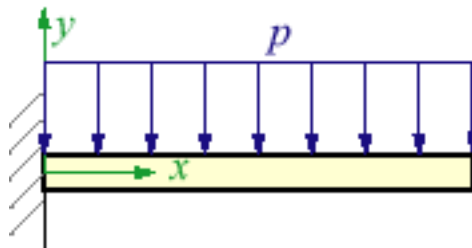
The Stoney equation is derived for the case of uniaxial stress in a surface film, parallel to the long axis of a beam. It relates the radius of curvature of the substrate to the film stress, in one dimension. In electronic materials applications, it is usually applied to experiments done on cantilever beams, shaped like diving boards.

1. What effects on the measured curvature do you expect from the existence of biaxial stress in the film? Consider the effect of the curvature about the long axis of the beam.
2. Does this cause any obvious experimental difficulties?
3. Does the Stoney equation give correct results if whole wafers are used rather than beams cut from them?

Useful formula: The standard result for 1-dimensional deflection of a cantilever beam under uniform load is

$$w(x) = -\frac{p x^2 (6L^2 - 4xL + x^2)}{24EI}$$

Where L is the length of the beam and I is its moment of inertia about the x -axis. E is Young's modulus.



COMPETING MODELS FOR EVOLUTION OF SIZES AND SHAPES OF SELF-ASSEMBLED Ge ISLANDS ON Si (001) SUBSTRATES

Question 1

One of the stated reasons to study the Ge / Si (100) system is that it is a “model” quantum dot system. However, Ge is an indirect band gap semiconductor, and most applications of quantum dots are in optoelectronics.

The question: name three fundamental differences between the physical properties of the Ge / Si (100) and the InAs / GaAs (100) systems, as relates to your discussion of size & shape distribution issues in “quantum dots”.

Question 2

What values are typical for the surface energies of solids?

Describe how these surface energies can be measured.

What is the difference between surface *energy* and surface *stress*, and what are the conditions under which they have the same value?

Question 3

In standard coarsening theory, there is a dependence on solute concentration, and mass is always conserved. In surface theory, the solute equivalent is adatom density.

- a) How would this difference, and the switch to 2-D from 3-D, be expected to affect the coarsening dependencies?
- b) If there is a finite desorption rate (i.e., chance of adatom disappearing from the system), how would this affect the outcome? Address particularly the upper end of island size distribution.

Question 4

In your document, you propose to conduct two groups of experiments. In the first group of experiments, the proposed temperatures are 500, 550, and 600 C. In the second group, the temperatures are 400 and 450 C, plus additional experiments at 550 and 600 C. Answer the following questions regarding these experiments:

- a. What type of temperature sensors would be used, and how accurate are they?
- b. Mathematically, can you calculate the sensitivity of your primary experimental outcome (e.g., particle shape) to annealing temperature?
- c. At what locations would you measure temperature?
- d. Assuming that the measured temperature location is not exactly on the surface, how would you assess and account for a lack of isothermal conditions in the annealing chamber?

Question 5

1. Coarsening theory (as modeled by Wagner, Lifshitz, and Slyozov) is a "mean field" theory. What does this theory assume, particularly the "mean field" assumption? How does this differ from the conditions of the actual experiments? Give a few suggestions about how the theories you presented might be modified to account for non-uniform driving forces.
2. In Figures 1 and 2 and Table 1 you have given some information on the shape and dimension transitions as a function of temperature and Ge coverage. What specific features of the transitions could be used to test the various theories?
3. The pyramid size distribution is very narrow. You discussed how there might be a barrier to growth due to nucleation of the next layer on a facet. There are also not many small pyramids. Could there also be a barrier to dissolution? Under what conditions, if any, might contribute to such conditions.

Question 6

In the plot of normalized excess surface energy vs. lattice mismatch (from K.N. Tu via Ohring), delineating the boundaries between F-vdM, S-K, and V-W growth modes, why is the excess interfacial free energy not included in the normalized excess surface energy?

How would you extend the diagram into the other three quadrants?

METAMORPHIC EPITAXY

Question 1

1. What factors must be considered in order to determine the optimum thickness for a metamorphic buffer layer?
2. If we are growing Ge on Si, does the size of the Si wafer have an effect on the process?

Question 2

1. In your presentation you had mentioned that the interface between the uppermost SiGe layer and the final Ge layer exhibited strain fields and that dislocations were prevented from threading to the Ge layer¹ by these strain fields.
 - a) What is the evidence that the contrast features you pointed to show “strain”?
 - b) By what mechanisms would strain fields cause dislocation termination?
 - c) The subsequent HRTEM image you showed was presented as evidence of a defect free epitaxial layer. Are you comfortable with that conclusion, and if so, why?

Question 3

Consider a lattice matched III-V heteroepitaxial layer with the zincblende structure grown on the (100) surface of a diamond cubic (group IV) substrate.

Describe the defects that you might expect to find in the vicinity of such an interface.

How might these defects limit the application of such heterointerfaces in electronic devices?

Question 4

1. Why is a balanced normal (i.e., hydrostatic) stress normally considered to have no effect on dislocation motion, while an unbalanced pure normal stress state does?
2. How might a hydrostatic stress affect the Peierls barrier?

Question 5

1. Describe the Matthews-Blakeslee mechanism for the formation of misfit dislocations.
2. Comment on the thermal stability of metamorphic layers. What would happen to the dislocation density if you annealed a metamorphic layer?

THICKNESS EFFECTS IN FERROELECTRICS

Question 1

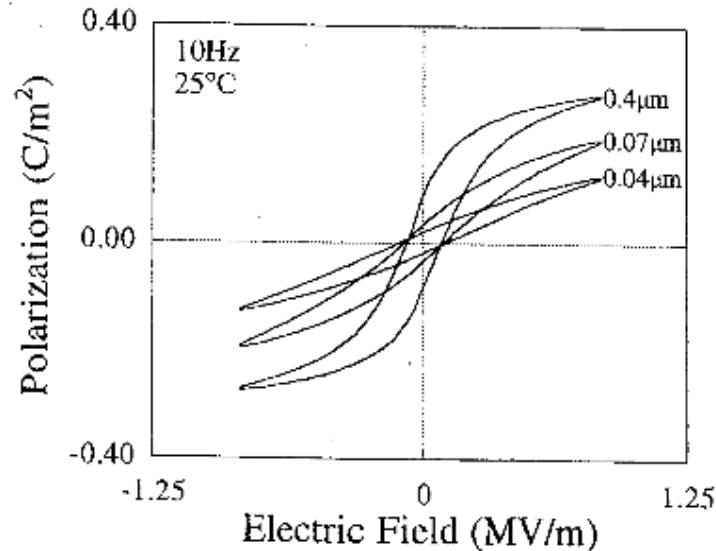
1. X-ray diffraction can be used to evaluate the peak splitting that occurs on the formation of tetragonal phase from a cubic one. What type of peak splitting would we see if we went from a tetragonal to an orthorhombic phase that is slightly distorted from the tetragonal phase?
2. Assume there is biaxial compression in the formation of a thin film. Although we usually look at films in a reflection mode, some investigators do transmission measurements. What does a transmission measurement allow you to measure that we cannot measure in reflection?

3. If there is biaxial compression in a polycrystalline, cubic film which orientations would you expect transform first as you cool below the Curie temperature?

Question 2

1. What controls the average ferroelectric domain size for a material like PZT?
2. Explain the microstructural processes involved in poling when the material has a grain size that is smaller than the average domain size, and describe the effects on the hysteresis loop.
3. Describe any additional effects that might be expected when the grain size is approximately the same as the domain size.

Question 3



The data shown above is for BaTiO₃.

1. Is this data consistent with the behavior of bulk ferroelectric or a thin film ferroelectric?
2. What implications does this data have for the discussion of thickness effects in ferroelectrics?

Question 4

For a perovskite ferroelectric material in thin film form ((001) oriented), draw a crystal unit cell and show the different changes that it will experience as you apply an electric field. In particular, show: **a)** The different configurations of the unit cell at different points in a stress-free hysteresis loop (polarization versus electric field), and the butterfly loop (strain versus electric field); **b)** what you expect will happen to the unit cell if you stretch it or compress it along the c-axis. What will happen to the hysteresis and the butterfly loop? **c)** What will happen to the hysteresis and butterfly loops if the stress is biaxial (compressive) and contained within the (001) plane? **d)** Based on what you have done so far, what do you expect will happen to the hysteresis and butterfly loops if the thickness of the ferroelectric film increases? What will happen if it decreases?

Question 5

- a) If a dielectric film has stochastic (random, statistical) variations in the breakdown field, what factor(s) would be most important in the breakdown voltage of the overall film?
- b) Describe *briefly* one possible breakdown mechanism for such a film.
- c) Would any changes in breakdown voltage be observed if the contact pads (measurement electrodes) were quite small?

SUPPRESSION OF GLASS TRANSITION TEMPERATURE DUE TO NANOCONFINEMENT

Question 1

- 1) In your document you wrote about how polystyrene doped with a pyrene methacrylate was used for fluorescence experiments. How would such a material be synthesized (assume a random doping)? If instead of a random copolymer, how would you dope the middle part between two blocks in a block copolymer of PS and PMMA?
- 2) In the document mention is made to how PMMA interacts with silica, but this effect was not seen in observations of Bolline.
 - a) Using the chemical structures of PMMA and silica, describe the origin of the interaction.
 - b) It is commonly known that the strength of adhesion of PMMA to silica is strongly influenced by pretreatment of the silica. Based on the results of 2 a), how would pretreatment of the silica with acid and base affect the adhesion?

Question 2

Describe the origins and evolution of stress during the spin coating process for a polymeric material. How is film stress relaxed? Compare/contrast with a vapor deposited polycrystalline metal film.

Question 3

- 1) An analogy between nanocomposites and thin films has been presented by Schadler et al. [MRS Bulletin, April 2007] as shown in the figure below. From your reading of this topic, discuss possible reasons for the change in T_g in bulk nanocomposites as compared to thin films.

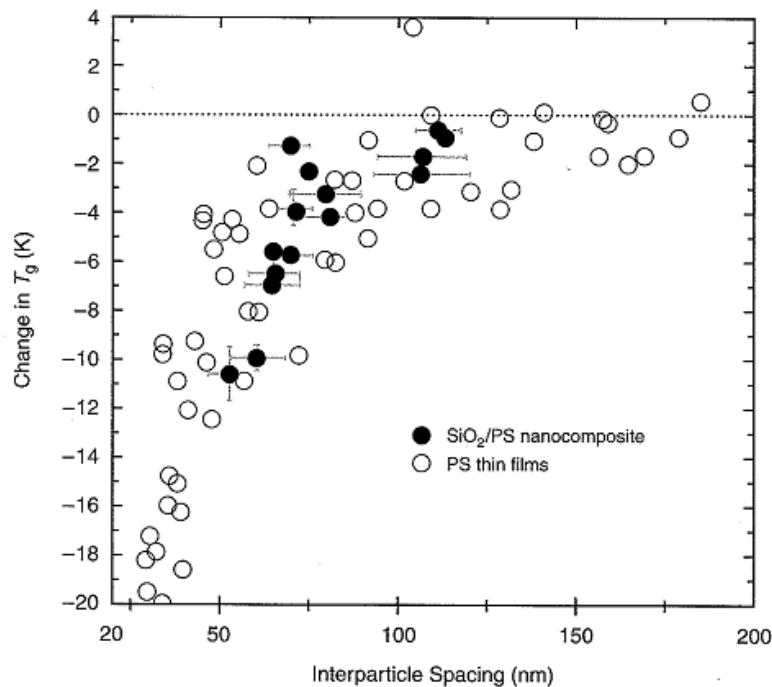


Figure 2. Comparison between the glass-transition response of polystyrene nanocomposites and polystyrene thin films as a function of interparticle spacing, which represents the film thickness for thin films and an average interparticle spacing in the nanocomposites. The x-error bars represent a 95% confidence level. Data from literature on freestanding ultrathin films²⁹ and supported films³⁰ are shown as open circles. (Taken from Reference 31.)

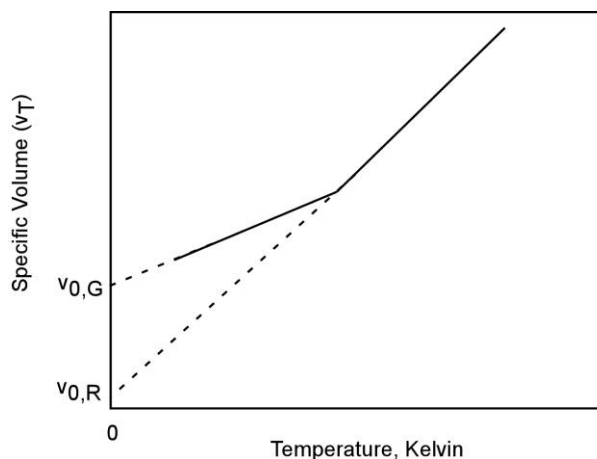
- 2) For glassy polymers the stress needed to initiate plastic deformation, such as shear banding or crazing, is different in compression and tension. Is the yield stress higher in compression or tension? Explain your answer.

Question 4

- 1) Schematically illustrate the typical behaviors of (i) specific volume versus temperature and (ii) specific enthalpy versus temperature, upon cooling of a polymer in the liquid state through the (a) glass and (b) crystallization transition temperature.
- 2) You stated that “The glass-rubber transition ... is often assumed to be a second order thermodynamic transition” (lines 9 – 11, page 6). Explain the typical patterns of behavior in the DSC traces that signify first-order and second-order phase transitions. Using the DSC data shown in Figure 2, discuss the reason(s) why the glass transition is often considered as a second-order transition.
- 3) As discussed on page 28 (line 16), in glassy polymers (i.e., $T < T_g$), properties depend on the thermal history of the material. This phenomenon called “aging” is often problematic, because it causes unwanted drifts in the mechanical properties of the polymer materials. Interestingly, this aging always leads to densification of the glass. Explain why the densification occurs in thermodynamic terms.

Question 5

- 1) Please provide a working definition for free volume. How is it different or the same than porosity?
- 2) The figure is a plot of specific volume versus temperature. Please answer the following questions:
 - (i) Write a simple expression for the total volume of the polymer (v_T).
 - (ii) What does $v_{0,G}$ represent? Explain.
 - (iii) What does $v_{0,R}$ represent? Explain.
 - (iv) An expression for specific free volume, v_f , near the glass transition is given as $(\alpha_R - \alpha_G)T_g$, where α is the volume expansion coefficient. Indicate the location of α on the graph; indicate the free volume above and below the T_g on the graph. Discuss any implications.
- 3) Can the T_g of a material be changed without altering its chemical structure (ie. MW, pendent groups, etc)? Explain. If yes, how is this related to the free volume of the polymer?
- 4) Would you expect to see suppression of the glass transition temperature due to nanoconfinement in high density polyethylene?
- 5) Is glass transition a first order or second order thermodynamic transition? Explain.



THE EXPANSION OF Li-BASED RECHARGEABLE BATTERY CATHODE MATERIALS BEYOND LiCoO_2

Question 1

1. You are given an oxide ceramic material and asked to perform experiments to determine if the oxide is an ionic or electronic conductor. What experiment(s) would you perform and what results would allow you to reach a conclusion about the mechanism of electrical conduction?
2. Ni-Cu alloys exhibit complete solid solubility. Sketch a plot of the electrical resistivity of Ni-Cu alloys as a function of composition ranging from pure Ni to pure Cu. Assume that pure Ni has a higher resistivity than pure Cu.

- Al-Cu alloys exhibit a limited range of solid solubility. Sketch a plot of the electrical resistivity of Al-Cu alloys as a function of composition ranging from pure Al to pure Cu. Assume that pure Al has a higher resistivity than pure Cu.

Question 2

- What are the similarities and differences between ordinary semiconductivity and polaron conductivity?
- How can the important parameters of each (e.g., energy gaps / trap depths and density of states / carrier density) be measured?

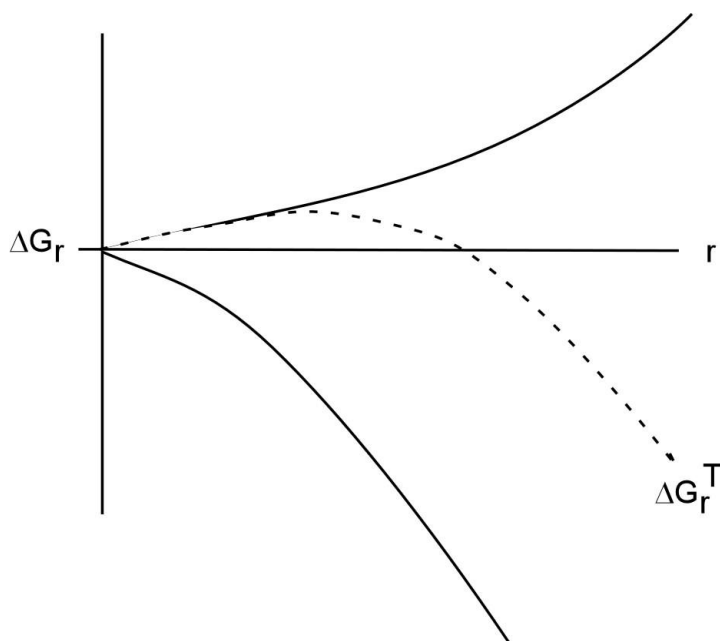
Question 3

- You write LiFePO_4 is based on a distorted HCP lattice. What do you mean by a distorted HCP lattice? Is it common to refer to Triphylite as being HCP?
- You and others refer to these compounds as Olivine. What is the crystal structure of the mineral series called Olivines that range from Fayalite (Fe_2SiO_4) to Forsterite (Mg_2SiO_4)? Why are these battery materials called Olivines?
- For the microstructure shown in Figure 9 describe a quick way that you could discern that you had formed the two "distinct" phases shown. Explain how you could tell the crystal structure of the two phases.

Question 4

Consider the nucleation of a small spherical particle of phase β within a matrix of the parent phase α . Below is a figure illustrating the relationship between the change in free energy of the new β crystal with radius r (ΔG_r) versus the radius of the β crystal (given as r in the figure).

- What affects the ΔG_r^T term (this is the total free energy change in the β particle of radius r)? You might start by labeling the upper and lower curves (drawn with solid lines in the figure below) and attaching a physical significance to them.
- Develop a mathematical expression for ΔG_r^T
- What is the significance of the inflection point on the ΔG_r^T curve?



Question 5

You proposed that an "optimum" cathode microstructure would consist of "small crystallites connected by necks creating a porous structure..." and you pointed out that reducing the particle size would decrease the diffusion distance for Li^+ (Fig. 9).

- (a) Derive an expression for the specific surface area of spherical particles of radius r and true density ρ .
- (b) Explain how decreasing the particle (grain) size would affect the surface (interface) area over which the cathode reaction would occur?
- (c) Sketch a microstructure showing necks that form between particles during sintering under conditions that resulted in no shrinkage. Indicate the possible mass transport pathways for this sintering process.

EFFECT OF GRAIN BOUNDARIES ON THE ELECTRICAL PROPERTIES OF POLYCRYSTALLINE SILICON

Question 1

Describe the structure of a small-angle grain boundary, by answering the following questions:

- a) How does the dislocation content vary with the misorientation angle?
- b) How does the energy of the boundary vary with the misorientation angle? (Provide an approximate derivation of the energy, based upon the dislocation content).

Question 2

Screw dislocations should have no dangling bonds, and edge dislocations in Si also usually reconstruct into 5-7 rings with no unsaturated bonds. What aspects of these dislocations would affect carrier recombination/generation or transport?

Question 3

Consider the crystal growth of a dilute copper alloy in a Bridgman furnace. Assuming that the alloying addition has lowered the melting temperature, and that a planar solid-liquid interface is maintained during growth, sketch the change in the composition profile along the length of the ingot. How does the profile change for complete mixing of the liquid versus the case of limited liquid diffusion and no convection?

Question 4

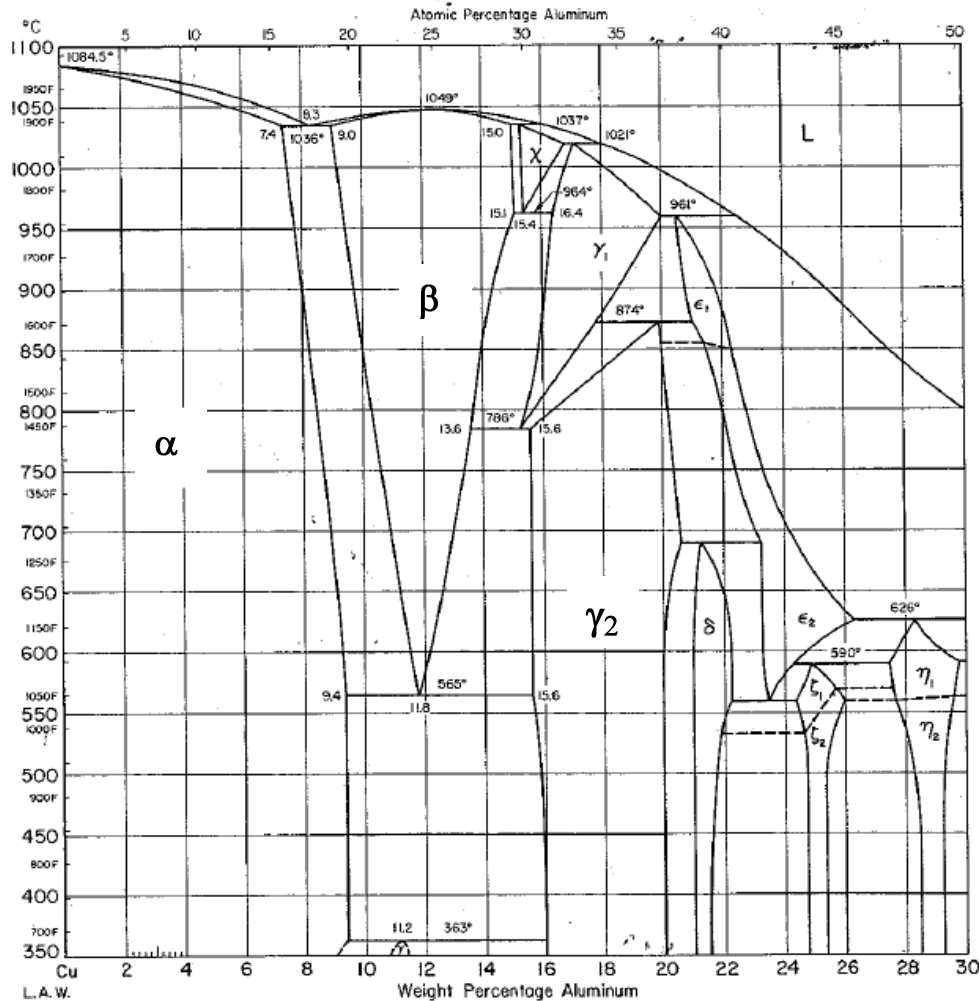
Two identical diffusion couples are assembled with disks of two alloys A and B in a binary system of components 1 and 2. The two couples are annealed at temperature $T^\circ\text{C}$, one couple for time t_1 and the other for time t_2 .

- 1. Draw schematic concentration profiles for the two couples diffusion-annealed for times of t_1 and t_2 . Indicate any assumptions you would like to make.
- 2. What relationship do you expect between the two profiles and why?
- 3. If you were to get inside the diffusion zone and hang on to a concentration level of your choosing at some section x , with what velocity do you expect to move at any time t of diffusion?
- 4. At what section in the diffusion zone would you expect the interdiffusion fluxes of the components to be maximum and why?

PYRAMIDAL DEFECTS OBSERVED IN Mg-DOPED GaN

Question 1

- 1) With reference to the attached phase diagram, sketch the TTT-diagram for the decomposition of the β -phase for a Cu-11.8 wt% Al alloy. Note a martensitic phase can form for this alloy.
- 2) Explain the shape and position of the curves.
- 3) What changes in the TTT-diagram would occur for alloys of lower Al content (say Cu-11.0 wt% Al)?



Question 2

Compare and contrast fcc and hcp crystal structures in terms of the following:

- 1.) stacking of close-packed planes
- 2.) coordination number
- 3.) packing factor
- 4.) first nearest neighbor distance
- 5.) second nearest neighbor distance.

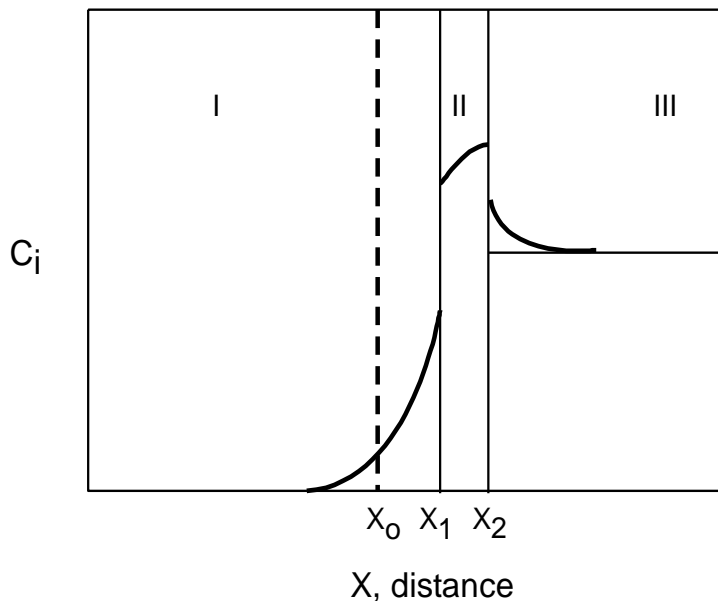
Question 3

- 1.) What determines the slip plane of a dislocation?
- 2.) What determines the movement direction of a dislocation?
- 3.) For two dislocations on the same slip plane and with the same (+/-) direction of motion, what factors would influence their interaction?

Question 4

1. A schematic concentration profile, (C_i vs x), for a multiphase diffusion couple, assembled with alloys I and III and isothermally annealed at temperature T for time t , is shown below. A phase identified as II develops in the diffusion zone and the interfaces x_1 and x_2 move parabolically with time. X_0 is the location of the Matano plane.

(a) Show a mass balance on the plot that justifies the location of the Matano plane.
(b) Draw a schematic profile for the interdiffusion flux of component i as a function of x .
(c) Any comments on the plot drawn as answer to (b).



POLYMER-CLAY NANOCOMPOSITES “THE PROCESSING CHALLENGES OF A NATURALLY OCCURRING REINFORCEMENT”

Question 1

Consider your Au nanowire arrays in porous anodic alumina. If you were to perform a coupled theta-2*theta XRD scan and found only 111 and higher order reflections (e.g., 222, 333 etc.) from fcc Au, what could you conclude about the microstructure of the sample? What conclusions could you draw only with more information? What additional XRD experiments would you perform?

If instead, you found that the original theta-2*theta scan revealed that the 111 and 200 reflections (and their higher order reflections) were conspicuously absent, but the 220 reflection and 422 reflections were present, what could you conclude?

Question 2

1. Derive Bragg's Law.
2. What variables can influence the intensity of a diffraction pattern?

Question 3

A) In adding these micron-sized clay particles to polymers, this process seems similar to heterogeneous nucleation in polymer melts. Explain heterogeneous nucleation. Draw a graph of the free energy of nucleation versus nuclei size and explain the factors influencing the shape.

B) In many of these systems, crystallization rate and degree are actually suppressed. Propose a mechanism for why such behavior occurs. What role does the surface interaction of the clay with the polymer play? How would a strong interaction differ from a weak interaction?

Question 4

Consider a composite material consisting of a nanoscale conductor dispersed in a non-conducting (electrically) polymer. Suppose that a closely interconnected network of the conductor (without polymer) has a conductance of G_1 , and that the polymer has a low conductance of G_2 . How would you expect the conductance of the composite to vary with percentage of the nanoscale conductor (consider the various regimes, as appropriate).

Question 5

- 1) Explain the major differences between x-ray and electron diffraction.
- 2) Discuss the similarities and differences in applying these techniques to the analysis of nanometer scale polycrystalline materials.

MODELS MAGMA GRAMENTATION VIOLENT PLINIAN ERUPTION

Question 1

In the early stage of boiling water in a pan on a stove and in freshly poured champagne, bubbles tend to form at isolated points on the pan/glass surface.

- A. Qualitatively describe the nucleation mechanism and energetics of this process and show why crevices or pits in a solid surface can act as much more potent nucleation sites than flat surfaces. Highlight the role of the contact angle.
- B. Quantitatively describe the forces and pressures at play in the above process of bubble formation and subsequent motion in the liquid.

Question 2

Describe the rationale for using the Schmid factor in describing the deformation of single crystals tested in a tensile frame.

What approach would be used to find the resolved shear stress for more complicated loading conditions (3-D state of stress)?

Question 3

Solid state sintering of ceramics is an important research area as it provides a means to densify materials with high melting temperatures or no melting temperature at all. The following questions are related to this topic.

1. Draw a schematic of two or three powder particles on the marker board after some time at a temperature of approximately $0.6 T_m$. Use the schematic to indicate the movement of material during sintering, differentiating between the two primary transport mechanisms. Which transport mechanism is most relevant for making, for example, dense alumina?

2. There is a thin shell of SiO_2 around each silicon nitride powder that reacts with sintering aids (like Y_2O_3) to form a glassy phase during sintering. How could this glassy phase affect the transport mechanism(s) during densification?
3. The starting powders to make silicon nitride parts are usually composed of equiaxed grains of $\alpha\text{-Si}_3\text{N}_4$. During sintering these grains transform to $\beta\text{-Si}_3\text{N}_4$. How would this phase transformation assist or be a detriment for densification?
4. When pressureless sintering does not result in a dense part, other processing techniques are available. Discuss a couple of these and how they might be used to densify, for example, silicon nitride powders without sintering aids.

Question 4

1. In general, what is the effect of strain rate on fracture toughness?
2. No material is perfectly brittle. How do you justify the use of linear elastic fracture mechanics in real materials which exhibit plasticity?
3. Consider two collinear cracks in an elastic-plastic material under remote tension. Assume that one crack is much larger than the other and they are within the “interactive range.” At a certain load level the two cracks would move toward each other, which crack would move first?

Question 5

If a glass contains isolated spheroid cavities with small cracks as shown in Figure 13(a) how much do you expect the fracture stress from external applied stress to be reduced versus a glass that had only the cracks?

Give an estimate followed by an explanation for your reasoning.

Question 6

What mechanism(s) would atomic diffusion occur by in silicon nitride?
Would this be changed between single crystal and amorphous?
How would this be affected by purity/doping?

PHASE-SEPARATIONS IN III-V ALLOY NANOSTRUCTURES

Question 1

In your presentation you argued that the observations of phase separation in III-V nanostructures are a result of the presence of kinetic miscibility gaps in both the AlGaAs and AlGaN systems. In each of these cases, the epitaxial strain is non-existent, due to lack of a growth substrate to provide the source of coherency strain.

Please discuss how one might grow nanostructures that have coherency strains, and whether you might be able to prevent phase separations through the application of coherency strain.

Question 2

The core/shell structure of the GaN/(Al,Ga)N nanowires is intriguing. From your report, I learned that the GaN cores are 5-40 nm in diameter, and the $\text{Al}_{0.73}\text{Ga}_{0.23}\text{N}$ sheath is typically 50-200 nm. The lattice mismatch should be about 3% along the c direction, and about 1.9% in the basal plane. The electron diffraction pattern (Fig. 14D) suggests that the core and shell are coherent.

Please comment on the state of strain in these core/shell nanowires.

If the heterostructure were to relax (reduction of elastic strain energy by defect introduction), how might this occur?

How would you expect the strain energy to affect the dimensions (core diameter and sheath thickness) of the nanowire?

Question 3

- 1) Plot the free energy (G) versus temperature (T) for the solid and liquid of a pure metal. Label the melting temperature.
- 2) Draw another plot to show how the melting temperature would change if pressure is increased (assume the solid is the denser phase).
- 3) Show how the melting temperature would change due to curvature.

Question 4

- a) If a screw dislocation penetrated through an elastically strained spinodally-developed interface, what would happen?
- b) Would the composition gradient across a spinodally-induced interface differ if the interface became incoherent (versus normally coherent)? Why?

Question 5

The phase separation patterns (structure, composition, etc.) that have been observed in the growth of Al-Ga-N and Al-Ga-As nanowires are different. You proposed that further experiments are needed to determine the mechanisms operating in both of these cases. You gave a list of extrinsic parameters on page 30 to examine what mechanisms are operating.

For Al-Ga-N, describe how the growth and phase separation behavior might change with changes in temperature, gas pressure, and particle size of the catalyst?

For Al-Ga-As, describe how the growth and phase separation behavior might change with changes in temperature, gas pressure, and particle size of the catalyst?

What dopants would you add to Al-Ga-As to increase the coherency strain effect? What dopants would you add to Al-Ga-N to increase the coherency strain effect?

THE INTRINSIC STRESS OF POLYCRYSTALLINE THIN FILMS

Question 1

Silicon thin films can be made amorphous in many different ways, although the crystalline form is always the stable structure, and transformation to the crystalline phase occurs upon heating the film. Describe how the transformation from the amorphous to the crystalline phase proceeds, by answering the following questions:

- a) How does the fraction of the material that has transformed vary with time?
- b) How would a single particle of crystalline material grow? (How would the growth rate vary with time?)
- c) If the amorphous silicon was unstressed, what state of stress would the film have, after it has crystallized?

Question 2

1. What would a reasonable value be for the yield stress of Cu?
2. How is this related to the maximum stress you would expect to see in a thin film?
 - a. What assumptions are you making?
 - b. What effects would be present from the type of film formation process?
3. Are dislocations more or less important in the generation of film stresses than grain boundaries? What mechanisms of dislocation formation are present in films?

Question 3

If the residual stress in a film were nonuniform, how could you measure that stress (BOTH mean and local)?

Question 4

1. Estimate the strain caused by surface stress on a 10 nm spherical gold particle.
2. What stress would this strain cause in the substrate? What value of the “lock down” radius would lead to the observed compressive stress in the pre-coalescence stage?
3. Explain in simple terms why for most materials the lattice parameter decreases with decreasing system size; i.e. why is the surface stress typically positive?

Question 5

Whether a film delaminates from its substrate or not depends on the "strength of the interface", the residual stress state of the film, the film thickness, and the elastic moduli of the film. What is the (qualitative) nature of each of these dependencies? i.e., if the thickness of the film is increased and everything else remains the same, is the film more or less likely to delaminate?

Time permitting:

How would you apply a simple Griffith/Orowan-type brittle fracture analysis to the case of a thin film? (i.e., pre-existing flaw, no plastic deformation, etc.). Can you derive an expression for the critical residual stress necessary for delamination? What assumptions are you making? How does this situation differ from the bulk fracture case?

THE COHERENCY STRAIN THEORY AS THE DRIVING FORCE FOR DIFFUSION INDUCED GRAIN BOUNDARY MIGRATION

Question 1

Consider the motion of an interphase boundary between two disks of alloys α (fcc) and β (bcc) bonded together and isothermally annealed at temperature T for time t .

1. Draw a schematic concentration, C_i , of component i versus distance x diagram for the annealed diffusion couple. Indicate all the assumptions made.
2. How is the velocity of motion of the interphase boundary related to the interdiffusion fluxes, \tilde{J}_i^α and \tilde{J}_i^β , of a component i on either side of the boundary?
3. Can you apply the concepts developed in question (2) to the motion of the grain boundary in DIGM?

Question 2

1. What is η in Eq. (6 [in your document])? Please conduct a units analysis on this equation. Why does the use of this equation require the assumption of ideal solution behavior?
2. On page 14. “(i) a grain boundary is a thermodynamic phase with its own Gibbs energy.” What is a phase? What is Gibbs energy?” “....(this assumption) allows the grain boundary to be treated as if it were a very thin film of liquid....” What is the principal difference between a solid and a liquid? What is hot shortness? What causes hot shortness?
3. What is “the diffusion distance”?

Question 3

- 1) Define the terms C_{11} , C_{12} , and C_{44} used in the expression for the orientation dependent elastic modulus for cubic symmetry given on page 12 (of your document). What is the meaning of the subscripts?
- 2) Given values for C_{11} , C_{12} , and C_{44} , describe (for cubic symmetry) how you would find the shear modulus in the (111) plane in the $[\bar{1}10]$ direction. Please set up the problem.

Question 4

1. What do the two major terms in Equation (7 [of your document]) describe? What makes this equation and these terms different for a liquid film and for a grain boundary?
2. If you were to examine data from diffusion experiments, for example, in the Cu-Ni-Zn system, how could you tell whether DIGM had occurred? What about diffusion induced recrystallization (DIR)?
3. You mentioned that symmetric copper grain boundaries showed DIGM when exposed to Zn vapor. What other factors might be present that could be responsible for breaking the boundary symmetry?

Question 5

Consider a one dimensional, single phase, binary alloy with an initial composition distribution, $C_o(x)$ and impermeable boundaries at $x = 0$ and $x = L$. We want to calculate the diffusion of solute through the domain using numerical methods. The governing equation for the diffusion is

$$\frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) = \frac{\partial C}{\partial t}.$$

- (1) Explain how a finite difference discretization of this equation would be done.
- (2) Explain how a finite volume discretization of this equation would be done.
- (3) In parts (1) and (2), did you assume an explicit or an implicit numerical scheme? What are the advantages and disadvantages of each?
- (4) How would you solve the set of discretized equations?
- (5) Consider the diffusion that can occur near a phase boundary and how that is related to the movement of the phase boundary. Discuss what you would change from the single phase formulation above to calculate diffusion in a one dimensional, *two* phase system with a sharp interface between the two phases.

TIN WHISKERS: AN ANALYSIS OF THE PROBABLE GROWTH MECHANISMS

Question 1

Consider whisker growth by the vapor-liquid-solid (VLS) mechanism. It has been observed experimentally that, for a given set of growth conditions (substrate temperature, precursor partial pressure, initial catalyst size distribution, etc.), the whisker growth rate depends on whisker diameter. Specifically, there is a minimum whisker diameter, below which whiskers are not observed. For diameters larger than the minimum, the growth rate increases and then saturates with increasing whisker diameter.

- 1) Explain these observations qualitatively
- 2) Derive an expression for the minimum whisker diameter

Question 2

- 1a). Why would an edge dislocation in a dielectric have an associated charge?
- 1b). Would this still be true in an intermetallic?
- 1c). Would this still be true for a screw dislocation?

Question 3

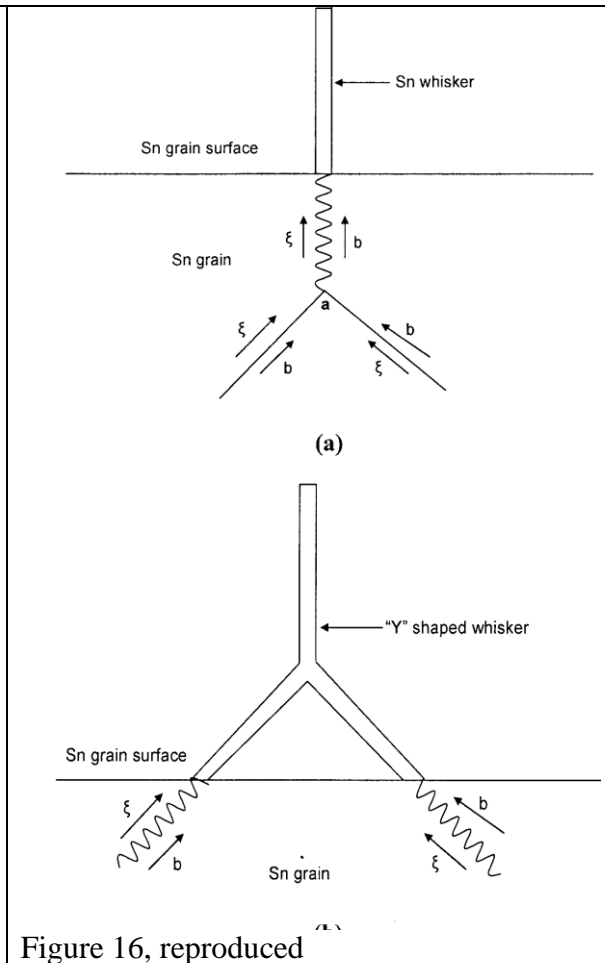
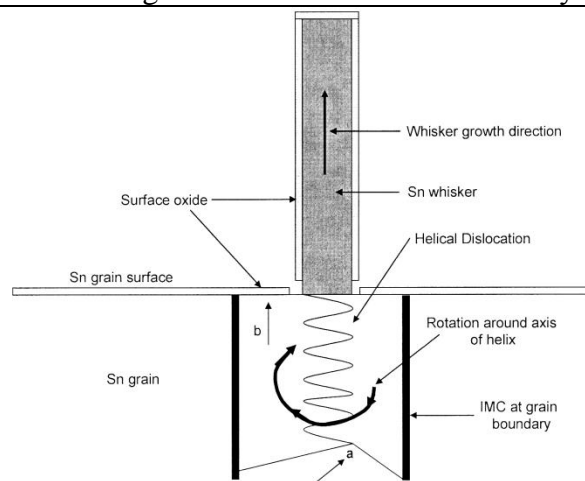
1. Does the diameter of a whisker correlate with the crack diameter of a disruption in the Sn oxide? Comment on the characteristics of an oxide that would be more protective of Sn (e.g. thickness, density, chemistry). If an oxide were deposited onto Sn and patterned, would whiskers grow and, if so, would all openings in the oxide yield whiskers?
2. Do the whiskers have a preferred texture or orientation? Please provide some insight into why or why not.

Question 4

In a recent graduate seminar, the observed strain aging behavior of cold worked austenitic stainless steel in which a large increase in strength was found after long-time aging at room temperature was argued to result from the formation of tetragonal-defects consisting of carbon-vacancy pairs. During the question and answer period, a question was raised as to why tetragonal defects are needed for strengthening. Answer this question by discussing why tetragonal defects produce more hardening in solid solutions than do symmetrical ones.

Question 5

In Figures 12 and 16 of your report (reproduced below), you have proposed two dislocation mechanisms that could give rise to the whisker features you've reviewed.



What techniques would you propose to use to validate this mechanism? (no bounds on available time, equipment or support)

Please consider aspects of sample preparation as well as characterization.

Question 6

1. Sketch a polycrystalline microstructure in a typical metal or ceramic material. Assume the material is isotropic.
2. Write an expression for the chemical potential of an atom adjacent to the grain boundary.
3. Consider a pore trapped within a grain and a pore sitting on a grain boundary. What factors determine the shape of the pore?
4. When the grain boundary moves during grain growth, what happens to the pore?

THE GROWTH OF MINERAL CRYSTALS IN AQUEOUS SOLUTIONS CONTROLLED BY SOLUBLE ORGANIC SPECIES

Question 1

A capillary is partially filled with a perfectly wetting liquid having a surface tension value of 1 N/m. The capillary is open at both ends to vapor at 0.1 MPa (~1 atm).

- At what capillary radius will the pressure in the liquid be zero?
- How and why will the melting/freezing temperature of the liquid be different from that when the liquid is in bulk form.

Question 2

- Page 15 of your document contains the statement – “Then the osmotic pressure due to the polymer solution becomes unbalanced, resulting in an attraction of the two crystals.”

What is an osmotic pressure? What causes it to develop? Explain why it becomes unbalanced in the polymer solution and why does it cause an attraction between the two crystals?

- What is a zeta potential, and how is it measured?

Question 3

- How would adsorption kinetics differ between an inorganic complex (e.g., NH_3) and an organic molecule of greater size (e.g., $\text{C}_{10}\text{F}_{18}$)?
- How would adsorption kinetics be affected by surface size between a 50 nm particle and a 5 μm particle?

Question 4

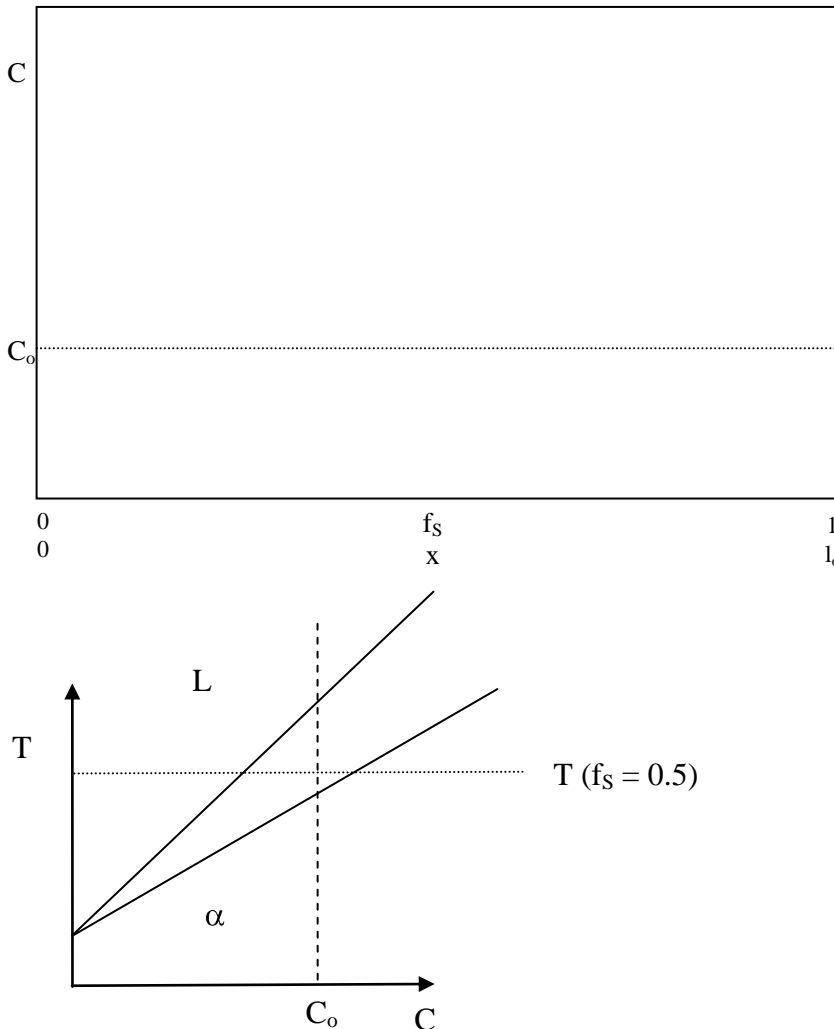
- One possible mechanism for additive effect on growth is by preferential adsorption to a crystal facet slowing the growth of that plane. Draw a diagram showing the $(1\bar{1}0)$ plane in a cubic structure. Sketch the expected two dimensional $(1\bar{1}0)$ section of a three dimensional single crystal particle (Wulff Construction) considering the following solid-vapor interfacial energies: $\sigma_{111} = \sigma_{110} \ll \sigma_{001}$. If polymer is added it selectively adsorbs to the σ_{001} face slowing it down resulting in interfacial energies of $\sigma_{001} \ll \sigma_{111} = \sigma_{110}$, what would the crystal look like?
- In the growth by aggregation mechanism, it seems that additives act as heterogeneous nuclei in the supersaturated solution. Draw a graph of the free energy of nucleation versus nuclei size and explain the factors influencing the shape. How might the degree of supersaturation affect the shape?

Question 5

Referring to Fig. 16 of the Prelim document, assume that the copper TEM grid is in intimate contact with the hammer, which is also made of copper and has dimensions of 1cm x 1cm x 1cm. The hammer and grid move through the liquid nitrogen ($T = 77\text{K}$) at a velocity of 2 cm/sec. We wish to determine how quickly this system quenches. Based on the information above, *explain how you would determine whether or not a lumped thermal analysis would be appropriate for solving the transient temperature profile of the grid. You do not need to solve for the actual temperature profile.*

Question 6

- Using the phase diagram, *sketch* the composition profiles in the solid and liquid at time (t) when $f_s = 0.5$. Assume limited diffusion in the solid, infinite diffusion in the liquid.
- Sketch the profiles that occur at a slightly later time ($t + dt$) and at the same temperature as in part (a).
- Sketch the profiles that occur at a slightly later time than part (a) ($t + dt$) and at a slightly lower temperature than part (a).
- Using the sketch in part (c), derive an equation governing the relationship between the change in fraction solid.



A ROLE OF SHEAR IN AGGLOMERATION

Question 1

- The interaction free energy associated with van der Waals forces between molecules has the functional form $w = -\frac{C}{r^6}$ where C is a constant and r is the separation distance between molecules. The interaction free energy associated with van der Waals forces between a sphere of radius R and a surface has the functional form $W = -\frac{AR}{6D}$ where A is the Hamaker constant, R is the sphere radius, and D is the separation distance between the sphere and the surface. Please explain why the functional forms have different separation distance dependencies.
- Sketch a plot of shear stress vs. shear rate for a particulate suspension in which van der Waals attractions dominate the interparticle forces. Explain the behavior represented by your plot.

- Describe at least two ways in which a suspension may be modified such that repulsive interparticle forces dominate rather than attractive interparticle forces.

Question 2

- On pages 13 and 14 of your document it is written that hydration forces can adjust DLVO theory and cause more repulsion than is predicted. Explain in physical terms this effect with attention paid to the boundaries of hydrophilic particles and hydrophobic particles.

Question 3

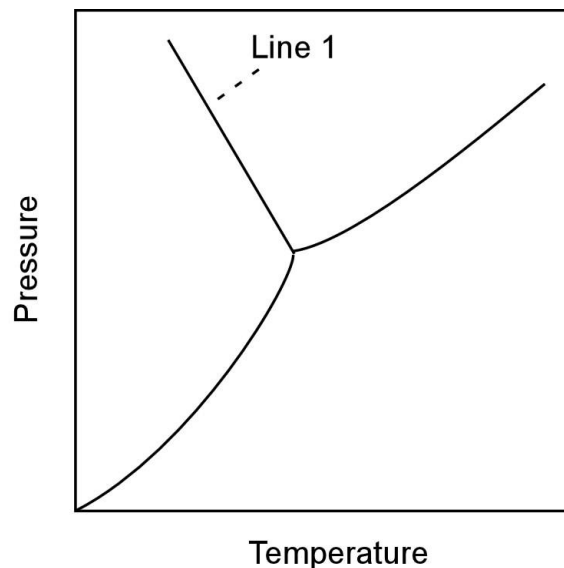
- Sketch a deformation mechanism map for a fcc metal and identify the different fields. For a similar grain size, when maps of bcc metals are compared to those of fcc metals the Nabarro-Herring and dislocation creep fields in the bcc maps are enlarged at the expense of the Coble creep field. Please explain.

Question 4

- Make a list of as many different techniques for measuring powder particle size distributions as you can. Describe the principle of each technique and discuss their relative advantages and disadvantages.

Question 5

- Answer the following questions pertaining to the P vs. T diagram below for water.



- What is true about ice (s) and water (liquid) phases all along line 1?
- What can be said about the relative densities of ice and water? It might be helpful to remember the Clapeyron equation stating:

$$\left. \frac{dP}{dT} \right|_{\text{equilibrium}} = \frac{\Delta H}{T\Delta V}$$

- How many invariant reactions are indicated on the plot? Show using Gibb's phase rule that the degree of freedom is zero.

Question 6

- What are major differences in agglomeration by shear for micron compared to nanometer particles?
- What are the mathematical expressions for relating shear rate to viscosity for curves a - c in Figure 2 of your document?
- How would equation 2 of your document change for particles of unequal sizes?
- Explain the initial part of Figure 6 of your document when repulsion forces drastically change to attractive forces which then drastically change to repulsive forces.

5. What types of crystallization and chemistries can be created in cementation regions? How can this be used to improve a desired application? What unique structures can be created?
6. How can shear mediated agglomeration be used to improve biomedical applications?

GRAIN GROWTH IN LIQUID PHASE SINTERED SILICON NITRIDE

Question 1

β -Silicon nitride demonstrates some obvious faceting which is attributed by you to different growth rates of planes. You also state that minimization of the surface energy could be used to predict crystal shapes. The following questions deal with this in more detail.

1. Why do materials have a γ_{sv} - a solid-vapor surface energy?
2. If the bond energy, ϵ , is equal to $\Delta H_{\text{sublimation}}/6N_a$, estimate the γ_{111} for an FCC metal. Start by drawing a 111 plane.
3. How would the γ_{100} compare to γ_{111} ? What are the implications on the shape of the crystal – which plane would you form more of?

Question 2

- 1) Sketch and label a possible deformation mechanism map for a fine grained FCC metal.
- 2) Discuss how the boundaries between the different regions are determined.
- 3) How would the boundaries shift if the map was redrawn for a metal with a much larger grain size?

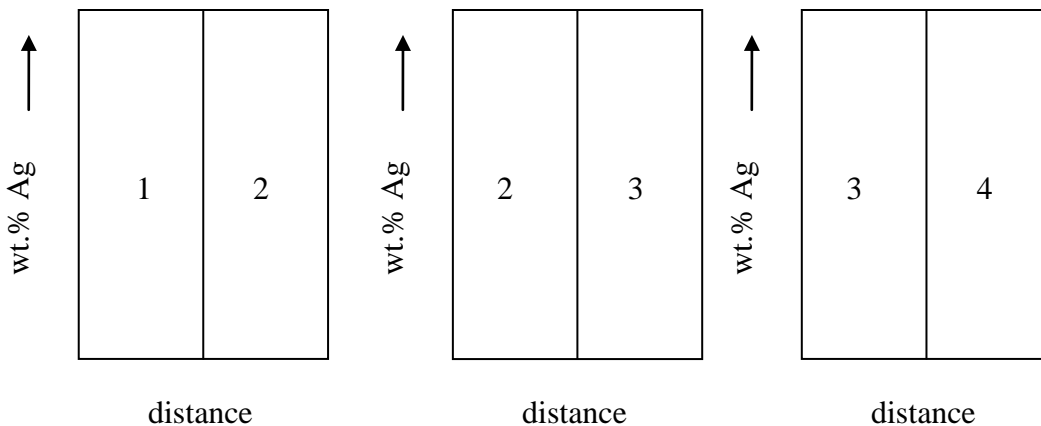
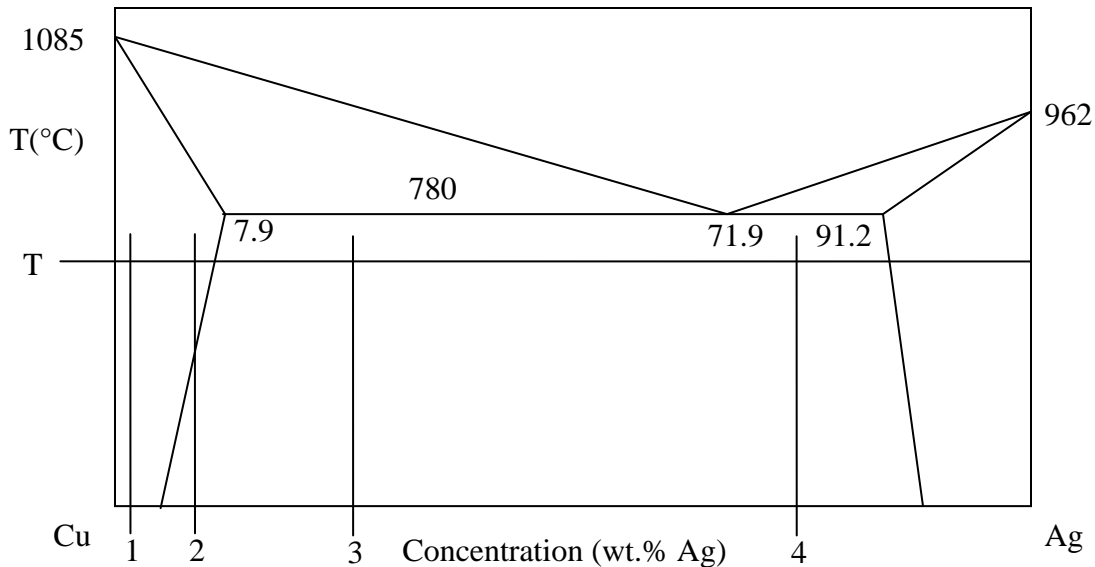
Question 3

Consider a polycrystalline material that is dense aside from a few per cent of isolated porosity. Some of the pores are found within grains while others reside along the grain boundaries.

- a) Sketch what this microstructure might look like paying attention to the shape of the pores.
- b) If you heat the material to a temperature where grain growth occurs, what happens to the pores that reside along the grain boundaries?

Question 4

Using the copper-silver phase diagram below, sketch the concentration profiles across the diffusion couples between the indicated alloys (1-4) after annealing at temperature, T , for three different times: $t = 0$, $t = \text{an intermediate time}$, and $t = \text{equilibrium}$.



Question 5

Starting with an initial state of randomly packed, mixed powders (one powder has a much lower melting temperature than the other), describe the stages of liquid phase sintering. Sketch the microstructural changes in each stage and describe the physical mechanisms that cause those changes. Sketch a curve of densification vs. time and identify the location of each stage on that curve.

FORMATION MECHANISMS AND ELIMINATION OF MICROPIPE DEFECTS IN SINGLE CRYSTALS OF SILICON CARBIDE

Question 1

Let's consider a WEDGE DISCLINATION:

Use a simple Volterra model to deduce the strain as a function of the wedge angle, and the distance from the core of the defect.

Wedge disclinations have been observed in crystals in a few special cases. Is it likely that these defects would have hollow cores? Can you demonstrate how you would deduce the core radius?

Question 2

A solid-solid diffusion couple is assembled with disks of 75Cu-25Zn brass and pure Cu with inert markers placed at the initial contact or weld plane. The couple is annealed in vacuum at 800°C for 5 days.

1. Draw a schematic diagram of the Zn concentration profile (C_{Zn} vs. x) after diffusion and identify the locations of the Matano plane and the marker plane.
2. Indicate a method to evaluate the interdiffusion flux \tilde{J}_{Zn} of Zn at any section x from the concentration profile without using Fick's law. Draw a schematic profile of the interdiffusion flux \tilde{J}_{Zn} of Zn as a function of x .
3. How would you determine the intrinsic flux J_{Zn} of Zn at the marker plane at $t = 5$ days from your (C_{Zn} vs. x) diagram?
4. What is the relation between the intrinsic and interdiffusion fluxes, J_{Zn} and \tilde{J}_{Zn} ?

Question 3

For an ordering transition, how could you tell experimentally whether the transition is 1st order or higher order? What are the strengths and drawbacks of the technique(s)?

Question 4

In the derivation of the energy per unit length of a screw dislocation, one must integrate dr/r from r_{min} to r_{max} . r_{max} is determined by the extent of the strain field. r_{min} is generally chosen to be a fraction of the burgers vector (a smaller fraction for a covalent crystal than for a metal). The assumptions of linear elasticity fail at a greater distance from the core than r_{min} . How is r_{min} chosen and what is its physical significance (if any).

Question 5

Describe the difference between Physical Vapor Transport growth for bulk SiC, and Chemical Vapor Deposition for SiC epitaxy.

POLYMER-CLAY NANOCOMPOSITES "THE PROCESSING CHALLENGES OF A NATURALLY OCCURRING REINFORCEMENT"

Question 1

Consider your Au nanowire arrays in porous anodic alumina. If you were to perform a coupled theta-2*theta XRD scan and found only 111 and higher order reflections (e.g., 222, 333 etc.) from fcc Au, what could you conclude about the microstructure of the sample? What conclusions could you draw only with more information? What additional XRD experiments would you perform?

If instead, you found that the original theta-2*theta scan revealed that the 111 and 200 reflections (and their higher order reflections) were conspicuously absent, but the 220 reflection and 422 reflections were present, what could you conclude?

Question 2

1. Derive Bragg's Law.
2. What variables can influence the intensity of a diffraction pattern?

Question 3

- A) In adding these micron-sized clay particles to polymers, this process seems similar to heterogeneous nucleation in polymer melts. Explain heterogeneous nucleation. Draw a graph of the free energy of nucleation versus nuclei size and explain the factors influencing the shape.
- B) In many of these systems, crystallization rate and degree are actually suppressed. Propose a mechanism for why such behavior occurs. What role does the surface interaction of the clay with the polymer play? How would a strong interaction differ from a weak interaction?

Question 4

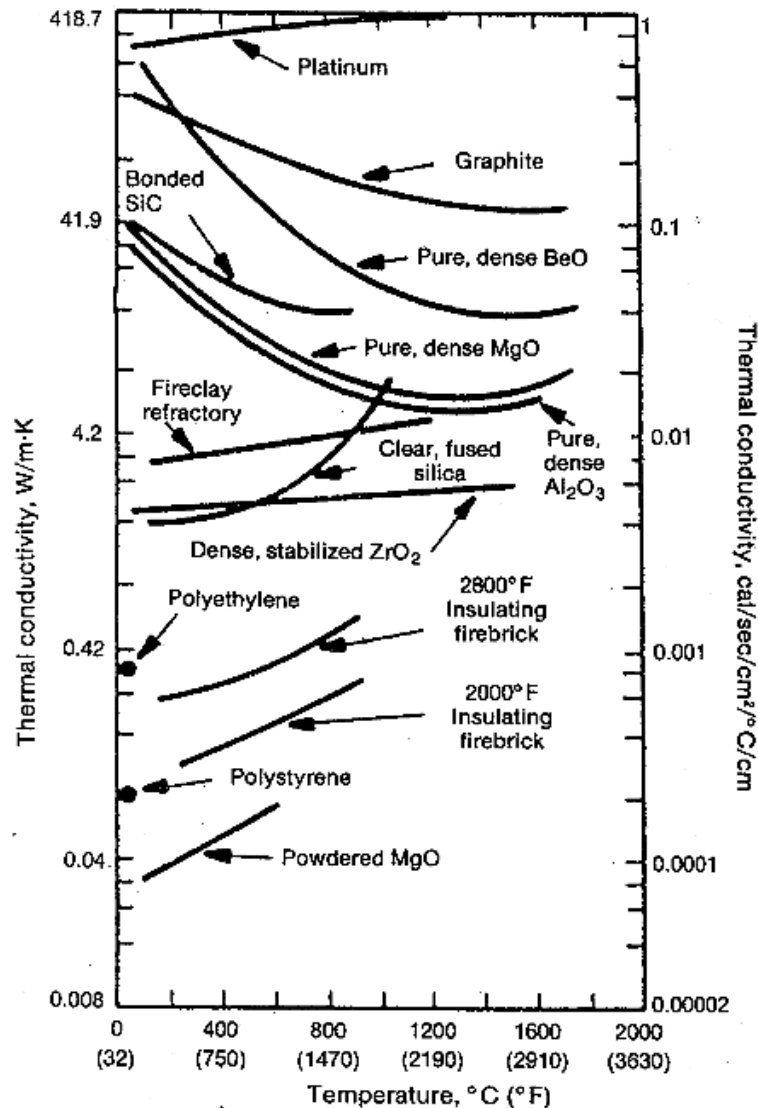
Consider a composite material consisting of a nanoscale conductor dispersed in a non-conducting (electrically) polymer. Suppose that a closely interconnected network of the conductor (without polymer) has a conductance of G_1 , and that the polymer has a low conductance of G_2 . How would you expect the conductance of the composite to vary with percentage of the nanoscale conductor (consider the various regimes, as appropriate).

Question 5

- 1) Explain the major differences between x-ray and electron diffraction.
- 2) Discuss the similarities and differences in applying these techniques to the analysis of nanometer scale polycrystalline materials.

MATERIALS FOR UNCOOLED MICROLOMETER INFRARED DETECTORS

Question 1



1. The plot above contains thermal conductivity data as a function of temperature for several materials.
 - a. Please explain the relative magnitudes of thermal conductivity values at a given temperature (e.g., 400°C). For example, powdered MgO and dense MgO.
 - b. Please explain the temperature dependence of the thermal conductivity data. Just to start consider the behavior of firebrick; pure, dense BeO; and dense, stabilized zirconia.

Question 2

- 1) In the document, you mentioned that aerogels could be used to reduce thermal conduction. How would you construct a device such as Figure 5 with an aerogel film? In other words, how would you synthesize a silica aerogel film on top of silica?
- 2) Commonly silica aerogels have reported stability up to 500 °C. a) Why does the aerogel have this low stability temperature when compared to xerogel silica? b) Describe the densification process and what factors are important.
- 3) While reported stability is 500 °C, it is possible to embed silica aerogel in aluminum by pouring molten Al into a form of silica aerogel with minimal collapse of the aerogel. How is this possible?

Question 3

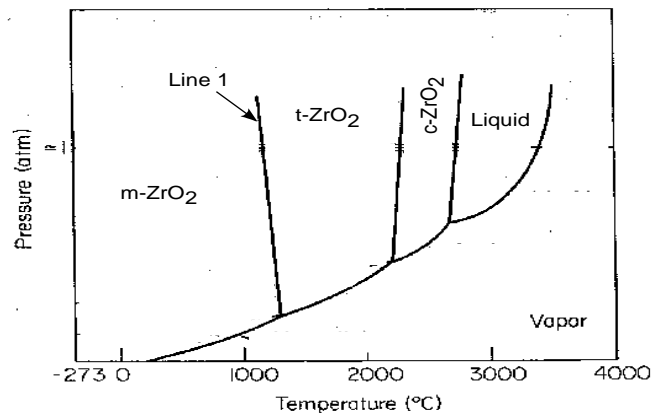
Semiconducting oxides are often selected as the materials for sensing elements in bolometers and microbolometers.

- Explain what characteristics make these materials attractive for this application.
- Is the TCR positive or negative for these materials?
- How is the resistivity of an oxide affected by its stoichiometry?
- How is the TCR affected by the stoichiometry?
- If the material is a polycrystalline thin film, what effects may be imposed by its structural features?

Question 4

Answer the following questions using the P vs. T diagram below for zirconia, ZrO_2 .

- What can be said about the relative densities of m- ZrO_2 and the t- ZrO_2 ? Why?
- Explain Gibb's phase rule. Use Gibb's phase rule to show the number of invariant reactions on the plot.



Question 5

Using the Au-Nb phase diagram, sketch concentration profiles across diffusion couples after annealing at 900°C . Neglect any density differences and molar volume changes. Show the initial concentration profile (t_0), the concentration profile at a representative intermediate time (t_{int}) and at compositional equilibrium (t_{eq}) for the following three couples (wt.%):

- 100% Nb | 100% Au
- 100% Nb | 80% Nb
- 40% Nb | 20% Nb

NATIVE POINT DEFECTS AND REASONS FOR n-TYPE CONDUCTIVITY IN ZnO

QUESTION 1

In your presentation you mentioned alumina as a "natural substrate" for ZnO. Provide a crystallographic and strain basis for your statement.

Describe how diffusion of Zn and O in pure ZnO varies as a function of oxygen partial pressure for a given temperature.

What are typical levels of impurities in the ZnO crystals and films that you described in your presentation? At what concentrations should they be noticeable/important in terms of affecting the concentrations of point defects in ZnO?

QUESTION 2

- Based on Eq. (1) of your write-up, the equilibrium concentration n of vacancies in a crystal of N lattice sites at temperature T is given by

$$n = N \exp(-E^f/kT) \quad \text{Eq. (1)}$$

where E^f is energy of formation of a vacancy.

(a) Indicate the basic steps and assumptions employed in the derivation of this equation.

(b) Can this equation be improved and if so, how?

2. For equilibrium concentration of divacancies, how would you modify Eq. (1)?

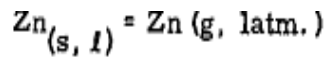
QUESTION 3

4. You are given an oxide ceramic material and asked to perform experiments to determine if the oxide is an ionic or electronic conductor. Unfortunately, your equipment to measure the Hall effect is broken. What experiment(s) would you perform and what results would allow you to reach a conclusion about the mechanism of electrical conduction?

5. The conductivity of metals decreases with increasing temperature while the conductivity of semiconductors and insulators increases with increasing temperature. Please explain.

QUESTION 4

Using the standard vapor pressure data below, plot the log P vs. T equilibrium phase diagram for zinc and label the phase fields, triple point, and normal boiling point.



T, °K	P	ΔG_T	ΔH_T	P	T, °K
298.15	2.40×10^{-17}	22673	31170	10^{-10}	420
400	1.54×10^{-11}	19789	31047	10^{-9}	448
500	3.75×10^{-8}	16990	30904	10^{-8}	480
600	6.60×10^{-6}	14223	30735	10^{-7}	516
692.655(s)	2.06×10^{-4}	11684	30550	10^{-6}	559
692.655(l)	2.06×10^{-4}	11684	28800	10^{-5}	610
700	2.56×10^{-4}	11503	28781	10^{-4}	670
800	3.37×10^{-3}	9052	28528	10^{-3}	749
900	2.45×10^{-2}	6632	28275	10^{-2}	852
1000	1.18×10^{-1}	4241	28022	10^{-1}	988
1100	4.24×10^{-1}	1875	27768	1	1180
1180	1.00	0	27565	$\Delta S_{v, 1180} = 23.360$ $(\pm .08)$ $\Delta H_{v, 0} = 31039$ (± 100)	
1200	1.22	- 467	27515		
1300	2.95	- 2790	27262		
1400	6.23	- 5090	27009		
1500	11.87	- 7375	26756		
1600	20.75	- 9641	26503		
1700	33.80	-11893	26250		

QUESTION 5

- a) Is epitaxial ZnO on Al₂O₃ a single crystal or polycrystalline?
- b) How would you show this?
- c) Since Si can be grown in similar ways with only part-per-billion impurities: why, how, and from where would ZnO acquire significant impurities, especially metallic (not H or N) impurities?

Radiation Damage in Electron Microscopy

QUESTION 1

- a) Provide an equation that describes the behavior of an electron.
- b) Describe how this equation leads to the origin of band gaps in semiconducting and insulating materials.
- c) Describe how this equation leads to the diffraction of electrons from a crystalline solid.

QUESTION 2

- a) In what ways can the presence of defects, such as vacancies, interstitials, dislocations, stacking faults and grain boundaries affect the rate at which electron beam damage occurs in a crystalline specimen? Would you expect any particular defect or defects to be more effective at changing the rate than others?
- b) In your document you have addressed issues that result from the charge and the momentum of the electrons used in electron microscopes. Does the wave nature of the electron have any effect on radiation damage processes in perfect crystalline specimens?

QUESTION 3

- a) What is contrast in TEM and how can we define it quantitatively? What specimen parameters influence the mass-thickness contrasts?
- b) Define the electron dose in TEM. How is electron dose influenced by the brightness?

QUESTION 4

The drawing below shows a spherical pore sitting on a flat grain boundary. What is wrong with this drawing?



QUESTION 5

- a) Optical microscopists can recreate a three-dimensional image of transparent specimen by using a series of images, each focused only at a narrow depth slice. Explain how/ whether this is how 3-D stereology is performed in the TEM.
- b) Explain whether this effect would be enhanced or not by use of an immersion objective lens (i.e., with higher numerical aperture).

Conductance Switching Mechanism of High-Density Non-Volatile Bi-Stable Memory Based on (2) Rotaxane Molecule

QUESTION 1

Let's consider the electric force exerted on the metallic plates of a simplified design where two parallel plates are separated by a 2 nm-thick BL film and with 2 Volts applied across them.

Remember that the electric field generated by an infinite plate is: ———

Where ϵ_0 is the permittivity of vacuum (8.85×10^{-12} C/N/m), ϵ is the relative permittivity of the film and Q/A is the charge per unit area.

- Calculate an expression for the force exerted on the plates in terms of geometrical parameters and the applied voltage. Give a numerical estimate of this force per unit area. Is the force attractive or repulsive?
- Describe how you expect the film to deform under the applied force.
- Can mechanical forces explain some of the observed behavior in the switches?

QUESTION 2

- A ferroelectric material is undergoing 180° switching. The applied field is aligned perfectly along the polarization direction. Describe what happens to the physical arrangement of atoms or ions within the material to change the polarization.
- How might the magnitude of the polarization (for the example above) be affected by application of a tensile load along the polarization direction? A compressive load? (As you begin your answer, consider first how an elastic tensile load affects a material and what changes it produces. First describe these changes.)
- Imagine the ferroelectric material is a thin film that possesses a tensile stress within the surface of the film from processing – how would this affect the polarization?
- How would stresses affect the conductance switching mechanism?

QUESTION 3

- In your presentation, you describe that the Rotaxane molecule uses the electric-field induced switching between a stable and a metastable state as a means to set the memory unit. During your review, did you find any work that attempts to explore the possibility of modifying the molecule to stabilize both states? If you did, please discuss it. If not, what would you do to functionalize the molecule to make it bistable? What would you do to the molecule to make it switch faster?
- Propose other feasible molecular configurations inspired on the Rotaxane molecule to build a stable memory switch.
- For the proposed deposited Rotaxane film experiment that you proposed, what would be the crystal structure of the layer? To what degree will the crystallinity affect the response? If crystalline, would you expect this monolayer crystal to have a center of symmetry? What would

be the properties in the crystal? If the monolayer is polycrystalline, would you expect the switching to be the same at both grain boundaries and bulk?

QUESTION 4

A) Give the iron carbon phase diagram below, please perform the following steps:

- 1) If you form a semi-infinite diffusion couple between carbon and an initial Fe-C alloy with a carbon concentration of 0.01 wt%C at 1000°C, what is the surface concentration of the carbon at 1000°?
- 2) After diffusion for some amount of time slowly cool the alloy at 600°C. Sketch the expected microstructural regions from the surface to the interior where the carbon concentration has not changed.
- 3) If you had quenched the diffusion couple to room temperature instead of slowly cooling it from 1000°C, what changes would you expect to see in the microstructure?

QUESTION 5

Consider the following materials

1. Dielectric (example MgO)
2. Piezoelectric (example Quartz)
3. Ferroelectric (example PZT)
4. Rotaxane molecule
5. Metal (example Si)
 - A. Sketch and describe the polarization as a function of applied electric field. Consider both single crystals and polycrystalline materials.
 - B. How does the initial polarization cycle differ from the following cycles? Describe the physical processes that can occur during the cycles.
 - C. Sketch and describe the strain as a function of applied field. What processes contribute to the strain observed? How would the strain change if the field is applied in different directions?

BONE INGROWTH INTO POROUS IMPLANTABLE DEVICES, A CRITICAL REVIEW OF SCAFFOLD STRUCTURE AFFECTING OSSEOINTEGRATION AND CURRENT IMAGING LIMITATIONS

QUESTION 1

1. What is the resolution limit to conventional tomography, and which parameters cause the limit?
2. (a) How are the slices in computed tomography differentiated, and
(b) what factors limit how narrow the slices can be?

QUESTION 2

For the sake of argument, let's assume we are designing a screw for use in the vertebrae.

- A. Describe how you would characterize the mechanical strength of the bone-screw interface. Could it change over time?
- B. Would it be possible to relate the interfacial strength to certain parameters of the bone ingrowth that could be measured histologically or radiographically?

- C. How do implant integration studies in rats, rabbits, and dogs relate to implant integration studies in humans? What additional factors need to be considered in humans?

QUESTION 3

1. Explain how are the main signals that are used in the SEM generated and what information about the specimen does each of the signals provide?
2. Describe the organization of a typical bone.

THE QUALITATIVE NATURE OF HOT TEARING CRITERIA

QUESTION 1

We will be discussing the transient fluid flow and heat transfer near an infinite vertical flat plate in the short time after a heat flux is suddenly generated by the surface. The fluid is initially quiescent and it and the wall are at the temperature T_o . At $t = 0$, a constant and uniform heat flux, q_o'' , is turned on at the wall ($y = 0$) and the fluid is heated.

- (a) Write the equations for conservation of energy, momentum in the x direction (along the wall), and mass. Assume that gravity acts in the negative x direction, the pressure gradient term is negligible, and the thermophysical properties are constant and uniform.
- (b) Write the boundary conditions for u , v , and T at $y = 0$ and $y = \infty$. Neglect any terms you can using the fact that the plate can be treated as infinitely long.
- (c) Assuming $Pr = 1$, sketch the temperature and vertical velocity profiles, $T(y)$ and $u(y)$, at two successive times.
- (d) Find the exact solution to the continuity equation for the velocity normal to the surface, $v(y)$.
- (e) Using a scaling analysis of the governing equations and boundary conditions, find estimates as a function of time for
 - (i) the thermal penetration depth, δ ,
 - (ii) the temperature difference, $T_{wall} - T_o$, and
 - (iii) the vertical velocity, u_o .

QUESTION 2

- 1) Which crystal structure is more susceptible to strain-rate deformation effects – a FCC or a BCC metal? What is the mechanism behind this strain-rate deformation sensitivity?
- 2) Would you expect crystal structure to play a part in the Rappaz et al. model for strain-rate based hot tearing? Why or why not?

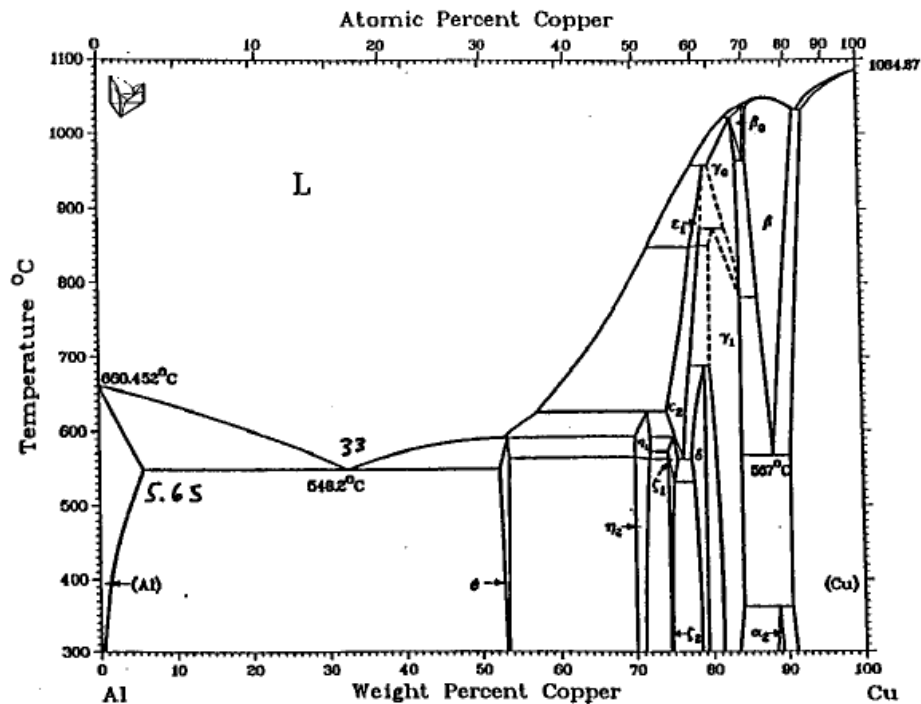
QUESTION 3

In your document you proposed to use an organic crystal as a surrogate material to learn more about the mechanisms that govern hot tearing in metallic alloys. Assuming that the conditions present during casting of a metal can be reproduced in the surrogate system, the lessons learned could only be applied if the mechanisms of crack nucleation and propagation in the two materials are similar. So let's talk about crack propagation.

- 1) Please describe Griffith's approach to crack propagation in brittle materials. The model compares two energy contributions and establishes a criterion for crack propagation. What are the two energy terms? Under what conditions will a crack with a simple geometry propagate?
- 2) What need to change in the model to describe a ductile material? Do you need to spend more or less energy to propagate a crack? What additional energy term comes to play? What happens ahead of the crack?

QUESTION 4

- 1) Consider the Al-Cu system and briefly describe the application of the constitutional supercooling criterion to predict the morphological instability of a planar solid-liquid interface as a function of alloy composition for a given thermal gradient and interface velocity. If solute transport in the liquid is by diffusion only, what is the interface temperature for planar growth of a specific alloy (e.g., 2 wt% Cu)?
- 2) Discuss why the various hot-tearing models predict similar compositions for the peak in the lambda curve for hot tearing susceptibility. Sketch the microstructure for this case and indicate the temperature with respect to the Al-Cu phase diagram.
- 3) Estimate the pressure difference to homogeneously nucleate a pore in the melt. Note the energy of the liquid/gas interface is on the order of 1 J/m^2 . Is this likely to occur? If not, discuss how and where the pore would nucleate.



QUESTION 5

Two perfectly parallel solid plates 2 cm in diameter are held at a separation of 10 μm . Between them is a film of a perfectly wetting liquid 1 cm in diameter. The surface tension of the liquid is 1 N/m and the system is in an inert gas at 0.1 MPa (~ 1 atm).

- (a) Are the plates held together or repelled by the presence of the liquid between them?
- (b) Describe the origin of this force.
- (c) Using the Laplace equation, calculate the capillary pressure ($\Delta P = P_L - P_V$).
- (d) Estimate the magnitude of the force holding the plates at this separation.
- (e) Apply these results to the concepts of hot tearing.

DENDRITE FORMATION IN RECHARGEABLE LITHIUM BATTERIES

QUESTION 1

During your presentation you described differences in the Li ordering of the LiCoO_2 structure the charging and discharging cycles of Li-ion batteries. The loss of Li ions (deintercalation) has been suggested to lead to a first order change in the crystal structure from a hexagonal structure to a monoclinic structure.

1. Please describe the primary symmetry elements that would be expected in a hexagonal structure. A crystal structure model is given below:

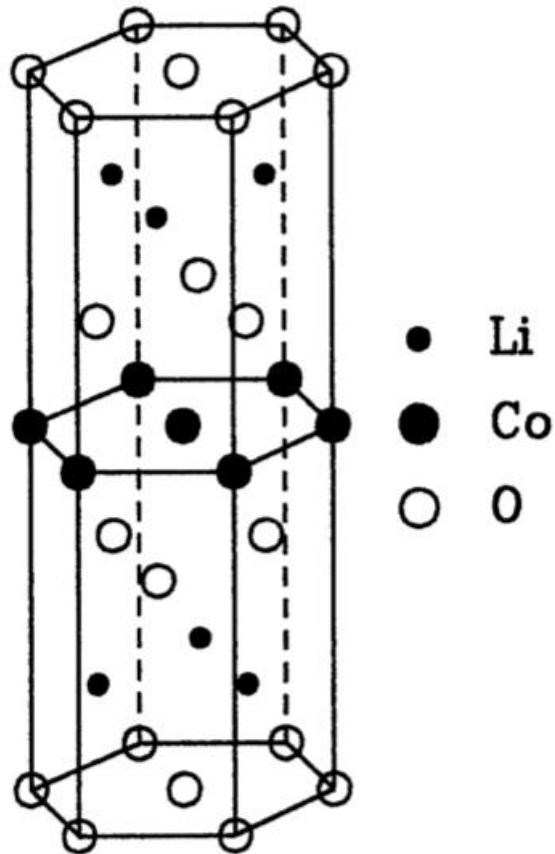


Fig. 1. Schematic diagram of the layered LiCoO_2 structure showing the . . . ABCABC . . . stacking of the O-Li-O-Co-O-Li-O layers.

2. Please describe the primary symmetry elements for a monoclinic structure.
3. Please describe some techniques that would allow one to investigate this first-order transition?

QUESTION 2

- 1) Write the energy balance for nucleation in a liquid-liquid phase transformation. What aspects might need to be added for a solid-solid transformation?
- 2) Describe three different heterogeneous nucleation sites, and describe the energy balance in nucleation at one of these.

QUESTION 3

Sketch an eutectic phase diagram, label each phase, and pick three temperatures: 1) above the highest melting point of pure A and pure B, 2) between the eutectic temperature and the lowest melting point, and another one below the eutectic temperature.

--For each temperature sketch the associated free energies and associated common tangent construction.

--If you abut a single-crystal sample of pure A against a single-crystal sample of pure B, what will the concentration fields be after a 0.1 times the characteristic diffusion time of the couple?

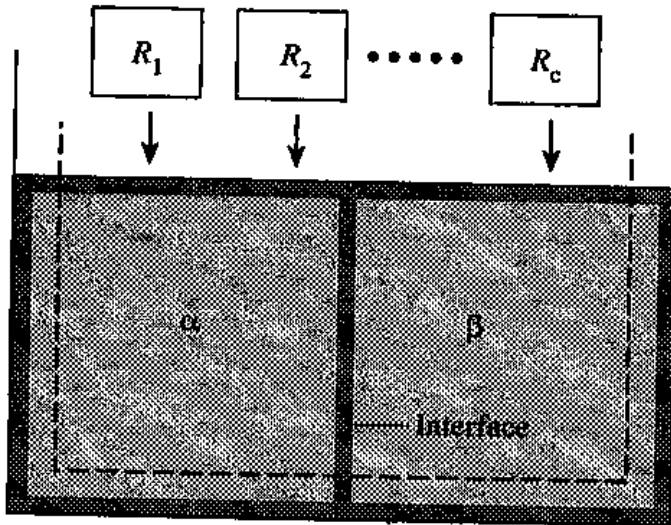
QUESTION 4

Please discuss the possible mechanisms responsible for dendritic branching in solidification and in electrodeposition. How are these two cases similar/different?

QUESTION 5

1. Thermodynamics of Interfaces

Consider a bicrystal containing two bulk phases, α and β in contact along a planar interface. For the addition of material to the system from reservoirs (R_i) at constant T, P, μ_i



a) write an expression for the increase in internal energy, due to the addition of material, of the bicrystal region, dotted region above.

b) Write an expression for the increase in the internal energy per unit interface area at constant S, V, N_i . What is this term called?

c) Write the Gibbs free energy for the bicrystal region

d) Write an equivalent expression to part b) for the increase in the internal energy per unit interface area using the Gibbs free energy. What are the variables held constant?

2. For a crystalline material, the interfacial energy depends on orientation.

a) Give the orientation variables that are necessary to describe an interface between two crystalline materials.

b) Describe the Wulff construction for an isolated particle

c) Does Neumann's principle apply to Wulff shapes?

d) For a tetragonal material, 4mm, can the Wulff shape be a cube? Can it be a sphere? What about for a hexagonal material?

THERMOELECTRICITY OF SI NANOWIRES

QUESTION 1

You presented micrographs and data on two different Si nanowire types with different surface roughnesses that were prepared by two different techniques: vapor-liquid-solid growth and an electroless etching technique starting with Si single crystals.

1. Describe vapor-liquid-solid growth process for Si. Draw the physical geometry for different steps in the growth process. Draw the Au-Si phase diagram and describe how it relates to VLS process.
2. Describe the electroless etching technique. Draw the physical geometry and the various phases and compositions involved in the etching process.

QUESTION 2

Consider a polycrystalline sample of Silver of grain size g and grain boundary thickness δ .

1. Sketch-out the chemical diffusivity of the grain boundaries phase and the chemical diffusivity of the single-crystal (grain) phase as a function of temperature. Please explain which one should be higher at what temperature and why.
2. Given your answer above, sketch out how a dopant will diffuse at low temperatures, intermediate temperatures, and high temperatures. Please justify your answer.

QUESTION 3

1. Explain the differences between diffusive, ballistic, and coherent transport of quasi-particles in a solid. Quasi-particles to consider: electrons and phonons.
2. What are the differences between these quasi-particles?
3. How do the quasi-particles interact with each other - within the same species - across the different species?

QUESTION 4

These questions deal with epitaxial films and coherency limits.

1. Sketch the diamond crystal structure. What are the Burgers vectors for bcc, fcc and diamond crystals?
2. Now consider a thin film grown epitaxially on a substrate with a lattice parameter smaller than that of the film.
Using a simple schematic diagram explain how an edge dislocation on the interfacial plane releases epitaxial strain.
3. Calculate the density of interfacial edge dislocations (number of dislocations per unit length that cut a plane formed by the interface normal and the Burgers vector of the dislocations) that leads to the most efficient strain relaxation.
4. Coherency limit: Under what conditions would it be favorable to nucleate the dislocations in 3?

QUESTION 5

1. How would measuring the size and roughness of nanowires differ from measurements of a thin 2-D layer?
2. What parameters would you want quantified for each?

EFFECT OF AGING ON THE MECHANICAL PROPERTIES AND MICROSTRUCTURES OF Sn-AG-CU (SAC) LEAD FREE SOLDER

QUESTION 1

1. You used an exponential function (Boltzmann factor) to describe atomic diffusivity in growth kinetics:

$$K_0 \exp(-Q/kT)$$

Q represents an activation energy (or energy barrier) and I would like for you to discuss the atomic processes that this energy barrier corresponds to in the case of diffusion in crystalline metals.

- i) Sketch a perfect crystal and describe the atomic processes that lead to mass diffusion
 - ii) Repeat i) for mass diffusion through a grain boundary. In which case (bulk or grain boundary) do you expect a lower activation energy?
2. (Time permitting.) You used a similar expression to describe mobility of dislocations. Could you sketch a simple dislocation in terms of atoms and describe the process associated with the energy barrier?

QUESTION 2

1. Describe the grain size dependence of yield strength for ductile materials - what is the basis and what relationship do you expect?
2. What other mechanisms are available to change the yield strength of solder materials? How would you implement them?

QUESTION 3

1. Describe the formation process of intermetallic compounds.
2. What are the key parameters that affect the formation process.
3. What do you think a possible lead-free alloy that may be thermally more stable?

QUESTION 4

1. Give a definition of coarsening using a simple model system of alpha particles in a beta matrix.
2. What is the free energy difference between two alpha particles of different sizes?

3. How does this lead to equation (3) in your paper?
4. In your paper you discussed coarsening and phase formation in Sn-Ag-Cu alloys. Using the information from your literature review, roughly sketch the Cu-Sn phase diagram from 150°C to room temperature. What are the phases that form?
5. In the microstructures that form during solidification of Sn-Ag-Cu alloys (for example SAC405), what phase forms first as the alloy is cooled?

QUESTION 5

1. What determines the melt temperature of Sn-Ag-Cu? 217°C
2. How is wetting of Sn-Ag-Cu to copper determined? How is adhesion affected by wetting?
3. What is thermal migration?
4. What is the scale of the microstructure?

IRRADIATION SWELLING OF METALS: A COMPARISON OF THEORY AND EXPERIMENTS FOR THE EFFECT OF COLD WORKING

QUESTION 1

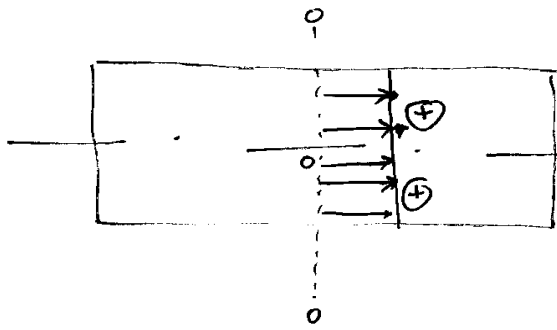
Iron is alloyed with about 10 to 20 wt% chromium to produce ferritic stainless steels. Nickel also can be added, typically at 8 to 12 wt.%, to produce austenitic stainless steel.

- A. Sketch and label ball-and-stick models of the unit cell structures for these two solid solution alloys. Label the appropriate number of atoms in each unit cell to represent compositions in the ranges given above. You may neglect atomic weight differences.
- B. Pick one of these structures and show possible positions for carbon atoms in the lattice.
- C. For a typical carbon concentration of 0.1 wt.% (~0.5 atomic %), is it possible to represent this composition in a single unit cell model?

QUESTION 2

- 1) What does it mean when we say a body has residual stresses?
- 2) The attached figure shows 3 different types of residual stress distributions (through the thickness) 'estimated' in a block of material. Which, if any, of these would you be inclined to disregard as 'an infeasible distribution(s)'?

Stress distributions

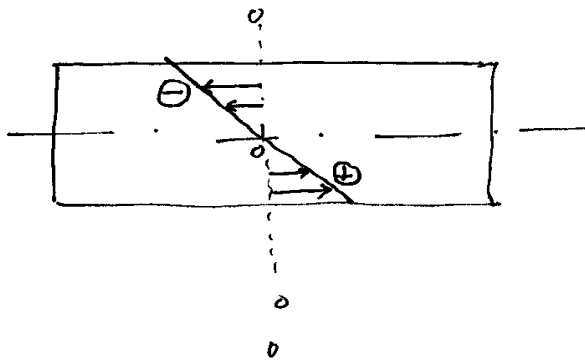


(a)

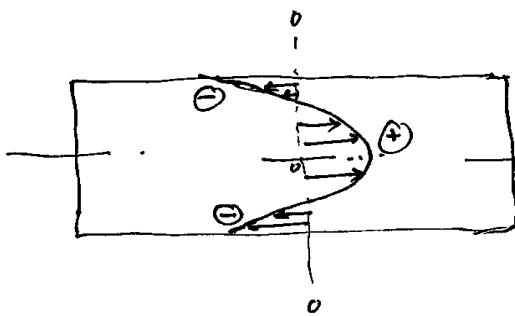
o-o is zero level.

(+) → Tensile stress

(-) → Compressive stress



(b)



(c)

QUESTION 3

In the paper you state that at low doses the sink strength ratio, $Q \gg 1$, consists of dislocations as the dominant sink. At intermediate doses $Q = 1$ and higher doses ($Q \ll 1$), voids and neutral sinks become dominant.

- 1) Helium will be a primary product of burning plasma fusion reactors. Describe the fundamental mechanisms and synergy (if any) of helium irradiation and fast neutron (14.1 MeV) irradiation (from nuclear fusion reaction) on the swelling process and in particular the incubation period described in your paper. Use sketches and equations to aid in your overall explanation of the balance of defect behavior under these operating conditions.

QUESTION 4

- 1) Figure 12 from your document shows some TEM micrographs of iron. Tell me what you see in part (a). Describe in as detailed a way as possible how you could quantify the features shown in part(a).
- 2) How does part (b) differ from part (a)?
- 3) How are the features in (a) and (b) dependent on sample preparation for the TEM?

QUESTION 5

Differing fcc materials (Cu, Al, SS) have very different stacking fault energy.

- 1) How do stacking faults form in these materials during irradiation?
- 2) What influence would the stacking fault energy have on loop formation?
- 3) Could the fault energy influence the tendency to form voids?

ULTIMATE LIMITS ON THE SPATIAL RESOLUTION OF ELECTRON ENERGY LOSS SPECTROSCOPY OBTAINED WITH A SCANNING TRANSMISSION ELECTRON MICROSCOPE

QUESTION 1

1. Draw a band diagram for GaN/InGaN/GaN light emitting diode in equilibrium.
2. Connect this diagram to appropriate applied voltages so that you achieve a condition where carriers recombine in the base.
3. What would we need to make this light emitting diode become a laser?

CREEP BEHAVIOR OF 9Cr MAODS MARTENSITIC STEELS

QUESTION 1

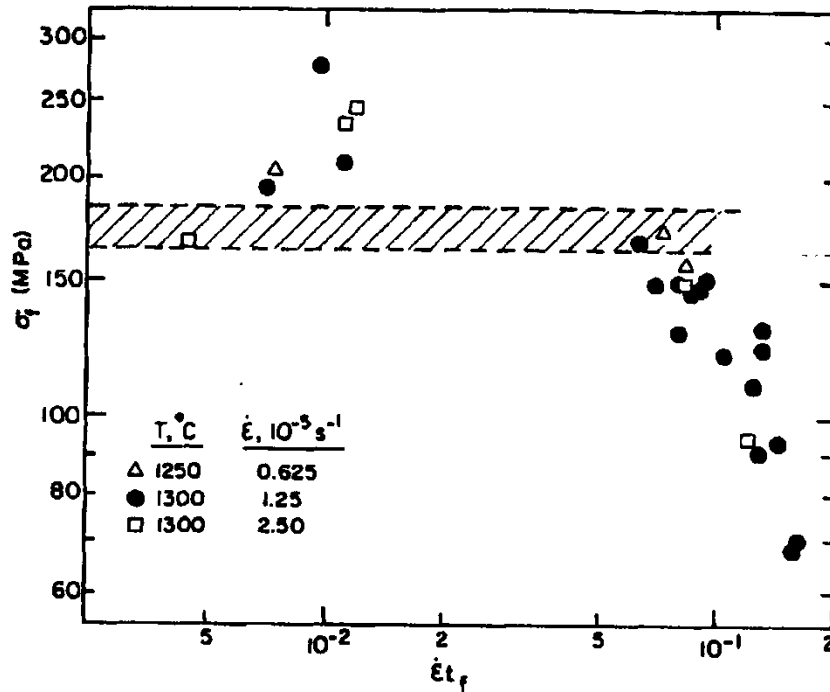
1. Sketch and label a deformation mechanism map for a common fcc metal.

- Discuss how a deformation mechanism map for a bcc metal would compare to your sketch. What remains the same? What are the differences?

QUESTION 2

Ceramic Society—Dalglish et al.

Vol. 68, No. 11



The plot above shows creep rupture data (failure stress vs. the product of the applied strain rate and the failure time) for polycrystalline Al_2O_3 bars tested in 3-point bending at elevated temperature. The bars were tested at a constant applied strain rate (e.g., the cross head speed of the mechanical test frame was constant).

Although the bend bars were all made from the same material, the data displayed a bimodal distribution of failure times and stresses. Please attempt to explain the observed duality in creep rupture behavior of the Al_2O_3 bend bars.

QUESTION 3

- As a model of the ODS alloys, derive a simple estimate for the average spacing, λ , between particles in terms of their radius, r , and volume fraction, V , by assuming a simple cubic lattice (ball-and-stick model) of particles with lattice parameter λ .
- Describe two physical, chemical or mechanical characteristics of oxide dispersion particles that tend to give better creep strengthening effects compared to carbide or intermetallic precipitates.

QUESTION 4

1. Beginning with an equation of the form (similar to equation 3 in your document):

Describe how you would measure the stress exponent using a series of experiments (i.e. What would you plot on the X and Y axis and what testing variable(s) would you keep constant, and how would you interpret the results?)

2. Would you expect the activation energy for these alloys to change? What variable in your equation would have to change for that to happen?

QUESTION 5

1. Sketch an edge dislocation approaching a spherical precipitate
2. Explain how (which direction) the dislocation would climb if the particle is under hydrostatic tension.
3. What effects would these cause on the interaction:
shear strain within particle, anisotropic particle/matrix interface energy

DENDRITE FORMATION IN RECHARGEABLE LITHIUM BATTERIES

QUESTION 1

During your presentation you described differences in the Li ordering of the LiCoO_2 structure the charging and discharging cycles of Li-ion batteries. The loss of Li ions (deintercalation) has been suggested to lead to a first order change in the crystal structure from a hexagonal structure to a monoclinic structure.

1. Please describe the primary symmetry elements that would be expected in a hexagonal structure. A crystal structure model is given below:

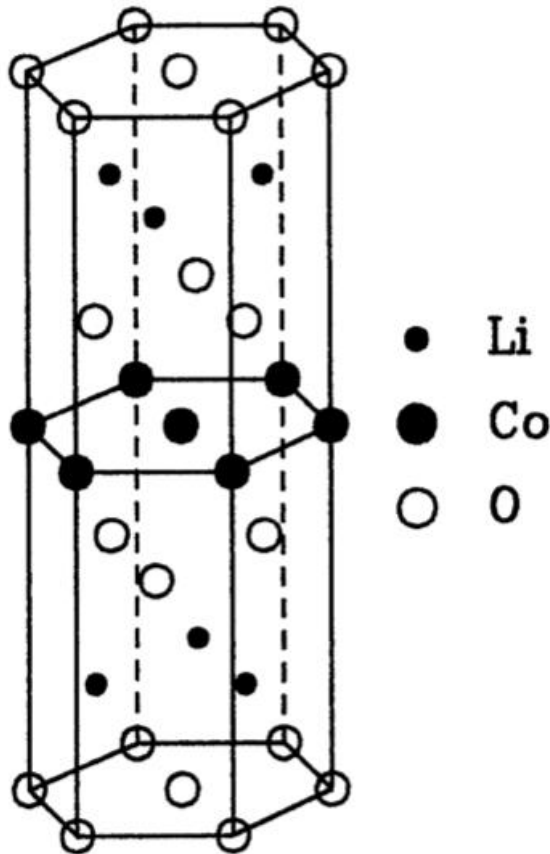


Fig. 1. Schematic diagram of the layered LiCoO_2 structure showing the . . . ABCABC . . . stacking of the O-Li-O-Co-O-Li-O layers.

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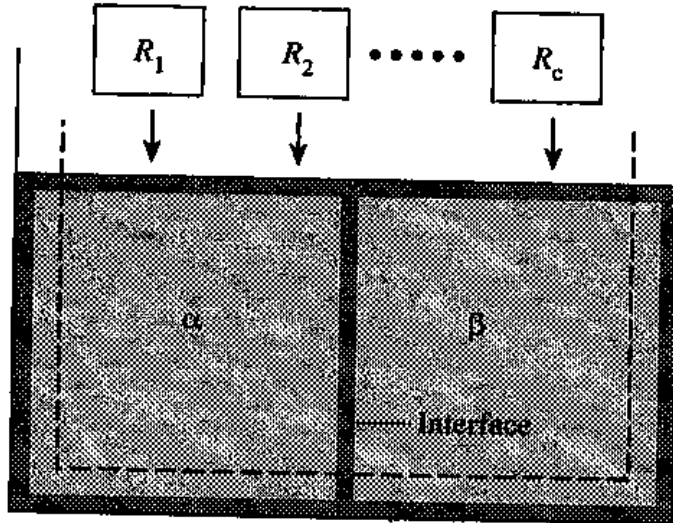
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THE QUALITATIVE NATURE OF HOT TEARING CRITERIA

QUESTION 1

We will be discussing the transient fluid flow and heat transfer near an infinite vertical flat plate in the short time after a heat flux is suddenly generated by the surface. The fluid is initially quiescent and it and the wall are at the temperature T_o . At $t = 0$, a constant and uniform heat flux, q_o'' , is turned on at the wall ($y = 0$) and the fluid is heated.

- (a) Write the equations for conservation of energy, momentum in the x direction (along the wall), and mass. Assume that gravity acts in the negative x direction, the pressure gradient term is negligible, and the thermophysical properties are constant and uniform.
- (b) Write the boundary conditions for u , v , and T at $y = 0$ and $y = \infty$. Neglect any terms you can using the fact that the plate can be treated as infinitely long.
- (c) Assuming $Pr = 1$, sketch the temperature and vertical velocity profiles, $T(y)$ and $u(y)$, at two successive times.
- (d) Find the exact solution to the continuity equation for the velocity normal to the surface, $v(y)$.
- (e) Using a scaling analysis of the governing equations and boundary conditions, find estimates as a function of time for
 - (i) the thermal penetration depth, δ ,
 - (ii) the temperature difference, $T_{wall} - T_o$, and
 - (iii) the vertical velocity, u_o .

QUESTION 2

- 1) Which crystal structure is more susceptible to strain-rate deformation effects – a FCC or a BCC metal? What is the mechanism behind this strain-rate deformation sensitivity?
- 2) Would you expect crystal structure to play a part in the Rappaz et al. model for strain-rate based hot tearing? Why or why not?

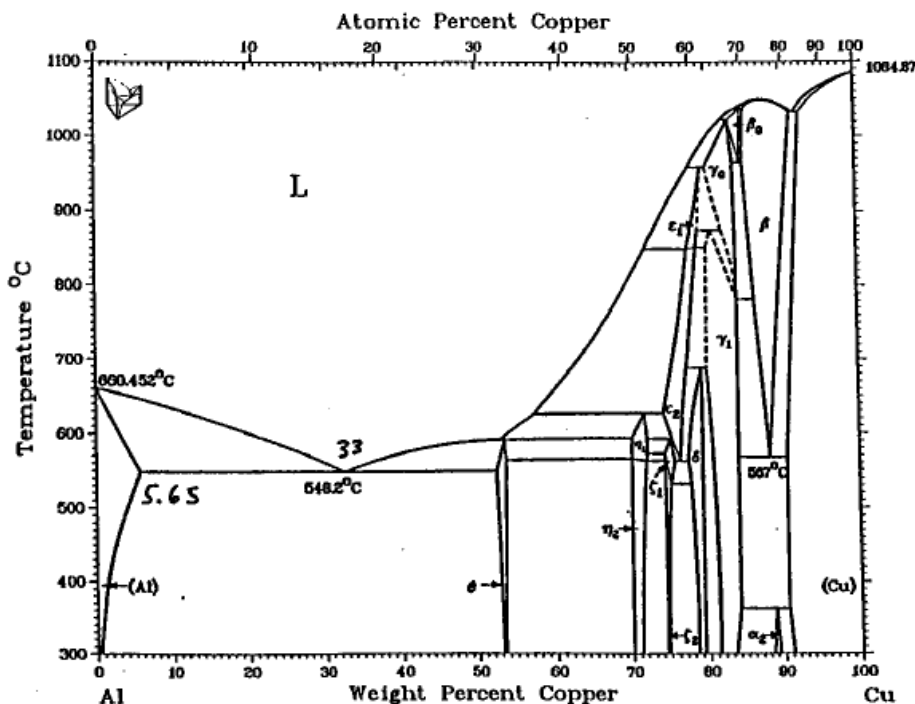
QUESTION 3

In your document you proposed to use an organic crystal as a surrogate material to learn more about the mechanisms that govern hot tearing in metallic alloys. Assuming that the conditions present during casting of a metal can be reproduced in the surrogate system, the lessons learned could only be applied if the mechanisms of crack nucleation and propagation in the two materials are similar. So let's talk about crack propagation.

- 1) Please describe Griffith's approach to crack propagation in brittle materials. The model compares two energy contributions and establishes a criterion for crack propagation. What are the two energy terms? Under what conditions will a crack with a simple geometry propagate?
- 2) What need to change in the model to describe a ductile material? Do you need to spend more or less energy to propagate a crack? What additional energy term comes to play? What happens ahead of the crack?

QUESTION 4

- 1) Consider the Al-Cu system and briefly describe the application of the constitutional supercooling criterion to predict the morphological instability of a planar solid-liquid interface as a function of alloy composition for a given thermal gradient and interface velocity. If solute transport in the liquid is by diffusion only, what is the interface temperature for planar growth of a specific alloy (e.g., 2 wt% Cu)?
- 2) Discuss why the various hot-tearing models predict similar compositions for the peak in the lambda curve for hot tearing susceptibility. Sketch the microstructure for this case and indicate the temperature with respect to the Al-Cu phase diagram.
- 3) Estimate the pressure difference to homogeneously nucleate a pore in the melt. Note the energy of the liquid/gas interface is on the order of 1 J/m^2 . Is this likely to occur? If not, discuss how and where the pore would nucleate.



QUESTION 5

Two perfectly parallel solid plates 2 cm in diameter are held at a separation of $10 \mu\text{m}$. Between them is a film of a perfectly wetting liquid 1 cm in diameter. The surface tension of the liquid is 1 N/m and the system is in an inert gas at 0.1 MPa ($\sim 1 \text{ atm}$).

- (a) Are the plates held together or repelled by the presence of the liquid between them?
- (b) Describe the origin of this force.
- (c) Using the Laplace equation, calculate the capillary pressure ($\Delta P = P_L - P_V$).
- (d) Estimate the magnitude of the force holding the plates at this separation.

(e) Apply these results to the concepts of hot tearing.

THERMOELECTRICITY OF SI NANOWIRES

QUESTION 1

You presented micrographs and data on two different Si nanowire types with different surface roughnesses that were prepared by two different techniques: vapor-liquid-solid growth and an electroless etching technique starting with Si single crystals.

1. Describe vapor-liquid-solid growth process for Si. Draw the physical geometry for different steps in the growth process. Draw the Au-Si phase diagram and describe how it relates to VLS process.
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QUESTION 2

Consider a polycrystalline sample of Silver of grain size g and grain boundary thickness δ .

1. Sketch-out the chemical diffusivity of the grain boundaries phase and the chemical diffusivity of the single-crystal (grain) phase as a function of temperature. Please explain which one should be higher at what temperature and why.
2. Given your answer above, sketch out how a dopant will diffuse at low temperatures, intermediate temperatures, and high temperatures. Please justify your answer.

QUESTION 3

1. Explain the differences between diffusive, ballistic, and coherent transport of quasi-particles in a solid. Quasi-particles to consider: electrons and phonons.
2. What are the differences between these quasi-particles?
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QUESTION 4

These questions deal with epitaxial films and coherency limits.

1. Sketch the diamond crystal structure. What are the Burgers vectors for bcc, fcc and diamond crystals?
2. Now consider a thin film grown epitaxially on a substrate with a lattice parameter smaller than that of the film.
Using a simple schematic diagram explain how an edge dislocation on the interfacial plane releases epitaxial strain.
3. Calculate the density of interfacial edge dislocations (number of dislocations per unit length that cut a plane formed by the interface normal and the Burgers vector of the dislocations) that leads to the most efficient strain relaxation.

4. Coherency limit: Under what conditions would it be favorable to nucleate the dislocations in 3?

QUESTION 5

1. How would measuring the size and roughness of nanowires differ from measurements of a thin 2-D layer?
2. What parameters would you want quantified for each?

CRATER FORMATION PHENOMENA IN HYPERVELOCITY IMPACTS ON COPPER TARGETS

QUESTION 1

1. When a ball is pressed against the surface of a large block of material, what are the differences in the target deformation processes when the ball initially flies at high speed as compared to the ball is statically pressed into the material.
2. What is the definition of Mach number? Do you think this number defined with the wave speed in the target material is important and why? Do you know how fast the deformation can occur in the target material?

QUESTION 2

The research you reviewed indicates that the crater rim undergoes large-strain extensional flow to the point of plastic instability or necking.

- a) Draw an engineering stress-strain curve for an annealed ductile metal all the way to fracture and show the point on the curve where the material would exhibit plastic instability or necking.
- b) Sketch on the same plot the corresponding true stress-strain curve. On sketches of the test specimen before and after necking, indicate the portion of the specimen gage length where the true stress-strain relationship occurs.
- c) Explain how and why plastic instability occurs.
- d) Another specimen of the same alloy is tested, but this time it is strain-hardened by 50% reduction before the specimen is cut out. Sketch the full engineering stress-strain curve you would expect compared to the annealed specimen and explain the differences.

QUESTION 3

1. Consider a free-free uniform homogeneous metallic rod with cross-sectional area A , modulus E , length L , and density ρ :
 - a. Derive the differential equation that describes the small amplitude longitudinal dynamic response $u(x,t)$ of this rod at position x as a function of time t due to forces $f(x,t)$ that act upon the rod using Newton's second law of motion (please state your assumptions in the derivation).
 - b. Calculate the natural frequencies and mode shapes of the rod as it longitudinally displaces.

- c. How can these modal properties be used to calculate the dynamic response of the rod along with a forcing function $f(x,t)$?
2. In the study you presented during part 1 of your preliminary examination on hyper velocity impact of copper,
 - a. What role does deductive reasoning play in the study of hyper velocity impact events? In contrast, your talk focused on inductive reasoning.
 - b. What are the principal uncertainties in laboratory tests that aim to simulate such on-orbit impact events? Which of these uncertainties is most influential in generalizing the findings reported to practice, and why?
 - c. What are the time scales involved in the various processes that occur during such an impact event? Deformation, thermal, re-crystallization, etc.

QUESTION 4

1. The Tsai-Wu failure criterion has been shown to accurately predict the off-axis tensile strength of a composite material. How does it predict laminate strength and what issues govern laminate strength?
2. Describe the test method for determining the interlaminar fracture toughness of a unidirectional composite material.

QUESTION 5

Explain how small second phase particle in an alloy affect the mechanical response, especially how they could (a) strengthen or (b) weaken the material. Quantify this if possible, particularly with regard to the size of the particles.

ELECTROMIGRATION INFLUENCED GROWTH ON Sn-Cu INTERMETALLICS RELATED TO ELECTRONIC RELIABILITY

QUESTION 1

Ternary phase diagrams

Consider two different ternary phase diagrams:

Phase Diagram 1

In one (elements A, B, and C) form a ternary phase diagram. Each binary is a simple binary eutectic with some solid solubility.

- (1) Draw an isothermal section below the eutectic marking the phase fields and the tie lines
- (2) Draw an isothermal section above the ternary eutectic temperature but below any of the binary eutectic temperatures
- (3) Draw an isothermal section above the binary eutectic temperatures.

Phase Diagram 2

Now for A, B, and C. A and B and A and C form simple binary eutectics with some solubility. B and C solids form a complete solid solution (isomorphous).

Draw an isothermal section below the binary eutectic temperatures marking the phase fields and tie lines.

QUESTION 2

1. Give an expression for the diffusion coefficient, D , in terms of jump frequency, lattice spacing, geometry, etc.
2. Describe the difference in D due to
 - a) 1D vs 3D
 - b) crystal structure
 - c) diffusion mechanism
3. Describe how the presence of a chemical potential, stress or electric potential driving force changes the free energy of diffusion.
3. How is the diffusion coefficient affected as the temperature is changed?

QUESTION 3

1. Describe other property changes that should result to produce the embrittled material shown in Fig.6.
2. If loading is in pure shear, describe the expected fracture geometry for the embrittled material.

QUESTION 4

1. Describe the micromechanical origin of the strengthening that originates from grain boundaries in metals. What is the key parameter that determines the strengthening, and how does this parameter scale?
2. Let's suppose that the efforts in the Handwerker group on the creation of 'nanosolders' were to work. Describe how these small grained structures would either increase or decrease the formation of the intermetallics you described in your Prelim document.

QUESTION 5

1. Why does the phase order in the Sn-Cu couples always appear to mimic the phase diagram order?
2. Why are the interfaces not always flat? Would they always be flat for isotropic materials?
3. Discuss how anisotropy would affect the mechanical integrity of the interfaces.

WETTING AND SPREADING OF RARE EARTH ELEMENT MICRO-ALLOYED Sn-BASED Pb FREE SOLDERS

QUESTION 1

1. In thin film deposition, the microstructure evolution as the film thickens/grows has been described in the literature according to "structure zone models." Choose any method of thin film formation (for example, physical vapor deposition, electrodeposition, ...) and discuss how the microstructure is expected to evolve with thickness for different film deposition conditions, including temperature and some composition variable.

2. Assume now that you have a thin film on a thick substrate for which the deposition temperature was T_1 . Now heat the film+substrate to a new temperature T_2 . Assuming only elastic deformation, draw schematically changes to the lattice parameters of the film. Give an rough estimate of the resulting elastic energy of the thin film.

QUESTION 2

1. If you are asked to create a hydrophilic surface by geometrical modification of the surface, how would you achieve it?
2. Consider a plate with center crack of length " $2a$ " loaded in uniaxial tension. Write down the expression for the total potential energy from which the surface energy coefficient can be derived under steady crack propagation. Explain how you would obtain the steady state energy release rate from the expression. Hint: Subtract the work of adhesion for the crack from the total potential corresponding to the plate without the crack.

QUESTION 3

Consider a binary diffusion couple assembled with polished disks of an alloy α (bcc) and an alloy β (fcc). The couple is annealed at a temperature T for some time t for interdiffusion to occur and to develop an interface between the two alloys.

1. Assuming local equilibrium at the α/β interface, draw a schematic concentration profile for the couple.
2. How is the motion of the interface related to the interdiffusion fluxes of the components at the interface?
3. Can a two-phase layer develop in the diffusion zone? Justify your answer.
4. If the alloys α and β are ternary alloys, draw schematic diagrams for possible interface morphologies and diffusion structures.

QUESTION 4

1. Why does a metal pulled to 0.1% strain show a substantially increased yield stress in compression?
2. Why does a small-grained polycrystal, with more grains closer to the ideal Schmid factor, have a HIGHER yield stress than a larger-grained polycrystal?
3. Would you expect a single crystal to have a different yield point and work hardening exponent than a polycrystal?

MECHANISM OF BAINITE TRANSFORMATION IN HIGH CARBON STEELS

QUESTION 1

Zr undergoes a martensitic phase transformation between bcc (austenite) and hcp (martensite). In this transformation a (110) bcc plane transforms into the closed packed plane of the hcp phase.

1. Sketch a (110)_{bcc} plane and a closed packed hcp plane and describe how one can transform into the other. Can one phase be strained into the other without atomic relaxation? Hint: Consider the stacking sequence (show as many atomic planes as necessary) in each phase.
2. Based on these two structures: do you expect Zr to exhibit shape memory?
3. How does dislocation-based plastic deformation affect shape memory?

QUESTION 2

1. Give the definition of a phase. What are the equilibrium phases in the Fe-C system? Describe the metastable phases in the system.
2. Describe the morphological differences between upper and lower bainite.
3. Describe how single crystals are grown using the Bridgman-Stockbarger technique. What is happening as the solid-liquid interface? How would a fully austenite specimen be stabilized upon cooling? How and at what temperature is bainite formed?
4. Describe the general relationship between yield stress and fracture toughness within a given class of materials. Explain why a good fracture toughness is measured for NANOBAIN steels.

QUESTION 3

1. Sketch the relevant part of the Fe-Fe₃C phase diagram and use it to speculate on the solubility of carbon in austenite, relative to that in ferrite, below the eutectoid.
2. Sketch ball-and-stick models of the unit cell of ferrite and austenite and describe the interstitial positions in these structures.
3. The diffusivity of carbon in ferrite at 200°C is $\sim 1 \times 10^{-12} \text{ cm}^2/\text{s}$. Estimate the “diffusion distance” in 10,000 s and comment on the implications for the bainite transformation mechanisms described in your paper.

QUESTION 4

A Fe-0.77wt%C steel is quenched from above the eutectoid temperature to a temperature just below it, where it is held long enough for a complete solid-solid phase transformation to take place.

1. What is this phase transformation? Where in the microstructure does it typically begin?
2. Assume the carbon-rich phase nucleates first and describe its growth before the nucleation of the second phase. What controls the movement of the interface of the new and parent phases?

3. Where does the second phase tend to nucleate? Why?
4. Describe the growth of the two new phases into the parent phase. What controls the growth rate and the spacing of the two new phases?
5. How does the relative coherence of the interfaces affect their velocities in the phase transformations you described in (a)-(d)?

QUESTION 5

1. Sketch the Fe-C free energy - composition diagram for $T \sim 300$ K, including the two stable and two metastable phases.
2. Use this diagram to explain the variation in C concentrations over time seen in Figure 10.

THE INTERACTION OF TITANIA PARTICLES IN NONPOLAR SOLVENTS

QUESTION 1

1. What is the dependence of the Debye length on the dielectric constant of the continuous fluid?
2. Comment on the influence of the Debye length on particle packing and what do you think will be the effect of having a large Debye length in the bi-stability of electrophoretic displays?

QUESTION 2

1. From your document you state that the response time is (coupling the two equations)

$$t \sim d^2 \eta / \epsilon \zeta V$$

where d is the diameter, η is the viscosity, ϵ is the dielectric constant of the fluid, ζ is the zeta potential of the particle, and V is the applied voltage. Based on this the optimal system is one where there are small particles, a low viscosity fluid, a high dielectric constant fluid, and a large zeta potential particle.

- A. Currently, non-polar organic fluids are used as the carrier fluid for EPD. For what reasons may these materials be used? (Consider their dielectric constant and viscosity). Why not use water?
- B. Consider that diameter of the particle is a squared relationship and therefore the more important factor. What factors limit the ultimate lower limit in choosing materials for the particle? What does this imply in the selection of TiO_2 and graphite?
- C. Considering that these suspensions are not dilute (and at low Re flow), what impact does this have on the response time (ie how will it reduce the equation) and why? What limitation does this place on concentration of particles and what does this do to the functional design of the EPD?

QUESTION 3

1. Define the colloidal state; what makes a particle a “colloid” as opposed to just a particle?
2. Describe the phenomenon of Brownian motion and its origins.
3. In a gravitational field, if colloidal particles and the liquid medium have different densities, what two phenomena oppose each other to give a concentration gradient of particles at equilibrium. Use a sketch to explain.
4. Make sketches of a colloidal suspension showing qualitatively how it would evolve from a non-equilibrium initial particle distribution of your choosing to the equilibrium distribution of particles.

QUESTION 4

1. What is the crystal structure of rutile?
2. If the Titania particles exhibit some degree of surface energy anisotropy, what are some particle shapes that are consistent with the symmetry of titania?
3. What effects would you expect this to have on polymer absorption?
On your surface force measurements?

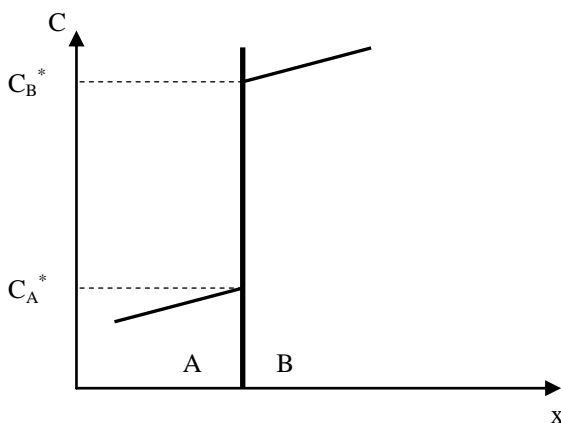
QUESTION 5

What size restriction is required to noticeably affect the light emission from a quantum well LED?
Explain this quantitatively.

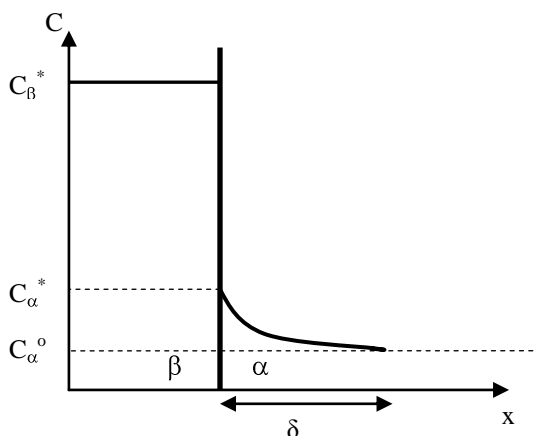
A CRITICAL REVIEW OF THE NUGGET ZONE MICROSTRUCTURE FORMATION OF FRICTION STIR WELDING

QUESTION 1

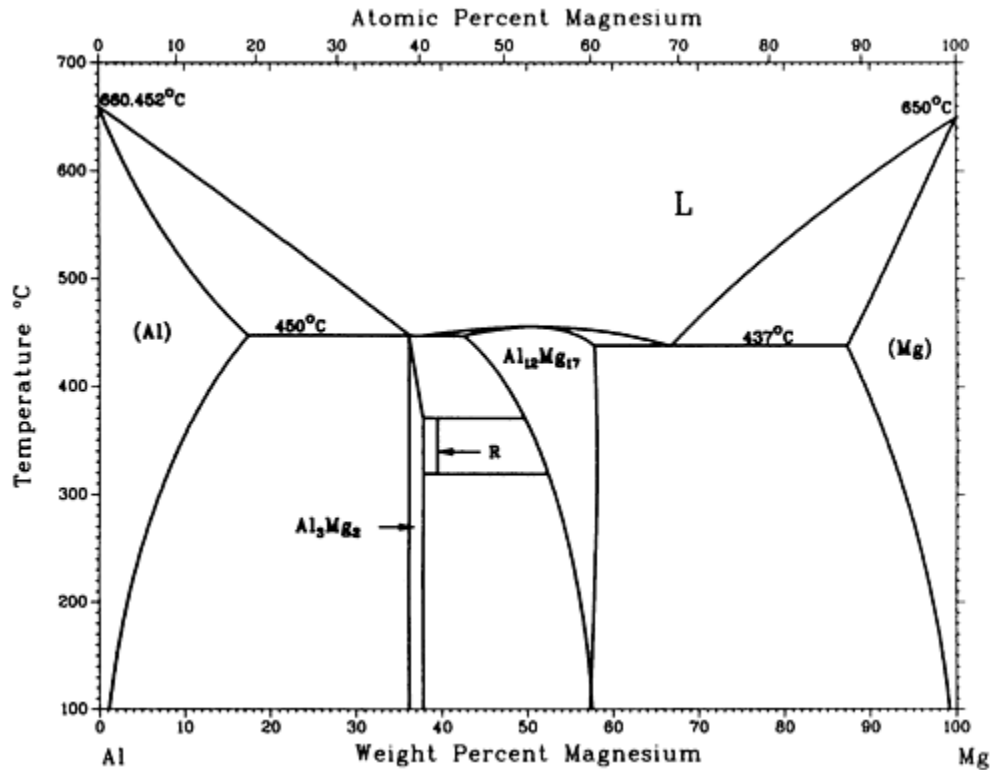
- (a) **Derive** equation for the velocity of the interface between phases A and B in figure on the left below.
(b) **Estimate** for the time for the β phase in the figure on the right above to grow into the α phase from x



$= 0$ to $x = x_0$.



(c) For an Al-1wt%Mg alloy, how long would it take to dissolve a β precipitate 4 microns in width(from figure 13), using $D = 10^{-13} \text{ m}^2/\text{s}$? Using this result, comment on the likelihood of the dissolution and reprecipitation process described on p. 23 of your document.



QUESTION 2

1) Sketch an Ashby deformation mechanism map for a pure FCC metal. Do not include any strain rate contours. What are the mechanisms governing deformation in each region? Discuss how a map for a BCC metal would compare to that for FCC.

2) Discuss the development of residual stresses in a friction stir welded plate. Clearly define your coordinate system.

QUESTION 3

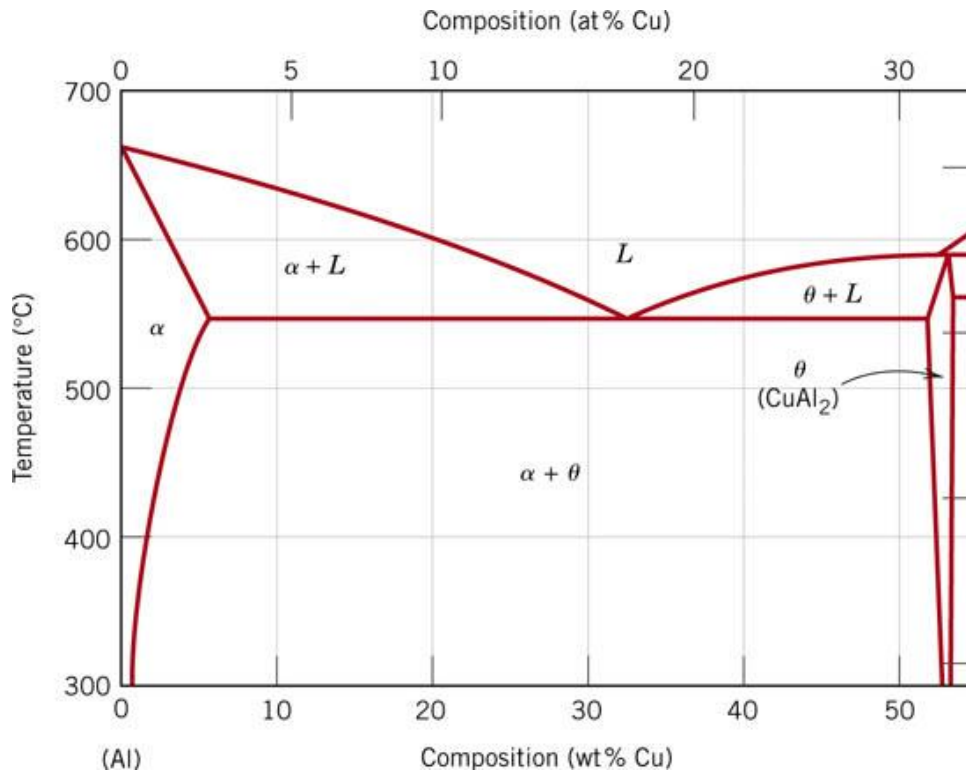
Approximating Al 2024 as an Al-4.4 wt.% Cu binary alloy, consider the solution-treatment and aging process used for precipitation-hardening.

(a) What is the purpose of the solution-treatment step and why is it necessary for precipitation-hardening?

(b) On a sketch of the phase diagram (below) indicate an appropriate solution-treatment temperature.

(c) Draw a particle of θ in the α matrix with coordinate axes of wt.% Cu versus distance from the center of the particle (origin) and sketch a series of profiles showing how the Cu concentration would vary with time at the solution-treatment temperature.

(c) Consider an alloy that has been fully solution-treated and then quenched to room temperature. On the same type of coordinate axes as in part (b), sketch a series of profiles showing how the Cu concentration would vary with time around a θ precipitate growing in the α matrix at the aging temperature of 300°C.



QUESTION 4

Describe the spacing selection mechanism for primary dendrites/cells. What determines the minimum stable spacing of dendrites in a dendrite array? When the maximum stable spacing occurs in a dendrite array?

QUESTION 5

If the OR structure was suspected caused by impurities, which atom types would you expect in each (Cu or Al-based) case?

How could you go about looking for these impurities?

DYNAMIC FAILURE OF BOROSILICATE GLASS UNDER VARIOUS LOADING CONDITIONS

QUESTION 1

1. You used an exponential function (Boltzmann factor) to describe atomic diffusivity in growth kinetics:

$$K_0 \exp(-Q/kT)$$

Q represents an activation energy (or energy barrier) and I would like for you to discuss the atomic processes that this energy barrier corresponds to in the case of diffusion in crystalline metals.

i) Sketch a perfect crystal and describe the atomic processes that lead to mass diffusion

ii) Repeat i) for mass diffusion through a grain boundary. In which case (bulk or grain boundary) do you expect a lower activation energy?

2. (Time permitting.) You used a similar expression to describe mobility of dislocations. Could you sketch a simple dislocation in terms of atoms and describe the process associated with the energy barrier?

QUESTION 2

1. Describe the grain size dependence of yield strength for ductile materials - what is the basis and what relationship do you expect?
2. What other mechanisms are available to change the yield strength of solder materials? How would you implement them?

QUESTION 3

1. Describe the formation process of intermetallic compounds.
2. What are the key parameters that affect the formation process.
3. What do you think a possible lead-free alloy that may be thermally more stable?

QUESTION 4

1. Give a definition of coarsening using a simple model system of alpha particles in a beta matrix.
2. What is the free energy difference between two alpha particles of different sizes?
3. How does this lead to equation (3) in your paper?
4. In your paper you discussed coarsening and phase formation in Sn-Ag-Cu alloys. Using the information from your literature review, roughly sketch the Cu-Sn phase diagram from 150°C to room temperature. What are the phases that form?
5. In the microstructures that form during solidification of Sn-Ag-Cu alloys (for example SAC405), what phase forms first as the alloy is cooled?

QUESTION 5

1. What determines the melt temperature of Sn-Ag-Cu? 217°C
2. How is wetting of Sn-Ag-Cu to copper determined? How is adhesion affected by wetting?
3. What is thermal migration?
4. What is the scale of the microstructure?

MORPHOLOGY CONTROL OF CUPROUS OXIDE AND ITS PHOTOCATALYTIC PROPERTIES

QUESTION 1

1. a. What are important considerations you need to make when preparing a sample for SEM imaging? Describe how the sample can be prepared for SEM analysis if the sample is:
 - i. A fine powder of alumina
 - ii. A small piece of Ti alloy. You need backscattering electron analysis of this sample.
- b. Can any sample be imaged directly in the SEM, for instance cheese? Explain.
- c. Describe how the microscope voltage can contribute to the charging effect under the SEM.

QUESTION 2

Consider 400-nm metal oxide colloids in an aqueous suspension at a pH far from the isoelectric point (i.e., significant magnitude of zeta potential). List the different types of forces that act on the particles, their origin(s) and their consequences. Use sketches where possible.

QUESTION 3

1. Explain the mechanism of organic molecule photodegradation on the Cu₂O surface.
2. What is the driving force for surfactant adsorption on the Cu₂O surface?

QUESTION 4

How is heterogeneous nucleation different from homogeneous nucleation? What is the key aspect of heterogeneous nucleation that makes it more likely to occur?

1b. Estimate what the new equations for Gibbs free energy change (ΔG), and critical radius for nucleation (r^*). You may use simplifying assumptions (ie heterogeneous nucleation of a spherical shaped precipitate on a flat surface, etc)

1c. List the variables that should be include in Item #1b to make it more applicable to the Cu₂O system. How will changes in the solution or heterogeneous nucleation sites influence heterogeneous nucleation?

QUESTION 5

The Al-Si system is a simple eutectic. The Si dendrites are distinctly faceted at their tip, while Al dendrites have no facets during solidification. How would this affect the cooperative growth at the eutectic composition? If the Si facets form to exhibit the {111}, would the dendrites have a preferred growth direction?

PERFORMANCE AND METALLURGICAL INFLUENCES ON LOW-TEMPERATURE SENSITIZATION OF AUSTENITIC STAINLESS STEEL 304LN

QUESTION 1

Solid nickel dissolves oxygen up to a maximum concentration of ~0.2 at.% at 1440°C, where the saturated solid solution is in equilibrium with solid NiO and liquid containing ~0.9 at.% O. Pure Ni melts at 1455°C.

A. Using the information above, sketch and label the Ni end of the Ni-O phase from 0 to ~10 at.% O. Write the equilibrium (reaction) and name the type of invariant at 1440°C.

B. Bulk, solid, pure Ni is reacted with oxygen gas at 1 atm at 700°C.

i) Write the equilibrium for this reaction.

ii) Make a series of sketches showing how the microstructure will develop, including how the concentrations of Ni and O will vary across the reaction system. Show the concentrations semi-qualitatively

iii) Once the NiO scale becomes sufficiently thick, its thickness, x , will increase with time according to the well-known parabolic rate law, $x = kt^{1/2}$. Make a simple derivation of this rate law, starting with the assumption,

$$\frac{dx}{dt} \propto J_{Ni^{2+}},$$

where $J_{Ni^{2+}}$ is the flux of nickel through the scale.

QUESTION 2

1. In the 304LN alloy studied in your prelim, an additional amount of nitrogen is added to the 18 Cr/8 Ni steel alloy. There is a range of nitrogen (0.1-0.16 wt.%) and carbon (less than 0.03 wt.%) in the alloy. Discuss how the nitrogen or carbon would fit into the austenitic matrix of the stainless steel. Where would the solute atoms reside or sit? Do they distort the matrix? Prove using calculations. Assume $r_{\text{carbon}} = 0.08 \text{ nm}$ and $r_{\text{nitrogen}} = 0.07 \text{ nm}$. Assume the size of an iron atom is 0.124 nm.
2. Comment on whether the interstices are larger or smaller for α -iron. Is this surprising? Why or why not?
3. Would the size of the atom make a difference in the value of D , the diffusion coefficient? Why or why not? Do the nitrogen atoms “beat” the carbon atoms to the grain boundary?

QUESTION 3

1. Sketch a schematic isothermal transformation (TTT) diagram for precipitation of CuAl_2 from Al/Cu solid solution at some specified copper content c_0 ($< 5 \text{ wt\% Cu}$). Indicate the schematic solvus temperature at c_0 . Superimpose a thermal history that will produce a precipitation hardened alloy. Sketch the copper concentration profile in the vicinity of a growing precipitate.

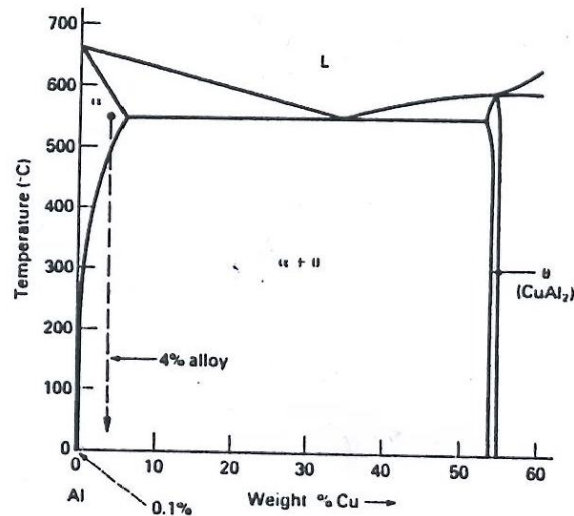


Fig. 10.3. The aluminium end of the Al-Cu phase diagram.

2. Sketch a TTS curve from your Figure 4 at some fixed carbon content. Discuss similarities and differences in construction and interpretation between the TTT diagram for CuAl_2 and the TTS diagram.
3. Consider the desensitization process in Figure 4 for your chosen carbon content. The model in Figure 8 indicates that carbide growth continues concurrent with Cr concentration recovery of the CDZ. Figure 8 suggests a time-dependent phase-boundary composition which seems inconsistent with a diffusion-control (equilibrium at the interface) model. Please explain.
4. LTS in a BWR is occurring in the same environment as the concurrent IGC. How do your models isolate these processes?

QUESTION 4

1. Discuss if the fusion zone of welded austenitic stainless steel is susceptible to sensitization or low temperature sensitization. What metallurgical factors must be considered?
2. Rocksalt is cubic and slips on $\{110\}\langle 110\rangle$. Which slip system(s) are expected to operate if the tensile axis is $[\bar{1}23]$. Sketch the stereographic projection showing the expected slip system(s).

QUESTION 5

1. Is there a way to estimate the stored energy of cold work from the dislocation density?
2. Should this energy be uniformly distributed?
3. Why can very low temperature deformation induce some austenitic stainless steels to become ferritic?

