HOMEWORK 5.

P R O J E C T   W O R K

DUE DATE: Ongoing

- **Prepare a project plan.** This week, you will form a new project team and begin your materials research and project planning. Once you settle onto a team, start working on your project proposal, do some research on your alloy system, and explore the application areas for your alloy. As you develop your project plan, consider these questions:

  1. What are the main questions you are asking?
  2. What raw materials do you need?
  3. What do you need to do in the lab or machine shop in terms of processing? What are the steps involved in getting a material into the form you need for your analyses? How long will the processing take?
  4. What technical information do you need to learn to understand your alloy(s) and process(es)? Where will you find this information – textbooks, reference books, under a piece of aged gouda?
  5. What tests will you perform? What are the goals of each test?
  6. What sustainability-related questions will you explore for your metal or alloy system?
  7. What will you have to show after four weeks of this project?

- **Research your metals and alloys.** Use ASM Handbook (http://products.asminternational.org/hbk/index.jsp) to research the composition and properties of your alloy(s). Volume 1 includes a section on iron alloys. Volume 2 has sections on all other alloys under "Specific Metals and Alloys" and on pure metals in the "Pure Metals" section. Do some web or library searching for various practical applications of your alloy.

- **Get a head start on phase diagrams.** In Volume 4 of ASM Handbook, locate a binary phase diagram for the two primary constituents of the alloy systems you are studying in your project. For example, if you are studying bronze, find the phase diagram for copper-tin alloys. If you know the composition of your alloy, try to locate it on the phase diagram and attempt to glean some information (e.g., phases at different temperatures, melting temperature) from the diagram.

R E A D I N G S

This week, we have a couple of readings that serve as a setup for the metals project. The first is on solid-state imperfections, or defects. Defects play a key role in determining the properties and performance of metals and alloys (and other materials), and they help us understand more complex topics such as diffusion and the kinetics and thermodynamics of phase transformations. Which brings us to the second topic for this week: solid-state diffusion. You and your teammates are about to subject an alloy to mechanical and thermal treatments, as part of your project work. When you do so, the atoms in your alloy are going start moving around in particular ways. Getting a grasp on the basics of solid-state diffusion will help you understand and explain the changes you'll see in your alloys as a function of processing.

Imperfections in Solids. Callister Chapter 4 (Imperfections in Solids), or Ashby *Engineering Materials 1* Chapter 9 (Dislocations and Yielding in Crystals) and *Engineering Materials 2* Chapter 2 (Metal Structures)

Diffusion. Callister Chapter 5 (Diffusion), or *Ashby Engineering Materials 1* Chapter 21 (Kinetic Theory of Diffusion)

Look over the brief "Stolk's Take on the MatSci Readings," if you like.

STOLK'S TAKE ON THE MATSCI READINGS

Chapter 4 – Imperfections in Solids

Defects matter. Small or large, the number and type of imperfections in solid materials can have enormous effects on properties and performance. Sometimes these changes are highly desirable (e.g., increases in strength or ductility, reduction in melting temperature to facilitate processing, increases in electrical conductivity), and sometimes they are not (e.g., increased brittleness, decreased electrical conductivity, increased corrosion rates). I'll give you some examples. First, let's consider **point defects (1D)** in, say, copper. Copper is my favorite metal, by the way. Why, you ask? I consider Cu an underdog in the ultra-competitive, high-stakes world of engineering materials… and I always root for the underdog. I also like the smell of copper oxide, but we don't have time to explore that particular tangent. Okay, so if you measure the electrical conductivity of pure copper, you get a very high value – third best among materials. But if you add even minuscule amounts of iron to your pure copper, the conductivity drops like a rock. I'm talking orders of magnitude decreases in Cu conductivity resulting from a little dissolved iron. This dramatic effect was the bane of my existence for three years of my graduate school career (it's a long and very sad story that left me crumpled in the corner of a dark lab, reciting the Cars' "You Might Think" lyrics to my small collection of worthless nanoscale ternary alloys… *oh I think that you're wild…and so-o uniquely styled…you might think I'm crazy, but all I want is you…*). Emotional distress and mild delirium aside, the fact that tiny amounts of dissolved impurities have such enormous effects on properties is a pretty interesting materials phenomenon. Speaking of dissolved impurities, let's talk **solid-state solubility** for a moment. I love the way this topic connects back to atomic scale characteristics and to information from the periodic table. Did you think you could look at a periodic table, read off things like electronegativity, atomic radius, crystal structure and valence, and then predict how well elements will get along with each other in the solid state? Very cool.

Line defects (2D), or **dislocations,** are discussed next in the reading. As imperfections go, dislocations are definitely my favorite. Give me a chunk of copper loaded with dislocations, and I'm in heaven. You can't see these defects by eye, or even with optical microscopes, but they are present in large amounts in commercial materials. Hey, here's a riddle for you to share with your friends and family: I am easy to create but difficult to destroy. I form while my surroundings deform. I make metals both weaker and stronger. What am I? A dislocation! Okay, that was perhaps the worst riddle ever. My apologies. Anyway, the thing to remember about dislocations is that (1) they are created when we "cold work", or strain harden, metals, (2) their movement is responsible for the plastic deformation, or "slip", that occurs in metals when we apply a stress, and (3) they interact with each other, and with other types of defects. If you can get a handle on how dislocations interact with point defects (e.g., solute atoms such as Zn in Cu alloys), other dislocations, grain boundaries, and volume defects (e.g., precipitates in a metal), you will be able to control the properties of alloys in amazing ways. You'll be able to strengthen or weaken metals at will. Yes, indeed. More on this later.

Surface (planar, 2D). Grain boundaries are surface defects separate different crystal orientations in a polycrystalline solid, and they can affect properties by interacting with dislocations and messing with diffusion rates in the solid. I make the distinction between grain boundaries and phase boundaries. Phase boundaries act similarly to grain boundaries in terms of their interaction with dislocations, but sometimes we can have two phases (with boundaries in between) that stack up to create a single grain. Does grain size matter? Why yes it does! What happens to yield strength when we decrease the grain size? It increases according to the Hall-Petch equation:

$$\sigma_y = \sigma_o + \frac{k_y}{\sqrt{d}}$$

where σ_y is the yield stress, σ_o is a materials constant for the starting stress for dislocation movement (or the resistance of the lattice to dislocation motion), k_y is a material constant, and d is the average grain diameter. Increasing the strength of materials by shrinking the grain size was a hot topic in the early days of nanoscale materials research. It was all the rage, in fact. Back in the day, if you busied yourself with the creation of new alloys with nanoscale grains, you were invited to all the great mat sci parties. I'll never forget the time Professor Van Vlack set up a transmission electron microscope and x-ray diffractometer in his backyard, so the gang could grill burgers and play bocce ball while guessing space group symmetries of unknown materials based on nothing more than Kijuchi lines or spot patterns. That was freakin' awesome.

Volume defects (3D). Volume imperfections include things like pores, voids, cracks, precipitates, and inclusions. It probably seems obvious that things like cracks and pores can affect material properties, but the extent to which a given size of volume defect such as a pore depends on the fracture toughness of the material. Metals can deal with pores and cracks much more effectively than ceramics and glasses. Think about it… if you put a dent in your car door, you're not worried that the thing will crack in half while you're driving down the road. But what if you get a small chip or crack in your car window. Big trouble. As another example, think about how you go about cutting glass. All you need to do is introduce a volume defect in the form of a "score," or scratch, and the glass pane will fracture along your line.

Unfortunately, ceramics and glasses – and to a lesser extent, brittle metals – are highly susceptible to premature failure as a result of *internal* volume defects (e.g., pores, voids, and inclusions). Thankfully, we can use nondestructive testing methods, such as ultrasound and x-ray, to detect and characterize volume defects in critical components.

Chapter 5 – Diffusion

Shoot, I forgot to write a Stolk's Take on the solid-state diffusion topic. Sorry. But let's face it, the diffusion chapter is fairly straightforward, so I can probably summarize diffusion with a few key points.

- Diffusion coefficient – What factors affect diffusivity (or diffusion coefficients)? If we look at the equation (which has an Arrhenius form), we can quickly identify the things that matter to diffusivity: (1) temperature, (2) activation energy for diffusion, aka the energy barrier, for the diffusing species in the host lattice (3) a pre-exponential constant that depends on the material system (look this up in a table).
- Diffusion mechanisms. You need to consider the different paths atoms can take through different solids, and the associated energy barriers. What paths are available for atomic motion in solids? Are we talking about self-diffusion or impurity diffusion? Are we dealing with small atoms that move from interstitial site to interstitial site, or are we talking about large atoms that require vacancies for movement? Do atoms move through the bulk of the grains, or along grain boundaries or dislocations? Which paths offer the easiest solid-state diffusion, and which require more energy?
- Steady-state diffusion (Fick's first law). What drives steady-state diffusion? In what applications do we see steady-state diffusion – can you think of any examples where this equation might be useful?
- Nonsteady-state diffusion (Fick's second law). Compared to steady-state diffusion, non-steady state diffusion is a lot more common and thus more important to materials science work. Unfortunately, it's also a lot more challenging to calculate different scenarios, given the partial differential equation expression and some crazy solutions to the equation with certain boundary conditions. Try to get a handle on the basics, e.g, how do various factors (temperature, time, concentration, activation energy) affect concentration profiles of diffusing species in host lattices? If you can sketch out what you might expect to see as a function of time and temperature for a given diffusing species, you'll be well on your way.

Atoms move around within solids. Got it. Weakly bonded atoms move more easily. Got it. Atoms move more at higher temperatures. Got it. Smaller interstitial atoms move more easily than larger substitutional atoms. Got it. Grain boundaries and dislocations provide fast diffusion paths. Got it. There are not too many confusing concepts here, and just a few key equations that are useful when calculating diffusivities, concentrations of diffusing species, and diffusion distances. But if you want to test your skill at applying concepts in diffusion, give the textbook problems shown below a try. When you work through the practice problems, consider how the concepts may apply to your Part II project. You're your processing technique provide for solid state atomic motion? How might your processing parameters or other experimental variables affect the rates of atomic motion?

P R O B L E M S

Textbook Problems: Imperfections in Solids

1. Askeland 4-67. Why is most "gold" or "silver" jewelry made out of gold or silver alloyed with copper, i.e, what advantages does copper offer?

2. Solid state solubility. Of the elements in the chart below, name those that would form each of the following relationships with copper (non-metals only have atomic radii listed):

    a. Substitutional solid solution with complete solubility
    b. Substitutional solid solution of incomplete solubility
    c. An interstitial solid solution

Element	Atomic Radius (nm)	Crystal Structure	Electronegativity	Valence
Cu	0.1278	FCC	1.9	+2
C	0.071			
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Pt	0.1387	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

3. Vacancies. Calculate the fraction of atom sites that are vacant for pure lead at room temperature (25 °C) and at 310 °C (just below its melting temperature). The activation energy for vacancy formation is about 53 kJ/mole. How do you think the difference in the fraction of vacant sites will affect self-diffusion (diffusion of the atoms within their own crystal)?

4. Strain fields around dislocations. Sketch the distortion of a crystal lattice around an edge dislocation, and show the preferred regions for (i) large substitutional atoms, (ii) small substitutional atoms, and (iii) interstitial atoms. HINT: Determine the type of distortion (tension or compression) that the large and small substitutional atoms will have on a perfect lattice, then think of how the distortion around a dislocation could best be balanced or relieved by the distortion caused by the substitutional atoms.

Open-Ended Problem: Imperfections in Solids

1. Askeland Problems 2-38 and 21-31. *NOTE: Only one answer is required, as they are very similar problems.*
    (2-38) Turbine blades used in jet engines can be made from such materials as nickel-based superalloys. We can, in principle, even use ceramic materials such as zirconia or other alloys based on steels. In some cases, the blades also may have to be coated with a thermal barrier coating (TBC) to minimize exposure of the blade material to high temperatures. What design parameters would you consider in selecting a material for the turbine blade and for the coating that would work successfully in a turbine engine? Note that different parts of the engine are exposed to different temperatures, and not all blades are exposed to relatively high temperatures. What problems might occur? Consider the factors such as temperature and humidity in the environment that the turbine blades must function.

    (21-31) What design constraints exist in selecting materials for a turbine blade for a jet engine that is capable of operating at high temperatures?

Textbook Problems: Diffusion

1. Let's harden some steel by adding carbon near the surface! A carburizing process is carried out on a 0.10% C steel by introducing 1.0% C at the surface at 980 °C. At this temperature, the iron has a face-centered cubic (fcc) crystal structure. Calculate the carbon content at 0.01 cm, 0.05 cm, and 0.10 cm beneath the surface after 1 h, and plot these values on a graph of carbon composition versus position (distance into the steel). Assume that the carbon content at the surface remains constant.

2. Diffusivity. Values for the diffusion of carbon in bcc and fcc iron are given in the following table:

Materials	D_o (cm²/sec)	Q_d (kJ/mole)
C in bcc Fe	0.0079	83
C in fcc Fe	0.21	141

   a. Calculate the diffusion coefficients for C in both fcc and bcc iron at 900 °C.
   b. Explain why you think the values are different.

3. Askeland Problem 5-38. Using data on diffusion coefficients of different ions in oxides (Figure 5-21 in Askeland), calculate the activation energy of diffusion of K ions in beta alumina.

   Hint: Use the slope of the line.

   Why would anyone care about diffusion of ions in alumina? Materials such as beta alumina show rapid transport of ions and have been considered for batteries based on sodium and sulfur.
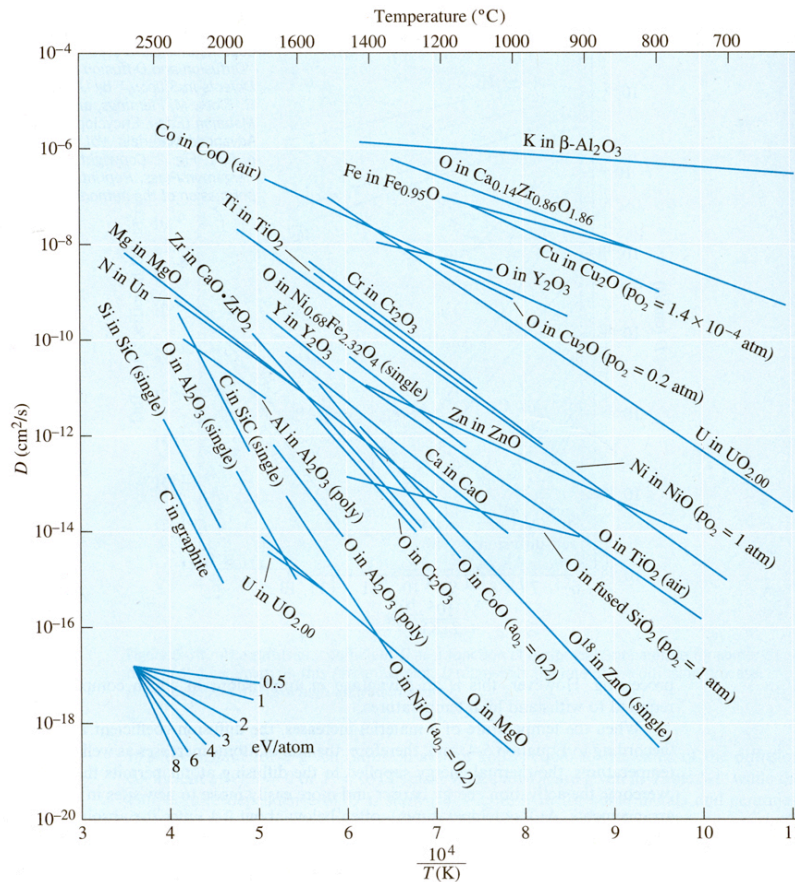
Figure 5-21   Diffusion coefficients of ions in different oxides. (*Source: Adapted from* Physical Ceramics: Principles for Ceramic Science and Engineering, *by Y.M. Chiang, D. Birnie, and W.D. Kingery, Fig. 3-1. Copyright © 1997 John Wiley & Sons. Adapted with permission.*)