HOMEWORK 3.

P R O J E C T   W O R K

DUE DATE: Ongoing

By now, your team has likely developed a detailed testing approach, set up some experiments, and perhaps even collected some laboratory data on your materials. This week, you will continue your materials research and your experimentation, and hopefully make some good progress toward answering questions about your consumer product's materials, properties, and impacts. As I mentioned last week, it is okay to use project time to explore different testing approaches, but try to use specific goals to guide your materials science experiments: if you run a test, do it because you believe it could give you relevant data for your analysis. Try analyzing your data and synthesizing your evidence as you go. This will highlight missing pieces of your analysis, bring important questions to the forefront early in the process, and lower the anxiety as the poster deadline approaches.

This week's readings and exam are related to the chemistry, structure, and bonding of the material(s) used in your consumer product. The big questions we hope to answer are:

What's the chemical composition, i.e., what atoms, ions, or molecules make up your material?
How do the atoms, ions, and molecules interact with each other (bonding)?
How are the atoms, ions, and molecules arranged?
What does any of this have to do with the various properties we observe or measure?

M A T E R I A L S   S C I E N C E   R E A D I N G S

DUE DATE: Monday, September 22

1. **Atomic structure and bonding**. Callister Chapter 2 (*Atomic Structure and Interatomic Bonding*) or Ashby Engineering Materials 1, Chapter 4 (*Bonding between Atoms*). This chapter will be a lot of chemistry review for most of you, but it may include some interesting solid state material science angles that you haven't seen in the past. Worth a quick read, since you'll be connecting properties to bonding in your materials.

2. **Crystallography.** Callister Chapter 3 (*The Structure of Crystalline Solids*) or Ashby Engineering Materials 1, Chapter 5 (*Packing of Atoms in Solids*). Look through the chapter, but *don't get too bogged down in the details*. There's a lot of information here that may or may not be useful to your project work. Remember that the goal here is to develop your knowledge of the connections among material composition/structure, properties, and performance in the materials used in your consumer products; so look for ways to connect the concepts in this chapter with the materials in your consumer products.

3. **Polymer structures**. Callister Chapter 14 (*Polymer Structures*) or Ashby Engineering Materials 2, Chapter 22 (*The Structure of Polymers)*. This chapter deals with polymeric materials, which are quite a bit different than the metallic materials discussed in the "crystalline solids" readings. Since most of you are focused on polymer structures for your project work, this chapter will be much more relevant than the readings on crystal structures of metals.

4. Look over the brief "Stolk's Take on the MatSci Readings" later in this document... and love it (or not).

STOLK'S TAKE ON THE MATSCI READINGS:

Chapter 2 – Atomic Structure and Bonding. Atoms, ions, and molecules – now we're talking. Or, as the Doobie Brothers like to say, we're "Takin' it to the Streets" (the "streets" in this case being the atomic-scale characteristics of materials). Chapter 2 begins with a review of concepts you've probably seen before, so I'm not going to spend time discussing atomic models, quantum numbers, and electron configurations here. The Doobie Brothers are not fans of this sort of review, and since I model all of my behaviors after the Doobie Brothers, neither am I.

Chapter 2 starts to get interesting with the discussion of bonding, for it is here that we begin to forge some links between atomic-scale characteristics and the physical properties of materials. Check out the force and energy versus interatomic separation curves, for example. With these simple graphs, we can illustrate the energy or force required to separate atoms by a certain distance (slope of force curve is related to stiffness or Young's modulus); the bonding energy at the equilibrium atomic spacing (depth of the energy well is related to melting temperature); and the amount a material expands upon heating or contracts upon cooling (width of the energy well relates to thermal expansion). Yes, indeed, you can capture a lot of material properties with this graph! Try comparing a few of the materials used in your consumer products by sketching energy versus interatomic spacing curves for each material on the same set of axes. To add a little excitement, try humming the tune of Terence Trent D'Arby's "Wishing Well" while you're doing this.

When we're considering bonding in materials, we need to go a bit beyond the interactions between two individual atoms. Bonding strength is important for understanding material properties, but so is the **bonding type** (covalent, ionic, metallic, and secondary). These different bond types can provide for some very different arrangements of atoms in 3D space (structure), and some very different responses when we start to apply some energy to the atoms. For example, let's compare a substance with strong ionic bonding, like NaCl (3.3 eV/atom), to a substance with about the same strength of metallic bond, such as aluminum (3.4 eV/atom). Do these materials behave similarly? Not on your life. You can break the strong ionic bonds in salt pretty easily, right? Go ahead and try it. Pour out some salt on a tabletop and smash it with your spoon or fork. Note that what you're doing is breaking billions and billions of bonds. Now imagine doing this with aluminum. Sorry, but finely powdered aluminum has been known to spontaneously combust and start massive fires, so we don't tend to keep it in our salt shakers. It doesn't taste all that great on food, either. Not good for the brain, either. This ability of aluminum to react with air is related to its chemical properties, of course. Aluminum has an enormous affinity for oxygen, and it would much rather form covalent bonds with oxygen (Al_2O_3) than hang out with its own kind. But back to our powder smashing. Think you can break millions of Al bonds in the same way you can break NaCl bonds? What would happen when you pound on Al powder, or any other metal for that matter, with your spoon or fork? Could you point to any evidence of broken bonds? What's going on here?

While we're on the topic of bonding, let's talk about diamonds. Paul Simon likes diamonds on the soles of his shoes (I'm told it helps him lose those walking blues). I prefer them in my saw blades. Why? Just take a look at the bonding energy of diamond: an enormous 8.8 eV/atom! This makes diamond strong and hard, and able to act as the aggressor when it comes to interacting with metals or just about any other material. Diamond grinding wheels are used to sharpen extremely hard sapphire (Al_2O_3) and zirconia (ZrO_2) knife blades, and the diamond saw blades we use in the materials lab saws are good for sectioning just about anything. But ponder this for a moment: the carbon-carbon covalent bonds in diamond are present to a slightly lesser extent in graphite, and these same bonds dominate the bonding along the "backbone" of most synthetic (e.g., polypropylene, nylon, polystyrene) and natural (e.g., silk, leather, cotton) polymers. These materials much weaker and softer than diamond, of course, so this tells us that we need to think beyond the covalent bonds along the polymer chains to the bonds that exist *between* chains.

In most polymers, **secondary bonds** hold the long chains together in a solid (although some polymers have stronger covalent bond **crosslinks**). The strength of these secondary bonds depends a lot on the degree of **polarity** in the molecules, with highly polar molecules such as amides providing stronger interaction between chains than we find for non-polar molecules. But as I mentioned in last week's homework, polymer behavior is complex, and it depends on more than just the type of bonding. We also need to consider the chain shape, presence of different chemical groups within the chain or in side groups, molecular weight, degree of crystallinity, etc. It turns out that depending on the polymer chemistry, bonding, and chain configuration, polymeric materials may wind up completely amorphous (or "glassy"), semicrystalline (some amorphous and some ordered regions), or nearly all crystalline. Understanding the degree of crystallinity in a polymer can help you explain properties ranging from density to mechanical strength to optical transparency. And you can determine if a polymer is crystalline or amorphous using some simple thermal analysis, such as differential scanning calorimetry (DSC). If it shows a distinct melting point, it's likely to be highly crystalline. No melting point? Then it's probably amorphous. Somewhere in between? Semicrystalline.

While we're on the topic of experimental analysis, I think it's about time we discussed some of our wonderful materials lab equipment. One of the interesting aspects of atoms and molecules is that they all have characteristics that make them identifiable. That's right, they all have distinct "fingerprints" that we can see with our laboratory instruments, but we need to be clever enough to know which analytical technique to select, and how to analyze the data. For example, we know that different elements have electrons moving in orbitals of varying energy, and we know that through **absorption** and **emission** of energy, electrons can move from one orbital to another. Imagine we blast a solid sample with enough energy (with, say, an electron beam or some x-rays) to cause a bunch of electrons in the atoms in the material to get excited (absorption). Those excited electrons will want to quickly dump this excess energy and return to their equilibrium or lowest-energy state, and they can accomplish this energy dump by emitting the absorbed energy as x-rays. But here's the kicker: all those x-rays coming off the sample will have energy values that correspond exactly to certain transitions in the atoms from our material. If we use an x-ray detector to collect the x-rays and a computer system to sort the x-ray energies, as in our energy dispersive x-ray spectrometer (EDS) and x-ray fluorescence (XRF) systems, we can determine which elements are present, and in what amounts. This works great for detecting particular elements, but what about groups of molecules like those found in polymers and other organic materials? Molecules tend to absorb energy in the infrared range through vibration, and different types of bonds (e.g., C=O vs. C-H) require different amounts of energy to vibrate. A Fourier transform infrared (FTIR) spectrometer blasts samples with a range of IR wavelengths and shows which energies the material absorbs, and which simply pass through the material. With this absorption versus IR energy (or wavelength or wave number) spectrum, we can match our unknown organic material to spectra from known materials compiled in a database. Voila! We now have an analytical method that may help us determine why 3M™ Post-it® notes are stickier than off-brand post-it notes.

Chapter 3 – Crystallography. If you made it through Chapter 3 without falling asleep or refueling on sugary snacks, give yourself a pat on the back. If you heard an angelic choir singing while you navigated Chapter 3, you may want to consider checking yourself into a hospital. In terms of pure entertainment value, this may be the worst chapter of the entire textbook. It's what I'd call a building block chapter – one that contains a bunch of detailed information that seems like it'll be important at some point, but that doesn't have obvious practical significance now. Instead of engineering applications to chew on, you get a mouthful of terminology – Bravais lattices, Miller indices, crystallographic directions and planes, lattice parameters, unit cells, coordination number, atomic packing factor, crystal structures, etc. Why are these things important? First off, these terms give materials science folks a way of communicating with each other. Imagine being a fly on the wall for this conversation:

> Jeong: I'm trying to deposit an epitaxial <100> copper film on a <100> silicon wafer, but the film stress is too high and the films keep failing. I want this layer to be fairly thick, so maintaining ductility is important.
> Pam: You may have too much lattice mismatch between the Cu (100) and the Si (100). Have you tried the Cu <111> orientation?
> Jeong: No, but I'll give it a try. Will the lower surface energy of the Cu(111) cause any problems with deposition?
> Pam: I don't think so, and you'll definitely get a Cu layer with lower stress. But if you have time for more experiments, I've heard that Cu can be successfully grown with the (111), (111), and (001) planes oriented to Si(111), so you may want to give that a try. Can you get your hands on some Si(111) wafers?
> Jeong: Yeah, no problem. Hey, I was also considering molybdenum layers. What do you think?
> Pam: I thought you said you wanted *ductile* films! Moly is bcc, and it has much higher bond energy compared to Cu, so I wouldn't expect a ductile film with that approach. And geez, have you even looked at the lattice parameters for Mo? I think you're going to have a heck of a time getting an epitaxial layer to grow, and you might even see some reactions at the Mo and Si interface. Stick with the fcc metals if you're looking for ductility. And pay attention to those lattice parameters.
> Jeong: Speaking of lattice parameters, do you know that song "You Spin Me Round (Like a Record)" by Dead or Alive? For some reason, that song always of reminds me of thin films research.
> Pam: Yeah, that song is awesome, and I know what you mean about the connection to thin films.

Do materials scientists really converse in this manner? Yes, indeed. Is it disturbing? Yes, indeed. As in any discipline, knowledge of the terminology simply enables people to speak precisely, without having to explain all the little details. Instead of referring to "the plane in the copper structure that is at the top of the unit cell and that has lower planar density, edges equal to the lattice parameter, and higher surface energy," we can simply say "Cu(100)." Do you need to be able to speak like Jeong and Pam by the end of this course? No, but I would very much like you to try using the formal terminology when discussing material structures and properties. Using the terminology in this course won't make you an expert, but I can pretty much guarantee that avoiding the terminology won't help you communicate effectively with materials experts after the course is complete.

Near the end of Chapter 3, we find a few pages on **x-ray diffraction** (XRD). This is a great topic to spend some time understanding. . In fact, **Bragg's law** ($n\lambda = 2d\sin\theta$) makes my top ten list of useful materials science equations. Take a

look at how Bragg's law is used in the determination of lattice parameters and analyzing x-ray diffraction patterns for crystalline substances, and think about how you might use x-ray diffraction to analyze components of your modern artifact. Also, check out the equation that relates interatomic spacing to the lattice parameter and Miller indices, as this is key to connecting the "d" in Bragg's law to planes in specific crystal structures (bcc, fcc, etc.).

Of course, it's important for you to form your own impressions and develop your own views, rather than memorizing and repeating my take on things. Build your understanding by synthesizing all this information in a way that makes sense to you, and that is meaningful to your own context.

P R O B L E M S

Open-ended Problems. Here's a selection of problems that get at conceptual understanding of the atomic bonding and structure readings. These problems require an application of different materials science concepts, and some use of higher-level thinking (e.g., analysis, evaluation, synthesis) about the ideas.

1. (from Askeland's book) Materials such as silicon carbide (SiC) and silicon nitride (Si_3N_4) are used for grinding and polishing applications. Rationalize the choice of these materials for this application (discuss structure-property connections).

2. (from Askeland's book) Would you expect Al_2O_3 or aluminum to have a higher coefficient of thermal expansion? Explain.

3. Consider the following graph of the bond-energy curves for two different materials.
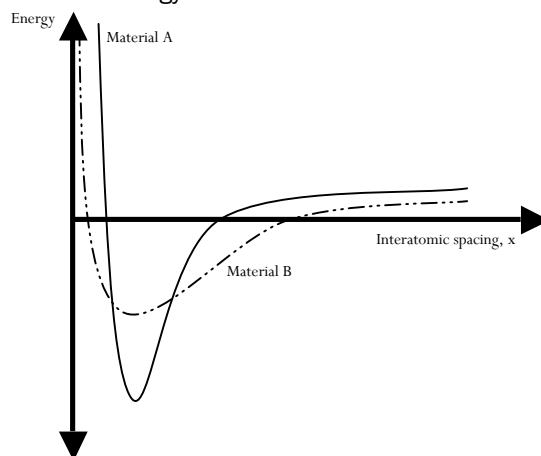
    a. Which of the two materials will have the lowest coefficient of thermal expansion over a given change in temperature? Justify your answer.
    b. Which of the two materials will have a higher melting temperature? Justify your answer.
    c. Which of the two materials will have a higher Young's modulus? Justify your answer.
    d. If Material B is a metal, do you think that Material A is a metal, ceramic, or polymer? Justify your answer.

4. An unforeseeable reaction has just destroyed the metal lining of your high temperature vacuum furnace. You can't afford to purchase a new lining, so you've decided to make a new lining in the Olin shop. The lining is basically a 6-inch metal cube with a wall thickness of 0.125 inches. One problem: you don't know the material used for the furnace lining. You think you can safely assume it's a pure metal, but other than that, you're at a loss.

    To determine the unknown metal, you run a standard x-ray diffraction scan, the results of which are shown in the following figure. Crystallographic planes (hkl) are indexed on the pattern. The copper radiation used in the x-ray diffraction test had a wavelength of 0.1542 nm.
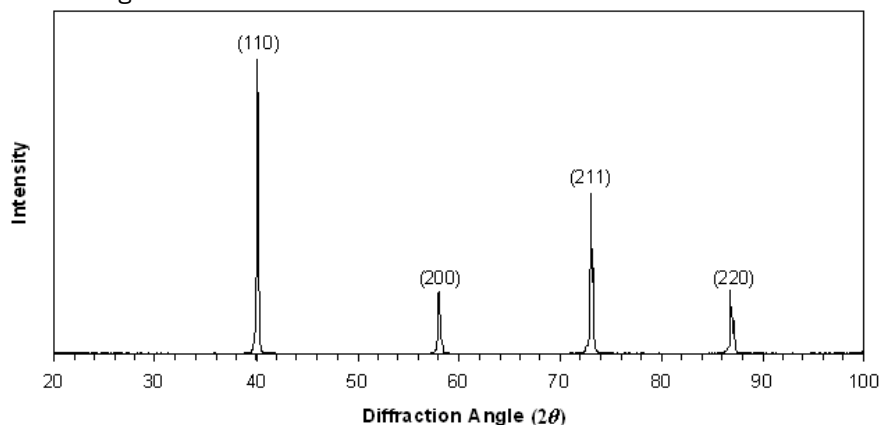
  a. Given the XRD data, what is the likely crystal structure of the unknown metal?

  b. What is the lattice parameter of the unknown metal?

  c. Based on your answers in parts (a) and (b), which of the following materials is the most likely match for the unknown metal?
     i.   Tantalum
     ii. Nickel
     iii. Sodium
     iv. Zirconium
     v.   Tungsten
     vi. Chromium

  d. Do you think you would be able to fabricate the material in the Olin machine shop? Briefly explain your answer.

5. Noncrystalline SiO_2 is optically transparent. Polycrystalline SiO_2 is opaque or translucent. Single crystal SiO_2 is optically transparent. Explain.

Classic Textbook Problems. If you're interested in experiencing materials science in a more conventional form, take a look at these textbook problems on crystallography. If you were in a traditional lecture-based materials science class, you'd have to work a bunch of these problems to show that you understand the ins and outs of atomic arrangements in crystalline solids.

The next few problems won't do much for your critical thinking, but they might address some low level cognitions, such as knowledge acquisition and application. Do these problems if you're looking for a more traditional approach to crystallography topics – classic materials science.

6. (from Askeland's book) Beryllium has a hexagonal crystal structure, with a_o = 0.22858 nm and c_o = 0.35842 nm. The atomic radius is 0.1143 nm, the density is 1.848 g/cm^3, and the atomic weight is 9.01 g/mol. Determine
    a. The number of atoms in each unit cell; and
    b. The packing factor in the unit cell

7. (from Askeland's book) Explain why polycrystalline materials usually exhibit isotropic properties.

8. Crystallographic planes. Sketch an fcc unit cell. Within the unit cell, sketch and label the following:
    a. $(0\,0\,1)$ b. $\left(2\,0\,\overline{1} \right)$ c. $\left[1\,\overline{2}\,0 \right]$

9. Crystallographic planes and directions. Sketch a bcc unit cell. Within the unit cell, sketch and label the following:
    b. $[\,0\,1\,0\,]$ b. $[\,2\,2\,1\,]$ c. $(\,0\,0\,1\,)$

10. Nickel has the fcc structure and a lattice parameter of a = 0.3517 nm.
    a. Determine the atomic radius in nm. Compare this value to that shown in the front of your textbook.
    b. Determine the atomic volume Ω in nm^3 (assume a spherical atom shape).
    c. Determine the density in g/cm^3 and compare this answer to the Ni density value given in the table at the front of your textbook.

11. Sketch an fcc unit cell.
    a. Determine the planar density for the (1 1 1).
    b. Determine the planar density for the (1 1 0).
    c. Determine the linear density for the $\left[0\,1\,\overline{1} \right]$
    d. Determine the linear density for the [1 0 0].
    e. Given the densities you calculated for (a)-(d), which planes and directions would provide the easiest path for edge dislocation motion, or "slip"?