HOMEWORK 7.

PROJECT WORK

By now, most of you have metallic physical artifacts in hand, and you're ready to do some testing and analysis. Your project work this week will likely involve some sample preparation, property testing, and microstructural analysis, and perhaps some additional processing of your alloys. Hopefully, by the end of the week you'll have some laboratory data as well as some cross-sectional samples that you've started to analyze via optical or electron microscopy. Are your test data and microstructural analyses starting to come together? Can you begin to explain **how** your compositional or processing variables are affecting the alloy properties, and **why** the compositional or processing variables are having these effects on your alloys?

READING

This week, I suggest focusing your reading on phase transformations that are relevant to your project experiments. If you chose to process metals by casting, focus your attention on solidification kinetics and thermodynamics. If your metals underwent solid-state phase transformations (e.g. steel forging), then focus on the kinetics and thermodynamics of solid-state reactions in steel alloys.

- **Textbook Reading**

  Focus your reading on sections that help you with your project analyses. Some suggestions are provided below.

  Readings relevant to all teams:

  - o Ashby *Engineering Materials 2*: Chapter 6 (Driving Force for Structural Change)
  - o Ashby *Engineering Materials 2*: Sections 7.4-7.6 (Kinetics 1 - Diffusive Transformations)
  - o Callister: 10.1 – 10.4 (Kinetics of Phase Transformations) and 11.9 (Precipitation hardening)

  Readings relevant to specific teams:

  - o Steel teams. Callister: Sections 10.5 – 10.9, 11.7-11.8, **or** Ashby *Engineering Materials 2*: Chapter 9 (Kinetics 3 - Displacive Transformations)
  - o Casting teams. Ashby *Engineering Materials 2*: Chapter 8 (Kinetics 2 - Nucleation)

- **Key Concepts in Phase Transformations**

  There are a few key concepts in kinetics, nucleation, and growth to consider as you interpret your project results.

  - o Energy is everything! Why do materials change phases? Because the product phase(s) have a lower Gibbs free energy than the parent phases(s). How do we know what phases are lowest energy? The phase diagram is a great place to start – simply find the point of interest on the phase diagram (composition, temperature), and read which phases are supposed to be present under those conditions. Note the emphasis on the "supposed to" here. Phase diagrams typically show *thermodynamic equilibrium* conditions, or what is supposed to happen if the material is able to reach its lowest energy state. But most phase transformations in materials are diffusional reactions, and diffusion takes time. Sometimes a lot of time. Sometimes far more time than we provide.

    Low temperature solid-state reactions, in particular, can be quite sluggish due to slow motion of atoms in the solid state. When the reaction kinetics are slow, a few of different things can happen. First, you could simply wind up with the higher temperature phase(s) showing up in your alloys, even though they are not supposed to.

This happens when the driving force for the phase transformation isn't high enough, i.e., the higher temperature phase(s) are comfortable enough to hang out at lower temperatures. Diamond at room temperature is a good example of this. Second, the high-to-low phase transformation could happen, but the products could show up in an unexpected morphology. Maybe you're expecting to see striped grains, but because the alloy needs more time to diffuse into stripes, it instead forms speckles. Third, you could form entirely different phase(s) via a diffusional reaction. The diffusional formation of "metastable phase(s)" is surprisingly common in alloys: we frequently see this in wrought aluminum alloys, and we can take advantage of these phases to strengthen aluminum alloys. The "aircraft aluminum" alloys, as well as 6061-T6 aluminum, are strong due to the formation of metastable phases. Finally, you could form a metastable phase through a **diffusionless,** or **athermal**, reaction. Diffusionless reactions often form upon fast quenching of a high temperature phase, and they involve an incredibly fast shifting of atoms into a different crystal structure. The most common diffusionless reaction is the formation of martensite during the fast quenching of high temperature (austenite) steel.

o Let's talk casting, or the nucleation and growth of a solid phase from a liquid phase. Your textbooks present a couple of different scenarios for nucleation: homogeneous and heterogeneous. Homogeneous nucleation is about at rare as good Tex-Mex food in Boston, but it is interesting to consider from a theoretical perspective. The equation for Gibbs free energy of homogeneous nucleation has two terms:

$$G = \frac{4\pi}{3}r^3 G_v + 4\pi r^2 \gamma$$

The first term in this equation is the volume of a sphere times the **volume free energy** term. Volume free energy is the difference in Gibbs free energy between the parent (liquid) phase and the product (solid) phase. If your metal is below the melting temperature (or solidification temperature, if you prefer), this volume free energy term is negative. You want negative. You need negative. Without negative changes in Gibbs free energy, nothing's going to happen. The other part of the equation is what I call the **surface energy** term. Surface energy has an important effect in phase changes. I like to consider this as the price you have to pay in order to get a new phase to form. For example, to nucleate some solid in a liquid, as in solidification during casting, you have to create a new solid-liquid interface that was not previously there. This surface has a certain amount of energy associated with it. That means that this term is positive. With one negative and one positive term in this equation, you can imagine a situation in which the surface energy term is higher than the volume free energy term, right? If this is the case, your solid won't nucleate – the price it has to pay is too high. This is why you can have things like "superheated water" or "supercooled metal": the payoff (volume free energy) isn't yet high enough to warrant the cost (surface energy).

o Solidification structures in cast alloys. Not much to discuss here, except that in cast alloys you will typically three solidification zones: the chill zone, the columnar zone, and the equiaxed zone. If you add nucleating agents (aka inoculants), you can reduce the columnar zone and get mostly small equiaxed grains. If you want to make me angry, ask me about the time I spent hours polishing a huge bronze ingot in order to create a cool desk ornament that showed the three solidification zones, only to find that a nucleating agent was used in the metal. Painful memories.
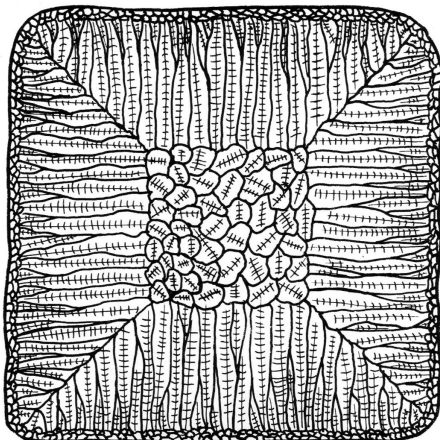

Fig. 1. Schematic cross section of a steel ingot, showing typical macrostructure: an outer chill zone, a columnar zone, and a central equiaxed zone

(image from ASM Handbooks, 8th ed.)

- o   Dendritic growth: What do the dendritic microstructures look like? Like trees, silly. Everybody knows that.[†]

- o   TTT diagrams. Given that most transformations in materials are diffusional reactions, the transformation **time** and transformation **temperature** have dramatic effects on microstructure and properties. Nucleation rate, growth rate, and overall transformation rate are all a function of the transformation temperature, since temperature determines both the driving force for the phase change (how badly a new phase wants to form) and the rates of diffusion (how long it will take for atoms to change from the old phase to the new phase). In general, higher temperatures will give you fewer, larger grains; and lower temperature transformations will provide for more, smaller grains. With more time, comes more diffusion, and this results in stuff either getting larger (if it is stable), or stuff heading toward the more stable state. To turn those fine grains into huge grains, just add time and temperature.

- o   Finally, I feel compelled to say a word or two about supersaturated solid solutions. If you take a high temperature solid solution and rapidly quench it, you can oftentimes "freeze" the higher temperature phase by not allowing sufficient diffusion time for the lower temperature phases to nucleate and grow. But here's where things get interesting. If you want to change the properties of the alloy, you can use time and temperature to encourage the lower temperature phase(s) to form in a specific shape or size or distribution. The best example of this is aluminum age hardening. If you heat certain aluminum alloys to the "solutionizing" temperature to dissolve all of the alloy additions in a single phase (Al) solid solution, you can easily quench the material in water to lock in this phase. But the properties of this solid solution are pretty lousy, so we don't want to stop there. What we'd like is to encourage the formation of tiny little precipitates (which happen to be metastable phases in most Al alloys) that give us an alloy with high strength and hardness, through a process called precipitation hardening, or age hardening. We can do this in one of two ways. The most common approach is called artificial aging, which involves tossing the aluminum in an oven at a specified temperature and for a specified time. Another approach is natural aging – just leave it on a shelf, and your aluminum will change properties over time. Crazy, huh? Almost as crazy as Brad Pitt in *12 Monkeys*.

Brad Pitt, artificial aging:

Brad Pitt, natural aging:
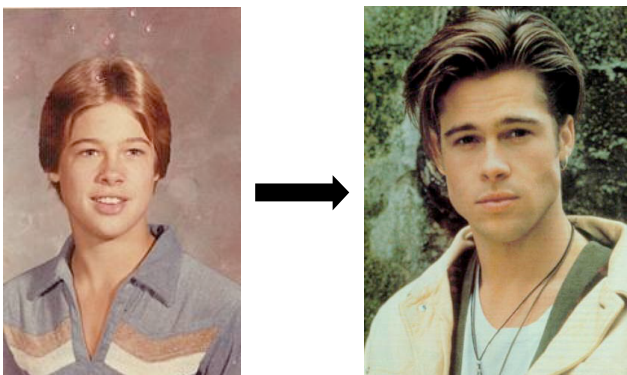
[†] In all honesty, some dendrites look more like brains or snowflakes than trees.

PROBLEMS

1. What roles do nucleation and growth play in determining the properties of the alloy(s) you are studying for your second project? What processing parameters affect the rates of nucleation and growth in your alloy(s)? How does varying these parameters provide for different microstructures in your material(s)?

2. Pure titanium has two allotropic forms: β-Ti (high temperature) and α-Ti (low temperature). For equilibrium heating conditions, the low temperature α phase transforms to the high temperature β phase at 883 °C (1156K). Let's consider what size of a β-Ti nucleus we would have to form in order for it to be stable at a temperature *just above* the transformation temperature.
   a. Calculate the critical radius r* and the activation free energy ΔG* for a body-centered cubic beta phase nucleus in a superheated alpha titanium matrix at 1165 K. Assume a spherical nucleus (homogeneous nucleation), ΔG_v (1165 K) = -0.095 J/m³, and σ_{sl} = 0.2 J/m².
   b. Given your answer in part (a), explain why nucleation of the beta phase is unlikely to occur if you heat the titanium to the 1165 K temperature. What can you do to make nucleation more likely to occur?

3. For inspiration only… look at these cool microstructures from ASM Handbook!
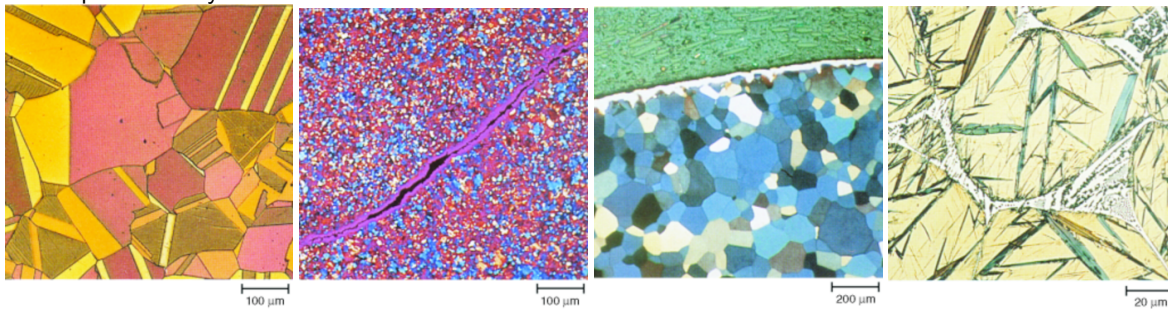
Pretty cool, huh? Why don't my microstructures ever turn out looking this awesome?

4. The following two micrographs are from a hypoeutectic (less than 12.6% Si) aluminum-silicon alloy that was melted and poured into two different molds – a sand mold, and a metallic mold.
   a. Which photo – left or right – is from the sample that cooled in the metallic mold? How do you know?
   b. Based on the microstructure, estimate the composition of the Al-Si alloy. The phase diagram is provided below for reference.
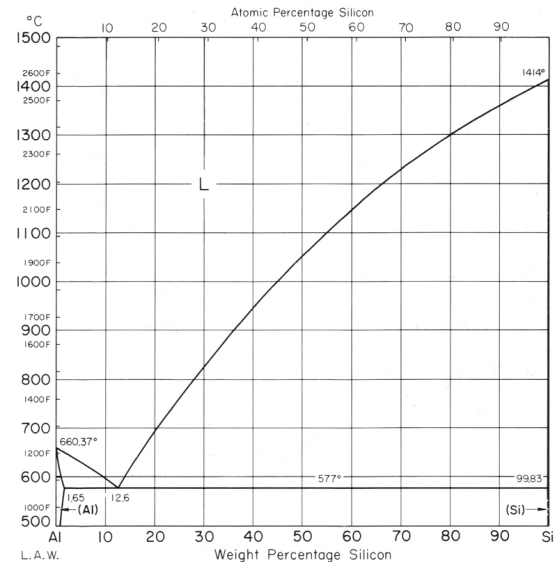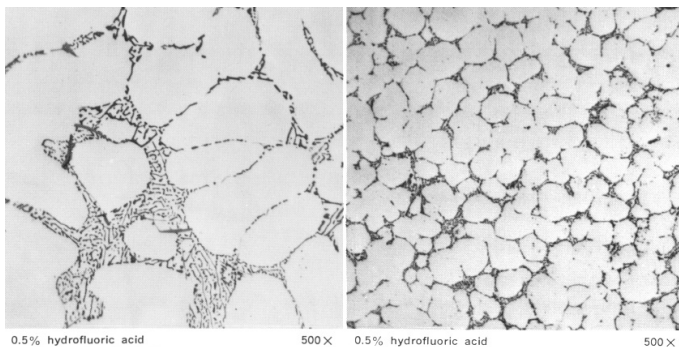
5. Pure titanium undergoes a crystallographic transformation at 883 °C. Below this temperature, pure titanium has a hexagonal close packed structure known as alpha (α); above it, titanium exists as the body centered cubic beta (β) phase. Addition of certain alloying elements to pure titanium results in significant changes in the phase transformation temperatures and in the stability of the alpha and beta phases. The most common titanium alloy is Ti-6-4, which is composed of titanium with 6 weight percent aluminum and 4 weight percent vanadium. A schematic, pseudo-binary phase diagram for Ti-Al-V alloys is shown below.

    c.   Based on the schematic Ti-Al-V phase diagram, what phases do you expect to see in room temperature alloys of Ti-6Al-4V?

    d.   In the four boxes, sketch the expected microstructure in the Ti-6Al-4V alloy. Label the phases in your sketches. Assume furnace (very slow) cooling.

    e.   Would the Ti-6Al-4V alloy provide any property advantages over single-phase alpha alloys? Briefly explain your answer.