SOLUTIONS

UNIVERSITY OF CALIFORNIA
College of Engineering
Department of Materials Science & Engineering
Professor R. Gronsky Fall Semester 2014

Engineering 45

Midterm 03

This is a 50 minute examination with 4 equally weighted problems.

Instructions

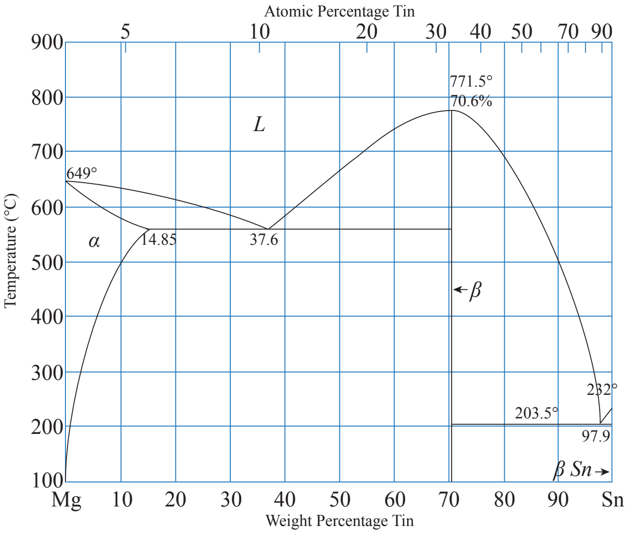
WAIT! Do not open these pages until “START” is announced.

While you are waiting please
PRINT your name **clearly** and **legibly** at the top of this page,
SILENCE your mobile phones and other electronic devices,
STORE all belongings under your seat and out of sight, and
NOTE the following rules.

ONLY writing instruments / eraser / straightedge are allowed.
Calculators are NOT allowed.
Questions during the exam are NOT allowed.
You ARE held to your Honor Code!

Problem (1)

A start-up company in Palo Alto named *CalNESIUM*® has just won a multi-million-dollar contract to design a high-tech wheelchair with superior properties and ultra-low weight, based on alloying magnesium ($Z = 12$, $\rho = 1.74$ g/cm^3) with tin ($Z = 50$, $\rho = 7.29$ g/cm^3) for higher strength. You are hired as Senior Design Engineer on the project, and you begin your analysis, as always, by consulting the equilibrium phase diagram provided by ASM (*Metals Handbook*, Volume 8) and reproduced here.



(**a**) Your supervisor, whose MBA includes no technical training, asks you to submit a written report, due tomorrow, on what is meant by a "eutectic microstructure," something she'd read about in the *Wall Street Journal*, and if it can be obtained in this alloy system. What do you write?

(**b**) A widely-read junior colleague mentions over a coffee break that she remembers a paper in *Acta Materialia* reporting on a very brittle intermetallic compound with stoichiometry Mg_2Sn that might be found in this binary system. Do you include this in your report to your supervisor? Explain.

(**c**) and (**d**) After a more detailed reading of her *Wall Street Journal* article, your supervisor asks you to submit a separate written report, due tomorrow, comparing and contrasting "hypoeutectic" and "hypereutectic" alloys as candidates for your wheelchair design. What do you write in your report?

(**e**) After reading your expertly-crafted reports, your supervisor concedes that she should have just asked you for your opinion on the best way to achieve *CalNESIUM*'s design goals. She sheepishly requests one more report from you, detailing your recommendations, which she promised to honor, "without wasting any more of your time." What do you write?

Answer (1)

(a) Your report should be a pedagogical one, reading as follows. The term "eutectic" is derived from the Greek word for "**easily melted.**" **A "eutectic microstructure" is an intergrowth of two phases resulting from solidification of an alloy with a specific composition having a melting point lower than any of its components.** For this reason, it is a preferred composition for shape-casting, so that the liquid phase can penetrate all parts of a mold with complex shape before it cools enough to solidify. The eutectic microstructure has a very characteristic appearance, most often **alternating lamellae** of the constituent phases, that sets it apart in any metallographic examination.

In the Mg-Sn alloy system there are **two eutectic reactions**, one at ≈560°, where liquid of 37.6 wt% Sn solidifies into α phase of 14.85 wt% Sn + β phase of 70.6 wt% Sn, and the other at ≈204°, where liquid of 97.9 wt% Sn solidifies into β phase of 70.6 wt% Sn and the β-tin phase of ≈99 wt% Sn.

(b) **Yes**; this must be included in your report because the Mg_2Sn phase with 33.3 at% Sn (70.6 wt% Sn), is the β phase, which appears in **both** eutectics. This phase is an ordered intermetallic compound with the highest melting point on the phase diagram, signifying strong bonding, a potential reason for its brittleness reported in the scientific literature. Consequently, if brittleness is to be avoided in the wheelchair frame, **microstructural control is needed to minimize the volume fraction of β phase**.

Answer (1) continued

(c) < combined with (d) >

(d) Compared to the eutectic composition, **hypoeutectic compositions are solute-lean and hypereutectic compositions are solute-rich. Both have pro eutectic constituents appearing in the microstructure in addition to the lamellar eutectic product.**
For the eutectic isotherm at ≈560°C, a hypoeutectic alloy will contain proeutectic α phase, while a hypereutectic alloy will contain proeutectic β phase.
For the eutectic isotherm at ≈204°C, a hypoeutectic alloy will contain proeutectic β phase, while a hypereutectic alloy will contain proeutectic β-tin phase.
One important consideration of a proeutectic constituent in the Mg-Sn system is mitigating the brittleness associated with the Mg_2Sn β phase, so **any proeutectic β phase should be avoided,** especially because it is most **likely to nucleate at grain boundaries, leading to intergranular fracture.**

(e) Recognizing that the primary design objective of this project is **ultra-low weight**, the alloy chosen for the wheelchair frame **should be Mg-rich**. Because the ≈560° eutectic product will contain continuous films of β phase, **the eutectic should be avoided**, making a **dilute alloy** (less than 14.85 wt% Sn) the **preferred** choice. On these guidelines, the following protocol is offered.

Synthesize an alloy of Mg-5 wt%Sn and solutionize at 550°C.

Quench to room temperature to generate a supersaturated solid solution of α phase.

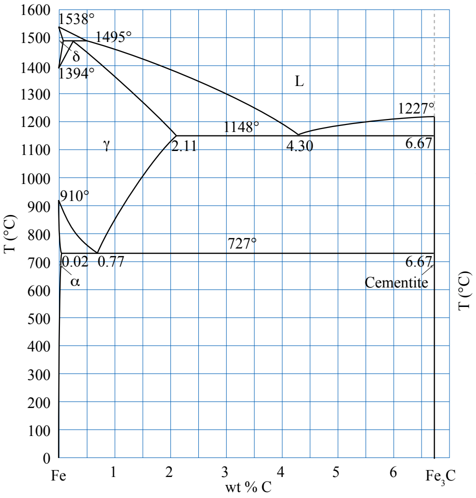
Age at 200°C to generate a fine dispersion of β phase in the α phase matrix.

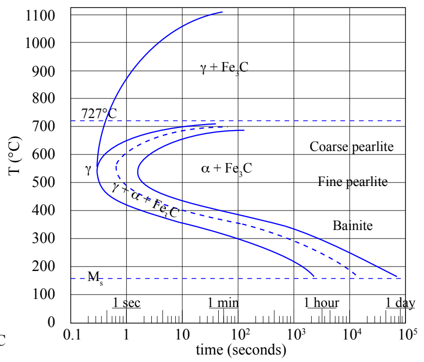
The result is an ultra low weight product with superior strength generated by precipitation hardening.

Problem (2)

(**a**) The TTT curve at right is derived from isothermal treatments of a 2.0 wt% C steel used to make kitchen knives. You are responsible for design an austenitizing treatment for a large order of new blades that must be shipped for the Thanksgiving Holiday season, so time is of the essence. What temperature do you choose? Explain.

(**b**) Your company traditionally makes kitchen knives by isothermal aging at 650°C. The lead technician on the job, who was never trained in TTT curves, anxiously asks you how long it will take to "finish the precipitation of proeutectoid cementite" at this temperature. What do you answer?





(**c**) Hearing your response, the same lead technician asks if isothermal aging at 910°C would speed up the transformation to proeutectoid cementite, causing it to finish more quickly. What do you say?

(**d**) A batch of old meat cleavers from the local butcher ship is returned to the company for reconditioning. The blades are austenitized, instantaneously quenched to 300°C, and held for one hour. Does this protocol avoid quench cracking of such large blades? Explain.

(**e**) Is it feasible to expect a 100% martensitic microstructure in a batch of carving knives made from this steel? Explain.

Answer (2)

(a) **Austenitizing temperature = 1150°C**. This is an especially delicate heat treatment because at 2 wt% carbon, the solvus temperature for the appearance of cementite lies at ≈1130°C, and the solidus temperature for the appearance of liquid phase lies at ≈1160°C. The choice of an austenitizing temperature must thread this needle; too low a temperature and you'll precipitate cementite, too high a temperature and you'll melt your knives!

(b) "**I don't know.**" The TTT curve for isothermal aging at 650°C shows that proeutectoid cementite will **start** to form in less that half a second, but there is **no** "finish" time for its generation. So you cannot say when the precipitation of cementite will "finish." Austenite and cementite remain in equilibrium until the next curve crossed during isothermal aging at 650°C, when, at ≈ 1second, austenite begins to decompose into ferrite and cementite, in a coarse pearlite morphology.

(c) "**That's right!**" At 910°C, diffusion is much more rapid than at 650°C, so proeutectoid cementite will certainly form more rapidly. However, there are no other reactions occurring at 910°C. The phase diagram confirms that austenite and cementite are in equilibrium at that temperature, and remain so indefinitely. Additional cooling is necessary, and **how** that cooling occurs in very important! The reason our company uses 650°C for its thermal treatment is to generate a **pearlitic** microstructure.

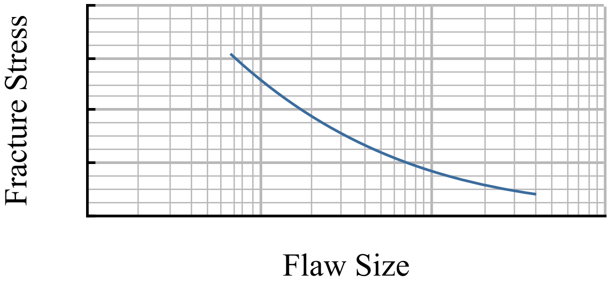
Answer (2) continued

(d) **Yes**. This is the treatment we discussed in lecture known as "**austempering**." Because there is no large temperature differential between surface and interior regions of the knife blades during the transformation to martensite, quench-cracking is avoided. In the case, the resulting microstructure is bainitic, offering a good combination of strength and toughness.

(e) **No**. The only way to avoid the generation of ferrite and cementite is to quench instantaneously to room temperature in less than 0.3 seconds. For large carving knives, this could be very difficult. But there is a more significant clue in the TTT plot. It labels the martensite "start" temperature at about 160°C, but there is **no indication of a martensite "finish" temperature**. Consequently it can be expected that no matter how rapid the quench, there will be **retained austenite** at room temperature.

Problem (3)

Sometimes the most significant property associated with engineering materials is their “damage tolerance,” or ability to bear loads even when they contain cracks and/or internal fissures. This realization led to the development of a sub-discipline known as “fracture mechanics,” with its definition of “fracture toughness.” Each material has a “critical stress intensity factor” (K_{IC}) under mode I (uniaxial) loading, relating the amount of stress needed to cause catastrophic failure (σ_f) in a material suffering a surface crack of length (a),



$$K_{IC} = Y\sigma_f\sqrt{\pi a},$$

where Y is a geometrical constant of order 1. In the language of fracture mechanics, materials with a high K_{IC} possess high fracture toughness, and are therefore more damage tolerant.

(**a**) How is K_{IC} determined? Explain.

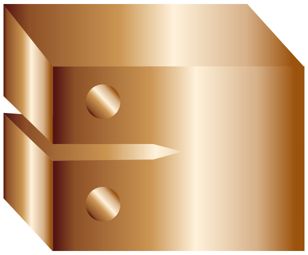
(**b**) Steels used in turbine rotor applications have K_{IC} values above 200 MPa√m, while crystalline alumina has a K_{IC} value less than 5. Using your knowledge of the microstructural mechanisms of deformation under load, how would you rationalize this large difference in fracture toughness?

(**c**) Soda glass (Na_2O-SiO_2) suffers from especially low fracture toughness, $K_{IC} < 1$, and can fail catastrophically under NO load, when it experiences something called “thermal shock.” Explain.

(**d**) The fracture toughness of ceramics is sometimes increased by the presence of microcracks. Is the same true for metals? Explain.

(**e**) From the *Wikipedia* entry for “stress intensity factor” comes the following quotation: “Typically, if a crack can be seen it is very close to the critical stress state predicted by the stress intensity factor.” Critique this statement from the perspective of a design engineer.

Answer (3)



(a) The critical stress intensity factor K_{IC} is determined **empirically,** by measuring the uniaxial tensile load (mode I) that causes failure of a specimen with **known crack size** (a). From the **known specimen geometry**, the fracture stress (σ_f) is calculated, and the equation given in the problem statement is used to calculate K_{IC}. A common sample geometry is the one shown on the worksheet page and reproduced here. Pins through those holes are used to pull the sample in tension along the vertical direction in the figure, while the crack grows left-to-right.

(b) Steel deforms by **dislocation motion**, allowing for appreciable **accommodation** of stress and an associated **blunting** of any cracks in damaged materials. Steels are therefore more tolerant of damage because crack growth is delayed by **deformation of the material around the crack tip**. Alumina has **no** such dislocation motion, consequently there is **no accommodation of stress at the crack tip**, resulting in rapid crack growth, leading to catastrophic failure.

Answer (3) continued

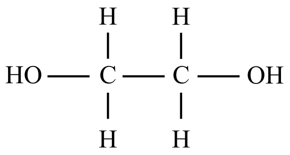
(c) Thermal shock results from a combination of two components: **thermal conductivity** and **thermal expansion**. When subjected to a **rapid** ("shock") **change in temperature**, a material with poor thermal conductivity establishes a **steep temperature gradient**. The gradient causes **differential thermal expansion**, a portion of material undergoing **expansion at high temperature**, and another portion of the material undergoing **contraction at low temperature**. Because these two effects compete against one another within a monolithic solid, an **effective stress** is generated, resulting in failure when a tensile component of that stress acts to open pre-existing surface flaws. In glasses with well-known surface flaws, the most serious form of thermal shock occurs when the surface is placed in tension. This would result when a hot glass is rapidly cooled.

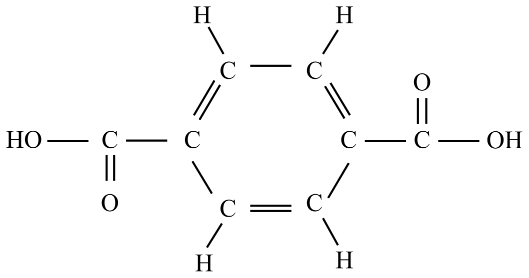
(d) Microcracks increase fracture toughness by a small amount in **glass** and **ceramic materials** due to **crack deflection** at the tip of a flaw that would otherwise continue growing in straightforward fashion without interruption until complete failure. Microcracks are **not** effective in increasing fracture toughness in **metals** because their presence is **diminished by the dominant effect of dislocation slip** causing crack blunting. In the worst case, those microcracks assist fracture in metals by linking up with the primary crack, extending its size.

(e) A reputable design engineer would **NEVER** make such a statement regarding his or her product. The expression "if a crack can be seen" suggests a **small crack**, barely perceptible, and if such a small crack is already at its **fracture toughness limit** (specified by the equation for K_{IC}), there is NO room for error. What if the inspector has poor eyesight? The reputable design engineer would instead choose a material with **high enough K_{IC} to bear load in service with a flaw of MUCH larger dimension** than being "barely visible." We refer to such design as having a "**safety factor,**" guarding against surprise failure.

Problem (4)

One of the most widely used engineering polymers is “polyester,” the same product woven as fibers into “no-iron” (“permanent press”) clothing, but also used to make Mylar™ insulating wraps, tear-resistant tarpaulins, rescue kayaks, recreational canoes, liquid crystal displays, credit card holograms, purification filters, and “shrink-wrap” dielectric insulators, among other engineering products. The most prevalent engineering polyester is known by the chemical name polyethylene terephthalate, or more commonly, PET. It is produced by co-polymerization of monoethylene glycol ($C_2H_6O_2$), and terephthalate acid ($C_6H_4[COOH]_2$), schematically illustrated here.

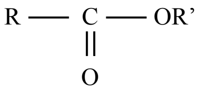




(**a**) By what polymerization reaction would you expect PET to form? Explain.

(**b**) PET is a “block copolymer.” Explain what this means, and show with a sketch the structure you anticipate for PET.

(**c**) An “ester” functional group has a molecular structure illustrated at right. Using your sketch from part (**b**) show and explain why PET is a “polyester.”



$\mathrm{R-\underset{\underset{\displaystyle O}{\|}}{C}-OR'}$

(**d**) Would you expect PET to be a thermoplastic or thermosetting polymer? Explain.

(**e**) Are your answers above consistent with the fact that PET is recyclable? Explain.

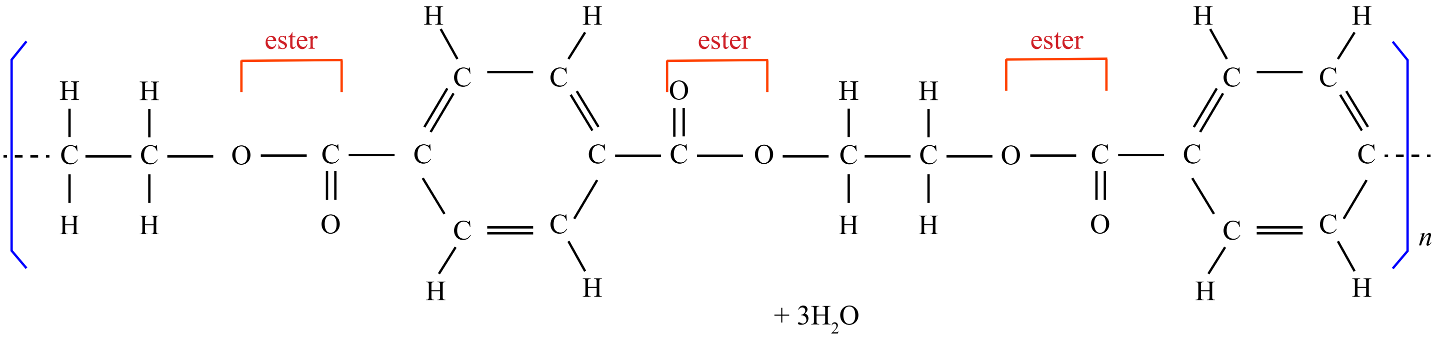
Answer (4)

(a) **PET would from by condensation polymerization, also known as step-growth polymerization**. The obvious clue here is the face-to-face hydroxyl groups, one from each molecule, in the sketch above. These can readily react to form **water**, leaving one oxygen available to link the two molecules through a common oxygen atom. The water produced in this way is the “**condensation**” product associated with a **step-growth polymerization reaction**. As the reaction continues, each step addition to the polymer (each pairing of two mers) condenses another H_2O molecule. This is illustrated in a sketch of the structure (shown in (c) below) resulting in the linking of four molecules *via* three “pairings,” generating three H_2O molecules as a result.

(b) The mers contributing to PET **share the same backbone chain,** the distinguishing feature of a **block copolymer** that sets it apart from a polymer blend, an intermixing of chains of two or more fully polymerized compounds. Block copolymers are reacted after the individual components are mixed, while polymer blends are mixed after they are reacted. In the case of PET, the reaction generates water as its condensation product, signifying the occurrence of a polymerization reaction. The structure is illustrated by a sketch in (c) below.

Answer (4) continued

(c) The sketch below shows the most regular block copolymer configuration of PET, with periodic alteration of monoethylene glycol (C2H6O2), and terephthalate acid (C6H4[COOH]2) mers. Labels also identify the **ester groups** along the backbone chain, and because there are **many** of them, the resulting product is called a "polyester."



(d) **Most polymers generated by condensation reactions are anticipated to be thermosets**, so that would be the normal expectation here, too. However, the list of applications in the problem statement includes a significant **clue**. The fact that PET can be used as a "shrink-wrap" (apply heat and it changes shape), alters the "normal" expectation to one that is more rational, based upon its actual performance. **The amended expectation is therefore that PET is thermoplastic**!

(e) This is another important clue informing your expectation of PET in (d) above, and it is OK to go back and change your answer! Only **thermoplastic polymers** are recyclable because they can be heated to soften them (they become "plastic"), allowing them to be reformed into new shapes. So, yes, all responses to the questions here **are** consistent.