UNIVERSITY OF CALIFORNIA
College of Engineering
Department of Materials Science and Engineering

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Fall Semester 2

ENGINEERING 45

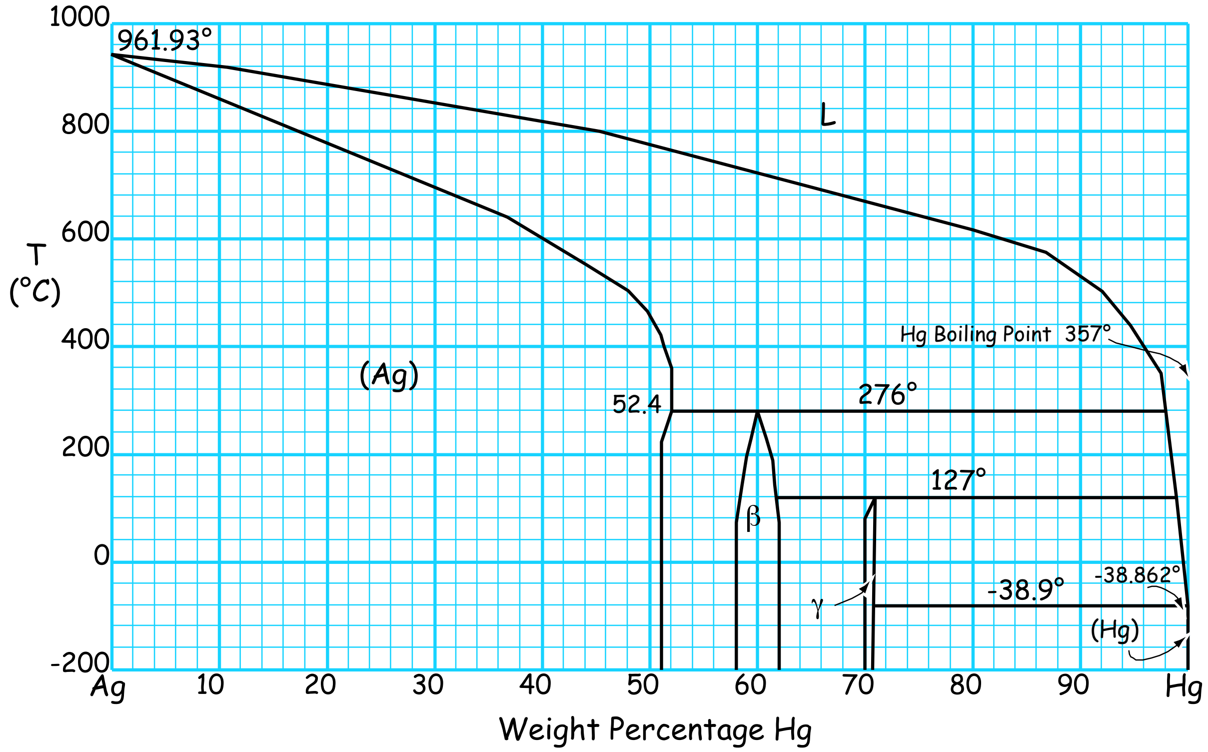
Midterm #2

SOLUTIONS

Question 1 The silver-mercury system forms the basis of an important **biomaterial** known as dental *amalgam*, which has been used for decades in restorative dental fillings. The term "amalgam" is frequently used to depict many different alloys of mercury, originating from the "amalgamation" process to refine ores of the precious metals, primarily silver and gold. The finely crushed ores in aqueous solution are mixed with mercury, allowing the mercury to alloy with the precious metals, forming an amalgam. When the amalgam is heated, the mercury is driven off as a vapor (collected and recycled of course), leaving behind pure precious metal "sponge."

Silver (*Ag*, Z = 47) is fcc and melts at 961.93°C, mercury (*Hg*, Z = 80) freezes at −38.862°C. The equilibrium β phase has AgHg stoichiometry and an hcp Bravais lattice. The equilibrium γ phase has Ag_2Hg_3 stoichiometry and a bcc Bravais Lattice.

Use this information and the equilibrium phase diagram for the silver-mercury binary system due to M. Hanson (*Constitution of Binary Alloys*, 2nd. Edition, McGraw –Hill, 1958) shown below to choose the *best* answers for 2 points each.



a. The number of components in this binary system is
☐ one (1)
☒ two (2)
☐ three (3)

b. The phase called (*Ag*) is actually
☐ pure silver
☒ a silver-mercury solid solution
☐ a metastable phase

c. Based upon the Gibbs Phase Rule ($P+F = C+2$), the number of degrees of freedom available to pure Hg at 357°C in this system is
☒ zero (0)
☐ one (1)
☐ two (2)

d. The number of degrees of freedom available to a 40 wt.% Ag alloy at 276°C is
☒ zero (0)
☐ one (1)
☐ two (2)

e. The maximum solubility of mercury in silver is
☐ infinitesimally small
☐ undefined because mercury is a liquid at room temperature
☒ established by the highest temperature reaction isotherm

f. Both β phase and γ phase are in equilibrium with liquid Hg at a
☐ monotectic
☐ eutectic
☒ peritectic

g. When β phase of 60 wt% Hg melts, it
☒ disappears completely
☐ passes through a β + L two-phase equilibrium
☐ generates mercury vapor

h. A dental hygienist "mixes" amalgam immediately before the dentist applies it so that it will "harden" as a complete filling. The hardening process is due to
☒ solid state diffusion
☐ solidification of liquid Hg
☐ dislocations created during mixing

i. An amalgam of 20 wt % Hg in equilibrium will decompose when heated above
☐ 276°C
☐ 576 °C
☒ 776°C

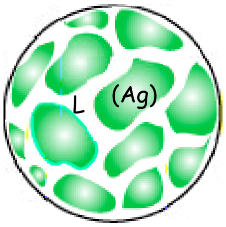
j. Dental fillings made of silver amalgam are at risk of leaking mercury into the mouth if the equilibrium mercury concentration exceeds
☐ 52.4%
☐ 62.4%
☒ 72.4%

Question 2 Use the same phase diagram to now sketch the microstructures expected during equilibrium solidification of the following alloys. The *lever rule* construction is important here. Draw a vertical line on the phase diagram for the specified composition and show all tie lines used to establish your equilibrium microstructures. Remember that the high temperature microstructure influences the lower temperature microstructure. Clearly label all phases for full credit.

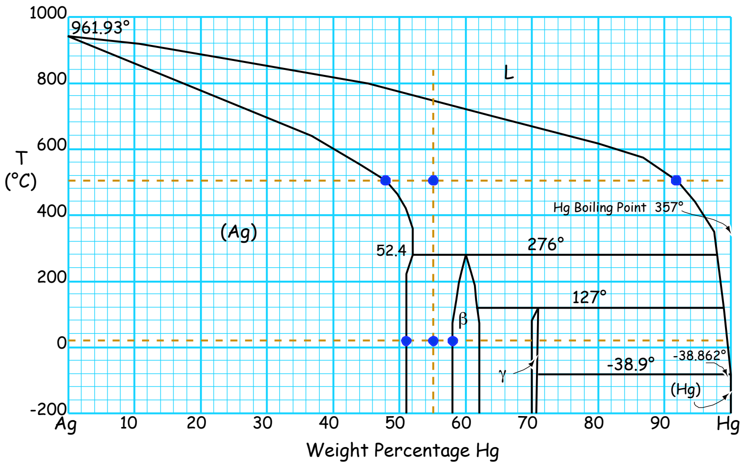
Each sketch is worth 5 points.

a. Ag-55 wt% Hg

T = 500°C
85% (Ag)
+ 15% L

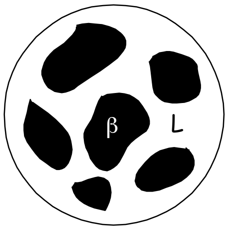


T = 25°C
40% (Ag)
+ 60% β

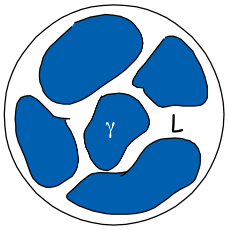


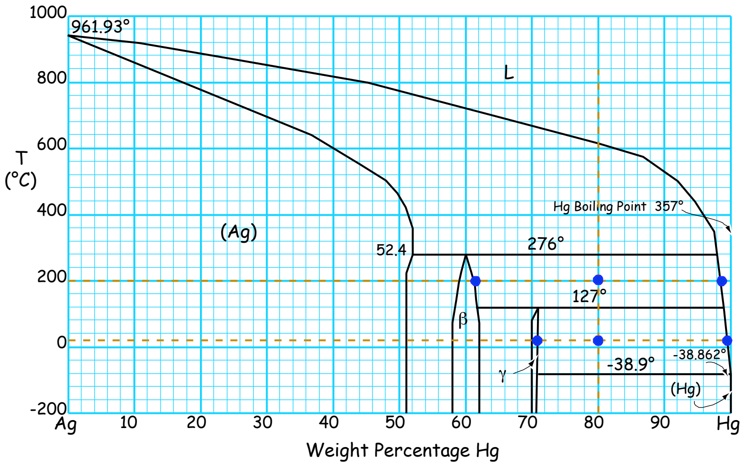
b. Hg-20 wt% Ag

T = 200°C
50% L
+ 50% β



T = 25°C
33% L
+ 67% γ



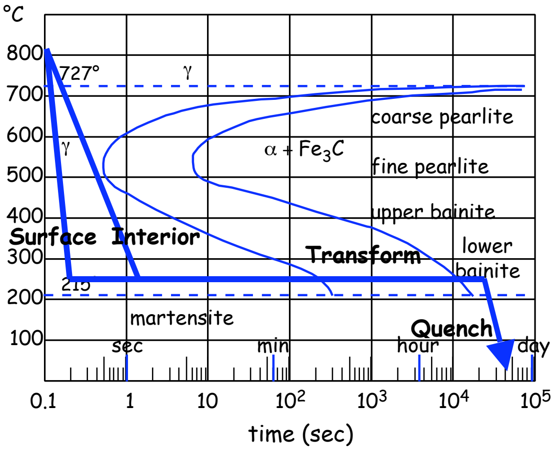


Note that in all cases here, there are no microstructural remnants from higher temperature reactions to influence the products. All are peritectic reactions, which require longer times to reach equilibrium, but time is not a factor here since we are working from an equilibrium phase diagram.

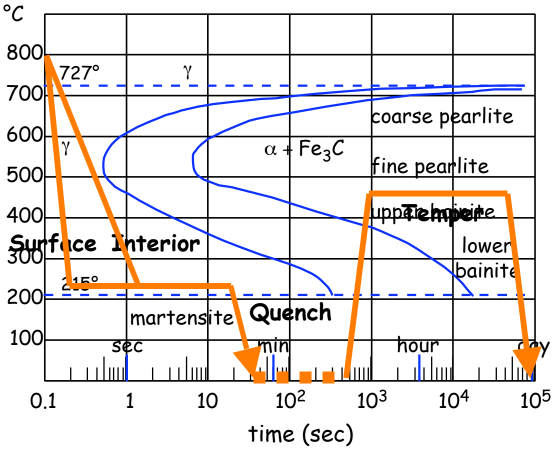
Question 3 The same TTT curve for a plain carbon steel of eutectoid composition is reproduced multiple times below. Draw directly on these plots the cooling curves corresponding to the specified treatments. Remember that TTT curves are appropriate for *isothermal transformations* only. The actual start and termination of the decomposition of austenite during continuous cooling occurs at slightly lower temperatures and longer times than shown here.

Each curve is worth 5 points.

a. Austempering, a commercial treatment used to avoid quench cracking. Show and label the curves corresponding to both the surface and the interior of a thick cross section steel beam.

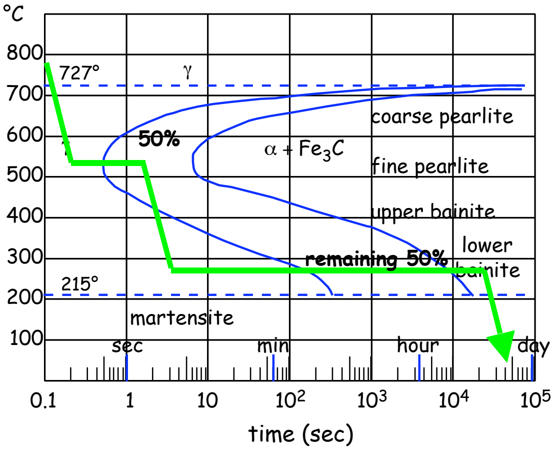


b. Martempering, a commercial treatment used to avoid quench cracking. Show and label the curves corresponding to both the surface and the interior of a thick cross section steel beam.



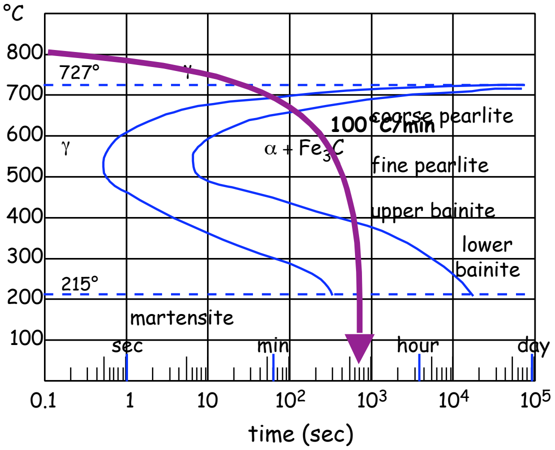
Both (**a**) and (**b**) are the classic, traditional methods used widely throughout the engineering community to prevent quench-cracking in large cross-section steel components.

c. An "interrupted quench" technique that would generate a final microstructure of 50% lower bainite and 50% fine pearlite. In this case the workpiece is a small diameter rod to be used as an axle in a motor-generator set.



The only way this treatment can be an "interrupted quench" is to begin with the high temperature transformation (fine pearlite), holding isothermally until the reaction progresses half way between the start and finish lines. Note that this amounts to only a few seconds. The untransformed austenite is then lowered in temperature and held isothermally until it fully transforms to lower bainite as shown.

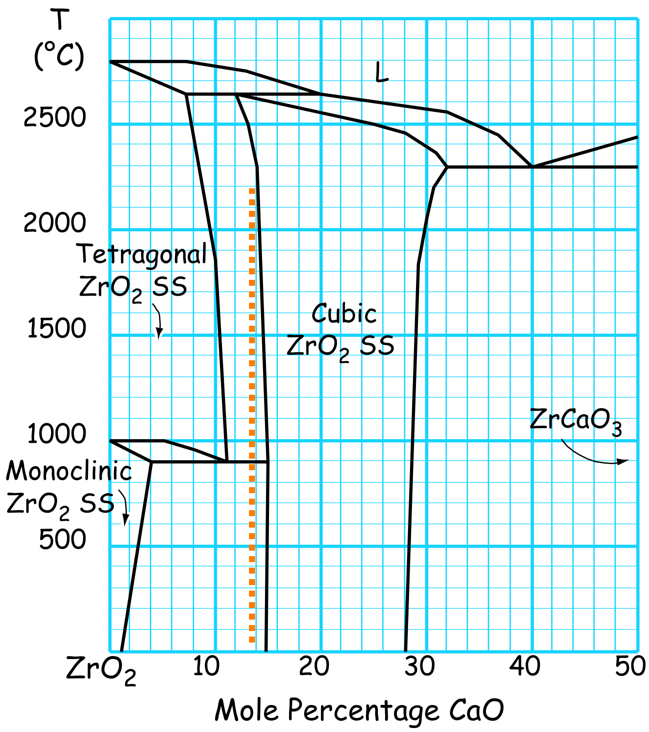
d. An approximation. Show without compensation for continuous cooling the T-t trajectory for a sample that was left in the furnace during a power outage. The initial temperature was 800°C at midnight when the power failed. The cooling rate for the well-insulated furnace was previously calibrated at 100°C / minute. The sample was recovered 8 hours later at the start of the daylight shift.



In question (d), note that a linear rate of 100°C / min is dramatically curved on the log scale used here. Although this is only an "approximation" because the cooling treatment is not isothermal, it is reasonable to expect that the final microstructure would be fully pearlitic, and rather coarse.

Question 4 Pure zirconia undergoes an allotropic transformation at 1000°C from a high temperature tetragonal structure to a low temperature monoclinic structure. A massive volume expansion upon cooling through the tetragonal-to-monoclinic transformation literally results in the self destruction of the crystal. Thermal cycling through the transformation temperature pulverizes the material into a fine powder.

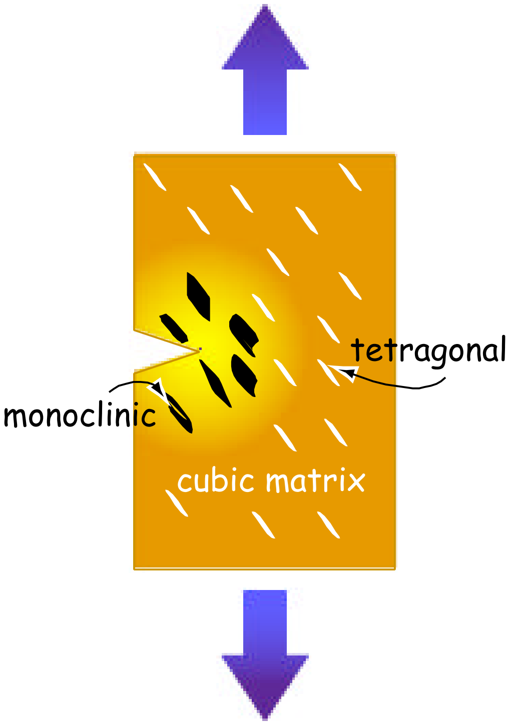
However, alloying zirconia with 25 mol % calcia yields a cubic phase that persists up to its melting point with no structural instabilities. This "stabilized" zirconia is a very popular structural ceramic for that reason.



a. Using this information, explain how "partially-stabilized" zirconia, which contains some cubic, some tetragonal, and some monoclinic phases, is prepared. Be specific, using the equilibrium phase diagram above and your understanding of phase transformation kinetics for 10 points.

The phase diagram indicates that it is not possible to find all three phases (cubic, tetragonal and monoclinic) <u>in equilibrium</u>. So this is a problem involving <u>kinetics</u>. At CaO concentrations less than 15 mol%, monoclinic and cubic phases are in equilibrium at room temperature. To include a tetragonal phase at room temperature, all that is required is to <u>heat above the eutectoid temperature</u> (900°C) where tetragonal phase is in equilibrium, <u>then "quench"</u> to retain it kinetically at lower temperature.

b. For another 10 points, explain in detail how the partially-stabilized zirconia structure leads to "transformation toughening" of an otherwise brittle ceramic material. Comment specifically on the volume expansion associated with the tetragonal to monoclinic transformation, and its role in causing an increase in fracture toughness. Recall that fracture toughness refers to the performance of a material with pre-existing flaws, and focus your attention on the crack shown in the following sketch.



Recalling from above that only the cubic and monoclinic phases are in equilibrium at room temperature, the metastable tetragonal phase becomes the key constituent in this problem.

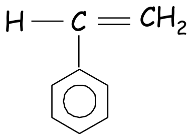
As the crack advances through the forest of tetragonal precipitates, it relaxes the constraints of the cubic matrix confining the tetragonal particles. This relaxation induces the <u>transformation of the metastable tetragonal phase to the equilibrium monoclinic phase</u> in the vicinity of the crack tip. The resulting volume expansion (as described in the problem statement) exerts a <u>closing force</u> on the crack tip, retarding its progress through the ceramic. It is for this reason that the mechanism described here is known as "transformation toughening." The transformation from the tetragonal to monoclinic phases gives partially stabilized zirconia (PSZ) the highest fracture tougnhness of all structural ceramics.

Question 5 Polymers or "many mers" may result from chain growth, also known as addition polymerization, which generates linear or branched polymers, or from step growth, also known as condensation polymerization, which generates network polymers. The mechanical properties of polymers are, like all materials, linked to their structure.

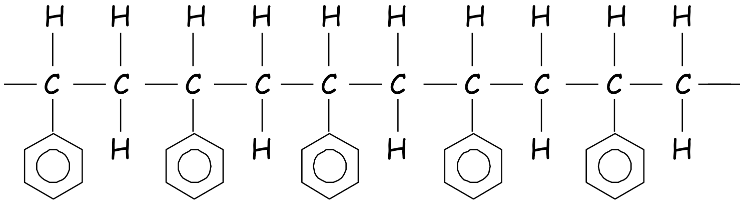
(**a**) The styrene mer is shown schematically below. Show how polystyrene results from a polymerization reaction by sketching the final product containing at least five mers. Is polystyrene a (check all that apply)

☒ linear,
☐ branched, or
☐ network polymer?

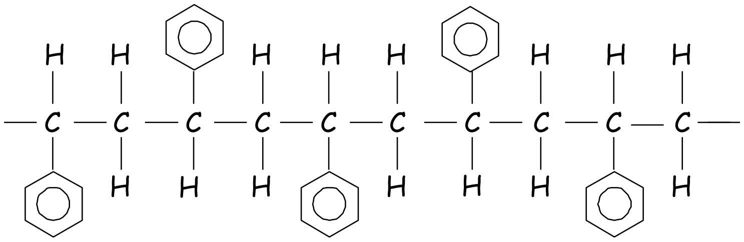
Showing the correct polymeric structure and checking the correct box(es) above earns 10 points.



The signature feature of the styrene mer that marks it as a candidate for polymerization is its double carbon bond. Conversion of this bond into two single bonds functionalizes the mer. Its resulting bifunctional character makes it a candidate for chain growth into a linear polymer, just like polyethylene. A segment of the polymer backbone chain is shown below.

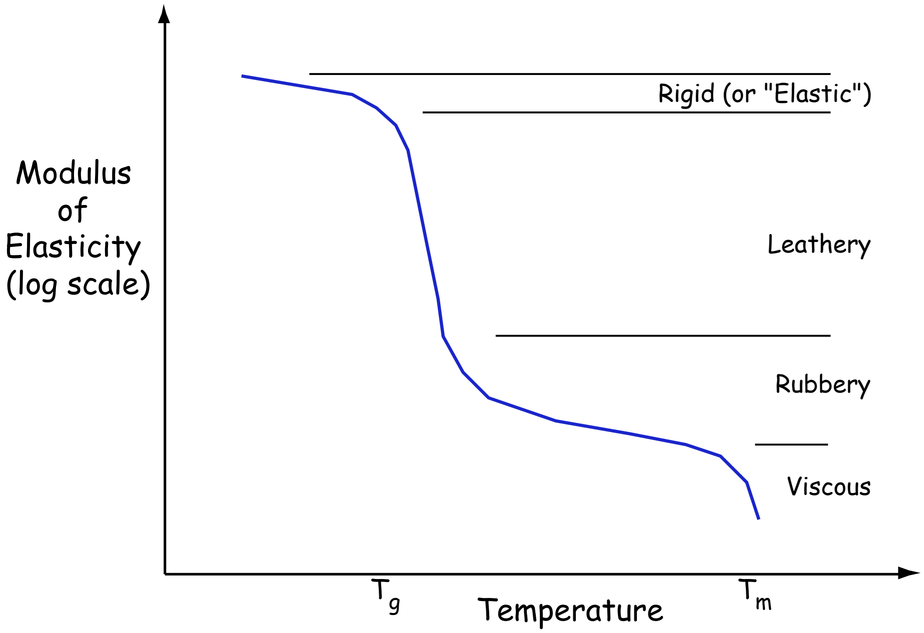


This particular configuration is the isotactic one, with all of the large side groups on the same side. The syndiotactic configuration shown below, and the atactic configuration (random) are also acceptable.



(**b**) Polymers, like metals and ceramics, can be described by a lattice and motif, but they are never fully crystalline. In fact, numerous polymers are completely amorphous. Those that possess some crystallinity have their polymeric chains arranged in a regular, parallel alignment, and these crystallites or "fringed micelles" are embedded in an amorphous matrix.

A partially crystallized thermoplastic polymer shows "viscoelastic" mechanical behavior. Using the coordinate axes below, plot the elastic modulus as a function of temperature for a viscoelastic polymer. Note particularly the changes seen at the glass transition temperature and the melting temperature. On your plot, label the four distinct regions of behavior associated with viscoelasticity, that is, rubbery, viscous, leathery, and rigid (or elastic). A correctly labeled plot is worth 10 points.



In its traditional definition, the glass transition temperature marks the transition from rigid "crystal-like" to viscous "glass-like" mechanical behavior. Crystals deform by dislocation motion, glasses deform by the viscous flow.

At the melting point, viscous flow is most obvious because the material cannot sustain its own weight against gravity. The elastic modulus drops to zero.