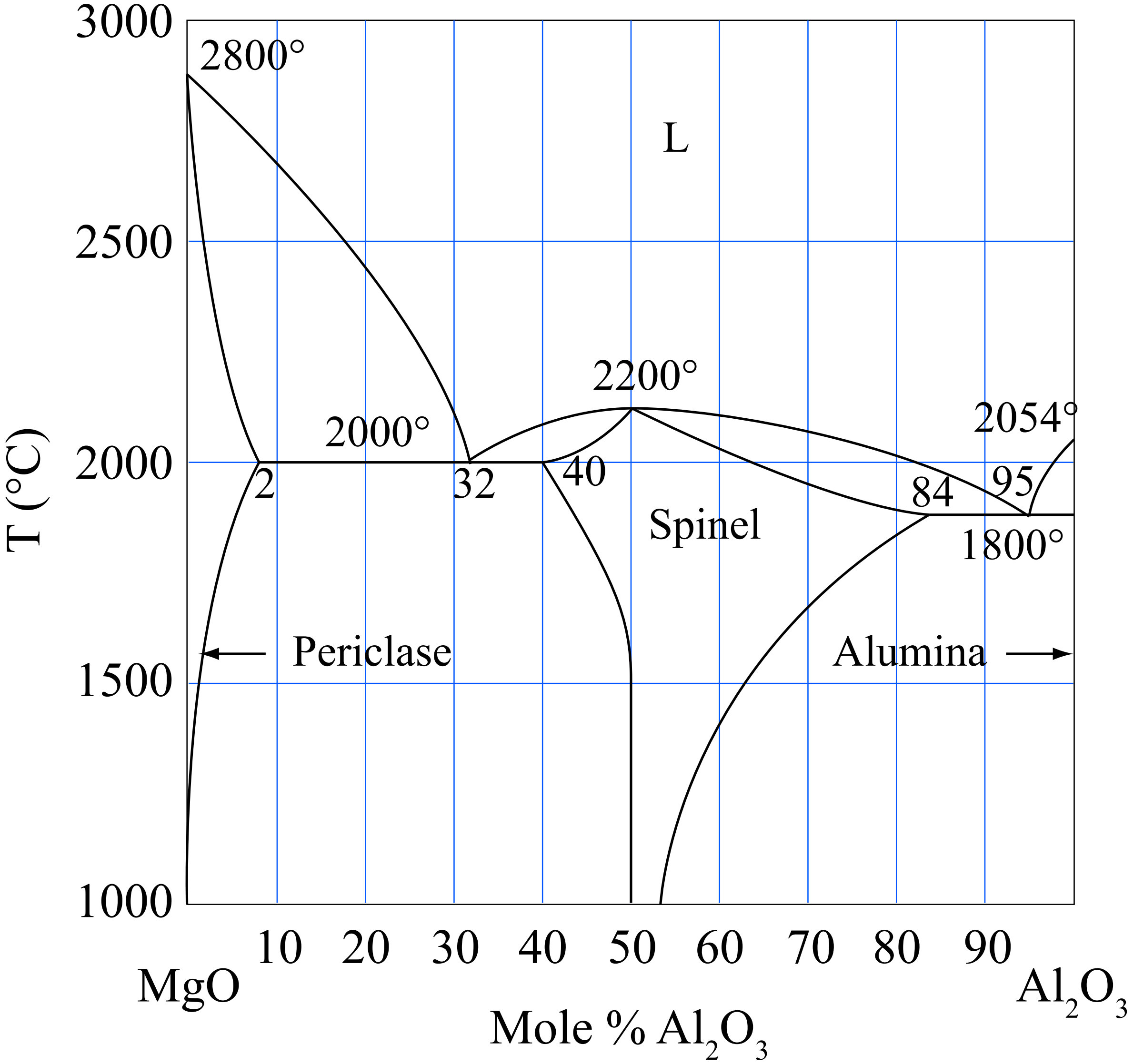
1. Phase Diagrams (20 points)

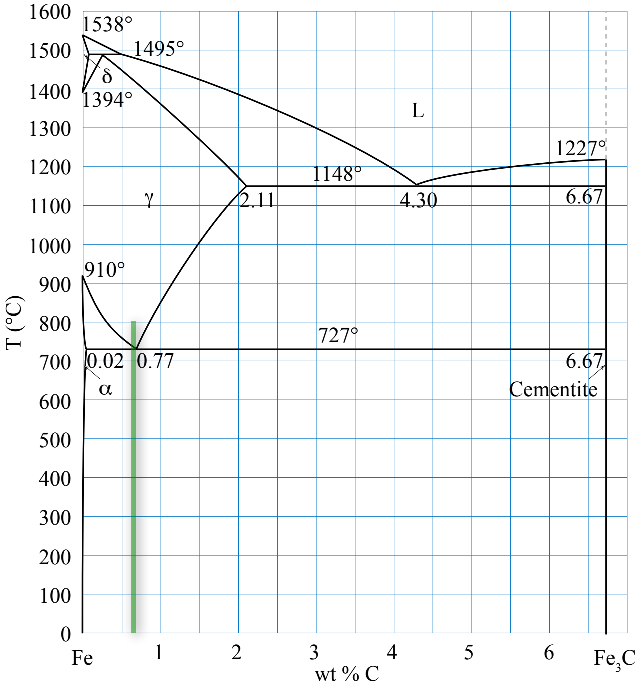
Industrial applications of refractories for thermal protection include a large quantity of ceramics based upon the MgO-Al_2O_3 ceramic alloy system. Using the grid below, construct the magnesia–alumina binary alloy phase diagram from the following experimental observations. All compositions are expressed in mole percentage. Be sure to label all single phase fields.

- Pure magnesia melts at 2800°C.
- Pure alumina melts at 2054°C.
- Magnesia can dissolve up to 2% alumina, the maximum solubility occurring at 2000°C. The name given to this solid solution of alumina in magnesia is "periclase."
- Magnesia has no solubility in alumina.
- "Spinel" is the name normally associated with the compound $MgAl_2O_4$, but it is also the name of a phase in the magnesia-alumina binary system with solubility ranging from 40% alumina (at 2000°C) to 84% alumina (at 1800°C). The spinel phase with a composition of 50% alumina melts congruently at 2200°C.
- At 2200°C, an 82% magnesia alloy is partially solidified, consisting of equal parts periclase and liquid.
- At 2000°C, a 68% magnesia alloy transforms on cooling from a liquid phase to two solid phases. One of the solid phases is periclase with 2% alumina content and the other is spinel with 40% alumina content.
- At 2000°C, a 73% alumina alloy is half liquid and half spinel.
- At 1800°C, a 95% alumina alloy solidifies on cooling into two solid phases, one a spinel of 84% alumina, and the other, pure alumina.
- At 1000°C, a 75% magnesia alloy has equal parts periclase, with a composition of 100% magnesia, and spinel, with a composition 50% magnesia.
- At 1000°C, a 77% alumina alloy has equal parts alumina phase and spinel phase, the latter with a composition of 54% alumina.

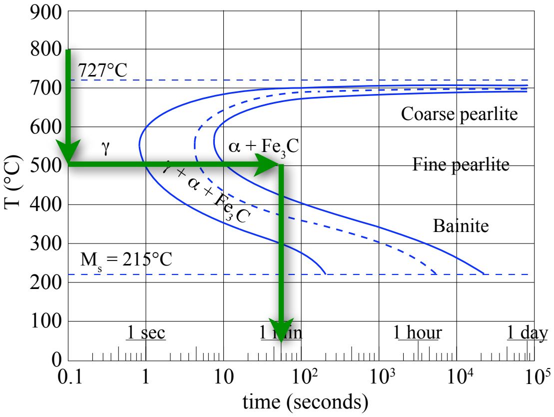

3000
2500
2000
1500
1000
T (°C)
2800°
L
2200°
2000°
2054°
2
32
40
84
95
1800°
Spinel
Periclase
Alumina
10
20
30
40
50
60
70
80
90
MgO
Al_2O_3
Mole % Al_2O_3

2. Kinetics (20 points)

a. A 1080 steel is austenitized at 800°C for 4 hours in preparation for an isothermal treatment to develop a uniform microstructure of 100% fine pearlite.
Plot directly on the TTT curve below the kinetic path of a treatment that would achieve the desired result *within one hour*.



ANSWER: The cooling path is shown on the plot below. There is some leeway in the hold time at 500°C (10 seconds to several minutes), but holding too long could coarsen the pearlite.



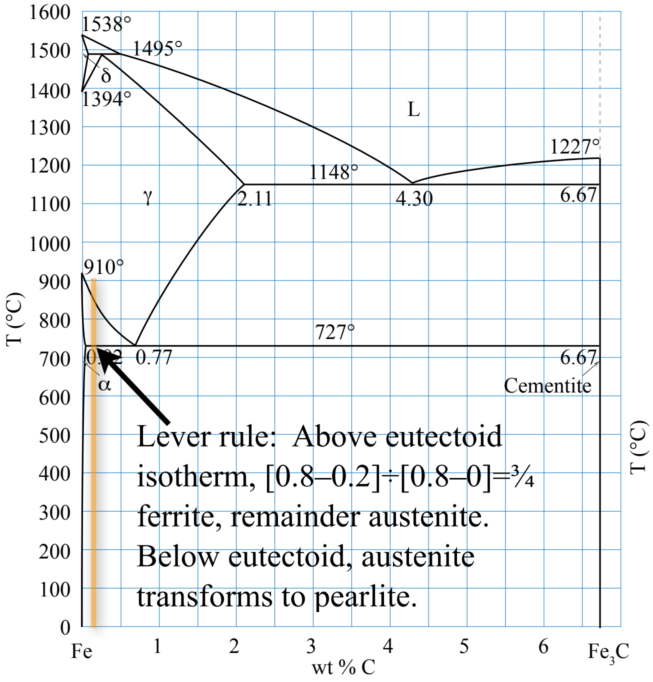
b. Now *describe* your heat treatment in succinct terms as though you were giving instructions to your furnace shop manager, explaining how to achieve each temperature-time segment of your kinetic path traced above.

ANSWER: Place the 1080 steel workpiece in a furnace at **800°C and hold for 4 hours** until fully austenitized. Transport quickly to second furnace operating **at 500° C and hold for one minute** (no shorter than 10 seconds, but 60 seconds gives adequate buffer time) to complete the transformation to pearlite. Remove from the furnace and **quench** to preserve fine pearlite.

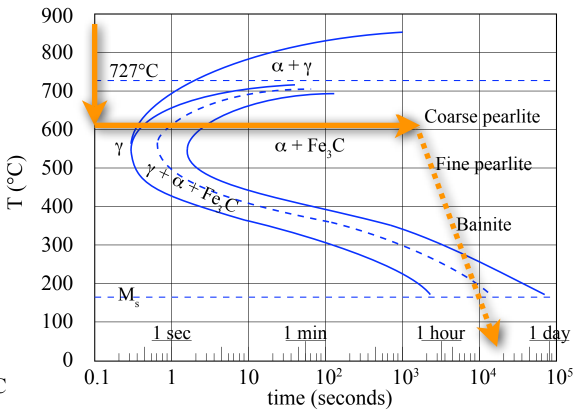
2.

c. A fully austenitized 1020 steel is held isothermally at 600°C for 30 minutes, removed from the furnace, and allowed to air cool to room temperature over the next several hours.
Describe the resulting microstructure in *quantitative* terms, citing the *relative amounts* of all constituents, and comment on its overall strength and ductility for structural applications.

ANSWER: The final microstructure will be approximately 75% proeuctoid ferrite and 25% coarse pearlite, a relatively soft and ductile product that would NOT be appropriate for structural load-bearing applications, since it would deform relatively easily.



Lever rule: Above eutectoid isotherm, [0.8–0.2]÷[0.8–0]=¾ ferrite, remainder austenite. Below eutectoid, austenite transforms to pearlite.



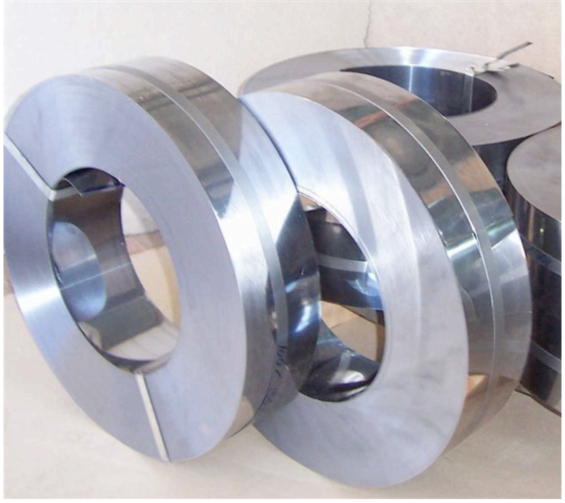
d. How would the microstructure of the same fully austenitized 1020 steel change if, instead of the above heat treatment, it was plunged directly into an iced brine quenching bath at 0°C? How would its strength and ductility differ from (**c**)? *Explain*.

ANSWER: An iced brine bath results in a very rapid quench (the brine enables the water bath to remain liquid at 0°C by depressing the freezing point). Rapid quenching would generate a microstructure of 100% martensite, a very strong product that could be used for bearing large loads with very little deformation. It would also be very brittle, so impact loading should be avoided.

3. Metallic Alloys (20 points)

a. Plain carbon steels (AISI designation 10XX) are used for many load-bearing applications, such as this assortment of small rods, in a "quenched and tempered" state.
Explain why this is a preferred heat treatment, citing the effects of processing on the microstructure and properties of products with relatively small section size.

ANSWER: This heat treatment begins with solutionizing the part by holding it at sufficiently high temperature to be above all solvus lines and fully within the austenite single phase field. "Quenching" refers to very rapid cooling from a fully austenitic microstructure to generate martensite. In small section sizes, such rapid cooling is readily achieved because the "interior" is very close to the surface. This also reduces the danger of quench cracking. "Tempering" is a lower temperature thermal treatment (≈300°C) to restore some ductility by allowing carbon diffusion, precipitation of carbides, and restoration of a cubic structure with more slip systems than the tetragonal martensitic structure. This enables the final part to withstand even aggressive impact loading.

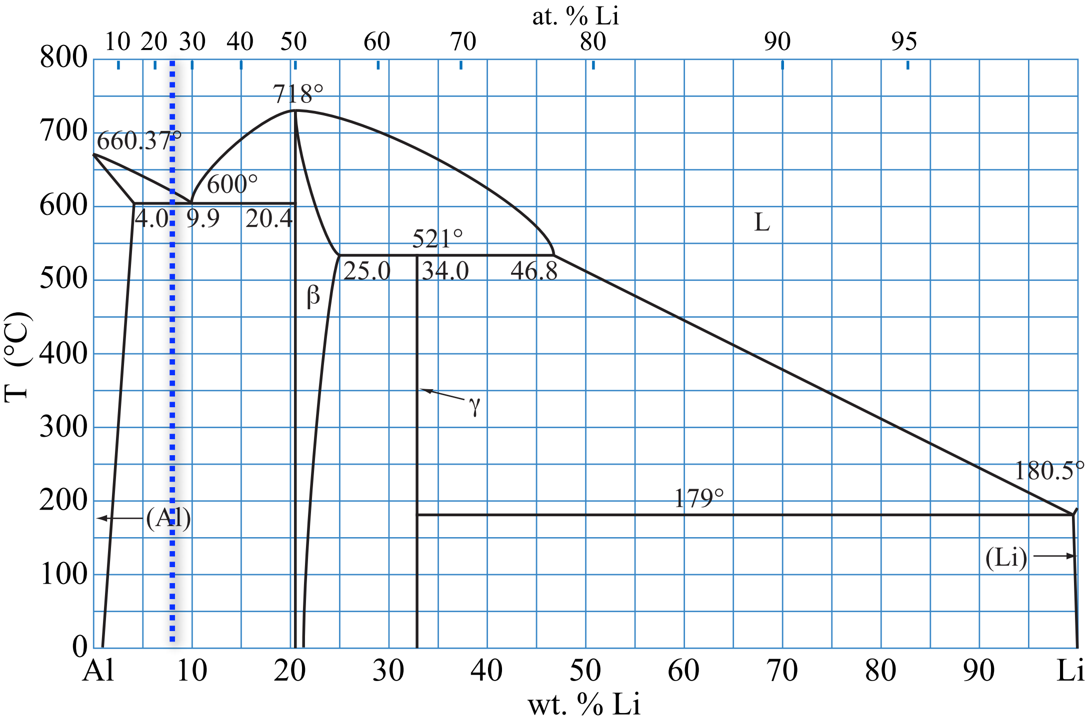


b. Sheet steel used for appliance housings is sometimes subjected to a processing treatment known as "strain hardening." Use your understanding of stress-strain behavior and the microstructural origins of hardening to explain this process. What makes it an attractive processing option?

ANSWER: Sheet product is deformed between rollers into its final shape. If the rolling operation is done "cold," the deformation process serves two purposes. It achieves final dimensional control and it increases the dislocation density. Such sheet products are strained due to their reduction in thickness, and they are "hardened" (strengthened) by the many obstacles to dislocation motion presented by the higher dislocation density. The result is therefore a very efficient process for generating a functional engineering product.

3.

c.

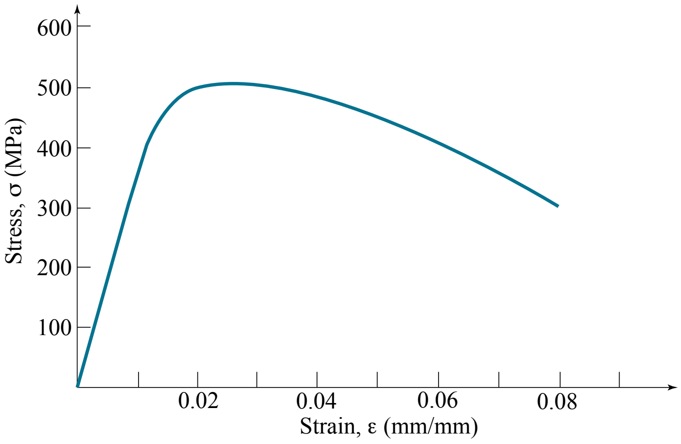


The aircraft industry has been interested in light weight Al-Li alloys for several years because they can be heat treated to high strength. Microstructural investigations reveal the origin of their strength to be a high density of ordered Al_3Li precipitates. Refer to the equilibrium Al-Li phase diagram above (from *ASM Metals Handbook*, Volume **8**, 1973, p. 261) and specify an *alloy composition* and *heat treatment* that will generate the favored microstructure. Be specific.

ANSWER: Guided by the labels at the **top** of the phase diagram, stoichiometric Al_3Li (25 at% Li, dotted line above) is NOT FOUND on the phase diagram; rather (Al) + γ are the expected phases. Recall that martensite is also not found on the Fe-C phase diagram. The reason is that phase diagrams are "equilibrium" diagrams, so Al_3Li, like ferrous martensite, must be a "**metastable**" phase. The processing protocol therefore becomes one of AVOIDING the equilibrium phase and allowing the kinetically favored metastable phase to form. But unlike martensite, which occurs by quenching, Al_3Li is a "precipitate," so a precipitation-hardening treatment is required.
To produce precipitates of Al_3Li in an Al-rich matrix, begin with an alloy having no more than 3 wt.% (approx. 10 at.%) Li, and **solutionize** it for several hours at 500°C. **Quench** to preserve a supersaturated solid solution, then **age at low temperature** (no more than 100°C) for **short times** (minutes) to encourage precipitation of the metastable Al_3Li phase. Too high a temperature or too long an aging time will precipitate the equilibrium γ phase instead.

3.

d. If a metallic alloy can be strengthened by work-hardening or age-hardening, why not both? *Describe* the microstructures resulting from (*i*) a work-hardening treatment followed by age-hardening and (*ii*) an age-hardening treatment followed by work-hardening. Which sequence would you expect to yield a stronger alloy, and why?



ANSWER: (i) Work hardening generates a high density of dislocations. Subsequent age hardening employs an elevated temperature to encourage diffusion and precipitate growth, but the precipitates are most likely to nucleate heterogeneously on the existing dislocations, reducing precipitate density and dispersion compared to a homogeneously-nucleated product. Moreover, diffusion will also cause some annealing, removing some of the original dislocations in the microstructure.
(ii) Age hardening in the absence of dislocations generates a homogeneously-nucleated product with high density and uniform dispersion. Subsequent work hardening adds dislocations to the microstructure that are themselves pinned by the existing precipitate dispersion.
The stronger alloy results from (ii) because of its overall higher density of obstacles to dislocation motion.

4. Ceramics & Glasses (20 points)

a. The poor fracture toughness of ceramics is reflected in low values of the critical stress intensity factor (K_{IC}) defined by

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

where Y is a dimensionless geometrical factor ≈ 1, σ_f is the applied tensile stress that causes failure and a is the length of a surface crack, or half the length of an internal crack. Values of K_{IC} for alumina can be two orders of magnitude lower than fully annealed copper. *Explain* this difference, citing the role of *dislocations*.

ANSWER: Under an applied tensile stress, crystalline alumina is unable to deform by dislocation motion, so its response to the applied stress is bond breaking at the point of highest stress concentration, the crack tip, which lengthens the crack. Fully annealed copper responds to the same applied stress by the nucleation and propagation of multiple dislocations that accommodate the applied stress by elongation of the sample, blunting the crack by increasing its opening instead of its length, hindering crack growth.

b. In his more detailed investigation of brittle fracture, aeronautical engineer Alan Griffith proposed that the sharpness of the crack, defined by the crack tip radius ρ establishes the value of the maximum stress σ_m at the tip of a crack of length a under a macroscopic tensile stress of σ, according to the relation

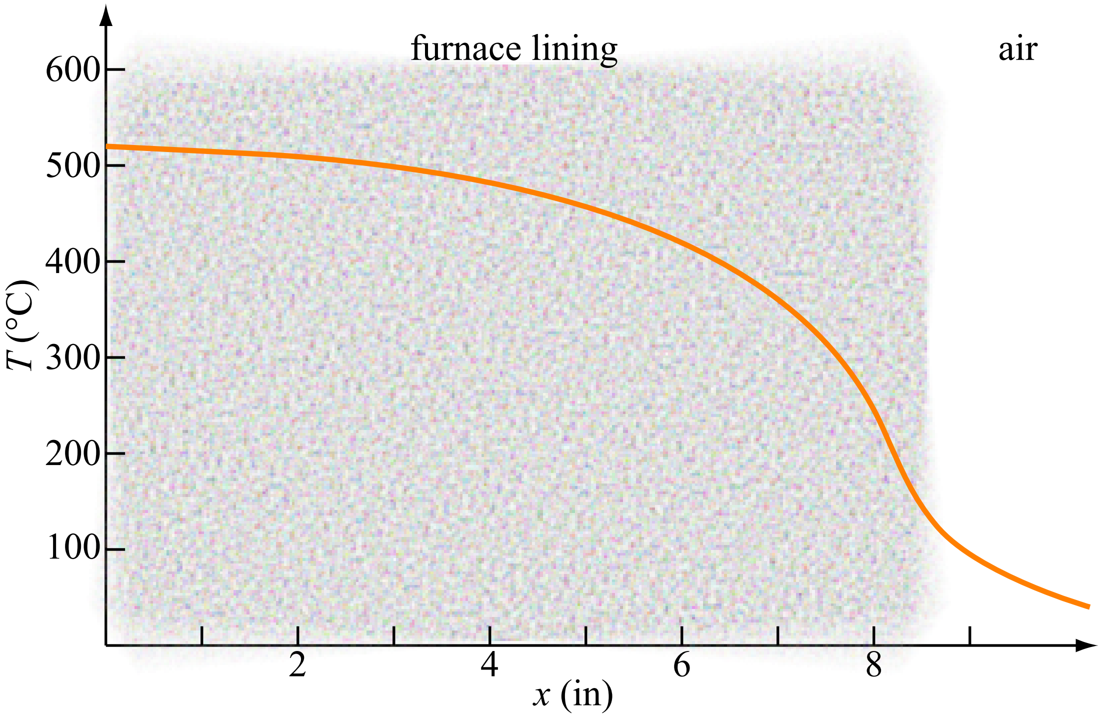
$$\sigma_m = \simeq 2\sigma \sqrt{\frac{a}{\rho}}$$

How, based upon this model, does the *microcrack* toughening mechanism work in ceramic materials? Be specific.

ANSWER: Microcracks in ceramic materials dissipate the energy release rate during crack growth by dispersing the fracture over many internal sites. Moreover, when the primary crack joins up with the microcracks ahead of it, the primary crack is blunted, increasing the crack tip radius in Griffith's equation, reducing the maximum stress at the crack tip.

4.

c. Many ceramics are susceptible to thermal shock, complete or partial fracture resulting from a sudden change in temperature, usually cooling. Consider a crystalline fireclay refractory furnace lining that is suddenly subjected to a rush of cold air as the furnace door is open, leading to the following temperature gradient across its thickness.

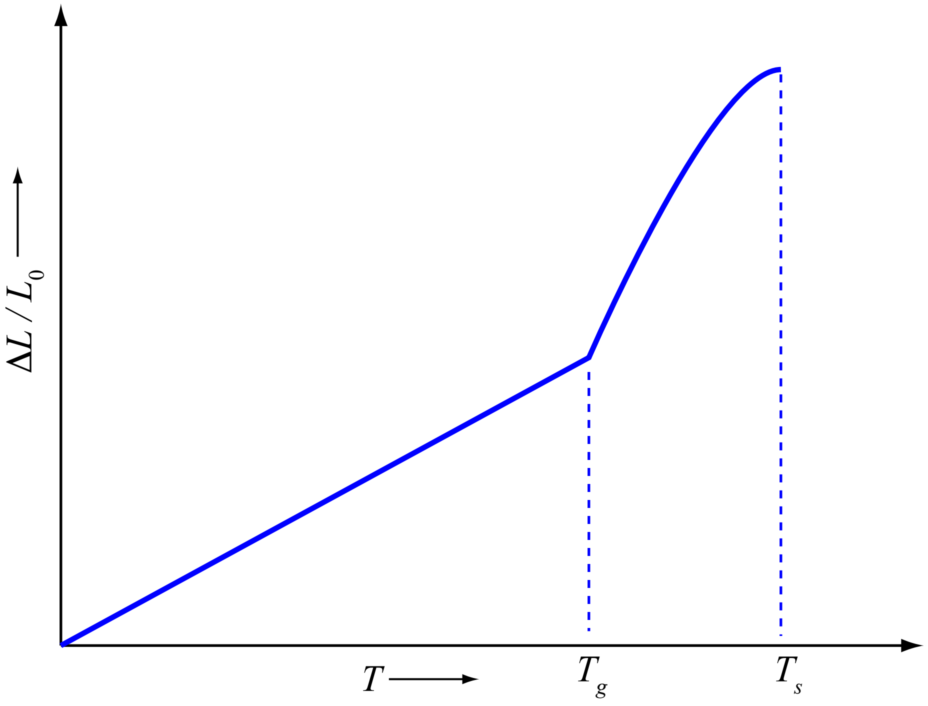


Using concepts of thermal conductivity and thermal expansion, relate this temperature gradient to a *stress gradient* that results in fracture.

ANSWER: The severe temperature gradient from surface to interior is the problem here. At the surface, the cooler fireclay contracts in response to its temperature drop. Due to relatively poor thermal conductivity, the interior cannot shed its heat so quickly, and it remains hot, and in a state of full thermal expansion. Because there is a large volume of fireclay at elevated temperature in the interior, the outer surface experiences a TENSILE load. This stress gradient results in fracture or spalling of the surface layers.

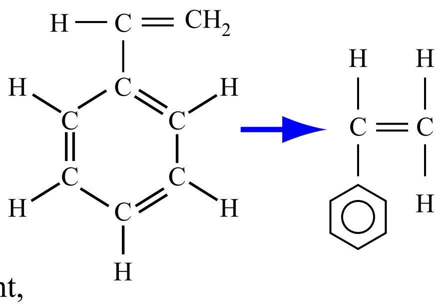
4.

d. Would it matter if the furnace lining was instead made of a vitreous (non-crystalline) ceramic with a glass transition temperature T_g of 100°C? Explain.



ANSWER: For a vitreous furnace lining, an even lower thermal conductivity is expected due to poor phonon dissipation. However, since the entire furnace lining, including its outermost surface layers, would be above its 100°C glass transition temperature, any tensile stress exerted on the surface by the interior would be relaxed by differential strain in the surface. The surface would flow easily in response to the tensile stress exerted by the hot interior, minimizing the danger of spalling.

5. Polymers (20 points)

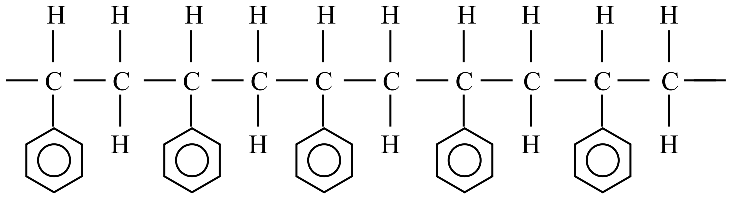


a. Polystyrene is used in many applications including laboratory Petri dishes, CD and DVD "jewel" cases, picnic cutlery, smoke detector housings, and license plate frames. One popular version has the fifty-year-old Dow Chemical trade name Styrofoam® used as building insulation panels. The styrene monomer is shown here in its full expansion on the left and in "shorthand" on the right, representing the phenol group by its hexagonal ring symbol. Is polystyrene a more likely candidate for synthesis by chain growth or step growth? Explain.

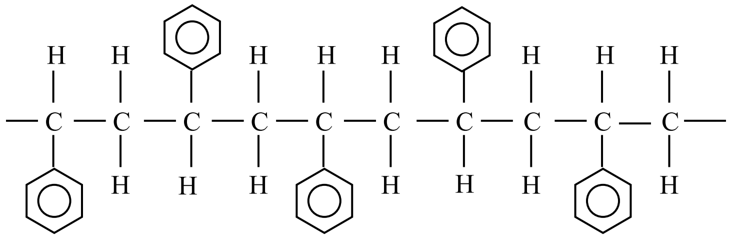
ANSWER: The styrene mer is bifunctional with a double carbon bond, making it a prime candidate for chain growth by addition polymerization.

b. Now sketch polystyrene in both its isotactic and syndiotactic conformations.

Isotactic

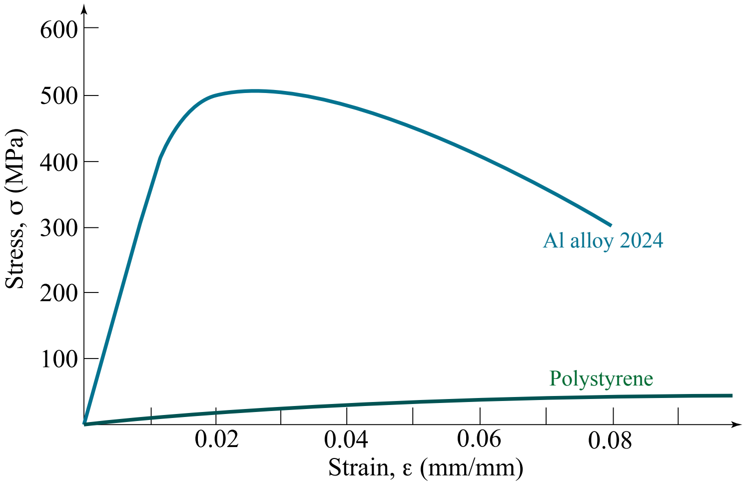


Syndiotactic



5.

c. The stress-strain behavior of polystyrene is compared here to aluminum alloy 2024. Polystyrene fails at a total elongation of approximately 1%, at a tensile strength of less than 50 MPa. Explain the deformation behavior of polystyrene, citing the microstructural mechanisms responsible for the shape of its *σ*–*ε* curve and obvious differences compared to the curve for the aluminum alloy.



ANSWER: Polystyrene shows no clear transition between elastic and plastic deformation and no clear "ultimate" tensile strength (necking behavior) as seen for aluminum alloys. Deformation in polystyrene proceeds on the microstructural level by the uncoiling and sliding of polymer chains past one another as weak secondary van der Waals bonds are broken. This accounts for the low strength of polystyrene. A dislocation model of plasticity, as used for aluminum alloys, is NOT appropriate for polystyrene because, like most polymers, it lacks crystallinity. Failure ultimately occurs when polymer chains are separated as elongation and sliding reach their physical limits.

d. From your answer to parts **a** and **b** above, would you expect polystyrene to be a thermoplastic or a thermoset? Is it recyclable? Why do you suppose the city of Berkeley banned all foamed polystyrene coffee cups within its metropolitan limits?

ANSWER: Polystyrene is a thermoplastic because it is a linear polymer. It is therefore recyclable. The city of Berkeley is more concerned about the fact that polystyrene is not biodegradable, and in foamed form, can be blown around the environment by even a light wind. A recycling program would be a reasonable alternative, but apparently more costly than enforcing a ban on foamed polystyrene.