1. **Grain Growth/Solid Solutions**

   a) At 400˚C, magnesium alloy AZ31 has empirical grain growth parameters of $K=4.4 \times 10^4 \mu m^n s^{-1}$ and $n=4$. If you are given AZ31 with an average grain size of 4µm, what is the average grain size after 44 minutes of annealing at 400˚C? (4 pts)

   \[
   d^n - d_0^n = Kt \Rightarrow d = \sqrt[n]{Kt + d_0^n} = \sqrt[n]{(4.4 \times 10^4) \times 44 \times 60 + 4^4} = 103.82 \mu m
   \]

   b) If the Hall-Petch constants of AZ31 are $k_y = 0.5 \text{ MPa.m}^{1/2}$ and $\sigma_0 = 3 \text{ MPa}$, what is the yield strength of the alloy from part (a) as-received, and after the annealing? (4 pts)

   The Hall-Petch equation relates grain size to yield strength.

   \[
   \sigma_y = \sigma_0 + k_y d^{-1/2}
   \]

   Using the as-received $d=4\mu m$ and the annealed $d=103.82\mu m$. (And being sure to note units when doing the math.)

   As Received
   \[
   \sigma_y = 3 + 0.5 \times (4 \times 10^{-6})^{-1/2} = 253 \text{ MPa}
   \]

   Annealed
   \[
   \sigma_y = 3 + 0.5 \times (103.82 \times 10^{-6})^{-1/2} = 52.1 \text{ MPa}
   \]

   c) You are given two as-rolled samples, A and B, of AZ31 and anneal them under the aforementioned conditions. Curiously, the grains in Sample B are larger, with a more uniform size distribution than Sample A. You are told by a colleague that one of the samples was known to have AlN impurities, which are insoluble in Mg. Which of the samples do you think has the impurities? How do aluminum nitride impurities in the magnesium alloy affect grain growth kinetics? (3 pts)

   Sample A is likely the impure AZ31. Grain growth is greatly affected by diffusion kinetics and the ability of dislocations forming the boundary to move and grow. Insoluble particles will hinder this growth. (see: Zener pinning.) Their random dispersion throughout the material means that they will affect some grains and not others. This explains the size distribution.

   d) Derive a relation for the force a particle exerts on a grain boundary as the boundary moves across it. Let $\Upsilon$ be the surface energy (per unit area) of the grain boundary. In the diagram below, assume the grain boundary is a plane extending into the page and that the particle is spherical with radius $r$. (9 pts)
The length of the grain boundary in contact with the particle is the circumference of the circle at that part of the particle. If \( \gamma \) is the surface energy per area, then the force per unit length on the boundary is \( \gamma \sin(\theta) \). (Note: energy/area = force/length.) Multiplying these together, we get:

\[
F_{\text{pinning}} = 2\pi r \cos \theta \times \gamma \sin \theta
\]

2. Diffusion and Fick's Law

a) Plot the diffusion coefficient vs. reciprocal temperature for Cu in Ni from 500 °C to 1000 °C. Use Log base 10. (8 pts)

Using Mathematica:

```
D0 = 2.7 \times 10^{-5};
Qd = 256 \times 10^3 \text{ (eV/mol)};
R = 8.31 \text{ (eV/mol K)};

Plot[Log10[D0] - Qd/(2.3 R x), {x, 1/273.15, 1/773.15}, AxesLabel -> {1/x, Log[D]}]
```

b) Calculate the Cu diffusion flux in Ni for steady state at 800 °C. Two concentrations of Cu beneath the Ni surface are 2.3 kg/m³ and 1.8 kg/m³ at 3 mm and 7 mm respectively. (5 pts)

\[
D = D_0 \exp \left( -\frac{Q_d}{RT} \right) = 2.7 \times 10^{-5} \times \exp \left( -\frac{256 \times 10^3}{8.31 \times (800 + 273.15)} \right)
\]

\[
D = 9.21 \times 10^{-18}
\]
\[ J = -D \frac{C_A - C_B}{x_A - x_B} = 9.21 \times 10^{-18} \times \frac{2.3 - 1.8}{(3 - 7) \times 10^{-3}} = 1.15 \times 10^{-15} \text{kg/m}^2\text{s} \]

c) Suppose we are in a nonsteady-state situation and the surface concentration of Cu is held at 1.12 wt % Cu. Initially, the Cu concentration in the Ni is 0.23 % wt Cu, spread uniformly throughout the Ni. Find the concentration at a depth of 0.005 mm after 72 hours at 800 °C. (7 pts)
\[
C_x = \left(1 - \text{erf} \left( \frac{x}{2\sqrt{D}t} \right) \right) (C_s - C_0) + C_0
\]
\[
= \left(1 - \text{erf} \left( \frac{0.005 \times 10^{-3}}{2\sqrt{72} \times 60 \times 60 \times 9.21 \times 10^{-18}} \right) \right) (1.12 - .23) + .23
\]
\[
= \left(1 - \text{erf}(1.6) \right) (.89) + .23 = (1 - .9763)(.89) + .23 = .251 \text{ wt % Cu}
\]

3. Strain Hardening
In penning the timeless classic Lord of the Rings (LOTR), J.R.R. Tolkien neglected to mention that Sauron utilized strain hardening – or cold working –to strengthen the One ring. Though the Dark Lord of Mordor in name, truly he was just an unheralded, underappreciated, and thus frustrated Materials Scientist who was millennia ahead of his time.

a) After spending an incredible Valentine’s Day together and reconciling your differences, the bond between you and your love is stronger than ever. Moreover, while testing the mechanical properties of your ring last week you were inadvertently cold working your ring and making it stronger (Sauron would be proud). Recall that the ring is unfurled and can be approximated as a rod with a length of 0.628 meters with a radius of 1 mm. This radius corresponds to a cross sectional area of 3.15 mm². Right before necking, the lateral tensile strain was 0.2. Poisson’s ratio for gold is 0.42. Compute the percent cold work in the ring assuming the strain was uniform. (7 pts)
\[
0.42 = \frac{\varepsilon_y}{\varepsilon_z} = -\frac{\varepsilon_y}{0.2} \rightarrow \varepsilon_y = -0.084
\]
\[
-0.084 = \frac{\Delta d}{d}, \rightarrow \Delta d = -.168 \text{ mm}
\]
\[
A_d = \pi (0.916)^2 = 2.635 \text{ mm}^2
\]
\[
\%CW = \frac{3.15 - 2.635}{3.15} \times 100 = 16.3\%
\]

b) Briefly describe the mechanism of strain hardening. (7 pts)
*Dislocation density in a metal increases with deformation or cold work. On average, dislocation-dislocation strain interactions are repulsive. The net result is that the motion of a dislocation is hindered by the presence of other dislocations, and as the density of dislocations increases this resistance becomes more pronounced. Thus the imposed stress necessary to deform a metal increases with increasing cold work.*

c) Draw (qualitatively), the stress/strain curve of the ring before and after cold working. Be sure to indicate which one is which. (6 pts)
4. Diffusion in Materials Processing
   a) Below are pairs of materials systems. In each pair, state which will diffuse faster. State the main reason for the difference. (5 pts)
      I. Carbon into α-Fe or γ-Fe (α-Fe because more open BCC structure)
      II. Fe in α-Fe at 500°C or at 900°C (900°C because temperature has a big influence on diffusion rates)
      III. Fe or H in α-Fe (H because smaller diffusing atom)
      IV. Si vacancy in Si or He in Si (He is Si because interstitial diffusion is faster than vacancy diffusion)
      V. H in Pt or H in Mg (Mg because it has atomic larger radius and both are close packed structures)
   b) As the armies of Middle Earth prepare for battle against Sauron, they realize that their regular steel armor is beginning to rust. The always wise Gandalf advises them that adding chromium as an alloying element in the steel will increase its resistance to corrosion. For the data below, the diffusion of chromium into steel, determine the temperature-independent pre-exponential $D_0$ and the activation energy for diffusion $Q_d$ (4 pts)
c) Sauron realizes the armies of Middle Earth are re-alloying their armor so he sets out to come up with computers to be able to model battle field strategy. To make a primitive computer, n and p type semiconducting materials are needed. He tries to create an n-type semiconductor. Arsenic can be diffused into silicon using a drive-in diffusion treatment to create an n-type semiconducting material. First Sauron pretreats silicon to obtain arsenic doping of $5.1 \times 10^{20}$ atoms/m$^2$ on the surface. (This value is $Q_0$ as seen on page 139 of the text.) Then he wants to drive the arsenic in for 6 hours at 1000C. What will the concentration of arsenic atoms be at a depth of 0.5µm into the Si wafer when he is done? Additionally, the values of $D_0$ and $Q_d$ are $5.5 \times 10^{-4}$ m$^2$/s and 4eV/atom, respectively. (5 pts)

$$D = D_0 \exp \left[ \frac{Q_d}{RT} \right] = (5.5 \times 10^{-4} \text{ m}^2/\text{s}) \exp \left[ \frac{-12.8}{8.6 \times 10^{-5} \text{ eV}/\text{atomK}} \times 1273 \text{K} \right] = 8.11 \times 10^{20} \text{ m}^2/\text{s}$$

Following Eq. 5.11,

$$C(x, t) = \frac{Q_0}{\sqrt{\pi D_d t}} \exp \left[ \frac{-x^2}{4D_d t} \right] = \frac{0.51 \times 10^{21} \text{ atoms/m}^2}{\sqrt{\pi \times (8.11 \times 10^{-20} \text{ m}^2/\text{s}) \times 6 \text{ hr} \times \frac{3600 \text{ s}}{1 \text{ hr}}}} \exp \left[ \frac{-(0.5 \times 10^{-6} \text{ m})^2}{4 \left(8.11 \times 10^{-20} \text{ m}^2/\text{s}\right) \times 6 \text{ hr} \times \frac{3600 \text{ s}}{1 \text{ hr}}} \right] = 2.15 \times 10^{12} \text{ atoms/m}^3$$

d) If Sauron is successful in transforming the Mordorian economy with his computer technology, surely an international energy crisis will follow. The United States decides to create a hydrogen economy to help mediate the crisis. A 1400 mile pipeline from Houston, TX to Washington, DC is constructed from steel to transport the hydrogen. The diffusion coefficient for hydrogen in this steel at 22°C is $2 \times 10^{-11}$ m$^2$/s. The pipe has a constant inner diameter of 100 cm and an outer diameter of 115 cm. Assuming a constant hydrogen pressure of 2 MPa in the pipe over the entire distance, calculate the mass of hydrogen lost during 1 year of transport. Assume steady state diffusion for the entire year. (Hint: first find the concentration of hydrogen inside the pipe and assume the concentration of hydrogen outside the pipe is zero.) (6 pts)

Find the concentration of hydrogen molecules.

$$PV = nRT \rightarrow \frac{n}{V} = \frac{P}{RT} \rightarrow \frac{\text{#molecules}}{\text{Volume}} = \frac{2 \times 10^6 \text{Pa}}{8.31 \text{ J/molK} \times 300 \text{K} \times 6.02 \times 10^{23} \text{ molecules/mol}}$$

$$= 4.82 \times 10^{26} \text{ molecules/m}^3$$
Assume that the concentration of $H_2$ outside of the pipe is approx. zero and solve for the diffusion flux of hydrogen out through the walls of the pipe.

\[
J = -D \frac{dc}{dx} = \frac{c_{outer} - c_{inner}}{x_{outer} - x_{inner}} = \left( \frac{2 \times 10^{-11} \text{m}^2}{s} \right) \times \frac{0 - 4.82 \times 10^{26} \text{molecules/m}^3}{1.15m - 1.00m} = 6.4 \times 10^{16} \text{molecules/m}^2\text{s}
\]

\[
J = \frac{M}{At} \rightarrow M = f(2\pi r_{inner} L) t
\]

\[
M = \left( 6.4 \times 10^{16} \frac{\text{molecules}}{m^2s} \right) * (2\pi * 1.00m * 2.253 * 10^6m)(3.154 * 10^7s)
\]

\[
= 2.85 \times 10^{31} \text{ molecules}
\]

\[
2.85 \times 10^{31} \text{ molecules} * \frac{\text{mol}}{6.02 \times 10^{23} \text{ molecule}} * \frac{2g}{\text{mol} H_2} = 9.5 \times 10^7 g = 9.5 \times 10^4 kg
\]

5. Phase Diagrams

After failing at the computer, the Dark Lord turns back to metallurgy. In his desire to forge the One Ring to rule over all Men, Elves and Dwarves the Dark Lord Sauron considered many materials. Two materials under consideration were titanium and aluminum. The Dark Lord commenced on an investigation of how these materials could be mixed. Below is the phase diagram of a solid solution of Al in Ti. Each phase is labeled. Unlabeled regions have a mixture of phases.

![Ti-Al Phase Diagram](image)

a) What phase(s) did the Dark Lord Sauron find at the following temperatures and concentrations of Al in atomic percent? (5 pts)
All information found on the plot above. Each part (i)-(v) uses distinct line colors as noted below.

I. 700 °C, 10% Al (Green Lines) The temperature and concentration (T,C) point is in the α-Ti phase.

II. 1100 °C, 50% Al (Blue Lines) The T,C point is in the TiAl phase.

III. 1300 °C, 30% Al (Pink Lines) The T,C point is in the β-Ti phase.

IV. 1400 °C, 46% Al (Red Lines) The T,C point lies in a region containing a mixture of β-Ti and TiAl.

V. 1600 °C, 38% Al (Orange Lines) The T,C point lies in a region containing a mixture of β-Ti and liquid (L)

b) For (i)-(v) in part a: If there is a mixture of phases found, what is the atomic percent aluminum of each part in the mixture? What percent of each phase will be present in the mixture with respect to atomic composition? (5 pts)

(i) and (ii) fall in single phases.

(iv) This T,C point falls in a mixture of β-Ti and TiAl. First draw a tie line (between the outer red vertical lines) from the β-Ti region edge to the TiAl region edge along the T=1400 °C line. The tie-line intersections with each phase region occurs at the concentration of Al found for that phase’s part in the mixture.

Atomic % Al in β-Ti here is ~44.9%.

Atomic % Al in TiAl here is ~49.8%.

To find the fraction (with respect to atomic composition) of β-Ti in the mixture at this T,C point we use the inverse lever rule. We find the fraction of the tie line which runs from the general concentration of Al (46%) to the edge of the opposite phase (TiAl here) region.

\[
\% \text{β-Ti} = \frac{49.8 - 46}{49.8 - 44.9} \times \frac{3.8}{4.9} = 0.776 = 77.6%
\]

\[
\% \text{TiAl} = \frac{100}{100-77.6} = 22.4\% \quad \text{or} \quad \% \text{TiAl} = \frac{46 - 44.9}{49.8 - 44.9} \times \frac{1.1}{4.9} = 0.224 = 22.4\%
\]

(v) This T,C point falls in a mixture of β-Ti and L. Draw a tie line (between the outer orange vertical lines) from the β-Ti region edge to the liquid region edge along the T=1600 °C line. The tie-line intersections with each phase region occurs at the concentration of Al found for that phase’s part in the mixture.

Atomic % Al in β-Ti here is ~35%.

Atomic % Al in L here is ~39.5%.

Find percent of each phase in the mixture with the inverse lever rule again:

\[
\% \text{β-Ti} = \frac{39.5 - 38}{39.5 - 35} \times \frac{1.5}{4.5} = 0.333 = 33.3%
\]

\[
\% L = \frac{100}{100-33.3} = 66.7\% \quad \text{or} \quad \% L = \frac{38 - 35}{39.5 - 35} = \frac{3}{4.5} = 0.667 = 66.7\%
\]

c) A β-Ti sample containing 10% (atomic percent) Al is being considered for use in making the One Ring. One form of processing considered by the Dark Lord Sauron to make the ring have a high strength to weight ratio involves cooling the material from 1100 °C to
1000 °C slowly. Describe the phase and composition before and after this processing. How would it be different if it were cooled fast? (5 pts)

At the start the sample will contain β-Ti. Grains of α-Ti will form in the cooling process. When cooled slowly the β-Ti will contain roughly 8.5 atomic percent Al and the α-Ti grains will contain about 11 atomic percent Al.

If it were cooled fast the grains formed would be composed of layers of different composition of Al unlike a slowly cooled sample which would have a roughly constant concentration through each grain. Also the grains will be smaller for the faster cooled.

d) Describe the expected change in mechanical properties of the material after processing as described in part c with respect to dislocation motion? (5 pts)

By precipitating grains of α-Ti, dislocations may be slowed or even stopped from gliding past these grain boundaries. This decrease in the ease of dislocation motion causes the material to be harder. In other words, it has been precipitation hardened.