

## Problem Distribution

| Chapter | Problems Covered |
| :---: | :---: |
| $\mathbf{7}$ | $7.1,7.2,7.3,7.4,7.5,7.6,7.7,7.8,7.9$ |
| $7.10,7.11$ |  |
| $\mathbf{8}$ | $8.2,8.7,8.8,8.10,8.13,8.14$ |
| $\mathbf{9}$ | $9.4,9.7,9.8,9.9,9.12,9.13$ |
| $\mathbf{1 0}$ | $10.5,10.6,10.15,10.16,10.17$ |
| $\mathbf{1 1}$ | $11.7,11.8$ |
| $\mathbf{1 2}$ | 12.9 |
| $\mathbf{1 3}$ | $13.1,13.2,13.5$ |
| $\mathbf{1 4}$ | 14.4 |
| $\mathbf{1 5}$ | $15.1,15.2,15.3,15.4,15.5$ |
| $\mathbf{1 6}$ | $16.5,16.6,16.8,16.11,16.13$ |

## Problems

## ■ Chapter 7 - Diffusion

## Problem 7.1

A steel plate component operates in a carburizing atmosphere on one side and a decarburizing one on the other at $700^{\circ} \mathrm{C}$ in a condition of steady state. Calculate the diffusion flux of carbon through the plate if the concentrations of carbon at positions of 5 and 10 mm beneath the carburizing surface are 1.2 and $0.8 \mathrm{~kg} \mathrm{~m}^{-3}$, respectively. Assume a diffusion coefficient of $3 \times 10^{-11} \mathrm{~m}^{2} \mathrm{~s}^{-1}$.
Problem 7.2
Assuming that the vacancy concentration of a close-packed metal is $10^{-4}$ at its melting point and that $D_{0}=10^{-4} \mathrm{~m}^{2} \mathrm{~s}^{-1}$ where $D=D_{0} \exp \left(-E_{D} / k T\right)$ and $D$ is the selfdiffusion coefficient, answer questions (a) to (f), which relate to diffusion by a vacancy mechanism in a close-packed metal:
(a) What are the vacancy concentrations at $1 / 4,1 / 2$, and $3 / 4 T_{m}$ (in kelvin)?
(b) Estimate the diffusion coefficient of the vacancies at $1 / 4,1 / 2$, and $3 / 4 T_{m}$.
(c) Estimate the self-diffusion coefficient for the metal at $1 / 4,1 / 2$, and $3 / 4 T_{m}$.
(d) How far does a vacancy diffuse at $T_{m} / 2$ in 1 h ?
(e) How far does an atom diffuse at $T_{m} / 2$ in 1 h ?
(f) If copper melts at $1065^{\circ} \mathrm{C}$, estimate $E_{\text {f }}$. (Boltzmann's constant $k_{B}=8.6 \times 10^{-5} \mathrm{eV}$ $\mathrm{K}^{-1}$ ).
Problem 7.3
The diffusivity of lithium in silicon is $10^{-9} \mathrm{~m}^{2} \mathrm{~s}^{-1}$ at 1376 K and $10^{-10} \mathrm{~m}^{2} \mathrm{~s}^{-1}$ at 968 K . What are the values of $E_{D}$ and $D_{0}$ for diffusion of lithium in silicon? ( $E_{D}$ is the activation energy for diffusion in $\mathrm{J} \mathrm{mol}^{-1}$ and $R=8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$.)
Problem 7.4
The diffusion coefficients for copper in aluminum at 500 and $600^{\circ} \mathrm{C}$ are $4.8 \times 10^{-14}$ and $5.3 \times 10^{-13} \mathrm{~m}^{2} \mathrm{~s}^{-1}$, respectively. Determine the approximate time at $500^{\circ} \mathrm{C}$ that will produce the same diffusion result (in terms of concentration of Cu at some specific point in Al ) as a 10 h heat treatment at $600^{\circ} \mathrm{C}$.

## Problem 7.5

The structure of an as-cast Cu-Ni alloy has a dendrite arm spacing of $120 \mu \mathrm{~m}$. If the activation energy for diffusion in this system is $120 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and the preexponential factor is $6.5 \times 10^{-9} \mathrm{~m}^{2} \mathrm{~s}^{-1}$, estimate the temperature at which this alloy needs to be 'soaked' in order to achieve homogenization in 24 h .
Problem 7.6
In carburizing an alloy that initially has a uniform carbon concentration of 0.25 $\mathrm{wt} \%$ and is to be treated at $950^{\circ} \mathrm{C}(1223 \mathrm{~K})$, if the concentration of carbon at the surface is suddenly brought to and maintained at $1.20 \mathrm{wt} \%$, how long will it take to achieve a carbon content of $0.80 \mathrm{wt} \%$ at a position 0.5 mm below the surface? The diffusion coefficient for carbon in iron at this temperature is $1.6 \times 10^{-11} \mathrm{~m}^{2} \mathrm{~s}^{-1}$. Assume that the steel piece is semi-infinite

## Problem 7.7

Base Si wafer characteristics are developed by diffusing in B or P. Diffusion of $P$ into Si forms $n$-type semiconductor material and can take place from a gaseous atmosphere. Estimate the time taken at $1200^{\circ} \mathrm{C}$ to develop a doping level of $10^{21}$ atoms per cubic meter at a depth of $1 \mu \mathrm{~m}$, if the gaseous atmosphere generates a surface $P$ concentration of $2 \times 10^{22}$ atoms per $\mathrm{m}^{3}$.
Diffusion of P in Si: $D_{0}=7.5 \times 10^{-5} \mathrm{~m}^{2} \mathrm{~s}^{-1}, Q=3.35 \mathrm{eV}, R=8.314 \mathrm{~kJ} \mathrm{~mol}^{-1}$, Avogadro's number: $6.02 \times 10^{23}$.

## Problem 7.8

Another alternative route to Problem 7.7 is to coat the pure Si wafer with a $\mathrm{Si}-10$ at. \% P coating of thickness $1 \mu \mathrm{~m}$ and diffusing P in at $1200^{\circ} \mathrm{C}$. Estimate the change in process time compared with the gaseous route. Given: density of $\mathrm{Si}=$ $2300 \mathrm{~kg} \mathrm{~m}^{-3}$, atomic weight of $\mathrm{Si}=28.09$.

## Problem 7.9

Ion implantation followed by diffusion is a modern method of surface enrichment. If nitrogen ions are implanted to a depth of $0.1 \mu \mathrm{~m}$ producing a surface layer of 10 $\mathrm{wt} \% \mathrm{~N}$ and a maximum hardness requires a nitrogen content of $0.25 \mathrm{wt} \%$, calculate the time required to produce a $1 \mu \mathrm{~m}$ hardened layer by diffusion at $1000^{\circ} \mathrm{C}$ when $D=9.6249 \times 10^{-12} \mathrm{~m}^{2} \mathrm{~s}^{-1}$.

## Problem 7.10

A thin layer of radioactivity doped gold has been sputtered on the end of a gold block and held at $1000^{\circ} \mathrm{C}$ for 16 h . The specimen was then sectioned and the radioactive count of each slice determined as a function of distance from the sputtered end. The variation of activity with distance was:

| Counts ( $\mathrm{min}^{-1}$ ) | Distance from sputtered end $\left(\times 10^{-4} \mathrm{~m}\right)$ |
| :---: | :---: |
| 8164 | 1 |
| 6413 | 2 |
| 4042 | 3 |
| 2350 | 4 |
| 828 | 5 |

Plot the data and calculate the self-diffusion coefficient of Au at $1000^{\circ} \mathrm{C}$. Problem 7.11
A thin film of radioactive gold was deposited on the end of a gold bar and annealed for 24 h near $T_{m}$. The specimen was then sectioned and the radioactivity of each slice measured as follows. Determine $D$.

| Distance from end of bar <br> to center of slice $(\boldsymbol{\mu m})$ | 10 | 20 | 30 | 40 | 50 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Activity | 83.8 | 66.4 | 42.0 | 23.6 | 8.74 |

## ■ Chapter 8 - Physical Properties

Problem 8.2
Given that the resistivity of copper at $0^{\circ} \mathrm{C}$ is $1.67 \times 10^{-8} \Omega \cdot \mathrm{~m}$ and the temperature coefficient of resistivity $\alpha$ is $6.8 \times 10^{-3}{ }^{\circ} \mathrm{C}^{-1}$, calculate the conductivity at $-100^{\circ} \mathrm{C}$.

## Problem 8.7

The resistivity of intrinsic germanium is $0.028 \Omega \cdot \mathrm{~m}$ at 385 K and $2.74 \times 10^{-4} \Omega \cdot \mathrm{~m}$. at 714 K . Assume that the hole and electron mobilities both vary as $T^{-3 / 2}$.
(a) Determine the band gap energy $E_{g}$.
(b) At what wavelength would you expect the onset of optical absorption?

## Problem 8.8

An $n$-type semiconductor has an electron concentration of $5 \times 10^{17} \mathrm{~m}^{-3}$ and drift velocity of $500 \mathrm{~m} / \mathrm{s}$ in an electric field of $1500 \mathrm{~V} / \mathrm{m}$. Calculate the conductivity.
Problem 8.10
For Si the room temperature electrical conductivity is $4 \times 10^{-4}(\Omega \cdot \mathrm{~m})^{-1}$, the electron and hole mobilities are respectively $0.14 \mathrm{~m}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}$ and $0.05 \mathrm{~m}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}$. Calculate the intrinsic carrier concentration $n$ at room temperature.

## Problem 8.13

If Nb is to be used in an MRI with a magnetic field of $40.0 \mathrm{~mA} \mathrm{~m}^{-1}$, what temperature must be achieved to maintain superconductivity? The temperature $T$ below which superconductivity occurs for a magnetic field is given by Eq. (8.14). For $\mathrm{Nb}, H_{c}=156.77 \mathrm{~mA} \mathrm{~m}^{-1}$ and $T_{c}=9.25 \mathrm{~K}$.

## Problem 8.14

The magnetic susceptibility ( $\chi$ ) of iron is temperature dependent according to $\chi \propto$ $1 /\left(T-T_{c}\right)$, where $T_{c}$ is the Curie temperature. At $900^{\circ} \mathrm{C}, \chi$ has a value of $2.5 \times 10^{-4}$. $T_{C}$ for iron is $770^{\circ} \mathrm{C}$. Determine the susceptibility at $800^{\circ} \mathrm{C}$.

## ■ Chapter 9 - Plastic Deformation and Dislocation Behaviour

## Problem 9.4

Estimate the shear stress at the upper yield point and the yield drop (shear stress) that occurs when the mobile dislocation density increases by two orders of magnitude from the initial density of $10^{5} \mathrm{~cm}^{-2}$. (Take the strain rate to be $10^{-3} \mathrm{~s}^{-1}$, $\tau_{0}$ the stress for unit dislocation velocity of $1 \mathrm{~cm} / \mathrm{s}$ to be $2.8 \times 10^{4} \mathrm{~N} \mathrm{~cm}^{-2}, n$ to be 20 and $b$, the Burgers vector, to be $2 \times 10^{-8} \mathrm{~cm}$.)

## Problem 9.7

The resolved shear stress for copper is $0.69 \mathrm{MN} \mathrm{m}^{-2}$ with a dislocation density of $10^{10} \mathrm{~m}^{-2}$. Estimate the resolved shear stress when the copper is deformed to an increased dislocation density of $10^{12} \mathrm{~m}^{-2}$. Take $n$ to be 10 .

## Problem 9.8

The Vickers hardness of a steel is $2.0 \mathrm{GN} \mathrm{m}^{-2}$. Estimate its yield stress.
Problem 9.9
A copper alloy has a true stress $\sigma_{T}$ of 414 MPa at true strain $\varepsilon_{T}=0.15$ and $\sigma_{T}$ of 483 MPa at true strain $\varepsilon_{T}=0.25$. What is the value of $\sigma_{T}$ at $\varepsilon_{T}=0.2$ ?
Problem 9.12
By assuming Ludvig strain hardening equation $\sigma=K \varepsilon^{n}$ for the true stress and strain. Show that the engineering (nominal) tensile strength is given by $\sigma_{T S}=$ $K n^{n} / e^{n}$.
Problem 9.13
An alloy has a strain hardening relation given by $\sigma=630 \varepsilon^{0.4} \mathrm{MPa}$. Estimate its nominal tensile strength. In a tensile experiment, the actual tensile strength recorded is 230 MPa . Comment on any difference.

## - Chapter 10 - Surfaces, Grain Boundaries and Interfaces

 Problem 10.5The strengthening of a polycrystalline metal is provided by grain refinement and dispersion of particles. The tensile yield stress of the metal is 400 MPa when the grain size is 0.32 mm and 300 MPa when $d=1 \mathrm{~mm}$. Calculate the average distance between the particles. Assume the shear modulus of the metal $\mu=80 \mathrm{GPa}$ and $b=$ 0.25 nm .

Problem 10.6
A steel with a grain size of $25 \mu \mathrm{~m}$ has a yield stress of 200 MPa and with a grain size of $9 \mu \mathrm{~m}$ a yield stress of 300 MPa . A dispersion of non-deformable particles is required to raise the strength to 500 MPa in a steel with grain size $100 \mu \mathrm{~m}$. What would be the required dispersion spacing? (Assume the shear modulus $\mu=80 \mathrm{GPa}$, and the Burguers vector $b=0.2 \mathrm{~nm}$.)

## Problem 10.15

The strengthening of a polycrystalline metal is provided by grain refinement and dispersion of particles. The tensile yield stress of the metal is 400 MPa when the grain size is 0.32 mm and 300 MPa when $d=1 \mathrm{~mm}$. Calculate the average distance between the particles. Assume the shear modulus of the metal $\mu=80 \mathrm{GPa}, b=$ 0.25 mm .

## Problem 10.16

Assume that strengthening of a low-carbon steel is achieved by grain size refinement and by fine carbide dispersions. Uniaxial tensile tests show that the tensile yield stress is 380 MPa when the grain diameter $d$ is 0.32 mm and 276 MPa when $d$ is 1.0 mm . What is the average distance of closest approach between the particles? The shear modulus is $11.98 \times 10^{10} \mathrm{~Pa}, b=2 \times 10^{-10} \mathrm{~m}$.

## Problem 10.17

A steel with a grain size of $25 \mu \mathrm{~m}$ has a yield stress of 200 MPa and with a grain size of $9 \mu \mathrm{~m}$ a yield stress of 300 MPa . A dispersion of non-deformable particles is required to raise the strength to 500 MPa in a steel with grain size $100 \mu \mathrm{~m}$. What would be the required dispersion spacing? (Assume the shear modulus $\mu=80 \mathrm{GPa}$, the Burgers vector $b=0.2 \mathrm{~nm}$.)

## ■ Chapter 11 - Work Hardening and Annealing

Problem 11.7
Copper is $50 \%$ recrystallized in the following times at the different temperatures. Calculate the activation energy for the process.

| Time (min) | Temperature $\left.{ }^{( }{ }^{\circ} \mathbf{C}\right)$ |
| :---: | :---: |
| 75 | 102 |
| 21 | 119 |
| 9 | 135 |

## Problem 11.8

The kinetics of recrystallization obey the Avrami relationship $f=1-\exp \left(-K t^{n}\right)$, where $f$ is the fraction recrystallized in time $t$ and $K, n$ are constants. Using the fraction transformed data given below, determine the total time required for $95 \%$ recrystallization.

| Fraction <br> recrystallized | Time, $\boldsymbol{t}(\mathbf{s})$ |
| :---: | :---: |
| 0.2 | 280 |
| 0.6 | 450 |

## Chapter 12 - Steel Transformations

## Problem 12.9

The kinetics of the austenite-to-pearlite transformations obey the Avrami relationship $f=1-\exp \left(-K t^{n}\right)$, where $f$ is the fraction transformed in time $t$ and $K, n$ are constants. Using the fraction transformed-time data given below, determine the time required for $95 \%$ of the austenite to transform to pearlite.

| Fraction <br> transformed | Time (t) |
| :---: | :---: |
| 0.2 | 280 |
| 0.6 | 425 |

Estimate the values of $K$ and $n$

## ■ Chapter 13 - Precipitation Hardening

Problem 13.1
During age hardening of an aluminum alloy the maximum hardness could be achieved by ageing at $327^{\circ} \mathrm{C}$ for 10 h or 280 h at $227^{\circ} \mathrm{C}$. How long would it take at $257^{\circ} \mathrm{C}$ ? If the alloy then contains precipitates $10^{-7} \mathrm{~m}$ diameter separated by $10^{-6}$ m , estimate the tensile yield stress.
Problem 13.2
In certain Al-Cu alloys, enhanced diffusion occurs following quenching from an elevated temperature. From the data given below for an Al-4 wt\% Cu alloy, calculate the energies of formation, $E_{f}$, and motion, $E_{m}$, of vacancies by assuming that the activation energy for diffusion in an annealed alloy equals $E_{f}+E_{m}$. For an alloy at $25^{\circ} \mathrm{C}$ show graphically how the factor $R e$ by which quenching increases diffusivity, varies with quenching temperature, $T_{q}$, between $25^{\circ} \mathrm{C}$ and $550^{\circ} \mathrm{C}$. Diffusion coefficients of Cu in Al-4 wt\% Cu:

| $\boldsymbol{T}^{\mathbf{}} \mathbf{C}^{\mathbf{1}}$ | $\boldsymbol{D}^{\mathbf{- 2}} \mathbf{s}^{\mathbf{1}}$ | Heat treatment |
| :---: | :---: | :---: |
| 500 | $3.63 \times 10^{-14}$ | Annealed |
| 25 | $8.61 \times 10^{-30}$ | Annealed |
| 25 | $2.76 \times 10^{-21}$ | Quenched from $500^{\circ} \mathrm{C}$ |

Problem 13.5
In an Al-Ag precipitation hardening alloy with spherical particles, the zone size increases from 2 to 5 nm in 3 h at $120^{\circ} \mathrm{C}$ and to 10 nm after 5 h at $160^{\circ} \mathrm{C}$.
Determine the activation energy for diffusion of Ag in Al .

## ■ Chapter 14 - Selected Alloys

## Problem 14.4

The surfaces of steel specimens can be hardened by enrichment in their nitrogen content. One route is to maintain a nitrogen-rich atmosphere around a heated steel specimen. If this atmosphere gives a constant $N$ content of 1.53 wt . \% at $1000^{\circ} \mathrm{C}$ and the minimum hardness requires a nitrogen content of $0.25 \mathrm{wt} . \%$, calculate the time required to achieve a hardened depth of (a) $1 \mu \mathrm{~m}$ and (b) 1.75 $\mu \mathrm{m}$ under these conditions.
Data: Diffusion of N in $\gamma$-Fe: $D_{0}=9.1 \times 10^{-5} \mathrm{~m}^{2} \mathrm{~s}^{-1}, Q=170 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Values of the error function are tabulated below.

| $z$ | 0.85 | 0.90 | 0.95 | 1.0 | 1.1 | 1.2 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\operatorname{erf}(z)$ | 0.770 | 0.797 | 0.8209 | 0.8427 | 0.8802 | 0.910 |
| $z$ | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 |
| $\operatorname{erf}(z)$ | 0.934 | 0.9523 | 0.9661 | 0.9763 | 0.9838 | 0.9891 |

## - Chapter 15 - Creep, Fatigue and Fracture

## Problem 15.1

A thick steel plate had a microcrack of 5 mm and a fracture toughness $K_{c} \sim 40$ $\mathrm{MN} \cdot \mathrm{m}^{-3 / 2}$. Determine the stress at which fast fracture takes place.
Problem 15.2
The crack growth rate equation in a steel component $d a / d N=c(\Delta K)^{m}$ has values of $a=0.1 \mathrm{~mm}, \mathrm{c}=2 \times 10^{-13}\left(\mathrm{MN} \cdot \mathrm{m}^{-2}\right)^{-4} \mathrm{~m}^{-1}, \mathrm{~m}=4$ and $K_{c}=54 \mathrm{MN} \cdot \mathrm{m}^{-3 / 2}$. Calculate the lifetime to failure if the component is subjected to an alternating stress from 0 to $180 \mathrm{MN} \cdot \mathrm{m}^{-2}$ about the mean $\Delta \sigma / 2$.

## Problem 15.3

The deformation mechanism map in the figure below shows three fields of creep for each of which the creep rate $\dot{\varepsilon}\left(s^{-1}\right)$ is represented by an expression of the form $\dot{\varepsilon}=A \sigma^{n} \exp (-Q / R T)$. The constant $A$ is $1.5 \times 10^{5}, 5.8 \times 10^{5} / d^{2}$ and $10^{-9} / d^{3}$ for dislocation creep, Herring-Nabarro creep and Coble creep, respectively ( $d=$ grain size in meters), while the stress exponent $n$ is 5,1 and 1 and the activation energy $Q\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ is 550,550 and 400 . The stress $\sigma$ is in MPa. Assuming that the grain size of the material is 1 mm and given the gas constant $R=8.3 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$,
(a) Label the three creep fields.
(b) Calculate the stress level $\sigma$ in MPa of the boundary AB.
(c) Calculate the temperature (K) of the boundary AC.


## Problem 15.4

In a high temperature application an alloy is observed to creep at an acceptable steady-state rate under a stress of 70 MPa at a temperature of 1250 K . If metallurgical improvements would allow the alloy to operate at the same creep rate but at a higher stress level of 77 MPa , estimate the new temperature at which the alloy would operate under the original stress conditions. Take stress exponent $n$ to be 5 , and activation energy for creep $Q$ to be $200 \mathrm{~kJ} \mathrm{~mol}^{-1}$.

Problem 15.5
Cyclic fatigue of an aluminum alloy showed it failed under a stress range $\Delta \sigma=280$ MPa after $10^{5}$ cycles, and for a range 200 MPa after $10^{7}$ cycles. Using Basquin's law, estimate the life of the component subjected to a stress range of 150 MPa .

## ■ Chapter 16 - Oxidation, Corrosion and Surface Engineering

## Problem 16.5

Iron oxidizes parabolically with time and the constant $k$ is given by

$$
k=2.5 \times 10^{-5} \times \exp \left(-\frac{72.4 \mathrm{~kJ} \mathrm{~mol}^{-1}}{R T}\right) \mathrm{cm}^{2} \mathrm{~s}^{-1}
$$

(a) What is the value of $k$ at $500^{\circ} \mathrm{C}$ ?
(b) What is the depth to which oxidation will occur at $500^{\circ} \mathrm{C}$ in 1 year?

## Problem 16.6

Assuming that oxidation of Fe to FeO obeys parabolic kinetics calculate the weight of metal lost at $600^{\circ} \mathrm{C}$ after 1 year if the oxidation constant is $2 \times 10^{-7} \mathrm{~kg}^{2} \mathrm{~m}^{-4} \mathrm{~s}^{-1}$. What thickness does this correspond to?

## Problem 16.8

A thin film of radioactive copper was electroplated on the end of a copper cylinder. After a high temperature anneal of 20 h , the specimen was sectioned and the activity of each section counted. The following results were obtained:

| Counts/minute | Distance from <br> Plated end (10 <br> $\mathbf{- 4}$ <br> $\mathbf{~ m})$ |
| :---: | :---: |
| 5012 | 1 |
| 3981 | 2 |
| 2512 | 3 |
| 1413 | 4 |
| 525 | 5 |

Plot the data and determine the self-diffusion coefficient of Cu at the temperature of the experiment.

## Problem 16.11

Ion implantation followed by diffusion is a modern method of surface enrichment. If nitrogen ions are implanted to a depth of $0.1 \mu \mathrm{~m}$ producing a surface layer of 10 $\mathrm{wt} \% \mathrm{~N}$ and a maximum hardness requires a nitrogen content of $0.25 \mathrm{wt} \%$, calculate the time required to produce a $1 \mu \mathrm{~m}$ hardened layer by diffusion at $1000^{\circ} \mathrm{C}$ when $D=9.6249 \times 10^{-12} \mathrm{~m}^{2} \mathrm{~s}^{-1}$. (Hint: the 'thin-surface-film' solution of Fick's second law is $C_{x, t}=(\alpha / \sqrt{\pi D t}) \exp \left(-x^{2} / 4 D t\right)$, where $\alpha$ is the amount of impurity per unit area present in the initial surface layer, $D$ is the diffusivity, $x$ is distance and $t$ is time.)

## Problem 16.13

The strain energy within a thin, flat oxide layer which remains attached to a thick metal substrate during cooling from the oxidation temperature, $T_{o x,}$ is

$$
W^{*}=E_{o x}\left(1-v_{o x}\right)(\Delta T)^{2}(\Delta \alpha)^{2}
$$

where $W^{*}$ is the strain energy density $\left(\mathrm{J} \mathrm{m}^{-3}\right)$ within the oxide, $E_{o x}$ is Young's modulus of the oxide ( Pa ), $v_{o x}$ is its Poisson ratio, $\Delta T=T_{o x}-T$ is the temperature $\operatorname{drop}(\mathrm{K})$ and $\Delta \sigma\left(=\left[\alpha_{\text {metal }}-\alpha_{\text {ox }}\right]\right)$ is the difference $\left(\mathrm{K}^{-1}\right)$ between the linear thermal expansion coefficient of metal and oxide.
(a) Derive this equation for $W^{*}$ assuming that the oxide is stress-free at the oxidation temperature and that the oxide layer experiences equal bi-axial, in-plane strains during cooling.
(b) Show how the expression for $W *$ can be used to predict the critical temperature drop, $\Delta T_{c}$, to initiate oxide spallation. (Hint: assume that there is no change in strain energy within the alloy substrate when spallation is initiated. Let the effective fracture energy of the oxide-metal interface be $\gamma_{f}, \mathrm{~J} \cdot \mathrm{~m}^{-2}$, and the oxide thickness be $h$, m.)
(c) Calculate the value of $\gamma_{f}$ using the following values: $E_{o x}=380 \mathrm{GPa}, v_{\mathrm{ox}}=0.27$, $\Delta \alpha=8.0 \times 10^{-6} \mathrm{~K}^{-1}, h=5 \times 10^{-6} \mathrm{~m}, \Delta T_{c}=671 \mathrm{~K}$. Why does this value of $\gamma_{f}$ differ from the intrinsic value of $2 \mathrm{~J} \cdot \mathrm{~m}^{-2}$ for fracture of the oxide/metal interface?

## Solutions

## ■ P7.1

This is a straightforward application of Fick's first law:

$$
J=-D \frac{\Delta c}{\Delta x}=-\left(3 \times 10^{-11}\right) \times \frac{1.2-0.8}{0.005-0.01}=-2.4 \times 10^{-9} \mathrm{~kg} \mathrm{~m}^{-2} \mathrm{~s}^{-1}
$$

## ■ P7.2

Part (a): We know that $D_{0}=10^{-4}=\exp \left(-E_{f} / k_{B} T_{m}\right)$. Calculations for other temperatures are shown next.

$$
\begin{aligned}
& \text { at } \frac{T_{m}}{4}: \exp \left(-\frac{E_{f}}{k_{B} \times\left(T_{m} / 4\right)}\right)=\left[\exp \left(-\frac{E_{f}}{k T_{m}}\right)\right]^{4}=\left(10^{-4}\right)^{4}=10^{-16} \\
& \text { at } \frac{T_{m}}{2}: \exp \left(-\frac{E_{f}}{k_{B} \times\left(T_{m} / 2\right)}\right)=\left[\exp \left(-\frac{E_{f}}{k T_{m}}\right)\right]^{2}=\left(10^{-4}\right)^{2}=10^{-8} \\
& \text { at } \frac{3 T_{m}}{4}: \exp \left(-\frac{E_{f}}{k_{B} \times\left(3 T_{m} / 4\right)}\right)=\left[\exp \left(-\frac{E_{f}}{k T_{m}}\right)\right]^{\frac{4}{3}}=\left(10^{-4}\right)^{\frac{4}{3}}=4.64 \times 10^{-6}
\end{aligned}
$$

Part (b): Noting that $D_{v}=D_{o} \exp \left(-E_{m} / k_{B} T\right)$ and assuming $E_{m}=E_{f}$, we can use the results in part (a) to compute the diffusion coefficients of vacancies:

$$
\begin{array}{r}
\text { at } \frac{T_{m}}{4}: D_{v}=D_{0} \exp \left(-\frac{E_{m}}{k_{B} T}\right)=10^{-4} \times 10^{-16}=10^{-20} \mathrm{~m}^{2} \mathrm{~s}^{-1} \\
\text { at } \frac{T_{m}}{2}: D_{v}=D_{0} \exp \left(-\frac{E_{m}}{k_{B} T}\right)=10^{-4} \times 10^{-8}=10^{-12} \mathrm{~m}^{2} \mathrm{~s}^{-1} \\
\text { at } \frac{3 T_{m}}{4}: D_{v}=D_{0} \exp \left(-\frac{E_{m}}{k_{B} T}\right)=10^{-4} \times\left(4.64 \times 10^{-6}\right)=4.64 \times 10^{-10} \mathrm{~m}^{2} \mathrm{~s}^{-1}
\end{array}
$$

Part (c): Note that

$$
D=D_{0} \exp \left[-\frac{\left(E_{f}+E_{m}\right)}{k_{B} T}\right]=D_{v} \exp \left(-\frac{E_{f}}{k_{B} T}\right)
$$

Using the vacancy concentrations determined in part (a) and the diffusion coefficients determined in part (b), we may write

$$
\begin{array}{r}
\text { at } \frac{T_{m}}{4}: D=10^{-20} \times 10^{-16}=10^{-36} \mathrm{~m}^{2} \mathrm{~s}^{-1} \\
\text { at } \frac{T_{m}}{2}: D=10^{-12} \times 10^{-8}=10^{-20} \mathrm{~m}^{2} \mathrm{~s}^{-1} \\
\text { at } \frac{3 T_{m}}{4}: D=\left(4.6 \times 10^{-10}\right) \times\left(4.6 \times 10^{-6}\right)=2.12 \times 10^{-15} \mathrm{~m}^{2} \mathrm{~s}^{-1}
\end{array}
$$

Part (d): Using the diffusivity determined in the second calculation of part (b), the diffusion length is found as

$$
x=\sqrt{D_{v} t}=\sqrt{10^{-12} \times 3600}=6.0 \times 10^{-5} \mathrm{~m}=60.0 \mu \mathrm{~m}
$$

Part (e): Using the diffusivity determined in the second calculation of part (c), the diffusion length is found as

$$
x=\sqrt{D t}=\sqrt{10^{-20} \times 3600}=6.0 \times 10^{-9} \mathrm{~m}=6.0 \mathrm{~nm}
$$

Part (f): Solving for $E_{f}$, we have

$$
\begin{gathered}
10^{-4}=\exp \left(-\frac{E_{f}}{k_{B} T_{m}}\right) \rightarrow E_{f}=-\ln \left(10^{-4}\right) k_{B} T_{m} \\
\therefore E_{f}=-\ln \left(10^{-4}\right) \times\left(8.6 \times 10^{-5}\right) \times(1065+273)=1.06 \mathrm{eV}
\end{gathered}
$$

■ P7.3
The diffusion coefficient is given by the Arrhenius-like law $D=D_{0} \exp \left(-E_{D} / R T\right)$, so that

$$
\ln D=\ln D_{0}-\frac{E_{D}}{R T}
$$

and

$$
\ln \left(\frac{D_{1}}{D_{2}}\right)=-\frac{E_{D}}{R}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)
$$

Solving for the activation energy for diffusion,

$$
\begin{gathered}
\ln \left(\frac{D_{1}}{D_{2}}\right)=-\frac{E_{D}}{R}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right) \rightarrow E_{D}=-\frac{R \ln \left(D_{1} / D_{2}\right)}{\left(1 / T_{1}-1 / T_{2}\right)} \\
\therefore E_{D}=-\frac{8.314 \times \ln \left(10^{-9} / 10^{-10}\right)}{(1 / 1376-1 / 968)}=62,500 \mathrm{~J} \mathrm{~mol}^{-1}=62.5 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{gathered}
$$

Lastly, we can determine $D_{0}$ :

$$
D_{0}=D \exp \left(\frac{E_{D}}{R T}\right)=10^{-10} \times \exp \left(\frac{62,500}{8.314 \times 968}\right)=2.36 \times 10^{-7} \mathrm{~m}^{2} \mathrm{~s}^{-1}
$$

## ■ P7.4

We may assume that the diffusion length $\sqrt{D t}$ is the same for both situations described in the problem statement. Letting $t_{500}$ denote the time at $500^{\circ} \mathrm{C}$ that will yield the same diffusion result as a 10 -hour treatment at $600^{\circ} \mathrm{C}$, it follows that

$$
\begin{gathered}
D_{500} t_{500}=D_{600} t_{600} \rightarrow t_{500}=\frac{D_{600}}{D_{500}} t_{600} \\
\therefore t_{500}=\frac{5.3 \times 10^{-13}}{4.8 \times 10^{-14}} \times 10=110 \mathrm{hr}
\end{gathered}
$$

## ■ P7.5

The soaking temperature can be estimated from the diffusion coefficient, which in turn can be determined by dint of the diffusion length equation $x=\sqrt{D t}$. For a dendrite arm spacing of $120 \mu \mathrm{~m}$, the diffusion distance will be $120 / 2=60 \mu \mathrm{~m}$, so that

$$
\begin{aligned}
& x=\sqrt{D t} \rightarrow D=\frac{x^{2}}{t} \\
& \therefore D=\frac{\left(60 \times 10^{-6}\right)^{2}}{24 \times 3600}=4.17 \times 10^{-14} \mathrm{~m}^{2} \mathrm{~s}^{-1}
\end{aligned}
$$

In turn,

$$
\begin{gathered}
D=D_{0} \exp \left(-\frac{Q}{R T}\right) \rightarrow T=-\frac{Q / R}{\ln \left(D / D_{0}\right)} \\
\therefore T=-\frac{120,000 / 8.314}{\ln \left[\left(4.17 \times 10^{-14}\right) /\left(6.5 \times 10^{-9}\right)\right]}=1210 \mathrm{~K}
\end{gathered}
$$

## ■ P7.6

In this unsteady diffusion problem, the concentration $c(x, t)$ of carbon varies according to equation (7.10):

$$
\frac{c(x, t)-c_{0}}{c_{s}-c_{0}}=1-\operatorname{erf}\left(\frac{x}{2 \sqrt{D t}}\right)
$$

Substituting the given data,

$$
\begin{gathered}
\frac{0.80-0.25}{1.20-0.25}=1-\operatorname{erf}\left(\frac{5 \times 10^{-4}}{2 \sqrt{\left(1.6 \times 10^{-11}\right) \times t}}\right) \\
\therefore 0.579=1-\operatorname{erf}\left(\frac{62.5}{\sqrt{t}}\right) \\
\therefore \operatorname{erf}\left(\frac{62.5}{\sqrt{t}}\right)=0.421
\end{gathered}
$$

The number $X$ for which $\operatorname{erf}(X)=0.421$ can be obtained in an error function table, or by using a computer algebra system such as Mathematica:

```
In[207]:= Solve[Erf[x] == 0.421, x]
```

$\cdots$ Solve: Inverse functions are being used by Solve, so some solutions may not
be found; use Reduce for complete solution information. Out[207] $=\{\{x \rightarrow 0.392335\}\}$

Finally,

$$
\begin{aligned}
\frac{62.5}{\sqrt{t}} & =0.392 \rightarrow t=\left(\frac{62.5}{0.392}\right)^{2} \\
\therefore t & =25,400 \mathrm{~s}=7.06 \mathrm{hr}
\end{aligned}
$$

## ■ P7.7

The concentration $c(x, t)$ of P in Si varies according to equation (7.10), which, for an initial concentration $c_{0}=0$, can be restated as

$$
\begin{gather*}
c(x, t)=c_{0}+\left(c_{s}-c_{0}\right)\left[1-\operatorname{erf}\left(\frac{x}{2 \sqrt{D t}}\right)\right] \\
\therefore c(x, t)=c_{s}\left[1-\operatorname{erf}\left(\frac{x}{2 \sqrt{D t}}\right)\right] \text { (I) } \tag{I}
\end{gather*}
$$

We proceed to compute the diffusivity of P in Si :

$$
\begin{gathered}
D=D_{0} \exp \left(-\frac{Q}{R T}\right)=\left(7.5 \times 10^{-5}\right) \times \exp \left[-\frac{3.35 \times\left(1.60 \times 10^{-19}\right) \times\left(6.02 \times 10^{23}\right)}{8.314 \times 1473}\right] \\
\therefore D=2.71 \times 10^{-16} \mathrm{~m}^{2} \mathrm{~s}^{-1}
\end{gathered}
$$

Substituting this quantity in $(I)$, along with $c(x, t)=1 \times 10^{21}$ and $c_{s}=2 \times 10^{22} \mathrm{~m}^{-3}$, we have

$$
\begin{gathered}
10^{21}=\left(2 \times 10^{22}\right) \times\left[1-\operatorname{erf}\left(\frac{1.0 \times 10^{-6}}{2 \sqrt{\left(2.71 \times 10^{-16}\right) \times t}}\right)\right] \\
\therefore \frac{10^{21}}{2 \times 10^{22}}=1-\operatorname{erf}\left(\frac{1.0 \times 10^{-6}}{2 \sqrt{\left(2.71 \times 10^{-16}\right) \times t}}\right) \\
\therefore 0.05=1-\operatorname{erf}\left(\frac{30.4}{\sqrt{t}}\right) \\
\therefore \operatorname{erf}\left(\frac{30.4}{\sqrt{t}}\right)=0.95
\end{gathered}
$$

Using Mathematica as we did in the previous problem:

```
In[213]:= Solve[Erf[x] == 0.95,x]
Out[213]= {{x->1.3859} }
```

Therefore,

$$
\begin{aligned}
& \operatorname{erf}\left(\frac{30.4}{\sqrt{t}}\right)=0.95 \rightarrow \frac{30.4}{\sqrt{t}}=1.386 \\
& \therefore t=\left(\frac{30.4}{1.386}\right)^{2}=481 \mathrm{~s}=8.02 \mathrm{~min}
\end{aligned}
$$

## ■ P7.8

In this case, the equation that governs the diffusion process is (7.18):

$$
c(x, t)=\frac{\alpha}{\sqrt{\pi D t}} \exp \left(-\frac{x^{2}}{4 D t}\right)
$$

where $\alpha$ is the initial amount of $P$ in a thin layer. Now, note that one mole of Si (density $=2300 \mathrm{~kg} / \mathrm{m}^{3}$ ) weighs 28.09 g and occupies a volume $\left(28.09 \times 10^{-3}\right) / 2300$ $=1.22 \times 10^{-5} \mathrm{~m}^{3}$. Then, one cubic meter of Si contains $\left(6.02 \times 10^{23}\right) /\left(1.22 \times 10^{-5}\right)=$ $4.93 \times 10^{28} \mathrm{P}$ atoms. Since the wafer is made of a 10 at. $\% \mathrm{P}$ coating, the number of $P$ atoms per cubic meter becomes $10 \% \times 4.93 \times 10^{28}=4.93 \times 10^{27}$. For an unit area of surface, $1-\mu \mathrm{m}$ thickness of alloy contains $4.93 \times 10^{27} \times 10^{-6}=4.93 \times 10^{21} \mathrm{P}$ atoms $/ \mathrm{m}^{2}$. Accordingly, $\alpha=4.93 \times 10^{21} \mathrm{at} / \mathrm{m}^{2}$. Substituting the pertaining data into (I),

$$
\begin{gather*}
10^{21}=\frac{4.93 \times 10^{28}}{\sqrt{\pi \times\left(2.71 \times 10^{-16}\right) \times t}} \exp \left(-\frac{\left(10^{-6}\right)^{2}}{4 \times\left(2.71 \times 10^{-16}\right) \times t}\right)  \tag{I}\\
\therefore 10^{21}=\frac{1.69 \times 10^{29}}{\sqrt{t}} \exp \left(-\frac{923}{t}\right)
\end{gather*}
$$

This transcendental equation can be solved with Mathematica's FindRoot command using an initial guess of, say, $t=100 \mathrm{sec}$ :

$$
\begin{aligned}
\operatorname{In}[221]:= & \text { FindRoot }\left[1 \mathbf{0}^{21}-\frac{1.69 * 10^{29}}{\sqrt{t}} * \operatorname{Exp}[-\mathbf{9 2 3} / t],\{t, \mathbf{1 0 0}\}\right] \\
& \cdots \text { FindRoot: The line search decreased the step size to within tolerance } \\
& \text { specified by AccuracyGoal and PrecisionGoal but was unable to find a } \\
& \text { sufficient decrease in the merit function. You may need more than } \\
& \text { MachinePrecision digits of working precision to meet these tolerances. }
\end{aligned}
$$

As shown, $t \approx 54.5 \mathrm{sec}$. This is about $89 \%$ less than the pure-Si wafer situation examined in Problem 7.7.

## ■ P7.9

Much like the previous problem, this one involves equation (7.18):

$$
c(x, t)=\frac{\alpha}{\sqrt{\pi D t}} \exp \left(-\frac{x^{2}}{4 D t}\right)
$$

Here, for a surface layer of $10 \mathrm{wt} \% \mathrm{~N}$ with $0.1-\mu \mathrm{m}$ thickness, we may write

$$
\alpha=10 \times\left(0.1 \times 10^{-6}\right)=10^{-6} \mathrm{wt} \%
$$

Substituting the pertaining data into (I), we get

$$
0.25=\frac{10^{-6}}{\sqrt{\pi \times\left(9.6249 \times 10^{-12}\right) \times t}} \exp \left[-\frac{\left(10^{-6}\right)^{2}}{4 \times\left(9.6249 \times 10^{-12}\right) \times t}\right]
$$

$$
\therefore 0.25=\frac{0.182}{\sqrt{t}} \exp \left(-\frac{0.0260}{t}\right)
$$

This transcendental equation can be solved with help of Mathematica's FindRoot command:

$$
\begin{aligned}
& \operatorname{In}[226]:=\operatorname{FindRoot}\left[0.25=\frac{0.182}{\sqrt{t}} * \operatorname{Exp}\left[-\frac{0.026}{t}\right],\{t, 1\}\right] \\
& \text { Out[226] }=\{t \rightarrow 0.475031\}
\end{aligned}
$$

Thus, $t=0.475 \mathrm{~s}=475 \mathrm{msec}$.
■ P7. 10
This is a thin film problem, hence the concentration at distance $x$ from the sputtered end after heating for time $t$ is given by equation (7.18):

$$
c(x, t)=\frac{\alpha}{\sqrt{\pi D t}} \exp \left(-\frac{x^{2}}{4 D t}\right)
$$

Taking natural logarithms on both sides,

$$
\ln c(x, t)=\ln \left(\frac{\alpha}{\sqrt{\pi D t}}\right)-\frac{x^{2}}{4 D t}
$$

Hence, a plot of $\ln [c(x, t)]$ versus $x^{2}$ should yield a straight line of slope $-1 / 4 D t$. The data are processed and plotted in continuation.

| Counts $\left(\mathrm{min}^{-1}\right)$ |  |  | $\ln$ (Counts) |
| :---: | :---: | :---: | :---: |
|  | $\boxed{*}\left(\times 10^{-4} \mathrm{~m}\right)$ | $x^{2}(\mathrm{~m})$ |  |
| 8164 | 9.007 | 1 | $1.00 \mathrm{E}-08$ |
| 6413 | 8.766 | 2 | $4.00 \mathrm{E}-08$ |
| 4042 | 8.304 | 3 | $9.00 \mathrm{E}-08$ |
| 2350 | 7.762 | 4 | $1.60 \mathrm{E}-07$ |
| 828 | 6.719 | 5 | $2.50 \mathrm{E}-07$ |



As shown in the plot, the slope of the trendline is found to be $-9.404 \times 10^{6}$. It follows that

$$
\begin{gathered}
\text { Slope }=-\frac{1}{4 D t}=-9.404 \times 10^{6} \\
\therefore \frac{1}{4 \times D \times(16 \times 3600)}=9.404 \times 10^{6} \\
\therefore D=\frac{1}{4 \times(16 \times 3600) \times\left(9.404 \times 10^{6}\right)}=4.62 \times 10^{-13} \mathrm{~m}^{2} \mathrm{~s}^{-1}
\end{gathered}
$$

## ■ P7. 11

This problem is similar to 7.10; we must find the slope of the linear fit

$$
\ln c(x, t)=\ln \left(\frac{\alpha}{\sqrt{\pi D t}}\right)-\frac{x^{2}}{4 D t}
$$

The data are processed and plotted below.

| Activity |  |  | $\ln$ (Activity) |  | $x(\mu \mathrm{~m})$ |  | $x^{2}\left(\mu \mathrm{~m}^{2}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 83.8 | 4.428 | 10 | $1.00 \mathrm{E}+02$ |  |  |  |  |
| 66.4 | 4.196 | 20 | $4.00 \mathrm{E}+02$ |  |  |  |  |
| 42 | 3.738 | 30 | $9.00 \mathrm{E}+02$ |  |  |  |  |
| 23.6 | 3.161 | 40 | $1.60 \mathrm{E}+03$ |  |  |  |  |
| 8.74 | 2.168 | 50 | $2.50 \mathrm{E}+03$ |  |  |  |  |



As shown, the slope of the linear fit is $-9.35 \times 10^{-4} \mu \mathrm{~m}^{-2}=-9.35 \times 10^{8} \mathrm{~m}^{-2}$. Solving for diffusivity, we obtain

$$
\begin{gathered}
-9.35 \times 10^{8}=-\frac{1}{4 D t} \\
\therefore 9.35 \times 10^{8}=\frac{1}{4 \times D \times 86,400} \\
\therefore D=\frac{1}{4 \times\left(9.35 \times 10^{8}\right) \times 86,400}=3.09 \times 10^{-15} \mathrm{~m}^{2} \mathrm{~s}^{-1}
\end{gathered}
$$

## ■ P8. 2

The resistivity can be assumed to vary with temperature according to the relationship

$$
\rho_{T}=\rho_{0}(1+\alpha \Delta T)
$$

Using the resistivity at $0^{\circ} \mathrm{C}$ as the base value, we may write

$$
\rho_{T}=\left(1.67 \times 10^{-8}\right) \times\left[1+\left(6.8 \times 10^{-3}\right) \times(-100-0)\right]=5.34 \times 10^{-9} \Omega \cdot \mathrm{~m}
$$

Since conductivity is the reciprocal of resistivity,

$$
\kappa=\frac{1}{5.34 \times 10^{-9}}=1.87 \times 10^{8}(\Omega \cdot \mathrm{~m})^{-1}
$$

■ P8.7
Part (a): Firstly, we write, for the conductivity of a semiconductor such as germanium

$$
\rho=\frac{1}{\kappa}=\frac{1}{n_{e} e \mu_{e}+n_{h} e \mu_{h}}
$$

where $n$ denotes concentration, $\mu$ denotes mobility, and $e$ is the elementary charge. Assuming that the concentrations of electrons and holes are equal, we may write

$$
\rho=\frac{1}{n_{e} e \mu_{e}+n_{h} e \mu_{h}}=\frac{1}{n_{e} e\left(\mu_{e}+\mu_{h}\right)}
$$

Next, assuming that mobility is dependent on temperature $T^{-3 / 2}$,

$$
\rho=\frac{1}{n_{e} e\left(\mu_{e}+\mu_{h}\right)}=\frac{1}{n_{e} e B T^{-3 / 2}} \text { (I) }
$$

where $B$ is a constant. Next, note that electron concentration varies with temperature as

$$
n_{e}=A T^{3 / 2} \exp \left(-\frac{E_{g}}{2 k_{B} T}\right)
$$

where $A$ is a constant, $E_{g}$ is bandgap energy, and $k_{B}$ is Boltzmann's constant. Substituting in (I) brings to

$$
\begin{aligned}
\rho=\frac{1}{n_{e} e B T^{-3 / 2}} & =\frac{1}{A T^{3 / 2} \exp \left[-E_{g} /\left(2 k_{B} T\right)\right] B T^{-3 / 2}} \\
\therefore \rho & =\frac{1}{A B \exp \left[-E_{g} /\left(2 k_{B} T\right)\right]} \\
& \therefore \rho=C \exp \left(\frac{E_{g}}{2 k_{B} T}\right)
\end{aligned}
$$

where we have condensed constants $A$ and $B$ into a single constant $C$. Applying logarithms to the equation above, we have

$$
\begin{gathered}
\ln \rho=\ln C+\ln \left[\exp \left(\frac{E_{g}}{2 k_{B} T}\right)\right] \\
\therefore \ln \rho=\ln C+\frac{E_{g}}{2 k_{B} T}
\end{gathered}
$$

Denoting two specific data points with subscripts 1 and 2,

$$
\ln \left(\frac{\rho_{1}}{\rho_{2}}\right)=\frac{E_{g}}{2 k_{B}}\left(\frac{1}{T_{1}}-\frac{1}{T_{2}}\right)
$$

Solving for bandgap energy,

$$
\begin{gathered}
E_{g}=\frac{2 k_{B} \ln \left(\rho_{1} / \rho_{2}\right)}{\left(1 / T_{1}-1 / T_{2}\right)}=\frac{2 \times\left(1.38 \times 10^{-23}\right) \times \ln \left[0.028 /\left(2.74 \times 10^{-4}\right)\right]}{1 / 385-1 / 714}=1.07 \times 10^{-19} \mathrm{~J} \\
\therefore E_{g}=1.07 \mathrm{eV}
\end{gathered}
$$

Part (b): Optical absorption ensues when the energy of the incident photon is greater than or equal to the bandgap energy $E_{g}$ :

$$
\begin{gathered}
h v=E_{g} \rightarrow \frac{h c}{\lambda}=E_{g} \\
\therefore \lambda=\frac{h c}{E_{g}}=\frac{\left(6.63 \times 10^{-34}\right) \times\left(3.0 \times 10^{8}\right)}{1.07 \times 10^{-19}}=1.86 \times 10^{-6} \mathrm{~m}=1860 \mathrm{~nm}
\end{gathered}
$$

## ■ P8.8

We first solve equation (8.11) for electron mobility $\mu_{e}$ :

$$
\begin{gathered}
v_{d}=\mu_{e} E \rightarrow \mu_{e}=\frac{v_{d}}{E} \\
\therefore \mu_{e}=\frac{500}{1500}=0.333 \mathrm{~m}^{2} / \mathrm{V} \cdot \mathrm{~s}
\end{gathered}
$$

Then, the conductivity $\sigma$ follows from equation (8.12):

$$
\sigma=n e \mu_{e}=\left(5 \times 10^{17}\right) \times\left(1.60 \times 10^{-19}\right) \times 0.333=0.0266(\Omega \cdot \mathrm{~m})^{-1}
$$

## ■ P8. 10

Assuming concentrations $n_{e}=n_{h}=n_{i}$, we solve equation (8.13) for intrinsic carrier concentration to obtain

$$
\begin{gathered}
\sigma=n_{e} e \mu_{e}+n_{h} e \mu_{h} \rightarrow n_{i}=\frac{\sigma}{e\left(\mu_{e}+\mu_{h}\right)} \\
\therefore n_{i}=\frac{4 \times 10^{-4}}{\left(1.60 \times 10^{-19}\right) \times(0.14+0.05)}=1.32 \times 10^{16} \mathrm{~m}^{-3}
\end{gathered}
$$

## ■ P8. 13

All we have to do is solve equation (8.14) for temperature:

$$
\begin{gathered}
H_{c}=H_{0}\left[1-\left(\frac{T}{T_{c}}\right)^{2}\right] \rightarrow 40.0=156.77 \times\left[1-\left(\frac{T}{9.25}\right)^{2}\right] \\
\therefore \frac{40}{156.77}=1-\left(\frac{T}{9.25}\right)^{2} \\
\therefore 0.255=1-\frac{T^{2}}{85.6} \\
\therefore \frac{T^{2}}{85.6}=1-0.255 \\
\therefore T=\sqrt{85.6 \times(1-0.255)}=7.99 \mathrm{~K} \approx 8.0 \mathrm{~K}
\end{gathered}
$$

■ P8. 14
Per the problem statement, the magnetic susceptibility $\chi$ is expressed as

$$
\chi=\frac{c}{T-T_{C}}
$$

where $T_{c}$ is the Curie temperature and $c$ is a constant. For iron, $T_{c}=770^{\circ} \mathrm{C}$; also, we were told that $\chi=2.5 \times 10^{-4}$ for a temperature of $900^{\circ} \mathrm{C}$. We can use this information to compute constant $c$ :

$$
\begin{aligned}
& \chi=\frac{c}{T-T_{C}} \rightarrow 2.5 \times 10^{-4}=\frac{c}{900-770} \\
& \therefore c=\left(2.5 \times 10^{-4}\right) \times(900-770)=0.0325
\end{aligned}
$$

Lastly, the susceptibility $\chi$ at $800^{\circ} \mathrm{C}$ becomes

$$
\chi=\frac{c}{T-T_{C}}=\frac{0.0325}{800-770}=1.0833 \times 10^{-3}
$$

## ■ P9.4

After yielding, the plastic strain rate is much larger than the elastic strain rate, so we may assume that the total strain rate consists of a plastic component only, i.e., $\dot{\varepsilon}_{\text {total }} \approx \dot{\varepsilon}_{p}$. At the upper yield point, noting that $\dot{\varepsilon}=\varphi b \rho_{m} \bar{v}$, we may write

$$
\begin{gathered}
\dot{\varepsilon}_{\text {total }}=10^{-3}=\varphi b \rho_{m} \overline{\bar{v}}=\frac{1}{2} \times\left(2 \times 10^{-8}\right) \times 10^{5} \times\left(\frac{\tau}{\tau_{0}}\right)^{n} \\
\therefore\left(\frac{\tau}{\tau_{0}}\right)^{n}=1 \mathrm{~cm} / \mathrm{s}
\end{gathered}
$$

But we were told that the stress for a unit dislocation velocity of $1 \mathrm{~cm} / \mathrm{s}$ is $2.8 \times 10^{4}$ $\mathrm{N} \mathrm{cm}^{-2}$. Therefore, $\tau=2.8 \times 10^{4} \mathrm{~N} / \mathrm{cm}^{2}$. Assuming now that the dislocation density increases from $10^{5}$ to $10^{7} \mathrm{~cm}^{-2}$ (i.e., a two-order-of-magnitude increase), we may write

$$
\begin{gathered}
\dot{\varepsilon}_{\text {total }}=10^{-3}=\varphi b \rho_{m} \bar{\nu}=\frac{1}{2} \times\left(2 \times 10^{-8}\right) \times 10^{7} \times\left(\frac{\tau}{\tau_{0}}\right)^{n} \\
\therefore\left(\frac{\tau}{\tau_{0}}\right)^{n}=10^{-2} \\
\therefore \tau=\left(10^{-2}\right)^{\frac{1}{n}} \tau_{0} \\
\therefore \tau=\left(10^{-2}\right)^{\frac{1}{20}} \times\left(\tau_{0}\right)=\left(10^{-2}\right)^{\frac{1}{20}} \times\left(2.8 \times 10^{4}\right)=2.224 \times 10^{4} \mathrm{~N} \mathrm{~cm}^{-2}
\end{gathered}
$$

Accordingly, the yield drop is about $5760 \mathrm{~N} \cdot \mathrm{~cm}^{-2}$ or $\sim 20.6 \%$.

## ■ P9.7

Since the dislocation velocity is given by $v=\left(\tau / \tau_{0}\right)^{n}$ and the shear rate may be expressed as $\dot{\gamma}=\rho b v$, we have

$$
\left(\frac{\tau}{\tau_{0}}\right)^{n}=\frac{\dot{\gamma}}{\rho b}
$$

so that, for the same shear rate, $\tau^{n} \propto 1 / \rho$ or $\frac{\tau_{2}}{\tau_{1}}=\left(\frac{\rho_{1}}{\rho_{2}}\right)^{\frac{1}{n}}$, giving

$$
\begin{aligned}
& \frac{\tau_{2}}{\tau_{1}}=\left(\frac{\rho_{1}}{\rho_{2}}\right)^{\frac{1}{n}} \rightarrow \tau_{2}=\tau_{1}\left(\frac{\rho_{1}}{\rho_{2}}\right)^{\frac{1}{n}} \\
\therefore \tau_{2} & =0.69 \times\left(\frac{10^{10}}{10^{12}}\right)^{\frac{1}{10}}=0.435 \mathrm{MN} \cdot \mathrm{~m}^{-2}
\end{aligned}
$$

## ■ P9. 8

The Vickers hardness can be estimated to be $\approx 3.3$ times the yield stress; accordingly,

$$
\begin{gathered}
H_{V} \approx 3.3 \sigma_{y} \rightarrow \sigma_{y}=\frac{H_{V}}{3.3} \\
\therefore \sigma_{y}=\frac{2.0}{3.3}=0.606 \mathrm{GPa}=606 \mathrm{MPa}
\end{gathered}
$$

## ■ P9.9

In general, true stress and true strain are related by the exponential law $\sigma_{T}=K \varepsilon_{T}^{n}$. Dividing one of the given data points by the other and solving for exponent $n$, we obtain

$$
\begin{gathered}
\frac{\left(\sigma_{T}\right)_{1}}{\left(\sigma_{T}\right)_{2}}=\left[\frac{\left(\varepsilon_{T}\right)_{1}}{\left(\varepsilon_{T}\right)_{2}}\right]^{n} \rightarrow \ln \left[\frac{\left(\sigma_{T}\right)_{1}}{\left(\sigma_{T}\right)_{2}}\right]=n \times \ln \left[\frac{\left(\varepsilon_{T}\right)_{1}}{\left(\varepsilon_{T}\right)_{2}}\right] \\
\therefore n=\frac{\ln \left[\left(\sigma_{T}\right)_{1} /\left(\sigma_{T}\right)_{2}\right]}{\ln \left[\left(\varepsilon_{T}\right)_{1} /\left(\varepsilon_{T}\right)_{2}\right]}=\frac{\ln (414 / 483)}{\ln (0.15 / 0.25)}=0.3018
\end{gathered}
$$

Using this exponent and one of the given data points, we proceed to compute the flow stress at $\varepsilon_{T}=0.2$,

$$
\left(\sigma_{T}\right)_{3}=\left(\sigma_{T}\right)_{1} \times\left[\frac{\left(\varepsilon_{T}\right)_{3}}{\left(\varepsilon_{T}\right)_{1}}\right]^{n}=414 \times\left(\frac{0.2}{0.15}\right)^{0.3018}=452 \mathrm{MPa}
$$

## ■ P9. 12

In a tensile test, since volume is conserved, the product area $\times$ length is conserved, giving

$$
A_{\text {true }} \ell_{\text {true }}=A_{\text {original }} \ell_{\text {original }}
$$

Denoting the mechanical load as $P$, the nominal stress becomes

$$
\begin{gathered}
\sigma_{n}=\frac{P}{A_{\text {original }}}=\frac{P}{\frac{A_{\text {true }} \ell_{\text {true }}}{\ell_{\text {original }}}} \\
\therefore \sigma_{n}=\underbrace{\frac{P}{A_{\text {true }}}}_{=\sigma} \times \underbrace{\left(\frac{\ell_{\text {original }}}{\ell_{\text {true }}}\right)}_{=\frac{1}{\left(1+\varepsilon_{n}\right)}} \\
\therefore \sigma_{n}=\frac{\sigma}{1+\varepsilon_{n}}(\mathrm{I})
\end{gathered}
$$

But the nominal strain $\varepsilon_{n}$ is related to the true strain $\varepsilon$ by $\varepsilon=\ln \left(1+\varepsilon_{n}\right)$, so that $1+$ $\varepsilon_{n}=e^{\varepsilon}$. Substituting in (I),

$$
\sigma_{n}=\frac{\sigma}{1+\varepsilon_{n}}=\frac{\sigma}{e^{\varepsilon}} \text { (II) }
$$

Noting that breakage occurs when $d \sigma / d \varepsilon=\sigma$, we can substitute Ludvig's law to obtain

$$
\begin{aligned}
& \frac{d \sigma}{d \varepsilon}=\sigma \rightarrow \frac{d}{d \varepsilon}\left(K \varepsilon^{n}\right)=\sigma \\
& \therefore n K \varepsilon^{n-1}=\sigma \\
& \therefore n \frac{K \varepsilon^{n}}{\varepsilon}=\sigma \\
& \therefore n \frac{\sigma}{\varepsilon}=\sigma \\
& \therefore n \times \frac{1}{\varepsilon}=1 \\
& \therefore \varepsilon=n
\end{aligned}
$$

Lastly, we substitute into (II) to obtain

$$
\sigma_{n}=\frac{\sigma}{e^{\varepsilon}}=\frac{K \varepsilon^{n}}{e^{\varepsilon}}=\frac{K n^{n}}{e^{n}}
$$

as we intended to show.

## ■ P9. 13

The nominal tensile strength can be estimated using the formula derived in Problem 9.12:

$$
\sigma_{n}=\frac{K n^{n}}{e^{n}}=\frac{630 \times 0.4^{0.4}}{e^{0.4}}=292.7 \approx 293 \mathrm{MPa}
$$

This is substantially greater than the experimental tensile strength of 230 MPa . This is due to local weakness in the sample, which leads to necking. The Considère construction used to derive $\sigma_{T S}=K n^{n} e^{-n}$ assumes uniform reduction in crosssectional area without necking.

## ■ P10.5

We have two data points to substitute in the Hall-Petch equation, namely:

$$
\left.\begin{array}{c}
\sigma_{y}=\sigma_{i}+k_{y} d^{-1 / 2} \\
400=\sigma_{i}+k_{y} \times\left(0.32 \times 10^{-3}\right)^{-1 / 2} \\
300=\sigma_{i}+k_{y} \times\left(1.0 \times 10^{-3}\right)^{-1 / 2}
\end{array}\right\} \begin{aligned}
& \therefore\left\{\begin{array}{l}
400=\sigma_{i}+55.9 k_{y} \text { (I) } \\
300=\sigma_{i}+31.6 k_{y} \text { (II) }
\end{array}\right.
\end{aligned}
$$

Rearranging equation (II), we get $k_{y}=9.48-0.0316 \sigma_{i}$. Substituting in (I) and solving for friction stress, we obtain

$$
\begin{gathered}
400=\sigma_{i}+55.9 \times\left(9.48-0.0316 \sigma_{i}\right) \\
\therefore 400=\sigma_{i}+530-1.77 \sigma_{i} \\
\therefore-130=-0.77 \sigma_{i} \\
\therefore \sigma_{i}=\frac{-130}{-0.77}=169 \mathrm{MPa}
\end{gathered}
$$

Finally, we can solve the Orowan equation for the particle spacing $\ell$; a factor of 2 is included because the stress in question is tensile rather than shear.

$$
\begin{gathered}
\sigma_{D}=\frac{2 \mu b}{\ell} \rightarrow \ell=\frac{2 \mu b}{\sigma_{D}} \\
\therefore \ell=\frac{2 \times\left(80 \times 10^{9}\right) \times\left(0.25 \times 10^{-9}\right)}{169 \times 10^{6}}=2.37 \times 10^{-7} \mathrm{~m}=237 \mathrm{~nm}
\end{gathered}
$$

## - P10.6

We have two data points to substitute in the Hall-Petch equation, so that

$$
\begin{gathered}
\sigma_{y}=\sigma_{i}+k_{y} d^{-1 / 2} \\
\left\{\begin{array}{c}
300=\sigma_{i}+k_{y} \times\left(9 \times 10^{-6}\right)^{-1 / 2} \\
200=\sigma_{i}+k_{y} \times\left(25 \times 10^{-6}\right)^{-1 / 2}
\end{array}\right.
\end{gathered}
$$

Subtracting the second equation from the first and solving for $k_{y}$, we obtain

$$
\begin{aligned}
& 300-200=\not \partial+k_{y} \times\left(9 \times 10^{-6}\right)^{-1 / 2}-\not \subset \dot{x}-k_{y} \times\left(25 \times 10^{-6}\right)^{-1 / 2} \\
& \therefore 100=k_{y} \times\left[\left(9 \times 10^{-6}\right)^{-1 / 2}-\left(25 \times 10^{-6}\right)^{-1 / 2}\right] \\
& \therefore k_{y}=\frac{100}{\left[\left(9 \times 10^{-6}\right)^{-1 / 2}-\left(25 \times 10^{-6}\right)^{-1 / 2}\right]}=0.75 \mathrm{MN} \cdot \mathrm{~m}^{-3 / 2}
\end{aligned}
$$

Substituting $k$ in the first equation gives the lattice friction stress:

$$
\begin{gathered}
300=\sigma_{i}+0.75 \times\left(9 \times 10^{-6}\right)^{-1 / 2} \\
\therefore \sigma_{i}=300-0.75 \times\left(9 \times 10^{-6}\right)^{-1 / 2}=50 \mathrm{MPa}
\end{gathered}
$$

Assuming that strengthening by dispersion is additive, we may write

$$
\begin{gathered}
500 \mathrm{MPa}=50 \mathrm{MPa}+\frac{0.75}{\sqrt{100 \times 10^{-6}}} \mathrm{MPa}+\sigma_{D} \\
\therefore 500=50+75+\sigma_{D} \\
\therefore \sigma_{D}=375 \mathrm{MPa}
\end{gathered}
$$

Finally, solving the Orowan equation for spacing $\ell$, we get

$$
\begin{gathered}
\sigma_{D}=\frac{2 \mu b}{\ell} \rightarrow \ell=\frac{2 \mu b}{\sigma_{D}} \\
\therefore \ell=\frac{2 \times\left(80 \times 10^{9}\right) \times\left(0.2 \times 10^{-9}\right)}{375 \times 10^{6}}=8.53 \times 10^{-8} \mathrm{~m}=85.3 \mathrm{~nm}
\end{gathered}
$$

## ■ P10.15

Using the Hall-Petch equation as we did in previous problems, we write:

$$
\begin{gathered}
\sigma_{y}=\sigma_{i}+k_{y} d^{-1 / 2} \\
\left\{\begin{array}{l}
400=\sigma_{i}+k_{y} \times\left(0.32 \times 10^{-3}\right)^{-1 / 2} \\
300= \\
\sigma_{i}+k_{y} \times\left(1.0 \times 10^{-3}\right)^{-1 / 2}
\end{array}\right.
\end{gathered}
$$

The solution to this system of linear equations is straightforward and has been exemplified in problems 10.5 and 10.6. We can speed things up using MATLAB's fsolve function:

```
function \(F=\) hallpetch(x)
\(F(1)=400-x(1)-x(2)^{*}(0.32 e-3)^{\wedge}(-0.5)\);
\(F(2)=300-x(1)-x(2)^{*}(1 e-3)^{\wedge}(-0.5)\);
>> fun = @hallpetch;
\(x 0=[100,1] ;\)
\(x=\) fsolve(fun, \(x 0\) )
x =
    169.75214 .1188
```

As shown in the code snippet, $\sigma_{i} \approx 170 \mathrm{MPa}$. Then, using the Orowan equation,

$$
\begin{gathered}
\sigma_{D}=\frac{2 \mu b}{\ell} \rightarrow \ell=\frac{2 \mu b}{\sigma_{D}} \\
\therefore \ell=\frac{2 \times\left(80 \times 10^{9}\right) \times\left(0.25 \times 10^{-9}\right)}{170 \times 10^{6}}=2.35 \times 10^{-7} \mathrm{~m}=235 \mathrm{~nm}
\end{gathered}
$$

## ■ P10.16

The equation to use is, you guessed it, the Hall-Petch equation:

$$
\begin{gathered}
\sigma_{y}=\sigma_{i}+k_{y} d^{-1 / 2} \\
\left\{\begin{array}{l}
380=\sigma_{i}+k_{y} \times\left(0.32 \times 10^{-3}\right)^{-1 / 2} \\
276=\sigma_{i}+k_{y} \times\left(1.0 \times 10^{-3}\right)^{-1 / 2}
\end{array}\right.
\end{gathered}
$$

As in the previous problem, we can speed things up using MATLAB's fsolve command:

```
function F = hallpetch(x)
F(1) = 380-x(1) - x(2)*(0.32e-3)^(-0.5);
F(2) = 276 - x(1) - x(2)*(1e-3)^(-0.5);
>> fun = @hallpetch;
x0 = [100, 1];
x = fsolve(fun, x0)
x =
\[
140.5422 \quad 4.2836
\]
```

As shown in the code snippet, $\sigma_{i} \approx 141 \mathrm{MPa}$. Substituting this and other data into the Orowan equation, we get

$$
\begin{gathered}
\sigma_{D}=\frac{2 \mu b}{\ell} \rightarrow \ell=\frac{2 \mu b}{\sigma_{D}} \\
\therefore \ell=\frac{2 \times\left(11.98 \times 10^{10}\right) \times\left(2 \times 10^{-10}\right)}{141 \times 10^{6}}=3.40 \times 10^{-7} \mathrm{~m}=340 \mathrm{~nm}
\end{gathered}
$$

## ■ P10.17

The equation to use is, wait for it, the Hall-Petch equation:

$$
\begin{gathered}
\sigma_{y}=\sigma_{i}+k_{y} d^{-1 / 2} \\
\left\{\begin{array}{c}
200=\sigma_{i}+k_{y} \times\left(25 \times 10^{-6}\right)^{-1 / 2} \\
300=\sigma_{i}+k_{y} \times\left(9 \times 10^{-6}\right)^{-1 / 2}
\end{array}\right.
\end{gathered}
$$

We can easily solve these two equations for $\sigma_{i}$ and $k_{y}$ using Mathematica's Solve command:

```
In[245]:= Solve[{200== 的 + k* (25*10-6 )-0.5, 300 == 和 + k* (9*10-6}\mp@subsup{)}{}{-0.5}},{\mp@subsup{\sigma}{i}{},k}
Out[245]= {{\mp@subsup{\sigma}{i}{}->50., k }->0.75}
```

As shown, the solutions are $\sigma_{i}=50 \mathrm{MPa}$ and $k_{y}=0.75 \mathrm{MN} \cdot \mathrm{m}^{-3 / 2}$. Assuming strengthening by dispersion is additive, we may write

$$
\begin{gathered}
500 \mathrm{MPa}=50 \mathrm{MPa}+\frac{0.75}{\sqrt{100 \times 10^{-6}}} \mathrm{MPa}+\sigma_{D} \\
\therefore \sigma_{D}=375 \mathrm{MPa}
\end{gathered}
$$

Using the Orowan equation, dispersion spacing $\ell$ is determined as

$$
\begin{gathered}
\sigma_{D}=\frac{2 \mu b}{\ell} \rightarrow \ell=\frac{2 \mu b}{\sigma_{D}} \\
\therefore \ell=\frac{2 \times\left(80 \times 10^{9}\right) \times\left(0.2 \times 10^{-9}\right)}{375 \times 10^{6}}=8.53 \times 10^{-8} \mathrm{~m}=85.3 \mathrm{~nm}
\end{gathered}
$$

## ■ P1 1.7

The recrystallization process can be modelled with the Arrhenius-like equation

$$
\text { Rate }=A \exp \left(-\frac{Q}{k_{B} T}\right)
$$

which implies that a plot of $\operatorname{In}($ Rate) versus reciprocal temperature should yield a straight line with slope $-Q / k_{B}$. The present data are processed and plotted below.

| Time (min) | Rate $\left(\mathbf{m i n}^{\mathbf{- 1}}\right)$ | $\boldsymbol{\operatorname { l n } ( \text { Rate } )}$ | $\mathbf{T}\left({ }^{\circ} \mathbf{C}\right)$ | $\mathbf{T}(\mathbf{K})$ | $\mathbf{1 / T}\left(\mathbf{K}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 75 | 0.013333 | -4.317488 | 102 | 375 | 0.0026667 |
| 21 | 0.047619 | -3.044522 | 119 | 392 | 0.002551 |
| 9 | 0.111111 | -2.197225 | 135 | 408 | 0.002451 |



As shown, the slope of the line obtained is $\mathbf{- 9 8 6 0 . 7}$. Then, the activation energy $Q$ is calculated to be

$$
\begin{gathered}
\text { Slope }=-\frac{Q}{k_{B}}=-9860.7 \\
\therefore Q=9860.7 \times k_{B}=9860.7 \times\left(8.62 \times 10^{-5}\right)=0.850 \mathrm{eV}
\end{gathered}
$$

## ■ P1 1.8

The Avrami equation can be adjusted to yield

$$
f=1-\exp \left(-K t^{n}\right) \rightarrow-K t^{n}=\ln (1-f)
$$

Dividing one of the given data points by the other and solving for $n$, we have

$$
\begin{gathered}
\left(\frac{450}{280}\right)^{n}=\frac{\ln (1-0.6)}{\ln (1-0.2)} \\
\therefore\left(\frac{450}{280}\right)^{n}=4.11 \\
\therefore n \times \ln \left(\frac{450}{280}\right)=\ln (4.11) \\
\therefore n=\frac{\ln (4.11)}{\ln (450 / 280)}=2.98
\end{gathered}
$$

Then, coefficient $K$ can be obtained from either of the two data points:

$$
\begin{gathered}
-K t^{n}=\ln (1-f) \rightarrow K=-\frac{\ln (1-f)}{t^{n}} \\
\therefore K=-\frac{\ln (1-0.6)}{450^{2.98}}=1.14 \times 10^{-8}
\end{gathered}
$$

Thus, the recrystallization process is described by the Avrami kinetic equation

$$
f=1-\exp \left[-\left(1.14 \times 10^{-8}\right) \times t^{2.98}\right]
$$

Solving for $t$, we can determine the time required for $f=0.95$ :

$$
\begin{aligned}
& K=-\frac{\ln (1-f)}{t^{n}} \rightarrow t=\left[-\frac{\ln (1-f)}{K}\right]^{\frac{1}{n}} \\
\therefore t & =\left[-\frac{\ln (1-0.95)}{1.14 \times 10^{-8}}\right]^{\frac{1}{2.98}}=669 \mathrm{~s}=11.2 \mathrm{~min}
\end{aligned}
$$

## ■ P12.9

Substituting the two data points and rearranging, we obtain

$$
\begin{aligned}
& 0.2=1-\exp \left(-K \times 280^{n}\right) \\
& \therefore \exp \left(-K \times 280^{n}\right)=0.8 \\
& \therefore K \times 280^{n}=-\ln (0.8)(\mathrm{I}) \\
& 0.6=1-\exp \left(-K \times 425^{n}\right) \\
& \therefore \exp \left(-K \times 425^{n}\right)=0.4 \\
& \therefore K \times 425^{n}=-\ln (0.4)(\mathrm{II})
\end{aligned}
$$

Dividing (II) by (I) and solving for $n$, we get

$$
\begin{gathered}
\frac{X \times 425^{n}}{\not X \times 280^{n}}=\frac{\ln (0.4)}{\ln (0.8)} \\
\therefore\left(\frac{425}{280}\right)^{n}=4.11 \\
\therefore n \times \ln \left(\frac{425}{280}\right)=\ln (4.11) \\
\therefore n \times 0.417=1.41 \\
\therefore n=3.38
\end{gathered}
$$

Substituting the newly obtained value of $n$ into (I) and solving for $K$,

$$
\begin{gathered}
K \times 280^{3.38}=-\ln (0.8) \\
\therefore K=-\frac{\ln (0.8)}{280^{3.38}}=1.19 \times 10^{-9}
\end{gathered}
$$

Accordingly, the austenite-to-pearlite transition can be described by the Avramikinetic relationship

$$
f=1-\exp \left[-\left(1.19 \times 10^{-9}\right) \times t^{3.38}\right]
$$

To find the time required for $95 \%$ transformation, we write

$$
\begin{aligned}
& 0.95=1-\exp \left[-\left(1.19 \times 10^{-9}\right) \times t^{3.38}\right] \\
& \therefore \exp \left[-\left(1.19 \times 10^{-9}\right) \times t^{3.38}\right]=0.05 \\
& \therefore\left(1.19 \times 10^{-9}\right) \times t^{3.38}=-\ln (0.05) \\
& \therefore t^{3.38}=\frac{-\ln (0.05)}{1.19 \times 10^{-9}} \\
& \therefore t=\left[-\frac{\ln (0.05)}{1.19 \times 10^{-9}}\right]^{\frac{1}{3.38}}=604 \mathrm{~s}
\end{aligned}
$$

The transition will reach $95 \%$ completion within approximately 10 minutes.

## ■ P13.1

Any two age hardening times $t_{1}$ and $t_{2}$ are related by Arrhenius-like equation

$$
\ln \left(\frac{t_{2}}{t_{1}}\right)=\frac{Q}{R}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)
$$

In the present case, we have $t_{1}=10 \mathrm{~h}, T_{1}=600 \mathrm{~K}, t_{2}=280 \mathrm{~h}$, and $T_{2}=500 \mathrm{~K}$, so that

$$
\begin{gathered}
\ln \left(\frac{280}{10}\right)=\frac{Q}{R}\left(\frac{1}{500}-\frac{1}{600}\right) \\
\therefore 3.33=\frac{Q}{R} \times\left(3.33 \times 10^{-4}\right) \\
\therefore \frac{Q}{R}=1.0 \times 10^{4} \mathrm{~K}
\end{gathered}
$$

It follows that the time $t_{3}$ required to achieve age hardening at a temperature $T_{3}=$ $257^{\circ} \mathrm{C}=530 \mathrm{~K}$ is

$$
t_{3}=t_{2} \exp \left[\frac{Q}{R}\left(\frac{1}{T_{3}}-\frac{1}{T_{2}}\right)\right]=280 \times \exp \left[10^{4} \times\left(\frac{1}{530}-\frac{1}{500}\right)\right]=90.26 \mathrm{~h}
$$

Now, the source length is $10^{-6}-10^{-7}=0.9 \times 10^{-6}$. For aluminum, $\mu=40 \mathrm{GPa} ; b$ may be taken as 0.25 nm . Then, the tensile stress can be estimated with the Orowan equation:

$$
\sigma=\frac{2 \mu b}{\ell}=\frac{2 \times\left(40 \times 10^{9}\right) \times\left(0.25 \times 10^{-9}\right)}{0.9 \times 10^{-6}}=2.22 \times 10^{7} \mathrm{~Pa}=22.2 \mathrm{MPa}
$$

## ■ P13.2

In general, diffusivity varies as a function of temperature according to the following Arrhenius-like equation:

$$
D=D_{0} \exp \left(-\frac{E_{a}}{R T}\right)
$$

For substitutional diffusion, energy $E_{a}$ is constituted of a component $E_{f}$ for vacancy formation and a component $E_{m}$ for vacancy movement, so that

$$
\begin{aligned}
D= & D_{0} \exp \left(-\frac{E_{a}}{R T}\right)=D_{0} \exp \left(-\frac{E_{f}+E_{m}}{R T}\right) \\
& \therefore D=D_{0} \exp \left(-\frac{E_{f}}{R T}\right) \exp \left(-\frac{E_{m}}{R T}\right)
\end{aligned}
$$

Consider first specimens diffusing at $25^{\circ} \mathrm{C}$. As the metal is annealed at $25^{\circ} \mathrm{C}$, vacancies are formed at $25^{\circ} \mathrm{C}$ and move at this same temperature, so we can write

$$
D_{1}=D_{0} \exp \left(-\frac{E_{f}}{298 \times T}\right) \exp \left(-\frac{E_{m}}{298 \times T}\right)
$$

In turn, as the metal is quenched from $500^{\circ} \mathrm{C}$, vacancies are formed at $500^{\circ} \mathrm{C}$ and move at $25^{\circ} \mathrm{C}$, so we may write

$$
D_{2}=D_{0} \exp \left(-\frac{E_{f}}{773 \times T}\right) \exp \left(-\frac{E_{m}}{298 \times T}\right)
$$

Dividing (II) by (I) and using the diffusivity data that accompanies the problem statement, we have

$$
\begin{gathered}
\frac{D_{2}}{D_{1}}=\frac{2.76 \times 10^{-21}}{8.61 \times 10^{-30}}=\frac{D_{2} \exp \left(-\frac{E_{f}}{773 \times T}\right) \exp \left(-\frac{E_{f}}{298 \times T}\right) \exp \left(\frac{E_{m}}{298 \times T}\right.}{298 \times T} \\
\therefore \frac{D_{2}}{D_{1}}=\frac{2.76 \times 10^{-21}}{8.61 \times 10^{-30}}=\exp \left[-\frac{E_{f}}{R}\left(\frac{1}{773}-\frac{1}{298}\right)\right] \\
\therefore 3.21 \times 10^{8}=\exp \left[-\frac{E_{f}}{R}\left(\frac{1}{773}-\frac{1}{298}\right)\right] \\
\therefore 3.21 \times 10^{8}=\exp \left(0.00206 \times \frac{E_{f}}{R}\right) \\
\therefore \ln \left(3.21 \times 10^{8}\right)=0.00206 \times \frac{E_{f}}{R} \\
\therefore E_{f}= \\
\frac{\ln \left(3.21 \times 10^{8}\right) \times 8.314}{0.00206}=79,050 \mathrm{~J} \mathrm{~mol}^{-1} \\
\therefore E_{f}=79.05 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{gathered}
$$

It remains to find the energy of motion $E_{m}$. Note that for a specimen annealed at $500^{\circ} \mathrm{C}$, vacancies are formed and move at $500^{\circ} \mathrm{C}$, so that

$$
D_{2}=D_{0} \exp \left(-\frac{E_{f}}{773 \times T}\right) \exp \left(-\frac{E_{m}}{773 \times T}\right)(\text { III })
$$

Dividing (II) by (I) and using the diffusivity data given in the problem statement, we have

$$
\frac{D_{3}}{D_{1}}=\frac{3.63 \times 10^{-14}}{8.61 \times 10^{-30}}=\frac{\not D Q \exp \left(-\frac{E_{f}}{773 \times T}\right) \exp \left(-\frac{E_{m}}{773 \times T}\right)}{\text { DQ } \exp \left(-\frac{E_{f}}{298 \times T}\right) \exp \left(-\frac{E_{m}}{298 \times T}\right)}
$$

$$
\begin{gathered}
\therefore 4.22 \times 10^{15}=\exp \left[-\frac{\left(E_{f}+E_{m}\right)}{R}\left(\frac{1}{773}-\frac{1}{298}\right)\right] \\
\therefore 4.22 \times 10^{15}=\exp \left[0.00206 \times \frac{\left(E_{f}+E_{m}\right)}{R}\right] \\
\therefore \ln \left(4.22 \times 10^{15}\right)=0.00206 \times \frac{\left(E_{f}+E_{m}\right)}{R} \\
\therefore 36.0=0.00206 \times \frac{\left(E_{f}+E_{m}\right)}{R} \\
\therefore 36.0=0.00206 \times \frac{\left(79,050+E_{m}\right)}{8.314} \\
\therefore E_{m}=66,200 \mathrm{~J} \mathrm{~mol}^{-1}=66.2 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{gathered}
$$

Lastly, we note that factor $\Re$ varies with temperature according to the exponential law

$$
\mathfrak{R}=\frac{D_{0} \exp \left(-E_{f} / R T_{2}\right) \exp \left(-E_{m} / R T_{1}\right)}{D_{0} \exp \left(-E_{f} / R T_{1}\right) \exp \left(-E_{m} / R T_{1}\right)}=\exp \left[-\frac{E_{f}}{R}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)\right]
$$

Alternatively, we can apply logarithms to both sides and write

$$
\ln \mathfrak{R}=-\frac{E_{f}}{R}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)
$$

which indicates that the logarithm of $\mathfrak{R}$ varies linearly with reciprocal temperature; the two foregoing equations should be familiar to those who have taken a class on chemical kinetics during an elementary chemistry course.


■ P13.5
The Ostwald ripening equation for coarsening reads

$$
\bar{r}_{t}^{3}-\bar{r}_{o}^{3}=\frac{8 \gamma c v_{m} D t}{9 R T}
$$

With the surface free energy $\gamma$, the solute concentration $c$ and the molar volume $v_{m}$ assumed independent of temperature, the process is governed by the diffusivity $D$, which of course follows the Arrhenius-like law $\operatorname{Aexp}\left(-Q / k_{B} T\right)$. Therefore, at $120^{\circ} \mathrm{C}$, we write

$$
\begin{gathered}
\frac{\bar{r}_{t}^{3}-\bar{r}_{o}^{3}}{\Delta t}=A \exp \left(-\frac{Q}{k_{B} T}\right) \\
\therefore \frac{5^{3}-2^{3}}{3}=A \exp \left(-\frac{Q}{k_{B} \times 393}\right) \\
\therefore 39=A \exp \left(-\frac{Q}{k_{B} \times 393}\right) \text { (I) }
\end{gathered}
$$

$$
\begin{aligned}
& \frac{10^{3}-2^{3}}{5}=A \exp \left(-\frac{Q}{k_{B} \times 433}\right) \\
& \therefore 198=A \exp \left(-\frac{Q}{k_{B} \times 433}\right) \text { (II) }
\end{aligned}
$$

Dividing (II) by (I) and solving for activation energy,

$$
\begin{gathered}
\frac{198}{39}=\frac{X \exp \left(-\frac{Q}{k_{B} \times 433}\right)}{X \exp \left(-\frac{Q}{k_{B} \times 393}\right)} \\
\therefore \frac{198}{39}=\exp \left[\frac{Q}{k_{B}}\left(\frac{1}{393}-\frac{1}{433}\right)\right] \\
\therefore \ln \left(\frac{198}{39}\right)=\frac{Q}{k_{B}}\left(\frac{1}{393}-\frac{1}{433}\right) \\
\therefore 1.62=\frac{Q}{k_{B}} \times 2.35 \times 10^{-4} \\
\therefore \frac{Q}{k_{B}}=\frac{1.62}{2.35 \times 10^{-4}}=6890 \\
\therefore Q=6890 \times\left(8.62 \times 10^{-5}\right)=0.594 \mathrm{eV}
\end{gathered}
$$

■ P14.4
This question involves the infinite couple solution of Fick's second law for a constant surface concentration, which is discussed in section 7.2.2 of the textbook. The equation to use is

$$
c(x, t)=c_{0}+\left(c_{s}-c_{0}\right)\left[1-\operatorname{erf}\left(\frac{x}{2 \sqrt{D t}}\right)\right]
$$

Assuming the initial bulk nitrogen concentration to be 0 , then for $c_{s}=1.53 \mathrm{wt} \%$ and $c(x, t)=0.25$ :

$$
\begin{gathered}
0.25=0+(1.53-0)\left[1-\operatorname{erf}\left(\frac{x}{2 \sqrt{D t}}\right)\right] \\
\therefore 0.25=1.53\left[1-\operatorname{erf}\left(\frac{x}{2 \sqrt{D t}}\right)\right] \\
\therefore \frac{0.25}{1.53}=1-\operatorname{erf}\left(\frac{x}{2 \sqrt{D t}}\right) \\
\therefore \operatorname{erf}\left(\frac{x}{2 \sqrt{D t}}\right)=1-\frac{0.25}{1.53} \\
\therefore \operatorname{erf}\left(\frac{x}{2 \sqrt{D t}}\right)=0.837
\end{gathered}
$$

Interpolating values in the given table or using a computer algebra system such as Mathematica, we have:

## $\operatorname{In}[311]:=$ Solve[Erf[z] == 0.837, z]

... Solve: Inverse functions are being used by Solve, so some solutions may not be found; use Reduce for complete solution information.

Out[311] $=\{\{z \rightarrow 0.986451\}\}$
Therefore,

$$
\begin{aligned}
\operatorname{erf}\left(\frac{x}{2 \sqrt{D t}}\right)= & 0.837 \rightarrow \frac{x}{2 \sqrt{D t}}=0.9865 \\
& \therefore \frac{x^{2}}{4 D t}=0.973 \\
& \therefore t=\frac{x^{2}}{3.89 D} \text { (I) }
\end{aligned}
$$

Pausing for a moment to compute the diffusion coefficient, we have

$$
D=D_{0} \exp \left(-\frac{Q}{R T}\right)=\left(9.1 \times 10^{-5}\right) \times \exp \left(-\frac{170,000}{8.314 \times 1273}\right)=9.62 \times 10^{-12} \mathrm{~m}^{2} \mathrm{~s}^{-1}
$$

Substituting in (I) with $x=1 \mu \mathrm{~m}=10^{-6} \mathrm{~m}$,

$$
t=\frac{\left(10^{-6}\right)^{2}}{3.89 \times\left(9.62 \times 10^{-12}\right)}=0.0267 \mathrm{~s}
$$

Similarly, with $x=1.75 \times 10^{-6} \mathrm{~m}$,

$$
t=\frac{\left(1.75 \times 10^{-6}\right)^{2}}{3.89 \times\left(9.62 \times 10^{-12}\right)}=0.0818 \mathrm{~s}
$$

## ■ P15.1

Solving the fracture toughness equation for stress $\sigma$, we obtain

$$
\begin{gathered}
K_{c}=\sqrt{\pi a} \sigma \rightarrow \sigma=\frac{K_{c}}{\sqrt{\pi a}} \\
\therefore \sigma=\frac{40}{\sqrt{\pi \times\left(5 \times 10^{-3}\right)}}=319 \mathrm{MPa}
\end{gathered}
$$

■ P15.2
Noting that $\Delta K=\Delta \sigma \sqrt{\pi a}$, the crack growth rate equation can be restated as

$$
\frac{d a}{d N}=c(\Delta K)^{m}=2 \times 10^{-13}(\Delta \sigma)^{4} \pi^{2} a^{2}
$$

Substituting the alternating stress amplitude $\Delta \sigma=180 \mathrm{MPa}$,

$$
\frac{d a}{d N}=2 \times 10^{-13} \times(180)^{4} \times \pi^{2} \times a^{2}=2.072 \times 10^{-3} a^{2}
$$

Separating variables and integrating,

$$
\begin{gathered}
\frac{d a}{d N}=2.072 \times 10^{-3} a^{2} \rightarrow \frac{1}{2.072 \times 10^{-3}} \frac{d a}{a^{2}}=d N \\
\therefore 483 \int_{a_{i}}^{a_{f}} \frac{d a}{a^{2}}=\int d N \\
\therefore N_{f}=483\left(\frac{1}{a_{i}}-\frac{1}{a_{f}}\right)
\end{gathered}
$$

where $a_{i}=0.1 \mathrm{~mm}=10^{-4} \mathrm{~m}$ and

$$
a_{f}=\frac{1}{\pi}\left(\frac{K_{c}}{\sigma_{\max }}\right)^{2}=\frac{1}{\pi} \times\left(\frac{54}{180}\right)^{2}=0.0287 \mathrm{~m}
$$

so that

$$
N_{f}=483\left(\frac{1}{10^{-4}}-\frac{1}{0.0287}\right)=4.81 \times 10^{6} \text { cycles to failure }
$$

The steel component can withstand 4.8 million cycles before failure ensues.

■ P15.3
Part (a): The area delimited by $A B C$ represents Herring-Nabarro creep. The area below DAC represents Coble creep. The area above BAD represents dislocation creep.
Part (b): At the dislocation creep/Herring-Nabarro creep boundary the creep rate given by the two mechanisms are equal. Accordingly, we may write

$$
\begin{gathered}
\left.\therefore 1.5 \times 10^{5} \sigma^{5} \exp -\frac{550,000}{\dot{\varepsilon}_{\text {Disl }}=\dot{\varepsilon}_{\mathrm{H}-\mathrm{N}}}=\frac{5.8 \times 10^{5}}{d^{2}} \sigma \exp -\frac{550,000}{R T}\right) \\
\therefore 1.5 \times 10^{5} \sigma^{5}=\frac{5.8 \times 10^{5}}{d^{2}} \sigma \\
\therefore \sigma^{4}=\frac{5.8 \times 10^{5}}{d^{2} \times\left(1.5 \times 10^{5}\right)} \\
\therefore \sigma=\left[\frac{5.8 \times 10^{5}}{\left(10^{-3}\right)^{2} \times\left(1.5 \times 10^{5}\right)}\right]^{\frac{1}{4}}=44.3 \mathrm{MPa}
\end{gathered}
$$

Part (c): For the Herring-Nabarro/Coble creep boundary, we may write

$$
\begin{gathered}
\dot{\varepsilon}_{\mathrm{H}-\mathrm{N}}=\dot{\varepsilon}_{\mathrm{C}} \\
\therefore \frac{5.8 \times 10^{5}}{d^{2}} \not \subset \mathrm{exp}\left(-\frac{550,000}{R T}\right)=\frac{10^{-9}}{d^{3}} \not \not \mathrm{~d} \exp \left(-\frac{400,000}{R T}\right) \\
\therefore \frac{5.8 \times 10^{5} d}{10^{-9}}=\frac{\exp (-400,000 / R T)}{\exp (-550,000 / R T)} \\
\therefore \frac{5.8 \times 10^{5} \times 10^{-3}}{10^{-9}}=\exp \left(\frac{150,000}{R T}\right) \\
\therefore 5.8 \times 10^{11}=\exp \left(\frac{150,000}{8.3 \times T}\right) \\
\therefore 5.8 \times 10^{11}=\exp \left(\frac{18,100}{T}\right) \\
\therefore \ln \left(5.8 \times 10^{11}\right)=\frac{18,100}{T} \\
\therefore T=\frac{18,100}{\ln \left(5.8 \times 10^{11}\right)}=66 \mathrm{~K}
\end{gathered}
$$

For completeness, we could establish the stress-temperature relationship for the dislocation creep/Coble creep boundary:

$$
\begin{gathered}
\dot{\varepsilon}_{\text {Disl }}=\dot{\varepsilon}_{\mathrm{C}} \\
\therefore 1.5 \times 10^{5} \sigma^{5} \exp \left(-\frac{550 \times 10^{3}}{R T}\right)=\frac{10^{-9}}{d^{3}} \sigma \exp \left(-\frac{400 \times 10^{3}}{R T}\right) \\
\therefore 1.5 \times 10^{5} \sigma^{4} \exp \left(-\frac{550 \times 10^{3}}{R T}\right)=\frac{10^{-9}}{d^{3}} \exp \left(-\frac{400 \times 10^{3}}{R T}\right) \\
\therefore \sigma^{4}=6.67 \times 10^{-6} \exp \left[150 \times 10^{3} /(8.31 \times T)\right] \\
\therefore \sigma=0.0508 \exp (4510 / T)[\mathrm{MPa}]
\end{gathered}
$$

## ■ P15.4

The steady-state creep equation is $\dot{\varepsilon}=A \sigma^{n} \exp (-Q / R T)$. After metallurgical improvements, the creep rate at $\sigma_{0}=77 \mathrm{MPa}$ and $T_{0}=1250 \mathrm{~K}$ is required to be the same as that at $\sigma_{1}=70 \mathrm{MPa}$ and a higher temperature $T_{1}$, so that

$$
\begin{gathered}
\sigma_{0}^{n} \exp \left(-\frac{Q}{R T_{0}}\right)=\sigma_{1}^{n} \exp \left(-\frac{Q}{R T_{1}}\right) \\
\therefore \frac{\sigma_{0}^{n}}{\sigma_{1}^{n}}=\frac{\exp \left(-Q / R T_{1}\right)}{\exp \left(-Q / R T_{0}\right)} \\
\therefore n \ln \left(\frac{\sigma_{0}}{\sigma_{1}}\right)=\frac{Q}{R}\left(\frac{1}{T_{0}}-\frac{1}{T_{1}}\right) \\
\therefore 5 \times \ln \left(\frac{77}{70}\right)=\frac{200,000}{8.314}\left(\frac{1}{1250}-\frac{1}{T_{1}}\right) \\
\therefore 1.98 \times 10^{-5}=\frac{1}{1250}-\frac{1}{T_{1}} \\
\therefore \frac{1}{T_{1}}=\frac{1}{1250}-1.98 \times 10^{-5} \\
\therefore \frac{1}{T_{1}}=7.80 \times 10^{-4} \\
\therefore T_{1}=\frac{1}{7.80 \times 10^{-4}}=1280 \mathrm{~K}
\end{gathered}
$$

## ■ P15.5

Assuming the fatigue behavior is represented by Basquin's law, we may surmise that $\Delta \sigma\left(N_{f}\right)^{a}=C$, where $\Delta \sigma$ is stress range, $N_{f}$ is the number of cycles to failure, and $a$ and $C$ are constants. We can substitute the two given data points and solve for exponent $a$ :

$$
\begin{gathered}
\Delta \sigma_{1}\left(N_{f, 1}\right)^{a}=\Delta \sigma_{2}\left(N_{f, 2}\right)^{a} \\
\therefore 280 \times\left(10^{5}\right)^{a}=200 \times\left(10^{7}\right)^{a} \\
\therefore\left(\frac{10^{5}}{10^{7}}\right)^{a}=\frac{200}{280} \\
\therefore\left(10^{-2}\right)^{a}=0.714 \\
\therefore a \times \ln \left(10^{-2}\right)=\ln (0.714) \\
\therefore a=\frac{\ln (0.714)}{\ln \left(10^{-2}\right)}=0.0732
\end{gathered}
$$

Using either of the two data points, we can determine constant $C$ :

$$
C=\Delta \sigma_{1}\left(N_{f, 1}\right)^{a}=200 \times\left(10^{7}\right)^{0.0732}=651 \mathrm{MPa}
$$

Lastly, we compute the number of cycles to failure at $\Delta \sigma=150 \mathrm{MPa}$ :

$$
\begin{aligned}
& C=\Delta \sigma\left(N_{f}\right)^{a} \rightarrow N_{f}=(C / \Delta \sigma)^{\frac{1}{a}} \\
\therefore & N_{f}=\left(\frac{651}{150}\right)^{\frac{1}{0.0732}}=5.12 \times 10^{8} \mathrm{cycles}
\end{aligned}
$$

## ■ P16.5

Part (a): Substituting $T=500^{\circ} \mathrm{C}=773 \mathrm{~K}$ in the given expression for $k$, we obtain

$$
k=2.5 \times 10^{-5} \times \exp \left(-\frac{72,400}{8.314 \times 773}\right)=3.20 \times 10^{-10} \mathrm{~cm}^{2} \mathrm{~s}^{-1}
$$

Part (b): Noting that 1 year $\approx 3.15 \times 10^{7} \mathrm{~s}$, the oxidation depth $\Delta x$ is calculated to be

$$
\begin{gathered}
(\Delta x)^{2}=k t \rightarrow \Delta x=\sqrt{k t} \\
\therefore \Delta x=\sqrt{\left(3.20 \times 10^{-10}\right) \times\left(3.15 \times 10^{7}\right)}=0.10 \mathrm{~cm}=1.0 \mathrm{~mm}
\end{gathered}
$$

## ■ P16.6

Noting that 1 year $\approx 3.15 \times 10^{7}$ s and $k_{p}=2 \times 10^{-7} \mathrm{~kg}^{2} \mathrm{~m}^{-4} \mathrm{~s}^{-1}$, the weight gain $\Delta m$ is determined as

$$
\begin{gathered}
(\Delta m)^{2}=k_{p} t \rightarrow \Delta m=\sqrt{k_{p} t} \\
\therefore \Delta m=\sqrt{\left(2 \times 10^{-7}\right) \times\left(3.15 \times 10^{7}\right)}=2.51 \mathrm{~kg} \mathrm{~m}^{-2}
\end{gathered}
$$

The number of oxygen atoms absorbed is $\frac{2.51}{\left(16 / N_{A}\right)}$, where 16 is the molar mass of oxygen and $N_{A}$ is Avogadro's number. Since the compound produced by oxidation is FeO , we surmise that the number of Fe atoms removed equals the number of O atoms absorbed. Then, the mass of Fe atoms removed is

$$
\text { Mass of Fe atoms removed }=\frac{2.51}{\left(16 / N_{A}\right)} \times \frac{55.9}{N_{A}}=8.77 \mathrm{~kg} \mathrm{~m}^{-2}
$$

where we have used $55.9 \mathrm{~kg} / \mathrm{kmol}$ as the molar mass of Fe . It remains to compute the thickness $\delta$ of iron removed,

$$
\delta=\frac{8.77}{7870}=0.00111 \mathrm{~m}=1.11 \mathrm{~mm}
$$

where we have used $7870 \mathrm{~kg} / \mathrm{m}^{3}$ as the density of iron.

## ■ P16.8

This problem is similar to 7.10. The key is to note that the thin-film diffusion equation

$$
c(x, t)=\frac{\alpha}{\sqrt{\pi D t}} \exp \left(-\frac{x^{2}}{4 D t}\right)
$$

can be adjusted to yield

$$
\ln c(x, t)=\ln \frac{\alpha}{\sqrt{\pi D t}}-\frac{x^{2}}{4 D t}
$$

so that a plot of $\log (c)$ versus $x^{2}$ should yield a straight line with slope $-1 / 4 D t$. The data are processed and plotted below.

| Counts (min) | $\operatorname{In}$ (Counts) | Dist. from <br> plated end $(\mathbf{m})$ | $\boldsymbol{x}^{\mathbf{2}}\left(\mathbf{m}^{\mathbf{2}}\right)$ |
| :---: | :---: | :---: | :---: |
| 5012 | 8.520 | $1.00 \mathrm{E}-04$ | $1.00 \mathrm{E}-08$ |
| 3981 | 8.289 | $2.00 \mathrm{E}-04$ | $4.00 \mathrm{E}-08$ |
| 2512 | 7.829 | $3.00 \mathrm{E}-04$ | $9.00 \mathrm{E}-08$ |
| 1413 | 7.253 | $4.00 \mathrm{E}-04$ | $1.60 \mathrm{E}-07$ |
| 525 | 6.263 | $5.00 \mathrm{E}-04$ | $2.50 \mathrm{E}-07$ |



As shown, the linear fit has slope $-9.34 \times 10^{6}$, hence,

$$
\begin{gathered}
-9.34 \times 10^{6}=-\frac{1}{4 D t}=-\frac{1}{4 \times D \times(20 \times 3600)} \\
\therefore D=\frac{1}{4 \times\left(9.34 \times 10^{6}\right) \times(20 \times 3600)}=3.72 \times 10^{-13} \mathrm{~m}^{2} \mathrm{~s}^{-1}
\end{gathered}
$$

■ P16.11
This problem is akin to Problem 7.9. The amount of impurity per unit area is $\alpha=10$ $\times\left(0.1 \times 10^{-6}\right)=10^{-6} \mathrm{wt} \%$. Substituting this and other data into the concentration distribution equation, we have

$$
\begin{gathered}
C(x, t)=\frac{\alpha}{\sqrt{\pi D t}} \exp \left(-\frac{x^{2}}{4 D t}\right) \\
\therefore 0.25=\frac{10^{-6}}{\sqrt{\pi \times\left(9.6249 \times 10^{-12}\right) \times t}} \exp \left(-\frac{\left(10^{-6}\right)^{2}}{4 \times\left(9.6249 \times 10^{-12}\right) \times t}\right) \\
\therefore 0.25=\frac{0.182}{\sqrt{t}} \exp \left(-\frac{0.0260}{t}\right) \\
\therefore \frac{0.182}{\sqrt{t}} \exp \left(-\frac{0.0260}{t}\right)-0.25=0
\end{gathered}
$$

This transcendental equation can be solved with MATLAB:

```
>> f = @(t) 0.182/sqrt(t)*exp(-0.026/t) - 0.25;
t0 = 1;
fsolve(f,t0)
ans \(=\)
\[
0.4750
\]
```

Therefore, $t \approx 0.475 \mathrm{sec}$.

## ■ P16.13

Part (a): Noting that the principal strain $\varepsilon_{o x}=\left(\sigma_{o x} / E_{o x}\right)\left(1-v_{o x}\right)$, we may write, for the biaxially-stressed oxide layer,

$$
W^{*}=\frac{1}{2} \sigma_{o x} \varepsilon_{o x}+\frac{1}{2} \sigma_{o x} \varepsilon_{o x}=\frac{\sigma_{o x}^{2}}{E_{o x}}\left(1-v_{o x}\right)
$$

But $\sigma_{\mathrm{ox}}=(\Delta T)(\Delta \alpha) E_{o x}$, giving

$$
\begin{gathered}
W^{*}=\frac{\sigma_{o x}^{2}}{E_{o x}}\left(1-v_{o x}\right)=\frac{\left[(\Delta T)(\Delta \alpha) E_{o x}\right]^{2}}{E_{o x}}\left(1-v_{o x}\right) \\
\therefore W^{*}=E_{o x}\left(1-v_{o x}\right)(\Delta T)^{2}(\Delta \alpha)^{2}
\end{gathered}
$$

as we intended to show.
Part (b): Assume oxide spallation will occur when the strain energy within the oxide layer, of thickness $h$, is equal to the energy required to produce decohesion over an interface area $A$. The volume of the oxide above area $A$ is $A h$ and the energy within this volume is $A h W^{*}$. The fracture energy required is $A \gamma_{f}$ and, so, using the given expression for $W^{*}$ within the energy balance:

$$
\begin{gathered}
E_{o x} h\left(1-v_{o x}\right)(\Delta T)^{2}(\Delta \alpha)^{2}=\gamma_{f} \\
\therefore \Delta T_{c}=\frac{1}{\Delta \alpha} \sqrt{\frac{\gamma_{f}}{E_{o x} h\left(1-v_{o x}\right)}}
\end{gathered}
$$

Part (c): Substituting the given data into equation (I), we obtain

$$
\begin{gathered}
\gamma_{f}=\left(380 \times 10^{9}\right) \times\left(5 \times 10^{-6}\right) \times(1-0.27) \times(671)^{2}\left(8 \times 10^{-6}\right)^{2} \\
\therefore \gamma_{f}=39.97 \approx 40.0 \mathrm{~J} \mathrm{~m}^{-2}
\end{gathered}
$$

This is much larger than the intrinsic value for interfacial fracture because much of the oxide strain energy is dissipated during cooling, mainly by creep deformation in the vicinity of the tips of cracks at the oxide/metal interface. Alloys weak in creep are expected to show greater resistance to oxide spallation (i.e. higher $\gamma_{f}$ and $\Delta T_{c}$ ) than strong alloys where creep relaxation will be more limited.


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