Please read the exam through before starting. Clearly show all work in the space provided below each question. Feel free to use the additional pages at the end of this packet if necessary. Calculators and one double-sided 8 ½ x 11 page of notes are permitted. It is suggested that you outline the solution to your problem wherever possible. Partial credit will be given for answers that follow a logical thought process. Good luck!

RETURN THIS EXAM WITH YOUR EQUATION SHEET
AT THE END OF THE EXAM PERIOD

Name

Question 1

Question 2

Question 3

Question 4

Question 5

Total

(out of 15) (out of 20) (out of 20) (out of 20) (out of 25) (out of 100)
Problem 1 (15 points)

A series of optical micrographs of Fe-6.5 wt% Si sheets are given below. The micrographs show microstructure progression after cold-rolling and heat treatment at different temperatures for 15 minutes (Data from YongFeng et al, Science China, 53(4), 1008-1011, 2010).

![Micrographs of Fe-6.5wt% Si sheets](image)

**Figure 2** Optical microstructures of Fe-6.5wt%Si sheets. (a) Cold-rolled, and heat-treated at (b) 350°C; (c) 450°C; (d) 550°C; (e) 650°C; (f) 750°C; (g) 900 °C for 15 min.

a) Explain the changes in these micrographs.

High dislocation density due to cold working. Recrystallization takes place, with subsequent grain growth.

b) Hardness values for these samples were measured and plotted as a function of heat treatment temperature. Explain the trend in this graph.

High hardness due to high dislocation density. Recrystallization produces dislocation free grains.

![Graph of micro-hardness evolution](image)

**Figure 3** Micro-hardness evolution of Fe-6.5wt%Si sheets with different annealing temperatures.
Problem 1 cont.
Problem 2 (20 points)

Studies were done to explore the nucleation behavior of aspirin crystals from supersaturated solution on various polymer coated glass surfaces. An array of many test tubes was assembled each with a polymer coated glass slide. Aspirin solution was placed in each tube before incubation. The polymer film is insoluble in the aspirin solution. The slides were examined microscopically at each time point to detect aspirin crystals. The probability $P$ for no crystallization event having taken place (fraction of test tubes without crystals) after a given time $t$ is shown below for four polymer films (Data from Y. Diao, 2010).

![Graph showing ln(P) vs. Time in Hours for polymers A, B, C, and D.]

a) Polymers $C$ and $D$ seem to be more effective at crystallizing aspirin from solution. What kind of nucleation is occurring?

Heterogeneous nucleation on defects and/or impurities.

b) There are some tubes for both polymer films $C$ and $D$ that are no more effective than polymers $A$ and $B$. Which parts of the curves are those tubes?

(should draw) the lower slope parts of the curves (Both regions are heterogeneous nucleation but the higher slope corresponds to greater surface activity for nucleation).

c) Shown below are atomic force microscopy (AFM) images from $D$ polymers films that are effective and that are not effective at nucleation of aspirin from solution. Explain why some surfaces are effective and why there are two slopes for effective films in the graph above.

Effective surfaces are those with defects, or those on which heterogeneous nucleation can take place. Non-effective surfaces are surfaces that don’t have defects; and must rely on heterogeneous nucleation on a flat surface, which makes nucleation of aspirin from solution much less effective.
The images are all from polymer films of composition $D$.

Shown at right is surface topology along line indicated in effective film.
Problem 2 cont.
Problem 3 (20 points)

Thermoelectric materials can be used in applications such as microprocessor cooling or power generation from waste heat. These materials must have low thermal conductivity and high electrical conductivity. Recently, it has been shown that the formation of heterostructures at nanoscale provides a scattering mechanism for mid to long wavelength phonons with little impact on electrical conductivity. This is because the phonon mean free path is larger than for the electrons. Thus, the manipulation of the material microstructure offers new degrees of freedom to tune thermal conductivity with weak side effects on electrical properties. As an example of how these structures are produced, consider an alloy of 36 mol% GeTe and 64 mol% PbTe that is cooled down from a liquid phase and processed in several different ways. The phase diagram of GeTe and PbTe for the temperature range 500-1200 K is given below as are the various heat treatments (Data from Gorsse, et al, Chemistry of Materials, 22, 988-993, 2010).

The microstructures of samples of Ge$_{0.36}$Pb$_{0.64}$Te that have been cooled from the liquid are shown below.
a) What has occurred to create the structure in micrograph a?

Quenched from the melt, producing normal nucleation of solid followed by dendritic growth.

b) Why does micrograph b look so inhomogeneous?

Only slightly more compositionally homogeneous than a. Dendritic growth inhomogeneity has not had sufficient time to homogenize by diffusion in the single phase region. The microstructure consists of different features, including the spinodes we see in different parts of the microstructure.

c) Describe the sequence of events that are occurring in micrographs c through h.

Figure 3. SEM-BSE images of an $\text{Pd}_{0.17}\text{Ge}_{0.83}$ alloy in the (a) quenched from the melt, (b) air-cooled from the melt, (c) solution treated at 600 °C and quenched, (d) solution treated, quenched, and aged at 500 °C for 1 min, (e) for 2 min, (f) for 10 min, (g) for 60 min, and (h) for 6000 min states. The bright and dark phases are $\text{Pd}_{0.17}\text{Ge}_{0.83}$ and $\text{GeTe(Pb)}$, respectively. Image magnifications depend on the microstructure size; they are ranked from the highest to the lowest as: c > d > e = f = g > h > b > a.
Micrograph c: most compositionally homogeneous as the inhomogeneity produced by the initial freezing has had sufficient time for diffusion.

Micrograph d: regions show evidence of spinodal decomposition. Possible thermal inhomogeneity because of short heat treatment times—chemically homogeneous but thermally inhomogeneous.

Micrograph e-g: clear evidence of spinodal decomposition.

Micrograph h: coarsening of the spinodal structure.
Problem 4 (20 points)

Polymers often crystallize in lamellar structures that involve the individual polymer molecules folding back on themselves as shown in the figure below. Individual lamellae grow laterally but periodically branch. Growth and repeated branching results in the spherulite structure you have seen (Data from Chan and Li, Advanced Polymer Science 188, 1-41, 2005).

![Fig. 8 Schematic showing edge-on and flat-on lamellae](image)

Nucleation, growth, and branching of lamella within initially amorphous films poly(bisphenol A-co-octane) (PB-C8) are shown in the AFM images below.

![Fig. 6 A series of AFM phase images obtained on a BA-C8 film at room temperature. a An embryo; b a short lamella (foundling lamella) developed from the embryo shown in a c-f. The growth of the foundling lamella; g-p branching and splaying apart of the subsidiary lamellae](image)

The growth of the foundling lamella; g-p branching and splaying apart of the subsidiary lamellae [61]
Problem 4 cont.

a) The AFM images can be used to measure the growth rate of lamellae at the temperature at which the image is acquired. The growth rate versus temperature for BA-C10, a different version of the same polymer, is shown below. Why does it go through a maximum?

![Graph of lamellar growth rate vs. temperature](image)

**Fig. 18** Lamellar growth rate of BA-C10 as a function of crystallization temperature, determined by AFM [64]

Lowering the temperature increases the undercooling which increases the growth rate. Too low a temperature, however, decreases diffusion and the growth rate begins to drop.

One mechanism by which a branch may form is shown below. A polymer molecule may be incompletely incorporated into the growing lamellae. It may then fold again to begin the order structure required to begin the growth of a new branch.

![Schematic of branch formation](image)

**Fig. 15** Schematic showing the proposed mechanisms of induced nucleation

b) It is observed that branches grow at the same rate as their founding lamellae. Thus, the time between subsequent branches along a given lamella can be estimated by measuring the distances between branches and dividing by the growth rate. The reciprocal of this time is plotted below for different annealing temperatures. Why does branching occur more frequently in a certain range of temperature?
The branching is essentially a nucleation process on the surface of an existing lamella. Thus, the branching rate should increase with undercooling until diffusion becomes limiting.
Problem 5 (25 points)

a) The evolution of Sn-rich solid particles in an isothermal Pb-Sn eutectic liquid is shown at constant magnification after 5, 75, and 1020 minutes. Explain this change in particle size over time.

Ostwald ripening or coarsening.

b) Draw a graph of free energy vs. particle size $d$, showing two scenarios: coherent nucleation and incoherent precipitates. Make sure to draw a large enough graph to show the differences between the curves.
Problem 5 cont.

Shown below is a micrograph within a single grain of a Ni-12 at.%Al alloy after 1 hour of aging time. The cubic particles are Ni₃Al (γ’). Note that the smaller γ’ particles formed upon quenching from the aging temperature, and only the larger cuboidal γ’ particles were there at the aging temperature (Data from Qiu, Y.Y., Journal of Alloys and Compounds, 270, 145-153, 1998).

\[ \text{Image of micrograph} \]

The large existing particles grow upon cooling and deplete the surrounding Ni of Al. Thus, this region has lower supersaturation than regions far from the surface of these existing particles. This means that it is easier to nucleate γ’ in the regions far from the existing γ’ particles.

c) Why is there a gap between the cubic particles formed during the quench and the particles present during aging?

The particles are coherent with the lattice.

d) The γ’ particles that appear after aging for one hour are all oriented in the same direction within the original Ni-Al grain. What does that say about these particles (refer back to part b)? Go back and label the appropriate curves in part b.
Problem 5 cont.

e) Shown below is the microstructure of γ' particles that have been aged for five hours. This microstructure shows that the particles have now split into octets; that is, each of the large particles has split into eight smaller particles (four seen in the micrograph view, four below). Therefore, the overall particle size has actually decreased! Can you explain why this would happen? What energy can explain the fact that the surface area has increased?

As the γ' particles coarsen the strain energy grows with $d^3$. Two options are apparent: 1) The particles can become incoherent, costing $6d^2\gamma_{\text{incoherent}}$ units of energy, or 2) split into eight smaller particles costing $2d^2\gamma_{\text{coherent}}$ units of energy. Option 2 is the option that gives the lower energy.
Problem 5 cont.