(write answers in here & we can scan & upload).

Engineering 45
The Structure and Properties of Materials
Midterm Exam
March 17, 2010

Key

**Problem 1: (25 points)**

15 (a) Describe how the $Cu_3Au$, NaCl and ß-ZnS structures are derived from FCC.

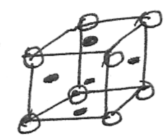
10 (b) Binary compounds with the $Cu_3Au$ structure are invariably metals, those with the ß-ZnS structure are usually semiconductors, and those with the NaCl structure are usually insulators. Why might you expect this behavior?

~~FCC crystal structure~~ ~~→ (+1)~~

a) $Cu_3Au$ 5

NaCl 5

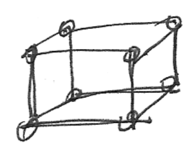
β ZnS 5



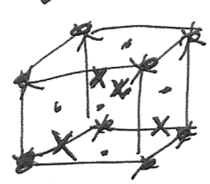
0 2.5 5

● = Cu

o = Au.



interlaced fcc.
fcc w/ two atom
fcc voids being filled.



FCC ½ tetras filled

FCC w/ 4 atom basis.

0 2.5 or 5.

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$Cu_3Au$ → 4pts. → ~~some~~ not ionic b/c Cu → Cu bond.
not covalent. b/c not tetrahedral. (like sea most cond)

ZnS 3pts → tetrahedral bonding. directional filled covalent. (1.5)

NaCl 3pts → Ionic bonding. (1.5) (+1) e⁻'s can be activated.

e⁻ tightly bound to atoms (+1)

tightly → maximize charge density (+1) (+ w/ -'s) ⇒ ionic
[no like charges adjacent] ⇒ insulator.

**Problem 2 (25 points):**

The Second Law of Thermodynamics states that the entropy of an isolated system can only increase. The change in entropy in an infinitesimal change of state is

$$dS = \frac{1}{T}\left[dE + PdV - \sum_k \mu_k dN_k\right] \qquad 2.1$$

where T is the temperature, E is the internal energy, P is the pressure, V is the volume, $\mu_k$ is the chemical potential of the $k^{th}$ component and $N_k$ is the mole number of the $k^{th}$ component.

14

(a) Let two solids have fixed volumes and chemical contents, and let their temperatures be different. Show that if they interact only with one another energy (heat) flows from the solid with higher T to the solid with lower T. [Hint: Remember that energy is conserved. If the solids interact only with one another, $dE_1 + dE_2 = 0$.]

11

(b) Let a solid have a fixed chemical content and be in thermal and mechanical contact with a reservoir that fixes its temperature and pressure. Show that the equilibrium of the system is governed by its Gibbs free energy,

$$G = E - TS + PV \qquad 2.2$$

which must decrease in any spontaneous change. [Hint: Let the solid and the reservoir together form an isolated system. Then the energy and volume are conserved in any interaction between them. Moreover, the reservoir is, by definition, so large that its temperature and pressure remain constant when it interacts with the system.]

a) $dS_{sys} = dS_1 + dS_2 \geq 0$

$3 \quad dS_1 = \frac{1}{T_1}[dE_1 + P_1 \cancel{dV_1} - \cancel{\mu_1 dn_1}]$ $\qquad dV_1 = dV_2 = 0 \; ①$

$dS_2 = \frac{1}{T_2}[dE_2 + P_2 \cancel{dV_2} - \cancel{\mu_2 dn_2}]$ $\qquad dn_1 = dn_2 = 0 \; ①$

$dE_2 = -dE_1 \; ①$

$dS_{sys} = \frac{dE_1}{T_1} + \frac{dE_2}{T_1} = \frac{dE_1}{T_1} - \frac{dE_1}{T_2} = dE_1\left(\frac{1}{T_1} \overset{①}{-} \frac{1}{T_2}\right) \boxed{\geq 0} \; ③$

if $T_1 > T_2$ then $\left(\frac{1}{T_1} - \frac{1}{T_2}\right) < 0$ and $dE_1 < 0$ $\quad dE_2 > 0 \; ②$

if $T_1 < T_2$ then $\left(\frac{1}{T_1} - \frac{1}{T_2}\right) > 0$ and $dE_1 > 0$ $\quad dE_2 < 0 \; ②$

including ~~plus~~ explanation

2b

½ $dE_2 = -dE_1$

½ $dV_2 = -dV_1$

½ $dn_1 = dn_2 = 0$

½ $T_1 = T_2 = T$

½ $P_1 = P_2 = P$

½ $dS_1 = \frac{1}{T}[dE_1 + PdV_1 - \mu_1 \cancel{dn_1}^{\,0}]$

½ $dS_2 = \frac{1}{T}[dE_2 + PdV_2 - \mu_2 \cancel{dn_2}^{\,0}]$

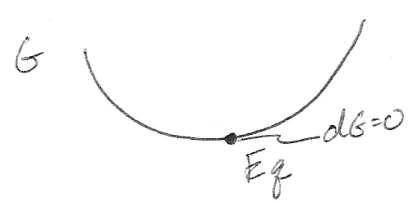
½ $dS_2 = -\frac{1}{T}[dE_1 + PdV_1]$

$$dS_{sys} = dS_1 + dS_2 = dS_1 - \frac{1}{T}[dE_1 + PdV_1] \quad ①$$

$$= -\frac{1}{T}[dE_1 - TdS_1 + PdV_1] \quad ①$$

$$dS_{sys} = -\frac{1}{T}\, d[\underbrace{E_1 - TS_1 + PV_1}_{G_1\ ①}] \le 0 \quad ②$$

At equilibrium
@ const $T, P, \{N\}$ $\qquad (dG_1)_{T,P,\{N\}} \ge 0$
G is at a minimum




Explanation: ②

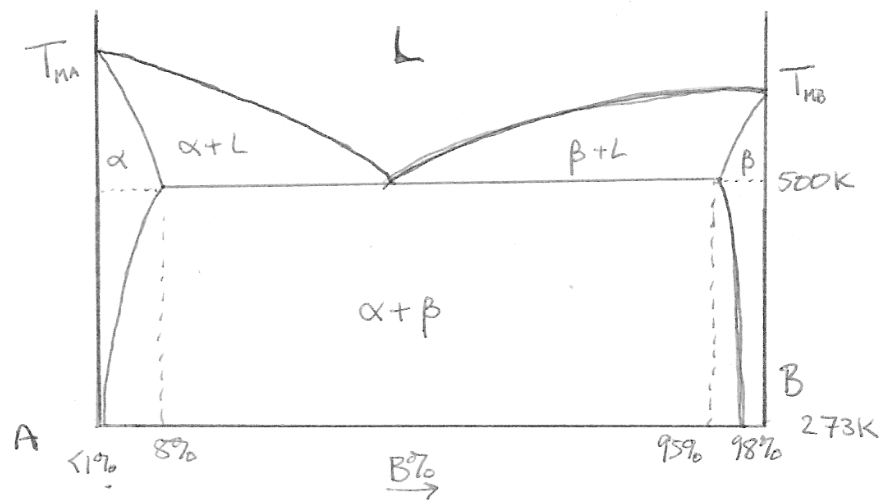
**Problem 3 (25 points):**

15 (a) A binary system of atoms of types A and B has a simple eutectic phase diagram. The A-rich solid solution ($\alpha$) has a maximum solubility of 8 atom percent B at the eutectic temperature (500 K), but dissolves much less than 1 atom percent B at room temperature (273 K). The B-rich solid solution ($\beta$) has a maximum solubility of 5 atom percent A at the eutectic temperature, and dissolves 2 atom percent A at room temperature. Show the qualitative form of the phase diagram and label the phase fields.

10 (b) You are given a sample of the solution that contains 4 atom percent B. You wish to process it into a homogeneous (supersaturated) $\alpha$ solid solution at room temperature. Starting from the liquid state, describe a thermal processing sequence that might achieve this, and explain why it might work.

3 (a)

$\boxed{15 \text{ pts}}$




2 pts → draw eutectic plot

1 pt → ~~use atomic percents for axis~~ label composition axis

6 pts → label 6 phase fields

2 pts → eutectic isotherm @ 500K

4 pts → key composition points (<1%, 8%, 95%, 98%)

↳ %B!

3(b)

$\boxed{10 \text{ pts}}$

1 pt → 4%B is less than max solubility at T=500K (8%)

1 pt → 4%B is greater than max solubility at T= 273K (<1%)

2pt → Cool from liquid to $\alpha$-phase field

2pt → Allow time for homogenization in '$\alpha$-regime'

2pt → QUENCH from $\alpha$-phase field to T=273K

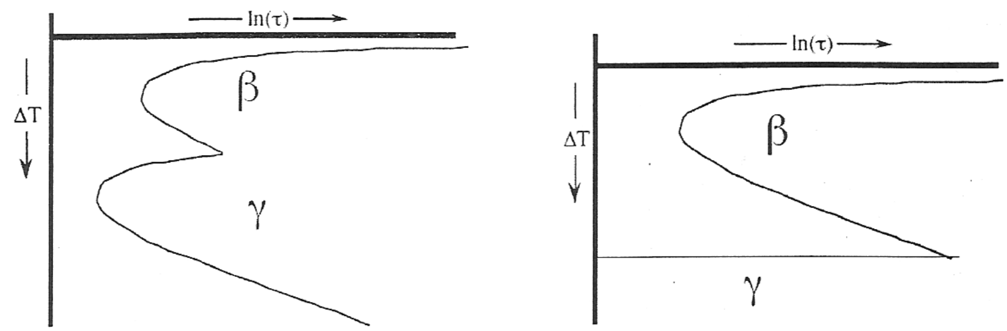
2pt → Quenching (rapid cooling) prevents diffusion from having time to occur & thus suppresses $\beta$ formation

☆ Goal of this question was to create a "homogenous (supersaturated) $\alpha$ solid solution" <u>with</u> <u>an</u> <u>overall</u> <u>composition</u> <u>of</u> <u>4%B</u>.

"Supersaturated" solutions are those which contain more solute than ~~the~~ the equilibrium amount due to kinetic barriers.

Purifying the sample to contain <1%B would <u>not</u> create "supersaturated" solution.

**Problem 4: (25 points)**




(a) (b)

A one-component material has three possible structures, α, ß and γ. At high T the system is α. If it is cooled slowly it transforms to ß at $T < T_{\alpha\beta}$, and remains ß for all lower temperatures. If it is cooled quickly it transforms to γ at $T_{\alpha\gamma} < T_{\alpha\beta}$.

(a) Suppose that both the α→β and α→γ transformations occur by nucleation and growth. Sketch plausible forms of the free energy vs. temperature curves for the three phases that might lead to this behavior.

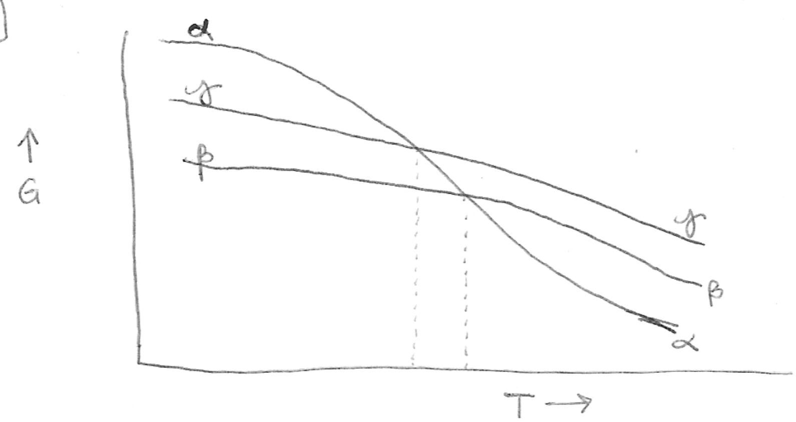
(b) Are the kinetics of the nucleated transformations more likely governed by fig. (a) or fig. (b)? Explain.

(c) Now consider the case in which phase α is a liquid, phase ß is a crystalline solid and phase γ is a glass. Are the kinetics of the transformation more likely governed by (a) or (b) in this case? Explain.

(d) While it is possible to suppress the α→β transformation by rapid cooling, it is not ordinarily possible to suppress the β→α transformation by rapid heating. Why?

4(a) See Figure 9.3 in the text.

10 pts




Correct axes - 2 pts
Three curves - 3 pts
Correct curvature - 2 pts
Correct order - 3 pts

4 (b) $\boxed{\text{5 pts}}$

Figure A (3 pts)

$\gamma$ has nucleation + growth c-curve (2 pts)

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4 (c) $\boxed{\text{5 pts}}$

Figure B (3 pts)

$\gamma$ occurs for any remaining $\alpha$ past $T_\gamma$

↳ does not require nucleation (2 pts)

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4 (d) $\boxed{\text{5 pts}}$

- as T decreases from $T_{TRANS}$

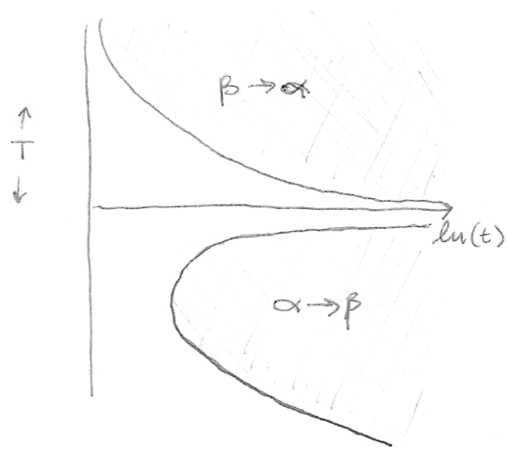
(2 pts) N↑ but D↓ (er, nucleation increases but diffusion/growth decreases)

- as T increases from $T_{TRANS}$

(3 pts) N↑ and D↑ ∴ no c-curve effect

★ See section 11.3.4 → "The Initiation Time"

Figure 11.6



# Graders

| | |
|---|---|
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| Q3 | Kathryn |
| Q4 | Kathryn |