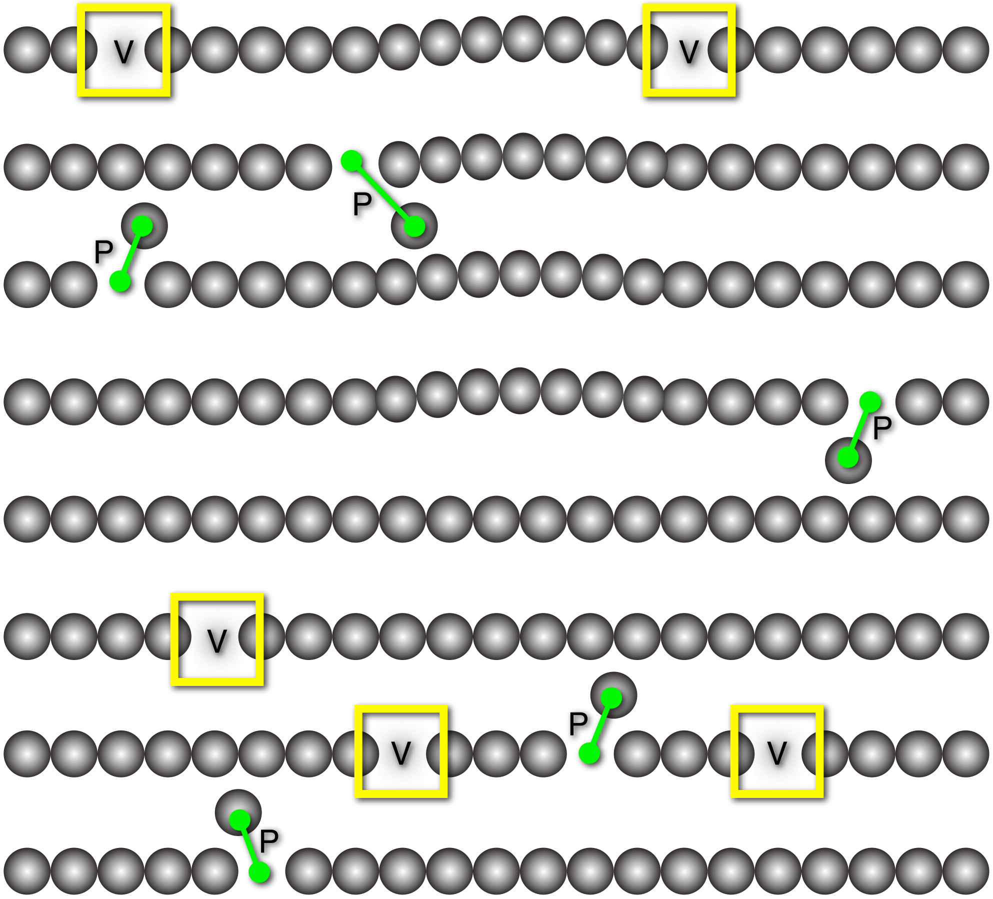
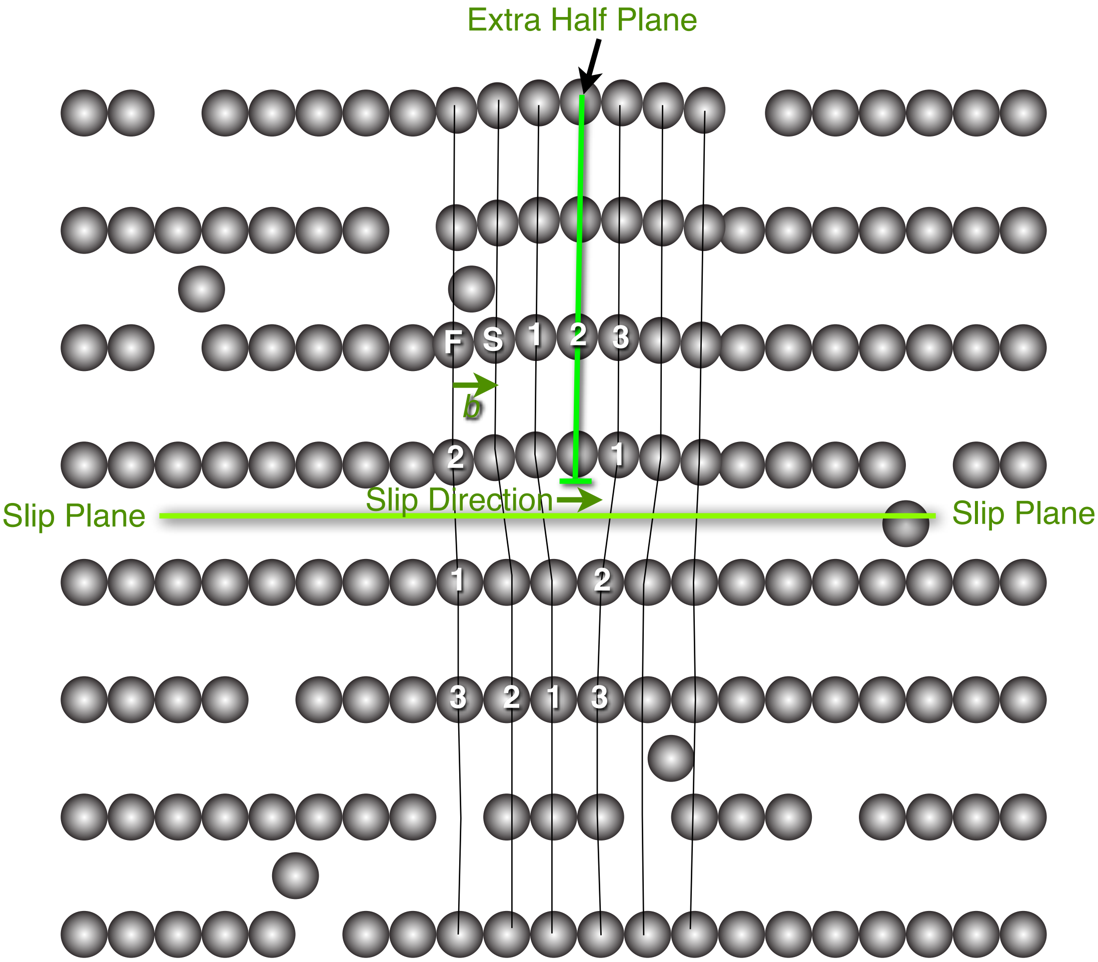
1. Defects in Solids (20 points)

The following figure is an atomic-level representation of a few dozen unit cells in an elemental metal that has been subjected to substantial cold work.



(**a**) The figure contains five (5) defects that appear as isolated vacancies, and five more than appear as Frenkel pairs.
(5 points) Locate and accurately label (*V* for isolated vacancy, *P* for Frenkel pair) all of them.



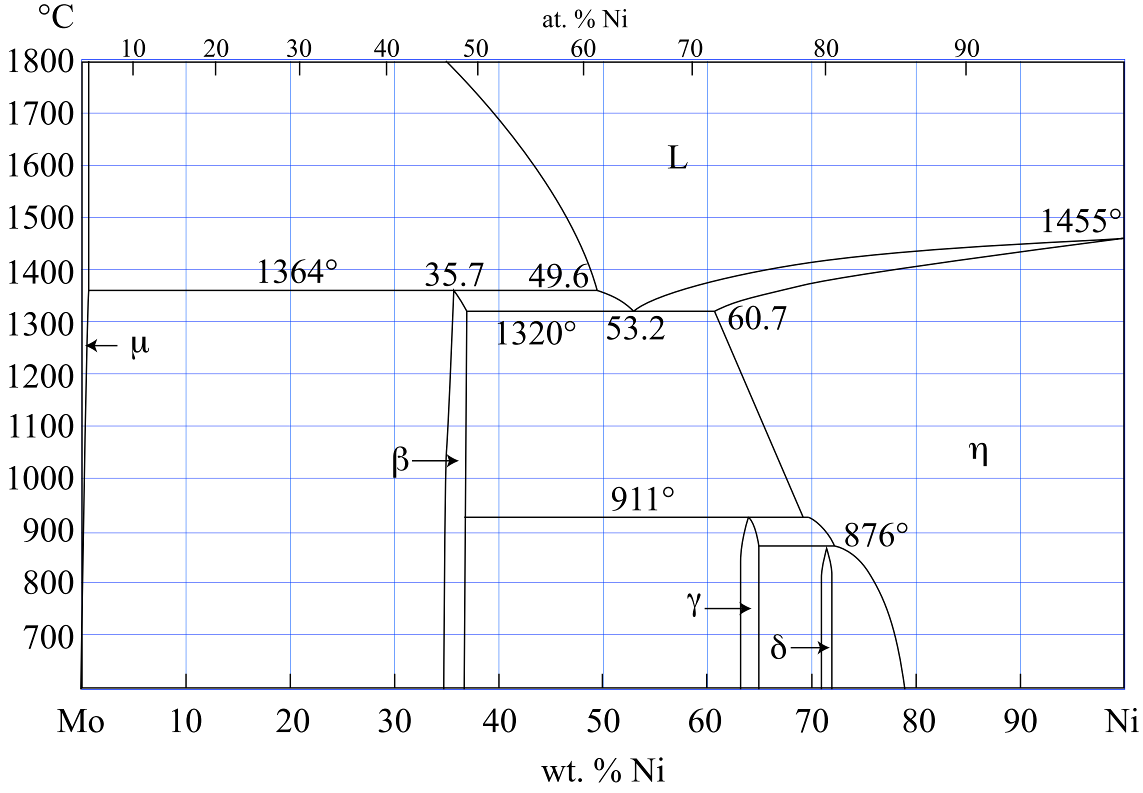
(b) (5 points) Locate and accurately label the extra half plane associated with an edge dislocation in this figure. **The extra half plane can be located at any of 4 or 5 different positions near the center of the figure, best illustrated by tracing the bending of contiguous planes around it, as shown above**.

(c) (5 points) Trace a Burgers circuit in the finish-to-start-right-hand (FSRH) convention and label the Burgers vector associated with this edge dislocation. **"Right hand" means a clockwise rotation, and the circuit must contain the same number of steps (3 are shown here) along equivalent crystallographic directions. The Burgers vector is labeled *b* above.**

(d) (5 points) Locate and accurately label the candidate slip plane on which this dislocation glides, and indicate its direction of motion in that slip plane. **The slip direction is always given by the Burgers vector direction, by definition.**

2. Phases and Phase Equilibria (20 points)

Refer to the following phase diagram from the *Metals Handbook*, 8th Edition, Volume **8**, American Society for Metals, Metals Park, Ohio (1973), to support your answers.



(a) Ni_3Mo is an ordered intermetallic compound with an orthorhombic structure at room temperature. What single-phase field does it occupy in the binary Mo-Ni system?

(5 points) *Answer*: γ **phase**

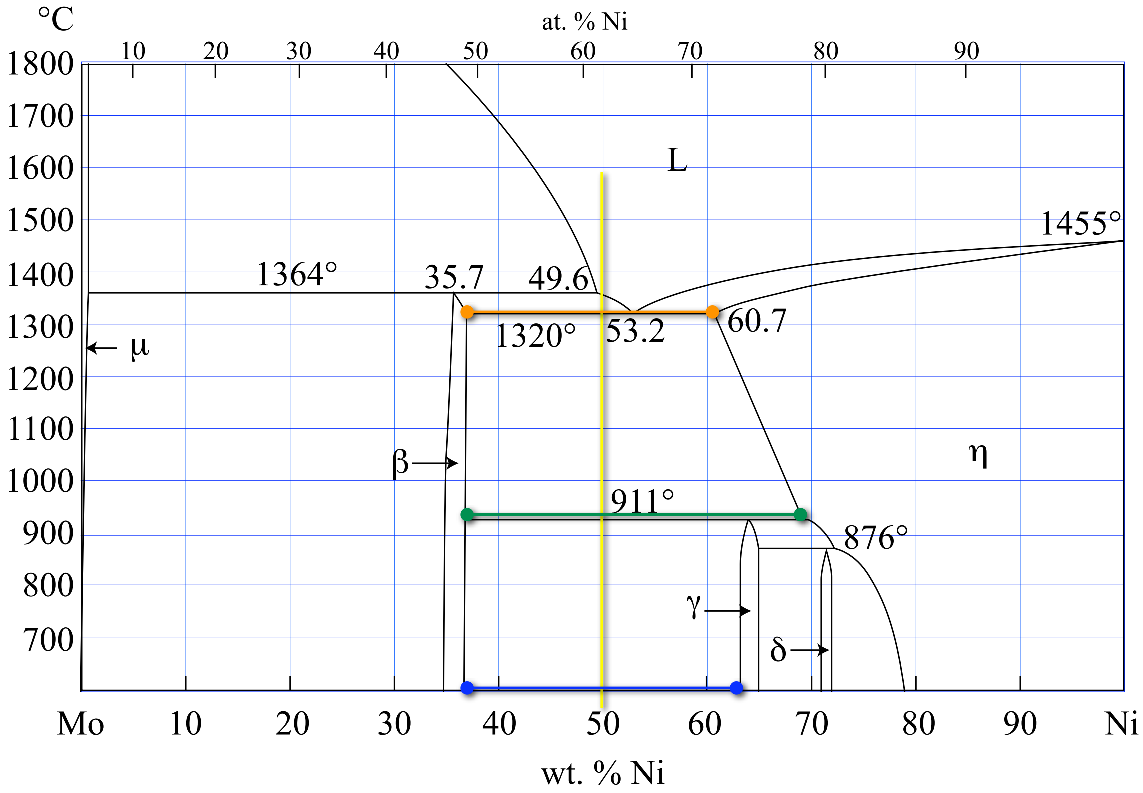
Ni_3Mo contains 75% at% Ni; use the atomic % scale (not wt%) appearing at the TOP of the figure to find it on the phase diagram. The phase field has some width on the phase diagram because γ phase has a (small) range of solubility.

(b) A 20% Ni alloy is slowly cooled through 1364°C. Specify the reaction that occurs at the peritectic isotherm.

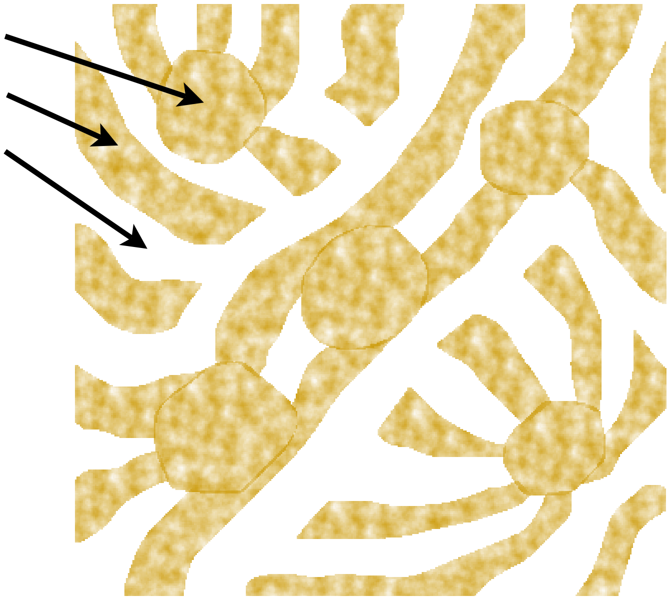
(5 points) *Answer*: $\mu + L \rightarrow \beta + \mu$

Note that this is the reaction that occurs in a 20% alloy on "slowly cooled through 1364°."

(c) The phase diagram shows that when a 50 wt.% alloy is solidified, it crosses a eutectic reaction isotherm at 1320°C and a peritectoid reaction isotherm at 911°C. Assume that the cooling rate is slow enough to sustain equilibrium conditions throughout and sketch the microstructure of the alloy when it is fully cooled at room temperature.



(10 points) *Show sketch here* ↓



Pro-eutectic *β* phase

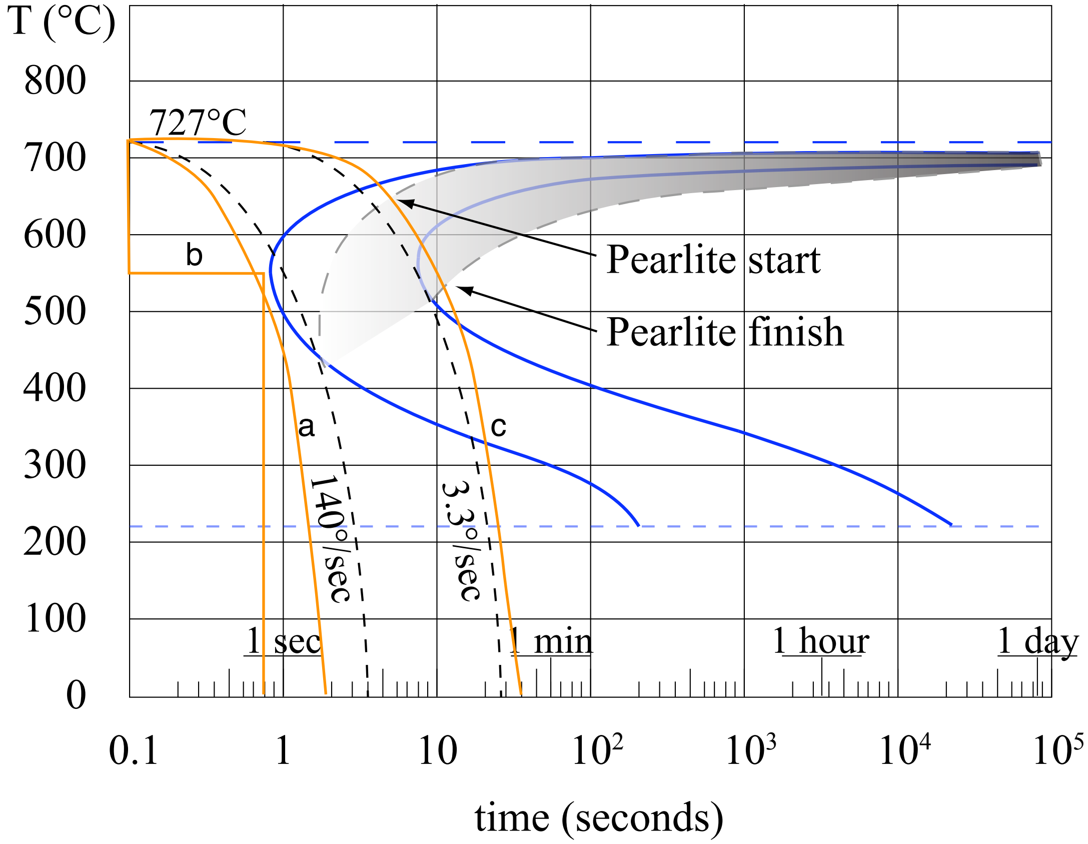
Eutectic / Pertectoid *β* phase

Peritectoid *γ* phase

Note that the peritectoid *γ* phase appears in the prior location of the eutectic *η* product, which was replaced by *β* + *γ* at the peritectoid isotherm. Final microstructure should be approximately 50% *β* (dark phase here) and 50% *γ* (light) by the lever rule.

3. Kinetics (20 points)

The following transformation curve for a steel of eutectoid composition was determined experimentally by R.A. Grange and J.M. Keifer in their classic paper "Transformation of Austenite on Continuous Cooling and Its Relation to Transformation at Constant Temperature," *Trans. Am Soc. Metals*, **29**, 85 (1941).



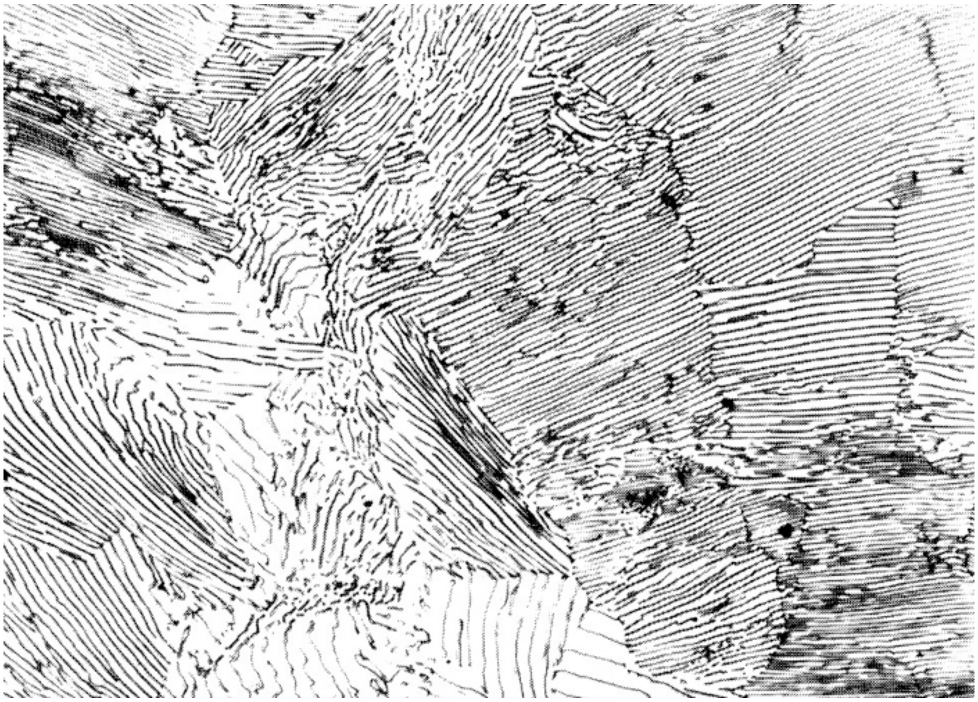
(**a**) Using Grange & Keifer's data, specify a continuous cooling rate for a fully austenitic sample that would generate a microstructure of 100% martensite in a eutectoid steel.

(5 points) *Answer*: **140°C/sec or faster**
An example curve is shown and labeled as "a" on the plot above.

(**b**) If a sample of a eutectoid steel was instantaneously quenched from the eutectoid isotherm to 550°C, how long could the sample remain at this temperature before a 100% martensite product was unachievable?

(5 points) *Answer*: **Approximately 0.8 seconds, as illustrated by curve "b".**

(c) The following microstructure (magnification 700X) was obtained from another sample of a eutectoid steel that was continuously cooled from the eutectoid isotherm.



Using Grange & Keifer's data, specify a continuous cooling rate for a fully austenitic sample that would generate this microstructure.

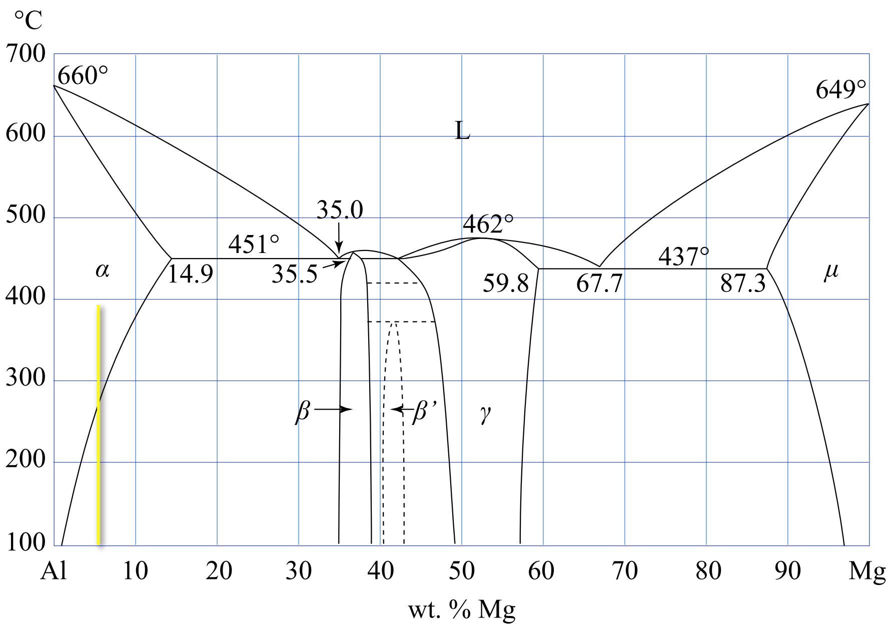
(5 points) *Answer*: **3.3 °C/sec or slower**
This microstructure contains 100% pearlite. An example cooling curve labeled "c" is shown directly on the plot.

(d) Explain, citing the competing effects of driving force and diffusion kinetics, why microstructures generated at higher temperatures are spatially "coarse," while those generated at lower temperatures are spatially "fine."

(5 points) *Answer*: **At high temperatures supersaturation is low, consequently the driving force for emergence of the new phase is low, causing fewer nuclei; but diffusion is favored, so those few nuclei grow very quickly, resulting in a coarse dispersion of micro-constituents. At low temperatures supersaturation is high, generating a high driving force and copious nucleation; but diffusion is hindered, so growth is stunted, resulting in a fine dispersion of micro-constituents.**

4. Metallic Alloys (20 points)

Binary Al-Mg alloys in the 5XXX series undergo substantial strengthening with good ductility as a result of cold work, in addition to excellent corrosion resistance and weldability. However, these alloys are also known as "non-heat-treatable" alloys because they do not show significant precipitation hardening at dilute (< 7%) alloy concentrations.



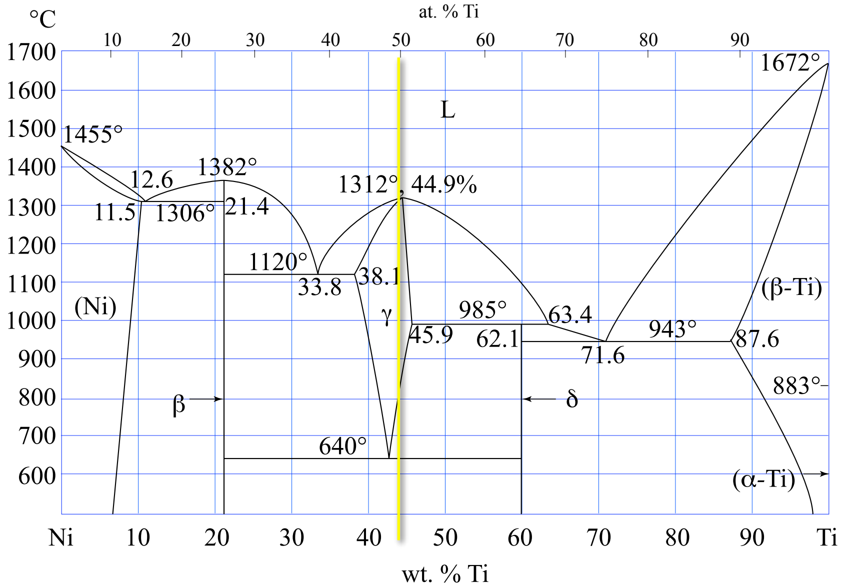
(**a**) Why does "cold work" result in substantial strengthening of the 5XXX series aluminum alloys? What causes the strength increase?

(5 points)? *Answer*: **"Cold work" is plastic deformation at temperatures below $T_m/3$, so recovery processes cannot occur. Because plastic deformation results from the creation and motion of dislocations, there is a high density of dislocations in cold-worked alloys. This is what causes "strengthening." The strength increase is due to the fact that dislocations act as barriers to other dislocations; their entanglement "pins" the dislocations, inhibiting their motion, making it more difficult to further deform the alloy.**

(**b**) Using a dilute 5 wt% Mg alloy for illustration, why does precipitation hardening not work? Explain why precipitates cannot be produced, or if they can (tell how), why they do not result in "hardening."

(5 points)? *Answer*: **The phase diagram shows that precipitates of β phase ARE produced in a 5% alloy when a supersaturated α phase is aged. However the phase diagram also shows that β phase is not that much different from α phase in Mg concentration (roughly 30%). When dislocations encounter β phase particles, the bond-breaking environment is very similar to that in the α phase; consequently, precipitates of β phase are ineffective barriers to dislocation motion.**

(c) The Ni-Ti binary alloy system is very popular in the medical device industry due to a peculiar property known as "shape-memory" that is exhibited by the stoichiometric NiTi intermetallic compound with an ordered cubic structure.



How would you produce a solid ingot of pure γ phase? Be specific, citing both composition(s) and heat treatments.

(5 points) *Answer*: **The problem statement identifies "stoichiometric" NiTi (50 at% of each) as the preferred composition for this alloy. Locating this composition on the phase diagram (as shown above) reveals that the ingot must be solution treated in the range of 900°C to 1200°C to generate 100% γ phase, then quenched rapidly to room temperature in order to retain γ phase in metastable equilibrium, otherwise the equilibrium phases β and δ will emerge.**

(d) The Food and Drug Administration (FDA) has approved NiTi for use as vascular stents, to be implanted in the blood vessels of human patients suffering from atherosclerosis. How do you rationalize this as a safe practice, based upon the information presented in the phase diagram above?

(5 points) *Answer*: **The phase diagram depicts EQUILIBRIUM. In general, "safe" means that the long term stability of a product is known, which in general means that it is in a state of "equilibrium." For the case of shape-memory NiTi, the phase diagram gives an opposing rationale -- γ phase is NOT an equilibrium phase. However, like ferrous martensite, the metastable NiTi γ phase can retain its stability as long as diffusion is restricted. Human body temperatures are well below $T_m/3$, so the FDA is convinced. Kinetics wins over thermodynamics this time.**

5. Ceramics & Glasses (20 points)

One of the more successful examples of structural ceramic materials is based upon the ternary oxide system Li_2O—Al_2O_3—SiO_2 and sold under the trade name Corningware™ (Corning). The product is shaped by conventional glass-forming routes, and its superior properties are due to precipitates of either β-spodumene with stoichiometry $Li_2O{\bullet}Al_2O_3{\bullet}4SiO_2$ and very small thermal expansion coefficient, or β-eucryptite with stoichiometry $Li_2O{\bullet}Al_2O_3{\bullet}SiO_2$ and a negative thermal expansion coefficient. Glass is known as a vitreous (*Latin* ***vitrum***= "glass") material and the process by which these products derive their superior properties is known as "devitrification."

(**a**) Explain what is meant by devitrification, and what thermal-mechanical processing steps are included to generate Corningware™ products. Include in your answer a schematic temperature-time plot to illustrate the sequencing of all steps in the process.

(10 points) *Answer*: **In this context, "devitrification" simply means "crystallization," because the crystalline state is the only other equilibrium state (other than "glassy") exhibited by solid ceramic materials. It should therefore be evident that Corningware™ is an example of the "glass-ceramic" materials that we have been addressing in class.**
Beginning with a "melt" of the ternary oxide constituents identified above, a molten charge is poured into the mold and mechanically shaped into its final (mostly "bowl" -- see illustration above) configuration while the material is still very soft, well above its glass transition temperature. After cooling to room temperature, it is given a relatively low temperature annealing treatment for short times to nucleate (N) the crystalline phase(s), then elevated to a higher growth (G) temperature so that the devitrification step can run to completion, the full cycle shown in the schematic on the Worksheet that follows.

(b) Sintering (*Greek* ***sintar*** = "ash") is another method used for the production of structural ceramics, including orthopedic implants, dental crowns, pacemaker electrodes, high temperature combustion feed-throughs, and (pictured) porous filters to remove particulates from high temperature liquid or gaseous streams.
Explain how the sintering process can be controlled to generate this product. In your answer, pay attention to ceramic powder sizing, compaction, and firing (temperature and time) during synthesis.

(10 points) *Answer*: **As shown in the illustration, the final sintered product is intentionally porous. To achieve and control such a structure the following steps should be taken.**
1. *Large particle size* Beginning with a large uniform particle size will cause relatively large pores because the size of the pores scales with the initial particle size, as long as they are all the SAME size. A range of particle sizes could cause the smaller particles to fill the holes between larger particles, decreasing porosity. The initial particle size offers the most control over the final pore size.
2. *No compaction* By not compacting the particles, the pores will remain open longer throughout the firing process.
2. *Low sintering temperature* The lower the temperature, the less diffusional bonding will occur, generating necks between sintered particles as needed for strength, but preserving adequate pore volume. It is also easier to maintain a uniform temperature over the entire part during sintering when the temperature is lower; at high temperature, local hot spots can occur, resulting in non-uniform sintering behavior (more sintering on the surfaces, less in the interior, for example).
3. *Short sintering time* This also diminishes the chances for pore closure, but must be carefully controlled so that there is sufficient time to sinter the powders into a monolithic part with sufficient mechanical strength to survive in-service pressures during fluid flow.

Worksheet

Problem 5(a)