Study Guide for Phase Transitions in Materials Science

Advanced Materials Engineering

December 1, 2025

Quiz: Short-Answer Questions

1. Distinguish between *displacive* and *reconstructive* phase transformations based on atomic motion and final composition.
2. What is the *thermodynamic basis* for the design of *high-entropy alloys*, and how does it promote the formation of a single phase?
3. Describe the *eutectic reaction* using the lead-tin ($\mathrm{Pb} - \mathrm{Sn}$) system as an example, specifying the phases involved and the conditions under which it occurs.
4. Explain the phenomenon of *uphill diffusion*. What specific feature of a solution's free energy curve is required for it to be possible?
5. Why is *heterogeneous nucleation* almost always favoured over *homogeneous nucleation* in practical scenarios?
6. Define *constitutional supercooling* and explain how it leads to the formation of *dendritic microstructures* during the solidification of alloys.
7. Compare the formation mechanisms and resulting structures of *pearlite* and *martensite* in steels.
8. What physical property is measured by *differential scanning calorimetry (DSC)*, and what does an *exothermic peak* on a DSC trace signify?
9. What is the physical origin of *piezoelectricity* in the tetragonal form of barium titanate?
10. Explain how the *common tangent construction* on a Gibbs free energy diagram is used to determine the equilibrium compositions of two phases in a binary alloy.

Answer Key

1. A *displacive transformation* involves a coordinated, **diffusionless** motion of atoms that homogeneously deforms the parent crystal into the product, resulting in a macroscopic shape change but **no change in composition**. In contrast, a *reconstructive transformation* is a **diffusion-controlled** process where atomic bonds are

broken and atoms rearrange into a new pattern, often leading to a **redistribution of solute** between the phases.

2. High-entropy alloys are designed by maximising the **configurational entropy** (ΔS_{config}) of mixing, achieved by combining five or more elements in roughly equiatomic proportions. This creates a large, negative entropy contribution ($-T\Delta S$) to the Gibbs free energy ($G = H - TS$), which **stabilises a single solid-solution phase** and reduces the thermodynamic tendency to form ordered intermetallic compounds.

3. A *eutectic reaction* is an invariant reaction where a single liquid phase transforms into two solid phases upon cooling ($\text{L} \rightarrow \alpha + \beta$). In the $\text{Pb} - \text{Sn}$ system, this occurs at a fixed temperature of 183°C and a composition of 61.9 wt% Sn, where the liquid transforms into a mixture of a lead-rich solid solution (α) and a tin-rich solid solution (β).

4. *Uphill diffusion* is the process where atoms migrate from a region of lower concentration to a region of higher concentration, moving **against the concentration gradient** but **down a chemical potential gradient**. It can occur in solutions with a positive enthalpy of mixing, which produces a free energy curve with a region of **negative curvature** ($\frac{\partial^2 G}{\partial x^2} < 0$) at certain temperatures and compositions.

5. *Heterogeneous nucleation* is favoured because it occurs on pre-existing defects like grain boundaries, surfaces, or foreign particles. The process **eliminates a portion of the high-energy interface**, which significantly lowers the **activation energy barrier** (G^*) for nucleation compared to forming a nucleus within a defect-free parent phase (*homogeneous nucleation*).

6. *Constitutional supercooling* is a condition in a solidifying alloy where solute partitioning enriches the liquid ahead of the solid-liquid interface, **depressing its liquidus temperature**. If the actual temperature gradient in the liquid is less steep than the liquidus temperature gradient, a supercooled zone forms, making a planar interface unstable and promoting the formation of **dendritic growth**.

7. *Pearlite* is a lamellar mixture of ferrite (α) and cementite (Fe_3C) that forms from austenite (γ) via a **reconstructive, diffusion-controlled eutectoid reaction**. *Martensite* is a single, metastable, body-centred tetragonal phase formed by a **displacive, diffusionless transformation** when austenite is cooled rapidly; it inherits the full carbon content of the parent austenite, making it extremely hard.

8. *Differential scanning calorimetry (DSC)* measures the **enthalpy change** (ΔH) of a material by monitoring the difference in heat flow required to increase the temperature of a sample and a reference. An **exothermic peak** represents a process where the sample **releases heat** ($\Delta H < 0$), such as the crystallisation of an amorphous metallic glass into a more ordered, lower-energy crystalline state.

9. Piezoelectricity in tetragonal barium titanate arises from its **asymmetric crystal structure** (non-centrosymmetric), where the titanium (Ti) and some oxygen (O) ions are slightly displaced from their symmetrical positions. This displacement creates a permanent electric dipole in the unit cell, and mechanical deformation shifts the centre of mass of the ions, generating a voltage.

10. The *common tangent construction* is a graphical method based on the principle that, at equilibrium, the **chemical potential (μ)** of each component must be equal in both coexisting phases. A single tangent line drawn to simultaneously touch the Gibbs free energy curves of two phases identifies the compositions at the points of tangency as the equilibrium compositions of those two phases.

Essay Questions

1. **Displacive vs. Reconstructive Transformations:** Compare and contrast the mechanisms of displacive and reconstructive transformations. Your answer should address the role of atomic diffusion, the resulting change in macroscopic shape, the thermodynamic driving forces and barriers (including strain energy), and the typical microstructures produced by each mechanism.

2. **Phase Diagram Construction from Free Energy:** Explain how a binary equilibrium phase diagram can be constructed from the Gibbs free energy curves (G vs. composition x) of the constituent phases at various temperatures. Discuss the concepts of chemical potential, the common tangent construction for defining two-phase regions, and the lever rule for determining phase proportions.

3. **Diffusion in Solids:** Describe the phenomenon of diffusion in solid materials. Discuss Fick's first and second laws as phenomenological descriptions of mass transport, and then explain the underlying atomic mechanisms, including vacancy-based and interstitial diffusion. How do crystal defects like grain boundaries affect the overall diffusion rate at different temperatures?

4. **Nucleation Theory:** Elaborate on the theory of nucleation as the initial step of a phase transformation. Differentiate clearly between homogeneous and heterogeneous nucleation, explaining the key terms: activation energy barrier (G^*), critical nucleus size (r^*), and driving force. Use the example of solidification to explain how nucleating agents (*inoculants*) can be used to control microstructure.

5. **Austenite Transformations in Steel:** Using the iron-carbon system as a basis, describe the transformation of austenite upon cooling. Explain the formation of two distinct microstructures: pearlite and martensite. Detail the conditions under which each forms, their crystal structures and compositions, and why martensite is typically much harder than pearlite. Furthermore, explain the process of *tempering* martensite and the concept of *secondary hardening.*

Glossary of Key Terms

- **Activation Energy Barrier (G^*):** The energy barrier that must be overcome for a phase transformation to nucleate or for an atom to diffuse. It is a critical factor in determining the rate of thermally activated processes.

- **Age Hardening:** The increase in hardness of an alloy over time, often at or near ambient temperature, due to the formation of fine precipitates from a supersaturated solid solution.

- **Allotrope:** Different crystal structures of the same pure element that are stable under different conditions of temperature and pressure. Iron, for example, has α, γ, δ, and ϵ allotropes.
- **Austenite (γ):** The high-temperature, face-centred cubic (FCC) phase of iron and iron-carbon alloys.
- **Bragg Law:** The equation $n\lambda = 2d \sin\theta$ that specifies the conditions for constructive interference of X-rays scattered by crystal planes.
- **Cementite (Fe_3C):** A hard, brittle iron carbide compound with an orthorhombic crystal structure, found in steels and cast irons.
- **Chemical Potential (μ):** The partial molar free energy of a component in a solution. At equilibrium, the chemical potential of each component is uniform across all coexisting phases.
- **Chill Zone:** A region of fine, equiaxed grains formed at the surface of a casting due to rapid nucleation and solidification when hot liquid contacts a cold mould wall.
- **Configurational Entropy:** The component of entropy related to the number of distinguishable ways atoms can be arranged on a crystal lattice. It is a driving force for the mixing of elements in solutions.
- **Constitutional Supercooling:** A condition where solute partitioning during alloy solidification creates a region of liquid ahead of the interface that is below its local liquidus temperature, leading to an unstable, dendritic growth front.
- **Coring:** Compositional gradients within individual grains that result from non-equilibrium solidification, where slow diffusion in the solid prevents homogenisation.
- **Critical Nucleus Size (r^*):** The minimum radius an embryonic particle of a new phase must attain to be thermodynamically stable and grow spontaneously. Nuclei smaller than r^* will redissolve.
- **Differential Scanning Calorimetry (DSC):** A thermal analysis technique that measures the difference in heat flow between a sample and a reference as a function of temperature, used to determine enthalpy changes associated with phase transitions.
- **Diffusion:** The net movement of atoms, ions, or other species driven by a chemical potential gradient, leading to mass transport. In solids, it occurs via mechanisms like vacancy or interstitial jumps.
- **Displacive Transformation:** A diffusionless phase transformation where the new crystal structure is formed by a coordinated, homogeneous deformation of the parent lattice, resulting in a macroscopic shape change. Martensite formation is a key example.
- **Enthalpy (H):** A thermodynamic property of a system, defined as $H = U + PV$. The change in enthalpy (ΔH) represents the heat absorbed or released in a process at constant pressure.

- **Entropy (S):** A measure of the disorder or randomness of a system. The second law of thermodynamics states that the entropy of an isolated system tends to increase over time.

- **Eutectic Reaction:** An isothermal, reversible reaction in which a liquid phase solidifies to form two different solid phases simultaneously upon cooling ($\mathrm{L} \to \alpha+\beta$).

- **Eutectoid Reaction:** An isothermal, reversible reaction in which a solid phase transforms into two different solid phases simultaneously upon cooling ($\gamma \to \alpha+\beta$). The formation of pearlite in steel is an example.

- **Ferrite (α):** The body-centred cubic (BCC) phase of iron, which is stable at low temperatures.

- **Ferroelectric:** A property of certain materials that have a spontaneous electric polarisation that can be reversed by an external electric field. Tetragonal $BaTiO_3$ is ferroelectric.

- **Fick's First Law:** An equation describing steady-state diffusion, stating that the diffusion flux (J) is proportional to the concentration gradient ($\partial C/\partial z$).

- **Fick's Second Law:** A partial differential equation describing how concentration changes with time during non-steady-state diffusion ($\partial C/\partial t = D\partial^2 C/\partial z^2$).

- **Free Energy (G):** A thermodynamic potential, defined as $G = H - TS$, that measures the "useful" work obtainable from a system at constant temperature and pressure. A process is spontaneous if it leads to a decrease in free energy ($\Delta G < 0$).

- **Glass Transition Temperature (T_g):** The temperature at which an amorphous solid (glass) transitions from a hard, "frozen" state to a more relaxed, rubbery state with increased atomic mobility.

- **Heterogeneous Nucleation:** Nucleation of a new phase that occurs at preferential sites such as grain boundaries, dislocations, impurities, or surfaces, which lower the activation energy barrier.

- **High-Entropy Alloys:** Alloys composed of five or more principal elements in high concentrations (often equiatomic), designed to maximise configurational entropy to favour the formation of simple solid solutions over complex intermetallic phases.

- **Homogeneous Nucleation:** Nucleation of a new phase occurring uniformly throughout the parent phase without the influence of any pre-existing defects or interfaces.

- **Ideal Solution:** A solution where the enthalpy of mixing (ΔH_mix) is zero, meaning there is no energetic preference for like or unlike atomic neighbours.

- **Inoculant:** Particles deliberately added to a molten metal to act as heterogeneous nucleation sites, promoting the formation of a fine, equiaxed grain structure upon solidification.

- **Kirkendall Effect:** The movement of the interface between two metals in a diffusion couple, caused by unequal diffusion rates of the atomic species. It provides evidence for the vacancy mechanism of diffusion.

- **Lever Rule:** A mathematical rule used on a binary phase diagram to calculate the mass fractions of the two phases present in a two-phase region at equilibrium.
- **Liquid Crystal:** A state of matter that has properties between those of a conventional liquid and a solid crystal, characterised by molecules that can flow but maintain some degree of long-range orientational order.
- **Liquidus:** A line on a phase diagram representing the temperatures above which a substance is completely liquid.
- **Martensite:** A hard, metastable phase formed by a displacive (diffusionless) transformation, typically upon rapid cooling. In steel, it is a body-centred tetragonal structure supersaturated with carbon.
- **Martensite-Start Temperature (M_s):** The temperature at which the martensitic transformation begins upon cooling.
- **Metallic Glass:** An amorphous metallic solid with a disordered, non-crystalline atomic structure, typically formed by very rapid cooling from the liquid state to prevent crystallisation.
- **Metastable Phase:** A phase that is not in its lowest possible energy state but is kinetically trapped, requiring an activation energy to transform to a more stable phase. Martensite is a metastable phase.
- **Pearlite:** A two-phase, lamellar microstructure of alternating layers of ferrite (α) and cementite (Fe_3C) that forms in steels by the eutectoid decomposition of austenite.
- **Phase:** A homogeneous and physically distinct region of a system, characterised by uniform physical and chemical properties.
- **Piezoelectricity:** The ability of certain crystalline materials to generate an electric voltage in response to applied mechanical stress.
- **Reconstructive Transformation:** A phase transformation that requires the breaking of atomic bonds and the rearrangement of atoms via diffusion to form the new crystal structure.
- **Regular Solution:** A solution model that assumes a non-zero enthalpy of mixing but maintains the ideal entropy of mixing.
- **Secondary Hardening:** An increase in the hardness of a steel during tempering at high temperatures (e.g., $> 500°C$), caused by the precipitation of fine, stable alloy carbides (e.g., Mo_2C, VC).
- **Solidus:** A line on a phase diagram representing the temperatures below which a substance is completely solid.
- **Tempering:** A heat treatment process applied to hardened steel (martensite) to decrease hardness and increase toughness by allowing the precipitation of carbides and recovery of the microstructure.

- **Tie-Line:** A horizontal line drawn across a two-phase region of a binary phase diagram that connects the compositions of the two phases in equilibrium at that temperature.

- **Time-Temperature-Transformation (TTT) Diagram:** An isothermal transformation diagram that plots temperature versus the logarithm of time, showing the kinetics of phase transformations from a parent phase (e.g., austenite) held at a constant temperature.

- **X-ray Diffraction:** A characterisation technique used to determine the atomic and molecular structure of a crystal, in which a beam of X-rays strikes a crystal and diffracts into many specific directions according to Bragg's law.