Introduction to Phase Transformations

Course: Phase Transformations
Level: 3rd Stage | Semester: 5
Department of Materials Engineering
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Learning Objectives

By the end of this lecture, students will be able to:

- Define fundamental terms: phase, system, components.
- Explain the concept of phase diagrams and phase transformations.
- Understand the role of thermodynamics in phase stability.
- Apply the Hall–Petch equation to analyze grain size effects.
- Interpret unary phase diagrams.
- Calculate atomic packing factor (APF).

Course References and Sources

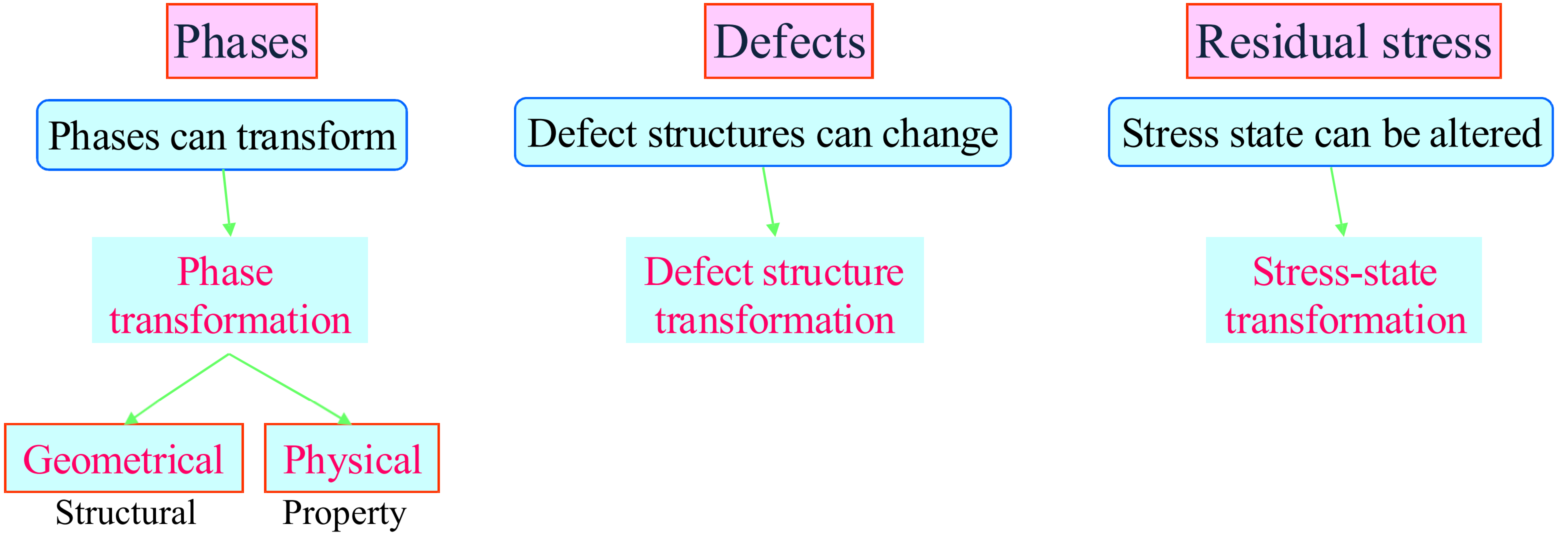
- Callister, William D., and David G. Rethwisch. Materials Science and Engineering: An Introduction. 9th Ed., Wiley, 2018.
- Askeland, Donald R., et al. The Science and Engineering of Materials. 6th Ed., Thomson Learning, 2010.
- Porter, David A., and Kenneth E. Easterling. Phase Transformations in Metals and Alloys. CRC Press, 2009.
- Supplemented by lecture materials from Osaka University (Japan), University of Sheffield (UK), and Delhi University (India).

Key Definitions

- System: A defined part of the universe under study; e.g., an alloy that can exist as a mixture of phases.
- Phase: A physically and chemically uniform region that is mechanically separable from others (e.g., solid, liquid, gas).
- Components: The elements or compounds that make up a system.

Transformations in Materials

In materials, several transformations occur – not just phases, but also defects and stresses. Let's see how…



Phases

Phases can transform

Phase transformation

Geometrical

Structural

Physical

Property

Defects

Defect structures can change

Defect structure transformation

Residual stress

Stress state can be altered

Stress-state transformation

Phases → Microstructure

Phases Transformations → Microstructural Transformations

Transformations in Materials

- **Phases can transform → Phase transformation**

Example: Austenite (γ, FCC) transforms to ferrite (α, BCC) in steels during slow cooling.
Example: Liquid → Solid in solidification (e.g., casting of aluminum).

- **Geometrical (structural change, e.g., FCC → BCC)**

Example: Austenite (FCC) → Martensite (BCT) via shear during quenching.
Example: Zirconia transformation: tetragonal → monoclinic, used in transformation-toughened ceramics.

- **Physical (property change, e.g., magnetic, electrical)**

Example: Iron: BCC α-Fe is ferromagnetic, but FCC γ-Fe is non-magnetic.
Example: VO_2 (vanadium dioxide) exhibits a semiconductor-to-metal transition near 68°C.

Transformations in Materials

- **Defects can transform → Defect structure transformation**

Example: Recovery in cold-worked metals reduces dislocation density (e.g., annealed copper).
Example: Climb of edge dislocations at high temperatures.

- **Residual stress can change → Stress-state transformation**

Example: Stress relief annealing in welded steel structures reduces internal stresses.
Example: Shot peening introduces compressive residual stresses to improve fatigue life.

- **Phases and microstructure are linked →**

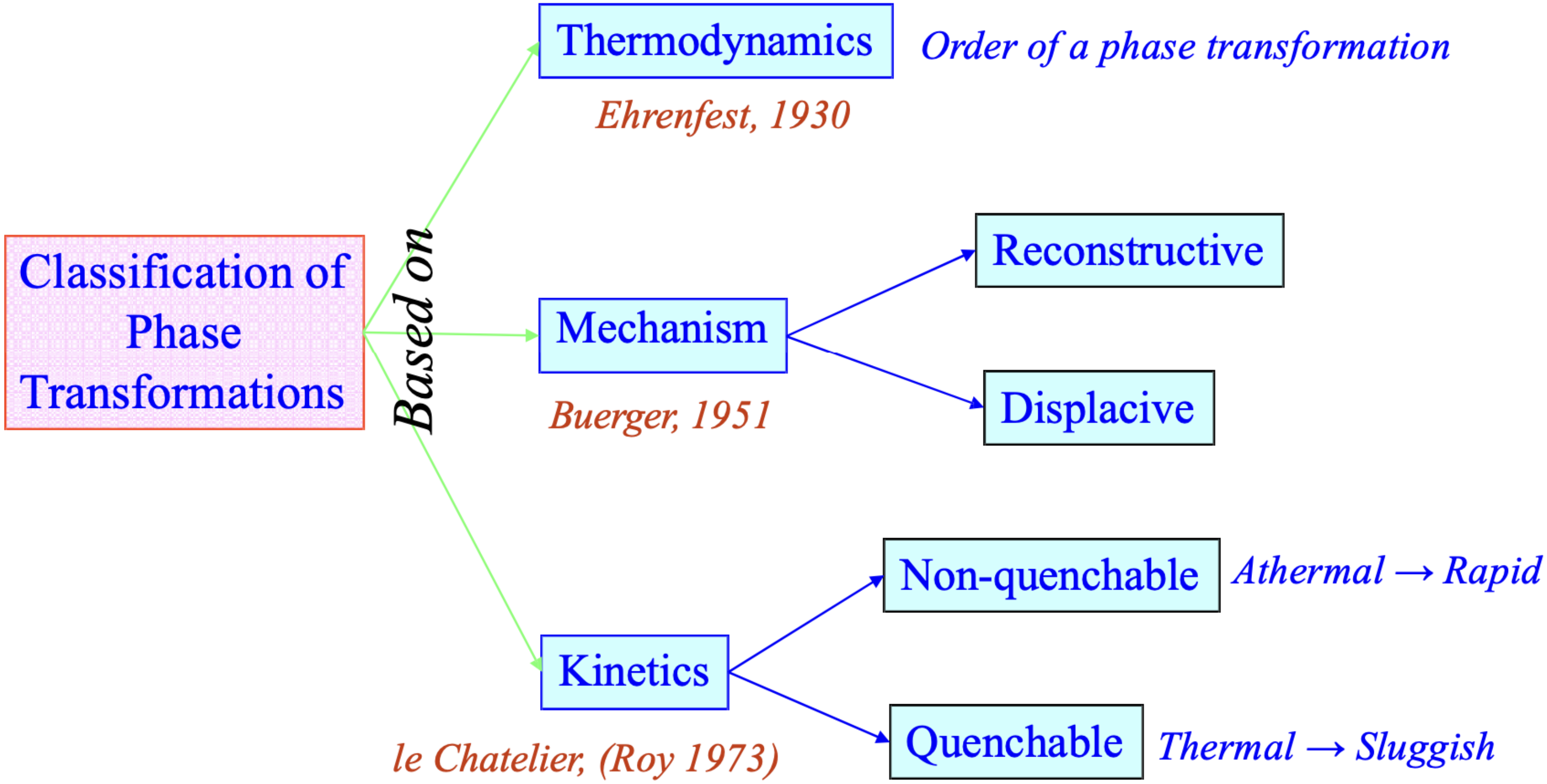
Example: In dual-phase steels, phase balance (ferrite + martensite) defines strength and ductility.

- **Phase transformations drive microstructural transformations**

Example: Precipitation of Mg_2Si in aluminum alloys during aging (T6 treatment) refines microstructure and increases strength.

Classification of Transformations

Now that we understand what can transform in a material, let's classify how these transformations occur based on scientific principles.



Classification of Phase Transformations

Based on

Thermodynamics

Order of a phase transformation

Ehrenfest, 1930

Mechanism

Reconstructive

Displacive

Buerger, 1951

Kinetics

Non-quenchable

Athermal → Rapid

Quenchable

Thermal → Sluggish

le Chatelier, (Roy 1973)

Classification of Transformations

1. **Thermodynamics (Ehrenfest, 1930)**
2. Depends on the **order of transformation** (1st order vs. 2nd order).
3. **Mechanism (Buerger, 1951)**
4. **Reconstructive** → bonds are broken and re-formed (slow, high activation energy).
5. **Displacive** → atoms shift cooperatively without breaking bonds (fast, low activation energy, e.g., martensitic transformation).
6. **Kinetics (Le Chatelier, Roy 1973)**
7. **Quenchable** → depends on cooling rate, sluggish (thermal).
8. **Non-quenchable** → athermal, occurs instantly when conditions are met (e.g., martensite).

Classification of Transformations

- The thermodynamic characteristics associated with the phase transformations can be used to classify transformations; in this classification methodology, if the n^{th} derivative of free energy (G) with respect to temperature (T) and pressure (P) is discontinuous, it is defined as the n^{th} order transformation.
- As shown in the Figure, in transformations such as melting, the first derivative has the discontinuity; hence, melting is a first order transformation; on the other hand, in some of the order/disorder transfor- mations, it is the second derivative which is discontinuous, making it the second order transformation.

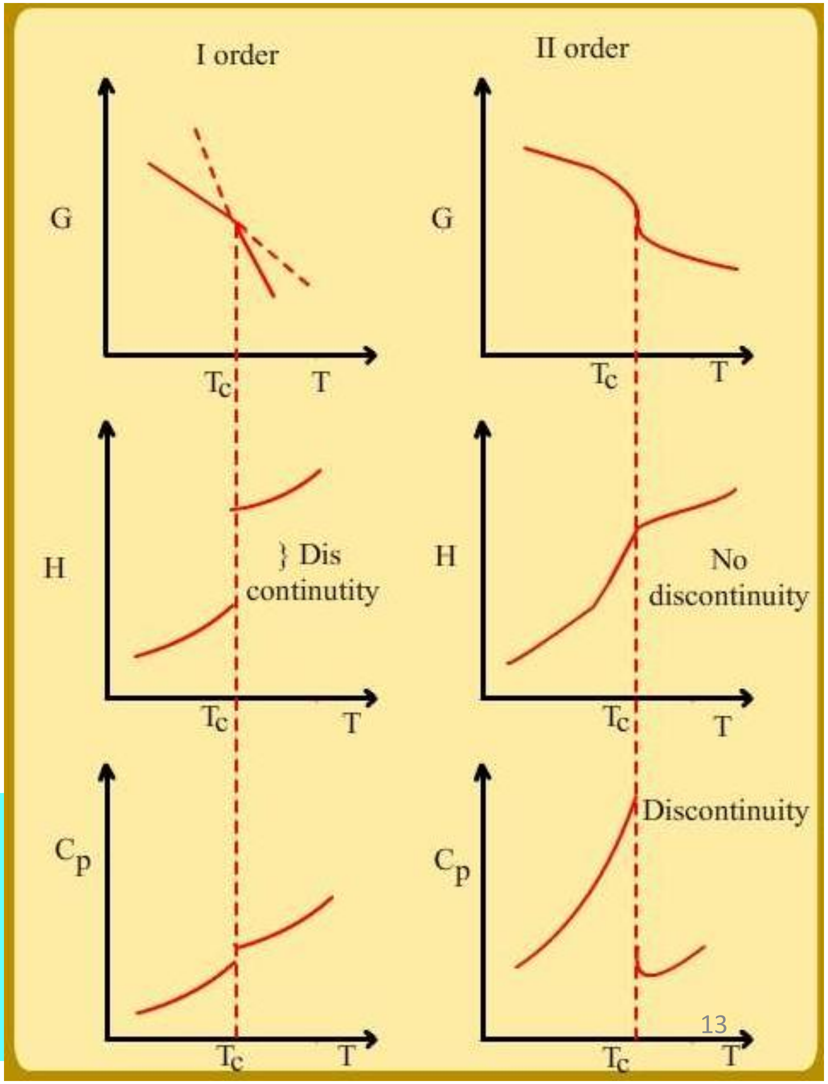


Figure: The thermodynamic classification of transformations: the first derivative of the free energy 'G' with respect to temperature 'T' , that is the enthalpy 'H' is discontinuous at the transformation temperature T_c as shown in the first column; the second derivative of the free energy with respective to temperature C_p is discontinuous while 'H' is not in the second column, making the order of transformation second.

- **Classification principle**:

If the **nth derivative** of Gibbs free energy (G) with respect to temperature (T) or pressure (P) is **discontinuous**, the transformation is called an **nth order transformation**.

- **First-order transformation**:

-First derivative (enthalpy H or volume V) shows a discontinuity.

-Example: **melting, vaporization, solidification**.

-Latent heat is involved.

- **Second-order transformation**:

-First derivative is continuous, but the **second derivative** (like heat capacity, Cp, or thermal expansion coefficient) is discontinuous.

-Example: **order–disorder transformation in alloys, Curie transition in ferromagnetic materials**.

-No latent heat.

Stability and Equilibrium

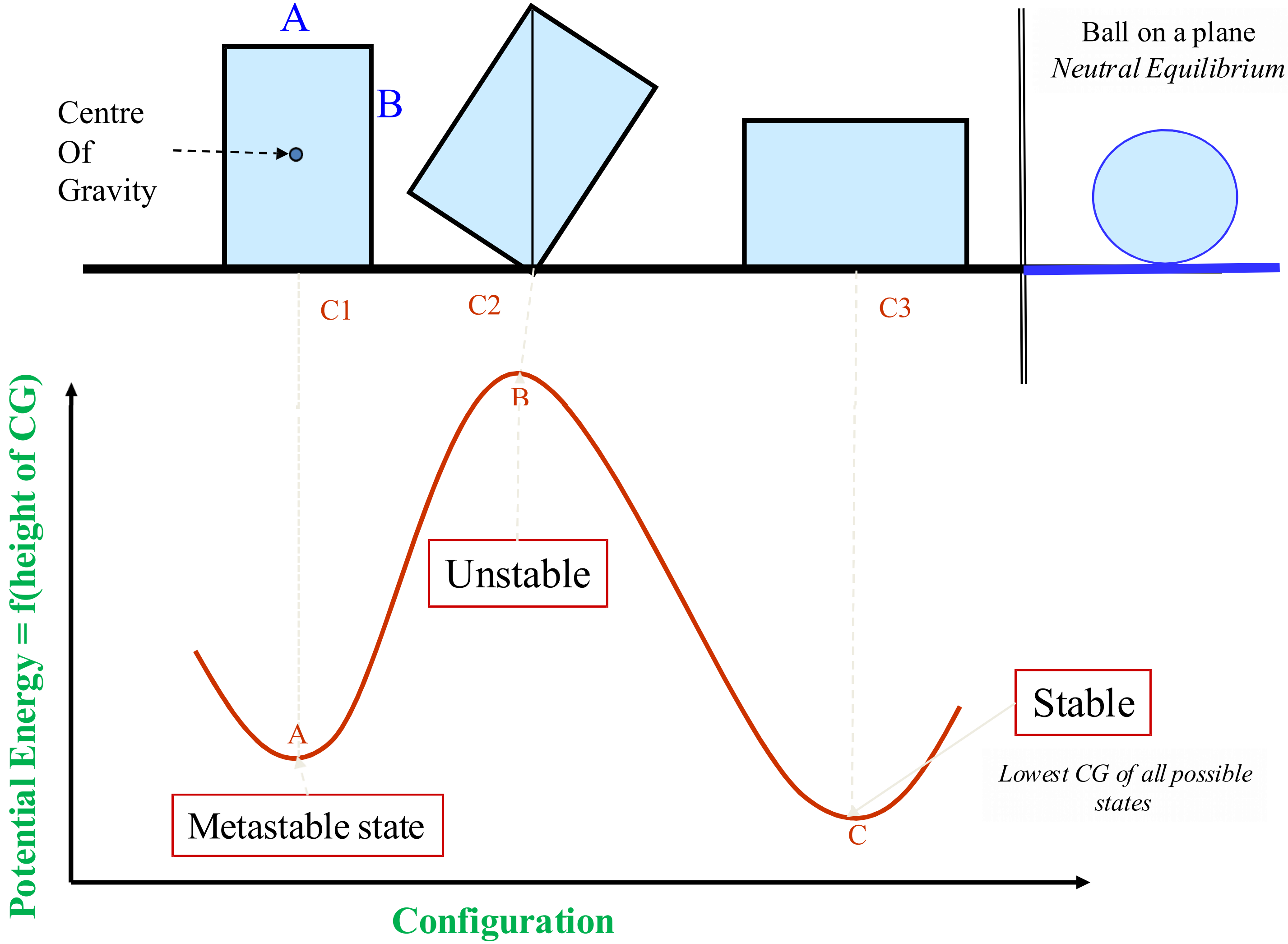
To understand why transformations occur or stop, we must understand equilibrium and stability — the driving forces behind transformations

- Equilibrium refers to a state → wherein there is a balance of 'forces'* (as we shall see equilibrium points have zero slope in a energy-parameter plot).
- Stability relates to perturbations (usually small perturbations** about an equilibrium state) (as we shall see stable relates to the curvature at the equilibrium points).
- Let us start with a simple mechanical system → a rectangular block *(Figure in next slide)* (under an uniform gravitational potential).
- The potential energy (PE) of the system depends on the height of the centre of gravity (CG).
- The system has higher PE when it rests on face-A, than when it rests on face-B.
- The PE of the system increases when one tilts it from C1 → C2 configuration.
- In configurations such as C1,C2 & C3 the system will be in equilibrium (i.e. will not change its configuration if there are no perturbations).
- In configuration C2 the system has the highest energy (point B) and any small perturbations to the system will take it downhill in energy → Unstable state.
- Configuration C3 has the lowest energy (point C) and the system will return to this state if there are small perturbations → the Stable state.

* *Force has been used here in a generalized sense (as an agent which can cause changes)*

** Perturbation is usually a small 'force/displacement' imposed in a short span of time.

Mechanical Equilibrium of a Rectangular Block



Centre Of Gravity

Ball on a plane
Neutral Equilibrium

Unstable

Metastable state

Stable

Lowest CG of all possible states

Stability and Equilibrium

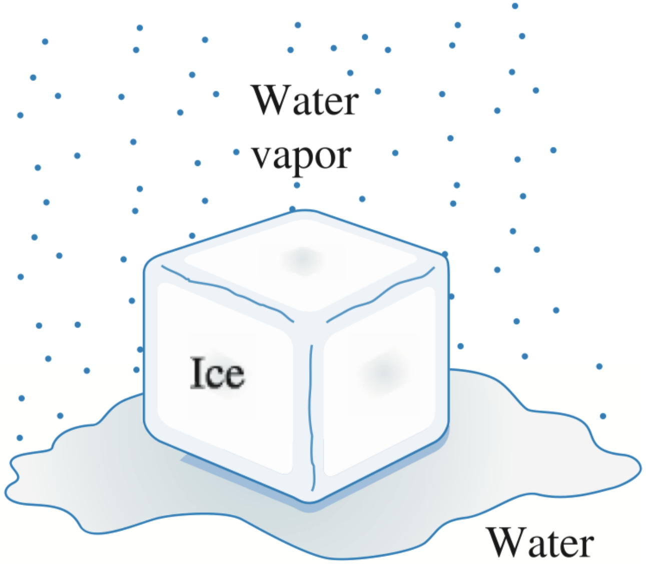
- ❑ Configuration C1 also lies in an 'energy well' (like point C) and small perturbations will tend to bring back the system to state C1. However this state is not the 'global energy minimum and hence is called a Metastable state.
- ❑ Additionally, one can visualize a state of neutral equilibrium, like a ball on a plane (wherein the system is in a constant energy state with respect to configurations).
- ❑ Points to be noted:
  - ➢ A system can exist in many states *(as seen even for a simple mechanical system: block on a plane)*
  - ➢ These states could be stable, metastable or unstable
  - ➢ Using the relevant (thermodynamic) potential the stability of the system can be characterized (In the case of the block it is the *potential energy*, measured by the height of the CG for the case of the block on the plane)
  - ➢ System will 'evolve' towards the stable state provided 'sufficient activation' is provided (in the current example the system will go from C1 to C3 by 'sufficient jolting/shaking' of the plane)

Three kinds of equilibrium (with respect to energy)

- ❑ Global minimum → STABLE STATE
- ❑ Local minimum → METASTABLE STATE
- ❑ Maximum → UNSTABLE STATE
- ❑ Constant energy → Neutral State/Equilibrium

Phases of Water (H_2O): An Example of Coexisting Phases

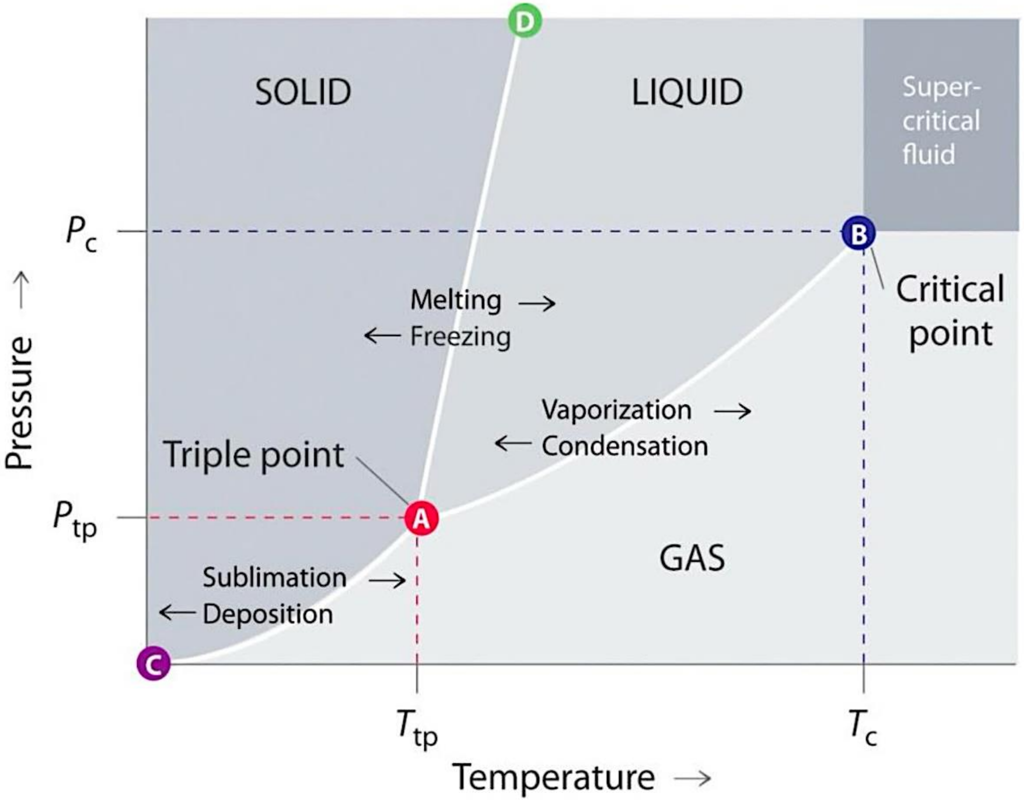
A block of ice in a vacuum chamber can simultaneously exist as solid, liquid, and vapor. Each phase is distinct in atomic structure and properties. This illustrates the concept of coexisting phases despite identical chemical composition.



Three phases of H_2O in vacuum chamber.

Phase Diagrams and Stability

- A Pressure–Temperature (P-T) diagram shows the regions of phase stability.
- Phase transformations occur when the system crosses phase boundaries (e.g., melting, vaporization).
- Transformations are driven by thermodynamic instability.

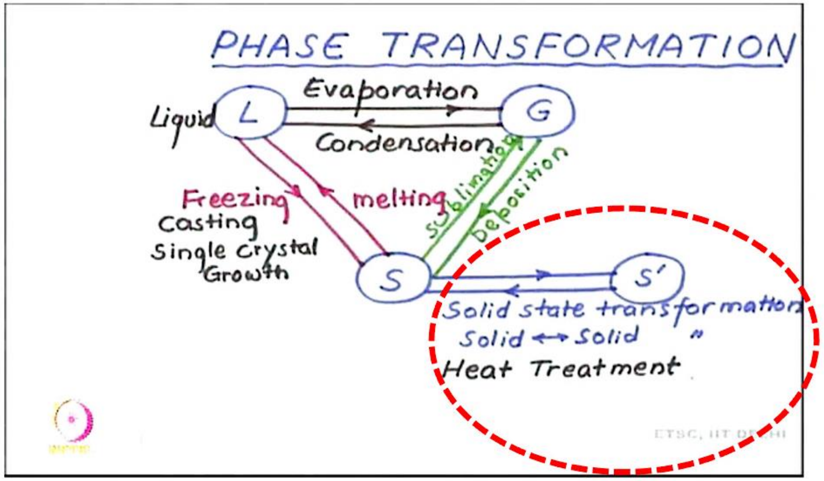


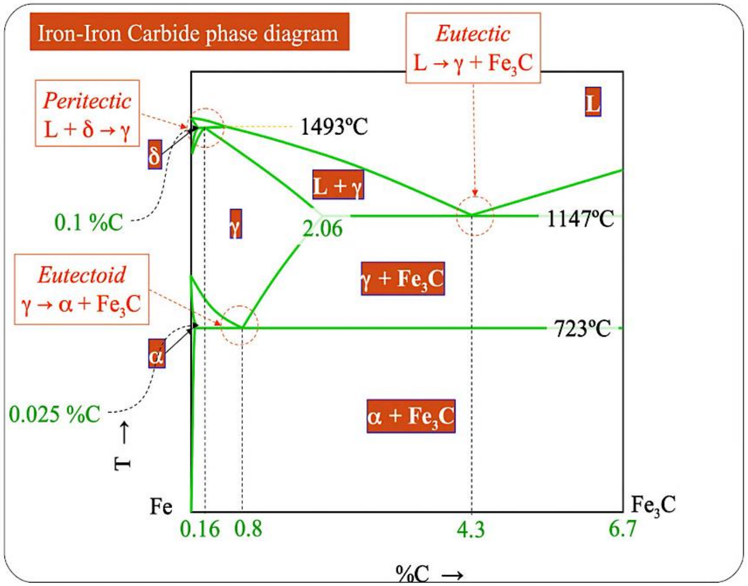
Pressure–Temperature (P–T) phase diagram of water (H_2O), showing phase stability regions and critical transitions such as sublimation, melting, and vaporization.

Why STUDY Phase Transformation?

- Tensile strength of iron–carbon alloy of eutectoid composition can be varied between 700 MPa and 2000 MPa, depending on the heat treatment employed.
- This shows that the desirable mechanical properties of a material can be obtained as a result of phase transformations using heat treatment processes.
- The time and temperature dependencies of phase transformations are represented on phase diagrams.
- It is important to know how to use these phase diagrams in order to design a heat treatment for an alloy to obtain the desired room-temperature mechanical properties.

Key Phase Transformations in Steels





Schematic illustration of general phase transformations (left), highlighting solid-to-solid transformations as the foundation of heat treatment processes. This is linked to the Iron–Iron Carbide (Fe–Fe_3C) phase diagram (right), which shows critical invariant reactions such as peritectic ($L + \delta \rightarrow \gamma$), eutectic ($L \rightarrow \gamma + Fe_3C$), and eutectoid ($\gamma \rightarrow \alpha + Fe_3C$) transformations central to the microstructural evolution of steels.

Example: Hall-Petch Equation and Grain Refinement

- This equation relates grain size to yield strength:
- $\sigma_\gamma = \sigma_0 + k_\gamma \cdot d^{-1/2}$
- Where:
- σ_γ = Yield strength
- σ_0, k_γ = Material-specific constants
- d = Average grain diameter
- Smaller grains → higher strength.

Example: Hall-Petch Equation and Grain Refinement

- Increasing the rate kinetics of phase transformation leads to finer microstructures.
- According to the **Hall–Petch equation**, a decrease in grain size increases the material's yield strength:
- $\sigma_\gamma = \sigma_0 + k_\gamma \cdot d^{-1/2}$

Where:

σ_γ = Yield strength

σ_0, k_γ = Material-specific constants

d = Average grain diameter

Smaller grains → higher strength.

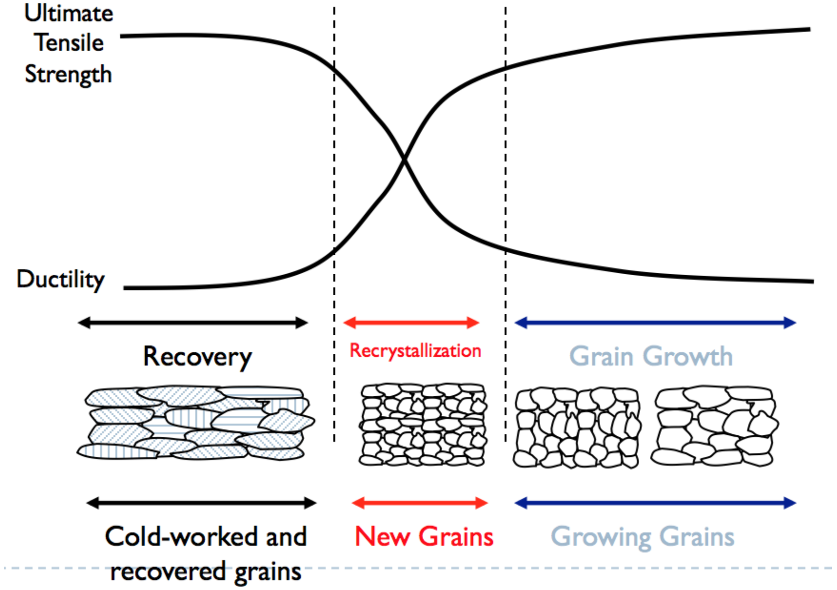


Diagram shows how strength increases and ductility decreases with grain refinement and recovery processes

Gibbs Phase Rule

A criterion for the number of phases that will coexist within a system at equilibrium

Number of phases present

$$P + F = C + N$$

Number of non-compositional variables (Temperature & Pressure)

Degree of freedom (externally controllable parameters: i.e. T, P, and C)

Number of components

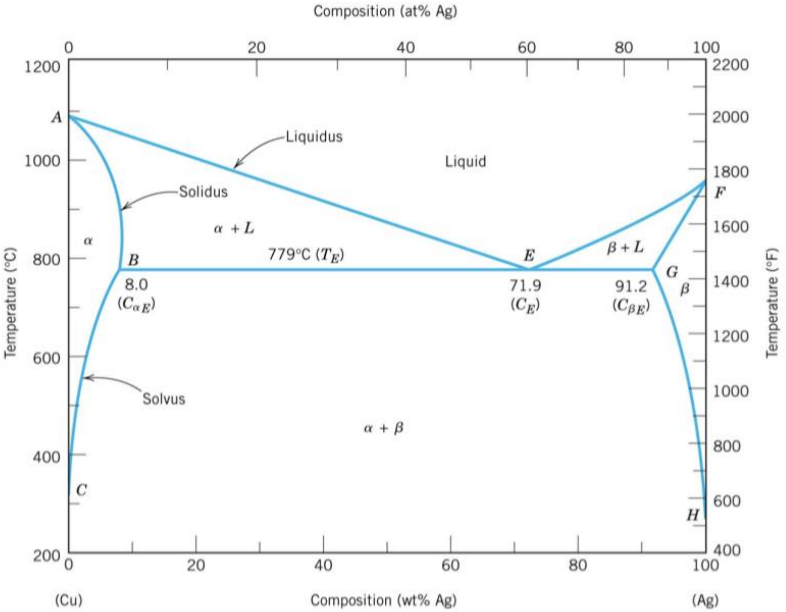


FIGURE 9.6 The copper–silver phase diagram. [Adapted from *Binary Alloy Phase Diagrams*, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

e.g. Cu-Ag phase diagram

Cu and Ag are the only components
-> $C = 2$

Temperature is the only non-compositional variable here (i.e. fixed pressure).
-> $N = 1$ (but in general $N = 2$)

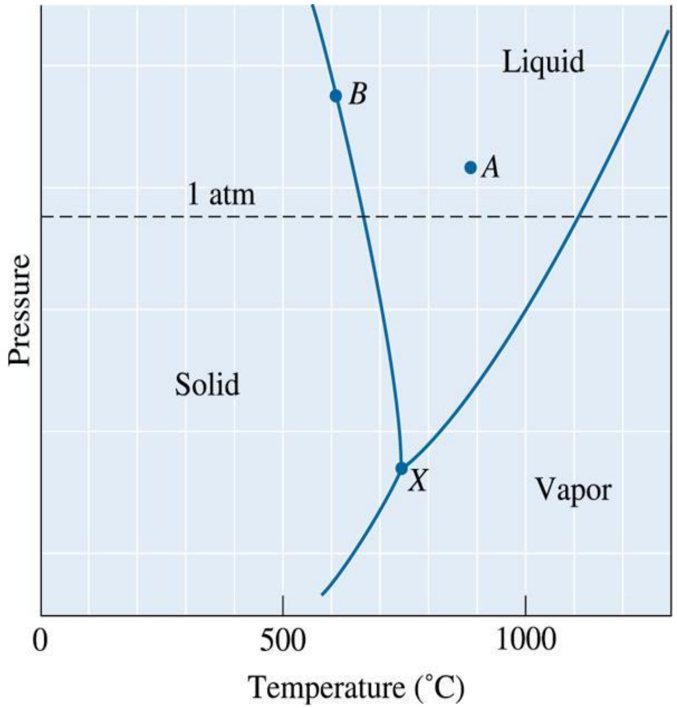
When 2 phases are present
-> $P = 2$ which leads to $\boldsymbol{F} = C+N-P = 2+1-2 = \mathbf{1}$

When only 1 phase is present.
-> $P = 1$ which leads to $\boldsymbol{F} = \mathbf{2}$

What does this mean? Why should you care?

Gibbs Phase Rule

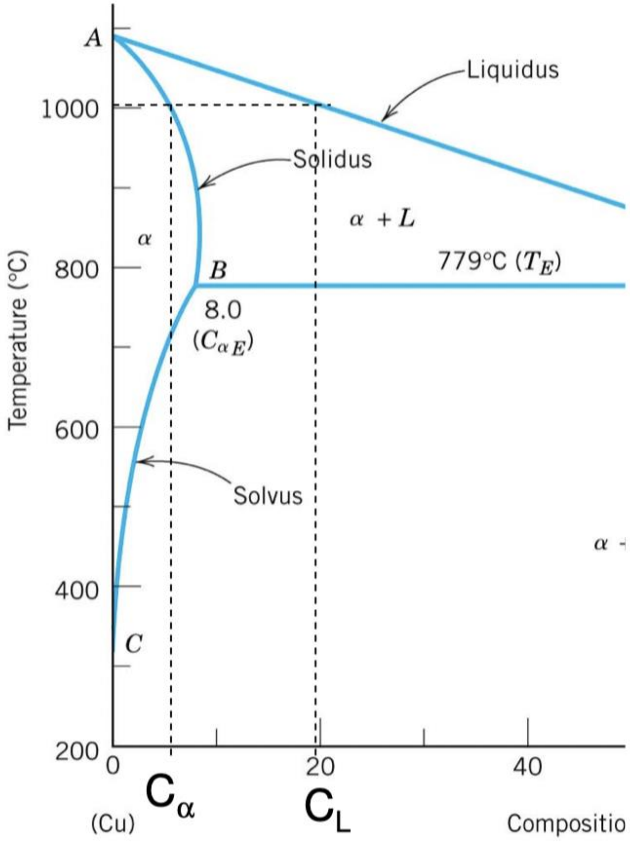
- Gibbs phase rule can be defined as the relationship between the number of components and the number of phases for a given system and the conditions that may be allowed to change. (e.g., temperature, pressure, etc.).
- P-T diagram - A diagram describing thermodynamic stability of phases under different temperature and pressure conditions (same as a unary phase diagram).



Schematic unary phase diagram for magnesium, showing the melting and boiling temperatures at one atmosphere pressure.

Gibbs Phase Rule

In the previous example of Cu-Ag phase diagram, when $F = 1$, only one parameter (T or C) needs to be specified to completely define the system.



→ e.g. (for α+L region)

If T is specified to be 1000°C, compositions are already determined (C_α and C_L).

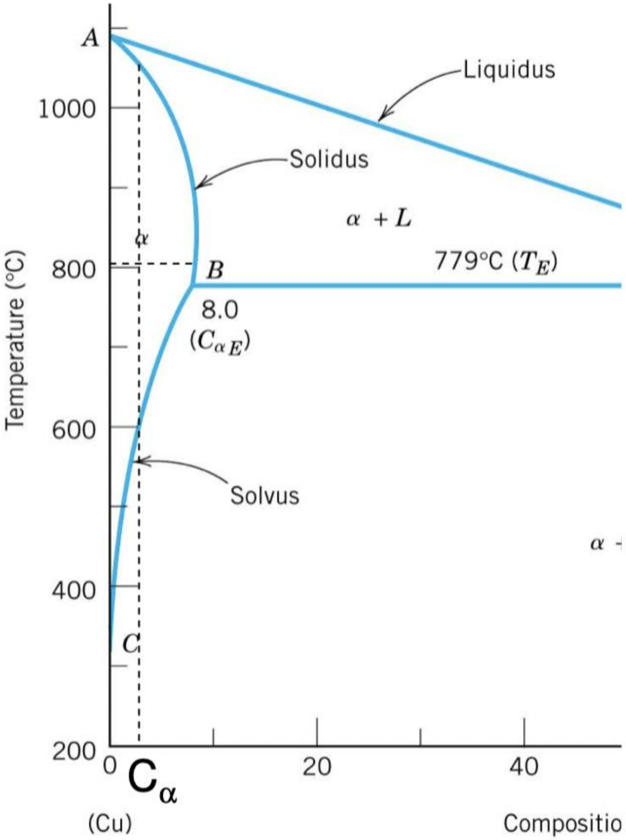
Or

If composition of the a phase is specified to be C_α then both T and C_L are already determined.

The nature of the phases is important, not the relative phase amounts.

Gibbs Phase Rule

When *F* = 2, both T and C have to be specified to completely define the state of the system.



→ e.g.(for α region)

If T is specified to be 800ºC, C_α can be any where between 0 to ~8 wt% Ag)

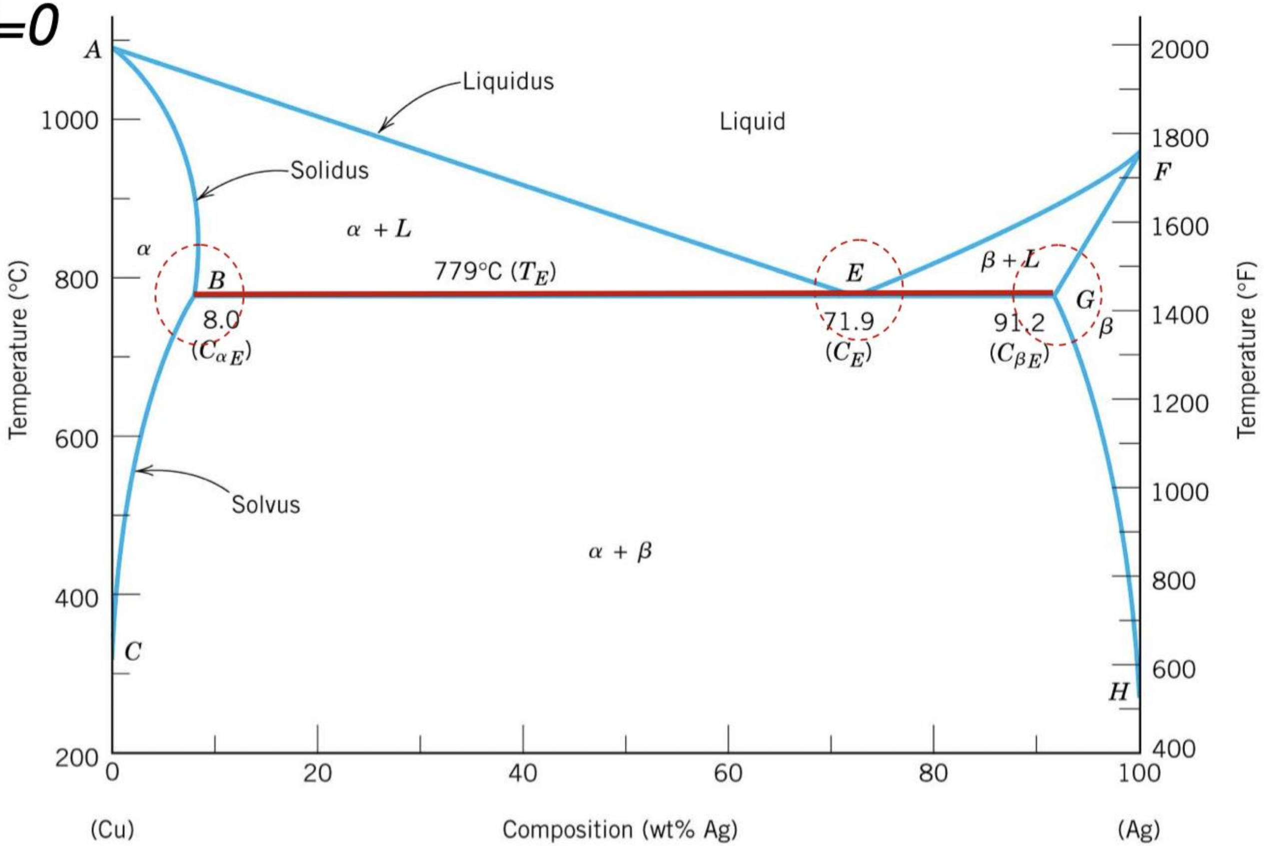
Or

If composition of the a phase is specified to be C_α = 3 wt%, then T and can be any where between ~600 to 1100ºC.

Gibbs Phase Rule

Where in the Cu—Ag diagram, is there a 0 degree of freedom?
(i.e. T, P, and C are all fixed)---eutectic isotherm

$F=3-P=0$



Example: Design of an Aerospace Component

Because magnesium (Mg) is a low-density material (ρ_{Mg} = 1.738 g/cm^3), it has been suggested for use in an aerospace vehicle intended to enter the outer space environment. Is this a good design?

SOLUTION:

- In space the pressure is very low. Even at relatively low temperatures, solid magnesium can begin to change to a vapor, causing metal loss that could damage a space vehicle.

- A low-density material with a higher boiling point (and, therefore, lower vapor pressure at any given temperature) might be a better choice.

- Other factors to consider: In load-bearing applications, we should not only look for density but also for relative strength. Therefore, the ratio of Young’s modulus to density or yield strength to density could be a better parameter to compare different materials.

Classifications of Phase Transformations

- Diffusion-dependent transformation (Simple)

✓ No change in number or composition of the phases present
✓ Solidification of a pure metal
✓ Allotropic transformations
✓ Recrystallization and grain growth

- Diffusion-dependent transformation

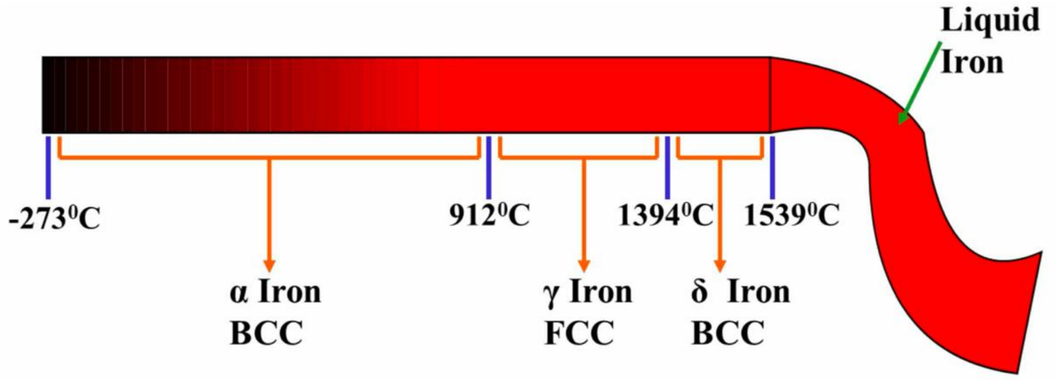
✓ Some alteration in phase compositions
✓ Often alteration in the number of phases present
✓ Final microstructure ordinarily consists of 2 phases
✓ Eutectoid reaction

- Diffusionless transformation

✓ Metastable phase is produced
✓ Martensitic transformation in some steel alloys

Polymorphism or Allotropy

- Polymorphism (in metals) or allotropy (in elements) is the ability of a material to exist in more than one crystalline form depending on temperature and/or pressure. The transformation from one structure to another is called an allotropic transformation.
- Iron exists in both BCC and FCC form depending on the temperature.



Allotropic transformation of iron showing phase changes with temperature. Iron exists in BCC (α, δ) and FCC (γ) structures depending on temperature before melting into liquid form.

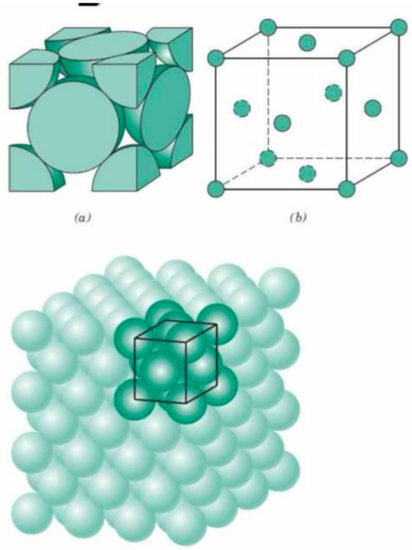
Why It Matters in Engineering

- **Allotropic transformations in iron are crucial for heat treatment processes**, especially when designing steels with specific mechanical properties.
- Different phases have different solubilities for carbon, which affects **phase transformation behavior**, **hardness**, and **microstructure**.
- Knowledge of these transformations is vital when using **TTT/CCT diagrams** and understanding critical temperatures during heating/co

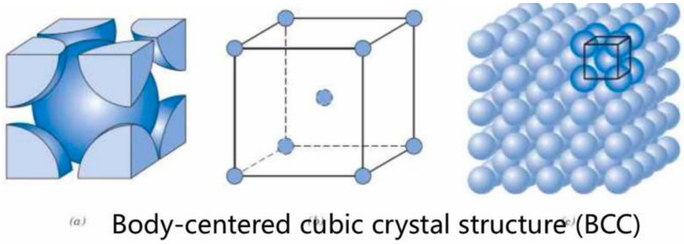
To fully understand allotropy, it is essential to examine the atomic arrangement of each phase. The crystal structure of iron changes with temperature—from BCC to FCC and back—which directly influences its physical properties and phase transformation behavior.

Crystal Structures and Atomic Packing Factor (APF)

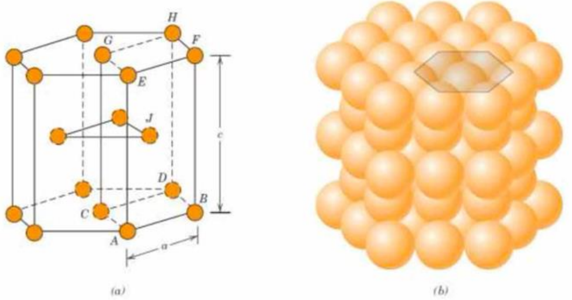
Metals have specific crystal structures that define how atoms are arranged in space. The most common metallic crystal structures are **Body-Centered Cubic (BCC)**, **Face-Centered Cubic (FCC)**, and **Hexagonal Close-Packed (HCP)**, as shown in Figure blow.



Face Centered Cubic Crystal Structure (FCC)

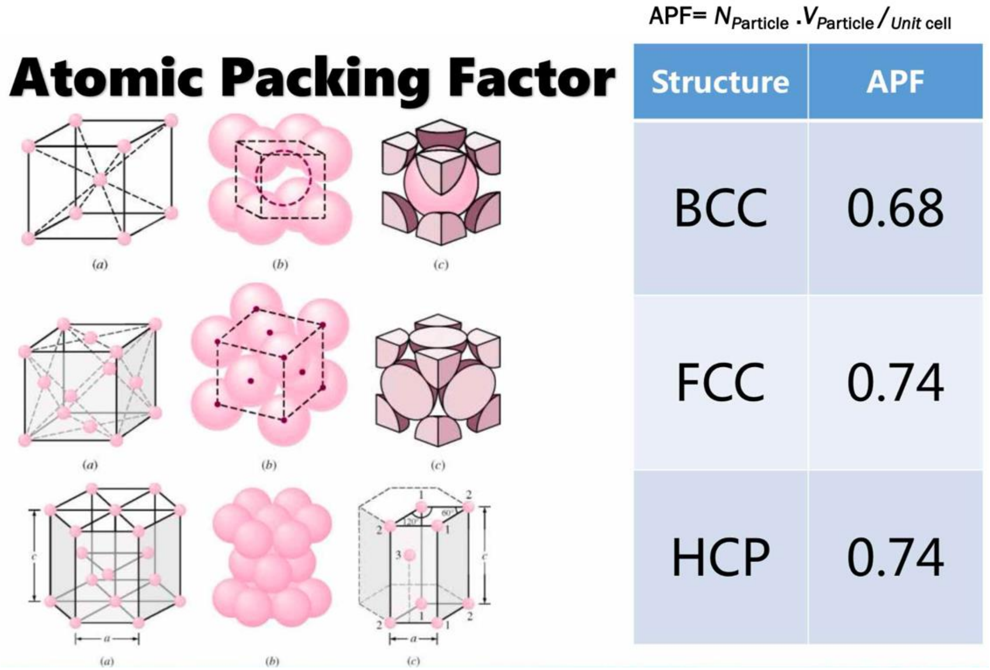


Body-centered cubic crystal structure (BCC)



Hexagonal close-packed crystal structure (HCP)

These structures influence many physical and mechanical properties of metals, including strength, ductility, and how easily atoms can diffuse during phase transformations. One key concept linked to these structures is the **Atomic Packing Factor (APF)**, which quantifies how efficiently atoms occupy space within the crystal lattice (Figure below).

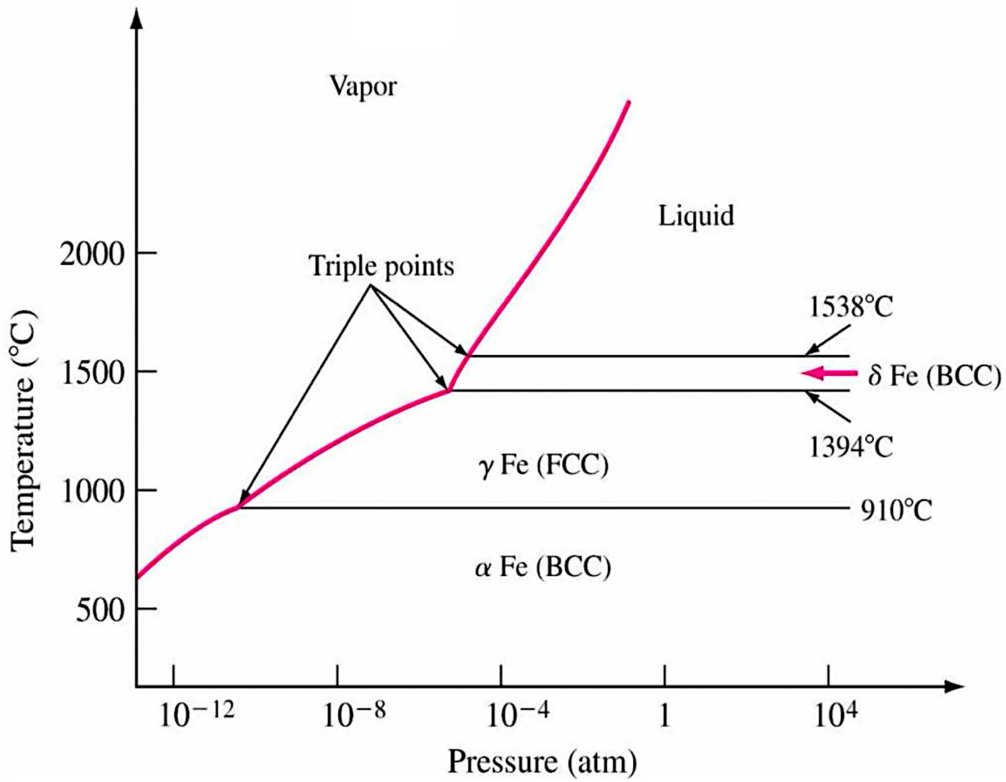

$APF= N_{Particle} . V_{Particle} / \textit{Unit cell}$

Atomic Packing Factor

Structure	APF
BCC	0.68
FCC	0.74
HCP	0.74

Allotropy in Pure Iron

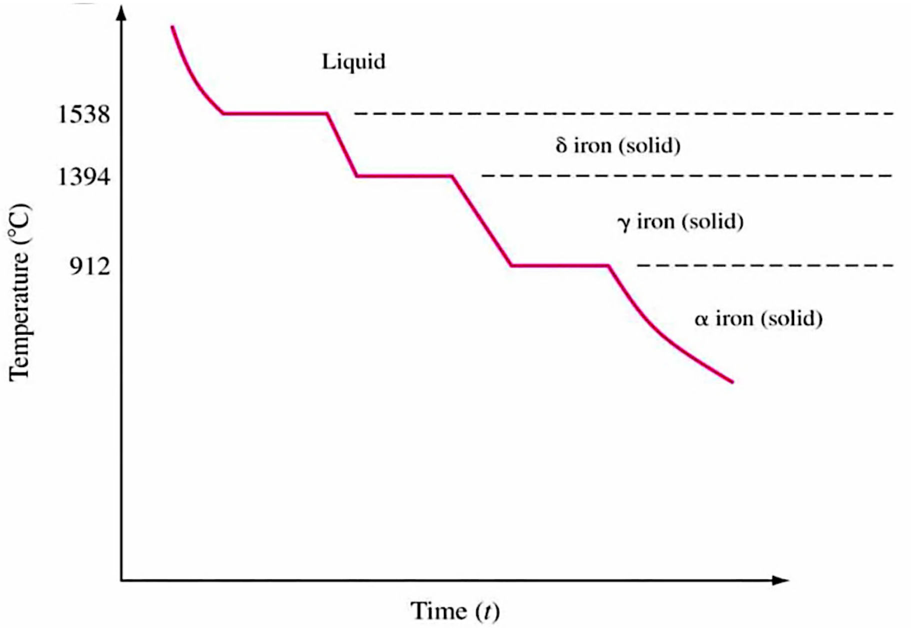
- **Iron changes its crystal structure with temperature.** This is known as **allotropy**.
- **Three Solid Phases of Iron:**
  - **Below 910°C: α-ferrite (BCC)**
    - Soft and magnetic.
  - **910°C to 1394°C: γ-austenite (FCC)**
    - Higher carbon solubility and more ductile.
  - **1394°C to 1538°C: δ-ferrite (BCC)**
    - Reverts back to the BCC structure before melting.
- **Why These Changes Matter:**
  - Understanding these transformations is crucial for **phase stability**, **diffusion**, and **heat treatment** of steels.



3 Solid Phases

1. α Fe (BCC)
2. γ Fe (FCC)
3. δ Fe (BCC)

- **Cooling curves** show how temperature changes as a material cools over time.
- **Thermal Arrests**: The flat, horizontal parts of the curve are called **thermal arrests**.
- The temperature stays constant here.
- This happens because **latent heat** is released during a phase transformation (like freezing), which counteracts the cooling.



Take times between Phases

Weekly Quiz – Lecture 1

1. Define a 'phase' in the context of materials science.
2. What is the Hall–Petch equation used for?
3. How many degrees of freedom exist in a unary system with two phases?
4. Why is magnesium not ideal for outer space structural use?
5. Write the formula for Atomic Packing Factor (APF).
6. What does each term represent in the Gibbs phase rule?
7. Which textbook defines phase transformations in metals and alloys in most detail?

- Answer Key:
- 1. A phase is a uniform portion of a system with consistent physical and chemical properties.
- 2. It relates grain size to the yield strength of a material.
- 3. $F = 1$ ($F = C - P + 2 \rightarrow 1 = 1 - 2 + 2$).
- 4. Mg can vaporize under low pressure, causing material loss.
- 5. APF = (N × V_particle) / V_unit_cell.
- 6. F = degrees of freedom, C = components, P = phases.
- 7. Porter and Easterling's 'Phase Transformations in Metals and Alloys'.