ME201N · B.TECH MECHANICAL · END TERM

Engineering Materials & Metallurgy

Master notes, solved PYQs and a 12-hour plan, aimed at 30 out of 40

Paper	40 marks · 3 hours · answer any **5 of 6** questions · 8 marks each
Split	Each question is 2 parts: 6+2, 5+3 or 4+4
Syllabus	6 units, per the DTU scheme (42 contact hours)
Sources	Callister, *Materials Science and Engineering* (10th ed.); DTU End Sem Nov 2024 (ME201n); Mid Sem Mar 2024

How to use: start with “Read this first” and the PYQ topic map, follow the 12-hour plan, and practise every diagram marked in the units by hand. Sections are tagged HIGH MEDIUM LOW by how likely they are to be asked.

READ THIS FIRST

How to score 30 out of 40

You answer 5 questions out of 6. You can skip one whole question, so prepare five question types thoroughly rather than six halfway.

The paper pattern

The Nov 2024 end-term (ME201n) had six 8-mark questions, each with an (a) and a (b) part. Every question mixed a long theory or diagram answer with a short derivation or numerical. Each question roughly maps to one syllabus area:

Q	Nov 2024 (what was asked)	Unit
1	(a) Fe–C diagram, all phases, reactions (6) · (b) Derive Gibbs' phase rule (2)	3
2	(a) Griffith theory, derive critical stress (6) · (b) Numerical: surface energy from K_{Ic} (2)	4
3	(a) Three powder-production methods + making cemented carbide tools (5) · (b) Annealing vs normalizing, microstructure (3)	6, 3
4	(a) Three stages of creep + mechanisms (4) · (b) TTT diagram of eutectoid steel, labelled (4)	4, 3
5	(a) Miller indices procedure, cubic and HCP, with examples (5) · (b) Numerical: vacancies in Cu at 200 °C (3)	1
6	(a) Reinforcements in polymer-matrix composites (6) · (b) Duralumin and brass: composition, properties, uses (2)	5/6, 2

STRATEGY

- **Must-prepare (guaranteed marks):** the Fe–C diagram with all three reactions, the TTT diagram, heat treatments, Griffith theory, the creep curve, and crystal numericals (APF, planar density, d-spacing, vacancies). These alone cover four questions.
- **Fifth question:** pick either powder metallurgy and composites (Units 5–6, short and descriptive) or steels, alloys and corrosion (Unit 2). Composites and PM are faster to learn.
- **Numericals are free marks.** The 2- and 3-mark parts are almost always one-formula problems. Learn the formula sheet at the end.
- **Draw a diagram in every long answer.** Examiners give roughly half the marks of a theory question for a correctly labelled figure.
- Write answers in numbered points with headings. Show units in every line of a numerical.

PYQ topic map

✓ = asked in that paper. Topics marked High below should not be skipped.

Topic	Mid 2024	End 2024	Priority	Unit
Iron–carbon diagram + invariant reactions	✓	✓	HIGH	3
TTT diagram, heat treatment (annealing, normalizing, hardening, tempering)		✓	HIGH	3
Gibbs' phase rule, lever rule		✓	HIGH	3

Griffith theory, fracture toughness numericals		✓	HIGH	4
Creep curve and mechanisms		✓	HIGH	4
APF, a–r relations, planar density	✓		HIGH	1
Interplanar spacing + Bragg’s law	✓		HIGH	1
Miller indices (cubic and HCP)		✓	HIGH	1
Imperfections, edge vs screw dislocation	✓		HIGH	1
Vacancy concentration numerical		✓	MEDIUM	1
Crystal systems: axial relations	✓		MEDIUM	1
Powder production, cemented carbides		✓	MEDIUM	6
Composites: reinforcements, rule of mixtures		✓	MEDIUM	5, 6
Non-ferrous alloys (duralumin, brass)		✓	MEDIUM	2
Fatigue, DBTT, ductile vs brittle fracture			MEDIUM	4
Case hardening, precipitation hardening			MEDIUM	3
Corrosion, galvanic cell, protection			MEDIUM	2
Recovery, recrystallization, cold/hot working			MEDIUM	1
Alloy, tool and stainless steels			LOW	2

Not covered in either 2024 paper but on the syllabus: corrosion, fatigue, case hardening, precipitation hardening, recovery and recrystallization. Since they haven't come up recently, expect at least one of them to appear.

12-hour study plan

Time	What to do	Output
Hour 0–0:30	Read this section, both solved PYQ papers (end of this PDF) and the formula sheet once, quickly. Don’t memorise yet.	Know the target
Hour 0:30–3:00	**Unit 3.** Fe–C diagram (draw it 3 times from memory), invariant reactions, lever-rule numericals, Gibbs’ phase rule derivation, TTT diagram, annealing, normalizing, hardening, tempering, case hardening.	Q1 + half of Q3/Q4 secured
Hour 3:00–5:00	**Unit 1.** Unit cells, a–r relations, APF, density, planar density, Miller indices (cubic and HCP), d-spacing and Bragg’s law, defects, dislocations, slip vs twinning. Solve every worked numerical yourself.	Q5 secured
Hour 5:00–5:20	Break. Walk, eat, no phone.	
Hour 5:20–7:20	**Unit 4.** Stress–strain and yield point, ductile vs brittle fracture, Griffith derivation (write it twice), K_{Ic} numericals, DBTT, fatigue (S–N curve), creep curve + mechanisms + creep-resistant materials.	Q2 + creep secured

Hour 7:20–9:00	**Units 5 + 6.** Composite classification tree, rule of mixtures, critical fibre length, fibres (glass, carbon, Kevlar) and matrices, coupling agents. Powder metallurgy steps, powder production, sintering, cemented carbides, advantages.	Q6 / PM secured
Hour 9:00–10:15	**Unit 2.** Plain carbon steels, effect of alloying elements (table), stainless and tool steels, non-ferrous alloy table (duralumin, brasses, bronzes), corrosion types, galvanic cell, rusting reactions, protection methods.	Backup question
Hour 10:15–11:15	Mock: write the Nov 2024 paper in 60 minutes without notes (attempt 5 questions). Check against the solutions.	Find gaps
Hour 11:15–12:00	Formula sheet, the must-draw diagrams list and the “Likely exam questions” boxes of each unit. Sleep if possible.	Final revision

Contents

Unit 1	Structure of metals: crystal structures, Miller indices, defects, dislocations, slip and twinning, cold/hot working, recovery and recrystallization	p. 5
Unit 2	Materials: plain carbon and alloy steels, tool and stainless steels, non-ferrous alloys; corrosion	p. 24
Unit 3	Solidification, phase diagrams, iron–carbon diagram, TTT, heat treatment, case hardening, precipitation hardening	p. 38
Unit 4	Yield and elastic modulus, fracture, Griffith theory, fracture toughness, DBTT, fatigue; creep	p. 58
Unit 5	Composite materials: classification, characteristics, rule of mixtures, applications	p. 73
Unit 6	Powder metallurgy; fibre-reinforced composites: fibres, matrices, coupling agents, fillers	p. 80
PYQs	End Sem Nov 2024 (ME201n) and Mid Sem Mar 2024, fully solved	p. 90
Revision	Formula sheet, key numbers, must-draw diagrams, answer-writing checklist	p. 100

UNIT 1 · ~7 CONTACT HRS

Structure of Metals

Most asked: APF and a–R relations, planar/linear density, Miller indices (cubic + HCP), Bragg's law numericals, number of vacancies, edge vs screw dislocation, recovery–recrystallization–grain growth.

HOW THIS UNIT IS EXAMINED

Usually 1–2 full questions (8 marks each, split 4+4, 5+3 or 6+2). There's almost always one numerical: planar density, Bragg/d-spacing, vacancies or density. Learn the **six worked numericals** in this unit. Between them they cover nearly every numerical type the paper uses.

1. Basic terms HIGH

DEFINITIONS

- **Crystalline solid:** atoms arranged in a repeating, periodic 3-D pattern over long distances (long-range order). All metals, most ceramics, some polymers.
- **Amorphous solid:** no long-range order (glass, many polymers).
- **Space lattice:** an infinite 3-D array of points in space where every point has identical surroundings. It is a *mathematical* concept.
- **Basis (motif):** the atom or group of atoms attached to every lattice point. **Crystal structure = Lattice + Basis.**
- **Unit cell:** the smallest repeating unit (a parallelepiped) that shows the full symmetry of the structure. Stacking it in 3-D generates the whole crystal. It is described by the **lattice parameters** a, b, c and α, β, γ.
- **Coordination number (CN):** number of nearest-neighbour (touching) atoms around an atom.
- **Atomic packing factor (APF):** fraction of the unit-cell volume occupied by atoms (hard spheres).
  $\text{APF} = (\text{no. of atoms per cell} \times 4/3\ \pi R^3) / V_{\text{cell}}$
- **Single crystal:** a solid in which the periodic arrangement extends **throughout the whole specimen without interruption**, i.e. no grain boundaries. All unit cells interlock in the same orientation. Examples: Si wafers, turbine blades (Ni superalloy), quartz, gem stones. Its properties are **anisotropic** (depend on direction).
- **Polycrystalline material:** made of many small crystals (grains) with different orientations, separated by grain boundaries. Most engineering metals are polycrystalline and nearly **isotropic** overall.
- **Polymorphism / allotropy:** the same element exists in more than one crystal structure, e.g. Fe: α (BCC, <912 °C) → γ (FCC, 912–1394 °C) → δ (BCC, 1394–1538 °C). Carbon: diamond and graphite.

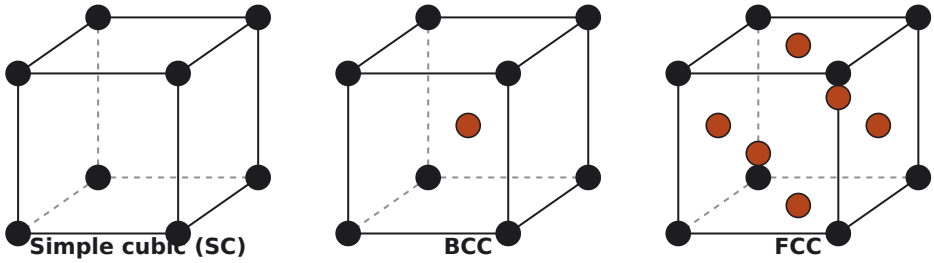
Seven crystal systems and 14 Bravais lattices Asked: End Sem 2024

Every crystal belongs to one of 7 systems, set by the **axial relationships** (a, b, c) and **inter-axial angles** (α between b and c, β between a and c, γ between a and b). Adding body-, face- and base-centring gives 14 Bravais lattices.

Crystal system	Axial relationship	Inter-axial angles	Bravais lattices (no.)	Example
Cubic	a = b = c	α = β = γ = 90°	P, I (BCC), F (FCC) — 3	Fe, Cu, NaCl
Tetragonal	a = b ≠ c	α = β = γ = 90°	P, I — 2	β-Sn, TiO_2
Orthorhombic	a ≠ b ≠ c	α = β = γ = 90°	P, I, F, C — 4	α-S, Ga
Hexagonal	a = b ≠ c	α = β = 90°, γ = 120°	P — 1	Zn, Mg, Ti
Rhombohedral (trigonal)	a = b = c	α = β = γ ≠ 90°	P — 1	Bi, calcite
Monoclinic	a ≠ b ≠ c	α = γ = 90° ≠ β	P, C — 2	gypsum
Triclinic	a ≠ b ≠ c	α ≠ β ≠ γ ≠ 90°	P — 1	$K_2Cr_2O_7$

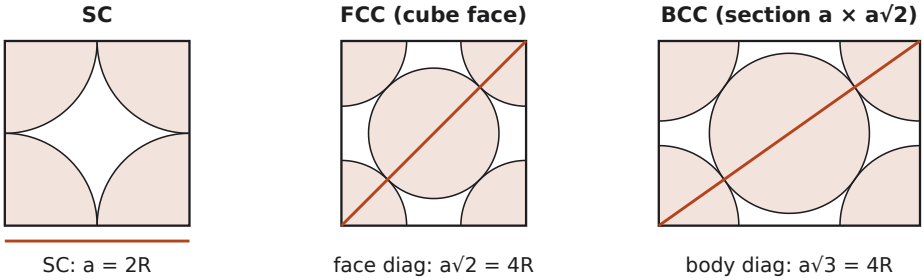
P = primitive (simple), I = body-centred, F = face-centred, C = base-centred. Total 3+2+4+1+1+2+1 = 14. Memory hook for most→least symmetric: *Cubic, Hexagonal, Tetragonal, Rhombohedral, Orthorhombic, Monoclinic, Triclinic*.

2. Metallic crystal structures: SC, BCC, FCC, HCP HIGH



Reduced-sphere unit cells. Corner atoms are dark; body-centre (BCC) and face-centre (FCC) atoms are in accent colour. Hidden edges are dashed.

Relationship between lattice parameter a and atomic radius R Asked: End Sem 2024



Atoms touch along the cube edge (SC), the face diagonal (FCC) or the body diagonal (BCC). Always draw this figure before writing the relation.

A–R RELATIONS

SC: atoms touch along edge → a = 2R

BCC: body diagonal √3 a = 4R → a = 4R/√3

FCC: face diagonal √2 a = 4R → a = 2√2 R

HCP: a = 2R, ideal c/a = 1.633

Atoms per unit cell

Count each atom by the share of it that lies inside the cell: corner = 1/8, face = 1/2, edge = 1/4, body = 1.

- SC: 8 × 1/8 = **1**
- BCC: 8 × 1/8 + 1 = **2**
- FCC: 8 × 1/8 + 6 × 1/2 = **4**
- HCP: 12 corners × 1/6 + 2 face centres × 1/2 + 3 inside = 2 + 1 + 3 = **6**

APF derivations (write these fully for 4–5 marks)

APF OF SC

n = 1, a = 2R, $V_c = 8R^3$

APF = $(1 \times 4/3\ \pi R^3)/8R^3 = \pi/6 =$ **0.52**

APF OF BCC

n = 2, a = 4R/√3 → $V_c = 64R^3/(3\sqrt{3})$

APF = $(2 \times 4/3\ \pi R^3)/(64R^3/3\sqrt{3}) = \sqrt{3}\pi/8 =$ **0.68**

APF OF FCC

n = 4, a = 2√2R → $V_c = 16\sqrt{2}\ R^3$

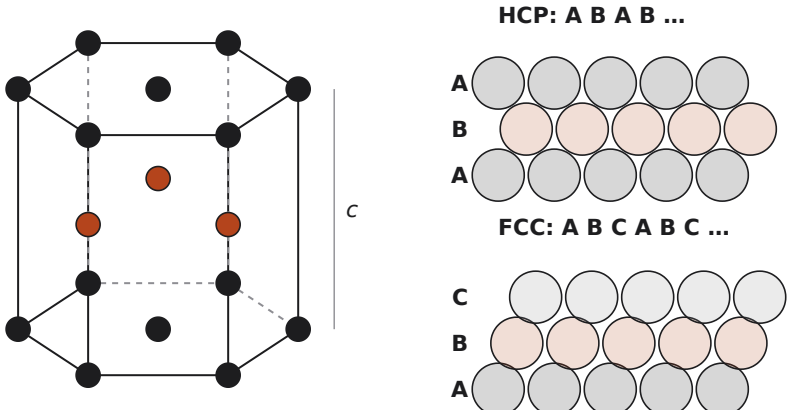
APF = $(4 \times 4/3\ \pi R^3)/(16\sqrt{2}R^3) = \pi/(3\sqrt{2}) =$ **0.74**

APF OF HCP

n = 6, a = 2R, c = 1.633a. Base area = $(3\sqrt{3}/2)a^2 = 6\sqrt{3}R^2$; V_c = base × c = $6\sqrt{3}R^2 \times 3.266R = 33.94R^3$.

APF = $(6 \times 4.189R^3)/33.94R^3 =$ **0.74**

Property	SC	BCC	FCC	HCP
Atoms / cell	1	2	4	6
a vs R	a = 2R	a = 4R/√3	a = 2√2R	a = 2R, c = 1.633a
Coordination no.	6	8	12	12
APF	0.52	0.68	0.74	0.74
Close-packed planes	—	none truly ({110} densest)	{111}	(0001) basal
Stacking	—	—	ABCABC…	ABAB…
Slip systems	—	12 (48 possible)	12	3
Ductility	—	moderate; ductile–brittle transition	very ductile, even at low T	limited (brittle-ish)
Examples	Po	α-Fe, Cr, Mo, W, V	Cu, Al, Ni, Ag, Au, γ-Fe, Pb	Zn, Mg, Ti, Cd, Co



HCP unit cell: 12 corner atoms, 2 basal face centres and 3 atoms in the mid-plane (accent). Right: stacking of close-packed layers. ABAB… gives HCP; ABCABC… gives FCC. Both have CN 12 and APF 0.74.

Density computation

THEORETICAL DENSITY

$$\rho = n\,A / (V_c\,N_A)$$

n = atoms per cell, A = atomic weight (g/mol), $V_c = a^3$ in cm³, $N_A = 6.022 \times 10^{23}$ atoms/mol.

WORKED NUMERICAL 1: DENSITY OF CU AND FE

Cu (FCC), R = 0.128 nm, A = 63.5 g/mol. $a = 2\sqrt{2}(0.128) = 0.3620$ nm $= 3.620 \times 10^{-8}$ cm, so $V_c = 4.745 \times 10^{-23}$ cm³.

$\rho = (4 \times 63.5)/(4.745 \times 10^{-23} \times 6.022 \times 10^{23}) = 254/28.58 =$ **8.89 g/cm³** (measured 8.94).

α-Fe (BCC), R = 0.124 nm, A = 55.85. $a = 4(0.124)/\sqrt{3} = 0.2864$ nm, so $V_c = 2.348 \times 10^{-23}$ cm³.

$\rho = (2 \times 55.85)/(2.348 \times 10^{-23} \times 6.022 \times 10^{23}) =$ **7.90 g/cm³** (measured 7.87).

Reverse form: given ρ, A and the structure, find R. Solve for $V_c = nA/(\rho N_A)$, then $a = V_c^{1/3}$, then R from the a–R relation.

3. Miller indices: directions and planes HIGH

Procedure for a crystallographic direction [uvw] (cubic)

1. Draw a vector through the origin, or note the coordinates of its **head** and **tail** in units of a, b, c.
2. Subtract: head − tail.
3. Multiply or divide by a common factor to get the **smallest integers**.
4. Enclose in square brackets without commas: **[uvw]**. A negative index is written with a bar, e.g. $[\bar{1}10]$.
5. Family of equivalent directions: **⟨uvw⟩**, e.g. ⟨100⟩ = [100], [010], [001], $[\bar{1}00]$…

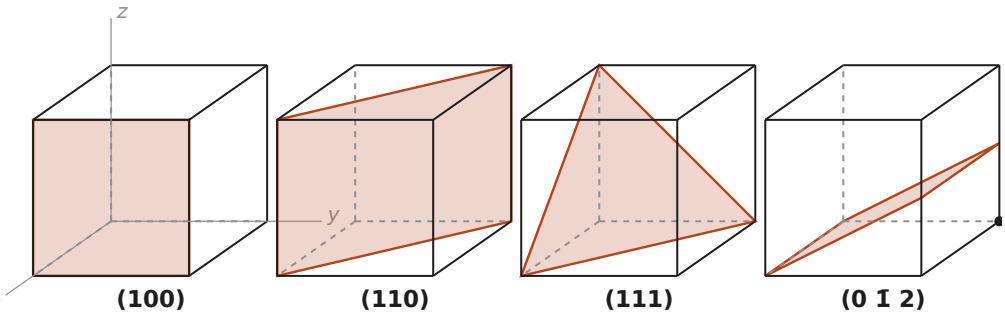
Procedure for a crystallographic plane (hkl) (cubic)

1. If the plane passes through the origin, shift the origin to a neighbouring corner (or draw a parallel plane).
2. Write the **intercepts** on the x, y, z axes in units of a, b, c. A plane parallel to an axis has intercept ∞.

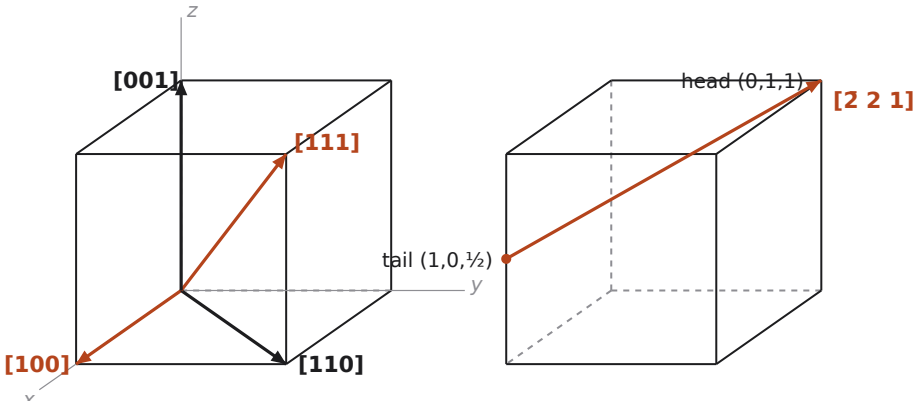
3. Take the **reciprocals** (1/∞ = 0).
4. Clear fractions to the smallest integers. Do not reduce further if the indices came from intercepts.
5. Write in round brackets: **(hkl)**. Family of planes: **{hkl}**, e.g. {111}.

MUST REMEMBER

In **cubic** crystals only, the direction [hkl] is **perpendicular** to the plane (hkl). Parallel planes have the same (or negative) indices.



Common planes in a cubic cell. In the 4th cube the plane would pass through the origin, so O′ is taken at (0,1,0). Intercepts are then ∞, −1, ½, reciprocals 0, −1, 2, giving (0 $\bar{1}$ 2).



Left: low-index directions from the origin. Right: head − tail = (0,1,1) − (1,0,½) = (−1, 1, ½). Multiplying by 2 gives [$\bar{2}$ 2 1].

WORKED NUMERICAL 2: MILLER INDICES

(a) Plane with intercepts x = ½, y = 1, z = ∞ → reciprocals 2, 1, 0 → **(210)**.

(b) Plane with intercepts x = 1, y = −1, z = ½ → reciprocals 1, −1, 2 → **(1 $\bar{1}$ 2)**.

(c) Plane with intercepts 2a, 3b, ∞ → reciprocals ½, ⅓, 0 → ×6 → **(320)**.

(d) Direction from tail (½, 0, 1) to head (0, 1, 0): head − tail = (−½, 1, −1) → ×2 → **[$\bar{1}$ 2 $\bar{2}$]**.

Miller–Bravais indices for HCP (4-index) Asked: End Sem 2024

HCP uses **four axes**: a_1, a_2, a_3 in the basal plane at 120° to each other, and z (c-axis) perpendicular to them. This makes equivalent planes and directions look equivalent in their indices, e.g. all prism planes are of the form {10 $\bar{1}$ 0}.

- **Planes (hkil):** find intercepts on a_1, a_2, a_3, z, take reciprocals and clear fractions. Always **i = −(h + k)**.

Conversion 3-index (hkl) → 4-index (hkil): just insert i = −(h+k). Example: (1 0 1) → (1 0 $\bar{1}$ 1); (1 1 0) → (1 1 $\bar{2}$ 0).

- **Directions [uvtw]** from 3-index [UVW]:
  u = (2U − V)/3, v = (2V − U)/3, t = −(u + v), w = W, then clear fractions.
- Important HCP planes: basal **(0001)**; prism **{10 $\bar{1}$ 0}**; pyramidal **{10 $\bar{1}$ 1}**. Main slip direction: **⟨11 $\bar{2}$ 0⟩**.

WORKED NUMERICAL 3: HCP CONVERSIONS

(a) Convert [010] to 4-index: U = 0, V = 1, W = 0. u = (0 − 1)/3 = −⅓; v = (2 − 0)/3 = ⅔; t = −(−⅓ + ⅔) = −⅓; w = 0. Multiply by 3 → **[$\bar{1}$ 2 $\bar{1}$ 0]**.

(b) Convert [111]: u = (2−1)/3 = ⅓; v = (2−1)/3 = ⅓; t = −⅔; w = 1. ×3 → **[1 1 $\bar{2}$ 3]**.

(c) Plane with intercepts $a_1 = 1$, $a_2 = -1$, $a_3 = \infty$, z = 1: reciprocals 1, −1, 0, 1 → **(1 $\bar{1}$ 0 1)**. Check: i = −(1 + (−1)) = 0 ✓.

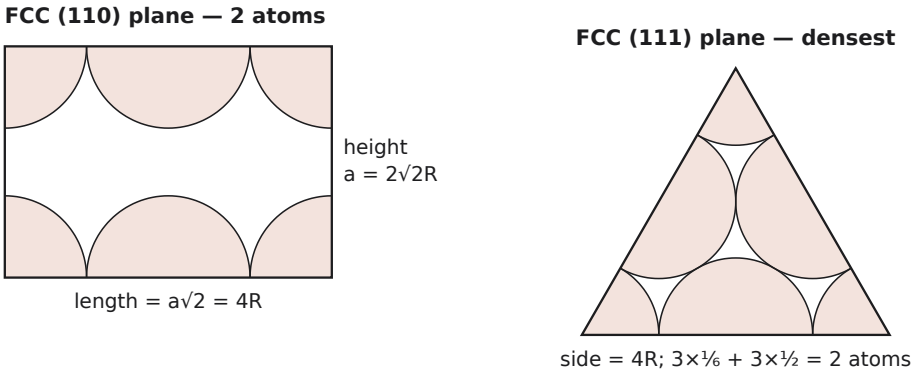
Linear and planar density Asked: End Sem 2024

FORMULAS

LD = (no. of atoms whose centres lie on the direction vector) / (length of vector)

PD = (no. of atoms centred on the plane, within the cell) / (area of plane within the cell)

Count only atoms whose **centres** lie on the line or plane. A plane corner atom contributes ¼ (rectangle) or ⅙ (60° triangle corner), an edge atom ½, and an atom at the centre of the plane 1.



FCC (110): a rectangle 4R × 2√2R holding 4 × ¼ + 2 × ½ = 2 atoms. FCC (111): a triangle of side 4R holding 2 atoms.

WORKED NUMERICAL 4: PLANAR DENSITY IN TERMS OF R (AND FOR CU, FE)

FCC (100): square of side a = 2√2R, area 8R². Atoms = 4 × ¼ + 1 = 2. **PD = 2/8R² = 1/(4R²) = 0.25/R²**

FCC (110): rectangle a√2 × a = 4R × 2√2R, area 8√2R². Atoms = 4 × ¼ + 2 × ½ = 2. **PD = 2/(8√2R²) = 1/(4√2R²) = 0.177/R²**

FCC (111): equilateral triangle of side 4R, area = (√3/4)(4R)² = 4√3R². Atoms = 3 × ⅙ + 3 × ½ = 2. **PD = 2/(4√3R²) = 1/(2√3R²) = 0.289/R²**. This is the densest plane, which is why FCC slips on {111}.

BCC (100): square of side a = 4R/√3, area 16R²/3. Atoms = 4 × ¼ = 1. **PD = 3/(16R²) = 0.1875/R²**

BCC (110): rectangle a × a√2, area √2a² = 16√2R²/3. Atoms = 4 × ¼ + 1 (centre) = 2. **PD = 3/(8√2R²) = 0.265/R²**. This is the densest BCC plane.

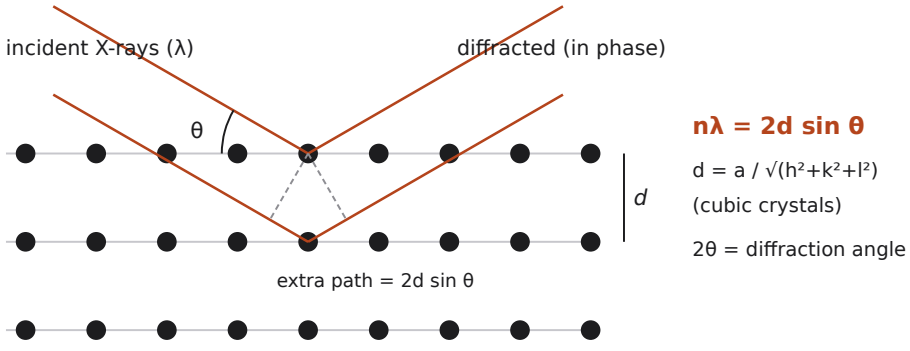
Numbers for Cu (R = 0.128 nm): PD(110) = 1/(4√2 × 0.01638) = **10.8 atoms/nm² = 1.08 × 10¹⁹ m⁻²**; PD(100) = 15.3 nm⁻²; PD(111) = 17.6 nm⁻².
Fe BCC (R = 0.124 nm): PD(110) = **17.2 nm⁻²** = 1.72 × 10¹⁹ m⁻²; PD(100) = 12.2 nm⁻².

LINEAR DENSITY

FCC [110] (face diagonal, length 4R): atoms = ½ + 1 + ½ = 2 → **LD = 2/4R = 1/(2R)**. For Cu: 1/(0.256 nm) = 3.91 nm⁻¹.
FCC [100] (edge, length a = 2√2R): 2 × ½ = 1 atom → LD = 1/(2√2R).
BCC [111] (body diagonal, 4R): 2 atoms → LD = 1/(2R). **BCC [100]**: LD = 1/a = √3/(4R).
Close-packed directions: FCC ⟨110⟩ and BCC ⟨111⟩, where LD = 1/2R (atoms touch).

Interplanar spacing and Bragg's law (X-ray diffraction) Asked: End Sem 2024

When X-rays of wavelength λ (comparable to atomic spacing, ~0.1 nm) hit a crystal, each set of parallel planes (spacing d) scatters them. The reflected waves from successive planes reinforce each other (constructive interference) only when their extra path length, 2d sin θ, equals a whole number of wavelengths.



Derivation of Bragg's law: the ray reflected from the lower plane travels an extra 2 × d sin θ.

BRAGG'S LAW AND D-SPACING

$n\lambda = 2\, d_{hkl} \sin\theta$ (n = order of reflection, usually 1)

$d_{hkl} = a / \sqrt{(h^2 + k^2 + l^2)}$ (cubic)

Uses: identifying crystal structure, measuring lattice parameter, finding phases and residual stresses. θ = Bragg angle; diffractometers report 2θ.

Reflection rules: SC: all planes. BCC: h + k + l even (110, 200, 211, 220…). FCC: h, k, l all odd or all even (111, 200, 220, 311…).

WORKED NUMERICAL 5: D-SPACING AND DIFFRACTION ANGLE

(a) BCC Fe, (220) planes, a = 0.2866 nm, λ = 0.1790 nm, n = 1.

$d_{220} = 0.2866/\sqrt{(4+4+0)} = 0.2866/2.828 =$ **0.1013 nm**

$\sin\theta = n\lambda/(2d) = 0.1790/(2 \times 0.1013) = 0.8833 \rightarrow \theta = 62.04°$. **Diffraction angle 2θ = 124.1°**

(b) FCC Al, (111) planes, a = 0.4049 nm, Cu Kα λ = 0.1542 nm, n = 1.

$d_{111} = 0.4049/\sqrt{3} =$ **0.2338 nm**; $\sin\theta = 0.1542/(2 \times 0.2338) = 0.3298 \rightarrow \theta = 19.26°$, **2θ = 38.5°**

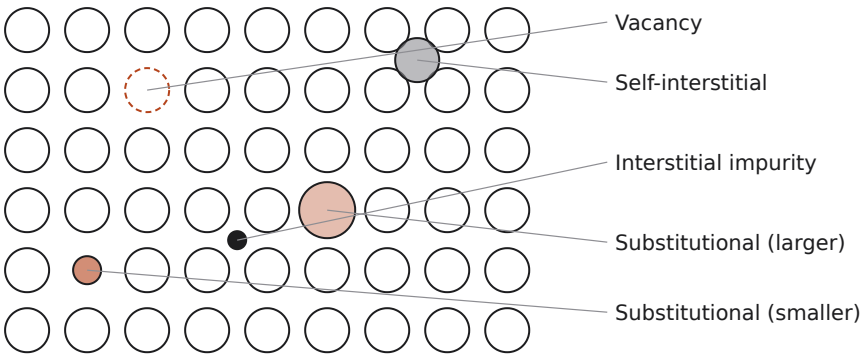
(c) Reverse problem: for a cubic metal, (211) diffracts at 2θ = 82.4° with λ = 0.1542 nm. θ = 41.2°, $\sin\theta = 0.6587$, $d = 0.1542/(2 \times 0.6587) = 0.1170$ nm, $a = d\sqrt{6} =$ **0.2867 nm** (this is α-Fe).

4. Crystal imperfections (defects) HIGH

A real crystal is never perfect. **Imperfections** are departures from the perfect periodic arrangement. Many properties are **structure-sensitive**, i.e. controlled by defects: yield strength, ductility, conductivity, diffusion, corrosion. Defects are classified by their dimension:

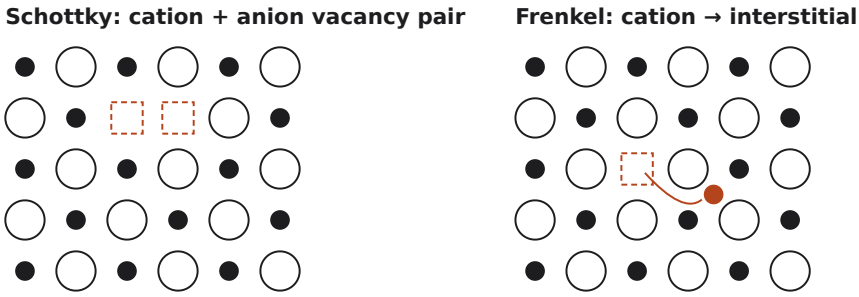
Class	Dimension	Examples
Point defects	0-D	vacancy, self-interstitial, substitutional and interstitial impurity, Frenkel, Schottky
Line defects	1-D	edge, screw and mixed dislocations
Surface (planar) defects	2-D	external surface, grain boundaries, twin boundaries, stacking faults, phase boundaries
Volume (bulk) defects	3-D	pores, cracks, voids, inclusions, precipitates

4.1 Point defects



Point defects in a metal.

- **Vacancy:** an empty lattice site. It is *thermodynamically necessary* because it raises entropy, so every crystal above 0 K has vacancies. Vacancies make diffusion in metals possible.
- **Self-interstitial:** a host atom squeezed into an interstitial void. It causes large distortion, so it is rare.
- **Substitutional impurity:** a foreign atom replaces a host atom, e.g. Zn in Cu (brass), Ni in Cu.
- **Interstitial impurity:** a small atom (C, N, H, B) sits in the voids, e.g. C in Fe (steel).
- **Schottky defect** (ionic solids): a cation vacancy and an anion vacancy as a pair, which keeps the crystal neutral. Lowers density. Example: NaCl.
- **Frenkel defect** (ionic): a cation leaves its site and moves into an interstitial position (vacancy + interstitial pair). Density is unchanged. Example: AgBr.



● cation (small) ○ anion (large) ▢ vacancy — ionic solids (NaCl, AgBr); stay neutral.

HUME-ROTHERY RULES (SUBSTITUTIONAL SOLID SOLUBILITY)

Extensive substitutional solubility needs: (1) atomic radius difference < ±15 %; (2) the same crystal structure; (3) similar electronegativity; (4) similar valence. Example: Cu–Ni satisfies all four, so they are completely soluble.

EQUILIBRIUM NUMBER OF VACANCIES

$$N_v = N \exp(-Q_v / kT) \quad N = N_A \rho / A$$

N = atomic sites per unit volume, Q_v = energy to form a vacancy, k = 8.62 × 10^{-5} eV/atom·K (= 1.38 × 10^{-23} J/atom·K), T in **kelvin**. Convert N to m^{-3}: multiply atoms/cm^3 by 10^6.

WORKED NUMERICAL 6: NUMBER OF VACANCIES **ASKED: END SEM 2024**

(a) Cu at 200 °C. Q_v = 0.9 eV/atom, ρ = 8.94 g/cm³, A = 63.55 g/mol.

Step 1: $N = N_A\rho/A = (6.022 \times 10^{23} \times 8.94)/63.55 = 8.47 \times 10^{22}$ atoms/cm³ = **8.47×10^{28} atoms/m³**

Step 2: T = 200 + 273 = 473 K; $kT = 8.62 \times 10^{-5} \times 473 = 0.04077$ eV; $Q_v/kT = 0.9/0.04077 = 22.07$

Step 3: $N_v = 8.47 \times 10^{28} \times e^{-22.07} = 8.47 \times 10^{28} \times 2.59 \times 10^{-10}$ = **2.2×10^{19} vacancies/m³**

(b) Cu at 1000 °C (ρ = 8.4 g/cm³ at that temperature): $N = 7.96 \times 10^{28}$ m⁻³; T = 1273 K; $Q_v/kT = 0.9/0.1097 = 8.20$; $N_v = 7.96 \times 10^{28} \times 2.74 \times 10^{-4}$ = **2.2×10^{25} vacancies/m³**. Raising T from 473 K to 1273 K increases vacancies by about a million times.

(c) Reverse: to find Q_v from a given N_v/N, use $Q_v = -kT \ln(N_v/N)$.

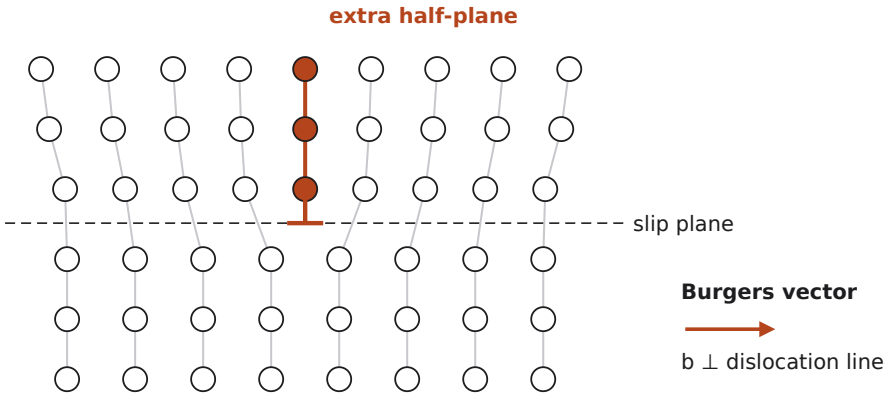
4.2 Line defects: dislocations and the theory of dislocation

DEFINITION

A **dislocation** is a linear defect around which some atoms are misaligned. It forms the boundary between the slipped and unslipped regions of a crystal. Its magnitude and direction of lattice distortion are given by the **Burgers vector b**.

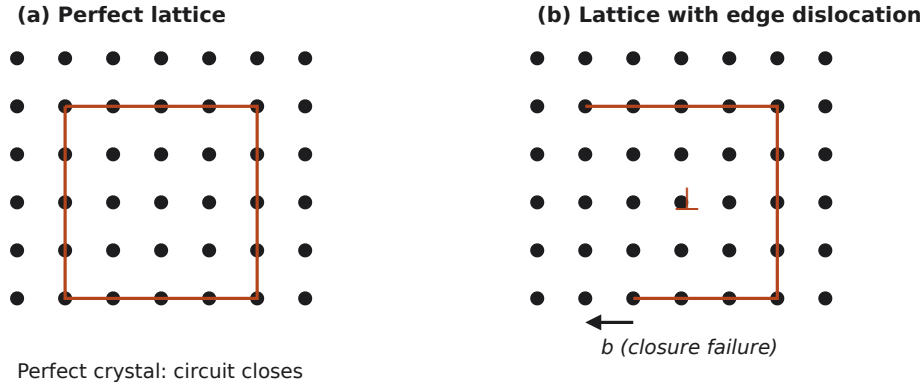
Why dislocations were proposed (theory of dislocation)

- The **theoretical shear strength** of a perfect crystal, where a whole plane of atoms slides over another at once, is $\tau_{th} \approx G/2\pi$ (realistically about G/30), i.e. thousands of MPa.
- Real metal crystals yield at about **$G/10^4$**, roughly 1000 times lower.
- In 1934 **Taylor, Orowan and Polanyi** explained this independently: slip happens by the **movement of dislocations**. Only one line of bonds breaks and re-forms at a time, like moving a carpet by pushing a ruck through it, or a caterpillar moving.
- Dislocations are present in all crystals: about 10^3 mm⁻² in carefully grown crystals, 10^5–10^6 mm⁻² in annealed metals, and 10^9–10^{10} mm⁻² in heavily cold-worked metals. They multiply during deformation, e.g. from a **Frank–Read source**.
- Plastic deformation = motion of large numbers of dislocations. **Strengthening = making dislocation motion difficult** (grain refinement, solid solution, strain hardening, precipitation).



Above slip plane: compression · Below: tension. ⊥ = dislocation line (into page).

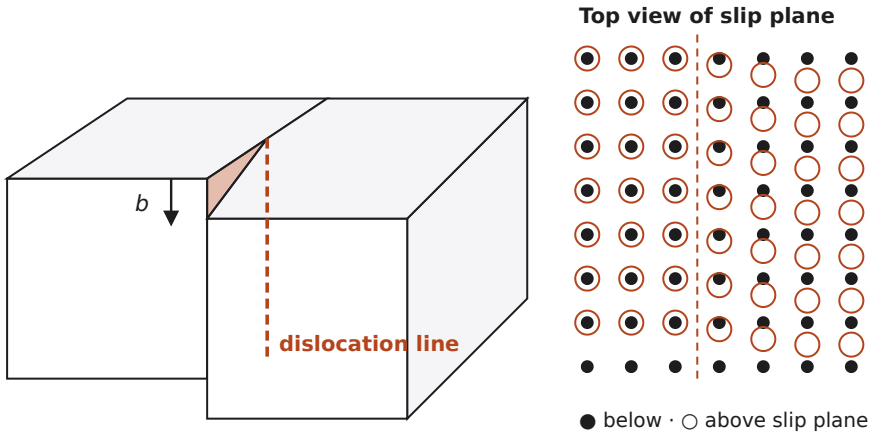
Edge dislocation: an extra half-plane of atoms (accent) ends inside the crystal. The line runs perpendicular to the page at ⊥.



Perfect crystal: circuit closes

Same steps around ⊥ fail to close

Burgers circuit. Taking the same number of atom-to-atom steps around the dislocation fails to close. The closure vector is b.



● below · ○ above slip plane

Front-right part sheared by b; step dies out at the line. b ∥ line.

Screw dislocation: the crystal is sheared by one atomic spacing. The atomic planes form a spiral ramp around the dislocation line, and b is parallel to the line.

Edge vs screw dislocation Asked: End Sem 2024

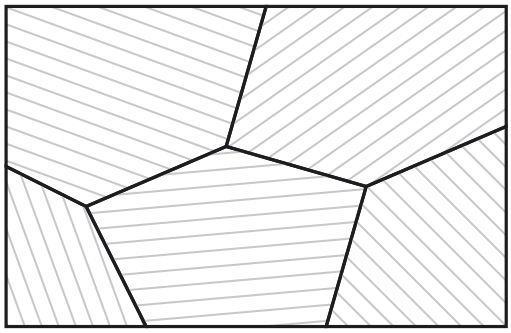
Feature	Edge dislocation	Screw dislocation
Description	Extra half-plane of atoms inserted, ending inside the crystal	Part of the crystal shifted by one atomic distance; planes form a helical ramp

Burgers vector vs line	**b ⊥ dislocation line**	**b ∥ dislocation line**
Direction of motion	Moves parallel to b (in the direction of shear stress)	Moves perpendicular to b (and to the applied shear)
Slip plane	Unique, defined by b and the line	Not unique, so it can **cross-slip**
Climb (non-conservative motion)	Possible, by adding or removing vacancies at high T	Not possible
Stress field	Compressive above, tensile below the slip plane	Pure shear strain
Symbol	⊥ (positive), ⊤ (negative)	↻ / ↺ (right- or left-handed spiral)
Interaction with solutes	Strong: solutes collect in the tensile or compressive region (Cottrell atmosphere → yield point)	Weak

Mixed dislocation: most real dislocations are curved, with an edge character at one end and a screw character at the other. b stays constant along the whole line.

Burgers vector magnitude: FCC b = (a/2)⟨110⟩, $|b| = a/\sqrt{2}$. BCC b = (a/2)⟨111⟩, $|b| = a\sqrt{3}/2$. HCP b = (a/3)⟨11 $\bar{2}$ 0⟩, |b| = a. b always lies along the close-packed direction.

4.3 Surface (interfacial) defects



Each grain = a crystal with its own lattice orientation (hairlines).

Thick lines = grain boundaries: disordered, ~2–3 atoms wide, higher energy; block dislocations.

Low-angle (<15°) boundary = array of edge dislocations (tilt) or screw dislocations (twist).

A polycrystal: grains with different lattice orientations, separated by grain boundaries.

- **External surface:** surface atoms are not bonded to the maximum number of neighbours, so they have higher energy (surface energy, J/m²).
- **Grain boundary:** the boundary between two grains of different orientation, a disordered region about 2–3 atoms wide. **Low-angle** (<10–15°) boundaries are arrays of dislocations (tilt boundary = edge dislocations; twist boundary = screw dislocations). **High-angle** boundaries are more disordered. Grain boundaries hinder dislocation motion (strengthening), are preferred sites for diffusion, precipitation and corrosion, and act as nucleation sites.
- **Twin boundary:** a special mirror-plane boundary. The atoms on one side are mirror images of those on the other. Mechanical twins form by shear in BCC and HCP; annealing twins form in FCC (brass, Cu).
- **Stacking fault:** an interruption in the stacking sequence of close-packed planes, e.g. ABCAB**A**BCABC in FCC, which is locally HCP-like.
- **Phase boundary:** the interface between different phases (e.g. ferrite/cementite in pearlite).

GRAIN SIZE: HALL–PETCH AND ASTM NUMBER

$\sigma_y = \sigma_0 + k_y\, d^{-1/2}$ $N = 2^{n-1}$

d = average grain diameter. A finer grain size gives higher yield strength *and* higher toughness. Grain refinement is the only strengthening method that improves both. N = grains per square inch at 100× magnification; n = ASTM grain size number.

WORKED NUMERICAL 7: HALL–PETCH AND ASTM

An alloy has σ_0 = 70 MPa and k_y = 0.74 MPa·$m^{½}$. For d = 0.01 mm = 1 × 10^{-5} m: $d^{-½}$ = 316.2 $m^{-½}$, so σ_y = 70 + 0.74 × 316.2 = **304 MPa**. Halving d to 5 μm gives σ_y = 70 + 0.74 × 447.2 = 401 MPa.

ASTM n = 6 → N = 2^5 = **32 grains/in² at 100×**. If 45 grains/in² are counted at 100×: n = 1 + log 45/log 2 = 1 + 5.49 = 6.5.

4.4 Imperfections: a 5-mark answer outline

MODEL ANSWER: "DISCUSS IMPERFECTIONS IN CRYSTALS IN DETAIL" (5 MARKS)

1. **Definition:** any deviation from perfect periodic atomic arrangement. Properties such as strength, ductility, conductivity and diffusion depend on defects.
2. **Classification** by dimension (draw the table): point, line, surface, volume.
3. **Point defects:** vacancy (equation $N_v = N\, e^{-Q_v/kT}$), interstitial, substitutional, Schottky and Frenkel. Draw the point-defect sketch.
4. **Line defects:** edge (b ⊥ line) and screw (b ∥ line) with sketches. Dislocations explain why real strength is much less than theoretical, and their motion is plastic deformation.
5. **Surface defects:** grain boundaries (Hall–Petch), twin boundaries, stacking faults, external surfaces.
6. **Volume defects:** voids, cracks, inclusions.
7. **Significance:** controlled defects are useful (alloying, strengthening); uncontrolled ones (cracks, pores) cause failure.

5. Plastic deformation: slip and twinning HIGH

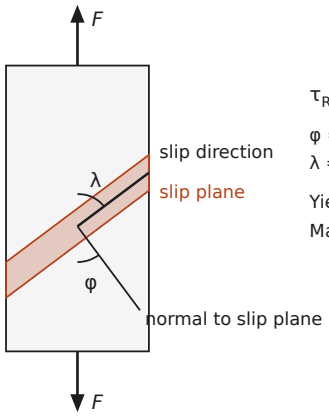
Slip

Slip is plastic deformation by the motion of dislocations, which makes one part of the crystal glide over another along specific **slip planes** in specific **slip directions**. A **slip system** = slip plane + slip direction. Slip occurs on the **most densely packed plane** along the **most densely packed direction**, because there the atoms move the smallest distance and the planes are farthest apart.

Structure	Slip plane	Slip direction	No. of slip systems	Ductility
FCC (Cu, Al, Ni)	{111}	⟨1 Ī 0⟩	4 planes × 3 = 12	High
BCC (α-Fe, W, Mo)	{110}, {211}, {321}	⟨Ī 1 1⟩	12 + 12 + 24 = 48	Moderate (needs higher stress)
HCP (Zn, Mg, Ti)	(0001) basal	⟨11 2 0⟩	1 × 3 = 3	Low, brittle in polycrystals

At least 5 independent slip systems are needed for a polycrystal to deform plastically (von Mises). That is why HCP metals are less ductile.

Resolved shear stress and Schmid's law



$\tau_R = \sigma \cos\varphi \cos\lambda$

φ = angle between F and slip-plane normal
λ = angle between F and slip direction

Yield when τ_R reaches τ_{CRSS}
Max Schmid factor = 0.5 at $\varphi = \lambda = 45°$

WORKED NUMERICAL 8: RESOLVED SHEAR STRESS

A BCC single crystal is loaded in tension along [010]. Slip is on (110) in the $[\bar{1}11]$ direction.

cos φ: angle between [010] and the plane normal [110] → $\cos\varphi = (0\cdot1 + 1\cdot1 + 0\cdot0)/(1 \times \sqrt{2}) = 0.707$ ($\varphi = 45°$)

cos λ: angle between [010] and $[\bar{1}11]$ → $\cos\lambda = (0\cdot(-1) + 1\cdot1 + 0\cdot1)/(1 \times \sqrt{3}) = 0.577$ ($\lambda = 54.7°$)

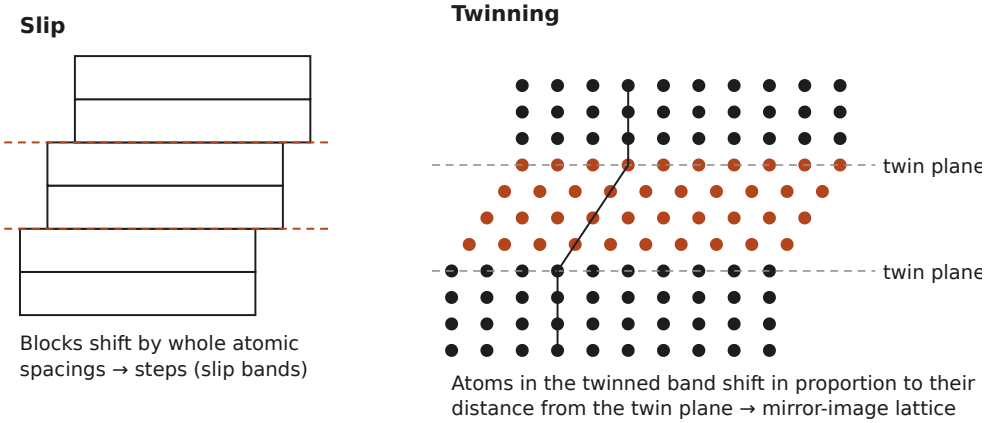
(a) At $\sigma = 52$ MPa: $\tau_R = 52 \times 0.707 \times 0.577 =$ **21.2 MPa**

(b) If $\tau_{CRSS} = 30$ MPa: $\sigma_y = 30/(0.707 \times 0.577) =$ **73.5 MPa**

Angle between two directions $[u_1v_1w_1]$ and $[u_2v_2w_2]$: $\cos\theta = (u_1u_2 + v_1v_2 + w_1w_2)/(\sqrt{(u_1^2+v_1^2+w_1^2)}\sqrt{(u_2^2+v_2^2+w_2^2)})$.

Twinning

Twinning is plastic deformation in which a shear force moves atoms in a region of the crystal so that this region becomes a **mirror image** of the parent lattice across a plane called the **twin plane**. Each atom moves a distance proportional to its distance from the twin plane, always a fraction of an atomic spacing. It happens in BCC and HCP metals at low temperature or high strain rate (shock), when slip is difficult.



Slip makes steps of whole atomic spacings. Twinning reorients a band of crystal into a mirror image.

Slip vs twinning

Slip	Twinning
Atoms move **whole multiples** of the interatomic distance	Atoms move **fractions** of the interatomic distance, proportional to distance from the twin plane
Orientation of the slipped region is **unchanged**	Twinned region becomes a **mirror image** with a different orientation
Occurs on widely spread planes (slip lines/bands)	Occurs in a definite region between twin planes
Needs a lower shear stress	Needs a higher shear stress
Relatively slow (ms)	Very fast (μs); may produce an audible "click" (tin cry)
Main mechanism in FCC and BCC; gives large strains	Common in HCP, and in BCC at low T or impact; gives small strains but reorients grains to favour slip
Slip lines seen under the microscope disappear on polishing	Twin bands remain visible after polishing and etching (different orientation)

6. Cold working and hot working MEDIUM

Cold working is plastic deformation **below** the recrystallization temperature (T_R), usually at room temperature. **Hot working** is deformation **above** T_R.

Strain (work) hardening

During cold work the dislocation density rises from about 10^6 to 10^{10} mm^{-2}. The dislocations tangle and their strain fields repel each other, so further motion needs more stress. The metal becomes stronger and harder but less ductile.

PERCENT COLD WORK

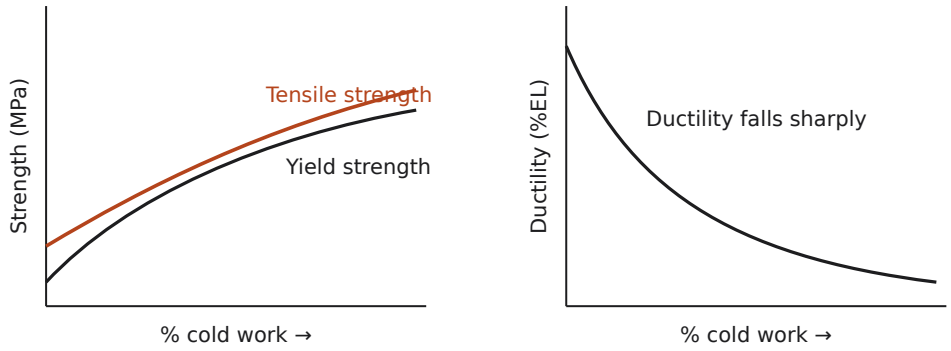
$$\%CW = (A_0 - A_d) / A_0 \times 100$$

A_0 = original cross-section area, A_d = area after deformation. For round bars $\%CW = [1 - (d_d/d_0)^2] \times 100$.

WORKED NUMERICAL 9: % COLD WORK

A Cu rod is drawn from 15.2 mm to 12.2 mm diameter. $\%CW = [1 - (12.2/15.2)^2] \times 100 = (1 - 0.644) \times 100 =$ **35.6 %**. From Callister Fig. 7.19 this gives a yield strength of about 300 MPa, compared with about 70 MPa when annealed.

Thickness reduction of a sheet from 10 mm to 7 mm (width constant): $\%CW = (10 - 7)/10 \times 100 = 30$ %.



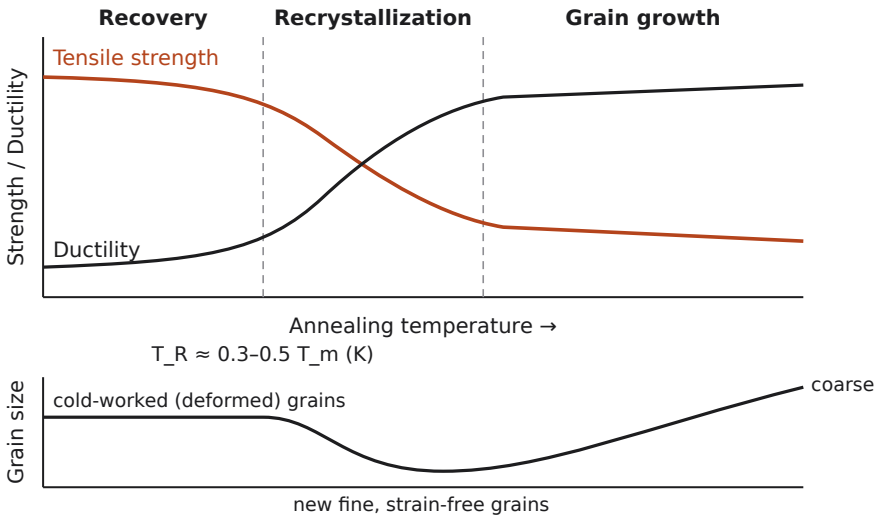
Effect of cold work: yield and tensile strength (and hardness) rise; ductility falls. Yield strength rises faster, so it approaches tensile strength.

Effects of cold working on properties: ↑ yield strength, ↑ tensile strength, ↑ hardness; ↓ ductility (%EL, %RA), ↓ impact toughness; ↓ electrical conductivity (slightly); ↓ corrosion resistance (stored energy); residual stresses; directional (anisotropic) properties from elongated grains and texture; good surface finish and close tolerances.

Basis	Cold working	Hot working
Temperature	Below T_R (usually room temp.)	Above T_R
Strain hardening	Yes: strength and hardness ↑, ductility ↓	No: recrystallization happens at the same time, so the metal stays soft
Grain structure	Grains elongated and distorted	Refined, equiaxed new grains
Force / energy needed	High	Low (larger deformation possible)
Surface finish and accuracy	Excellent, close tolerances	Poor (oxide scale), lower accuracy
Residual stresses	Present; need stress-relief annealing	Negligible
Defects	May crack if overworked	Closes porosity, breaks up the cast structure, removes inhomogeneity
Examples	Cold rolling, wire drawing, deep drawing, coining	Hot rolling, forging, extrusion, piercing

7. Recovery, recrystallization and grain growth HIGH

A cold-worked metal stores strain energy (dislocations, point defects). On **annealing** (heating) it softens in three stages:



Effect of annealing temperature on a cold-worked metal (fixed time, e.g. 1 h).

(1) Recovery

- Happens at low temperature. Some stored strain energy is released by **dislocation motion without grain-boundary motion**, helped by faster diffusion.
- Point defects are annihilated. Dislocations rearrange into low-energy arrays called sub-grain boundaries (**polygonization**), and opposite dislocations cancel.
- **Results:** internal (residual) stresses are relieved, and electrical and thermal conductivity are restored. Strength and hardness change very little, and the microstructure is unchanged. This is the basis of **stress-relief annealing**.

(2) Recrystallization

- New, **strain-free, equiaxed grains** with low dislocation density nucleate (at grain boundaries or highly deformed regions) and grow until they consume the whole cold-worked structure.
- **Driving force:** the stored strain energy difference between strained and unstrained material.
- **Results:** strength and hardness drop sharply; ductility is restored to the pre-cold-work level.
- **Recrystallization temperature T_R:** the temperature at which recrystallization is complete in 1 hour. $T_R \approx 0.3–0.5\ T_m$ (in kelvin), typically about $0.4\ T_m$.
- **Factors lowering T_R:** greater degree of prior cold work, higher purity (alloying raises T_R), finer initial grain size, longer annealing time. A **critical minimum cold work** (2–20 %) is needed, otherwise recrystallization does not occur.
- Examples (Callister Table 7.2): Pb −4 °C, Sn −4 °C, Zn 10 °C (these recrystallize at room temperature, so they cannot be work-hardened at RT), Al 80 °C, Cu 120 °C, Ni 370 °C, Fe 450 °C, brass (60Cu–40Zn) 475 °C, W 1200 °C.

(3) Grain growth

- After recrystallization, if heating continues, **larger grains grow at the expense of smaller ones** by grain-boundary migration.
- **Driving force:** reduction in total grain-boundary area, and so in grain-boundary energy.
- Strength and toughness fall further (Hall–Petch); the result is a coarse structure ("orange peel" surface on forming).

GRAIN GROWTH LAW

$d^n - d_0^n = K\,t$ ($n \approx 2$; K rises exponentially with temperature)

	Recovery	Recrystallization	Grain growth
Temperature	Low ($< T_R$)	$\approx T_R$ (0.3–0.5 T_m)	$> T_R$
Microstructure	No visible change; polygonization	New equiaxed strain-free grains	Grains coarsen
Strength / hardness	Slight decrease	Large decrease	Small further decrease
Ductility	Slight increase	Large increase	Slight increase / constant
Residual stress	Relieved	Fully removed	—
Driving force	Stored dislocation energy	Stored strain energy	Grain-boundary energy

Further reading: Callister Ch. 3 (structures, Miller indices, XRD §3.16), Ch. 4 (imperfections), Ch. 7 (dislocations, slip, strengthening, recovery and recrystallization §7.10–7.13).

Likely exam questions (Unit 1)

#	Question	Marks
1	Define APF and coordination number. Derive APF for SC, BCC and FCC (and HCP).	4–5
2	Derive the relation between a and R for SC, BCC and FCC with neat sketches.	3
3	Calculate the planar density of FCC (110) (or (100), (111)) and BCC (110) in terms of R.	3–4
4	State Bragg's law. For BCC Fe find d_{220} and the diffraction angle (a = 0.2866 nm, λ = 0.1790 nm, n = 1).	3–4
5	Tabulate the axial relationships and inter-axial angles of the seven crystal systems.	2–3
6	Explain the procedure to find Miller indices of planes and directions in cubic and HCP crystals with examples. Convert [010] and [111] to Miller–Bravais indices.	5
7	What is a single crystal? Discuss crystal imperfections in detail.	5
8	Compute the number of vacancies per m^3 in Cu at 200 °C (Q_v = 0.9 eV/atom, ρ = 8.94 g/cm^3, A = 63.55).	3
9	Differentiate between edge and screw dislocations with sketches. Define Burgers vector.	4
10	Differentiate between slip and twinning. Why are FCC metals more ductile than HCP?	4
11	Explain recovery, recrystallization and grain growth with a property-vs-temperature diagram. What factors affect recrystallization temperature?	5
12	Compare cold working and hot working. Explain the effect of cold work on mechanical properties.	4

MODEL ANSWER: WHY FCC IS MORE DUCTILE THAN BCC AND HCP (2–3 MARKS)

Ductility needs many active slip systems on close-packed planes. FCC has 12 slip systems on truly close-packed {111} planes (PD = 0.289/R^2) along ⟨110⟩, with a low Peierls stress, so dislocations move easily even at very low temperatures. BCC has 48 systems, but none of its

planes is truly close-packed, so it needs a higher, temperature-sensitive stress and shows a ductile–brittle transition. HCP has only 3 basal slip systems, fewer than the 5 independent systems needed for polycrystal plasticity, so it is the least ductile.

MODEL ANSWER: SINGLE CRYSTAL VS POLYCRYSTAL (2 MARKS)

A single crystal has a continuous, unbroken periodic lattice through the whole specimen with no grain boundaries, so its properties are anisotropic (e.g. E of Fe is 273 GPa along [111] and 125 GPa along [100]). A polycrystal consists of many randomly oriented grains separated by boundaries, so its properties are averaged and nearly isotropic. Uses of single crystals: Si wafers for ICs, Ni-superalloy turbine blades (no grain boundaries means better creep resistance), piezoelectric quartz.

MODEL ANSWER: MILLER INDICES OF A PLANE, WORKED IN THE EXAM LAYOUT (3 MARKS)

Plane intercepts: x = 1, y = ½, z = ⅓. Reciprocals: 1, 2, 3. No fractions to clear → **(123)**. Sketch: mark the points (1,0,0), (0,½,0), (0,0,⅓) in the cube and join them into a triangle. For a plane through the origin, first shift the origin to an adjacent corner, then repeat the steps.

UNIT 2 · ~8 CONTACT HRS

Engineering Materials & Corrosion

Most asked: composition, properties and uses of duralumin, brasses and bronzes (2-mark table); effect of alloying elements; stainless-steel types; galvanic cell and rusting of iron; methods of corrosion protection.

HOW THIS UNIT IS EXAMINED

This unit is mostly theory. Expect short parts (2–3 marks): "composition, properties and applications of duralumin / brass", "effect of Ni, Cr, Mo in steel", and one 4–5 mark corrosion part (mechanism of rusting, galvanic cell, protection methods). Learn the **alloy table in §5** and the **rusting reactions** word-perfect.

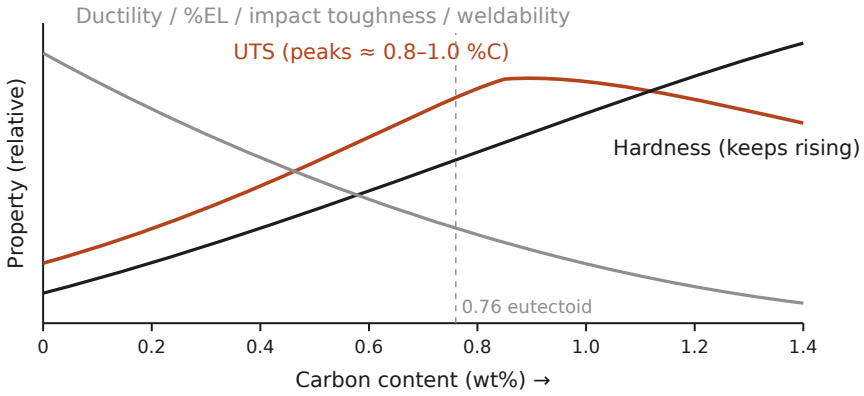
1. Plain carbon steels HIGH

DEFINITION

Plain carbon steel is an alloy of iron and carbon (up to 2.11 % C, practically ≤ 1.5 %). Its properties are controlled mainly by carbon. It contains only small residual amounts of Mn (≤ 1.0 %), Si (≤ 0.4 %), S and P (each ≤ 0.05 %), and no deliberately added alloying element.

Classification by carbon content

Type	% C	Microstructure (annealed)	Properties	Applications
Dead-mild steel	< 0.15	almost all ferrite	very soft, very ductile, excellent weldability and formability	wires, thin sheets, rivets, nails, tubes, car body panels
Low-carbon (mild) steel	0.15–0.30	ferrite + some pearlite	UTS ~ 400 MPa, ductile, tough, weldable, machinable; cannot be hardened by quenching	structural sections (I-beams, angles), bridges, ship plates, nuts and bolts, pipes, case-carburized gears
Medium-carbon steel	0.30–0.60	ferrite + pearlite (~ 50 %)	stronger, harder; good balance of strength and toughness; can be hardened and tempered	shafts, axles, crankshafts, connecting rods, gears, rails, forgings, machine parts
High-carbon steel	0.60–0.80	mostly pearlite	high strength and hardness, wear resistant, low ductility	springs, wire ropes, hammers, chisels, punches, rail wheels
Tool (very high-C) steel	0.80–1.5	pearlite + proeutectoid cementite	very hard, wear resistant, brittle; poor weldability	files, razors, drills, taps, knives, wood-working tools, ball bearings



Effect of carbon on the properties of annealed plain carbon steel. UTS peaks near the eutectoid region because a continuous cementite network forms at the grain boundaries above about 1 % C.

Role of residual elements

- **Mn (0.3–1.0 %):** deoxidizer. It combines with S to form MnS, preventing FeS and so preventing **hot shortness**. Also adds strength and hardenability.
- **Si (0.1–0.4 %):** deoxidizer (killed steel); strengthens ferrite.
- **S:** forms FeS, a low-melting film at grain boundaries that makes the steel crack during hot working (**hot shortness**). Kept below 0.05 %; added (0.1–0.3 %) only in free-cutting steels.
- **P:** strengthens ferrite but causes **cold shortness** (brittleness at room/low temperature). Kept below 0.05 %.

Designation: AISI/SAE 10xx, where xx = %C × 100 (1020 = 0.20 % C, 1045 = 0.45 % C, 1080 = 0.80 % C). Indian IS: 40C8 = 0.40 % C, 0.8 % Mn; also C45.

Limitations of plain carbon steels (why we alloy)

1. Low hardenability: they need a drastic water quench, which causes distortion and quench cracks, and thick sections do not harden through.
2. Strength above about 700 MPa is only possible with a large loss of ductility and toughness.
3. Poor corrosion and oxidation resistance.
4. Lose strength and creep resistance at high temperatures; soften quickly on tempering.
5. Poor impact toughness at low temperatures (ductile–brittle transition).

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2. Effect of alloying elements HIGH

An **alloy steel** contains deliberately added elements (Ni, Cr, Mo, W, V, Mn > 1 %, Si > 0.5 %…) to improve properties. Low-alloy steels have < 5 % total alloy; high-alloy steels have > 5–10 % (stainless, tool, Hadfield).

General effects

1. **Increase hardenability:** they shift the TTT curve to the **right** (slower transformation), so martensite forms even on oil or air cooling and thick sections harden through. Co is the exception: it shifts the curve to the left.
2. **Change the phase diagram:**
   - *Austenite (γ) stabilizers*: Ni, Mn, C, N, Cu, Co. They lower A_1/A_3 and widen the γ field (enough Ni or Mn gives austenitic steel at room temperature).
   - *Ferrite (α) stabilizers*: Cr, Si, Mo, W, V, Ti, Al, Nb. They raise A_3 and shrink the γ loop.
   - Almost all alloying elements shift the eutectoid point to **lower carbon**.

3. **Form carbides:** Ti, Nb, V, W, Mo, Cr (in decreasing tendency) form hard carbides, which add wear resistance and hot hardness. Ni, Si, Al and Co do not form carbides (they are *graphitizers*).
4. **Solid-solution strengthening** of ferrite (Si, Mn, Ni, P).
5. **Grain refinement** (V, Ti, Nb, Al), which gives better toughness.
6. **Resistance to tempering and secondary hardening** (Mo, W, V, Cr), so the steel keeps its hardness at high temperature.
7. **Lower M_s and M_f**, which may leave retained austenite.
8. **Corrosion and oxidation resistance** (Cr ≥ 11–12 %, Ni, Cu, Si, Al).

Element-wise effects (learn at least Ni, Cr, Mn, Si, Mo, W, V)

Element	Main effects	Typical use
Nickel (Ni)	γ-stabilizer; raises strength and **toughness, especially at low temperature**; raises hardenability; with Cr gives corrosion resistance; refines grain	Ni–Cr–Mo steels (4340), 18-8 stainless, cryogenic 9 % Ni steel
Chromium (Cr)	α-stabilizer, carbide former; raises **hardenability**, wear resistance and high-temperature strength; > 11–12 % gives **corrosion resistance** (passive Cr_2O_3 film)	bearing steel 52100 (1.5 % Cr), stainless, tool steels
Manganese (Mn)	deoxidizer and desulphurizer (MnS, prevents hot shortness); raises strength and hardenability; γ-stabilizer; 12 % Mn gives austenitic wear-resistant steel	all steels; Hadfield steel
Silicon (Si)	deoxidizer; strengthens ferrite; raises **elastic limit** (spring steels, 1.5–2 % Si); 3–4 % Si raises electrical resistivity and magnetic permeability and lowers hysteresis loss; graphitizer	Si–Mn spring steel, transformer (electrical) steel
Molybdenum (Mo)	raises hardenability strongly; raises **high-temperature strength and creep resistance**; reduces **temper embrittlement**; improves pitting resistance in stainless (316)	Cr–Mo boiler steels, HSS (M-series), 316 SS
Tungsten (W)	strong carbide former; **red hardness** (keeps hardness at 550–600 °C); wear resistance; fine grain	high-speed steel 18-4-1, hot-work dies
Vanadium (V)	strongest grain refiner; very hard carbides (VC) for wear resistance; toughness; secondary hardening	HSS, Cr–V tools (spanners), springs
Cobalt (Co)	raises red hardness in HSS; **lowers hardenability** (the only one); magnetic properties	super HSS, permanent magnets
Titanium (Ti), Niobium (Nb)	very strong carbide formers; grain refiners (micro-alloyed HSLA); **stabilize stainless steel** against weld decay (321, 347)	HSLA steel, stabilized SS
Copper (Cu)	0.2–0.5 % improves atmospheric corrosion resistance (weathering steel); precipitation strengthening	Corten steel
Boron (B)	only 0.001–0.003 % greatly raises hardenability	boron steels for bolts
Aluminium (Al)	deoxidizer, grain refiner; forms hard AlN in **nitriding** steels	Nitralloy
Lead (Pb), Sulphur (S)	improve machinability (chips break easily)	free-cutting steels

3. Tool steels MEDIUM

Tool steels are high-quality carbon or alloy steels used to make tools for cutting, forming, shaping and shearing other materials.

Requirements: high hardness; wear resistance; adequate toughness (shock resistance); **red / hot hardness** (keeps hardness at the high temperature of cutting); good hardenability with minimum distortion; machinability before hardening.

AISI group	Typical composition	Key feature	Uses
W water-hardening	0.6–1.4 C (plain carbon)	cheap, hard surface, tough core; low hardenability; loses hardness above 200 °C	files, chisels, wood-working tools, hand tools
O oil-hardening (O1)	0.9 C, 1.0 Mn, 0.5 Cr, 0.5 W	less distortion	gauges, dies, punches, taps
A air-hardening (A2)	1.0 C, 5 Cr, 1 Mo	minimum distortion	blanking and forming dies
D high-C high-Cr (D2)	1.5 C, 12 Cr, 1 Mo, 1 V	excellent wear resistance	long-run dies, shear blades, rolls
S shock-resisting (S1)	0.5 C, 1.5 Cr, 2.5 W	high toughness	chisels, punches, rivet sets, pneumatic tools
H hot-work (H13)	0.4 C, 5 Cr, 1.3 Mo, 1 V	resists softening and thermal fatigue	forging dies, die-casting dies, extrusion dies
T tungsten high-speed (T1 = 18-4-1)	0.75 C, 18 W, 4 Cr, 1 V	**red hardness to ~ 600 °C**; cuts at high speed	drills, lathe tools, milling cutters, broaches
M molybdenum high-speed (M2)	0.85 C, 6 W, 5 Mo, 4 Cr, 2 V	cheaper and tougher than T-type; most used HSS	twist drills, taps, end mills, saw blades
P mould steels (P20)	low C, Cr–Mo	easily machined, polished	plastic injection moulds

4. Stainless steels and wear-resistant steels HIGH

DEFINITION

Stainless steels are iron alloys with at least **10.5–12 % Cr**. The Cr forms a thin, adherent, self-healing **passive film of Cr_2O_3** that protects the metal from corrosion. Ni, Mo, N, Ti and Nb are added to improve particular properties.

Type	Composition	Structure	Properties	Grades and uses
Ferritic	12–27 % Cr, < 0.12 % C, no Ni	BCC ferrite	magnetic; not hardenable by heat treatment; good resistance to stress-corrosion cracking; moderate corrosion resistance; cheap	430, 409: automobile exhaust and trim, kitchen sinks, washing-machine drums

Martensitic	12–18 % Cr, 0.15–1.2 % C	BCT martensite after quench	magnetic; **hardenable** (Q + T); high strength and hardness; lowest corrosion resistance of the stainless steels	410, 420, 440C: cutlery, surgical instruments, valves, turbine blades, ball bearings
Austenitic	16–26 % Cr, 6–22 % Ni (18-8), < 0.08 % C	FCC austenite (Ni stabilizes γ)	non-magnetic; **best corrosion resistance**; very ductile and tough even at cryogenic temperature; strengthened only by cold work; prone to sensitization	304 (18Cr-8Ni), 316 (+2–3 Mo): kitchenware, food, dairy and chemical plant, cryogenic tanks, architecture
Duplex	22–25 % Cr, 5–7 % Ni, 3 % Mo, N	~ 50 % ferrite + 50 % austenite	about twice the yield strength of 304; excellent resistance to SCC and pitting; weldable	2205: oil and gas, desalination, chemical tankers, heat exchangers
Precipitation-hardening (PH)	17 % Cr, 4–7 % Ni + Cu / Al / Nb	martensitic or semi-austenitic + precipitates	very high strength (up to 1400 MPa) through ageing, with good corrosion resistance	17-4 PH, 17-7 PH: aircraft parts, springs, shafts, pump parts

SENSITIZATION (WELD DECAY) IN AUSTENITIC SS: FREQUENTLY ASKED

When 18-8 steel is heated in the range **425–870 °C** (e.g. near a weld), **chromium carbide $Cr_{23}C_6$** precipitates along the grain boundaries. The adjacent zone loses Cr below 12 % and is no longer stainless, so **intergranular corrosion** occurs. **Remedies:** (1) low-carbon grades (304L, 316L, C < 0.03 %); (2) stabilized grades with Ti (321) or Nb (347), which form TiC/NbC instead of Cr carbide; (3) solution anneal at about 1050 °C and quench to redissolve the carbides.

Wear-resistant steels

- **Hadfield manganese steel** (most important): **1.0–1.4 % C, 11–14 % Mn**. It is water-toughened (quenched from 1000–1100 °C) to keep it fully **austenitic** and tough. Under impact or abrasion its surface **work-hardens** from about 200 BHN to over 500 BHN while the core stays tough, so it is self-renewing. Non-magnetic. Hard to machine, so parts are cast or ground. *Uses:* rock and stone crushers, jaws of crushers, railway points and crossings, excavator and dredger bucket teeth, ball-mill liners, tractor treads, burglar-proof safes.
- **High-carbon high-chromium steels** (D2) and **Ni-hard cast iron**: abrasion-resistant liners and rolls.
- **Bearing steel** (AISI 52100: 1 % C, 1.5 % Cr): balls and races.
- **Case-hardened steels** (carburized, nitrided): hard wear-resistant surface with a tough core, e.g. gears and cams.

5. Non-ferrous alloys: Al, Cu, Zn HIGH

5.1 Aluminium and its alloys

Properties of Al: low density (2.7 g/cm³, about ⅓ of steel); FCC, so ductile and formable with no ductile–brittle transition; high electrical and thermal conductivity (about 60 % of Cu); excellent corrosion resistance from a protective Al_2O_3 film; non-toxic, non-magnetic; low melting point (660

°C); high specific strength in alloys. **Limitation:** low strength in the pure state, which is improved by alloying, cold work and **age (precipitation) hardening**.

Series	Main alloying element	Heat-treatable?	Example and uses
1xxx	≥ 99 % Al	No	1100: foil, electrical conductors, chemical equipment
2xxx	Cu (+ Mg)	**Yes**	2024 / 2017 (duralumin): aircraft structures, rivets, truck wheels
3xxx	Mn	No	3003: cooking utensils, beverage cans, heat exchangers
4xxx	Si	No	welding filler wire, brazing
5xxx	Mg	No	5052, 5083: marine and ship hulls, pressure vessels
6xxx	Mg + Si	**Yes**	6061, 6063: window frames, extrusions, bicycle frames, automobile parts
7xxx	Zn (+ Mg, Cu)	**Yes**	7075: highest strength (about 570 MPa); aircraft wings and spars

5.2 Copper and its alloys

Properties of Cu: excellent electrical and thermal conductivity (second only to Ag); FCC, so very ductile and malleable; good corrosion resistance; non-magnetic; density 8.96 g/cm³; easily joined; attractive colour. **Pure Cu** (electrolytic tough pitch, ETP, 99.9 %): electrical wiring, bus bars, heat exchangers. Brass = Cu + Zn. Bronze = Cu + Sn (more broadly Cu + any element other than Zn).

Brasses (Cu–Zn)

- **α-brasses** (up to about 36 % Zn): single-phase FCC, very ductile, cold-workable. Examples: gilding metal 95/5, red brass 85/15, cartridge brass 70/30, yellow brass 65/35.
- **α + β brasses** (36–45 % Zn): β is BCC, harder and less ductile; hot-workable. Example: Muntz metal 60/40.
- **Dezincification:** brass with more than 15 % Zn in seawater loses Zn selectively, leaving porous weak copper. It is prevented by adding 0.02–0.06 % As, Sb or P (inhibited brass), or 1 % Sn (Admiralty and naval brass).

Bronzes

- **Tin bronze** (Cu + 5–20 % Sn): stronger and more corrosion-resistant than brass, with good bearing properties.
- **Phosphor bronze** (Cu + 4–11 % Sn + 0.1–0.35 % P): P deoxidizes and hardens; springs, bearings, gears, bushes.
- **Aluminium bronze** (Cu + 5–11 % Al, + Fe, Ni): high strength, excellent seawater and oxidation resistance, gold colour; marine propellers, pump parts, coins.
- **Beryllium copper** (Cu + 1.7–2 % Be): age-hardenable to about 1400 MPa, the strongest Cu alloy; springs, diaphragms, **non-sparking tools** for mines and refineries.
- **Silicon bronze** (Cu + 3 % Si): marine hardware, boilers, fasteners.

5.3 Zinc and its alloys

Properties of Zn: HCP; density 7.14 g/cm³; low melting point (419 °C), so it is ideal for **die casting**; good fluidity; anodic to steel (sacrificial). Recrystallizes at about room temperature, so it cannot be work-hardened. **Uses:** about half of all Zn goes into **galvanizing** steel; also brass making, dry-cell cases, sacrificial anodes and roofing sheets.

Zamak die-casting alloys (Zn + 4 % Al + 0.04 % Mg; Zamak 5 adds 1 % Cu): good dimensional accuracy, thin sections, easy plating. Used for carburettor and fuel-pump bodies, door handles, locks, zip fasteners, toys and automobile trim. Zn–22 % Al is superplastic.

5.4 Master table: important non-ferrous alloys Asked: End Sem 2024

Alloy	Composition	Properties	Applications
Duralumin	Al + 3.5–4.5 % Cu, 0.4–0.8 % Mg, 0.4–0.7 % Mn, ~ 0.5 % Si	light (2.8 g/cm³); **age-hardenable** (solution treat about 500 °C, quench, age); UTS up to about 400–450 MPa, close to mild steel; good machinability; poorer corrosion resistance (hence **Alclad**: clad with pure Al)	aircraft structures and skins, rivets, automobile and truck parts, surgical and orthopaedic devices, high-speed train bodies
Y-alloy	Al + 4 % Cu, 2 % Ni, 1.5 % Mg	age-hardenable; **keeps strength at high temperature** (200–250 °C); good castability	IC-engine **pistons**, cylinder heads, crankcases
Brass (general)	Cu + Zn (5–45 %)	stronger and cheaper than Cu; good corrosion resistance; easily cast, machined and formed; gold-like colour	plumbing fittings, valves, radiators, musical instruments, electrical terminals, decorative items
Cartridge brass	70 % Cu, 30 % Zn (α)	maximum ductility of all brasses; excellent cold formability (deep drawing)	cartridge cases, radiator cores, lamp fittings, deep-drawn articles
Muntz metal	60 % Cu, 40 % Zn (α + β)	stronger and harder, less ductile; good hot-workability; cheap	condenser tube plates, ship sheathing, nuts and bolts, valve stems
Admiralty / naval brass	71Cu-28Zn-1Sn / 60Cu-39Zn-1Sn	Sn resists dezincification in seawater	condenser tubes, marine hardware, propeller shafts
Bronze (tin bronze)	Cu + 5–20 % Sn	harder, stronger and more corrosion-resistant than brass; good wear and bearing properties; low friction	bearings, bushes, gears, statues, coins, bells (bell metal ~ 20 % Sn)
Gun metal	88 % Cu, 10 % Sn, 2 % Zn	strong, tough, pressure-tight castings; good corrosion and wear resistance	bearings, valves, pump bodies, steam fittings, gears (historically guns)
Phosphor bronze	Cu + 4–11 % Sn + 0.1–0.35 % P	high strength and elasticity, fatigue and wear resistant, low friction	springs, bearings, worm wheels, electrical contacts
German silver (nickel silver)	~ 60 % Cu, 20 % Zn, 20 % Ni (no silver)	silvery-white, corrosion resistant, high electrical resistivity	cutlery, utensils, jewellery, musical instruments, resistance wires, keys
Cupronickel	70 % Cu, 30 % Ni (75/25 for coins)	excellent seawater corrosion resistance	marine condenser tubes, coins
Zamak 3	Zn + 4 % Al + 0.04 % Mg	low melting point, excellent castability	die-cast handles, locks, carburettors

BRASS VS BRONZE (2 MARKS)

	Brass	Bronze
Composition	Cu + Zn	Cu + Sn (or Al, Si, Be, P)
Colour	bright yellow (gold-like)	reddish brown
Strength and hardness	lower	higher
Corrosion resistance	good, but dezincification in seawater	better, especially in seawater
Friction and wear	moderate	low friction, so better for bearings
Cost and machinability	cheaper; excellent machinability	costlier (Sn)
Uses	fittings, radiators, cartridge cases	bearings, bushes, springs, propellers, statues

6. Corrosion: basics and types HIGH

DEFINITION

Corrosion is the destructive and unintentional deterioration of a metal by chemical or electrochemical reaction with its environment. In effect it is **extractive metallurgy in reverse**: the metal returns to its stable oxide or compound state.

Dry vs wet corrosion

Dry (chemical) corrosion	Wet (electrochemical) corrosion
Direct chemical attack by gases (O_2, Cl_2, H_2S, SO_2) at high temperature, with no liquid electrolyte	Needs an electrolyte (moisture, seawater, acid); anodic and cathodic areas form
Uniform; the product forms on the spot where attack occurs	Anode corrodes; the product forms between anode and cathode
Slow; adsorption and diffusion mechanism	Fast; electrochemical (galvanic cell) mechanism
e.g. oxidation of Fe in a furnace, tarnishing of Ag	e.g. rusting of iron, corrosion of ship hulls

Pilling–Bedworth ratio (dry oxidation): PBR = volume of oxide / volume of metal consumed = $A_{oxide}\rho_{metal}$ / (n A_{metal} ρ_{oxide}). If PBR < 1 (Mg, Na), the oxide is porous and non-protective. If 1–2 (Al, Cr, Ni, Ti), it is protective. If > 2 (Fe), it cracks and spalls off.

Electrochemical basis (wet corrosion)

Four things are needed: an **anode**, a **cathode**, an **electrolyte**, and a **metallic path** for electrons. Remove any one and corrosion stops (this is the basis of all protection methods).

REACTIONS

Anode (oxidation, corrodes): $M \rightarrow M^{n+} + n\ e^-$

Cathode, acid: $2H^+ + 2e^- \rightarrow H_2\uparrow$ (hydrogen evolution)

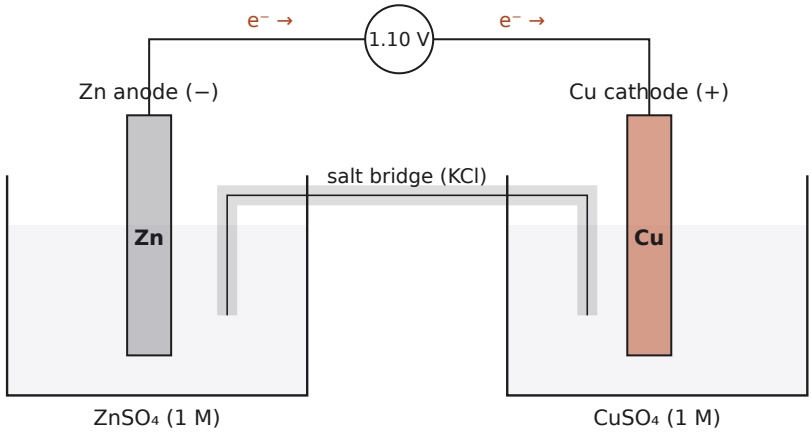
Cathode, acid + O_2: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Cathode, neutral/basic + O_2: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (oxygen absorption)

Metal-ion reduction: $M^{n+} + n\ e^- \rightarrow M$

Galvanic cell HIGH

When two dissimilar metals are electrically connected in an electrolyte, the more **active** metal (lower, more negative electrode potential) becomes the **anode** and corrodes. The more **noble** metal becomes the cathode and is protected. The Daniell cell (Zn–Cu) is the classic example.



Zn–Cu galvanic cell. $E_{cell} = E_{cathode} - E_{anode} = +0.34 - (-0.76) = 1.10$ V.

Electrode reaction	E° (V)
$Au^{3+} + 3e^- \rightarrow Au$	+1.420
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.229
$Ag^+ + e^- \rightarrow Ag$	+0.800
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.340
$2H^+ + 2e^- \rightarrow H_2$	0.000
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.136
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.250
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.403
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.440
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.763
$Al^{3+} + 3e^- \rightarrow Al$	−1.662
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.363

Standard EMF series (25 °C, 1 M). Top = noble (cathodic); bottom = active (anodic).

Galvanic series (practical ranking in **seawater**, including alloys):

More noble (cathodic) ↑
Platinum · Gold · Graphite · Titanium · Silver · 316 SS (passive) · 304 SS (passive) · Inconel / Nickel (passive) · Monel · Cupronickel · Bronzes · Copper · Brasses · Nickel (active) · Tin · Lead · 316 / 304 SS (active) · Cast iron · Iron and steel · Aluminium alloys · Cadmium · Pure aluminium · Zinc · Magnesium and its alloys
↓ More active (anodic)

EMF vs galvanic series: the EMF series is for pure metals in 1 M solutions of their own ions, a theoretical and fixed ranking. The galvanic series covers metals *and alloys* in a real environment (seawater), and the same alloy can appear in both an active and a passive position.

NERNST EQUATION (NON-STANDARD CONCENTRATIONS)

$\Delta V = (V_2^\circ - V_1^\circ) - (0.0592 / n) \log ([M_1^{n+}] / [M_2^{n+}])$ (25 °C)

Metal 1 is oxidized (anode); metal 2 is reduced (cathode).

WORKED NUMERICAL: CELL POTENTIAL

(a) Zn–Cu standard cell: E = 0.340 − (−0.763) = **1.10 V**; Zn corrodes.

(b) Ni in 10^{-3} M Ni^{2+} connected to Cd in 0.5 M Cd^{2+}. Cd (−0.403) is more active, so Cd is oxidized (metal 1) and Ni^{2+} is reduced (metal 2).
$\Delta V = (-0.250 - (-0.403)) - (0.0592/2) \log (0.5/10^{-3}) = 0.153 - 0.0296 \times 2.699 = 0.153 - 0.080 =$ **+0.073 V**. It is positive, so the reaction is spontaneous as written.

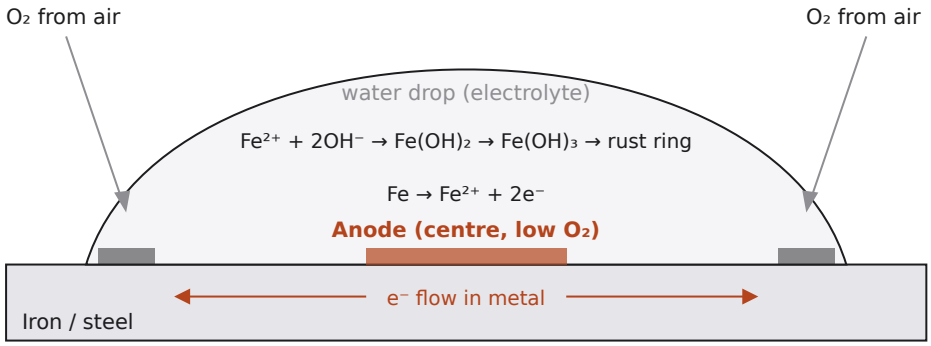
CORROSION PENETRATION RATE

$CPR = K\,W / (\rho\,A\,t)$ $K = 87.6 \rightarrow$ mm/yr (W in mg, ρ in g/cm³, A in cm², t in h)

Worked: a steel sheet (ρ = 7.9) of area 400 cm² loses 375 g in 1 year (8760 h). CPR = 87.6 × 375 000/(7.9 × 400 × 8760) = **1.19 mm/yr**.

Rusting of iron: mechanism HIGH

Rusting is the electrochemical corrosion of iron in the presence of **both water and oxygen**. Different parts of the same iron surface act as anode and cathode (impurities, stresses, or **differential aeration**). Under a water drop, the centre (poor in O_2) becomes the **anode** and the edge (rich in O_2) becomes the **cathode**.



Cathodes at the rim (O_2-rich): $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Differential-aeration cell under a water drop on iron.

REACTIONS (WRITE ALL OF THEM)

Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (×2)

Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Overall: $2Fe + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2$ (ferrous hydroxide, greenish)

Further oxidation: $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$ (ferric hydroxide)

Dehydration: $2Fe(OH)_3 \rightarrow Fe_2O_3 \cdot xH_2O$ (**rust**, reddish brown, hydrated ferric oxide)

In acidic water the cathode reaction is $2H^+ + 2e^- \rightarrow H_2$ (hydrogen evolution). Rust is porous and non-adherent (PBR > 2), so it does not protect the iron underneath and attack continues. Salt water corrodes faster because it is a better electrolyte.

Forms (types) of corrosion

Type	Description and cause	Example	Prevention

Uniform attack	Even corrosion over the whole exposed surface; most common, predictable	rusting of steel sheet, tarnish on silver	coatings, corrosion allowance, inhibitors
Galvanic (bimetallic)	Two dissimilar metals in contact in an electrolyte; the more active one corrodes. A **small anode with a large cathode** is very dangerous	steel bolts in copper plate, Zn–Cu	choose metals close in the galvanic series; insulate joints; large anode area; coat the cathode
Crevice	Concentration (O_2-depletion) cell in narrow gaps, under gaskets, washers and deposits	under rivet heads, bolt washers	welded joints instead of riveted; non-absorbing gaskets; avoid stagnant areas
Pitting	Localized attack forming small deep pits; autocatalytic; very dangerous because it is hard to detect	stainless steel in chloride (seawater)	add Mo (316 SS); polish surfaces; avoid Cl^-
Intergranular	Attack along grain boundaries because of Cr depletion (sensitization)	weld decay of 18-8 SS	low-C (L grades), Ti/Nb stabilization, solution anneal
Selective leaching	One element of an alloy is removed preferentially	**dezincification** of brass; graphitic corrosion of cast iron	As/Sb/P or Sn additions; change alloy
Erosion–corrosion	Combined chemical attack and mechanical abrasion by a fast-moving fluid that removes the protective film	pipe elbows, pump impellers, propellers	reduce velocity and turbulence; streamlined design; harder alloys
Stress corrosion cracking (SCC)	Cracking under tensile stress (applied or residual) together with a specific corrosive environment	brass in ammonia (season cracking); SS in hot chlorides	stress-relief anneal; lower stress; change environment; duplex SS
Hydrogen embrittlement	Atomic H diffuses into steel and lowers ductility, causing brittle failure	high-strength steel during pickling or electroplating	bake at about 200 °C; lower-strength steel; avoid H sources

Factors affecting the rate of corrosion

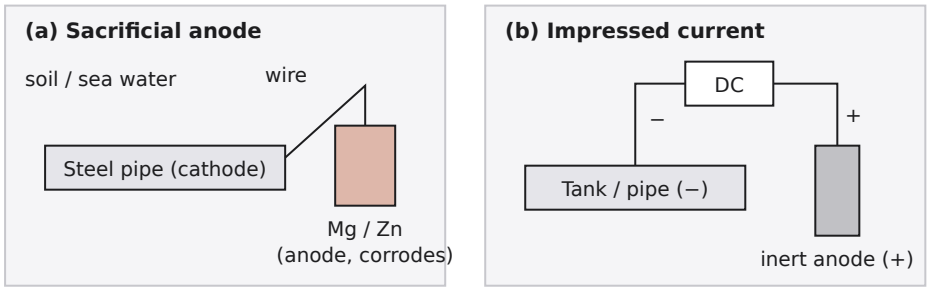
- **Nature of the metal:** position in the galvanic series (bigger potential difference means faster attack); **anode-to-cathode area ratio** (small anode and large cathode is severe); purity (impurities form local cells); nature of the oxide film (PBR); physical state (stressed or cold-worked areas are anodic; grain boundaries are anodic).
- **Nature of the environment:** temperature ↑ → rate ↑; humidity and moisture; pH (acids accelerate); dissolved O_2 and differential aeration; impurities such as Cl^-, SO_2, H_2S; conductivity of the electrolyte (seawater is faster than fresh water); fluid velocity.

7. Methods of protection from corrosion HIGH

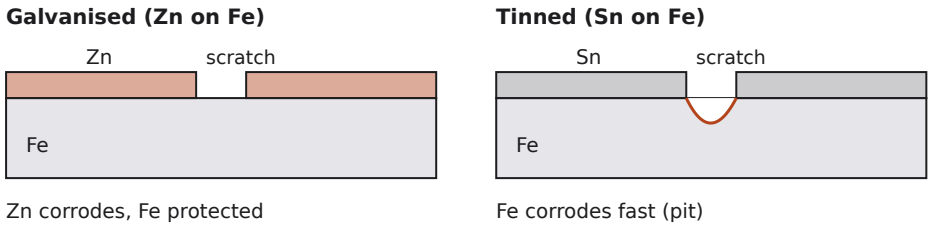
1. **Proper selection of material:** use noble or passive metals (SS, Ti, Cu alloys) or non-metals (plastics, ceramics) where economical. Use pure, homogeneous metal.
2. **Proper design:**

- avoid contact of dissimilar metals, or insulate them (gaskets, washers);
- if contact is unavoidable, make the **anode area large** and the cathode small;
- avoid crevices (weld rather than rivet), sharp corners and stagnant pockets;
- provide drainage; allow easy inspection, cleaning and replacement;
- add a corrosion allowance to the thickness; avoid residual stresses (stress-relieve).

3. **Modifying the environment:** lower the temperature and fluid velocity; remove O_2 (deaeration with hydrazine or Na_2SO_3 in boiler water); dehumidify; neutralize acids; add **inhibitors**.
   - *Anodic inhibitors* (chromates, phosphates, nitrites) form a passive film on the anode.
   - *Cathodic inhibitors* (Zn, Mg and Ni salts, organic amines) block the cathode reaction.
   - *Vapour-phase inhibitors* are used for packaging.
4. **Protective coatings:**
   - *Metallic, anodic coatings*: coating metal more active than the base, e.g. **galvanizing** (Zn on steel, hot dip at about 450 °C) or cadmium plating. They protect even when scratched.
   - *Metallic, cathodic coatings*: a nobler metal, e.g. **tinning** (Sn on steel), Ni or Cr plating. They protect only while unbroken.
   - Methods of applying: hot dipping, electroplating, metal spraying, cladding (Alclad), cementation (sherardizing with Zn powder, calorizing with Al, chromizing).
   - *Inorganic / chemical conversion coatings*: anodizing (thick Al_2O_3 on Al), phosphating (Fe/Zn phosphate under paint, e.g. car bodies), chromating, enamelling.
   - *Organic coatings*: paints (red-lead or zinc-chromate primer + top coat), varnishes, lacquers, epoxy, rubber and plastic linings.
5. **Cathodic protection:** make the structure the cathode so that it cannot corrode.
   - *Sacrificial anode method:* a more active metal (Mg, Zn, Al) is connected to the structure and corrodes instead. It is replaced periodically. Used for buried pipelines, ship hulls, water heaters and offshore platforms.
   - *Impressed current method:* a DC supply makes the structure the cathode, with an inert anode (graphite, high-Si iron, Pt-coated Ti) in the soil or water. Used for long pipelines, tanks and large structures.
6. **Anodic protection and passivation:** for metals that passivate (SS, Ti), applying an anodic potential or using oxidizing acids (HNO_3) keeps a stable passive film.



Cathodic protection: (a) sacrificial anode; (b) impressed current.



When the coating is scratched, Zn (anodic) protects the steel sacrificially. Sn (cathodic) makes the exposed steel a small anode next to a large cathode, so it pits rapidly.

Galvanizing	Tinning
Coating of **Zn** on steel (hot dip in molten Zn at about 450 °C)	Coating of **Sn** on steel (hot dip at about 230 °C or electrolytic)
Zn is **anodic** to Fe, giving sacrificial protection	Sn is **cathodic** to Fe, giving barrier protection only
Protects Fe even if the coating is scratched or broken	If scratched, Fe corrodes faster than uncoated steel
Zn dissolves in dilute acids and is toxic, so **not used for food**	Sn is non-toxic, so used for **food cans** and containers
Uses: roofing sheets, pipes, buckets, wires, fencing	Uses: food cans, utensils, copper wires (for soldering)

Further reading: Callister Ch. 11 (ferrous and non-ferrous alloys §11.2–11.3), Ch. 17 (corrosion §17.2–17.9).

Likely exam questions (Unit 2)

#	Question	Marks
1	Give the composition, properties and applications of (a) duralumin (b) brass (or gun metal, Y-alloy, German silver, Muntz metal).	2–3
2	Classify plain carbon steels. Give the properties and uses of each class. What are their limitations?	4
3	Discuss the effect of alloying elements (Ni, Cr, Mo, W, V, Mn, Si) on the properties of steel.	4–5
4	What are stainless steels? Classify them and give the composition, properties and applications of each. What is weld decay and how is it prevented?	5
5	Write short notes on (a) Hadfield manganese steel (b) high-speed steel (c) tool steels.	3
6	Differentiate between brass and bronze. Explain dezincification.	3
7	Explain the electrochemical mechanism of rusting of iron with reactions.	4
8	What is a galvanic cell? Distinguish between the EMF series and the galvanic series.	3–4
9	Describe the various forms of corrosion with examples.	5
10	Discuss methods of corrosion protection. Explain cathodic protection. Compare galvanizing and tinning.	5

MODEL ANSWER: DURALUMIN AND BRASS (2 MARKS, "ASKED: END SEM 2024" TYPE)

Duralumin: Al + 4 % Cu + 0.5 % Mg + 0.5 % Mn (+ 0.5 % Si). Light (2.8 g/cm³), age-hardenable to about 400 MPa (close to mild steel), good machinability, moderate corrosion resistance (clad with pure Al as Alclad). *Uses:* aircraft structures, rivets, automobile parts, surgical instruments.

Brass: Cu + Zn, e.g. cartridge brass 70Cu–30Zn and Muntz metal 60Cu–40Zn. Good strength and ductility, corrosion resistant, easily cast, machined and deep-drawn, attractive yellow colour. *Uses:* cartridge cases, radiator cores, plumbing fittings, valves, musical instruments, condenser plates.

MODEL ANSWER: MECHANISM OF RUSTING (4 MARKS)

Rusting is electrochemical (wet) corrosion of iron that needs both water and O_2. A differential-aeration cell forms: the region with less O_2 (e.g. the centre of a water drop) becomes the anode and the O_2-rich region becomes the cathode. Draw the water-drop figure.
Anode: $Fe \rightarrow Fe^{2+} + 2e^-$. Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$; $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$; $Fe(OH)_3 \rightarrow Fe_2O_3 \cdot xH_2O$ (rust).
Rust deposits between the anode and cathode. It is porous (PBR > 2), so attack continues. Salt and acids accelerate rusting. Prevented by paint, galvanizing and cathodic protection.

MODEL ANSWER: EFFECT OF NI, CR AND MO (3 MARKS)

Ni: austenite stabilizer; raises toughness (especially at low temperature), strength and hardenability; with Cr, gives austenitic stainless steel. **Cr:** carbide former; raises hardenability, wear resistance and high-temperature strength; ≥ 12 % gives corrosion resistance through a passive Cr_2O_3 film. **Mo:** raises hardenability and creep strength, prevents temper embrittlement, adds red hardness in HSS and pitting resistance in 316 SS.

UNIT 3 · ~8 CONTACT HRS

Solidification, Phase Diagrams & Heat Treatment

Most examined: the Fe–Fe_3C diagram and its reactions, the TTT diagram, annealing vs normalizing, Gibbs phase rule and lever-rule numericals. This unit alone can be worth 16 of your 40 marks.

HOW THIS UNIT IS EXAMINED (END SEM PATTERN: ANY 5 OF 6, 8 MARKS EACH)

- **Fe–C diagram: draw, mark phases, explain reactions (6 marks).** Asked in **both** Mid Sem 2024 and End Sem 2024. Practise drawing it from memory 3 times.
- **Gibbs phase rule derivation (2)**, **annealing vs normalizing microstructures (3)**, **TTT diagram of eutectoid steel (4)**.
- Typical splits are 6+2, 5+3 and 4+4. Short parts come from case hardening, tempering, Jominy and precipitation hardening.

1. Basic terms: phases in metal systems MEDIUM

DEFINITIONS

- **Component:** a pure metal or compound making up an alloy (Fe and C, or Cu and Ni). **System:** a series of alloys made from the same components.
- **Phase:** a physically and chemically homogeneous part of a system, separated from other phases by a definite boundary (e.g. α, γ, liquid, Fe_3C).
- **Solubility limit:** the maximum amount of solute that can dissolve in the solvent to form a solid solution at a given temperature.
- **Equilibrium:** the state of minimum free energy. A **phase diagram** (equilibrium diagram) maps the phases present against temperature and composition at constant pressure (1 atm), for very slow cooling.
- **Microstructure:** the number, proportion, size, shape and distribution of phases, as seen under a microscope.

Types of phases in alloys

Phase type	What it is	Example
Substitutional solid solution	Solute atoms replace solvent atoms on lattice sites	Cu–Ni (complete solubility), Cu–Zn (brass)
Interstitial solid solution	Small solute atoms (C, N, H, B) sit in interstitial voids	C in γ-Fe (austenite), C in α-Fe (ferrite)
Intermediate phase / intermetallic compound	Has a fixed (or narrow) composition and its own crystal structure; usually hard and brittle	Fe_3C, $CuAl_2$ (θ), Mg_2Pb
Mechanical mixture	Two or more phases intimately mixed	Pearlite (α + Fe_3C), eutectic Pb–Sn

HUME-ROTHERY RULES (COMPLETE SUBSTITUTIONAL SOLUBILITY)

(1) Atomic-size difference below about 15%. (2) Same crystal structure. (3) Similar electronegativity, otherwise intermetallics form. (4) Same valence; a metal dissolves a higher-valence metal more readily than a lower-valence one. Cu–Ni satisfies all four, so it is **isomorphous**.

2. Gibbs phase rule HIGH Asked: End Sem 2024 (2 marks: derivation)

FORMULA

$F = C - P + 2$ (general) $\quad F = C - P + 1$ (condensed: pressure fixed at 1 atm)

F = degrees of freedom: the number of variables (T, P, composition) that can be changed independently without changing the number of phases. C = number of components. P = number of phases in equilibrium.

MODEL ANSWER: DERIVE THE GIBBS PHASE RULE (2 MARKS)

Consider a system of **C** components distributed among **P** phases in equilibrium.

1. **Total variables.** The composition of each phase needs (C − 1) mole fractions, because the fractions add up to 1. For P phases that gives P(C − 1). Adding temperature and pressure: $\text{Variables} = P(C-1) + 2$.
2. **Equations (constraints).** At equilibrium, the chemical potential of each component is equal in every phase: $\mu_i^{\alpha} = \mu_i^{\beta} = \ldots$ gives (P − 1) equations per component. For C components: $\text{Equations} = C(P-1)$.
3. **Degrees of freedom** = variables − equations = P(C − 1) + 2 − C(P − 1) = PC − P + 2 − PC + C, so **F = C − P + 2**.
4. Metallurgical systems are studied at constant pressure (1 atm), which removes one variable, so **F = C − P + 1** (condensed phase rule).

WORKED EXAMPLES (CONDENSED RULE, BINARY C = 2)

Situation	P	F = C − P + 1	Meaning
Single-phase field (e.g. γ region)	1	2	T and composition can both vary (bivariant)
Two-phase field (e.g. α + L)	2	1	Fix T and the phase compositions are fixed by the tie-line (univariant)
Eutectic point, 1147 °C (L ⇌ γ + Fe_3C)	3	0	Invariant: T and all compositions fixed, so the cooling curve shows a plateau
Eutectoid point, 727 °C (γ ⇌ α + Fe_3C)	3	0	Invariant
Pure metal melting (C = 1, P = 2)	2	1 − 2 + 1 = 0	Melts at a fixed temperature
Triple point of water (general rule, C = 1, P = 3)	3	1 − 3 + 2 = 0	Unique T and P

3. Solidification of metals MEDIUM

Solidification happens in two steps: **nucleation** (tiny stable solid particles form) and **growth** (those nuclei grow into grains). A liquid must be **undercooled** ($\Delta T = T_m - T$) below the melting point before solid can form.

3.1 Homogeneous nucleation and the critical radius

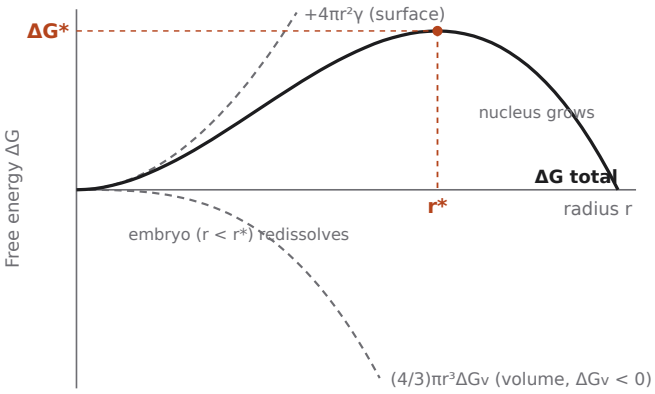
Homogeneous nucleation happens uniformly inside the pure liquid, with no foreign surfaces. For a spherical embryo of radius r:

$$\Delta G = (4/3)\pi r^3 \Delta G_v + 4\pi r^2 \gamma$$

ΔG_v = free-energy change per unit volume. It is negative below T_m (the driving force) and grows with ΔT. γ = solid–liquid surface energy per unit area (always positive).

$$r^* = -2\gamma / \Delta G_v \qquad \Delta G^* = 16\pi\gamma^3 / (3\Delta G_v^2)$$

Using $\Delta G_v = \Delta H_f \Delta T / T_m$: $r^* = -2\gamma T_m / (\Delta H_f \Delta T)$



ΔG against embryo radius. Below r* the embryo redissolves; above r* the nucleus grows because adding atoms lowers ΔG. (Callister §10.3)

- Set $d\Delta G/dr = 0$ to get r* (the critical radius) and ΔG^* (the activation energy barrier).
- More undercooling makes ΔG_v larger, so r* and ΔG^* get smaller. More nuclei form, giving **finer grains**, which is why fast cooling refines the grain size.
- Homogeneous nucleation needs very large undercooling, about $0.2T_m$ (hundreds of °C), so it is rare in practice.

WORKED NUMERICAL 1: CRITICAL RADIUS

Q. For a metal, $\gamma = 0.2$ J/m² and $\Delta G_v = -2 \times 10^8$ J/m³. Find r* and ΔG^*.

$r^* = -2\gamma/\Delta G_v = -2(0.2)/(-2 \times 10^8) = \mathbf{2 \times 10^{-9}\ m = 2\ nm}$.

$\Delta G^* = 16\pi\gamma^3/(3\Delta G_v^2) = 16\pi(0.008)/(3 \times 4 \times 10^{16}) = 0.4021/(1.2 \times 10^{17}) = \mathbf{3.35 \times 10^{-18}\ J}$.

WORKED NUMERICAL 2 (CALLISTER EXAMPLE 10.1, PURE GOLD)

$\Delta H_f = -1.16 \times 10^9$ J/m³, $\gamma = 0.132$ J/m², $T_m = 1064$ °C = 1337 K, undercooling $\Delta T = 230$ K.

$r^* = -2\gamma T_m/(\Delta H_f \Delta T) = -2(0.132)(1337)/[(-1.16 \times 10^9)(230)] = 352.97/(2.668 \times 10^{11}) = \mathbf{1.32 \times 10^{-9}\ m = 1.32\ nm}$.

$\Delta G^* = 16\pi\gamma^3 T_m^2/(3\Delta H_f^2 \Delta T^2) = \approx \mathbf{9.7 \times 10^{-19}\ J}$ (Callister gives 9.64×10^{-19} J). This nucleus is about 137 FCC unit cells, i.e. about 548 atoms.

3.2 Heterogeneous nucleation

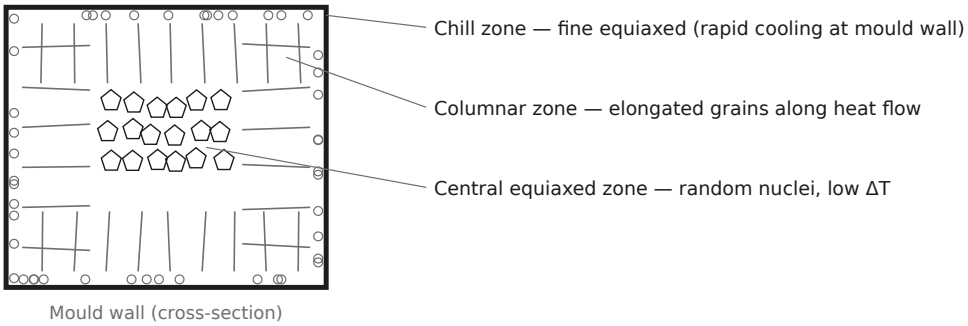
- Nuclei form on **existing surfaces**: mould walls, impurities, oxide particles, or deliberately added **inoculants** (grain refiners, e.g. Ti–B in Al, Mg/Ce in cast iron).
- The surface lowers the energy barrier: $\Delta G^*_{het} = \Delta G^*_{hom} \cdot S(\theta)$, where $S(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2/4 \leq 1$ and θ is the wetting (contact) angle. r* is the same, but much less undercooling

is needed (a few °C). This is how real castings nucleate.

3.3 Growth: planar and dendritic

- **Planar growth:** when the liquid ahead of the interface is hotter (positive temperature gradient), any bump on the solid melts back, so the interface stays flat. Typical of pure metals in a well-insulated mould.
- **Dendritic growth:** when the liquid is undercooled (negative gradient), a bump finds colder liquid and grows faster. It forms tree-like **dendrites** with primary, secondary and tertiary arms along preferred crystal directions (<100> in cubic metals). The latent heat flows into the undercooled liquid. Dendrites are the normal way alloys and castings solidify.
- A fast cooling rate gives finer dendrite arm spacing, finer grains, and better strength and toughness.

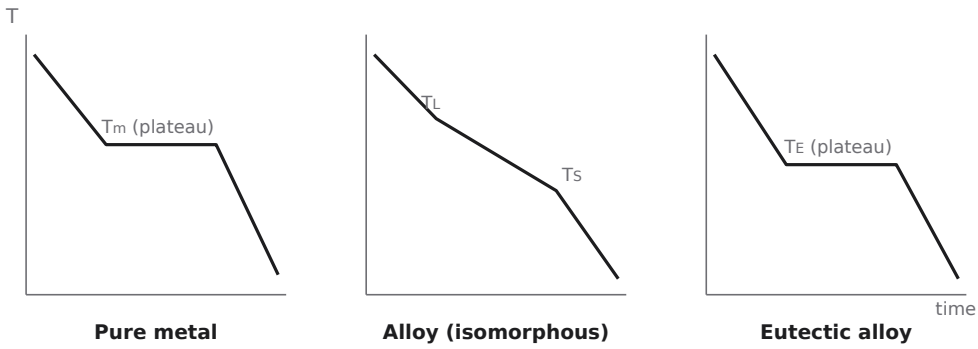
3.4 Cast (ingot) structure



Three zones in a cast ingot.

1. **Chill zone:** the liquid touching the cold mould wall cools very fast and nucleates heavily, giving a thin layer of fine, randomly oriented equiaxed grains.
2. **Columnar zone:** grains with favourable orientation grow inward, opposite to the heat flow, as long column-like grains. This zone gives anisotropic properties.
3. **Central equiaxed zone:** the remaining liquid has low undercooling. Broken dendrite arms and inoculants act as nuclei, giving coarse equiaxed grains. Shrinkage cavities (pipe) and segregation also gather here.

3.5 Cooling curves



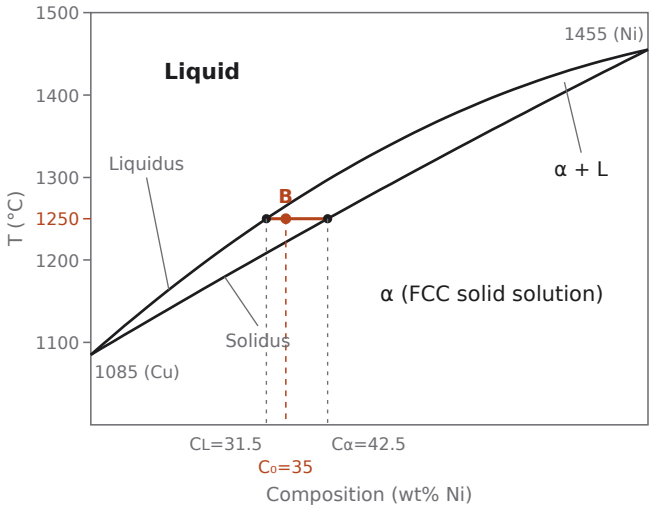
A pure metal and a eutectic alloy both freeze at a constant temperature (F = 0, plateau). An isomorphous alloy freezes over a range from T_L to T_S (F = 1, change in slope).

4. Binary isomorphous system and solidification of alloys HIGH

An **isomorphous** system has complete liquid and solid solubility, e.g. Cu–Ni (both FCC, Hume-Rothery rules satisfied). Its diagram has three regions: liquid, α (solid solution) and α + L, bounded by the **liquidus** (above it everything is liquid) and the **solidus** (below it everything is solid).

Three questions you can answer for any point (T, C_0):

1. **Phases present:** read off the region the point lies in.
2. **Phase compositions:** draw a horizontal **tie-line** across the two-phase field. Where it meets the liquidus gives C_L; where it meets the solidus gives C_α.
3. **Phase amounts:** use the **lever rule**.



Cu–Ni diagram with the tie-line at 1250 °C for a 35 wt% Ni alloy (point B). Data from Callister §9.8.

LEVER RULE (WITH DERIVATION)

Mass balance: $W_\alpha + W_L = 1$ and $W_\alpha C_\alpha + W_L C_L = C_0$. Solving these two equations:

$$W_L = (C_\alpha - C_0)/(C_\alpha - C_L) \qquad W_\alpha = (C_0 - C_L)/(C_\alpha - C_L)$$

Memory trick: each phase's fraction = **length of the opposite arm** of the tie-line ÷ total tie-line length, with the fulcrum at C_0.

WORKED NUMERICAL 3: CU–NI LEVER RULE

Q. A 35 wt% Ni–Cu alloy is held at 1250 °C. Find the phases, their compositions and their amounts.

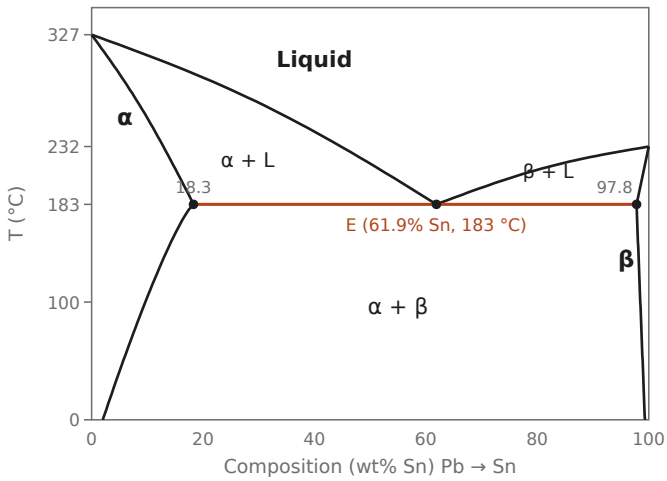
The point lies in the α + L field. Tie-line: C_L = 31.5 wt% Ni, C_α = 42.5 wt% Ni.

$W_L = (42.5 - 35)/(42.5 - 31.5) = 7.5/11 =$ **0.68**; $W_\alpha = (35 - 31.5)/11 = 3.5/11 =$ **0.32**.

Equilibrium and non-equilibrium solidification of an alloy

- **Equilibrium (very slow cooling):** solidification starts at the liquidus, with the first solid richer in the high-melting component (Ni). As T falls, the solid composition follows the solidus and the liquid follows the liquidus. Diffusion keeps each phase uniform. It finishes at the solidus with a uniform solid of composition C_0.
- **Non-equilibrium (practical cooling):** diffusion in the solid can't keep up, so each grain has a Ni-rich centre and Cu-rich outer layers. This is **coring** (micro-segregation). The grain boundaries may melt early on reheating. Fix it with **homogenization annealing** below the solidus.

5. Invariant reactions: eutectic, eutectoid, peritectic, peritectoid HIGH



Binary eutectic system (Pb–Sn), with limited solid solubility. α is Pb-rich and β is Sn-rich. Callister §9.11.

Key lines in a eutectic diagram: liquidus (two branches meeting at E), **solidus**, **solvus** (solubility limit of B in α and of A in β, decreasing as T falls) and the **eutectic isotherm** (183 °C).

Eutectic (Greek: "easily melted"): the composition with the lowest melting point. It freezes at one temperature into a lamellar mixture of α + β.

Alloys left of E are **hypoeutectic** (primary α + eutectic). Alloys right of E are **hypereutectic** (primary β + eutectic).

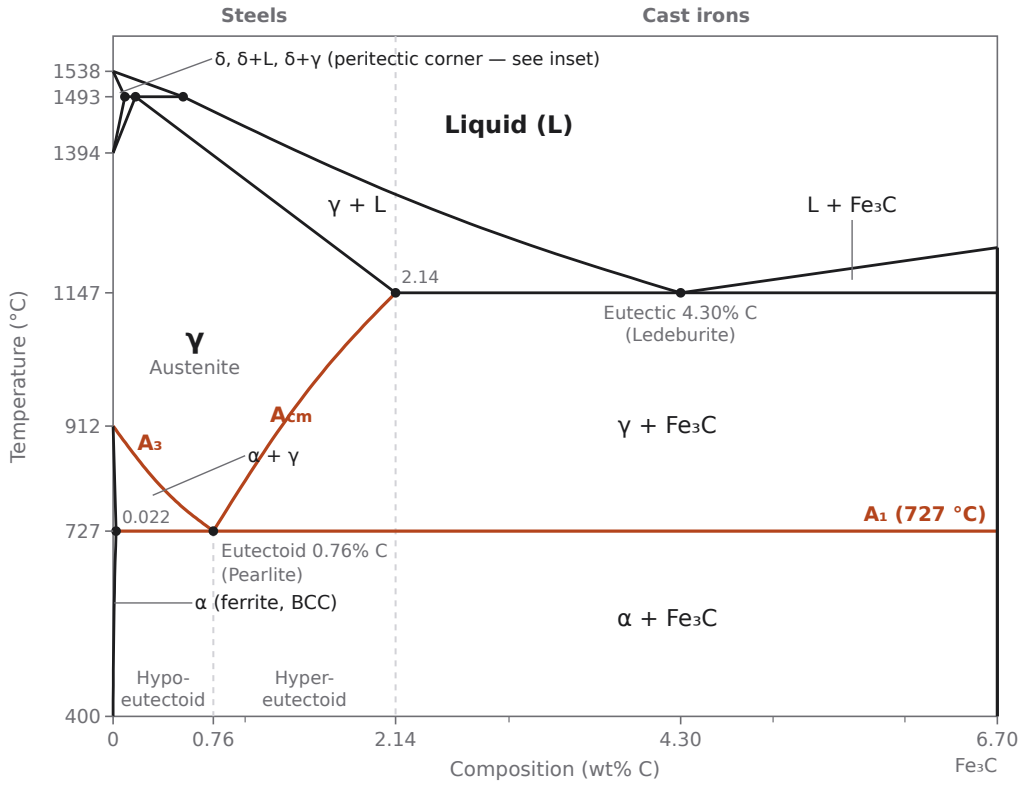
Soft solder (60Sn–40Pb) is close to the eutectic, so it melts sharply at a low temperature.

Reaction	On cooling	Example (T, compositions)
Eutectic	L ⇌ α + β (one liquid gives two solids)	Fe–C: L(4.30) → γ(2.14) + Fe_3C(6.70) at 1147 °C (ledeburite). Pb–Sn: L(61.9) → α(18.3) + β(97.8) at 183 °C
Eutectoid	γ ⇌ α + β (one solid gives two solids)	Fe–C: γ(0.76) → α(0.022) + Fe_3C(6.70) at 727 °C (pearlite). Cu–Zn: δ → γ + ε at 560 °C
Peritectic	L + α ⇌ β (liquid + solid give a new solid)	Fe–C: L(0.53) + δ(0.09) → γ(0.17) at 1493 °C. Cu–Zn: δ + L → ε at 598 °C
Peritectoid	α + β ⇌ γ (two solids give a new solid)	Rare; seen in a few systems (some Cu- and Ni-based alloys). Learn the form only.
Monotectic	L_1 ⇌ L_2 + α	Cu–Pb (≈ 955 °C)
Syntectic	L_1 + L_2 ⇌ α	Very rare (e.g. Na–Zn)
Congruent transformation	One phase changes to another of the same composition	Melting of an intermetallic compound; pure-metal allotropy (α-Fe ⇌ γ-Fe at 912 °C)

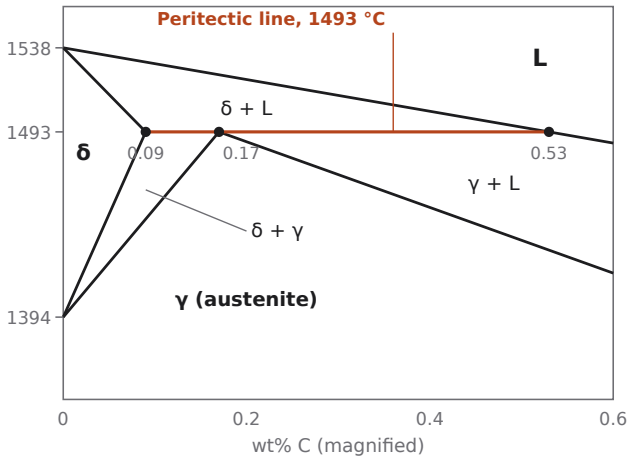
MEMORY RULE

"**-ic**" means a liquid is involved; "**-oid**" means everything is solid. **Eu-** means one phase splits into two on cooling; **Peri-** means two phases combine into one. All are invariant (F = 0, three phases in equilibrium) and show a horizontal line on the diagram.

6. The iron–iron carbide (Fe–Fe_3C) diagram HIGH Asked: Mid Sem 2024 and End Sem 2024 (6 marks)



Fe–Fe_3C phase diagram (metastable), after Callister Fig. 9.24. Orange lines are the critical lines used in heat treatment: A_1 (727 °C), A_3 (γ/α+γ) and A_{cm} (γ/γ+Fe_3C). Steels: up to 2.14% C. Cast irons: 2.14–6.70% C.



Peritectic (δ) corner, magnified.

Phases (learn all five)

Phase	Structure and max C	Properties
α-ferrite	BCC; 0.022% C at 727 °C (≈ 0.008% at room T)	Soft, ductile, magnetic below 768 °C
γ-austenite	FCC; 2.14% C at 1147 °C	Soft, ductile, non-magnetic; stable only above 727 °C in plain C steel
δ-ferrite	BCC; 0.09% C at 1493 °C	High-temperature form; little practical importance
Fe_3C (cementite)	Orthorhombic; 6.70% C	Very hard, brittle intermetallic; metastable (slowly turns into Fe + graphite)
Liquid	above the liquidus	—

The three invariant reactions

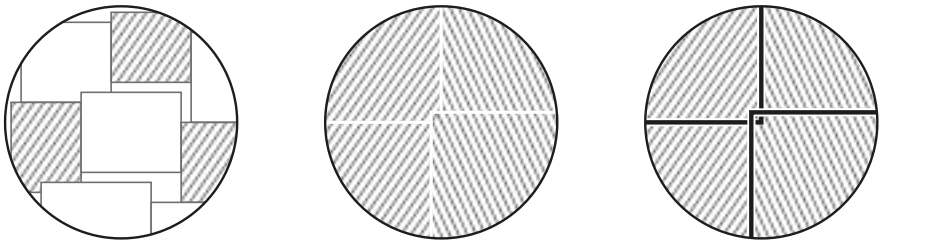
Reaction	Temperature	Equation (wt% C)	Product
Peritectic	1493 °C	L (0.53) + δ (0.09) → γ (0.17)	Austenite
Eutectic	1147 °C	L (4.30) → γ (2.14) + Fe_3C (6.70)	**Ledeburite** (cast irons)
Eutectoid	727 °C	γ (0.76) → α (0.022) + Fe_3C (6.70)	**Pearlite**: alternating lamellae of α and Fe_3C (about 8 : 1 by mass)

CRITICAL LINES AND OTHER TEMPERATURES

- **A_1**: eutectoid temperature, 727 °C (lower critical temperature).
- **A_3**: boundary between γ and α + γ (912 °C at 0% C falling to 727 °C at 0.76% C). It is the upper critical line for hypoeutectoid steels.
- **A_{cm}**: boundary between γ and γ + Fe_3C (727 °C at 0.76% C rising to 1147 °C at 2.14% C). It is the upper critical line for hypereutectoid steels.
- **A_2** = 768 °C is the Curie temperature: ferrite becomes non-magnetic above it. Pure iron: δ ⇌ γ at 1394 °C, γ ⇌ α at 912 °C, melts at 1538 °C.
- Subscripts: **c** (chauffage) for heating, e.g. Ac_1, Ac_3; **r** (refroidissement) for cooling, e.g. Ar_1, Ar_3.

Classification of iron–carbon alloys

Alloy	% C	Room-temperature microstructure (slow cooling)
Commercially pure iron	< 0.008	Ferrite
Hypoeutectoid steel	0.008–0.76	Pro-eutectoid ferrite + pearlite
Eutectoid steel	0.76	100% pearlite
Hypereutectoid steel	0.76–2.14	Pearlite + pro-eutectoid cementite (network at the prior austenite grain boundaries)
Hypoeutectic white cast iron	2.14–4.30	Pearlite (from primary γ) + transformed ledeburite + Fe_3C
Eutectic cast iron	4.30	Transformed ledeburite (pearlite + Fe_3C)
Hypereutectic white cast iron	4.30–6.70	Primary Fe_3C needles + transformed ledeburite



Schematic room-temperature microstructures of slowly cooled steels.

Cooling of a 0.4% C (hypoeutectoid) steel

1. Above about 800 °C (above A_3) the steel is **fully austenite** (γ).
2. On crossing A_3 (≈ 800 °C), **pro-eutectoid ferrite** starts forming at the γ grain boundaries. The carbon it rejects enriches the remaining austenite.
3. Between A_3 and 727 °C, the ferrite composition follows the α solvus and the austenite composition follows A_3 towards 0.76% C.
4. At 727 °C the remaining austenite (now 0.76% C) undergoes the **eutectoid reaction** and becomes pearlite.
5. At room temperature: **pro-eutectoid ferrite (≈ 49%) + pearlite (≈ 51%)**.

Cooling of a 1.0% C (hypereutectoid) steel

1. Above A_{cm} (≈ 800 °C for 1.0% C) the steel is fully γ.
2. Below A_{cm}, **pro-eutectoid cementite** precipitates along the γ grain boundaries. The austenite loses carbon, moving down A_{cm} towards 0.76%.
3. At 727 °C the remaining γ (0.76% C) becomes pearlite.
4. Final structure: **pearlite + a grain-boundary cementite network**. $W_{Fe_3C'} = (1.0 - 0.76)/(6.70 - 0.76) = 0.04$, i.e. 4% pro-eutectoid cementite and 96% pearlite. The brittle network is removed by normalizing or spheroidizing.

MODEL ANSWER: "DRAW THE FE–C DIAGRAM, MARK ALL PHASES AND EXPLAIN THE REACTIONS" (6 MARKS)

[Diagram, about 3 marks] Draw the figure above with axes T (°C) against wt% C (0 to 6.70). Mark 1538, 1493, 1394, 1147, 912 and 727 °C, and 0.022, 0.76, 2.14, 4.30 and 6.70% C. Label the fields L, δ, δ+L, δ+γ, γ, γ+L, L+Fe_3C, α, α+γ, γ+Fe_3C and α+Fe_3C, and the lines A_1, A_3 and A_{cm}.

[Phases, 1 mark] α-ferrite (BCC, max 0.022% C); γ-austenite (FCC, max 2.14% C); δ-ferrite (BCC, max 0.09% C); cementite Fe_3C (6.70% C, hard and brittle); liquid.

[Reactions, 2 marks]

- **Peritectic at 1493 °C:** L (0.53% C) + δ (0.09% C) → γ (0.17% C).
- **Eutectic at 1147 °C:** L (4.30% C) → γ (2.14% C) + Fe_3C (6.70% C). The eutectic mixture is called ledeburite.
- **Eutectoid at 727 °C:** γ (0.76% C) → α (0.022% C) + Fe_3C (6.70% C). The product is pearlite, made of alternate lamellae of ferrite and cementite.

Each is invariant: by the condensed phase rule $F = 2 - 3 + 1 = 0$. Alloys up to 2.14% C are steels (hypo- and hypereutectoid on either side of 0.76%); 2.14–6.70% C are cast irons. Strong finish: one line each on the room-temperature structures of 0.4% C, 0.76% C and 1.2% C steel.

Lever-rule numericals on Fe–C HIGH

FORMULAS JUST BELOW 727 °C (CALLISTER EQS. 9.20–9.23)

Hypoeutectoid ($C_0 < 0.76$): $W_p = (C_0 - 0.022)/(0.76 - 0.022) = (C_0 - 0.022)/0.738$ $W_{\alpha'} = (0.76 - C_0)/0.738$

Hypereutectoid ($C_0 > 0.76$): $W_p = (6.70 - C_0)/(6.70 - 0.76) = (6.70 - C_0)/5.94$ $W_{Fe_3C'} = (C_0 - 0.76)/5.94$

Total phases (any steel): $W_\alpha = (6.70 - C_0)/(6.70 - 0.022) = (6.70 - C_0)/6.678$ $W_{Fe_3C} = (C_0 - 0.022)/6.678$

WORKED NUMERICAL 4: 0.40% C STEEL JUST BELOW 727 °C

Pro-eutectoid ferrite: $W_{\alpha'} = (0.76 - 0.40)/0.738 = 0.36/0.738 =$ **0.488 (48.8%)**

Pearlite: $W_p = (0.40 - 0.022)/0.738 = 0.378/0.738 =$ **0.512 (51.2%)**

Total ferrite: $W_\alpha = (6.70 - 0.40)/6.678 = 6.30/6.678 =$ **0.943**; total cementite $W_{Fe_3C} =$ **0.057**.

Eutectoid ferrite (the ferrite inside pearlite) = total α − pro-eutectoid α = 0.943 − 0.488 = **0.455**.

WORKED NUMERICAL 5: 0.25% C STEEL

$W_{\alpha'} = (0.76 - 0.25)/0.738 = 0.51/0.738 =$ **0.691**

$W_p = (0.25 - 0.022)/0.738 = 0.228/0.738 =$ **0.309**

Mostly ferrite, so the steel is soft and ductile. Low-carbon steels are used for sheet and wire.

WORKED NUMERICAL 6: 1.2% C STEEL

$W_{Fe_3C'} = (1.2 - 0.76)/5.94 = 0.44/5.94 =$ **0.074**

$W_p = (6.70 - 1.2)/5.94 = 5.50/5.94 =$ **0.926**

Total α = 5.50/6.678 = **0.824**; total Fe_3C = **0.176**.

WORKED NUMERICAL 7: EUTECTOID STEEL

Ferrite and cementite in pearlite (0.76% C):

$W_\alpha = (6.70 - 0.76)/(6.70 - 0.022) = 5.94/6.678 =$ **0.889**; $W_{Fe_3C} =$ **0.111**, i.e. about 8 : 1. That is why the ferrite lamellae are much thicker than the cementite lamellae.

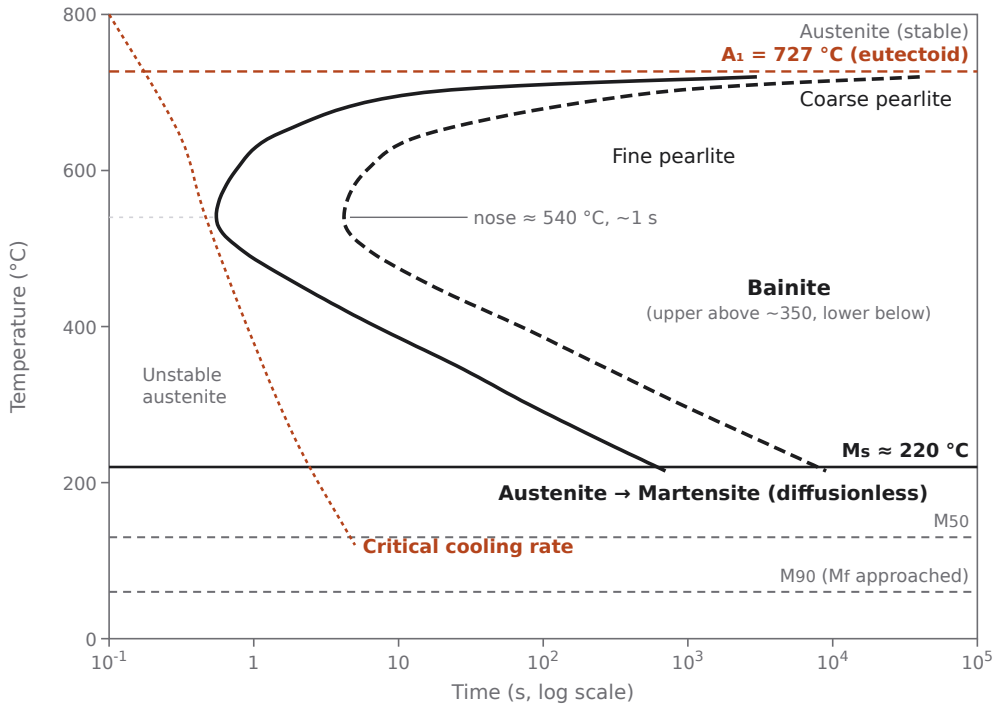
WORKED NUMERICAL 8: REVERSE PROBLEM

Q. A slowly cooled plain carbon steel shows 60% pearlite and 40% pro-eutectoid ferrite. Find its carbon content.

$W_p = (C_0 - 0.022)/0.738 = 0.60$, so $C_0 = 0.022 + 0.443 =$ **0.465 ≈ 0.46% C**.

7. TTT (isothermal transformation) diagram

HIGH Asked: End Sem 2024 (4 marks)



TTT diagram for eutectoid (0.76% C) steel, after Callister Fig. 10.23. Solid C-curve = start of transformation (1%); dashed curve = finish (99%). The dotted orange line is the critical cooling rate, just missing the nose. (Cooling curves strictly belong on a CCT diagram; examiners accept them on a TTT sketch.)

Construction

1. Prepare many small samples of eutectoid steel and **austenitize** them (above 727 °C, fully γ).

2. Quench each into a salt bath at a fixed sub-critical temperature (e.g. 700, 650, 600 … °C) and **hold isothermally**.
3. Remove samples after increasing times and quench them in water. Untransformed austenite becomes martensite, so the microscope shows how much austenite had already transformed.
4. Plot the times for 1% (start) and 99% (finish) transformation at each temperature on a log-time axis. The points form "C"-shaped curves (S-curves).

Why the C-shape?

Just below A_1 the undercooling is small, so the driving force (nucleation) is low and transformation is slow. At low temperature, diffusion is slow. At the **nose** (≈ 540 °C, under 1 s) the balance of driving force and diffusion gives the fastest transformation.

Regions and products

Transformation temperature	Product	Structure	Hardness (approx.)
727–650 °C	**Coarse pearlite**	Thick α + Fe_3C lamellae (high T, fast diffusion)	≈ HRC 15–20
650–540 °C	**Fine pearlite**	Thin lamellae	≈ HRC 30–40
540–350 °C	**Upper bainite**	Feathery: ferrite laths with Fe_3C between them	≈ HRC 40–45
350 °C to M_S	**Lower bainite**	Acicular (needle-like): ferrite plates with fine carbides inside	≈ HRC 50–60
Below M_S (≈ 220 °C)	**Martensite**	BCT supersaturated solid solution, needle/lath-like; diffusionless shear	up to HRC 65

- **M_S** (martensite start) and **M_f** (martensite finish) are horizontal lines. Martensite is **athermal**: how much forms depends only on the temperature reached, not on time. Austenite left untransformed below M_f is called **retained austenite**.
- **Critical cooling rate (CCR):** the slowest cooling rate that just misses the nose, giving 100% martensite. Cool faster than the CCR to harden.

Effect of carbon and alloying elements

- **Hypoeutectoid steels:** an extra pro-eutectoid ferrite curve appears above the nose, the nose moves left (shorter times, harder to harden) and M_S rises. **Hypereutectoid:** a pro-eutectoid cementite curve appears and M_S falls. M_S falls steadily as % C rises.
- **Alloying elements** (Cr, Mo, Ni, Mn, W, V…), except **Co**, shift the C-curves to the **right**. This lowers the CCR and increases hardenability, so thick sections or oil/air quenching can still give martensite. Elements like Cr and Mo also separate the pearlite and bainite noses. Most alloying elements lower M_S.

TTT vs CCT

TTT (isothermal transformation)	CCT (continuous cooling transformation)
Transformation at constant temperature	Transformation during continuous cooling (real heat treatment)
Used for austempering, martempering and isothermal annealing	Used for annealing, normalizing and quenching

C-curves further left and higher	Curves shifted **down and to the right** (longer times, lower temperatures)
Bainite region present	Bainite usually absent for plain-carbon eutectoid steel; the cooling path cuts off at the pearlite "nose"

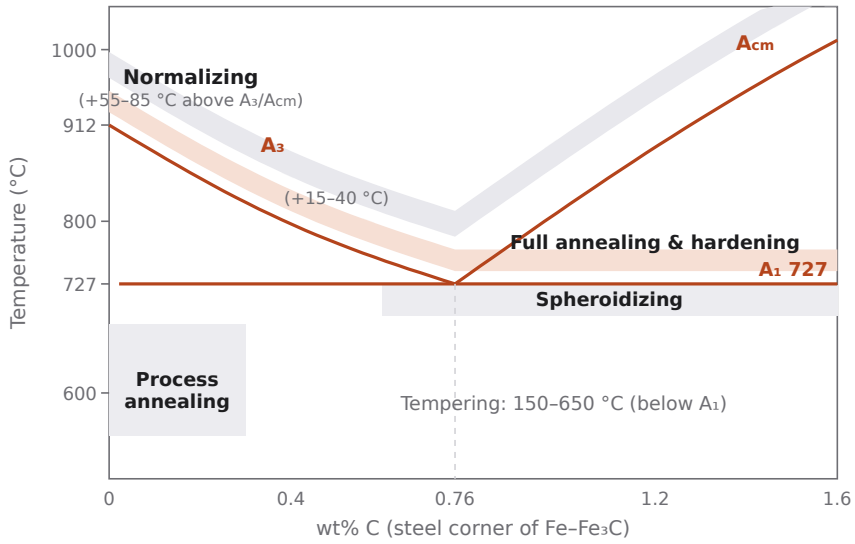
MODEL ANSWER: "DRAW THE TTT DIAGRAM FOR EUTECTOID STEEL, LABEL REGIONS AND PRODUCTS" (4 MARKS)

1. **Draw:** temperature (0–800 °C) against log time (0.1 to 10^5 s). Draw the A_1 line at 727 °C, the start (1%) and finish (99%) C-curves with the nose at ≈ 540 °C and ≈ 1 s, and horizontal lines M_s ≈ 220 °C, M_{50} and M_{90}.
2. **Label the regions:** stable austenite above A_1; unstable austenite left of the start curve; austenite + product between the curves; the transformed product right of the finish curve.
3. **Products:** coarse pearlite (727–650 °C), fine pearlite (650–540 °C), upper bainite (540–350 °C), lower bainite (350 °C to M_s), martensite below M_s (diffusionless).
4. Add one line on the critical cooling rate (tangent to the nose, gives 100% martensite) and one on the C-shape (nucleation vs diffusion).

	Pearlite	Bainite	Martensite
Forms at	727–540 °C	540 °C – M_s	below M_s
Mechanism	Diffusion (nucleation and growth)	Diffusion of C + shear of Fe	Diffusionless shear (athermal)
Phases	α + Fe_3C lamellae	α + fine Fe_3C (non-lamellar)	Single phase, BCT, C supersaturated
Properties	Soft–moderate, ductile	Strong and tough	Hardest, brittle; must be tempered

8. Heat treatment of plain carbon steels HIGH

Heat treatment means heating a metal in the solid state to a set temperature, holding it (soaking) and cooling it at a controlled rate to get the microstructure and properties you want.



Heat-treatment temperature ranges on the steel corner of the Fe–Fe_3C diagram (after Callister Fig. 11.10).

8.1 Annealing Asked: End Sem 2024 (with normalizing, 3 marks)

Type	Temperature	Cooling	Result and purpose
Full annealing	15–40 °C above A_3 (hypo) or above A_1 (hyper)	Very slow, in the furnace	Coarse pearlite (+ ferrite or cementite). Softest condition; best ductility and machinability for low/medium-C steel; refines a coarse cast structure; relieves stresses
Process (sub-critical) annealing	Below A_1, about 550–650 °C	Air	Recovery and recrystallization of **cold-worked** low-C sheet or wire, so it can be worked further; no phase change
Spheroidizing	Just below A_1 (≈ 700 °C) for 15–25 h, or cycling about A_1	Slow	Fe_3C becomes spheres in a ferrite matrix (**spheroidite**): softest, most ductile structure; best machinability for **high-C** (tool) steels
Stress-relief annealing	About 550–650 °C (below A_1)	Slow	Removes residual stresses from welding, machining, casting or cold work; no change in microstructure

Why hypereutectoid steels are not heated above A_{cm} for annealing: on slow cooling a continuous brittle Fe_3C network would form at the grain boundaries.

8.2 Normalizing

- Heat **55–85 °C above A_3** (hypo) or **above A_{cm}** (hyper), fully austenitize, then **cool in still air**.
- Gives **fine pearlite** with fine, uniform grains (grain refinement), so strength and hardness are a little higher than after annealing.
- Used to refine the coarse grains of castings, forgings and welds, to break the cementite network in hypereutectoid steel, and as a cheaper treatment before hardening.

MODEL ANSWER: "DISCUSS ANNEALING AND NORMALIZING IN TERMS OF THEIR EFFECTS ON MICROSTRUCTURE" (3 MARKS)

	Full annealing	Normalizing
Heating	15–40 °C above A_3 (hypo) / A_1 (hyper)	55–85 °C above A_3 / A_{cm}
Cooling	Furnace (very slow)	Still air (faster)
Microstructure	**Coarse pearlite** + pro-eutectoid phase; larger grains	**Fine pearlite**; finer, more uniform grains; cementite network broken up
Properties	Softer, more ductile, lower strength	Higher hardness, strength and toughness
Cost/time	Longer, costlier (furnace occupied)	Shorter, cheaper

Reason: faster air cooling means more undercooling, so austenite transforms at a lower temperature. Diffusion distances are shorter (thinner lamellae) and nucleation is more frequent (finer grains).

8.3 Hardening

- Heat **30–50 °C above A_3** (hypo) or **30–50 °C above A_1** (hyper), soak, then **quench** faster than the CCR. Media in decreasing severity: brine > water > oil > air.
- Product: **martensite**, hard and brittle with high internal stresses. Its maximum hardness depends on % C.

- Hypereutectoid steel is not heated above A_{cm}: that would coarsen the grains, give more retained austenite (lower M_s) and raise the risk of cracking. The undissolved Fe_3C particles add wear resistance.
- Defects to know: quench cracks, distortion/warping, soft spots, retained austenite.

8.4 Tempering

Reheat hardened steel **below A_1** (150–650 °C), hold, then cool. This relieves quenching stresses and trades a little hardness for toughness and ductility. The product is **tempered martensite**: fine Fe_3C particles in a ferrite matrix.

Stage	Temperature	Change
1	80–200 °C	ε-carbide ($Fe_{2.4}C$) precipitates; martensite loses some tetragonality; stresses are relieved (low-temperature tempering for tools: hardness kept)
2	200–300 °C	Retained austenite decomposes to bainite-like ferrite + carbide
3	250–400 °C	ε-carbide becomes cementite; martensite becomes ferrite + fine Fe_3C (troostite); medium-temperature tempering for springs
4	400–650 °C	Fe_3C coarsens and spheroidizes (sorbite); recovery of ferrite; high toughness for shafts, axles and gears

TEMPER EMBRITTLEMENT

- **Tempered martensite embrittlement** ("blue brittleness", ≈ 260–370 °C): toughness drops when tempering in this range. Avoid it.
- **Temper embrittlement** (alloy steels tempered at or slowly cooled through **375–575 °C**): impurities (Sb, P, As, Sn) segregate to the prior austenite grain boundaries, causing intergranular brittle fracture. Remedies: temper above 575 °C and cool fast through the range, keep impurities low, add Mo. It can be reversed by heating to about 600 °C and cooling fast. (Callister §10.8)

8.5 Martempering and austempering (isothermal treatments)

MARTEMPERING (MARQUENCHING)

Quench into a salt bath just **above M_s**.

Hold only until the temperature is uniform through the section (before bainite starts). Then air-cool through the M_s–M_f range, giving martensite, then temper.

Benefit: the surface and core turn to martensite together, so there is much less distortion, residual stress and cracking.

AUSTEMPERING

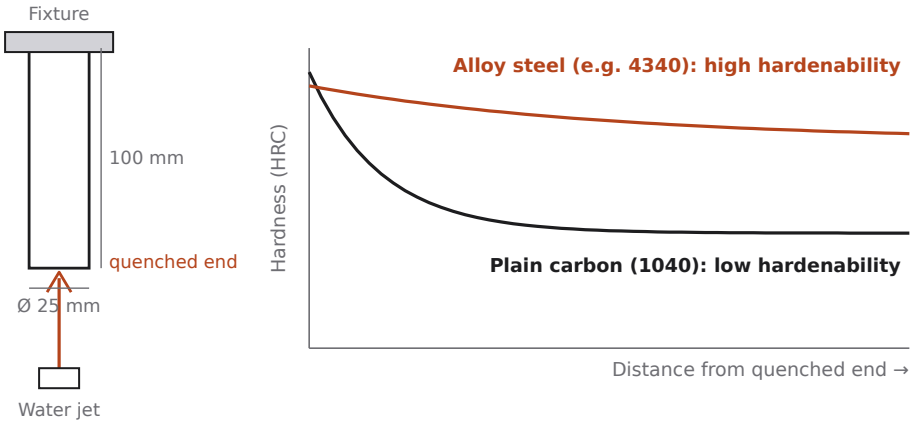
Quench into a salt bath **above M_s** (≈ 260–400 °C) and **hold until transformation to bainite is complete**, then air-cool.

Benefit: lower bainite has better toughness and ductility than tempered martensite at the same hardness, less distortion, and no tempering is needed. Limited to thin sections.

8.6 Hardenability and the Jominy end-quench test HIGH

DEFINITION

Hardenability is a steel's ability to form martensite **to a certain depth** when quenched. It is different from **hardness**, which is resistance to indentation; the maximum hardness depends mainly on % C. A high-hardenability steel hardens all the way to the core.



Jominy end-quench test: setup and hardness profile.

1. **Specimen:** a standard bar 25 mm (1 in.) in diameter and 100 mm (4 in.) long.
2. **Austenitize** it at the specified temperature for a specified time.
3. Mount it in a fixture and quench **only the bottom end** with a water jet of specified flow and temperature. The cooling rate is highest at the quenched end and falls along the length.
4. After cooling, grind a flat 0.4 mm deep along the length and measure **Rockwell C hardness every 1.6 mm (1/16 in.)** for the first 50 mm.
5. Plot the **hardenability curve** (hardness against distance from the quenched end). A flatter curve means higher hardenability.

Factors that increase hardenability: alloying elements (Cr, Mo, Ni, Mn, B), which shift the TTT curve right; higher carbon (up to eutectoid); coarser austenite grain size; homogeneous austenite. **Severity of quench** and **section size** decide the actual cooling rate.

8.7 Surface (case) hardening HIGH

Aim: a hard, wear-resistant surface (case) on a tough, ductile core, for gears, cams, camshafts and piston pins. There are two ways:

- **Thermochemical:** change the surface chemistry (carburizing, nitriding, cyaniding, carbonitriding).
- **Thermal (selective) hardening:** composition unchanged; heat only the surface and quench (induction, flame).

Process	Medium and temperature	Element added	Case depth	Quench?	Notes
Pack carburizing	Box with charcoal + energizer ($BaCO_3/Na_2CO_3$), 900–950 °C, several hours	C (surface ≈ 0.8–1% C)	0.5–2 mm	Yes, then temper	Low-C steels (0.1–0.2% C); simple, but slow and hard to control
Gas carburizing	CH_4/propane + carrier gas, 870–950 °C	C	0.1–1.5 mm	Yes (direct)	Accurate control, clean, mass production
Liquid carburizing	Molten cyanide-based salt bath, 815–900 °C	C (+ a little N)	0.1–0.8 mm	Yes	Fast, uniform heating; toxic salts
Cyaniding	Molten NaCN bath, 800–870 °C, 30–60 min	C + N	0.1–0.3 mm	Yes (direct water/oil)	Thin, hard case on small parts (screws, small gears); highly poisonous

Carbonitriding	Carburizing gas + NH_3, 750–900 °C	C + N	0.07–0.75 mm	Yes (oil)	Gas version of cyaniding; less distortion than carburizing
Nitriding	NH_3 gas, **500–590 °C** (below A_1), 10–100 h	N, forming hard nitrides with Al, Cr, Mo (Nitralloy)	0.1–0.6 mm	**No**	Hardest case (≈ 1000–1100 HV), minimal distortion, good fatigue and corrosion resistance; done after hardening and tempering; slow, costly

Induction hardening

A copper coil carries high-frequency AC around the part. Induced eddy currents heat a thin surface layer above A_3 within seconds, and a water spray quenches it to martensite. The **skin effect** means a higher frequency gives a shallower case. Used for medium-C steels (0.35–0.6% C): crankshafts, camshafts, gear teeth, axles.

Flame hardening

An oxy-acetylene flame heats the surface above the upper critical temperature, followed immediately by a water spray. Used for large or irregular parts that won't fit a furnace (lathe beds, large gears, rolls). Case depth depends on flame speed, intensity and dwell time.

Induction hardening	Flame hardening
Eddy-current heating; very fast (seconds)	Oxy-fuel flame; slower
Case depth precisely controlled by frequency and power (≈ 0.5–5 mm)	Less control; deeper cases (≈ 1.5–6 mm)
High equipment cost; ideal for mass production, easily automated	Cheap, portable; suits one-off and very large parts
Little scaling, decarburization or distortion	Risk of overheating, uneven hardness, some scaling

EXAM TIP: CARBURIZING VS NITRIDING (A FAVOURITE 3-4 MARK COMPARISON)

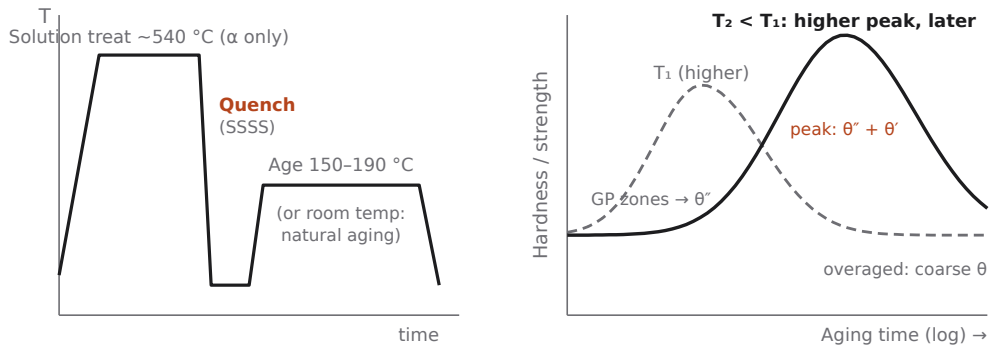
Carburizing: C, 900–950 °C (in the austenite range), quench needed, more distortion, case ≈ 60 HRC, cheaper, faster. Nitriding: N, 500–590 °C (ferrite range), no quench, minimal distortion, harder case (≈ 70 HRC), needs alloying elements (Al, Cr, Mo), slow (up to 100 h).

9. Precipitation (age) hardening of aluminium alloys HIGH

Precipitation hardening strengthens an alloy with extremely small, uniformly dispersed second-phase particles that block dislocation motion. It is the main strengthening method for Al alloys, which can't be hardened by martensite. (Callister §11.10)

REQUIREMENTS

(1) The maximum solubility of the solute must be fairly high. (2) The solubility must fall sharply as temperature drops. Al–Cu: maximum Cu solubility in α-Al is about 5.65% at 548 °C, dropping to nearly zero at room temperature. Al–4% Cu (duralumin-type 2014/2024 alloys) qualifies.



Left: precipitation-hardening heat-treatment cycle. Right: hardness against aging time at two temperatures ($T_2 < T_1$).

1. **Solution heat treatment:** heat Al–4% Cu to about 500–548 °C (into the single-phase α field, between solvus and solidus) and hold until all the θ ($CuAl_2$) dissolves.
2. **Quenching:** cool rapidly to room temperature (water). There is no time for θ to form, so you get a **supersaturated solid solution (SSSS)** of Cu in Al. It is soft and ductile, so it can be formed now (e.g. rivets).
3. **Aging: natural aging** at room temperature, or **artificial aging** at 100–200 °C. Precipitation proceeds in this sequence:

   $$\text{SSSS} \rightarrow \text{GP zones (GP-I)} \rightarrow \theta'' \text{ (GP-II)} \rightarrow \theta' \rightarrow \theta\ (CuAl_2)$$

   - **GP zones:** Cu-rich discs one or two atoms thick, fully **coherent** with the matrix.
   - **θ″:** coherent, tetragonal; produces large coherency strains. **θ′:** semi-coherent.
   - **Peak hardness** occurs when θ″/θ′ are present: coherency strain fields strongly resist dislocations.
   - **Overaging:** longer time or higher temperature gives coarse, incoherent equilibrium **θ**. The particles are farther apart and dislocations bypass them, so strength falls.

- A higher aging temperature (T_1) peaks **sooner but lower**. A lower temperature (T_2) peaks **later but higher**.
- **"Ice-box rivets"**: Al–Cu rivets are solution-treated and stored in a refrigerator to delay natural aging. They are driven while soft and then age-harden in service.
- Applications: aircraft structures (2014, 2024, 7075), truck frames, high-strength forgings. Other systems: Cu–Be, Al–Zn–Mg, maraging and PH stainless steels.

Quick revision: numbers to memorize HIGH

Item	Value	Item	Value
Fe melting	1538 °C	Eutectic	1147 °C, 4.30% C
δ → γ (pure Fe)	1394 °C	Max C in γ	2.14% at 1147 °C
γ → α (pure Fe)	912 °C	Eutectoid	727 °C, 0.76% C
Curie point (A_2)	768 °C	Max C in α	0.022% at 727 °C
Peritectic	1493 °C; 0.09 / 0.17 / 0.53% C	Fe_3C	6.70% C
Nose of TTT (eutectoid)	≈ 540 °C, ≈ 1 s	M_s (eutectoid steel)	≈ 220 °C
Nitriding	500–590 °C, NH_3, no quench	Carburizing	900–950 °C

Tempering range	150–650 °C	Al–Cu solution treatment	≈ 500–548 °C, age 100–200 °C

Likely exam questions

The typical DTU pattern, built from the topics above. These are practice questions, not reproduced past papers. Marks shown match the 8-mark question format (6+2, 5+3, 4+4).

1. Draw the Fe–Fe_3C equilibrium diagram, label all phases and temperatures, and write the invariant reactions. **(6)**
2. Derive the Gibbs phase rule. Apply it to the eutectoid point of the Fe–C system. **(2–3)**
3. Draw the TTT diagram for eutectoid steel and label the regions and products. What is the critical cooling rate? **(4–5)**
4. Discuss annealing and normalizing in terms of their effects on microstructure and properties. **(3–4)**
5. Calculate the amounts of pro-eutectoid ferrite, pearlite, total ferrite and total cementite in a 0.4% C steel just below 727 °C. **(3–4)**
6. State and derive the lever rule. For a 35 wt% Ni–Cu alloy at 1250 °C (C_L = 31.5, C_α = 42.5), find the phase fractions. **(4)**
7. Explain eutectic, eutectoid, peritectic and peritectoid reactions with one example of each. **(4)**
8. Differentiate homogeneous and heterogeneous nucleation. Derive the expression for the critical radius of a nucleus. **(5)**
9. What is hardenability? Describe the Jominy end-quench test with a sketch. **(4)**
10. Explain carburizing and nitriding, and compare them. **(4)**
11. Write short notes on (a) induction hardening, (b) flame hardening, (c) cyaniding. **(2 each)**
12. Explain the stages of tempering. What is temper embrittlement? **(4)**
13. Explain precipitation hardening of Al–4% Cu alloy with a neat sketch. What is overaging? **(5)**
14. Differentiate martempering and austempering. Compare pearlite, bainite and martensite. **(4)**

MODEL ANSWER: HOMOGENEOUS VS HETEROGENEOUS NUCLEATION, AND THE R* DERIVATION (5 MARKS)

Difference (2 marks): Homogeneous nucleation happens uniformly throughout the pure liquid without help from foreign surfaces, and needs large undercooling (≈ $0.2T_m$).

Heterogeneous nucleation happens on mould walls, impurities or inoculants. The surface lowers the barrier ($\Delta G^*_{het} = S(\theta)\Delta G^*_{hom}$), so only a few degrees of undercooling are needed. All practical castings nucleate this way.

Derivation (3 marks): $\Delta G = (4/3)\pi r^3 \Delta G_v + 4\pi r^2 \gamma$ (with $\Delta G_v < 0$). At the maximum, $d\Delta G/dr = 4\pi r^2 \Delta G_v + 8\pi r\gamma = 0$, so $\mathbf{r^* = -2\gamma/\Delta G_v}$. Substituting back: $\mathbf{\Delta G^* = 16\pi\gamma^3/(3\Delta G_v^2)}$. Since $\Delta G_v = \Delta H_f \Delta T/T_m$, $r^* = -2\gamma T_m/(\Delta H_f \Delta T)$: more undercooling means a smaller r*, more nuclei and finer grains. Sketch the ΔG–r curve.

MODEL ANSWER: CARBURIZING VS NITRIDING (4 MARKS)

	Carburizing	**Nitriding**
Element diffused	Carbon	Nitrogen

Temperature	900–950 °C (austenite)	500–590 °C (ferrite, below A_1)
Medium	Charcoal + $BaCO_3$ (pack), CH_4 (gas), cyanide salts (liquid)	Dissociated ammonia: $2NH_3 \rightarrow 2N + 3H_2$
Steel	Low-C (0.1–0.2%) plain or alloy	Alloy steels with Al, Cr, Mo (Nitralloy)
Post-treatment	Quench + temper required	No quench; done on hardened and tempered parts
Case hardness / depth	≈ 60 HRC; 0.5–2 mm	≈ 1000–1100 HV; 0.1–0.6 mm
Distortion, time	More distortion; a few hours	Minimal distortion; 10–100 h

MODEL ANSWER: PRECIPITATION HARDENING OF AL–4% CU (5 MARKS)

Draw the Al-rich corner of the Al–Cu diagram (solvus rising to 5.65% Cu at 548 °C) or the thermal cycle, plus the aging curve. Then three steps: (1) **solution treatment** at about 540 °C, giving single-phase α; (2) **quench**, giving a soft supersaturated α (SSSS); (3) **aging** at room temperature or 100–200 °C, with precipitation sequence GP zones → θ″ → θ′ → θ ($CuAl_2$). Coherent θ″/θ′ particles create strain fields that block dislocations, giving **peak hardness**. Prolonged aging gives coarse incoherent θ and **overaging** (softening). A lower aging temperature gives a higher peak after a longer time. Used in aircraft alloys 2014/2024.

UNIT 4 · ~6 CONTACT HRS

Fracture, Fatigue & Creep

Most examined: Griffith derivation (6 marks), K_{Ic} / surface-energy numericals (2–3 marks), creep curve with mechanisms, DBTT, S–N curve.

1. Elastic behaviour: Hooke's law, E, G, ν MEDIUM

DEFINITION

Elastic deformation is non-permanent: the material returns to its original shape when the load is removed. Inside the elastic region stress is proportional to strain (**Hooke's law**): $\sigma = E\varepsilon$. The constant **E (modulus of elasticity, Young's modulus)** measures *stiffness*, i.e. resistance to elastic deformation. Atomically, E is the slope of the interatomic force–separation curve at the equilibrium spacing, so it depends on **bond strength**.

FORMULAS

$\sigma = F/A_0 \quad \varepsilon = \Delta l/l_0 \quad \sigma = E\varepsilon \quad \tau = G\gamma$

$\nu = -\varepsilon_{lateral}/\varepsilon_{axial} = -\varepsilon_x/\varepsilon_z \quad E = 2G(1 + \nu)$

For most metals $\nu \approx 0.25$–0.35, so $G \approx 0.4E$. E falls slowly as temperature rises.

Material	E (GPa)	G (GPa)	ν
Steel	207	83	0.30
Copper	110	46	0.34
Aluminium	69	25	0.33
Tungsten	407	160	0.28
Ceramics (Al_2O_3)	380	—	0.22
Polymers	0.007–4	—	~0.4

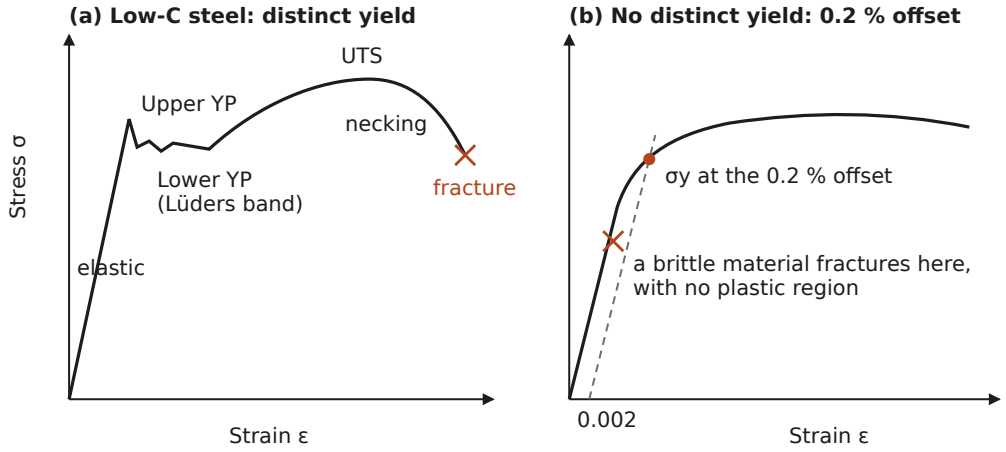
WORKED NUMERICAL

A copper bar (E = 110 GPa), originally 305 mm long, is pulled in tension with a stress of 276 MPa. The deformation is entirely elastic. Find the elongation.

$\Delta l = \sigma l_0/E = (276 \times 10^6 \times 305)/(110 \times 10^9)$ = **0.77 mm**.

Steel has E = 207 GPa and ν = 0.30, so $G = E/[2(1 + \nu)] = 207/2.6$ = **79.6 GPa**.

2. Yield point, strength & the stress–strain curve HIGH



Engineering stress–strain curves. Area under the elastic part is the resilience; area under the whole curve is the toughness.

Key points on the curve

- **Proportional limit (P):** the point where the curve first departs from linearity (Hooke's law ends).
- **Elastic limit:** the maximum stress that causes no permanent set.
- **Yield strength σ_y:** the stress at which noticeable plastic deformation begins. If there is no sharp yield point, draw a line parallel to the elastic portion starting at strain 0.002 (the **0.2 % offset**). Its intersection with the curve is σ_y.
- **Upper and lower yield points** (low-carbon steel). Interstitial C and N atoms form *Cottrell atmospheres* around dislocations and pin them. A higher stress (the **upper yield point**) is needed to tear the dislocations free. Once free they move at a lower stress (the **lower yield point**), and the strain proceeds as **Lüders bands** at roughly constant stress. σ_y is taken as the lower yield point. The same pinning causes *stretcher strains* in sheet steel.
- **Tensile strength (UTS):** the maximum engineering stress. Beyond it, deformation localises into a **neck**.
- **Fracture strength:** the engineering stress at fracture. It is lower than the UTS because the area has shrunk.
- **Ductility:** $\%EL = (l_f - l_0)/l_0 \times 100$ and $\%RA = (A_0 - A_f)/A_0 \times 100$. A material with fracture strain below about 5 % is called *brittle*.
- **Resilience:** energy absorbed elastically, $U_r = \sigma_y^2/2E$ (used for springs). **Toughness:** total energy absorbed up to fracture, i.e. the area under the curve.

TRUE STRESS AND TRUE STRAIN (VALID UP TO NECKING)

$\sigma_T = F/A_i = \sigma(1 + \varepsilon)$ $\quad \varepsilon_T = \ln(l_i/l_0) = \ln(1 + \varepsilon)$ $\quad \sigma_T = K\varepsilon_T^n$

n is the strain-hardening exponent. True stress keeps rising after the UTS because the actual area keeps shrinking.

WORKED NUMERICAL

At an engineering stress of 400 MPa the engineering strain is 0.20. Then $\sigma_T = 400(1.20) =$ **480 MPa** and $\varepsilon_T = \ln 1.20 =$ **0.182**.

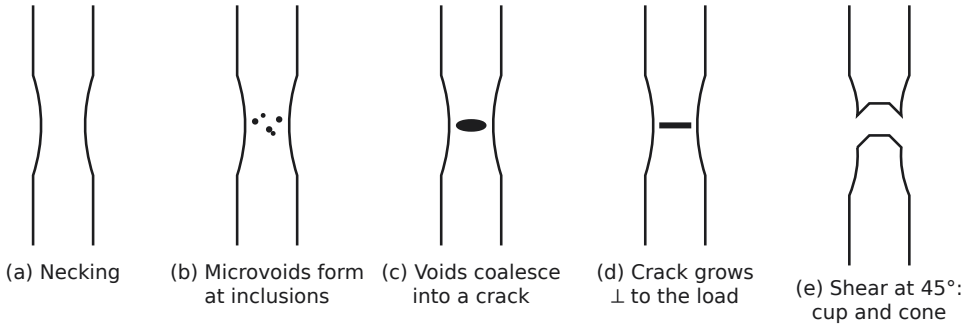
Resilience of a steel with $\sigma_y = 300$ MPa and $E = 207$ GPa: $U_r = (300 \times 10^6)^2/(2 \times 207 \times 10^9) =$ **2.17×10^5 J/m³**.

3. Fracture in ductile and brittle materials HIGH

DEFINITION

Fracture is the separation of a body into two or more pieces under a static stress, at temperatures that are low relative to T_m. It has two steps: **crack formation** and **crack propagation**. **Ductile fracture** involves extensive plastic deformation and a slow, *stable* crack that resists extension. **Brittle fracture** involves little or no plastic deformation and a fast, *unstable* crack that runs once it starts.

Ductile fracture: the cup-and-cone sequence



Stages of cup-and-cone fracture (Callister §8.3). The fibrous central region is surrounded by a 45° shear lip, where shear stress is maximum.

Under the SEM, a ductile fracture surface shows **dimples**: half-voids, spherical under uniaxial tension and parabolic under shear.

Brittle fracture

- The crack runs roughly **perpendicular to the applied stress** and the fracture surface is relatively flat and shiny.
- Chevron ("V") or fan-like ridge markings point back to the crack origin.
- **Transgranular (cleavage):** the crack passes *through* the grains by breaking bonds along specific crystallographic planes. It gives a faceted, grainy look. Typical in BCC and HCP metals at low temperature.
- **Intergranular:** the crack runs *along* the grain boundaries. It occurs when boundaries are weakened by segregation or precipitates (e.g. temper embrittlement, S/P segregation, hydrogen embrittlement).

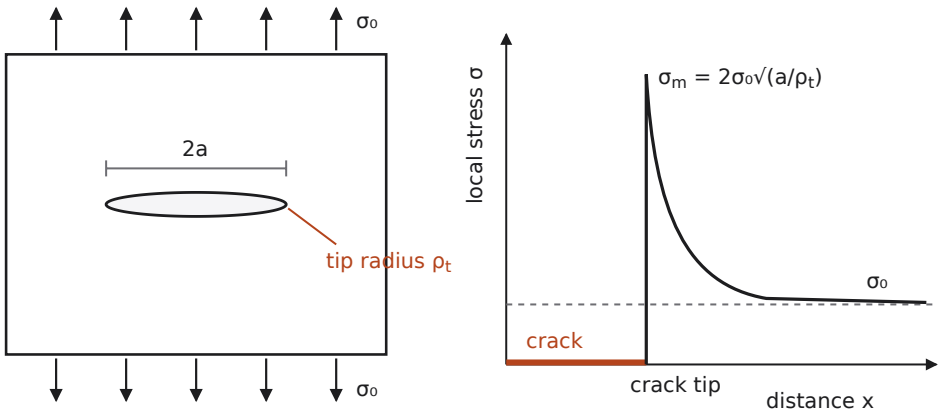
Feature	Ductile fracture	Brittle fracture
Plastic deformation	Extensive (necking)	Little or none
Crack growth	Slow and stable; needs increasing stress	Very fast and unstable; self-propagating

Energy absorbed	High (tough)	Low
Warning before failure	Yes (visible deformation)	No (catastrophic)
Fracture surface	Cup and cone, fibrous, dull, dimples	Flat, granular or shiny, chevron marks
Fracture plane	45° shear lip plus central fibrous zone	⊥ to the tensile axis
Examples	Mild steel, Cu, Al, Au at room temperature	Cast iron, glass, ceramics, steel below its DBTT

4. Griffith's theory of brittle fracture HIGH Asked: End Sem 2024 (6 marks)

Why real strength is far below theoretical strength

The theoretical cohesive strength of a solid is about E/10. Measured fracture strengths of brittle materials are 10 to 1000 times lower. Griffith (1920) explained this by the presence of very small microscopic **flaws or cracks**, always present at the surface and inside a body, which act as **stress raisers**.



An elliptical crack of length 2a in a plate under remote stress σ_0. The local stress peaks at the crack tip.

STRESS CONCENTRATION AT A CRACK TIP (INGLIS)

$$\sigma_m = 2\sigma_0 (a/\rho_t)^{1/2} \qquad K_t = \sigma_m/\sigma_0 = 2(a/\rho_t)^{1/2}$$

Here a is the length of a surface crack, or half the length of an internal crack. Long, sharp cracks (large a, small ρ_t) give the largest concentration. In ductile metals, plastic flow at the tip blunts the crack, so K_t is smaller.

MODEL ANSWER: GRIFFITH ENERGY-BALANCE DERIVATION (6 MARKS)

Assumptions. The material is ideally brittle and linear elastic. It is a thin infinite plate of unit thickness under plane stress. It contains a through-thickness elliptical crack of length 2a, normal to a uniform tensile stress σ.

Statement. A crack propagates when the elastic strain energy released by its growth is equal to, or greater than, the energy needed to create the new crack surfaces.

Step 1: strain energy released. Introducing the crack relaxes the stress in a region around it. For unit thickness, the stored elastic energy falls by

$$U_E = -\pi a^2 \sigma^2 / E$$

Step 2: surface energy gained. The crack has two faces, each 2a long (unit thickness), so the new surface area is 4a. With γ_s the specific surface energy (J/m²):

$$U_S = 4a\gamma_s$$

Step 3: total energy change.

$$\Delta U = 4a\gamma_s - \pi a^2\sigma^2/E$$

ΔU first rises with a (surface term dominates) and then falls (strain-energy term dominates). The crack becomes unstable at the maximum of ΔU.

Step 4: condition for propagation. Set d(ΔU)/da = 0:

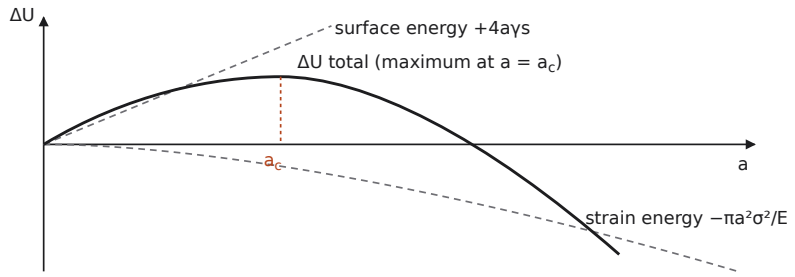
$$4\gamma_s - 2\pi a\sigma^2/E = 0 \;\Rightarrow\; \sigma^2 = 2E\gamma_s/(\pi a)$$

$$\sigma_c = (2E\gamma_s / \pi a)^{1/2}$$

Conclusions.

- $\sigma_c \propto 1/\sqrt{a}$, so larger flaws mean lower strength. This explains why fine glass fibres (small flaws) are very strong.
- Higher E and higher γ_s raise the strength.
- For plane strain, replace E by $E/(1-\nu^2)$.
- **Orowan–Irwin modification for metals:** replace γ_s by $(\gamma_s + \gamma_p)$, where γ_p is the plastic work done at the crack tip per unit area. γ_p is about 10^3–10^4 times γ_s, so $\sigma_c = [2E(\gamma_s + \gamma_p)/\pi a]^{1/2}$.
- Comparing with $K = \sigma\sqrt{(\pi a)}$ gives $K_{Ic} = \sqrt{(2E\gamma_s)}$, i.e. $G_c = 2\gamma_s = K_{Ic}^2/E$.

Draw: (i) the plate with the crack and the stress arrows, and (ii) the ΔU vs a curve with its maximum at the critical crack length a_c.



Energy versus crack length. Beyond a_c, crack growth lowers the total energy, so the crack runs unstably.

WORKED NUMERICAL 1: GRIFFITH CRITICAL FLAW SIZE (CALLISTER EX. 8.1)

A relatively large glass plate is loaded in tension at 40 MPa. Surface energy γ_s = 0.3 J/m² and E = 69 GPa. Find the maximum length of surface flaw possible without fracture.

$a_c = 2E\gamma_s/(\pi\sigma^2) = (2 \times 69 \times 10^9 \times 0.3)/(\pi \times (40 \times 10^6)^2) = (4.14 \times 10^{10})/(5.027 \times 10^{15}) =$ **8.2×10^{-6} m = 8.2 µm**.

WORKED NUMERICAL 2: SURFACE ENERGY FROM K_{Ic} (END SEM 2024 TYPE, 2 MARKS)

A material has fracture toughness 80 MPa√m and critical crack length 0.05 mm, with E = 120 GPa. Calculate the surface energy γ.

Griffith gives $\sigma_c^2 \pi a = 2E\gamma$. Since $K_{Ic} = \sigma_c\sqrt{(\pi a)}$, we get $K_{Ic}^2 = 2E\gamma$, so

$\gamma = K_{Ic}^2/(2E) = (80 \times 10^6)^2/(2 \times 120 \times 10^9) = 6.4 \times 10^{15}/2.4 \times 10^{11} =$ **2.67×10^4 J/m²**.

The crack length cancels out; it is needed only if you are also asked for σ_c. Here $\sigma_c = K_{Ic}/\sqrt{(\pi a)} = 80/\sqrt{(\pi \times 5 \times 10^{-5})} = 80/0.01253 =$ **6.38×10^3 MPa**. A value of 2.67×10^4 J/m² is far larger than a true surface energy (~1 J/m²). It is really ($\gamma_s + \gamma_p$), dominated by plastic work at the crack tip (Orowan). Write this line; it earns the remaining mark.

WORKED NUMERICAL 3: GRIFFITH FRACTURE STRESS

A glass (E = 70 GPa, γ_s = 1.0 J/m²) contains an internal crack 4 μm long (a = 2 μm). Find the fracture stress.

$\sigma_c = \sqrt{(2E\gamma_s/\pi a)} = \sqrt{(2 \times 70 \times 10^9 \times 1.0/(\pi \times 2 \times 10^{-6}))} = \sqrt{(2.228 \times 10^{16})} =$ **1.49×10^8 Pa ≈ 149 MPa**.

Compared with the theoretical strength E/10 = 7 GPa, the flaw lowers the strength about 47 times.

WORKED NUMERICAL 4: STRESS CONCENTRATION

A surface crack is 0.5 mm deep with tip radius 5×10^{-3} mm. The applied stress is 100 MPa.

$\sigma_m = 2\sigma_0\sqrt{(a/\rho_t)} = 2 \times 100 \times \sqrt{(0.5/0.005)} = 2 \times 100 \times 10 =$ **2000 MPa**, so $K_t =$ **20**.

WORKED NUMERICAL 5: CRITICAL CRACK LENGTH FROM E AND Γ

For a brittle ceramic, E = 300 GPa and γ_s = 0.8 J/m². What internal crack length 2a causes fracture at 200 MPa?

$a = 2E\gamma_s/(\pi\sigma^2) = (2 \times 300 \times 10^9 \times 0.8)/(\pi \times 4 \times 10^{16}) = 4.8 \times 10^{11}/1.257 \times 10^{17} = 3.82 \times 10^{-6}$ m, so the crack length 2a = **7.6 μm**.

5. Fracture toughness K_{Ic} HIGH

DEFINITION

The **stress intensity factor K** describes the stress field near a crack tip. **Fracture toughness K_c** is the critical value of K at which a crack propagates rapidly. It measures a material's resistance to brittle fracture when a crack is present. Units: MPa√m.

FORMULAS

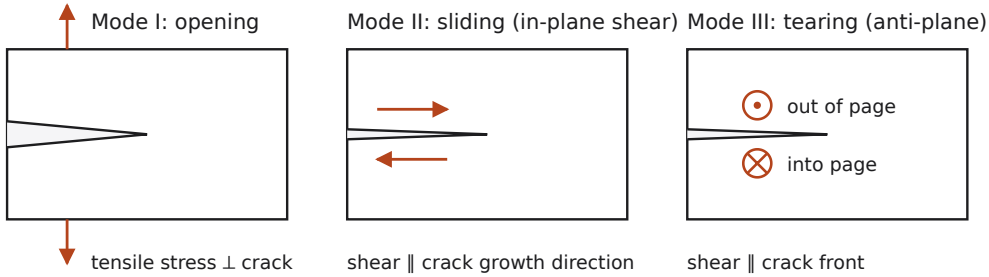
$K_c = Y\sigma_c\sqrt{(\pi a)}$ $\sigma_c = K_{Ic}/(Y\sqrt{(\pi a)})$ $a_c = (1/\pi)[K_{Ic}/(Y\sigma)]^2$

Plane-strain condition: $B \geq 2.5\ (K_{Ic}/\sigma_y)^2$

Y is a dimensionless geometry factor (≈ 1 for a centre crack in a wide plate; ≈ 1.1 for an edge crack). B is the specimen thickness.

- **Plane strain:** when the specimen is thick compared with the crack, there is no strain in the thickness direction. K_c then falls to a minimum, constant value called the **plane-strain fracture toughness K_{Ic}**. This is a material property and is the value used in design. Thin plates (plane stress) show higher K_c.
- **Factors that lower K_{Ic}:** lower temperature, higher strain rate, higher yield strength (strengthening by solid solution, dispersion or cold work), larger grain size. Refining the grain size *raises* K_{Ic}.
- **Design triangle:** K_{Ic} (material), σ (design stress) and a (largest flaw size). Fix any two and the third is determined. NDT sets the smallest flaw size that can be detected.

Modes of crack-surface displacement



Mode I (opening) is the most common in practice and the most severe. Hence the subscript "I" in K_{Ic}.

Material	σ_y (MPa)	K_{Ic} (MPa√m)
Al alloy 7075-T651	495	24
Ti-6Al-4V	910	55
4340 steel (tempered 260 °C)	1640	50
4340 steel (tempered 425 °C)	1420	87.4
Soda-lime glass	—	0.7–0.8
Al_2O_3	—	2.7–5.0
Concrete	—	0.2–1.4

Callister Table 8.1. Note the trade-off: the 4340 steel with higher σ_y has lower K_{Ic}.

WORKED NUMERICAL 6: K_{Ic} DESIGN

A steel plate has K_{Ic} = 50 MPa√m and Y = 1.1 (edge crack). (a) Find the critical crack length at a design stress of 250 MPa. (b) If NDT can detect cracks only down to 3 mm, what is the safe design stress?

(a) $a_c = (1/\pi)(K_{Ic}/Y\sigma)^2 = (1/\pi)(50/275)^2 = (1/\pi)(0.03306) =$ **0.0105 m ≈ 10.5 mm**.

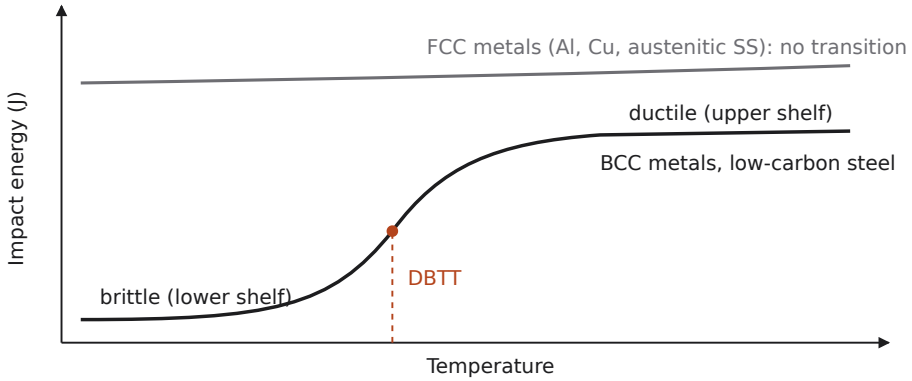
(b) $\sigma_c = K_{Ic}/(Y\sqrt{(\pi a)}) = 50/(1.1 \times \sqrt{(\pi \times 0.003)}) = 50/(1.1 \times 0.0971) =$ **468 MPa**. Cracks smaller than 3 mm cannot be detected, so the plate must be designed for σ < 468 MPa, with a factor of safety on top.

WORKED NUMERICAL 7: IS PLANE STRAIN VALID?

For 4340 steel tempered at 260 °C (σ_y = 1640 MPa, K_{Ic} = 50 MPa√m): $B \geq 2.5(50/1640)^2 = 2.5 \times 9.30 \times 10^{-4} = 2.3 \times 10^{-3}$ m. A plate thicker than **2.3 mm** is in plane strain.

6. Ductile-to-brittle transition (DBTT) HIGH

Impact tests (Charpy and Izod) measure the energy absorbed in breaking a notched bar struck by a swinging pendulum. The energy equals the drop in pendulum height × weight. In the **Charpy** test the specimen (10 × 10 × 55 mm, 2 mm V-notch) is simply supported as a beam and struck behind the notch. In the **Izod** test it is clamped vertically as a cantilever and struck above the notch. Severe conditions (notch, high strain rate, low temperature) bring out any tendency to brittle behaviour.



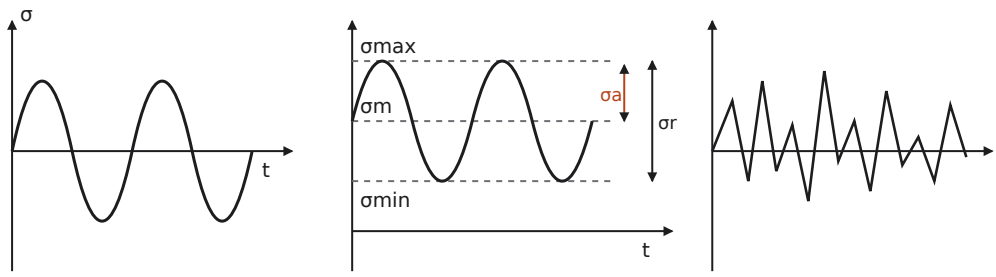
Impact energy versus temperature. The fracture surface changes from fibrous (shear) to granular (cleavage) as temperature falls (Callister §8.6).

- **DBTT** is the temperature (or range) over which the impact energy and the fracture mode switch from ductile to brittle. It is defined as the energy midpoint, a fixed energy (e.g. 20 J), or 50 % fibrous fracture.
- **BCC and HCP metals show a DBTT; FCC metals do not.** In BCC metals the yield stress (Peierls stress) rises steeply as temperature falls, because dislocation motion is thermally activated. Below the DBTT, cleavage takes less stress than yielding. FCC metals have many close-packed slip systems and a yield stress that varies little with temperature, so they stay ductile even at cryogenic temperatures.
- **Factors raising the DBTT** (bad): more carbon, P, S or N; coarse grains; thicker sections; sharper notches; higher strain rate; neutron irradiation.
- **Factors lowering the DBTT** (good): fine grain size, Ni and Mn additions, low C, deoxidised (killed) steel.
- **Case histories:** the WWII **Liberty ships** (welded hulls of low-carbon steel) split in two in cold seas. The **Titanic's** high-S, high-P hull steel was brittle in water at −2 °C. In both cases the steel was used below its DBTT.
- **Design rule:** choose a material whose DBTT is well below the lowest service temperature.

7. Fatigue HIGH

DEFINITION

Fatigue is failure under **fluctuating (cyclic) stresses** at a stress level much lower than the tensile or yield strength, after a long period of service. It causes about 90 % of metallic failures, for example in shafts, bridges, aircraft and springs. It is brittle-like (little gross deformation) and catastrophic.



(a) Reversed: σm = 0, R = −1 (b) Repeated: σm ≠ 0 (c) Random stress cycle

Types of fatigue stress cycle.

CYCLIC STRESS PARAMETERS

$\sigma_m = (\sigma_{max} + \sigma_{min})/2 \quad \sigma_r = \sigma_{max} - \sigma_{min} \quad \sigma_a = \sigma_r/2 = (\sigma_{max} - \sigma_{min})/2 \quad R = \sigma_{min}/\sigma_{max}$

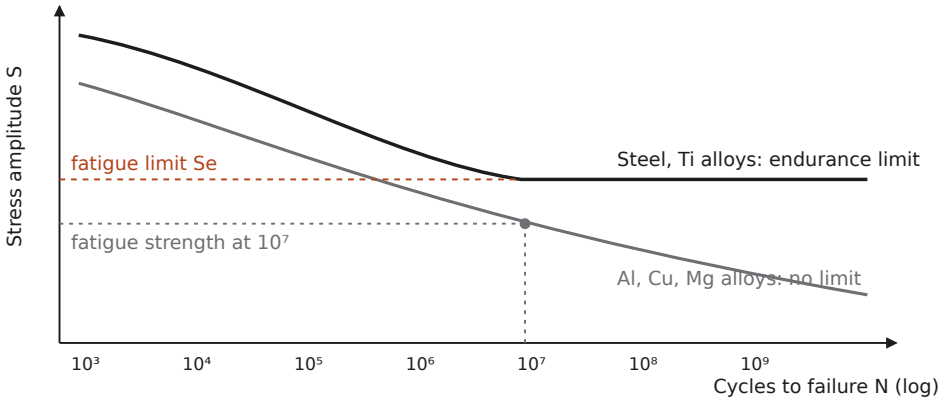
Tensile stresses are positive and compressive negative. Fully reversed loading: R = −1. Zero-to-tension: R = 0.

WORKED NUMERICAL 8

σ_{max} = 400 MPa, σ_{min} = −100 MPa. Then σ_m = (400 − 100)/2 = **150 MPa**, σ_r = **500 MPa**, σ_a = **250 MPa** and R = −100/400 = **−0.25**.

Reverse problem: given σ_m = 70 MPa and σ_a = 210 MPa, σ_{max} = 70 + 210 = **280 MPa**, σ_{min} = 70 − 210 = **−140 MPa** and R = **−0.5**.

S–N curve (Wöhler curve)



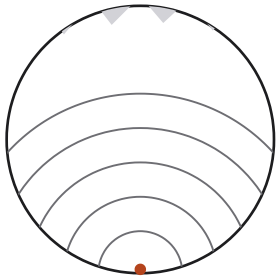
S–N curves: ferrous materials (typical) versus non-ferrous materials (Callister §8.8).

- **Fatigue (endurance) limit:** the stress amplitude below which fatigue failure never occurs. For steels it is typically 35–60 % of the tensile strength.
- **Fatigue strength:** for materials with no limit (Al, Cu, Mg), the stress at which failure occurs after a specified number of cycles, e.g. 10^7.
- **Fatigue life N_f:** the number of cycles to failure at a given stress. Low-cycle fatigue is N < 10^4–10^5 (high stress, plastic strain). High-cycle fatigue is N above that (elastic strains).
- Test data scatter widely, so S–N curves are often plotted as probability-of-failure curves.

Crack initiation and propagation

1. **Crack initiation:** a small crack forms at a point of high stress concentration on the surface: scratches, sharp fillets, keyways, threads, dents, or persistent slip bands (intrusions and extrusions).
2. **Crack propagation:** the crack advances by a small increment with each cycle. Stage I is slow, along slip planes. Stage II is faster, $\perp$ to the stress.
3. **Final failure:** very rapid, once the crack reaches its critical size, i.e. when K reaches K_c in the reduced section.

Beach marks (clamshell marks) are macroscopic, visible to the eye, concentric ridges. They form when loading is interrupted, and they mark the crack front positions. **Striations** are microscopic (SEM). Each striation is the crack advance in *one* cycle, and one beach mark contains thousands of striations. The final fast-fracture zone is rough and granular.



beach marks spread from origin
top: final rapid fracture

Fatigue fracture surface of a shaft.

CRACK GROWTH RATE (PARIS LAW)

$$da/dN = A(\Delta K)^m, \quad \Delta K = Y\sigma_r\sqrt{(\pi a)} \quad (m \approx 1\text{–}6)$$

Integrating from the initial crack size a_0 to the critical size a_c gives the fatigue life N_f.

Factors affecting fatigue life and design considerations

Factor	Effect and remedy
Mean stress	Higher σ_m shortens life at the same σ_a.
Design: stress raisers	Avoid sharp corners, holes, keyways and abrupt changes in section. Use generous **fillet radii**.
Surface finish	**Polishing** removes machining scratches and raises life.
Residual surface stress	**Shot peening** (small hard shot, 0.1–1 mm, blasted onto the surface) puts a thin layer in **compressive residual stress**, which offsets the tensile cycle and slows crack initiation.
Case hardening	Carburizing or nitriding gives a hard, wear-resistant case in compressive residual stress, so the fatigue life rises.
Decarburization	A soft surface lowers fatigue life, so avoid it.
Environment	**Thermal fatigue:** cycles of thermal stress $\sigma = \alpha E \Delta T$. Reduce restraint and temperature gradients. **Corrosion fatigue:** corrosion pits act as stress raisers. Use coatings, a less corrosive medium or shot peening.

MEAN-STRESS DESIGN LINES (BRIEF)

Goodman: $\sigma_a/S_e + \sigma_m/S_u = 1/n$ Soderberg: $\sigma_a/S_e + \sigma_m/S_y = 1/n$ Gerber: $\sigma_a/S_e + (\sigma_m/S_u)^2 = 1$

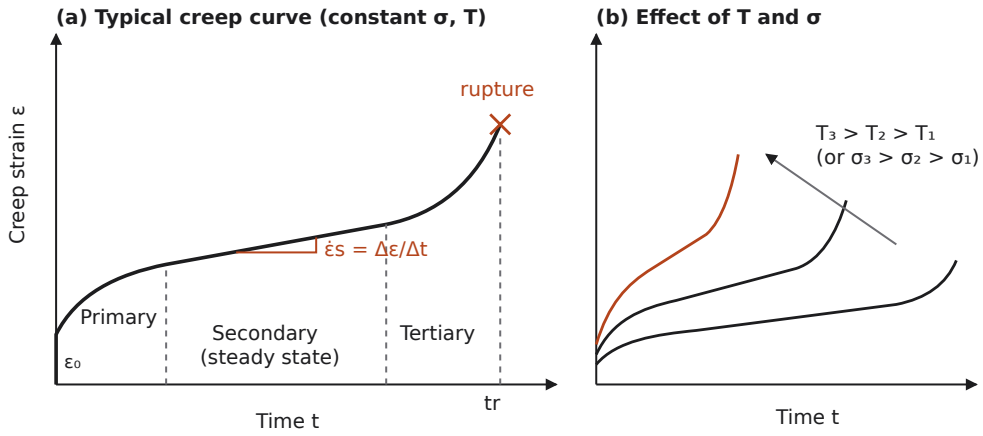
Soderberg is the most conservative. Example: S_e = 300 MPa, S_u = 700 MPa, σ_m = 150 MPa. Goodman (n = 1) gives allowable $\sigma_a = 300(1 - 150/700)$ = **236 MPa**.

8. Creep HIGH Asked: End Sem 2024 (4 marks)

DEFINITION

Creep is time-dependent, permanent deformation of a material under a **constant load or stress**, normally at elevated temperature. For metals it becomes important above about **0.4 T_m** (absolute temperature). Examples: turbine blades, steam-line pipes, boiler tubes, nuclear reactor parts. Polymers, and lead at room temperature, creep even at ambient temperature.

Creep curve: the three stages



Raising temperature or stress raises the instantaneous strain and the steady-state creep rate, and shortens the rupture life (Callister §8.12–8.13).

MODEL ANSWER: THREE STAGES OF CREEP AND THEIR MECHANISMS (4 MARKS)

Instantaneous strain ε_0 appears on loading. It is mostly elastic.

1. Primary (transient) creep: the creep rate *decreases* continuously with time, so the curve is concave downward. *Mechanism:* **strain hardening** dominates. Dislocations multiply and tangle, so deformation becomes harder as strain increases. Recovery is slower than hardening.

2. Secondary (steady-state) creep: the creep rate is *constant*, so the curve is linear. This is the longest stage. *Mechanism:* a **balance between strain hardening and recovery** (softening). Dislocations escape obstacles by **climb**, which is aided by vacancy diffusion, and annihilate. Its slope $\dot{\varepsilon}_s$ is the key design parameter for long-life parts.

3. Tertiary creep: the creep rate *accelerates* until rupture. *Mechanism:* **microstructural and metallurgical changes**: grain-boundary separation, formation of internal cracks, cavities and voids, necking (which raises the true stress), coarsening of precipitates, and recrystallization. Rupture is usually intergranular.

Draw: the curve with the three stages, ε_0, the slope $\dot{\varepsilon}_s$, the rupture point and t_r.

Effect of stress and temperature, and the creep-rate equation

FORMULAS

$\dot{\varepsilon}_s = K_1\sigma^n \quad (\text{constant T}) \qquad \dot{\varepsilon}_s = K_2\sigma^n \exp(-Q_c/RT)$

n is the stress exponent (about 3–8 for dislocation creep; 1 for diffusion creep). Q_c is the activation energy for creep, often about equal to that for self-diffusion. R = 8.314 J/mol·K.

WORKED NUMERICAL 9: CREEP RATE

(a) At constant temperature, the steady-state creep rate is 2.5×10^{-3} h^{-1} at 200 MPa, and n = 5. Find the rate at 250 MPa.

$\dot{\varepsilon}_2 = \dot{\varepsilon}_1(\sigma_2/\sigma_1)^n = 2.5 \times 10^{-3} \times (1.25)^5 = 2.5 \times 10^{-3} \times 3.052 =$ **7.63×10^{-3} h^{-1}**.

(b) Q_c = 270 kJ/mol. By what factor does $\dot{\varepsilon}_s$ rise from 800 K to 850 K at the same stress?

$\dot{\varepsilon}_2/\dot{\varepsilon}_1 = \exp[(Q_c/R)(1/T_1 - 1/T_2)] = \exp[(270000/8.314)(1/800 - 1/850)] = \exp(32475 \times 7.353 \times 10^{-5}) = \exp(2.388) =$ **≈ 10.9**. A 50 K rise makes creep about 11 times faster.

Mechanisms of creep

Mechanism	What happens	Dominant when
Dislocation glide	Dislocations move on slip planes, overcoming obstacles with thermal help	High stress
Dislocation climb (power-law creep)	Edge dislocations climb out of their slip plane by absorbing or emitting vacancies, bypass obstacles and then glide again. Rate is controlled by diffusion. n ≈ 3–8	Intermediate to high stress, $T > 0.4T_m$
Nabarro–Herring creep	Vacancies diffuse **through the lattice (grain interior)** from grain boundaries under tension to those under compression, so grains elongate. $\dot{\varepsilon} \propto \sigma/d^2$	Low stress, very high T
Coble creep	Same idea but diffusion **along grain boundaries**. $\dot{\varepsilon} \propto \sigma/d^3$	Low stress, lower T than N–H, fine grains
Grain-boundary sliding	Grains slide past each other along the boundaries, which needs accommodation by diffusion or dislocations. Causes wedge cracks and cavities at triple points	High T, fine grains, tertiary stage

A deformation-mechanism map (Ashby) plots σ/G against T/T_m and shows which mechanism dominates in each region.

Data extrapolation: Larson–Miller parameter

LARSON–MILLER PARAMETER

$$LM = T\,(C + \log t_r)$$

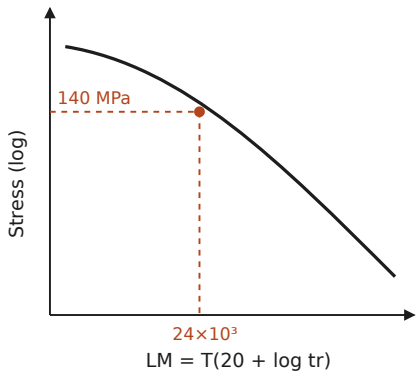
T in kelvin, t_r in hours, C ≈ 20. Short tests at higher temperature are used to predict long-term rupture life at lower temperature for the same stress.

WORKED NUMERICAL 10 (CALLISTER EX. 8.2)

Predict the rupture time of an S-590 alloy component at 800 °C (1073 K) and 140 MPa. From the LM plot, LM = 24.0 × 10³ at 140 MPa.

24 000 = 1073(20 + log t_r), so log t_r = 22.37 − 20 = 2.37 and t_r = **233 h (≈ 9.7 days)**.

Inverse: for 1000 h life at 700 °C, LM = 973(20 + 3) = **22.4 × 10³**. Read the allowable stress off the plot at this value.



Larson–Miller plot (sketch).

Effect of material variables and creep-resistant materials

Variable	Better creep resistance with…	Reason
Melting point	High T_m	At a given service T, the homologous temperature T/T_m is lower, so diffusion is slower.
Elastic modulus	High E	Stronger bonds
Grain size	**Large grains**, or no grain boundaries at all (single crystal)	Fewer boundaries means less grain-boundary sliding and Coble creep. This is the opposite of room-temperature strengthening.
Grain orientation	Directional solidification: grains elongated along the stress axis	No transverse boundaries normal to the stress
Solid-solution alloying	Yes	Solute atoms impede dislocation motion and slow diffusion.
Precipitates and dispersions	Fine, stable particles (e.g. γ′ $Ni_3(Al,Ti)$ in superalloys; ThO_2 in TD-nickel)	They pin dislocations and grain boundaries and must not coarsen at service T.

- **Creep-resistant materials:**
  - Ni- and Co-based **superalloys** (Inconel, Nimonic) for gas-turbine blades.
  - **Directionally solidified** and **single-crystal** turbine blades.
  - Stainless steels and Cr–Mo steels for boilers and steam pipes.
  - Refractory metals (W, Mo, Nb, Ta).
  - Ceramics (SiC, Si_3N_4, Al_2O_3): high T_m and strong bonds.
  - Thermal barrier coatings (yttria-stabilised zirconia) on blades.

- **Processing aids:** dispersion strengthening and directional solidification.

9. Design considerations: summary MEDIUM

Failure mode	Design parameter	Design measures
Brittle fracture	K_{Ic}, largest flaw a	Use K_{Ic} design. Use NDT to find flaws. Choose materials whose DBTT is below service temperature. Avoid notches.
Fatigue	S_e or fatigue strength at N cycles	Use fillets and a smooth finish. Shot peen or case harden. Avoid corrosive media. Check mean stress with Goodman or Soderberg.
Creep	$\dot{\varepsilon}_s$, t_r (LM parameter)	Use high-T_m, coarse-grained or single-crystal precipitation-hardened alloys, and limit the service temperature.

Likely exam questions

1. Explain Griffith's theory of brittle fracture and derive the expression for the critical stress to propagate a crack. (6)
2. A material has K_{Ic} = 80 MPa√m, critical crack length 0.05 mm and E = 120 GPa. Calculate its surface energy. (2)
3. Discuss the three stages of the creep curve with a diagram, and explain the mechanism in each stage. (4)
4. Differentiate between ductile and brittle fracture. Explain cup-and-cone fracture with sketches. (4)
5. Define fracture toughness. What is plane-strain fracture toughness? A plate with K_{Ic} = 50 MPa√m, Y = 1.1 carries 250 MPa: find the critical crack length. (5+3)
6. What is the ductile-to-brittle transition? Why do BCC metals show it and FCC metals do not? Explain the Charpy test. (4)
7. Draw S–N curves for steel and aluminium. Define endurance limit and fatigue strength. Explain the factors that improve fatigue life. (6)
8. Define σ_m, σ_a, σ_r and R. For σ_{max} = 400 MPa and σ_{min} = −100 MPa, find them. (2–3)
9. Explain the creep mechanisms: dislocation climb, Nabarro–Herring, Coble, grain-boundary sliding. How do material variables affect creep resistance? (4–6)
10. What is the Larson–Miller parameter? Find the rupture life at 1073 K if LM = 24 × 10^3. (3)
11. Explain the upper and lower yield points and the 0.2 % offset method. Relate E, G and ν. (4)

MODEL ANSWER: WHY BCC METALS SHOW A DBTT (4 MARKS)

In BCC metals there is no truly close-packed plane, so the Peierls (lattice friction) stress for dislocation motion is high and **strongly temperature-dependent**. Dislocation glide needs thermal activation. As temperature falls, the yield stress rises steeply, while the cleavage fracture stress changes little. Below the temperature where the two curves cross (the DBTT), the material cleaves before it can yield: low impact energy, flat granular fracture. FCC metals have 12 close-packed {111}⟨110⟩ slip systems and a low Peierls stress that hardly changes with temperature. Yielding always occurs before cleavage, so they remain ductile down to cryogenic temperatures. That is why austenitic stainless steel, Al and Cu are used for LNG tanks. Sketch the energy–temperature curve for both.

MODEL ANSWER: IMPROVING FATIGUE LIFE (4 MARKS)

1. **Design:** remove stress raisers. Use generous fillet radii, avoid sharp keyways, and drill crack-stopper holes.
2. **Surface finish:** polish to remove machining marks, where cracks start.
3. **Compressive residual stress:** shot peening, case hardening (carburizing, nitriding) or surface rolling. The compressive layer offsets the tensile part of the cycle.
4. **Mean stress:** reduce σ_m, keeping within the Goodman line.
5. **Environment:** prevent corrosion fatigue with coatings, inhibitors or a cathodic method, and minimise thermal-stress cycling.
6. **Material:** choose clean (inclusion-free), fine-grained alloys with a high endurance limit.

UNIT 5 · ~6 CONTACT HRS

Composite Materials

Most examined: classification by reinforcement (with tree diagram), rule of mixtures (isostrain/isostress) numericals, critical fibre length, applications.

1. What is a composite? HIGH

DEFINITION

A **composite** is a multiphase material, normally made artificially, in which the constituent phases are **chemically dissimilar** and separated by a **distinct interface**. It combines the best properties of its constituents. This is the **principle of combined action**: better property combinations come from a judicious mix of two or more distinct materials. Most composites have two phases. The **matrix** is continuous and surrounds the other phase. The **dispersed phase** (reinforcement) is embedded in it. Examples: wood (cellulose fibres in lignin), bone, concrete, GFRP, CFRP, WC–Co cermets.

The properties of a composite depend on the properties of the constituent phases, their relative amounts, and the **geometry of the dispersed phase**: particle shape, size, distribution and orientation.

Functions of the matrix

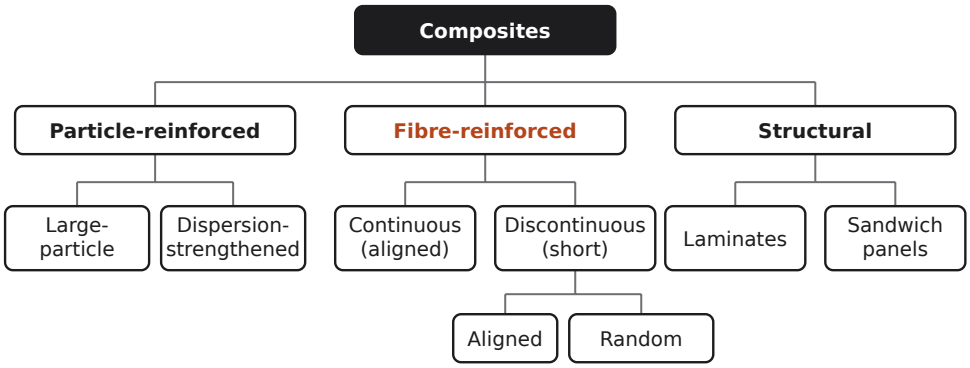
- Binds the fibres together and transmits and distributes the applied load to them.
- Protects the fibres from surface damage (abrasion, chemical attack).
- Separates the fibres, which stops cracks spreading from fibre to fibre. Cracks are blunted by the ductile matrix.
- Gives transverse strength, shape and the maximum service temperature.

Functions of the reinforcement

- Carries most of the load: high strength and stiffness.
- Raises E, strength, creep and fatigue resistance, and toughness (in ceramic-matrix composites).
- Particles improve wear resistance, hardness and dimensional stability, and lower cost.
- The fibre–matrix **bond** must be strong for load transfer. Coupling agents help (see Unit 6).

Classification by matrix	Example	Typical use
Polymer-matrix (PMC)	GFRP, CFRP, aramid–epoxy	Boat hulls, aircraft parts, sports goods
Metal-matrix (MMC)	Al–SiC, Al–B, Al–Al_2O_3 fibres	Engine pistons, brake rotors, drive shafts
Ceramic-matrix (CMC)	SiC–SiC, Al_2O_3–SiC whiskers	Cutting tools, turbine parts (higher toughness)
Carbon–carbon	Carbon fibres in a carbon matrix	Brake discs (aircraft, F1), re-entry nose cones

2. Classification based on reinforcement HIGH



Classification scheme for composites by reinforcement (Callister Fig. 16.2). Learn this tree: it is the opening diagram for almost every composite question.

2.1 Particle-reinforced composites

The dispersed phase is **equiaxed**: particle dimensions are about the same in all directions.

	Large-particle composites	**Dispersion-strengthened composites**
Particle size	Large (> 1 μm)	Very small, 0.01–0.1 μm (10–100 nm)
Mechanism	Particle–matrix interaction is not at the atomic level. Particles restrain the movement of the matrix near them, so the matrix transfers part of the load to the (stiffer) particles. Analysed by continuum mechanics.	Interaction at the atomic or molecular level, as in precipitation hardening. Particles **hinder dislocation motion**, so yield strength and hardness rise.
Volume fraction	Often large, 15–90 %	Small, typically < 15 %
Purpose	Improve stiffness, wear resistance and hardness; lower cost	Strength retained at **high temperature**. Particles are inert and do not coarsen or dissolve, unlike precipitates.
Examples	**Concrete** (gravel and sand in cement); **cermets** such as cemented carbide WC or TiC in a Co or Ni binder (cutting tools); **carbon black** in vulcanised rubber tyres (15–30 vol %, 20–50 nm); polymers with fillers	**TD nickel** (≈ 3 vol % ThO_2 in Ni); **SAP** (sintered aluminium powder, Al_2O_3 flakes in Al)

RULE OF MIXTURES FOR PARTICULATE COMPOSITES (BOUNDS)

Upper bound: $E_c(u) = E_m V_m + E_p V_p$ Lower bound: $E_c(l) = E_m E_p / (V_m E_p + V_p E_m)$

$V_m + V_p = 1$. The actual modulus lies between the bounds. Density always follows the linear rule: $\rho_c = \rho_m V_m + \rho_p V_p$.

WORKED NUMERICAL 1: PARTICULATE BOUNDS

A composite of 50 vol % tungsten particles (E = 407 GPa) in copper (E = 110 GPa). Find the upper and lower bounds on E_c.

Upper: 0.5(110) + 0.5(407) = **258.5 GPa**. Lower: (110 × 407)/(0.5 × 407 + 0.5 × 110) = 44 770/258.5 = **173.2 GPa**.

Density (ρ_{Cu} = 8.96, ρ_W = 19.3 g/cm³): ρ_c = 0.5(8.96) + 0.5(19.3) = **14.13 g/cm³**.

2.2 Fibre-reinforced composites HIGH

These are technologically the most important. The aim is high **specific strength** (strength/density) and **specific modulus** (E/density). The dispersed phase has a large length-to-diameter ratio. By diameter the reinforcement is either a **whisker** (very thin single crystal, nearly flaw-free, extremely strong, expensive), a **fibre** (polycrystalline or amorphous, small diameter), or a **wire** (metallic, larger diameter).

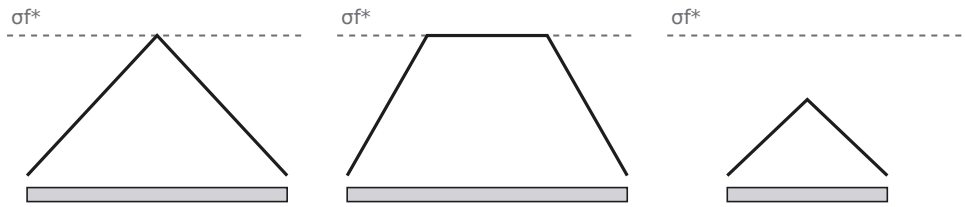
Influence of fibre length: critical fibre length l_c

The load is transferred from the matrix to the fibre by **shear at the fibre–matrix interface**. No load is transferred at the fibre ends. A minimum length, l_c, is needed for the fibre to be loaded to its full tensile strength σ_f^*.

CRITICAL FIBRE LENGTH

$$l_c = \sigma_f^* \, d / (2\tau_c)$$

d is the fibre diameter. τ_c is the fibre–matrix bond strength or the matrix shear yield strength, whichever is smaller. Fibres with $l \gg l_c$ (typically $l > 15\, l_c$) behave as **continuous**. Fibres with $l < 15\, l_c$ are **discontinuous (short)**. If $l < l_c$, there is hardly any reinforcement and the composite behaves like a particulate one.



(a) l = lc: σf* only at centre (b) l > lc: effective (c) l < lc: never reaches σf*

Stress along a fibre loaded to σ_f^* (Callister Fig. 16.7). The stress builds up from zero at each end over a distance $l_c/2$.

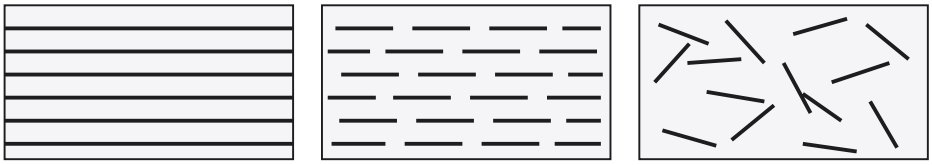
WORKED NUMERICAL 2: CRITICAL FIBRE LENGTH

Carbon fibres (d = 10 μm, σ_f^* = 3.5 GPa) are in an epoxy matrix with bond strength τ_c = 10 MPa. Find l_c and the minimum length for "continuous" behaviour.

$l_c = (3500 \times 10^6 \times 10 \times 10^{-6})/(2 \times 10 \times 10^6) = 35\,000/(2 \times 10^7)$ = **1.75×10^{-3} m = 1.75 mm**. Continuous behaviour needs $l > 15\, l_c \approx$ **26 mm**.

Inverse: if l_c = 1 mm for a 15 μm glass fibre with σ_f^* = 3.45 GPa, then $\tau_c = \sigma_f^* d/(2l_c) = (3450 \times 15 \times 10^{-6})/(2 \times 10^{-3})$ = **25.9 MPa**.

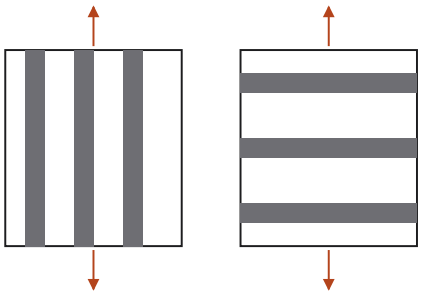
Influence of fibre orientation and concentration



(a) Continuous, aligned (b) Discontinuous, aligned (c) Discontinuous, random

Fibre arrangements. Aligned fibres give anisotropic properties: very high along the fibres, low across them. Random short fibres give isotropic but lower properties.

2.3 Continuous, aligned fibre composites: rule of mixtures HIGH



Isostrain (longitudinal) Isostress (transverse)

Grey = fibres. Load parallel to the fibres (left) or perpendicular to them (right).

Longitudinal loading: isostrain

The load is shared: $F_c = F_m + F_f$, so $\sigma_c A_c = \sigma_m A_m + \sigma_f A_f$. Divide by A_c: $\sigma_c = \sigma_m V_m + \sigma_f V_f$. With perfect bonding, $\varepsilon_c = \varepsilon_m = \varepsilon_f$. Dividing by ε gives the upper bound:

$$E_{cl} = E_m V_m + E_f V_f$$

Transverse loading: isostress

$\sigma_c = \sigma_m = \sigma_f$ and $\varepsilon_c = \varepsilon_m V_m + \varepsilon_f V_f$. This gives the lower bound:

$$1/E_{ct} = V_m/E_m + V_f/E_f$$

ALL FIBRE-COMPOSITE FORMULAS (MEMORISE)

$E_{cl} = E_m V_m + E_f V_f$ $E_{ct} = E_m E_f/(V_m E_f + V_f E_m)$

$F_f/F_m = E_f V_f/(E_m V_m)$ (load ratio, isostrain)

Longitudinal strength: $\sigma^*_{cl} = \sigma'_m(1 - V_f) + \sigma_f^* V_f$

Discontinuous aligned, $l > l_c$: $\sigma^*_{cd} = \sigma_f^* V_f(1 - l_c/2l) + \sigma'_m(1 - V_f)$

Discontinuous aligned, $l < l_c$: $\sigma^*_{cd'} = (l\tau_c/d)V_f + \sigma'_m(1 - V_f)$

Random / other orientation: $E_{cd} = K E_f V_f + E_m V_m$

σ'_m is the matrix stress at the strain where the fibres fail. K is the fibre efficiency: 1 for aligned (longitudinal), 0 for aligned (transverse), 3/8 for random in-plane (2-D), 1/5 for random 3-D.

Stress–strain behaviour (longitudinal). Stage I: both fibre and matrix are elastic, and the slope is E_{cl}. Stage II: the matrix yields, the curve is nearly linear but flatter, and the fibres carry almost all the extra load. Failure begins when the fibres break. The failure is gradual, not catastrophic, because fibres break at different points and the matrix still holds pulled-out fibres.

WORKED NUMERICAL 3: LONGITUDINAL MODULUS AND LOAD SHARING (CALLISTER EX. 16.1)

A continuous, aligned glass-fibre/polyester composite has 40 vol % glass fibres (E_f = 69 GPa) in a polyester matrix (E_m = 3.4 GPa). (a) Find E_{cl}. (b) If the cross-section is 250 mm² and the longitudinal stress is 50 MPa, find the load carried by each phase. (c) Find the strain in each phase.

(a) $E_{cl} = 3.4(0.6) + 69(0.4) = 2.04 + 27.6 =$ **29.6 GPa ≈ 30 GPa**.

(b) $F_f/F_m = (69 \times 0.4)/(3.4 \times 0.6) = 27.6/2.04 =$ **13.5**. Total $F_c = 50 \times 250 = 12\,500$ N. $F_m = 12\,500/14.5 =$ **862 N** and $F_f =$ **11 638 N**. The fibres carry 93 % of the load.

(c) $A_m = 150$ mm² and $A_f = 100$ mm², so $\sigma_m = 862/150 = 5.75$ MPa and $\sigma_f = 11\,638/100 = 116.4$ MPa. $\varepsilon_m = 5.75/3400 =$ **1.69×10^{-3}**; $\varepsilon_f = 116.4/69\,000 = 1.69 \times 10^{-3}$. They are equal, which confirms isostrain.

WORKED NUMERICAL 4: TRANSVERSE MODULUS

For the same composite: $E_{ct} = (3.4 \times 69)/(0.6 \times 69 + 0.4 \times 3.4) = 234.6/(41.4 + 1.36) = 234.6/42.76 =$ **5.5 GPa**. This is about 1/5 of E_{cl}, which shows the strong anisotropy.

WORKED NUMERICAL 5: DESIGNING V_F; LONGITUDINAL STRENGTH

(a) What fibre fraction of carbon (E_f = 230 GPa) in epoxy (E_m = 3.4 GPa) gives E_{cl} = 50 GPa?

$50 = 3.4(1 - V_f) + 230V_f$, so $V_f = (50 - 3.4)/(230 - 3.4) = 46.6/226.6 =$ **0.206 (20.6 %)**.

(b) Longitudinal tensile strength with $V_f = 0.6$, $\sigma_f^* = 4000$ MPa and $\sigma'_m = 15$ MPa: $\sigma^*_{cl} = 15(0.4) + 4000(0.6) = 6 + 2400 =$ **2406 MPa**.

(c) Random in-plane short glass fibres, $V_f = 0.3$: $E_{cd} = (3/8)(69)(0.3) + 3.4(0.7) = 7.76 + 2.38 =$ **10.1 GPa**.

WORKED NUMERICAL 6: DISCONTINUOUS ALIGNED STRENGTH

Fibres with $l = 5$ mm, $l_c = 1$ mm, $\sigma_f^* = 3.45$ GPa, $V_f = 0.3$ and $\sigma'_m = 20$ MPa. Since $l > l_c$:

$\sigma^*_{cd} = 3450(0.3)(1 - 1/10) + 20(0.7) = 931.5 + 14 =$ **945.5 MPa**.

A continuous composite would give 1035 + 14 = 1049 MPa. Short fibres reach about 90 % of that.

2.4 Structural composites MEDIUM

- **Laminar composites:** 2-D sheets or plies, each with a preferred high-strength direction (e.g. aligned-fibre prepregs), are stacked and bonded with the orientation changing from layer to layer.
  - Lay-ups: *unidirectional* (0°); *cross-ply* (0°/90°); *angle-ply* (+θ/−θ); *multidirectional* (0°/±45°/90°), which is nearly isotropic in the plane.
  - Examples: plywood, skis, aircraft wing skins.
- **Sandwich panels:** two strong, stiff outer **face sheets** (Al alloy, CFRP, GFRP, Ti, plywood) are bonded to a thick, lightweight, low-density **core** (polymer foam, balsa wood, or **honeycomb** of Al or aramid paper).
  - The faces carry in-plane bending loads (tension and compression).

- The core separates the faces, carries transverse shear, resists deformation perpendicular to the face, and gives high bending stiffness at low weight, like an I-beam web.
- Applications: aircraft floors, wings and stabilisers, helicopter rotor blades, roofs, walls, boat hulls, satellite panels.

3. Characteristics, advantages and limitations MEDIUM

Advantages

- Very high specific strength and specific stiffness, so they are light.
- Properties can be tailored by choosing the fibre type, V_f and orientation.
- Good fatigue and corrosion resistance (PMCs do not rust).
- Low thermal expansion (CFRP), so they are dimensionally stable.
- Good damping. Complex shapes can be moulded as single parts, which reduces fasteners.
- Toughness: crack blunting and fibre pull-out, especially in CMCs.

Limitations

- Anisotropic: weak in the transverse direction and between layers (delamination).
- High cost (carbon, aramid) and slow manufacture.
- PMCs have a low maximum service temperature and absorb moisture.
- Damage can be hidden (impact) and is hard to inspect and repair.
- Recycling is difficult (thermosets).
- Joining is difficult. Compressive strength is low for aramid.

4. Applications of composites in industry HIGH

Industry	Composite	Applications
Aerospace	CFRP, aramid–epoxy, honeycomb sandwich, C–C, CMCs	Boeing 787 and A350 fuselage and wings (~50 % composite by weight), helicopter rotor blades, control surfaces, rocket motor cases, brake discs, re-entry heat shields
Automotive	GFRP (SMC), CFRP, Al–SiC MMC, rubber + carbon black	Body panels, leaf springs, drive shafts, bumpers, F1 monocoque chassis, pistons, brake rotors, tyres
Sports	CFRP, GFRP, aramid	Tennis rackets, golf shafts, bicycle frames, fishing rods, skis, hockey sticks, pole-vault poles, helmets
Marine	GFRP, sandwich (foam/balsa core)	Boat and yacht hulls, decks, masts, minesweeper hulls (non-magnetic)
Construction and civil	Concrete, RCC, pre-stressed concrete, GFRP rebar, CFRP wraps	Buildings, bridges, column retrofit, pipes, tanks, window frames
Electrical	GFRP (non-conducting), Cu–W, Ag–W	Printed circuit boards (FR-4: glass–epoxy), insulator rods, switchgear, electrical contacts, wind-turbine blades
Cutting tools and wear	Cermets (WC–Co, TiC–Ni), Al_2O_3–SiC whisker	Cutting tool inserts, drill bits, dies, mining tools
Defence and protection	Kevlar (aramid), UHMWPE, ceramic/aramid	Bullet-proof vests, helmets, vehicle armour
Biomedical	CFRP, hydroxyapatite–polymer	Prosthetic limbs, bone plates, dental fillings (particulate)

Likely exam questions

1. Define a composite material. Classify composites on the basis of reinforcement, with a neat diagram, giving examples of each. (6)
2. Differentiate between large-particle and dispersion-strengthened composites. (3–4)
3. Derive the expressions for the modulus of a continuous, aligned fibre composite under isostrain and isostress conditions. (5)
4. A composite contains 40 % glass fibres (E = 69 GPa) in polyester (E = 3.4 GPa). Find E_{cl}, E_{ct} and the fraction of load carried by the fibres. (3–4)
5. What is critical fibre length? Derive or state l_c and explain its significance with stress profiles. (4)
6. Explain the influence of fibre length, orientation and concentration on composite properties. (4)
7. Write short notes on laminar composites and sandwich panels. (4)
8. Discuss the characteristics and applications of composite materials in industry. (4)
9. What are the functions of the matrix and the reinforcement in a composite? (3)

MODEL ANSWER: CLASSIFICATION OF COMPOSITES BASED ON REINFORCEMENT (6 MARKS)

Definition (1 mark): give the definition from §1. Then draw the **tree diagram** (2 marks) and explain each class briefly (3 marks):

1. **Particle-reinforced:** the dispersed phase is equiaxed.
   - *Large-particle:* particles over 1 μm restrain the matrix and share the load. Examples: concrete, WC–Co cermet, carbon black in tyres.
   - *Dispersion-strengthened:* 10–100 nm oxide particles block dislocations, and the strength is retained at high temperature. Examples: TD-Ni (ThO_2), SAP (Al_2O_3 in Al).
2. **Fibre-reinforced:** the dispersed phase has a high aspect ratio, and the fibres carry most of the load. These give the best specific strength and stiffness.
   - *Continuous aligned:* $l > 15\ l_c$. Highly anisotropic. Examples: CFRP, GFRP filament-wound tanks.
   - *Discontinuous:* short fibres, either aligned or randomly oriented (isotropic). Example: chopped-strand GFRP, SMC panels.
3. **Structural:** properties depend on the geometric design of the elements as well as the materials.
   - *Laminates:* plies stacked at different angles. Examples: plywood, CFRP skins.
   - *Sandwich panels:* stiff faces with a light core (honeycomb or foam). Example: aircraft floors.

MODEL ANSWER: LARGE-PARTICLE VS DISPERSION-STRENGTHENED (3 MARKS)

Size: > 1 μm versus 0.01–0.1 μm. Mechanism: mechanical restraint of the matrix and load sharing (continuum level) versus blocking of dislocation motion (atomic level). Volume fraction: high (up to 90 %) versus low (< 15 %). Aim: stiffness, wear and cost versus high-temperature strength. Examples: concrete and cemented carbide versus TD-Ni and SAP. Dispersoids, unlike precipitates, do not dissolve or coarsen at high temperature, so the strengthening lasts.

UNIT 6 · ~7 CONTACT HRS

Powder Metallurgy & Fibre-Reinforced Composites

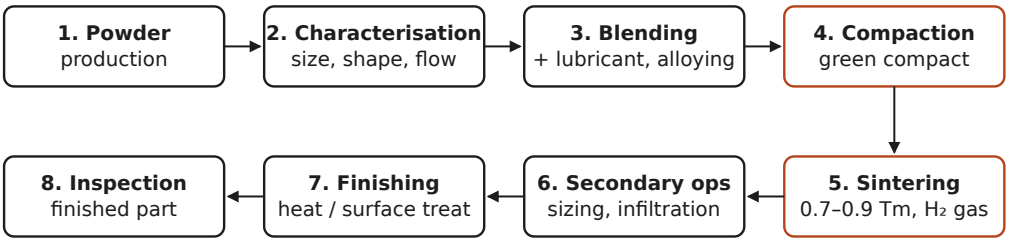
Most examined: powder production methods, P/M process steps, cemented carbide manufacture, sintering, self-lubricating bearings, fibres (glass, carbon, Kevlar 49) and matrices, coupling agents.

Part A · Powder Metallurgy (P/M)

DEFINITION

Powder metallurgy is the process of producing metal (or ceramic–metal) parts by **compacting fine powders** in a die into the required shape, and then **sintering** them: heating below the melting point of the main constituent in a controlled atmosphere, so that the particles bond by solid-state diffusion. The principle: the powder particles bond and densify by atomic diffusion, driven by the **reduction in surface energy**, without melting the bulk. It is the method of choice for refractory metals (W, Mo), for materials that do not mix in the liquid state (W–Cu, Cu–graphite), for controlled porosity, and for net-shape mass production.

1. P/M process: flow chart HIGH



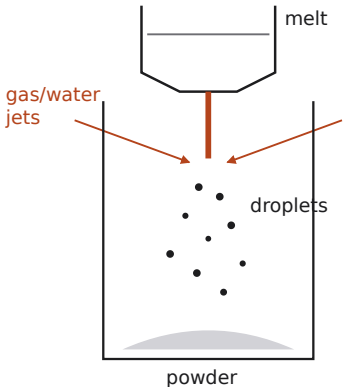
Sequence of operations in powder metallurgy. Compaction and sintering (accent) are the two essential steps.

2. Powder production methods HIGH Asked: End Sem 2024

(a) Atomization: the most widely used

A stream of **molten metal** is broken into fine droplets by high-pressure jets of **gas** (N_2, Ar, air) or **water**, or by a spinning disc or electrode (**centrifugal atomization**). The droplets solidify in flight into powder.

- Gas atomization gives **spherical** particles. Water atomization gives **irregular** particles, which are cheaper and have better green strength.
- Size range 10–1000 µm. Used for most alloys: steels, stainless steel, Al, Cu, bronze, superalloys.
- Pre-alloyed powders are possible.



Gas or water atomization.

(b) Reduction of oxides (chemical)

Metal oxides are reduced in the solid state by H_2 or CO gas, or by carbon, at temperatures below the melting point. The result is a spongy, porous, irregular powder with good compressibility and green strength. Examples: **W, Mo** ($WO_3 + 3H_2 \rightarrow W + 3H_2O$), Fe sponge powder (Höganäs process), Cu, Ni, Co.

(c) Electrolytic deposition

The metal is deposited at the cathode of an electrolytic cell under conditions (high current density, low metal-ion concentration) that give a loose, spongy or powdery deposit. The deposit is washed, dried, milled and annealed. The powder is of **very high purity** and dendritic, with excellent compressibility. Examples: Cu (most common), Fe, Ag, Ni, Ta.

(d) Mechanical methods: comminution and mechanical alloying

- **Crushing, milling and grinding** (ball mills, hammer mills, jaw crushers) are used for brittle materials such as oxides, carbides, intermetallics, and embrittled hydride Ti.
- **Mechanical alloying:** powders of different metals are milled together in a high-energy ball mill. Repeated cold welding and fracturing produce truly alloyed powders. Used for oxide-dispersion-strengthened (ODS) superalloys.
- Machining chips can also be ground (cheap but coarse powder).

(e) Carbonyl process (thermal decomposition)

Fe or Ni reacts with CO under pressure to form volatile carbonyls, $Fe(CO)_5$ or $Ni(CO)_4$. These are distilled and then decomposed by heating to give **very fine (1–10 µm), spherical, high-purity** powder. Used for magnetic cores and electronic parts.

(f) Others

Chemical precipitation from solution (Ag, Cu), granulation (pouring molten metal into water), and the hydride–dehydride process (Ti, Zr).

Method	Particle shape	Purity	Typical metals
Gas atomization	Spherical	High	Superalloys, stainless steel, Al, Ti
Water atomization	Irregular	Moderate (oxide skin)	Steels, Cu, Fe
Reduction	Spongy, porous	Moderate to high	W, Mo, Fe, Cu
Electrolytic	Dendritic	Very high	Cu, Fe, Ag
Mechanical (milling)	Flaky, angular	Contamination possible	Brittle carbides, oxides
Carbonyl	Fine spherical	Very high	Fe, Ni

3. Characterisation and blending MEDIUM

- **Particle size and size distribution:** measured by sieve analysis (mesh number) or laser diffraction. A mix of sizes packs better because fine particles fill the voids.
- **Particle shape:** spherical shapes flow and pack well but have low green strength. Irregular shapes interlock and give high green strength.
- **Flow rate** (Hall flowmeter: seconds for 50 g) governs how fast and uniformly the die fills. **Apparent density** and **tap density** are measured.
- **Compressibility** (green density at a given pressure), **green strength**, chemical purity and oxide content.

- **Blending and mixing:** gives uniformity, combines powders of different metals (e.g. Fe + Cu + graphite), and adds **lubricants** (zinc stearate, lithium stearate or wax, 0.5–1.5 %) to reduce die-wall friction and ejection force. Binders raise green strength. Mixing is done in a dry, inert atmosphere to avoid oxidation.

4. Compaction HIGH

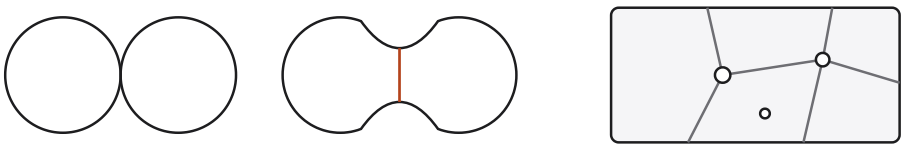
Powder is pressed in a die at pressures of 70–800 MPa (higher for steel) to form a **green compact**. The compact has the required shape and enough strength to be handled (green density about 70–90 % of theoretical). Particles first rearrange, then deform plastically at the contacts, and finally interlock and cold-weld.

- **Die pressing** (single-action or double-action, using mechanical or hydraulic presses): the most common method. Die-wall friction causes **density gradients**. Double-action pressing (top and bottom punches) gives more uniform density. The height-to-diameter ratio is limited.
- **Cold isostatic pressing (CIP):** powder in a flexible rubber or polyurethane mould is pressed equally from all sides by a fluid (water or oil) at 400–1000 MPa. This gives uniform density and allows complex and long shapes.
- **Hot isostatic pressing (HIP):** powder sealed in a metal can is subjected to high-pressure inert gas (Ar, ~100–200 MPa) at high temperature (e.g. 1100–1200 °C). Compaction and sintering happen at once, giving **~100 % density** and excellent properties. Used for superalloy turbine discs, Ti parts and sinter-HIP carbides.
- Other methods: **powder injection moulding** (PIM/MIM: fine powder + polymer binder injected, debinded and sintered; small complex parts), **powder rolling** (strip), **powder extrusion**, **hot pressing** and **spark plasma sintering**.

5. Sintering: mechanism and stages HIGH

DEFINITION

Sintering is heating the green compact to about **0.7–0.9 T_m** (absolute) of the main constituent, for a period of time (roughly 10 minutes to several hours), in a **protective atmosphere**: H_2, dissociated ammonia, endothermic gas, N_2-based gas, or vacuum. The particles bond metallurgically by atomic diffusion, so strength and density rise and porosity falls. Typical temperatures: Fe and steel 1100–1300 °C, Cu 750–1000 °C, bronze 760–870 °C, WC–Co 1400–1500 °C.



(a) Point contact after pressing

(b) Initial stage: neck formation and growth

(c) Final stage: grains with isolated spherical pores

Neck growth during sintering. The driving force is the reduction in total surface energy.

1. **Initial stage (bonding, neck formation):** atoms diffuse to the contact points and **necks** form and grow between particles. Densification is small at this stage, but strength rises sharply.

2. **Intermediate stage:** necks grow larger and the pores form an interconnected, cylindrical network along the grain edges. This is where most of the **densification and shrinkage** occurs, as particle centres approach one another. Grains begin to grow.
3. **Final stage:** the pores become **isolated**, spherical and closed (density above ~92 %). They shrink slowly and some are trapped inside grains. Grain growth continues.

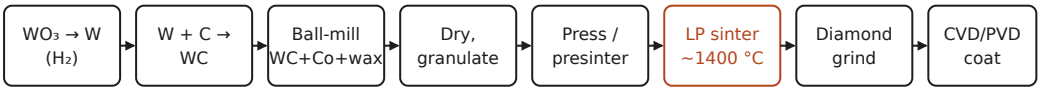
Diffusion paths: surface diffusion and evaporation–condensation make the neck grow without shrinkage. Grain-boundary diffusion and volume (lattice) diffusion transport material from the contact zone to the neck, which causes **shrinkage and densification**.

Liquid-phase sintering: a minor constituent with a lower melting point melts (e.g. Co in WC–Co, Cu in Fe–Cu), wets the solid particles and pulls them together by capillary force. This speeds up densification to near full density. **Activated sintering** uses small additions (e.g. Ni in W) to accelerate diffusion.

6. Secondary operations and surface treatment MEDIUM

Operation	Purpose
Sizing	Re-pressing a sintered part in a die to improve dimensional accuracy.
Coining and repressing	Re-pressing to raise density and strength, and to imprint surface detail. May be followed by re-sintering (double press, double sinter).
Infiltration	The pores of a sintered skeleton are filled with a molten metal of lower melting point by capillary action, e.g. **Cu into an Fe or steel skeleton** (raises strength, density, toughness, and seals pores) or Cu or Ag into W (electrical contacts).
Impregnation	The interconnected pores are filled with oil, grease, wax or polymer resin, by vacuum impregnation. **Self-lubricating bearings**: porous bronze (Cu–10Sn) or Fe bearings with 20–30 % porosity are impregnated with oil. In service, heat and pressure draw the oil to the surface. They need no external lubrication (fans, appliances, automobiles). Resin impregnation seals parts for pressure-tightness and plating.
Heat treatment	Quench-and-temper and carbonitriding of P/M steels. Steam treatment (≈ 550 °C) forms a **Fe_3O_4 (magnetite) layer** that seals surface pores and improves wear and corrosion resistance.
Surface treatment	Plating (after sealing), shot peening, case hardening (carburizing, nitriding), and coatings (PVD/CVD for carbides) give wear, corrosion and fatigue resistance.
Machining, joining	Cross holes, threads and grooves that cannot be pressed. Welding and brazing.

7. Cemented carbide (WC–Co) tools: production steps HIGH Asked: End Sem 2024



Production of cemented carbide (WC–Co) cutting-tool inserts.

1. **Tungsten powder:** WO_3 or ammonium paratungstate is reduced in hydrogen at 600–900 °C to give fine W powder.
2. **Carburization:** W powder is mixed with carbon black and heated to 1400–1600 °C in H_2, giving **WC powder** (1–10 µm). TiC, TaC or NbC may be added for grades that cut steel (they

resist cratering).

3. **Mixing and ball milling:** WC is milled with **3–25 % cobalt powder** (the binder) in an organic liquid (alcohol, acetone or hexane) for many hours. This coats the WC with Co and refines it. **Paraffin wax (1–2 %)** is added as a pressing lubricant and temporary binder.
4. **Drying and granulation:** spray drying gives free-flowing granules.
5. **Compaction:** die pressing (≈ 100–200 MPa), extrusion (rods for drills), or CIP produces an oversized green shape that allows for ~17–22 % linear shrinkage.
6. **Dewaxing and presintering** at 800–1150 °C in H_2 or vacuum removes the wax. The part reaches a chalk-like strength and can be **machined or shaped** at this stage.
7. **Final (liquid-phase) sintering** at **1350–1500 °C** in vacuum or H_2. Co (with dissolved WC; the eutectic is ~1320 °C) melts, wets the WC grains, draws them together by capillarity, and fills the pores, giving near-full density. Sinter-HIP removes any residual porosity.
8. **Finishing:** diamond grinding to size and edge honing.
9. **Coating:** CVD or PVD layers of TiN, TiC, TiCN or Al_2O_3 for wear resistance.

Properties: hardness about 90 HRA (1300–1800 HV), retained up to ~1000 °C. More Co gives a tougher but softer tool. Uses: cutting inserts, drills, dies, wire-drawing dies, rock and mining bits.

8. Applications, advantages and limitations of P/M HIGH

Application	Why P/M
Cemented carbide tools (WC–Co, TiC–Ni)	WC cannot be melted and cast. A Co binder is needed.
Self-lubricating porous bearings (bronze, Fe)	Controlled interconnected porosity holds oil.
Filters (bronze, stainless steel)	Controlled pore size and permeability.
Refractory metals: W lamp filaments, Mo heaters, Ta capacitors	Melting points too high for casting (W 3410 °C).
Automotive gears, sprockets, cams, connecting rods, synchroniser hubs	Net shape, mass production, little or no machining, low cost.
Magnets (Alnico, Nd–Fe–B, ferrites); soft-magnetic cores	Fine aligned grains; complex shapes.
Electrical contacts: W–Cu, Ag–W, Ag–CdO; brushes (Cu–graphite)	Combine materials that do not alloy in the liquid state.
Friction materials (clutch and brake linings: Cu or Fe + graphite + SiO_2)	Mixtures of metals and non-metals.
Aerospace: superalloy discs (HIP), Ti parts; ODS alloys	Fine, uniform microstructure; dispersion strengthening.

Advantages

- **Net or near-net shape:** little or no machining, and close to 97 % material use (minimal scrap).
- Can make parts from high-melting-point metals (W, Mo) and carbides.
- Can combine immiscible materials (W–Cu, metal–ceramic, metal–graphite).
- **Controlled porosity:** self-lubricating bearings and filters.

Limitations

- High cost of powders and dies, so it pays only for large production volumes (> ~10 000 parts).
- Size and shape limits: press capacity, and undercuts and cross holes cannot be pressed.
- Residual porosity gives lower strength, ductility and toughness than wrought parts (unless HIP is used).
- Density variations in tall parts.
- Some powders (Al, Mg, Ti, Zr) are fire and explosion hazards.

- Fine, uniform grain structure with no segregation (unlike casting).
- Good surface finish and tolerances. High production rates and automation.
- Skilled labour is not required. Energy-efficient.
- Powders oxidise and must be stored carefully.

Part B · Fibre-Reinforced Composites (FRC)

9. General characteristics and applications HIGH

- A fibre-reinforced composite consists of a strong, stiff, brittle **fibre** phase embedded in a more ductile, lower-modulus **matrix**. The fibre carries the load. The matrix binds, protects and transfers the load by interfacial shear (see Unit 5 for l_c and the rule of mixtures).
- Design goals: high **specific strength** (σ/ρ) and **specific modulus** (E/ρ).
- Characteristics: anisotropic (tailorable by lay-up), excellent fatigue resistance (especially CFRP), corrosion resistance, low thermal expansion, good damping, non-magnetic options (glass, aramid), and electrically insulating options (glass).
- Fibres must have small diameter (fewer flaws, so strength approaches theoretical), high E, high strength and good bonding with the matrix. $\mathbf{E_{fibre} \gg E_{matrix}}$.
- Applications: aircraft structures, rotor and wind-turbine blades, automotive panels and leaf springs, boat hulls, pressure vessels (filament-wound), pipes and tanks, sports goods, PCBs, ballistic armour, bridges and retrofitting.

10. Introduction to fibres HIGH

Property	E-glass	S-glass	Carbon (PAN, standard to high modulus)	Aramid (Kevlar 49)
Specific gravity	2.58	2.49	1.78–2.15	1.44
Tensile strength (GPa)	3.45	≈ 4.6	1.5–4.8	3.6–4.1
Elastic modulus (GPa)	72.5	≈ 86	228–724	131
Specific modulus (GPa)	28.1	≈ 34	106–407	91
Failure strain (%)	≈ 4.8	≈ 5.4	0.4–1.8	≈ 2.8
Cost	Lowest	Moderate	High	High
Key strength	Cheap, insulating, chemically resistant	Highest-strength glass	Highest stiffness, fatigue resistance, low CTE, conductive	Lowest density, toughness and impact resistance

Weakness	Low E, abrades	Cost	Brittle, low impact resistance, galvanic corrosion with Al	Poor compressive strength, UV and moisture sensitive, hard to cut

Callister Table 16.4; S-glass and failure-strain values are typical handbook figures.

Glass fibres

- Made by drawing molten glass (≈ 1260 °C) through fine holes in a platinum bushing at high speed into continuous filaments 3–20 μm in diameter. A **size** (coating plus coupling agent) is applied at once to protect the surface, because surface flaws would cut the strength.
- **E-glass** (electrical; calcium aluminoborosilicate, ~55 % SiO_2) is the cheapest and most widely used (≈ 90 % of glass fibre). **S-glass** (strength; magnesia–alumina–silicate) has higher strength, modulus and temperature resistance, for aerospace and pressure vessels. **C-glass** is for chemical resistance.
- GFRP (fibreglass): boat hulls, car bodies, pipes, tanks, PCBs, storage containers. Service temperature is limited to about 200 °C by the polymer matrix.

Carbon fibres

- Made from precursors: **PAN** (polyacrylonitrile, the most common), **mesophase pitch** (gives higher modulus) and rayon.
- PAN route:
  1. Spinning.
  2. **Stabilization**: oxidation in air at 200–300 °C *under tension*, to keep molecular alignment.
  3. **Carbonization** at 1000–1500 °C in an inert gas (H, N and O driven off).
  4. **Graphitization** at 2500–3000 °C, for high-modulus grades.
  5. Surface treatment and sizing.
- Structure: graphitic and turbostratic (disordered) carbon layers aligned along the fibre axis, which gives very high axial stiffness.
- Properties: the highest specific modulus and specific strength of all fibres, retained at high temperature (in inert atmospheres). Not affected by moisture, solvents, acids or bases. Low CTE. Electrically conducting.
- CFRP: aircraft wings and fuselage, sports goods, F1 chassis, pressure vessels, wind blades, rocket cases.

Aramid (Kevlar 49) fibres

- **Aramid** is an aromatic polyamide, poly(p-phenylene terephthalamide), DuPont trade name Kevlar. Its rigid, rod-like chains containing benzene rings are highly **aligned along the fibre axis** by spinning from a liquid-crystal solution, with hydrogen bonds between chains.
- **Kevlar 49** is the high-modulus grade used for composite reinforcement. (Kevlar 29 is the tougher grade used for ballistic fabrics and ropes.)
- Properties: very high tensile strength with the lowest density, so the highest specific strength among common fibres. Excellent toughness, impact and abrasion resistance. Non-conducting, non-flammable, stable from −200 to 200 °C. **Weak in compression** (fibrils buckle). Degraded by UV and strong acids and bases. Absorbs moisture.
- Uses: bullet-proof vests and helmets, aircraft fairings, pressure vessels, sporting goods (canoes, rackets), tyre cords, ropes and cables, brake and clutch linings, hybrid composites with carbon.

11. Matrix types HIGH

Matrix	Examples	Properties and role	Typical composites and uses
Polymer (PMC) most widely used	Thermosets: polyester (cheapest), vinyl ester, **epoxy** (better properties, moisture resistance), phenolics, polyimides (up to ~230 °C), bismaleimides. Thermoplastics: PEEK, PPS, PEI, nylon, PP	Light, easy to process at low temperature, corrosion resistant and cheap. Limited service temperature (polyester/epoxy < ~150–200 °C). Low E. Thermoplastics are tougher and recyclable.	GFRP, CFRP, aramid–epoxy: aircraft, boats, sports, auto, pipes
Metal (MMC)	Al, Mg, Ti, Cu alloys, superalloys	Higher operating temperature, non-flammable, good transverse strength, toughness, electrical and thermal conductivity, resistant to organic fluids. Expensive. Reinforcement–matrix reactions at high temperature are a concern.	Al–SiC (pistons, brake rotors, drive shafts), Al–B fibre (space shuttle struts), Al–C (antennas), Cu–C, superalloy–W
Ceramic (CMC)	SiC, Si_3N_4, Al_2O_3, ZrO_2, glass-ceramics	Very high temperature and oxidation resistance. Reinforcement (SiC fibres or whiskers) mainly raises **fracture toughness**, from ~3–5 to 6–20 MPa√m, by crack deflection, fibre bridging and fibre pull-out. Transformation toughening in ZrO_2.	Al_2O_3–SiC whisker cutting tools, SiC–SiC turbine and exhaust parts, heat engines
Carbon (C–C)	Carbon (from pyrolysed resin)	Retains strength above 2000 °C, high thermal-shock resistance. Expensive. Oxidises at high temperature unless coated.	Aircraft and F1 brakes, rocket nozzles, re-entry nose cones, hot-pressing dies

12. Coupling agents and fillers MEDIUM

COUPLING AGENTS

A **coupling agent** is a chemical applied to the fibre surface (as part of the **sizing**) that forms a **chemical bridge** between the inorganic reinforcement and the organic polymer matrix, and so improves **interfacial adhesion**. The most common are **organosilanes**, general formula **R–Si(OR′)$_3$**. The –Si(OR′)$_3$ end hydrolyses to silanol (–Si–OH) groups, which condense with –OH groups on the glass surface (Si–O–Si bonds). The organofunctional group R (vinyl, amino, epoxy, methacrylate) reacts or entangles with the resin. Others: titanates, zirconates, maleic-anhydride-grafted polymers (for natural fibres in PP).

- **Benefits:** efficient stress transfer from matrix to fibre (higher strength, especially transverse and interlaminar shear), much better **moisture and hot-wet resistance** (water cannot attack the interface), better fatigue life, and better wetting during processing.
- A poor interface leads to debonding, fibre pull-out with little load, and low strength. A very strong interface makes the composite brittle. An optimum bond is required.

FILLERS

Fillers are inexpensive, mostly inert, particulate materials added to the matrix resin, typically 10–50 %. Examples: calcium carbonate, talc, kaolin clay, silica, mica, glass microspheres, wood flour, carbon black and alumina trihydrate.

- They **reduce cost**, raise stiffness and hardness, reduce shrinkage and thermal expansion, and improve dimensional stability and surface finish.
- Special functions: fire retardancy (alumina trihydrate releases water), electrical conductivity (carbon black), lower density (hollow microspheres in syntactic foams), and UV resistance.
- Drawbacks: higher viscosity during processing and lower toughness.

Likely exam questions

1. Write any three methods of powder production. Describe the steps in the production of cemented carbide tools. (5) · End Sem 2024
2. Discuss the reinforcement materials commonly used in polymer-matrix composites and how their properties contribute to overall performance. (6) · End Sem 2024
3. Explain the powder metallurgy process with a flow chart. State its advantages, limitations and applications. (6)
4. What is sintering? Explain the mechanism and stages of sintering. What is liquid-phase sintering? (4)
5. Explain compaction, with cold and hot isostatic pressing. (3–4)
6. How are self-lubricating bearings made by P/M? Explain infiltration and impregnation. (3)
7. Compare glass, carbon and Kevlar 49 fibres. (4)
8. Discuss polymer-, metal- and ceramic-matrix composites with examples. (4–6)
9. What are coupling agents and fillers? Explain the role of silane coupling agents. (3)

MODEL ANSWER: THREE POWDER PRODUCTION METHODS + CEMENTED CARBIDE (5 MARKS: 3 + 2 OR 2.5 + 2.5)

1. Atomization: molten metal is poured as a thin stream and disintegrated by high-pressure gas or water jets into droplets that solidify as powder. Gas gives spherical particles, water gives irregular ones. Used for steels, Al, Cu and superalloys. It is the most common method.

2. Reduction: metal oxides are reduced by H_2, CO or carbon below the melting point, e.g. $WO_3 + 3H_2 \rightarrow W + 3H_2O$. The powder is spongy and porous with good compressibility. Used for W, Mo, Fe and Cu.

3. Electrolytic deposition: the metal is deposited as a loose, powdery layer on the cathode under high current density, then washed, dried and milled. The powder is very pure and dendritic. Used for Cu and Fe.

(Alternatives: mechanical milling or alloying; the carbonyl process for fine, pure Fe and Ni.)

Cemented carbide tool production:

1. Make WC by carburizing W powder with carbon at ~1500 °C.
2. Ball-mill WC with 3–25 % Co binder in alcohol, adding paraffin wax.
3. Dry and granulate.
4. Press to an oversized green shape.
5. Dewax and presinter at ~1000 °C, then shape it while it is chalk-like.

6. Liquid-phase sinter at 1350–1500 °C in vacuum or H_2. Co melts, wets the WC and densifies the part (~20 % linear shrinkage).
7. Diamond-grind and hone.
8. CVD/PVD coat with TiN or Al_2O_3.

Draw the flow chart.

MODEL ANSWER: REINFORCEMENTS IN POLYMER-MATRIX COMPOSITES AND THEIR CONTRIBUTION (6 MARKS)

Introduction: in a PMC the polymer (epoxy, polyester, vinyl ester, PEEK) is light and tough but weak (E ≈ 3 GPa). The reinforcement carries most of the load. The composite properties follow the rule of mixtures, $E_c = E_m V_m + E_f V_f$, so the fibre's E, σ and ρ dominate.

1. **Glass fibres (E- and S-glass; GFRP):** E ≈ 72 GPa, σ ≈ 3.45 GPa, ρ = 2.58. They give high strength at **low cost**, electrical insulation, chemical resistance and good impact behaviour (high strain to failure). Their modest stiffness limits use in stiffness-critical parts. Uses: boat hulls, pipes, car panels, PCBs.
2. **Carbon fibres (CFRP):** E = 230–720 GPa, σ up to 4.8 GPa, ρ ≈ 1.8. They give the **highest specific stiffness and strength**, excellent fatigue resistance, near-zero CTE (dimensional stability) and conductivity. They are brittle and expensive. Uses: aircraft structures, F1, sports goods.
3. **Aramid (Kevlar 49):** E = 131 GPa, σ ≈ 3.6–4.1 GPa, ρ = 1.44, the lowest density. It gives the highest specific tensile strength and outstanding **toughness, impact and ballistic resistance** and damage tolerance. Its compressive strength is poor. Uses: armour, pressure vessels, hybrid laminates.
4. **Others:**
   - UHMWPE (Spectra): very light, ballistic.
   - Boron: high E, stiff aerospace skins.
   - **Natural fibres** (jute, flax, hemp, sisal): cheap, low-density, renewable; used for auto interiors.
   - **Particulate fillers** ($CaCO_3$, talc, silica, glass microspheres, carbon black): raise stiffness and dimensional stability and cut cost.

How they contribute to overall performance:

- **Strength and stiffness:** fibres have high E and σ, and they carry most of the load (≈ 90 % at $V_f = 0.4$ for glass–polyester).
- **Low density** gives high specific properties and weight saving.
- **Form and orientation** (continuous, chopped, woven, multidirectional lay-up) tailor the anisotropy. Fibre length must exceed $l_c = \sigma_f * d / 2\tau_c$.
- **Fibre–matrix bonding** through silane coupling agents and sizing ensures stress transfer and hot-wet durability.
- Toughness comes from crack deflection and fibre pull-out. Fatigue, creep and thermal stability all improve.

Add a small fibre comparison table (E, σ, ρ). That alone is worth 1–2 marks.

PREVIOUS YEAR PAPER · FULLY SOLVED

End Term Exam, November 2024 (ME201n)

B.Tech (ME), 3rd semester · 3 hours · Max. marks 40 · answer any five, all questions carry equal marks

Answers are sized to their marks. Where a long figure is needed, the full drawing is in the unit named in brackets. Copy that figure into your answer.

Q1 (a) Draw the iron–carbon diagram, mark all phases and explain the reactions.

6 MARKS

MODEL ANSWER

Diagram: draw the Fe–Fe_3C diagram (Unit 3): temperature on the y-axis (up to 1600 °C), wt% C on the x-axis from 0 to 6.70. Mark these points: 1538 °C (Fe melting), 1493 °C peritectic, 1394 °C (δ→γ), 1147 °C eutectic, 912 °C (γ→α), 727 °C eutectoid; compositions 0.022, 0.76, 2.14, 4.30, 6.70 % C.

Phases:

- **α-ferrite**: BCC interstitial solid solution of C in Fe; max solubility 0.022 % C at 727 °C. Soft, ductile, magnetic below 768 °C.
- **Austenite (γ)**: FCC solid solution; max 2.14 % C at 1147 °C. Non-magnetic and ductile; does not exist below 727 °C in plain carbon steel.
- **δ-ferrite**: BCC, stable 1394–1538 °C, max 0.09 % C at 1493 °C.
- **Cementite (Fe_3C)**: intermetallic compound with 6.70 % C. Very hard and brittle.
- **Liquid (L)**, plus two-phase fields: L+δ, L+γ, δ+γ, α+γ, γ+Fe_3C, L+Fe_3C, α+Fe_3C.
- Microconstituents: **pearlite** (lamellar α + Fe_3C from the eutectoid reaction) and **ledeburite** (γ + Fe_3C from the eutectic reaction).

Invariant reactions (F = 0 at constant pressure, three phases in equilibrium):

Reaction	Temp.	Equation
Peritectic	1493 °C	δ (0.09 % C) + L (0.53 % C) → γ (0.17 % C)
Eutectic	1147 °C	L (4.30 % C) → γ (2.14 % C) + Fe_3C (6.70 % C) = ledeburite
Eutectoid	727 °C	γ (0.76 % C) → α (0.022 % C) + Fe_3C (6.70 % C) = pearlite

Classification: steels below 2.14 % C (hypoeutectoid < 0.76; eutectoid = 0.76; hypereutectoid 0.76–2.14); cast irons 2.14–6.70 % C. Critical lines: A_1 (727 °C), A_3 (γ/α+γ boundary), A_{cm} (γ/γ+Fe_3C boundary).

Q1 (b) Derive the equation for Gibbs' phase rule.

2 MARKS

MODEL ANSWER

Consider a system of **C** components distributed among **P** phases in equilibrium.

- **Variables:** the composition of each phase needs (C − 1) mole fractions, giving P(C − 1) in all, plus temperature and pressure. Total = P(C − 1) + 2.

- **Equations (constraints):** at equilibrium the chemical potential of each component is the same in every phase: $\mu_i^1 = \mu_i^2 = \ldots = \mu_i^P$. That is $(P - 1)$ equations per component, so $C(P - 1)$ in all.
- **Degrees of freedom** = variables − equations = $P(C - 1) + 2 - C(P - 1) = PC - P + 2 - PC + C$.

$$F = C - P + 2$$

At constant pressure (metallurgical systems, 1 atm): $F = C - P + 1$

Example: at the Fe–C eutectoid point, $C = 2$ and $P = 3$, so $F = 2 - 3 + 1 = 0$ (invariant: fixed T and compositions).

Q2 (a) Explain the Griffith theory of brittle fracture and deduce the critical stress for crack propagation. 6 MARKS

MODEL ANSWER

Idea: the measured fracture strength of brittle materials is 10–1000 times lower than the theoretical cohesive strength (≈ E/10). Griffith (1920) explained this by assuming every brittle solid contains tiny cracks. Stress concentrates at their tips, so a crack spreads when the elastic strain energy released by its growth is at least the surface energy of the new crack faces.

Setup: an infinite plate of unit thickness under uniform tensile stress σ, containing a through elliptical crack of length 2a perpendicular to σ (draw the plate, the crack 2a and arrows for σ; see Unit 4).

1. **Elastic strain energy released** by the crack (plane stress): $U_E = -\pi a^2\sigma^2/E$.
2. **Surface energy** of the two new crack faces, each of length 2a: $U_S = 2 \times (2a \times \gamma_s) = 4a\gamma_s$.
3. **Total energy change:** $U = 4a\gamma_s - \pi a^2\sigma^2/E$. U first rises with a, then falls (sketch U_S, U_E and U against a; the maximum is at a*).
4. **Condition for unstable growth:** $dU/da = 0$, so $4\gamma_s - 2\pi a\sigma^2/E = 0$.

$$\sigma_c = \sqrt{(2E\gamma_s / \pi a)} \text{ (plane stress)}$$

$$\sigma_c = \sqrt{(2E\gamma_s / \pi(1 - \nu^2)a)} \text{ (plane strain)}$$

Conclusions: (i) fracture stress $\propto 1/\sqrt{a}$, so bigger cracks fracture at lower stress; (ii) a material with higher E and γ_s is tougher. **Orowan's modification** for metals adds the plastic work γ_p: $\sigma_c = \sqrt{(2E(\gamma_s + \gamma_p)/\pi a)}$, where $\gamma_p \gg \gamma_s$. In fracture-mechanics form, $\sigma_c\sqrt{(\pi a)} = K_c = \sqrt{(2E\gamma)}$.

Q2 (b) K_{Ic} = 80 MPa√m, critical crack length 0.05 mm, E = 120 GPa. Find the surface energy γ. 2 MARKS

SOLUTION

Griffith: $\sigma_c = \sqrt{(2E\gamma/\pi a)}$ and fracture toughness $K_c = \sigma_c\sqrt{(\pi a)}$. Squaring and combining gives $K_c^2 = 2E\gamma$.

$\gamma = K_c^2 / 2E = (80 \times 10^6)^2 / (2 \times 120 \times 10^9) = 6.4 \times 10^{15} / 2.4 \times 10^{11}$

$\gamma \approx 2.67 \times 10^4$ J/m² (26.7 kJ/m²).

Check via the crack length: $\sigma_c = K/\sqrt{(\pi a)} = 80/\sqrt{(\pi \times 5 \times 10^{-5})} = 6383$ MPa, and $\gamma = \pi a\sigma_c^2/2E = \pi(5 \times 10^{-5})(6.383 \times 10^9)^2/(2.4 \times 10^{11}) = 2.67 \times 10^4$ J/m², the same. The crack length cancels out. The value is huge compared with a true surface energy (~1 J/m²) because it includes plastic work (Orowan). Mention this in one line.

Q3 (a) Any three methods of powder production; steps in producing cemented carbide tools. 5 MARKS

MODEL ANSWER

Powder production (any three):

1. **Atomization:** a stream of molten metal is broken into droplets by high-pressure water or gas (N_2, Ar) jets; the droplets solidify as powder. Used for steel, Al, Cu and alloys. Gas atomization gives spherical particles; water atomization gives irregular ones.
2. **Reduction of oxides:** metal oxides are reduced by H_2 or CO below the melting point, giving porous "sponge" powder (Fe, W, Mo, Cu). Example: $WO_3 + 3H_2 \rightarrow W + 3H_2O$.
3. **Electrolytic deposition:** metal is deposited at the cathode from an electrolyte as a brittle, spongy layer, then washed, dried and milled. Gives very pure dendritic powder (Cu, Fe, Ag).
4. Others: **mechanical comminution** (ball or hammer milling of brittle materials), **carbonyl decomposition** ($Ni(CO)_4 \rightarrow Ni + 4CO$), chemical precipitation.

Cemented carbide (WC–Co) tools:

1. Make WC powder: W powder (by H_2 reduction of WO_3) + carbon black, carburized at about 1400–1600 °C.
2. **Mixing / milling:** WC + 3–20 % Co (binder), ball-milled for hours in alcohol or hexane with 1–2 % paraffin wax as a pressing lubricant.
3. Drying and granulation (spray drying) into free-flowing granules.
4. **Compaction:** die pressing or cold isostatic pressing into "green" compacts.
5. **Presintering** at about 800–1000 °C in H_2: removes wax and gives chalk-like strength, so the blank can be shaped or machined.
6. **Liquid-phase sintering** at 1350–1500 °C in vacuum or H_2: Co melts and wets the WC grains. Expect 15–20 % linear shrinkage and near-full density. Optional HIP removes residual porosity.
7. **Finishing:** grinding with diamond wheels, brazing onto a steel shank or use as indexable inserts, then CVD/PVD coating (TiN, TiC, Al_2O_3).

Q3 (b) Annealing and normalizing: effects on microstructure. 3 MARKS

MODEL ANSWER

	Full annealing	Normalizing
Heating	15–40 °C above A_3 (hypoeutectoid) or above A_1 (hypereutectoid)	55–85 °C above A_3 or A_{cm} (fully austenitic)
Cooling	Slowly, in the furnace	In still air
Microstructure	Coarse pearlite + pro-eutectoid ferrite (or cementite); large grains	Fine pearlite, finer and more uniform grains, more pearlite; cementite network in hypereutectoid steel broken up
Properties	Softest, most ductile, best machinability, internal stresses removed	Higher strength and hardness than annealed, good toughness, uniform properties
Use	Before cold working or machining; to soften castings	Refine coarse cast/forged grain; before hardening

Add: process annealing (below A_1, 550–650 °C) restores ductility of cold-worked low-C steel by recrystallization; spheroidizing (just below A_1, long hold) turns the cementite into spheroids for maximum machinability.

Q4 (a) Three stages of the creep curve, with diagram and mechanisms. 4 MARKS

MODEL ANSWER

Creep is time-dependent, permanent deformation under constant load (or stress) at high temperature, $T > 0.4\ T_m$. Draw strain against time (Unit 4): instantaneous elastic strain ε_0, then three stages ending at rupture (×).

1. **Primary (transient) creep:** the creep rate decreases with time. Strain hardening outweighs recovery: dislocations multiply and tangle, and a sub-structure forms.
2. **Secondary (steady-state) creep:** constant, minimum creep rate $\dot{\varepsilon}_s$, the longest stage. There is a balance between strain hardening and recovery (dislocation climb, cross-slip, polygonization). Mechanisms: dislocation glide + climb (high σ), diffusion creep (Nabarro–Herring through the lattice, Coble along grain boundaries at low σ), grain-boundary sliding. $\dot{\varepsilon}_s = K\,\sigma^n \exp(-Q_c/RT)$ is the design parameter.
3. **Tertiary creep:** the creep rate accelerates until rupture. Causes: necking (reduced area), cavities and voids at grain boundaries, intergranular microcracks, and metallurgical changes (precipitate coarsening, recrystallization).

Higher stress or temperature raises ε_0 and $\dot{\varepsilon}_s$ and shortens rupture life.

Q4 (b) TTT diagram for eutectoid steel: label regions and products. 4 MARKS

MODEL ANSWER

Draw temperature (y) against log time (x) for 0.76 % C steel (Unit 3):

- A horizontal line at **727 °C** (A_1): stable austenite above it.
- Two C-shaped curves: **transformation start** (1 %) and **finish** (99 %). Between them is "austenite + product"; to the left of the start curve is unstable austenite.
- **Nose** at about 540 °C and about 1 s (fastest transformation).
- **Pearlite** above the nose: *coarse pearlite* at 650–727 °C, *fine pearlite* at 540–650 °C.
- **Bainite** below the nose, about 540 °C down to about 250 °C: *upper bainite* (feathery) at 350–540 °C, *lower bainite* (acicular) below about 350 °C.
- Horizontal lines **$M_s \approx 220$ °C**, M_{50}, M_{90} (M_f lower): **martensite** forms athermally (diffusionless) below M_s.
- **Critical cooling rate**: the cooling curve just tangent to the nose. Faster cooling gives 100 % martensite.

Hardness increases from coarse pearlite to fine pearlite to bainite to martensite. Show 2–3 cooling curves (furnace: coarse P; air: fine P; quench: M) for full marks.

Q5 (a) Procedure for Miller indices in cubic and HCP crystals, with examples.

5 MARKS

MODEL ANSWER

Cubic planes (hkl):

1. Choose an origin not on the plane (shift the origin if the plane passes through it).
2. Find the intercepts on the x, y, z axes in units of a, b, c (a plane parallel to an axis has intercept ∞).
3. Take reciprocals.
4. Clear fractions to the smallest integers; enclose in ( ) with no commas; write a negative index with a bar.

Examples: intercepts (1, ∞, ∞) give (100); (1, 1, ∞) give (110); (1, 1, 1) give (111); (½, 1, ∞) give reciprocals (2, 1, 0), so (210); (1, −1, ½) gives (1 $\bar{1}$ 2). A family is {hkl}.

Cubic directions [uvw]: head coordinates minus tail coordinates, in units of a; reduce to smallest integers; write in [ ]. Example: from (0,0,0) to (1,1,0) is [110]; from (1,0,0) to (0,1,1) gives (−1,1,1), so [$\bar{1}$11]. A family is ⟨uvw⟩.

HCP: Miller–Bravais indices (hkil), using four axes: a_1, a_2, a_3 at 120° in the basal plane, and c perpendicular to it.

1. Find the intercepts on a_1, a_2, a_3, c; take reciprocals; clear fractions.
2. The third index is redundant: **i = −(h + k)**. Convert from 3-index (hkl) by just inserting i.

Examples: basal plane (0001); prism plane (10$\bar{1}$0); pyramidal plane (10$\bar{1}$1).

HCP directions [UVW] to [uvtw]: u = (2U − V)/3, v = (2V − U)/3, t = −(u + v), w = W. Example: [100] gives u = 2/3, v = −1/3, t = −1/3, w = 0, so **[2 $\bar{1}$ $\bar{1}$ 0]**. [001] becomes [0001].

Q5 (b) Number of vacancies in copper at 200 °C. Q_v = 0.9 eV/atom, k = 8.62 × 10^{-5} eV/atom·K, ρ = 8.94 g/cm^3, A = 63.55 g/mol. 3 MARKS

SOLUTION

Step 1, atoms per unit volume: $N = N_A\rho/A = (6.022 \times 10^{23} \times 8.94)/63.55 = 8.47 \times 10^{22}$ atoms/cm^3 = **8.47×10^{28} atoms/m^3**.

Step 2, temperature: T = 200 + 273 = 473 K; $kT = 8.62 \times 10^{-5} \times 473 = 0.04077$ eV; $Q_v/kT = 0.9/0.04077 = 22.07$.

Step 3: $N_v = N \exp(-Q_v/kT) = 8.47 \times 10^{28} \times \exp(-22.07) = 8.47 \times 10^{28} \times 2.59 \times 10^{-10}$

$N_v \approx 2.2 \times 10^{19}$ vacancies/m^3 (= 2.2×10^{13} per cm^3). Fraction $N_v/N \approx 2.6 \times 10^{-10}$.

Q6 (a) Reinforcement materials used in polymer-matrix composites and how their properties contribute to performance. 6 MARKS

MODEL ANSWER

In a PMC (epoxy, polyester, vinyl ester, PEEK) the **fibres carry most of the load** while the matrix binds them, transfers load by shear at the interface and protects the fibres. Main reinforcements:

Fibre	ρ (g/cm^3)	σ_t (GPa)	E (GPa)	Key features → uses
E-glass (S-glass stronger)	2.58	3.45	72.5	Cheap, strong, good electrical insulator, corrosion resistant; low stiffness → GFRP boat hulls, pipes, tanks, car bodies, wind blades
Carbon (PAN / pitch)	1.78–2.15	1.5–4.8	228–724	Highest specific modulus, fatigue resistant, low thermal expansion; costly, brittle → aircraft structures, sports goods, F1
Aramid (Kevlar 49)	1.44	3.6–4.1	131	Highest specific strength, very tough, impact and cut resistant; poor compressive strength, absorbs moisture → body armour, helmets, ropes, tyres, pressure vessels
Others	Natural fibres (jute, flax: cheap, light, eco-friendly), UHMWPE, boron; particulate fillers (silica, $CaCO_3$, carbon black) for stiffness, cost and wear			

How they improve the composite:

- **Stiffness and strength** follow the rule of mixtures: $E_c = E_fV_f + E_mV_m$ (longitudinal). The load share is $F_f/F_m = E_fV_f/E_mV_m$, so stiff fibres take most of the load.
- **Low density** gives high specific strength and specific stiffness (weight saving).
- **Fibre length and orientation:** fibres longer than $l_c = \sigma_f{*}d/2\tau_c$ reinforce effectively. Aligned fibres give maximum longitudinal properties (anisotropic); random fibres give isotropic, lower properties.
- **Interface:** a good fibre–matrix bond (silane coupling agents on glass) is needed for load transfer.
- **Toughness:** fibres deflect and bridge cracks, and fibre pull-out absorbs energy (especially aramid).

- Fatigue, creep, dimensional stability and environmental resistance all improve (glass for corrosion, carbon for fatigue).

Q6 (b) Composition, properties and applications of duralumin and brass.

2 MARKS

MODEL ANSWER

	Duralumin	Brass
Composition	Al + 3.5–4.5 % Cu, 0.4–0.8 % Mg, 0.4–0.7 % Mn, ~0.5 % Si	Cu + Zn (e.g. 70/30 cartridge brass; 60/40 Muntz metal)
Properties	Age-hardenable; high strength-to-weight (UTS ~400–450 MPa); good machinability; poor corrosion resistance, so used clad (Alclad)	Ductile (α-brass cold-workable), good corrosion resistance, golden colour, easily machined (with Pb), good conductivity
Uses	Aircraft structures and skins, rivets, truck bodies, automobile parts	Cartridge cases, radiators, plumbing fittings, condenser tubes, musical instruments, coins

PREVIOUS YEAR PAPER · FULLY SOLVED

Mid Term Exam, March 2024

B.Tech 2nd sem, PE-104 Engineering Materials and Metallurgy · 1.5 hours · 20 marks. Same syllabus; questions like these appear as part (b)s in the end term.

Q1. Planar density of the (110) plane of FCC in terms of r. 2.5 MARKS

SOLUTION

The (110) plane in an FCC cell is a rectangle of sides a (cube edge) and a√2 (face diagonal).

Atoms centred on the plane: 4 corners × ¼ + 2 face-centre atoms (mid-points of the long sides) × ½ = **2 atoms**.

For FCC, a = 2r√2, so area = a × a√2 = (2r√2)(4r) = 8√2 r².

$$\mathbf{PD_{110} = 2 / (8\sqrt{2}\, r^2) = 1 / (4\sqrt{2}\, r^2) \approx 0.177 / r^2}$$

OR: Define APF and find it for simple cubic.

SOLUTION

APF = volume of atoms in a unit cell ÷ total unit cell volume (atoms taken as hard spheres).

SC: 8 corners × ⅛ = 1 atom; atoms touch along the edge, so a = 2r.

$$\text{APF} = (1 \times 4/3\ \pi r^3)/(2r)^3 = \pi/6 = \mathbf{0.52}$$

Q2. BCC iron, (220) planes: (i) interplanar spacing, (ii) diffraction angle. a = 0.2866 nm, λ = 0.1790 nm, n = 1. 5 MARKS

SOLUTION

(i) $d_{hkl} = a / \sqrt{(h^2 + k^2 + l^2)} = 0.2866 / \sqrt{(4 + 4 + 0)} = 0.2866 / 2.828 =$ **0.1013 nm**

(ii) Bragg's law nλ = 2d sin θ, so sin θ = (1 × 0.1790)/(2 × 0.1013) = 0.8833

θ = 62.04°, so diffraction angle $\mathbf{2\theta = 124.1°}$

(220) reflects in BCC because h + k + l = 4 is even (BCC rule). In FCC, h, k, l must be all odd or all even.

OR: Relationship between a and r for SC, BCC and FCC.

SOLUTION

Structure	Atoms touch along	Geometry	Result
SC	Cube edge	a = r + r	**a = 2r**
BCC	Body diagonal (a√3)	a√3 = 4r	**a = 4r/√3**
FCC	Face diagonal (a√2)	a√2 = 4r	**a = 2√2 r**

Draw the cube face (FCC) and the body-diagonal section (BCC) with the touching atoms (Unit 1).

Q3. Differentiate edge and screw dislocations with diagrams. 2.5 MARKS

MODEL ANSWER

Edge dislocation	Screw dislocation
Extra half-plane of atoms inserted in the crystal; symbol ⊥	Atoms arranged in a spiral (helical) ramp around the line; symbol ↻
Burgers vector **b** ⊥ dislocation line	Burgers vector **b** ∥ dislocation line
Moves (glides) parallel to b, in the direction of applied shear	Moves perpendicular to b (and to the shear stress)
Has a unique slip plane; can climb (by diffusion)	No unique slip plane, so can cross-slip; cannot climb
Compressive stress above the slip plane, tensile below	Pure shear strain field

Draw both with a Burgers circuit, showing the closure failure b (Unit 1). Real dislocations are usually **mixed**.

OR: Axial relationships and inter-axial angles of the crystal systems.

MODEL ANSWER

System	Axial lengths	Inter-axial angles	Example
Cubic	a = b = c	α = β = γ = 90°	Fe, Cu, NaCl
Hexagonal	a = b ≠ c	α = β = 90°, γ = 120°	Zn, Mg, Ti
Tetragonal	a = b ≠ c	α = β = γ = 90°	β-Sn, TiO_2
Rhombohedral (trigonal)	a = b = c	α = β = γ ≠ 90°	Calcite, Bi
Orthorhombic	a ≠ b ≠ c	α = β = γ = 90°	α-S, Ga
Monoclinic	a ≠ b ≠ c	α = γ = 90° ≠ β	Gypsum
Triclinic	a ≠ b ≠ c	α ≠ β ≠ γ ≠ 90°	$K_2Cr_2O_7$

7 crystal systems combine with lattice centring to give 14 Bravais lattices.

Q4. What is a single crystal? Discuss the various imperfections in a crystal. 5 MARKS

MODEL ANSWER

Single crystal: a solid in which the periodic, repeating atomic arrangement extends unbroken through the whole specimen, with no grain boundaries. Properties are anisotropic. Examples: silicon wafers, quartz oscillators, Ni-superalloy turbine blades (creep resistance). A polycrystal is made of many grains of different orientation separated by grain boundaries.

Imperfections, classified by dimension:

1. **Point (0-D):** vacancy (missing atom; $N_v = N \exp(-Q_v/kT)$); self-interstitial; substitutional and interstitial impurity atoms (solid solutions, Hume-Rothery rules); in ionic crystals the **Frenkel** defect (cation vacancy + cation interstitial pair) and **Schottky** defect (cation + anion vacancy pair).

2. **Line (1-D):** dislocations: edge (extra half-plane, b ⊥ line), screw (b ∥ line), mixed. They cause plastic deformation by slip at low stress; their interaction gives work hardening.
3. **Surface / planar (2-D):** external surfaces; grain boundaries (high- and low-angle, tilt and twist); twin boundaries (mirror-image lattice); stacking faults (ABCABABC in FCC); phase boundaries.
4. **Volume (3-D):** pores, cracks, voids, foreign inclusions, precipitates.

Draw: vacancy/interstitial/substitutional in a 2-D atom grid; edge dislocation; grain boundary and twin boundary (Unit 1).

Q5. Draw the iron–carbon phase diagram and describe the invariant reactions.

5 MARKS

Same as End Sem 2024, Q1(a) above. Drawing the diagram with the peritectic, eutectic and eutectoid reactions at their correct temperatures and compositions earns most of the marks.

LAST HOUR

Formula sheet & final revision

Everything you need for the 2- and 3-mark numerical parts on two pages. Read it right before entering the hall.

Unit 1: Crystal structure and defects

	SC	BCC	FCC	HCP
a in terms of r	2r	4r/√3	2√2 r	a = 2r, c/a = 1.633
Atoms per cell (n)	1	2	4	6
Coordination number	6	8	12	12
APF	0.52	0.68	0.74	0.74
Examples	Po	α-Fe, Cr, W, Mo	γ-Fe, Al, Cu, Ni, Au	Zn, Mg, Ti, Co

$\rho = nA / (V_c N_A)$, $N_A = 6.022 \times 10^{23}$

$d_{hkl} = a / \sqrt{(h^2 + k^2 + l^2)}$

Bragg: $n\lambda = 2d \sin\theta$

LD = atoms centred on line / line length

PD = atoms centred on plane / plane area

HCP: $i = -(h + k)$

[UVW]→[uvtw]: $u = (2U-V)/3$, $v = (2V-U)/3$, $t = -(u+v)$, $w = W$

$N_v = N \exp(-Q_v/kT)$, $N = N_A\rho/A$

$k = 8.62 \times 10^{-5}$ eV/K $= 1.38 \times 10^{-23}$ J/K

Schmid: $\tau_R = \sigma \cos\varphi \cos\lambda$

Hall–Petch: $\sigma_y = \sigma_0 + k_y\, d^{-½}$

$\%CW = (A_0 - A_d)/A_0 \times 100$

$T_{recryst} \approx 0.3\text{–}0.5\ T_m$ (in K)

Planar densities: FCC (100) = $1/(4r^2) = 0.25/r^2$; FCC (110) = $1/(4\sqrt{2}\, r^2) = 0.177/r^2$; FCC (111) = $1/(2\sqrt{3}\, r^2) = 0.289/r^2$ (densest); BCC (110) = $3/(8\sqrt{2}\, r^2) = 0.265/r^2$ (densest in BCC). **Linear:** FCC [110] = 1/(2r); BCC [111] = 1/(2r). **Slip systems:** FCC {111}⟨110⟩ 12; BCC {110}⟨111⟩ 12 (48 in total); HCP $(0001)\langle 11\bar{2}0\rangle$ 3. **Diffraction rules:** BCC: h + k + l even; FCC: h, k, l all odd or all even.

Unit 2: Corrosion

Anode (oxidation): $M \rightarrow M^{n+} + ne^-$

Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (neutral)

$2H^+ + 2e^- \rightarrow H_2$ (acid)

$E_{cell} = E°_{cathode} - E°_{anode}$

Rust: $Fe \rightarrow Fe^{2+} + 2e^-$; $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$ ($\rightarrow Fe_2O_3{\cdot}nH_2O$)

Faraday: $w = ItM / nF$, $F = 96\,500$ C/mol

$CPR = KW / \rho At$ ($K = 87.6 \rightarrow$ mm/yr)

The more active (anodic) metal corrodes. Small anode + large cathode = rapid attack. Protection methods: material selection, coatings (paint, galvanizing, tinning), cathodic protection (sacrificial Zn/Mg anode or impressed current), anodizing, inhibitors, good design (avoid crevices and dissimilar-metal contact).

Unit 3: Phase diagrams and heat treatment

Gibbs: $F = C - P + 2$ ($F = C - P + 1$ at const. P)

Lever rule: $W_L = (C_\alpha - C_0)/(C_\alpha - C_L)$

$W_\alpha = (C_0 - C_L)/(C_\alpha - C_L)$

$r^* = -2\gamma/\Delta G_v$, $\Delta G^* = 16\pi\gamma^3 / 3(\Delta G_v)^2$

$\Delta G_v = \Delta H_f(T_m - T)/T_m$

Hypo ($C_0 < 0.76$): $W_P = (C_0 - 0.022)/0.74$

$W_{\alpha'} = (0.76 - C_0)/0.74$

Hyper ($C_1 > 0.76$): $W_P = (6.70 - C_1)/5.94$

$W_{Fe3C'} = (C_1 - 0.76)/5.94$

Total: $W_\alpha = (6.70 - C_0)/6.68$, $W_{Fe3C} = (C_0 - 0.022)/6.68$

Key Fe–C numbers	Value	Key Fe–C numbers	Value
Peritectic	1493 °C: δ(0.09) + L(0.53) → γ(0.17)	Max C in α / γ	0.022 % (727 °C) / 2.14 % (1147 °C)
Eutectic	1147 °C: L(4.30) → γ(2.14) + Fe_3C	Fe_3C	6.70 % C
Eutectoid	727 °C: γ(0.76) → α(0.022) + Fe_3C	Fe melting / δ→γ / γ→α	1538 / 1394 / 912 °C
TTT nose (eutectoid)	~540 °C, ~1 s	M_s (eutectoid)	~220 °C

Heat treatment temperatures: full anneal A_3 + 15–40 °C (furnace cool); normalize A_3/A_{cm} + 55–85 °C (air cool) (Callister values; some Indian texts quote 30–50 / 40–60 °C, both accepted); harden A_3 + 30–50 °C (hypo) or A_1 + 30–50 °C (hyper), water/oil quench; temper 150–650 °C; process anneal 550–650 °C; spheroidize just below A_1. **Case hardening:** carburizing 870–950 °C; nitriding 500–550 °C (no quench); cyaniding 800–870 °C (NaCN bath). **Al–4 % Cu:** solution treat ~550 °C, quench, age (natural at RT, or artificial 100–200 °C). Sequence: GP zones → θ″ → θ′ → θ ($CuAl_2$); peak, then overaged.

Unit 4: Fracture, fatigue, creep

$\sigma = F/A_0$, $\varepsilon = \Delta l/l_0$, $E = \sigma/\varepsilon$

$E = 2G(1 + \nu)$

$\sigma_T = \sigma(1 + \varepsilon)$, $\varepsilon_T = \ln(1 + \varepsilon)$

Griffith: $\sigma_c = \sqrt{(2E\gamma_s/\pi a)}$

$\sigma_m = 2\sigma_0\sqrt{(a/\rho_t)}$, $K_t = \sigma_m/\sigma_0$

$K_{Ic} = Y\sigma\sqrt{(\pi a)}$; $K_c^2 = 2E\gamma$ (→ $\gamma = K^2/2E$)

Plane strain if $B \geq 2.5(K_{Ic}/\sigma_y)^2$

$\sigma_m = (\sigma_{max} + \sigma_{min})/2$

$\sigma_a = (\sigma_{max} - \sigma_{min})/2$, $\sigma_r = 2\sigma_a$

$R = \sigma_{min}/\sigma_{max}$ (fully reversed $R = -1$)

Paris: $da/dN = A(\Delta K)^m$

Creep: $\dot{\varepsilon}_s = K_1\sigma^n$; $\dot{\varepsilon}_s = K_2\sigma^n \exp(-Q_c/RT)$

LMP = $T(C + \log t_r)$, $C \approx 20$, T in K, t_r in h

Creep significant above ~0.4 T_m

a = surface crack length or half the internal crack length (internal crack = 2a). Units: MPa√m = MN·m$^{-3/2}$; γ in J/m². Use the same unit system throughout (Pa and m).

Units 5–6: Composites and powder metallurgy

Isostrain (longitudinal): $E_{cl} = E_m V_m + E_f V_f$

Isostress (transverse): $E_{ct} = E_m E_f / (V_m E_f + V_f E_m)$

$F_f/F_m = E_f V_f / E_m V_m$

$\rho_c = \rho_m V_m + \rho_f V_f$

Critical length: $l_c = \sigma_f^* \, d / 2\tau_c$

$\sigma^*_{cl} = \sigma'_m(1 - V_f) + \sigma^*_f V_f$

$l > l_c$: $\sigma^*_{cd} = \sigma^*_f V_f(1 - l_c/2l) + \sigma'_m(1 - V_f)$

Porosity $= 1 - \rho/\rho_{theoretical}$

Continuous fibres: $l > 15\, l_c$. Fibre efficiency factor K: aligned 1, random in a plane 3/8, random in 3-D 1/5. Fibres: E-glass E ≈ 72 GPa, carbon 230–720 GPa, Kevlar 49 131 GPa (ρ = 1.44, highest specific strength).

Must-draw diagrams checklist

- BCC, FCC, HCP unit cells; a–r geometry
- Miller planes (100), (110), (111) and directions in a cube
- Point defects grid; edge and screw dislocation with Burgers circuit
- Slip vs twinning
- Recovery → recrystallization → grain growth property curve
- Galvanic cell; rusting of iron (water droplet)
- Cooling curves: pure metal and alloy
- Isomorphous diagram with tie-line; binary eutectic
- **Fe–Fe_3C diagram (fully labelled)**
- **TTT diagram for eutectoid steel with cooling curves**
- Heat treatment ranges on the steel side of Fe–C; Jominy test
- Al–Cu aging curve
- Stress–strain curves (ductile with yield point, brittle)
- **Griffith crack and energy vs crack-length curve**
- DBTT curve; S–N curve (steel vs Al); fatigue stress cycles
- **Creep curve (3 stages)**; composite classification tree; PM flow chart

Answer-writing checklist

- Read all six questions first (5 minutes). Cross out the one you'll skip. Start with your strongest question.
- Budget about 32 minutes per question (3 hours ÷ 5, with 20 minutes spare).
- For long answers: definition, then a labelled diagram, then numbered points, then a one-line conclusion or example. Underline key terms.
- For numericals: write the formula, substitute with units, show the answer in a box with units. Convert °C to K and nm to m.
- For comparisons, always use a table.
- Carry a non-programmable scientific calculator, pencil and scale. Phones and smartwatches are not allowed (admit card).