SOLID - Atoms vibrating about their mean positions on fixed atomic sites.

SOLIDIFICATION:
- Centers of crystallisation consisting of space lattices appear
- The lattices grow by aggregation of more lattices
- The growth continues at the expense of the liquid
- The lattices expand in the directions of the axes until development is stopped by the vessel or adjacent grains
- Crystals meet & there are places where it is impossible for another lattice to develop.
- Resulting structure made up of irregularly shaped grains

If more than one phase is present in a given system, each will have its own distinct properties and a boundary separating the phases across which there will be an abrupt change in physical and/or chemical characteristics.

Important to know the natural characteristics and properties of the material under various conditions
- In what condition is the material?
- Is composition uniform?
- If not, how much of each component is present?
- Are there impurities or other elements?
- What happens if temperature, pressure varies?

BONDING
Primary - e.g. Ionic, Covalent, Metallic
Bond energies - 100-1000kJ/mol
Bond Length - 1-2 Angstrom

Secondary - e.g. Van der Waals, Hydrogen
Bond Energies - 1-50 kJ/mol
Bond Length - 2-5 Angstrom

IONIC Bonds - Formed between oppositely charged ions which are produced by the transfer of electrons from one atom to another. The ions are attracted together by the Coulomb attraction by virtue of their net electrical charge.

The bonding force is the same in all directions, therefore IONIC bonding is NON-DIRECTIONAL.
COVALENT Bonds - Occurs by sharing of electrons between neighbouring atoms. The bonding is between specific atoms and may exist in only one direction between one atom and another that participates in the electron sharing. Covalent bonds are **DIRECTIONAL**

METALLIC Bonds - An array of positive ions, with a common pool of electrons (free electron cloud) to which all atoms have contributed their outer electrons. The electrons shield the positively charged ion cores from mutually repulsive electrostatic forces. 
Electrons free to move anywhere in the lattice. Bonds **NON DIRECTIONAL**.

MIXED BONDING- In most materials, bonding between atoms is a mixture of 2 or more types. Iron e.g. is bonded by a combination of metallic and covalent bonding which prevents atoms from packing efficiently.

Compound formed from 2 or more metals may be bonded by a mixture of metallic and ionic bonds particularly when there is a large difference in electronegativity.

Many ceramics and semiconduction compounds have a mixture of covalent and ionic bonding. As electronegativity diff. between the atoms increases, the bonding becomes more ionic.

**Variation in bonding characteristics and properties:**
- Strongly bonded materials tend to have high melting and boiling temperatures.
- Covalent and ionic bonds are stronger than metallic bonds
- If a solid consists of molecules held together by secondary bonds, the melting and boiling points of the solid reflect only the strength of the secondary bonds between molecules

Thermal and electrical conductivities depend on the presence of free electrons
**Ionic and covalent bonds- materials are good thermal and electrical insulators**
**Metals are good conductors of heat and electricity**

**Mechanical properties depend on the bond strength and directional nature of the bond**
- Solids with strong and directional bonds tend to be brittle
- Metallic bonds are relatively weak and non directional
- Metals are soft, ductile, malleable
- Metals can change their shape permanently without breaking
- Ionic solids between covalent and metallic. They may exhibit a limited amount of ductility

**TRANSITION METALS**
In addition to s electrons, there are partially filled d orbitals which have directional characteristics and therefore impart a partial covalent character to the bonding.

**Their properties between covalent crystals and typical metals**
- **Thermal and electrical conductivities lower than typical metals**
- **Transition metals are hard and not so ductile as copper and silver**
- **Melting points higher than those of typical metals**

The interatomic spacing is the equm. distance between the atoms and is the result of a balance between repulsive and attractive forces. The min. energy is the binding energy.

CRystal STRUCTURE
A crystalline material is one in which the atoms are situated in a repeating or periodic array over large atomic distances. Instead of describing the arrangement of many millions of atoms in a grain, it is much easier to describe the unit cell. A non crystalline solid is known as an amorphous solid.
The **unit cell** is the basic structural unit or building block of the crystal structure and defines the crystal structure by virtue of its geometry and the atom positions within.

**Atomic hard sphere model**: atoms are thought of as being hard spheres with well defined diameters. Spheres representing nearest neighbour atoms touch one another.

To describe a unit cell

1. Atom positions or coordinates
2. Directions in the cell
3. Planes in the cell

**seven crystal structures**

1. Cubic (simple, face centred, body centred)
2. Hexagonal
3. Monoclinic (simple, end-centred)
4. Triclinic
5. Rhombohedral
6. Orthorhombic (simple, body-centred, end-centred, face-centred)
7. Tetragonal (simple, body-centred)

- Number of atoms associated with each unit cell
- Coordination number
- Atomic packing factor

\[
\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total volume of unit cell}}
\]

<table>
<thead>
<tr>
<th>Crystal Struct</th>
<th>Metals with this structure</th>
<th>Length of one side</th>
<th>Coord. No.</th>
<th>APF</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC</td>
<td>Po</td>
<td>2R</td>
<td>6</td>
<td>0.52</td>
</tr>
<tr>
<td>BCC</td>
<td>Fe, Ti, W, Mo, Nb, Ta, K, Na, V, Cr</td>
<td>4R/√3</td>
<td>8</td>
<td>0.68</td>
</tr>
<tr>
<td>FCC</td>
<td>Fe, Cu, Al, Au, Ag, Pb, Ni, Pt</td>
<td>4R/√2</td>
<td>12</td>
<td>0.74</td>
</tr>
<tr>
<td>HCP</td>
<td>Ti, Mg, Zn, Be, Co, Cd</td>
<td>a = 2R [\text{c/a} = 1.633]</td>
<td>12</td>
<td>0.74</td>
</tr>
</tbody>
</table>
This shows the relative sizes of the three different types of cubic crystal structures.

<table>
<thead>
<tr>
<th>X = (R_c/R_a)</th>
<th>Coordination</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>X &lt; 0.155</td>
<td>2</td>
<td>Linear</td>
</tr>
<tr>
<td>0.155 &lt; X &lt; 0.225</td>
<td>3</td>
<td>Plane-triangle</td>
</tr>
<tr>
<td>0.225 &lt; X &lt; 0.414</td>
<td>4</td>
<td>Tetrahedral, ZnS</td>
</tr>
<tr>
<td>0.414 &lt; X &lt; 0.732</td>
<td>6</td>
<td>NaCl</td>
</tr>
<tr>
<td>0.732 &lt; X &lt; 1</td>
<td>8</td>
<td>CsCl</td>
</tr>
<tr>
<td>X &gt; 1</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>
CRYSTAL IMPERFECTIONS:

Classified on basis of their geometry-

- Point imperfections
- Line imperfections (Dislocations)
- Surface imperfections
- Volume imperfections (pores, inclusions..)

Point imperfections are localised disruptions of the lattice. May be introduced by movement of atoms during processing of the material, by introduction of impurities or intentionally through alloying.

(i) Vacancy- one missing lattice atom. Since an atom vibrates about its lattice position, the tendency of an atom to jump out of its regular lattice position creating a vacancy increases rapidly with its energy i.e. temp. Possible to increase the number of vacancies by rapid cooling or extensive plastic deformation.

Equation: No. of vacancies $N_V = N \exp(-Q_V/kT)$

(ii) Interstitial defects- formed when an extra atom is inserted into the lattice structure at a normally unoccupied position. The defect causes lattice distortion.

Self interstitial- when the defect is an atom similar to those occupying the regular lattice sites.
(iii) Substitutional defects - when an atom is replaced by a different type of atom at a lattice site. The defect disturbs the surrounding lattice.

(iv) Frenkel Defect- A vacancy-interstitial pair formed when an ion jumps from a normal lattice point to an interstitial site, leaving behind a vacancy.

(v) Schottky defect is a pair of vacancies in an ionically bonded material; both an anion and a cation must be missing from the lattice structure if electrical neutrality is to be maintained.

- Parent Atom missing in the lattice is a Vacancy or Schottky Defect
- Different atom in a non lattice spot is an interstitial.
- Different atom in a lattice position is substitutional.
- Ionic compounds are charge balanced and hence defects occur in pairs.
- Parent ion moving to an interstitial site is a Frenkel Defect.
- In an ionic material Schottky defect occur in pairs to maintain neutrality. E.g. in LiF, a missing atom in the Li+ site has a -ve charge and a vacancy in the F− position has a +ve charge.

DISLOCATIONS:
(i) Edge dislocations- an extra plane of atoms above or below the dislocation line. Positive or negative. Causes localised lattice distortion and the dislocations can be displaced to the right or left by the application of suitable force. The dislocation can end -at a grain boundary - surface of a crystal -in another kind of dislocation.

ii) Screw dislocation can be illustrated by cutting partway through a perfect crystal, then skewing the crystal one atom spacing. The upper front of the crystal is shifted one atomic distance to the right relative to the bottom.

Burger’s vector- If a crystallographic plane is followed one revolution around the axis on which the crystal was skewed, starting at point 1 and travelling equal atomic spacings in each direction, we finish one atomic spacing below the starting point. The vector reqd. to complete the loop is the Burger’s vector. \( b \) parallel to screw dislocation and perpendicular to edge dislocation.

THE SLIP PROCESS: The process by which a dislocation moves and causes a material to deform is called the slip process. Deformation takes place by a gliding or shearing action on certain planes within the crystals. The gliding or shearing action is discontinuous and occurs by distinct movement on certain planes.

Easiest slip on planes of greatest planar density or in directions of greatest linear density.

IMPORTANT FACTORS:
- The stress required to cause the dislocation to move increases exponentially with the length of the Burgers’s vector. The slip direction should have a small repeat distance or high linear density.
- The stress reqd. to cause the dislocation to move decreases exponentially with the interpalnar spacing of the slip planes. Slip occurs most easily between planes of atoms that
are smooth and between planes that are far apart or have relatively large interplanar spacing. Planes with high planar density fulfils this requirement.

- Dislocations do not move easily in materials such as silicon or polymers which have covalent bonds. Because of the strengths and directionality of the bonds, the materials typically fail in a brittle manner before the force becomes high enough to cause appreciable slip.

- Materials with an ionic bond, including many ceramics such as MgO, also are resistant to slip. Movements of dislocations disrupts the charge balance around the cations and anions, requiring that bonds between anions and cations be broken. Brittle failure of material typically occur before dislocations move.

**SIGNIFICANCE OF DISLOCATIONS:**

- Slip explains why the strength of metals is much lower than the value predicted from the metallic bond. If slip occurs, only a tiny fraction of all metallic bonds across the interface need to be broken at any one time, and the force reqd. to deform the metal is small.
- Slip provides ductility in the metal.
- Can control the mechanical properties by interfering with the movement of dislocations. An obstacle introduced into the crystal prevents a dislocation from slipping unless higher forces is applied.

**CONTROL OF SLIP PROCESS**

(i) **Strain hardening** - Increasing the no. of dislocations increases the ability of the material to strain harden.

(ii) **Solid solution hardening** - Any of the point defects disrupt the perfection of the lattice can introduce substitutional or interstitial atoms by solid soln hardening.

(iii) **Grain size strengthening** - Surface defects such as grain boundaries disturb the lattice. By increasing the no. of grains or reducing the grain size, grain size hardening is achieved.

**TWINSING:** The rows of atoms parallel to what is called a twinning plane are displaced along the plane a distance from the twinning plane. Formation of a structure that is a mirror image of the lattice on the other side of the twinning plane. Occurs principally in BCC.

**IMPORTANCE OF POINT DEFECTS:**

Point defects disturb the perfect arrangement of the surrounding atoms, distorting the lattice for perhaps hundreds of atom spacings from the actual point defect. A dislocation moving through the general vicinity of the point defect encounters a lattice in which the atoms are not at their equilibrium. Positions. This disruption requires that a higher stress be applied to force the dislocation past the defect, therefore increasing the strength of the material.

**IMPORTANT NOTES**

- The strengthening of steels is to a large part due to interstitial carbon.
- At high temperature Fe exists as FCC and C occupies Octahedral interstitial positions.
- At low temperatures Fe exists as BCC and C occupies Tetrahedral interstitial positions.
- The resulting strain results in a change in structure from BCC to BCT.
• There is a 4% volume change associated with the FCC to BCC transition.

**Fig : A line defect**

**WHAT IS A PHASE?**

Any physically distinct, chemically homogeneous and mechanically separable portion of a substance.

An Equilibrium Diagram is defined as a plot of the composition of phases as a function of temperature in any alloy systems under equilibrium conditions.

**Phases and Additional information in Steel and other alloys**

**Body Centred Cubic**

BCC stands for Body Centred Cubic. It is a type of atomic arrangement and is a relatively "loosely" packed structure (atomic packing factor = 0.68). BCC can be formally termed a cubic lattice with the centre position fully equivalent to each of the eight corners. Body Centred Cubic structures are, as the name implies, based around a central atom with an atom at each of the corners of an imaginary cube.

**Face Centred Cubic**

FCC Stands for Face Centred Cubic. It is a type of atomic arrangement and is relatively "tightly" packed (atomic packing factor = 0.74). FCC is formally defined as a cubic lattice with the face positions fully equivalent to each of the eight corners. Face Centred Cubic structures are, as the name implies, based around "faces" of a cube with an atom at each of the corners and one at the centre of each face.

**Nucleation**

In terms of solidifying alloys, when the alloy (or a phase of the alloy) nucleates it starts to solidify a few atoms at a favourable site. These tiny solid lumps encourage more liquid to solidify onto them and these nucleation sites grow. Many of these sites form within the liquid which finally will become dendrites.

**Dendrite**

Primary phases often form as dendrites. These are solid structures forming from a liquid, which solidify in a branched manner because it is energetically favourable. Although a dendrite will rarely form in a completely regular manner, a diagram of such an idealised regular dendrite can be seen.
**Grain**
Grains are individual crystals of a microstructure. Grains grow from nucleation sites, with primary phases of metallic alloys commonly growing as dendrites. When grains meet during the solidification process they will produce a lattice mismatch as the orientations of the growing crystals will almost certainly be different. This mismatch forms a grain boundary.

Grain boundaries occur when growing grains meet.

**Alloy**
A metallic alloy is a mixture of a metal with other metals or non-metals. Ceramics can also be mixed to form alloys. Binary alloys are alloys of two elements only.

**Solid Solution.**
The addition of impurity atoms to a metal will result in the formation of a solid solution and/or a new second phase, depending on the kinds of impurity, their concentrations, and the temperature of the alloy.

A solid solution forms when, as the solute atoms are added to the host material, the crystal structure is maintained, and no new structures are formed. A solid solution has a uniform composition; the impurity atoms are randomly and uniformly dispersed within the solid.

Impurity point defects are found in solid solutions, of which there are two types: substitutional and interstitial.

**Intermetallic Compound**
An intermetallic solid (or compound) is a compound of two (or more) metals. Many have a fixed stoichiometric composition - cementite for example - but some do exist over a very small compositional range.

**Ferrite**
Ferrite is the name of a phase in steel alloys. Ferrite is the name given to the alpha phase of steel. It is a phase which occurs as a primary solid at compositions of carbon below the eutectic composition and at lower temperatures. Ferrite forms part of the eutectic solid (called pearlite). It is of BCC atomic arrangement and, more generally, ferritic steel is steel made mainly of ferrite.

**Cementite**
Cementite is the name of an intermetallic compound in steel alloys which has the chemical formula Fe$_3$C. It is important to note that Cementite is a phase which has a specific chemical formula unlike most phases which have ranges of chemical composition. Cementite is a hard brittle phase and steels containing high proportions of this phase will have increased strength/hardness but lower ductility.

**Austenite**
Austenite is the name of a phase in steel alloys. Austenite is the name given to the gamma phase of steel. It is a phase which, in simple steels, only occurs at fairly high temperatures - above 723°C. It is a Face Centred Cubic (FCC) structure of Iron with Carbon in solid solution. More generally Austenitic Steel can be defined as steel with a Face Centred Cubic Structure.

Carbon atoms sit in interstitial sites within the iron FCC lattice. As Carbon is too large to fit into the site the Iron atoms around it are distorted. This gives rise to solid solution strengthening.
**Pearlite**
Pearlite is the name of a phase mixture in steel alloys. Pearlite is the name given to the eutectoid mixture of steel - a lamellar mixture of ferrite (alpha) and cementite. Pearlite is so called because it looks like mother of pearl when viewed under a microscope.

**Eutectic**
A eutectic reaction is a three-phase reaction, by which, on cooling, a liquid transforms into two solid phases at the same time. It is a phase reaction, but a special one. For example: liquid alloy becomes a solid mixture of alpha and beta at a specific temperature (rather than over a temperature range). The eutectic solid is commonly lamellar (stripy) in form.

**Hypoeutectoid**
If an alloy is not of eutectoid composition then it is either hypereutectoid or hypoeutectoid. If the alloys' composition places it to the left of the eutectoid point on a phase diagram, then it's hypoeutectoid. If it is to the right of the eutectic point then it is called hypereutectoid. Note, though, that the phase diagram must have a eutectoid point to have hypoeutectoid or hypereutectoid alloys.

**Proeutectoid**
Proeutectoid signifies is a phase that forms (on cooling) before the eutectoid austenite decomposes. It has a parallel with primary solids in that it is the first phase to solidify out of the austenite phase. Thus, if the steel is hypoeutectoid it will produce proeutectoid ferrite and if it is hypereutectoid it will produce proeutectoid cementite.

**Phase**
Normally we consider there to be three phases, or states of matter: gas, liquid and solid. In materials science, the term has an additional, rather more specialised meaning. Gas phases are of no real relevance, and we concentrate on liquid and solid phases.

There can be many solid phases, distinguished by different greek letters, the difference between them being the nature of their atomic arrangement, or crystal structure. A phase can exist over a range of temperatures and compositions, but it's atomic structure will remain the same. There may be only one gas and one liquid phase for an alloy at a given temperature and composition, but there can be many solid phases. Another way of looking at a phase is that it is a structurally distinct part of a materials system.

**Phase Diagram**
A phase diagram is a temperature - composition diagram for two or more elements. It can be thought of as a "map" giving the microstructure of the resultant alloy at any given temperature and composition.
A binary phase diagram is a phase diagram of two elements.
**Fig 1: Lead–Tin Phase Equilibrium Diagram**

**Liquidus**
The Liquidus Line is the line (or lines) on a phase diagram above which only liquid is present. Technically it is "the locus of temperatures above which only liquid is stable".

**Solidus**
The Solidus Line is the line (or lines) on a phase diagram below which only solid is present. Technically it is "the locus of temperatures below which only solid is stable".

**Alpha**
With regard to phase diagrams: Alpha is the name given to a particular phase. The alpha phase is a mixture of the element on the left of the phase diagram and either the element on the right of the diagram (for a binary phase diagram) or an intermetallic compound.

**Beta**
With regard to phase diagrams, beta is the name given to a particular phase. The beta phase is a mixture of the element on the right of the phase diagram and either the element on the left of the diagram (for a binary phase diagram) or an intermetallic compound.

**Gamma**
With regard to phase diagrams, gamma is the name given to a phase. The gamma phase is a commonly a mixture of an intermetallic solid and either another intermetallic solid or an element. Gamma is also used to signify a high temperature solid. In steels the gamma (austenite) phase satisfies both of these definitions.

**Theta**
With regard to phase diagrams: theta is the name given to a phase. The theta phase is a commonly a mixture of an intermetallic solid and either another intermetallic solid or an element. In the Cu-Al phase diagram theta is an intermetallic solid of composition around 54wt%Cu.

**Microstructure**
The microstructure of an alloy consists of the structure of the grains and phases which the alloy possesses. An alloy normally requires metallographic preparation and magnification before its microstructure can be seen.
**Micrograph**  
A micrograph is a photograph or similar image taken through a microscope or similar device to show a magnified image of an item.

To produce a micrograph, a camera is affixed to a microscope either in place of the eyepiece or a specialist microscope is used which has a camera and eyepiece arrangement. A prepared specimen is put under the microscope in the usual way and photographs taken.

**Specimen Preparation** *(See set of notes for practicals in Metallurgy for more details)*  
Metallographic specimens are prepared using the following steps:

- Specimen is cut/sectioned.
- If the specimen is small, it is mounted in resin.
- The face to be studied is ground flat.
- The ground face is then polished using progressively finer particles of diamond (usually) until the required finish is obtained (commonly down to a micron or less).
- If required, the specimen is etched. Etchants usually attack a particular phase or a grain boundary to make it appear a different colour. Keller's etch is an exception to this rule as it deposits copper onto grain boundaries in Al-Cu alloys.

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**Phase and Phase Equilibrium Diagram**  
In a particular alloy system, the components may combine within certain temperature range to form two homogeneous coexisting portions. Each of these portions will be of different composition and will have different properties. However, each portion is homogeneous, throughout, and regardless of where a sample is taken in that portion, the composition will be the same. These homogeneous, physically distinct portions are called phases.
The phase in an alloy are not necessarily uniformly distributed throughout the structure. There are certain ways in which these phases may be associated to form the structure. The association of phases in a recognizably distinct fashion may be referred to as a structural constituent of the alloy.

A eutectic, e.g., is an intimate mechanical mixture of two or more phases having a definite melting point and a definite composition.

The study of the interrelation of phases in an alloy system at different temperatures and for different alloy compositions is of importance to understand the characteristics of alloys. An equilibrium diagram may be defined as a plot of the composition of phases as a function of temperature in an alloy system under equim. conditions.

**Equilibrium diagrams may be classified as**

1. Components completely soluble in liquid state;
   - Completely soluble in the solid state
   - Partially soluble in the solid state
   - Insoluble in the solid state.

2. Components partially soluble in the liquid state;
   - Partially soluble in the solid state
   - Completely insoluble in the solid state

3. Components completely insoluble in the liquid state;
   - Components insoluble in the solid state.

**Cooling curves:** One method of determining the temps. At which phase changes occur in a system consists of following the temp. as a function of time as diff. Alloys in the system are slowly cooled. This method is particularly useful in studying the changes that occur during the solidification of alloys and in some instances, may be used to advantage in determining transformations subsequent to solidification. However, in the latter case. The method may not be sufficiently sensitive; hence other procedures may be employed.

The LIQUIDUS curve is a plot of the composition of the liquid that will be in equilibrium with solid at any given temperature.

The grain size depends:
- The temperature from which metal is cast
- The cooling rate
- The nature of the metal

They will determine the
- The nucleation rate
- The rate of growth

The **LEVER** arm principle: The equim. Diagram indicates the composition of the phases that will be in equilibrium at any particular temp. At a particular temp. the composition of the phases present will always be the same whatever the composition of the alloy system. But the relative proportions of the phases in each alloy system will vary. The lever rule makes it possible to determine the proportions of each coexisting phases present.
The phase rule:
\[ F = C - P + 2 \]
- \( F \) - degrees of freedom
- \( C \) - Number of components
- \( P \) - Number of phases in equm. in a system

The variables of a system include 2 external parameters, temperature and pressure. Within the system variables that specify the composition of the phases present. No. of variables required to specify completely composition of a phase is \((C-1)\) where \( C \) is the number of components present.

**ALLOYING:** Metals seldom used in the pure state. Most metallic materials used in engineering are combination of metals known as alloys. Elements may combine in different ways to form alloys;
- Formation of solid soln.
- Compounds
- Mechanical mixtures

Solid Solution: Elements may combine to form alloys by completely dissolving in each other. The atoms of one element become part of the space lattice of the other element.

The addition of alloying elements is the principal method used to produce a variety of different alloys that are useable in a wide assortment of applications.

Main reason for alloying is to facilitate an improvement in the alloys’ physical and/or mechanical characteristics.

Typically the addition of alloying elements is to provide improvement in work hardening and/or precipitation hardening characteristics.

**BIBLIOGRAPHY:**
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