Thermal Equilibrium Diagrams for Alloys

Thermal equilibrium diagrams are special diagrams which contain information about changes that take place in alloys. The temperature at which a particular alloy changes from liquid to solid is an example of the type of thermal information contained in a thermal equilibrium diagram.

An alloy is a mixture or combination of two or more elements that produce a new element with improved properties.

During the solidification which takes place on cooling, the elements of an alloy combine in a particular way. This depends on the elements contained in the alloy in question. To understand this we will look at the cooling of a pure metal.

At 1500°C the pure metal is fully liquid. As time passes the temperature of the metal falls. At 1083°C for copper the liquid metal begins to change into solid. This change does not happen instantly but takes a little time. When this time has passed, the solidification ends and all of the metal has changed to solid. More cooling takes place until the metal reaches room temperature.

If a metal is 100% pure and contains no traces of other elements then some under cooling may occur before solidification begins. Under cooling is when the temperature drops below the liquid to solid temperature for a short period.
Constant Temperature Change
From the graph we can see that the temperature does not change while the metal is changing from liquid to solid. This is similar to when water changes into ice, which we call freezing. In metallurgy the term freeze point is used. Another example of this is the boiling of water. Water boils at 100°C. After this the water turns into steam but the temperature does not continue to rise. This extra heat that changes the water into steam is called latent heat.

Solid Solution Alloys
When metals combine they sometimes become completely soluble in each other. Metals which combine in this way are said to form solid solutions. When this type of alloy solidifies, only one type of crystal is formed. Under a microscope the crystalline structure of a solid solution alloy looks very like a pure metal. Solid solution alloys have similar properties to pure metals but have greater strength. They also have poorer electrical/thermal conductivity, greater hardness but not as elastic as pure metals.

The usual forms of solid solution are: substitutional solid solution and interstitial solid solution.

- Substitutional solid solution – this is when atoms of the parent metal are replaced or substituted by atoms of the second metal. In this case the atoms of the two metals are of similar size and direct substitution takes place.
- Interstitial solid solution – this is when the atoms of the parent metal are bigger than those of the alloying metal. The smaller atoms fit into the spaces (interstices) between the larger atoms.

![Typical Thermal Equilibrium Diagram](image-url)
Understanding Equilibrium Diagrams
There are a few different types of thermal equilibrium diagram. We have seen how a thermal equilibrium diagram for copper/nickel can be prepared from six graphs. There are three zones in this diagram:
- Liquid phase
- Solid phase
- Liquid + solid phase (pasty)
These are divided on the graph by the solidus and liquidus lines.

Eutectic Alloy
Another type of thermal equilibrium diagram is one that can be prepared from a eutectic alloy. In a eutectic alloy the two metals are completely soluble in the liquid phase but are insoluble in the solid phase. The cadmium/bismuth alloy is an example of a eutectic mixture. A thermal equilibrium diagram for cadmium/bismuth is built up in the same way as the solid solution diagram although they do differ. There is one point on the diagram where the liquid alloy changes to solid without going through a liquid/solid state is called the eutectic point. This is lowest melting point of any composition of the alloy. The temperature at which this occurs is very important as all alloys become solid at this temperature.

Partial Solubility Alloy
Some metals in an alloy only partially dissolve in each other. Solder (lead/tin alloy) is an example of this. The equilibrium diagram for this type of alloy is called a partial solubility thermal equilibrium diagram. It is a combination of the solid solution and eutectic diagrams and is a little more complex. The solvus line in the diagram plots the amount that metal ‘A’ that dissolves in metal ‘B’ up to a certain temperature. A solid
solution exists between the solidus line and the solvus line. These are present both on the left and right of the diagram.

**Intermetallic Compounds**

An intermetallic compound is a type of combination in binary alloys, formed when a chemical compound is created. They are also known as intermediate compounds or intermediate phases.

Two common types encountered in metallurgy are:

- Electron compounds
- Interstitial compounds

Electron compounds are very similar in structure to solid solutions and have metallic bonding. Compounds of this type tend to form between metals with similar electrochemical properties. An example is CuZn.

Interstitial compounds from between metals, or metals and non-metallic elements; with atom sizes similar to those that form interstitial solid solutions. One set of atoms fit into
the spaces (or interstices) between the other larger atoms. Iron carbide (Fe₃C) is an example, CuAl₂ is another.

In general intermetallic compounds are;
- Very hard and brittle
- Higher melting points than that of either of the elements contained in the compound

**Age Hardening**
It seems a contradiction that an alloy of Copper/Aluminium can be hard and brittle. This is as a result of age hardening. In 1906 A. Wilm discovered that when aluminium alloyed with copper is quenched from a high temperature its hardness will increase over time when left at room temperature.

**Solidifying Metal and Dendritic Growth**
When a molten metal cools, a point is reached when the temperature approaches solidification temperature. At this time the metal starts to become solid. Small particles become solid first, and then these grow as more metal becomes solid around them. Solidification takes place in a pattern and separate grains or crystals are formed. The small solidifying particles grow branches and eventually occupy a grain space. This is called dendritic growth. The formation of ice demonstrates this concept.

**Crystal Patterns and Unit Cells**
In metals, atoms bond together in a pattern which is repeated over and over, giving a crystalline structure. Most metals crystallise with one of the following crystalline structures:
- Body centred cubic structure (BCC) – copper, gold
- Face centred cubic structure (FCC) – zinc, cadmium
- Close packed hexagonal structure (CPH) – iron, tungsten

The BCC structure has atoms arranged so that their centres are positioned on the corners of a cube, with one atom in the centre. This unit cell is repeated to form a crystalline structure or pattern.
Atoms in the FCC and CPH unit cell are more tightly packed together than the atoms in a BCC structure. This helps to explain why different metals have different physical properties.

**Slip in BCC and FCC structures**
Slip means that part of a metal can slip over itself. Slip can take place in metals when they are subjected to certain shear type forces. If you take a look at the BCC and FCC structures you will see that slip is more likely in an FCC structure. This would explain why metals with an FCC structure are ductile and metals with a BCC structure are brittle.

**Atomic imperfections in metals**
Crystalline structures in metals have many imperfections. Atoms are not always where they should be if the crystal structure was adhered to. In reality there are often atoms missing, too many atoms, impure atoms, or distortions in the crystalline structure. These faults or defects are called crystal defects.

**Line defects in crystals**
If atoms are out of line in the grain body, or lattice, this is known as a line imperfection, or line defect. Line defects are called dislocations. Dislocations allow the grains to distort or slip under shear stress. Slip in metals is largely due to the presence of dislocations. Ductility in metals is a result of the distortion allowed by slip in metals.
A method of restricting the movement of a dislocation is to alloy it with another element OR to cold work the metal.

Point defects in metals
As already mentioned, it is rare that an ideal crystalline structure exists in a metal. Sometimes an atom may be missing from a line or a row and the lattice is placed under strain. When this occurs, a vacancy exists. Type of defect is known as a vacant site defect.

When an atom from another element, which is not the same size as the other atoms, is present it also causes distortion in the lattice. This atom can be larger or smaller than the other atoms. This type of defect is called a substitute defect.

If an atom from an impurity finds its way into a space or interstice in the lattice the defect caused is called an interstitial defect.

Allotropy of metals
This is the ability of some elements to exist in more than one crystalline structure. Steel can exist as BCC when cold and as FCC when heated above a certain temperature, depending on its carbon content.

Crystalline Structures
These have regular, repeating, geometrical molecular patterns.

Amorphous Structures
These have disorganised, irregular molecular patterns.