**3ME4-06 : MATERIAL SCIENCE AND ENGINEERING**

**Credit: 3 Max. Marks: 150 (IA:30, ETE:120) 3L+0T+0P**

**Subject notes**

**UT-2**

**Phase transformation**

Engineering materials possess mixtures of phases, e.g. steel, paints, and composites. The mixture of two or more phases may permit interaction between different phases, and results in properties usually are different from the properties of individual phases. Different components can be combined into a single material by means of solutions or mixtures. A solution (liquid or solid) is phase with more than one component; a mixture is a material with more than one phase. Solute does not change the structural pattern of the solvent, and the composition of any solution can be varied. In mixtures, there are different phases, each with its own atomic arrangement. It is possible to have a mixture of two different solutions! A pure substance, under equilibrium conditions, may exist as either of a phase namely vapor, liquid or solid, depending upon the conditions of temperature and pressure. A *phase* can be defined as a homogeneous portion of a system that has uniform physical and chemical characteristics i.e. it is a physically distinct from other phases, chemically homogeneous and mechanically separable portion of a system. In other words, a phase is a structurally homogeneous portion of matter. When two phases are present in a system, it is not necessary that there be a difference in both physical and chemical properties; a disparity in one or the other set of properties is sufficient.

There is only one vapor phase no matter how many constituents make it up. For pure substance there is only one liquid phase, however there may be more than one solid phase because of differences in crystal structure. A liquid solution is also a single phase, even as a liquid mixture (e.g. oil and water) forms two phases as there is no mixing at the molecular level. In the solid state, different chemical compositions and/or crystal structures are possible so a solid may consist of several phases. For the same composition, different crystal structures represent different phases. A solid solution has atoms mixed at atomic level thus it represents a single phase. A single-phase system is termed as homogeneous, and systems composed of two or more phases are termed as mixtures or heterogeneous. Most of the alloy systems and composites are heterogeneous.

It is important to understand the existence of phases under various practical conditions which may dictate the microstructure of an alloy, thus the mechanical properties and usefulness of it. Phase diagrams provide a convenient way of representing which state of aggregation (phase phases) is stable for a particular set of conditions. In addition, phase diagrams provide valuable information about melting, casting, crystallization, and other phenomena.

**Useful terminology:-**

**Component** – is either pure metal and/or compounds of which an alloy is composed. The components of a system may be elements, ions or compounds. They refer to the independent chemical species that comprise the system.

**System –** it can either refer to a specific body of material under consideration or it may relate to the series of possible alloys consisting of the same components but without regard to alloy composition.

**Solid solution** – it consists of atoms of at least two different types where solute atoms occupy either substitutional or interstitial positions in the solvent lattice and the crystal structure of the solvent is maintained.

**Solubility limit** – for almost all alloy systems, at a specific temperature, a maximum of solute atoms can dissolve in solvent phase to form a solid solution. The limit is known as solubility limit. In general, solubility limit changes with temperature. If solute available is more than the solubility limit that may lead to formation of different phase, either a solid solution or compound.

**Phase equilibrium** – it refers to the set of conditions where more than one phase may exist. It can be reflected by constancy with time in the phase characteristics of a system. In most metallurgical and materials systems, phase equilibrium involves just solid phases. However the state of equilibrium is never completely achieved because of very slow rate of approach of equilibrium in solid systems. This leads to non-equilibrium or meta-stable state, which may persist indefinitely and of course, has more practical significance than equilibrium phases. An equilibrium state of solid system can be reflected in terms of characteristics of the microstructure, phases present and their compositions, relative phase amounts and their spatial arrangement or distribution.

**Variables of a system** – these include two external variables namely temperature and pressure along with internal variable such as composition (*C*) and number of phases (*P*). Number of independent variables among these gives the degrees of freedom (*F*) or variance. All these are related for a chosen system as follows:

P+F=C+2

which is known as Gibbs Phase rule. The degrees of freedom cannot be less than zero so that we have an upper limit to the number of phases that can exist in equilibrium for a given system. For practical purpose, in metallurgical and materials field, pressure can be considered as a constant, and thus the condensed phase rule is given as follows:

P+F=C+1

**Phase Diagrams**

A diagram that depicts existence of different phases of a system under equilibrium is termed as phase diagram. It is also known as equilibrium or constitutional diagram. Equilibrium phase diagrams represent the relationships between temperature and the compositions and the quantities of phases at equilibrium. In general practice it is sufficient to consider only solid and liquid phases, thus pressure is assumed to be constant (1 atm.) in most applications.

Phase diagrams are classified based on the number of components in the system. Single component systems have unary diagrams, two-component systems have binary diagrams, three-component systems are represented by ternary diagrams, and so on. When more than two components are present, phase diagrams become extremely complicated and difficult to represent. This chapter deals mostly with binary phase diagrams.

**Unary phase diagramme**

In these systems there is no composition change (*C*=1), thus only variables are temperature and pressure. Thus in region of single phase two variables (temperature and pressure) can be varied independently. If two phases coexist then, according to Phase rule, either temperature or pressure can be varied independently, but not both. At triple points, three phases can coexist at a particular set of temperature and pressure. At these points, neither temperature nor the pressure can be changed without disrupting the equilibrium i.e. one of the phases may disappear. *Figure-1* depicts phase diagram for water



**Figure-1:** Unary phase diagram for water.

**Binary diagrams**: These diagrams constitutes two components, e.g.: two metals (Cu and Ni), or a metal and a compound (Fe and Fe3C), or two compounds (Al2O3 and Si2O3), etc. In most engineering applications, as mentioned before, condensed phase rule is applicable. It is assumed that the same is applicable for all binary diagrams, thus the presentation of binary diagrams becomes less complicated. Thus binary diagrams are usually drawn showing variations in temperature and composition only. It is also to be noted that all binary systems consist only one liquid phase i.e. a component is completely soluble in the other component when both are in liquid state.

Hence, binary systems are classified according to their solid solubility. If both the components are completely soluble in each other, the system is called *isomorphous* system. E.g.: Cu-Ni, Ag-Au, Ge-Si, Al2O3-Cr2O3. Extent solid solubility for a system of two metallic components can be predicted based on Hume-Ruthery conditions, summarized in the following:

- Crystal structure of each element of solid solution must be the same.

- Size of atoms of each two elements must not differ by more than 15%.

- Elements should not form compounds with each other i.e. there should be no appreciable

difference in the electro-negativities of the two elements.

- Elements should have the same valence.



**Figure-2:** Phase diagram for typical isomorphous binary system.

For the interpretation of the phase diagram, let’s consider the vertical line **ae** drawn corresponding to composition of 50%**A** +50%**B** and assume that the system is undergoing equilibrium cooling. The point **a** on the line **ae** signifies that for that particular temperature and composition, only liquid phase is stable. This is true up to the point **b** which lies on the liquidus line, representing the starting of solidification. Completion of solidification of the alloy is represented by the point, **d**. Point **e** corresponds to single-phase solid region up to the room temperature. Point **c** lies in the two-phase region made of both liquid and solid phases. Corresponding micro-structural changes are also shown in figure above liquidus only a liquid phase exists, and below the solidus single solid phase exists as completely solidified grains. Between these two lines, system consist both solid crystals spread in liquid phase. It is customary to use **L** to represent liquid phase(s) and Greek alphabets (**α**, **β**, **γ**) for representing solid phases. Between two extremes of the horizontal axis of the diagram, cooling curves for different alloys are shown in figure-3 as a function of time and temperature. Cooling curves shown in figure-3 represent **A**, **U’**, **X**, **V’** and **B** correspondingly in figure-2. Change in slope of the cooling curve is caused by heat of fusion. In fact these changes in slope are nothing but points on either solidus or liquidus of a phase diagram..

**Eutectic system:** Many binary systems have components which have limited solid solubility, e.g.: Cu-Ag, Pb-Sn. The regions of limited solid solubility at each end of a phase diagram are called terminal solid solutions as they appear at ends of the diagram. Many of the binary systems with limited solubility are of eutectic type, which consists of specific alloy composition known as eutectic composition that solidifies at a lower temperature than all other compositions. This low temperature which corresponds to the lowest temperature at which the liquid can exist when cooled under equilibrium conditions is known as eutectic temperature. The corresponding point on the phase diagram is called eutectic point. When the liquid of eutectic composition is cooled, at or below eutectic temperature this liquid transforms simultaneously into two solid phases (two terminal solid solutions, represented by **α** and **β**). This transformation is known as eutectic reaction and is written symbolically as:

Liquid (**L**) ↔ solid solution-1 (**α**) + solid solution-2 (**β**)



**iron – carbon system, phase diagramme**

A study of iron-carbon system is useful and important in many respects. This is because (1) steels constitute greatest amount of metallic materials used by man (2) solid state transformations that occur in steels are varied and interesting. These are similar to those occur in many other systems and helps explain the properties.

Iron-carbon phase diagram shown in figure-16 is not a complete diagram. Part of the diagram after 6.67 wt% C is ignored as it has little commercial significance. The 6.67%C represents the composition where an inter-metallic compound, cementite (Fe3C), with solubility limits forms. In addition, phase diagram is not true equilibrium diagram because cementite is not an equilibrium phase. However, in ordinary steels decomposition of cementite into graphite never observed because nucleation of cementite is much easier than that of graphite. Thus cementite can be treated as an equilibrium phase for practical purposes.

**Figure-** Iron – Iron carbide phase diagram.

The Fe-Fe3C is characterized by five individual phases and four invariant reactions. Five phases that exist in the diagram are: ***α***–ferrite (BCC) Fe-C solid solution, ***γ***-austenite (FCC) Fe-C solid solution, ***δ***-ferrite (BCC) Fe-C solid solution, Fe3C (iron carbide) *or* cementite - an inter-metallic compound and liquid Fe-C solution. Four invariant reactions that cause transformations in the system are namely eutectoid, eutectic, monotectic and peritectic.As depicted by left axes, pure iron upon heating exhibits two allotropic changes. One involves ***α***–ferrite of BCC crystal structure transforming to FCC austenite, ***γ***-iron, at 910ْC. At 14000c, austenite changes to BCC phase known as ***δ***-ferrite, which finally melts at 15360c

Carbon present in solid iron as interstitial impurity, and forms solid solution with ferrites / austenite as depicted by three single fields represented by **α**, **γ** and **δ**. Carbon dissolves least in **α**–ferrite in which maximum amount of carbon soluble is 0.02% at 723 ْC. This limited solubility is attributed to shape and size of interstitial position in BCC **α**–ferrite. However, carbon present greatly influences the mechanical properties of **α**–ferrite. **α**–ferrite can be used as magnetic material below 768 0C. Solubility of carbon in **γ**-iron reaches its maximum, 2.11%, at a temperature of 1147 0C. Higher solubility of carbon in austenite is attributed to FCC structure and corresponding interstitial sites. Phase transformations involving austenite plays very significant role in heat treatment of different steels. Austenite itself is non-magnetic. Carbon solubility in **δ**-ferrite is maximum (0.1%) at 1495 0C. As this ferrite exists only at elevated temperatures, it is of no commercial importance. Cementite, Fe 3C an inter-metallic compound forms when amount of carbon present exceeds its solubility limit at respective temperatures. Out of these four solid phases, cementite is hardest and brittle that is used in different forms to increase the strength of steels. ***α***–ferrite, on the other hand, is softest and act as matrix of a composite material. By combining these two phases in a solution, a material’s properties can be varied over a large range.commercial pure irons with less than 0.008%C; steels having %C between 0.008-2.11; while cast irons have carbon in the range of 2.11%-6.67%. Thus commercial pure iron is composed of exclusively **α**–ferrite at room temperature. Most of the steels and cast irons contain both **α**–ferrite and cementite. However, commercial cast irons are not simple alloys of iron and carbon as they contain large quantities of other elements such as silicon, thus better consider them as ternary alloys. The presence of Si promotes the formation of graphite instead of cementite. Thus cast irons may contain carbon in form of both graphite and cementite, while steels will have carbon only in combined from as cementite.

As shown in *figure-16*, and mentioned earlier, Fe-C system constitutes four invariant reactions:

**- peritectic** reaction at 1495 0C and 0.16%C, ***δ***-ferrite + ***L*** ↔ ***γ***-iron (austenite)

**- monotectic** reaction 1495 0C and 0.51%C, ***L*** ↔ ***L*** + ***γ***-iron (austenite)

**- eutectic** reaction at 1147 0C and 4.3 %C, ***L*** ↔ ***γ***-iron + Fe3C (cementite) [ledeburite]

- **eutectoid** reaction at 723 0C and 0.8%C, ***γ***-iron ↔ ***α***–ferrite + Fe3C (cementite)

Product phase of eutectic reaction is called ledeburite, while product from eutectoid reaction is called pearlite. During cooling to room temperature, ledeburite transforms into pearlite and cementite. At room temperature, thus after equilibrium cooling, Fe-C diagram consists of either ***α***–ferrite, pearlite and/or cementite. Pearlite is actually not a single phase, but a micro-constituent having alternate thin layers of ***α***–ferrite (~88%) and Fe3C, cementite (~12%). Steels with less than 0.8%C (mild steels up to 0.3%C, medium carbon steels with C between 0.3%-0.8% i.e. hypo-eutectoid Fe-C alloys) i.e. consists pro-eutectoid ***α***–ferrite in addition to pearlite, while steels with carbon higher than 0.8% (high-carbon steels i.e. hyper-eutectoid Fe-C alloys) consists of pearlite and pro-eutectoid cementite. Phase transformations involving austenite i.e. processes those involve eutectoid reaction are of great importance in heat treatment of steels.

In practice, steels are almost always cooled from the austenitic region to room temperature. During the cooling upon crossing the boundary of the single phase ***γ***-iron, first pro-eutectoid phase (either ***α***–ferrite or cementite) forms up to eutectoid temperature. With further cooling below the eutectoid temperature, remaining austenite decomposes to eutectoid product called pearlite, mixture of thin layers of ***α***–ferrite and cementite. Though pearlite is not a phase, nevertheless, a constituent because it has a definite

appearance under the microscope and can be clearly identified in a structure composed of several constituents. The decomposition of austenite to form pearlite occurs by nucleation and growth. Nucleation, usually, occurs heterogeneously and rarely homogeneously at grain boundaries. When it is not homogeneous, nucleation of pearlite occurs both at grain boundaries and in the grains of austenite. When austenite forms pearlite at a constant temperature, the spacing between adjacent lamellae of cementite is very nearly constant. For a given colony of pearlite, all cementite plates have a common orientation in space, and it is also true for the ferrite plates. Growth of pearlite colonies occurs not only by the nucleation of additional lamellae but also through an advance at the ends of the lamellae. Pearlite growth also involves the nucleation of new colonies at the interfaces between established colonies and the parent austenite. The thickness ratio of the ferrite and cementite layers in pearlite is approximately 8 to 1. However, the absolute layer thickness depends on the temperature at which the isothermal transformation is allowed to occur.

The temperature at which austenite is transformed has a strong effect on the inter-lamellar spacing of pearlite. The lower the reaction temperature, the smaller will be inter-lamellar spacing. For example, pearlite spacing is in order of 10-3 mm when it formed at 700 ْC, while spacing is in order of 10-4 mm when formed at 600 ْC. The spacing of the pearlite lamellae has a practical significance because the hardness of the resulting structure depends upon it; the smaller the spacing, the harder the metal. The growth rate of pearlite is also a strong function of temperature. At temperatures just below the eutectoid, the growth rate increases rapidly with decreasing temperature, reaching a maximum at 600 ْC, and then decreases again at lower temperatures.

Additions of alloying elements to Fe-C system bring changes (alternations to positions of phase boundaries and shapes of fields) depends on that particular element and its concentration. Almost all alloying elements causes the eutectoid concentration to decrease, and most of the alloying elements (e.g.: Ti, Mo, Si, W, Cr) causes the eutectoid temperature to increase while some other (e.g.: Ni, Mn) reduces the eutectoid temperature. Thus alloying additions alters the relative amount of pearlite and pro-eutectoid phase that form.

Fe-C alloys with more than 2.11% C are called cast irons. Phase transformations in cast

**Microstructures of Iron and Steels**

The microstructures of iron and steels is complicated and diverse which is influenced by composition, homogeneity, heat treatment, processing and section size. Microstructure of castings looks different than those of the wrought products even if the composition is same and even if the same heat treatment is given.

Pure iron is polymorphic. Two allotropic phases exist for pure iron in solid state depending on the temperature. One is bcc (body centered cubic) and the other is fcc (face centered cubic). The bcc crystalline form (?-iron) is stable until a temperature of 912 deg C when it is transformed to fcc (?-iron). The ?-iron remains stable until 1394 deg C, and then it reverts to bcc structure (?-iron). ?-iron is stable until the melting point of 1538 deg C. High purity iron is very weak. The ability of iron to accommodate heavy interstitials, namely carbon and nitrogen, is mostly responsible for the strength and the hardening effects.

**Ferrite**

Alpha – iron refers only to the bcc form of pure iron that is stable below 912 deg C. Ferrite is a solid solution of one or more elements in bcc iron. The carbon solubility of ferrite depends on the temperature: the maximum being 0.02 % at 723 deg C. Ferrite may precipitate from austenite in acicular form with certain cooling conditions. Ferrite is a very soft, ductile phase, although it loses its toughness below some critical temperature. ?-ferrite is magnetic below 768 deg C.

**Austenite**

Gamma – iron refers to fcc form of pure iron that is stable between 912 deg C and 1394 deg C. Austenite is a solid solution of one or more elements in fcc iron. Austenite is stable above 723 deg C depending upon C content. It can dissolve upto 2 % C. Austenite is not stable at room temperature in case of ordinary steels. However in case of Cr- Ni steels also known as austenitic stainless steels, austenite is stable at room temperature. There are other austenitic steels also such as Hadfield manganese steel and iron nickel magnetic grades. For heat treatment of steels, austenite is the parent phase for all transformation products that make steels so versatile and useful commercially. Austenite is a soft, ductile phase that can be work hardened to high strength levels. Austenite is non magnetic.For case hardened carburized steels and high carbon high alloy steels (e.g. tool steels), use of an excessively high austenitizing temperature dissolves excessive amount of carbide, which suppresses the temperatures where martensite begins and completes its transformation to such an extent that austenite is present at room temperature. This austenite is called retained austenite but it may not be necessarily stable.

Excessive retained austenite in tool steels is usually detrimental to die life since it may transform to fresh martensite and cause cracking or reduce wear resistance. Retained austenite in a carburized gear tooth is beneficial since teeth are not shock loaded.

When steels are heated during hot working, they are in austenitic condition. Subsequent cooling of hot steel results in the transformation of austenite to other phases or constituents. Air cooling (normalizing) of hot austenitized steel results into diffusion controlled transformation of austenite where ferrite precipitates first, followed by pearlite.

**Cementite**

Cementite is an intermetallic metastable compound of iron and carbon (iron carbide) with approximate formula Fe3C and an orthorhombic crystal structure. This compound contains 6.67 % of carbon by weight. Some substitution of other carbide forming elements such as Mn or Cr is possible. But only small amounts of the various carbide forming elements can be substituted before alloy carbides of other crystal structures and formulae are formed. Cementite decomposes (very slowly, within several years) into ?- ferrite and C (graphite) at 650-700 deg C.

Cementite is hard but brittle and can strengthen steels. Its hardness is 800 HV for pure Fe3C and upto around 1400 HV for highly alloyed carbide. Mechanical properties of steel depends on the microstructure, that is, how ferrite and cementite are mixed.

**Pearlite**

Pearlite is a fine mixture of ferrite and cementite arranged in lamellar form. It is stable at all temperatures below 723 deg C. Pearlite is formed due to eutectoid reaction. The eutectoid transformation is an isothermal, reversible reaction in which austenite is converted into two intimately fixed solid phases namely ferrite and cementite. With time and temperature, the cementite in the pearlite gets spheroidized which means that it changes from a lamellar to a spheroidal shape. Due to the spheroidizing action of cementite, the strength and hardness of the steel is reduced and its ductility increases. The degree of change is a function of the carbon content of the steel. Pearlite increases the strength of carbon steels. Mechanically, pearlite has properties intermediate to soft, ductile ferrite and hard, brittle cementite. Refining of the interlamellar spacing also increases the strength and the toughness. The hardness of fully pearlitic eutectoidal steel varies with the interlamellar spacing from about 250 HV to 400 HV as the spacing decreases.

**Bainite**

A different two phase constituent called bainite is formed if the cooling rate from austenitizing temperatures is faster than cooling in air, or if alloying elements are added to the steel to increase hardenability. Bainite is a metastable aggregate of ferrite and cementite that forms from austenite at temperatures below where martensite starts to form. The appearance of bainite changes with the transformation temperature. At high transformation temperatures the appearance of bainite is ‘feathery’. This bainite is also called upper bainite. At low transformation temperatures the appearance of bainite is ‘acicular’. This bainite is also called lower bainite. The feathery appearance of upper bainite is also influenced by carbon content and is most appropriate for grades with high carbon contents. Fig 1 shows microstructures of upper bainite and lower bainite.

**Martensite**

Martensite is formed if the cooling rate from the austenitizing temperature is rapid enough (a function of section size, hardenability and quench medium). Martensite is a generic term for the body centered tetragonal (bct) phase which is formed by the diffusionless transformation. The parent and product phases has the same composition and a specific crystallographic relationship. Martensite is formed in steel because the solute atoms of carbon occupy the interstitial sites of iron atoms. This produces substantial hardenability and a highly stained brittle condition. In carbon containing steels the appearance of the martensite changes with carbon in the interstitial sites. Low carbon steel produce ‘lath’ martensites while high carbon steels produce ‘plate martensite, often called ‘acicular’ martensite, when all the carbon is dissolved into the austenite.

The strength and hardness of martensite varies linearly with carbon in austenite upto about 0.5 % C. As the carbon in the austenite increases beyond 0.5 %, this curve starts to flatten and then goes downward due to the inability to convert the austenite fully to martensite (retained austenite becomes increasingly present). Hence when high carbon steels are heat treated, the austenitizing temperature is selected to dissolve no more than about 0.6 % C into the austenite.