

BASIC PRINCIPLES IN PHYSICAL METALLURGY - II

(Structure of solids and phase transformation)

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I. INTRODUCTION

The structure and stability of metallic materials needs to be understood before dealing them for a particular service. The materials depends on chemistry and processing condition. Various structures evolves during processing. Therefore one has to understand the distinction among the structures from crystallographic point of view. Here, we have presented a brief account relevant to the structural aspect. This will help in understanding and identification of the phases by metallographic techniques. The road maps for phase stability, which may be called as phase diagram have been discussed. From phase diagram, we can extract the information about the relative amounts of the various phases, which can be verified and confirmed from microstructures of the materials. The various invariant liquid state and solid state reactions have been introduced. A few examples of non-equilibrium structures such as nanocrystal, glass and quasicrystal etc. arising due to non-equilibrium processing has been highlighted. A brief mention has been made about diffusion, precipitation, order-disorder reaction and spinodal decomposition.

II. STRUCTURE OF SOLIDS

Solids are formed from liquid, by the process, called solidification. In liquid the atoms are random and not fixed in one position, whereas in solids atoms are rigidly fixed, which gives a definite shape and size of solids. There are no variety in liquid structure, but a lot of varieties are observed in solids. We can classify solid structure into two type - (1) Noncrystalline, (2) crystalline. We will spend most of our time in discussion of the crystalline structure. Before going into the detail of crystalline and non-crystalline structure, it is relevant to mention about the atomic forces and nature of bonds in metallic solids. Inter-atomic bonds are found to be of two types (i) directional, (ii) nondirectional. The bond strength is dependent on direction in directional case, otherwise independent. Covalent and permanent dipole bonds are directional but metallic, Ionic and Vander Walls bonds ideally are nondirectional. In metallic solids, the free electron cloud inside the materials makes the bands nondirectional. In ceramics, ionic bonding make the bonds nondirectional. Coming back to classification of solids, crystalline structure can be defined as a structure where atoms are regularly and periodically placed. The non-crystalline solid can be subdivided as (i) Glassy or amorphous, (ii) Quasicrystalline. In glassy structure atomic arrangements resembles liquid like structure; only atoms are frozen. In case of quasicrystals,

atoms are ordered but not periodically arranged. One must realize that quasicrystal structure is neither periodic nor random in atomic arrangement and it falls between crystal and glassy structure. Electron microscopy and diffraction technique can be used to distinguish these above three structures. The geometry of the crystalline structure will be discussed here.

II.1. CRYSTALLINE STRUCTURE

It has been stated earlier that atoms are periodically repeated in three dimension incase of crystalline structure. The smallest repeated unit, which is either a cube or distorted cube, is designated as unit cell. The unit cell contains the atoms in its various position. However, it should be emphasized that the unit cell without the atom is a part of the space lattice which is an infinite three dimensional array of points. All lattice points have an identical surroundings. A single atoms or a group of atoms can be used to decorate the lattice point and finally the unit cell. Unit cell may have one lattice point (in primitive case) or more (in nonprimitive case).

To give the idea of a lattice, (two dimension) a square lattice has been displayed in Fig.1. Here we can see that each dot point has similar neighbour. It has been established that lattice points in 3 dimension can be arranged in only 14 different ways. These 14 different lattices are called Bravais lattices. Fig.2 shows all the unit cells from the Bravais lattices. From three dimension geometry point of view, we can also realize that the 14 bravais lattices can fall into two categories - (1) Primitive lattice, (ii) Nonprimitive lattice. In primitive lattice, the lattice points in unit cell is one. There are seven such unit cells. These are (i) cubic, 2) Tetragonal, 3) Orthorhombic, 4) Hexagonal, 5) Rhombohedral, 6) Monoclinic, and 7) Triclinic. All these primitive lattices are also called simple lattices of those system. However, we can also have nonprimitive case, for an example, in cubic system, there are two other non primitive lattices - these are body centered cubic(BCC) and face centered cubic (FCC). In simple cubic system, the lattice points present in the corner of the unit cells. In BCC, the lattice points are present in body centered position, in addition to the corner position. In FCC, the lattice points are present in face centered position of cubic face and also in the corner. Similarly, depending on the system we have 7 nonprimitive cells. To describe the unit cell, we need to define the lattice parameters.

The cubic system is defined by the vectors along the 3 edges of the cube i.e. a , b , c (of equal length). The angle between b & c is α , and between c & a is β and between a & b is γ . The rotation about angle should be followed consistently. The geometry of all the unit cells is summerized in Table-1 and illustrated in Fig.2.

Table-1 : Lattice parameters of the unit cells of all systems

System	Lattice parameters	Materials
Cubic (P, I, F)	$a = b = c; \alpha = \beta = \gamma = 90^\circ$	Cu, Ag, Au
Tetragonal (P.I)	$a = b \neq c; \alpha = \beta = \gamma = 90^\circ$	β -Sn (white)
Orthorhombic (P, C, F, I)	$a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$	Fe ₃ C (cementite)
Hexagonal	$a = b \neq c; \alpha = \beta = 90^\circ, \gamma = 120^\circ$	Mg, Zn
Rhombohedral	$a = b = c; \alpha = \beta = \gamma \neq 90^\circ$	Sb, Bi
Monoclinic	$a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta$	β -S
Triclinic	$a \neq b \neq c; \alpha \neq \beta \neq \gamma$	K ₂ CrO ₇

Note : P represents simple or primitive, I denotes body centered, F indicates face centered and C means edge centered unit cells.

Most of the metallic structures fall into either cubic or hexagonal class. Engineering materials are mainly of BCC, FCC or HCP type. Among all these structures, FCC has good ductility and is favoured for metal working operation.

After discussing the crystal structure we are in a position to distinguish the microstructure of the metallic crystals. A solid material may be a single crystal or aggregates of crystals having different orientation. The former is called single crystal of a phase, which can be grown from liquid by controlled cooling. The latter one i.e. structure of aggregates of crystallites is called polycrystal. These individual crystallites are designated as grains and the junction between the crystallites are termed as grain boundary, which is observed under microscope after proper etching. Another type boundary, frequently observed in Cu-Zn alloys is twin boundary. The parallel sided regions with each grain are basically twins. One portion of the grain rotates to make a mirror image to other portion. The reflecting plane is called twin plane or twin boundary (Fig.3).

III. PHASE DIAGRAMS

Phase diagrams are the maps exhibiting the relative amounts of the phases, range of existence and stability region, as a function of temperature, pressure and composition. The phase diagrams are

constructed maintaining the equilibrium condition. Thus the phase diagram is referred as equilibrium diagram. Phases in a metallic material is understood in terms of microstructure, as regions that is different from other region either in composition or in structure or in both.

III.1. Phase Rule

We will discuss Gibbs phase rule before describing the phase diagram. Gibbs derived a relationship between the number of phases (P), that can coexist at equilibrium, the minimum number of components (C) that can be used to form the system, the degree of freedom (F) and the number of external variables (N). The relationship may be expressed in equation form as '

$$P + F = C + N \quad \text{..... (1)}$$

N = 2, considering pressure and temperature as variable, or
N = 1, considering pressure const. (atmospheric pressure) and temperature as variable - applicable to most metallurgical system.

The above relation (1) is called Gibbs phase Rule. Let us understand the significance of the above terms.

A phase is defined as a physically distinct, chemically homogeneous, mechanically separable region of a system. The components of a system can be elements, ions or compounds. They must be the independent chemical species comprising the system. In Cu-Ni system, the elements Cu and Ni are the components, whereas Al_2O_3 - Cr_2O_3 system the two oxides can be taken to be the components as oxygen will not be considered as independent component. In Fe-C system, iron and graphite can be two components but to our convenience for practical purpose iron and iron carbide (Fe_3C) are chosen as the components.

The external variables (N) of a system are basically temperature and pressure. However, within the system there are variables that specify the compositions of the phases present. If there are P phases in the system, the total number of composition variables is $P(C-1)$. Including the two external variables the total number of variables is $P(C-1) + 2$. The number of independent variables among these gives the degree of freedom (F). Naturally, F can not be greater than the total number of variables

$$\text{i.e. } F \leq P(C-1) + 2 \quad \text{.... (2)}$$

It can be logically understood that when one phase is present in a system, the degrees of freedom are equal to the total variable. As the number of phases increases the degrees of freedom decrease. The degree of freedom cannot be less than zero, so that we have the lower limit and upper limit of degree of freedom. Thus, the number of phases that can co-exist can be easily derived.

For binary diagram, where $C = 2$; we have computed the list of total variable and degrees of freedom as follows :

Table-2

No.of phases	Total variables	Degree of freedom
P	$P (C-1) + 2$	$F = C-P +2$
1	3	3
2	4	2
3	5	1
4	6	0

The binary system cannot have more than four phases in equilibrium when pressure and temperature both are external variables.

Phase diagram are classified on the basis of the number of components in the system. Single component system, two component system and three component systems are called as unary diagram, binary diagram and ternary diagram respectively. Among all these diagrams, binary diagram has been extensively studied.

III.2 Unary Diagram

The Gibbs phase rule $P + F = C + N$, can be reexpressed considering $C = 1$ and $N = 2$, as :

$$F = 3 - P \quad \dots (3)$$

As $F = 0$, the maximum number of phases which can co-exist can be ~ 3 .

In a single component system, there is composition variable and only temperature and pressure be variables.

The unary diagram for Fe is illustrated in Fig.4. X-axis and Y axis represent pressure and temperature respectively. Generally, in phase diagram, solid phases are denoted by Greek alphabets (α , β , γ etc.)

Let us consider the single phase regions on the diagram such as gas, liquid and several other crystalline forms of iron. From the phase rule, $C = 1$, $P=1$ and $F=2$. As the degree of freedom is $\leq$, it indicates that both temperature and pressure can be varied independently without sacrificing the phase.

If we consider the two phase region i.e. $P=2$, then $F=1$, which indicates that the degree of freedom is one i.e. either temperature and pressure can be varied dependently to stay on the phase boundary.

Three phase equilibrium exist at points on the phase diagram, where three phase boundaries meet. In this case $P=3$; so $F=0$ i.e. no

degree of freedom; neither pressure or temperature can be altered without sacrificing the phase.

The equilibrium structure of iron at ambient temperature and pressure is BCC (α). α -phase transforms to the FCC (γ) form at 910°C. At 1410°C, the FCC (γ) changes to BCC(δ) iron. As the pressure is increased the $\alpha \rightarrow \gamma$ transition temperature is lowered. At high pressure (HCP(ϵ) phase of Fe has also been experimentally observed.

III.3. Two component systems - Solid solubility

Two components are completely soluble in each other if they form a single phase in the equilibrium state. The structure of the single phase has to conform one of the parent structure. For example, copper and nickel are soluble in each other in all proportions, both in liquid and solid state whose structure is FCC. The structure of Cu and Ni is also FCC. The concept of a solid solution can be understood as very similar to that liquid solution. A solid solution may be either substitutional or interstitial depending on whether the solute atoms substitute for a solvent atoms or it may occupy an interstitial position available between the solvent atoms. So it is clear that in substitutional solid solutions the solutes occupy the lattice points. Hume-Rothery's rule has been prescribed to predict the possibility for solid solution formation in substitutional alloys.

Hume-Rothery's Rule - According to this rule the atoms of two components must show :

1. Less than 15% difference in size
2. the same crystal structure
3. No appreciable difference in electro-negativity
4. The same valence

If the Hume-Rothery's rule is not satisfied, the solid solution formation is unfavourable. In that case intermediate phase forms.

III.4. Binary Diagram

Gibb's rule can be re-expressed in binary diagram assuming pressure is constant and we are interested only in composition-temperature diagram. In fact most of the metallurgical systems are operated at atmospheric pressure.

Here, $C=2$, $N=1$

So, $F = 3-P$

..... (3)

We can see that maximum three phase can co-exist in equilibrium as $F=0$ in that case. Fig.5 shows a schematic phase diagram of two components A & B, which are completely soluble to each other in liquid and solid state. The diagram is composed of a single phase liquid region, a single phase solid region and two phase liquid plus solid region. The liquidus is the curve for the liquid phase that is in equilibrium with solid. The solidus is a curve for the solid phase that is

in equilibrium with liquid. The region between solidus and liquidus line indicates the mixture of solid and liquid phase. At a particular temperature, an horizontal line, which is drawn between solidus and liquidus, is called tie line. The two ends of the tie lines represents the composition of solid and liquid respectively (Fig.5). Now, we will discuss lever rule to predict the relative amount of solid and liquid phase at that temperature. Let us take the composition of the material be C_0 . At the temperature indicated by point C, C_1 and C_s are the composition of the liquid and solid phase. Hence we have to imagine a lever with a fulcrum at C_0 . According to this rule, the fraction of a phase having a composition indicated by one end of the lever is equal to the ratio of the length of the lever on the far side of fulcrum to the total lever length. These can be expressed as :

$$f_s \text{ (fraction of solid)} = \frac{ec}{ef} = \frac{C_0 - C_1}{C_s - C_1}$$

$$F_l \text{ (fraction of liquid)} = \frac{cf}{ef} = \frac{C_s - C_0}{C_s - C_1}$$

This lever rule can be applied to type of binary phase diagram.

III.5 Binary Eutectic Diagram

One of the most important phase diagram is eutectic phase diagram (Fig.6). Eutectic is a type of reaction where all the liquid transforms on cooling to two solid phase simultaneously. In Fig.6, at point e which is called eutectic point, all liquid transforms to alpha and beta phase. From the phase diagram it is clear that eutectic point is the lowest melting point of the system. On further lowering the temperature below eutectic temperature, the solid solubility of B in A and vice versa decreases with decreasing temperature reflected in the solvus which is also called maximum solubility line. If the solute concentration is lower than the eutectic composition (c_e) the alloy is called hypoeutectic alloy (C_0 , in Fig.6) in which case we have microstructure containing primary α in a matrix of eutectic. A material with composition higher than the eutectic is called hyper eutectic and in general a microstructure containing primary β in a matrix of eutectic is expected.

III.6 Invariant Reactions

There are numerous liquid state and solid state transformation which are invariant type i.e. the degree of freedom is zero. Equilibrium binary diagrams are not usually simple solid solution or eutectic diagrams discussed earlier. Instead they are composite diagrams containing a number of invariant reactions. Common invariant reactions have been discussed below :

1. On cooling one phase separates into two phases
2. On cooling two phases react to produce a third different phase

We can describe these reactions in equation form, where L represents a liquid phase and a Greek letter represents a solid phase (including compounds). These invariant reactions that belong to class (1) are :

- a) Eutectic : $L \longrightarrow \alpha + \beta$
- b) Eutectoid : $\gamma \longrightarrow \alpha + \beta$
- c) Monotectic : $L1 \longrightarrow \alpha + L2$

Those belong to class (2) are

- a) Peritectic : $\beta + L \longrightarrow \alpha$
- b) Peritectoid : $\beta + \gamma \longrightarrow \alpha$
- c) Syntectic : $L1 + L2 \longrightarrow \alpha$

Some of these important invariant reactions are displayed in Fig.7. The iron carbon diagram is an example, where the combination of peritectic, eutectic and eutectoid reactions are observed.

IV. NON EQUILIBRIUM PROCESSING

So far we discussed the equilibrium aspects of phase stability assuming equilibrium condition has been maintained to process the materials. However, in actual cases, due to non equilibrium processing (i.e. cooling rate higher than the equilibrium), equilibrium structures or microstructures do not result. Here we will discuss some of these non-equilibrium or metastable equilibrium microstructures and structures.

IV.1. Cooling

In practice, cooling rates are almost always rapid enough to prevent the equilibrium microstructure formation; such a microstructure is said to be cored because the first regions to solidify (cores) have solute lean composition, which is different from those of the last material to solidify containing solute rich composition. Since a chemical etch often attacks regions of different composition at different rates, cored regions can be delineated in a microstructure. A cored copper-nickel alloy is shown in Fig.8 (a) and the mechanism of its formation can be understood from Fig.8(b).

IV.2 Surroundings

Rapid cooling through a peritectic reaction a second type of non-equilibrium structure called surrounding developed in the material. Peritectic structure almost always show the departure from equilibrium condition due to its nature of reaction i.e.



The product when formed initially is adhered at the surface of α p phase, acts as a barrier between the parent phases. Hence the reaction process slows down and finally stops before completion. This can be depicted in Fig.9 where the solid layer acts as a barrier. Thus the peritectic reaction is never completed without continuous stirring or agitating the melt.

IV.3 Nanocrystals

From the melt, grains nucleate and grow in different sizes depending on cooling rate. If the cooling rate higher, nucleation rate is faster than growth and one expects finer grain size. However, there is a critical cooling rate beyond which grain size of the materials becomes in the order of nanometer (10^{-9} m) in size. The grain boundary area is more than the grain body. This type of structure is called nanocrystals, which have a special mechanical properties like high strength and high ductility. It is an exciting field of research presently.

IV.4 Metallic Glass

If the cooling rate is so high that the nucleation of crystalline phases is completely suppressed, the liquid is completely frozen and gives rise to the structure called metallic glasses or amorphous phases. Splat cooling or rapid solidification techniques are used to obtain metallic glasses. Typical 10^6 - 10^9 K/s is required to obtain metallic glasses in Fe-B-Si system. Further heat treatment shows that glass transforms to crystalline phase.

IV. 5 Quasicrystal

As we have discussed earlier that quasicrystal structures are different from that of crystals and glasses. However, in many aspects the property of quasicrystal lies in between crystals and glasses. In many system, Al-Mn/Fe/Cr system, by rapid solidification technique one can synthesis quasicrystals. Though in many systems quasicrystals are metastable, there are some system (Al-Cu-Co) where quasicrystals are believed to be stable. In Al-Mn-Si system, it has been found that cooling rate required for quasicrystal formation is lower than that for metallic glass formation. Quasicrystals are very hard and brittle and it can be used as a good coating material.

V. DIFFUSION PROCESS

Diffusion means movement of atoms in liquid or solid present in the system. The movement of atom from one place (higher concentration) to other place (lower concentration) take place if the phase is heated at considerable temperature and time. This process leads to homogenization of the elements in the phase and removes the segregation or coring effect. The diffusion also controls the rate of phase transformation i.e. when atoms are moving from one phase to other phase. The diffusion in liquid is faster than in solid. The carburization of steel and oxidation of a metal occurs due to the diffusion phenomena. From the knowledge of diffusion, one can

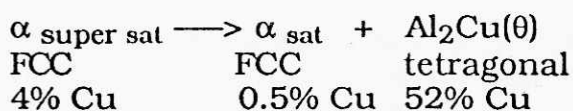
precisely calculate the time and temperature required in heat treatment schedule to achieve the particular phase transformation.

VI. PRECIPITATION PROCESS

We refer this process when the excess solute entrapped in the solvent starts coming out in a favourable situation. We have seen from the solvus in phase diagram that solid solubility decreases with temperature. Hence a solid solution saturated at high temperature becomes supersaturated at low temperature. The excess solute will come out as a precipitate of second phase. The precipitation can thus be written as :

Supersaturated solid solution $\rightarrow$ saturated S.S + precipitate

The precipitate particle first nucleates and then grows by the diffusions of solute atoms into it from matrix phase. One such example of precipitate in Al-Cu (duralumin) alloy was given



These particles $\text{Al}_2\text{Cu}(\theta)$ phases are coarse in size and can be identified in optical microscope.

VII. SOLID STATE TRANSFORMATION

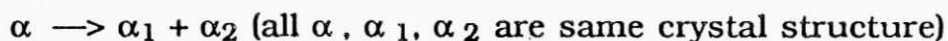
Besides eutectoid, peritectoid and precipitation type transformation there are many solid state transformation in metallic crystals. It is out of the scope of the present lecture to mention all. However, we will briefly mention about two important transformations such as (1) order-disorder, (2) spinodal decomposition. These processes will be discussed from the frame work lattice introduced earlier.

VII.1 Order-disorder Transformation

In binary solid solution, we understand that two atoms are intermixed and occupy the lattice points in random fashion. It is difficult to distinguish the atoms for a particular lattice points. This type of solid solution is called disordered solid solution. In many system example (Cu-Zn) the disordered phase transforms to ordered phase where the type of atoms is fixed for a particular position in the unit cell. The occupancy is no more random. At lower temperature ordered phase and at higher temperature disordered phase is stable. Ordered phases are stronger than disorder phases. Intermetallic compounds are ordered phase i.e. Ni_3Al . Many ordered phase solidifies from the melt directly without having the existence of disorderd phase. There is a particular temperature below which order-disorder transformation takes place. The lattice parameters generally change after this transformation. The lattice is called super lattice.

VII.2 Spinodal Decomposition

It is observed that a solid solution (say α phase), being stable at high temperature, decomposes to two phases (say, α_1 and α_2) at lower temperature. The structure of α , α_1 and α_2 phases are same only the composition is different. This type of transformation is called spinodal decomposition. The reaction is written as :



This transformation is not controlled by nucleation and growth mechanism. That's why it is different from eutectoid or precipitation type process. The mottled microstructure without having sharp interface between α_1 and α_2 phase are the characteristic of this transformation. Transmission Electron Microscope is required to identify this type of microstructure.

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Figure Captions (Basic principles in physical metallurgy-II)

Fig.1 : Two dimensional lattice and unit cell

F.g.2 : Conventional unit cells of the 14 Bravais space lattices. The capital letter refer to the type of cell. P-Primitive; C - edge centered i.e. lattice points in the centre of two parallel faces; F - lattice point in the centre of each face, I - lattice point in the centre of interior. All points indicated are lattice points.

Fig.3 : A reflected light photomicrograph of the microstructure of 70-30 brass (70% Cu, 30% Zn) showing many grains of different orientations and showing twins (parallel sided regions) within the grains, 500x.

Fig.4 : Pressure-temperature diagram for the one component system of iron

Fig.5 : Binary solid solution diagram : an equilibrium diagram for elements A and B which are completely soluble in each other in all proportion in both the liquid and solid state.

Fig.6: Hypothetical binary equilibrium diagram for elements A and B which are completely soluble in each other in all proportion in the liquid state but only to a limited extent in one solid state.

Fig.7 : Example of invariant reaction.

Fig.8 : a) The microstructure of a cored, cast 70-30 Cu-Ni alloys, 75x
(b) The alloy is not considered to be completely solid until its composition line crosses the non-equilibrium solidus at T_5 .

Fig.9 : Surrounding during non-equilibrium cooling. (a) The peritectic portion of a phase diagram. If an alloy C_0 is cooled rapidly, surrounding may result. (b) atom transport during a peritectic reaction.