

Indian Institute of Technology Kanpur

National Programme on Technology Enhanced Learning (NPTEL)

Course Title

Manufacturing Process Technology – Part- 2

Module- 10

by

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Hello and welcome to this manufacturing process technology part 1, Module 10.

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We were talking about solid solutions and we just started deciphering how you know there is a solvent phase and there is solute phase and then how the solute based on its sizes can go either into the interstice space or you can do substantial kind of mechanism using the solid solution.

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Equilibrium Phase Diagram

- The important metallurgical changes that take place when a mixture of different metals or materials is gradually cooled from a liquid state are best described with the help of equilibrium phase diagrams.
- Phases are characterized by boundaries across which there exists some discontinuities in physical properties.
- Even a pure metal can be in different phases namely solid, liquid or vapor.
- Even within a single phase there can be different phases each characterized by a different crystal structure.
- When cooling is sufficiently slow, we can assume that all the phases involved in a transformation process at a given temperature are in equilibrium with each other.
- Though, in general, the transformation of phases is governed by temperature, composition and pressure, the latter plays an insignificant role in the processes that we shall consider.

Let us now talk about equilibrium phase diagrams which is very important aspect of understanding the solutions so the important metallurgical changes that take place when a mixture of different metals or materials is gradually cooled from a liquid state are best described with the help of this equilibrium phase diagrams so phases are characterized by boundaries across which there exists some discontinuity in the physical properties I am going to come to come to this later when I actually explained the diagram.

So even a pure metal in different phases namely solid, liquid and vapor can be plotted into something called a phase diagram .so even within a single phase there may be different phase each characterized by different crystal structure for example as in the case of iron you have a you know FCC or a BCC structure at two different ranges and these materials are known as allotropes I think I describe this earlier.

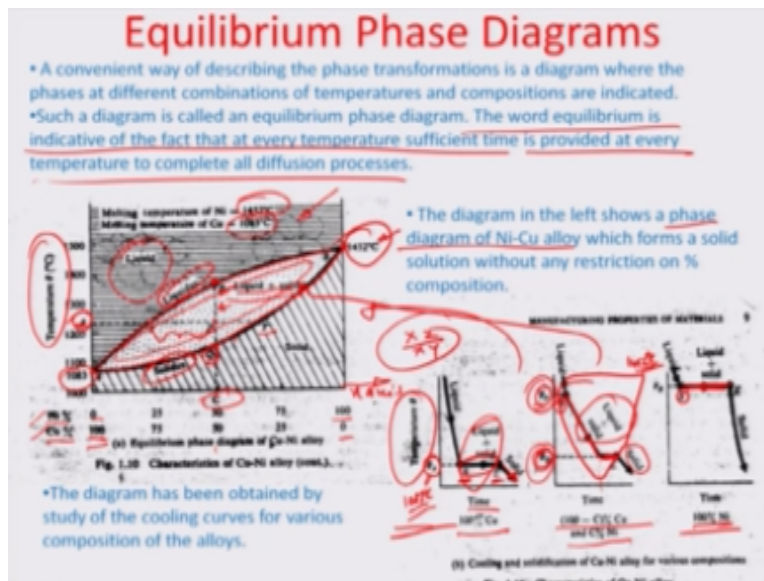
When we are talking about at the being about the engineering's okay so in a same manner you have to different structures which is the function of temperature of a certain material which can actually come in the way of how you take the material from the liquid state to the solid state through the various temperature regimes okay, so you have different phases even has a single phase material.

So when cooling is sufficiently slow we can assume that all the phases involved in a transformation process at a given temperature and equilibrium with each other and this what you take as a snapshot every time so that you can draw the equilibrated phase as a function of time of

a solidification process so through in general the transformation of phases is governed by temperature from position and pressure the later place and in significant role in the process that we shall consider.

So mostly we will worried about the once which have temperature meaning there by that temperature would be the most critical parameter that will get him.

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So let us look at the first model which is very simple it is a two phase system comprising of nickel copper as a convenient way of describing the phase transformation of the system is you can see here the concentration is plotted on the x axis and the temperature is on the y axis and you can see that the concentration of the nickel vis – a vis the copper varies between 0 ,100% to 100, 0% meaning there by beyond this 50 line the solute change into the solvent and vis a versa okay so that is how we are trying to see this diagram okay.

So the word equilibrium particular is indicative of the fact that every temperature sufficient time is provided so that you can complete all the mechanical slow diffusion driven process and then the material has come to a stable or equilibrated phase or state okay so you enough time that you are allowing at these points so the diagram in the left shows phase diagram of the nickel copper alloy okay now you can see there are various regions of this diagram this particular region is the liquid region.

Where you can see it by the this horizontally hatched region so the melting point or melting temperature of nickel is about 1452 °C and that of copper is about 1083°C obviously when you formulate an alloy the melting temperature would change based on the percentage of this nickel and copper because it is going to be taking a different thermal energy for the copper to get melted and a different thermal energy for the nickel to get melted as well.

So you have something called the liquidus line which basically gives you an illustration of the point beyond which the solidification will start to happen although not complete and solidus line which actually would give you an idea of when the solidification process is complete.

So you can see these dotted phase in-between which is actually related to a mixture of the solid and the liquid that means the liquids is partially solidified so there are some solid chances here and there and there till and until the unknown the temperature the let us say the temperature comes to this particular phase from p to q where it has completely solidified.

So complete liquid complete solid and in between this dotted line showing liquid plus solid that is how the phase diagram is mostly plotted and how will you plotted otherwise for a single phase for example you know that 100% copper phase, you have a single you know temperature beyond which the conversion would take place so here you can see on this particular diagram of the copper is 100%.

The temperature at the convergence is taking place exactly 1083°C which is the melting point of copper, so if you look at this particular time versus temperature plan you can see that this corresponds to the phase transition where it is changing from liquid to the solid state, but beyond this particular time everything is now converted into solid, but the temperature scale level changes this sheet is fixed as 1083°C which is the melting point of copper so but in this case obviously.

There is going to be some transition some change and there is also going to be a zone so in this particular case when there is some kind of a percentage of copper as suppose Nickel as you see there are two different points now one is θ_p value which is actually corresponding to when the solidifications starts to happen and then there is a solid plus liquid which comes up here in this particular zone and this really is the θ_q value where the complete solidification has happen so there is going to be a latent heat.

Phase in the solid and then it is going to go down, so basically what you are trying to do when the phase changes into two phases from a single phases that you are trying to take this region and splitted up into this you know fall in temperature versus time where there is partial liquid partial solid and the latent heat part which is separate and this latent heat part keeps on changing as the percentage nickel changes, so think of it that when we talk about 100% nickel obviously there is going to be 1452°C temperature.

Where it is going to be just as copper that there is going to be a solidus point so liquidus point beyond which this solid plus liquid would be there while it exist of the same, so the only difference that the phases making as that the temperature is changing because one of the phases is still in the liquid state and it will behave as if the you know as a normal liquid behaves on the time temperature transformation curve, so that is how we will explain that how a percentage copper or percentage nickel would make differences to the overall time temperature transformation and this can be further use this information to plot this so derive this.

So this PQ here the temperature difference is really the temperature difference which starts between this θ_P and θ_Q , okay so you can plot that is a function of the concentration and that brings you the array of such points which would be the liquidus in the array of such point which would be the solidus which would lead to the emergence of you know this curve from this curve write about here, okay so that is how equilibrium phase diagrams are plotted let us look at the interpretation.

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Equilibrium Phase Diagram

•The situation becomes more complex when two metals, having no restriction on solubility in the liquid state, are only partially soluble in the solid state.

•A solution of common salt and water falls in this category. (Figure on the left)

•From this diagram it is obvious that at a particular composition (i.e. 23.5% NaCl), the mixture, like a pure material, has a specific freezing point (-22 deg. C).

•This signifies simultaneous solidification of NaCl and H₂O.

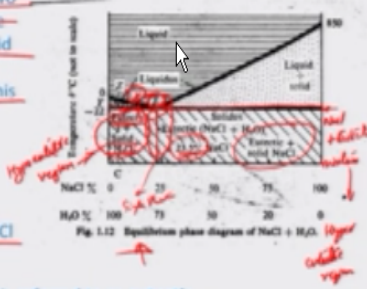
•This kind of mechanical mixture of two solids is referred to as eutectic.

•This eutectic composition is seen to have the minimum melting (freezing) temperature, and hence the name eutectic. (Greek word meaning easy melting)

•The solid portion is seen to be pure ice (H₂O) whereas the liquid has a composition given by the point X.

•On further cooling X shifts towards the eutectic point E.

•At -22 deg. C., the entire solid is ice and the liquid mixture has eutectic composition. As no mixture can remain liquid below this temperature the entire mixture on cooling solidifies simultaneously. Thus the solidus becomes the horizontal line through E.



To figure on the right describes you know the state of the mixture so, so physical state of the various phases here so you can see there is a liquid state there is a solid state and this you know representing by the liquid solid state and you know we may determine the relative proportion of liquid and solid in this by looking really at the ratio xz by zy let us look back this is the xz line corresponding to a particular temperature θ .

So we can think of it as if they so the nickel as already solidified, at the temperature θ because the melting point for the nickel is 1452°C so the amount of nickel as suppose to the amount of you know the total amount of liquid plus solid mass which is present can really be represented as xz by xy , so this ratio between this much length as suppose to the total, length here would give you the percentage of solid fraction which is there.

Okay so xz/zy obviously is solid to liquid portion so the composition of the solid portion of the temperature θ is given by the abscissa of the point y similarly the composition of the liquid portion at this temperature is given by the abscissa of the point x so it may be noted from the above figure that when there is no restriction on the solid solubility the solid state of an alloy, would look like a pure metal as probably here and such an alloy is always known as a single phase alloy where nothing but the grain boundaries are the only the distinguishable features and if there is some restriction on the solid solubility it may necessarily not look as a pure one phase system okay.

The situation becomes more complex when two metals having no restriction on solubility in the liquid state are only partially soluble in this solid phase. So obviously in this solid phase you have to throughout some material you know in order to make the solidification possible. a solution of this very commonly very use solution is common salt and water which falls in this category the figure on the right here you know describes such a physical equilibrium diagram.

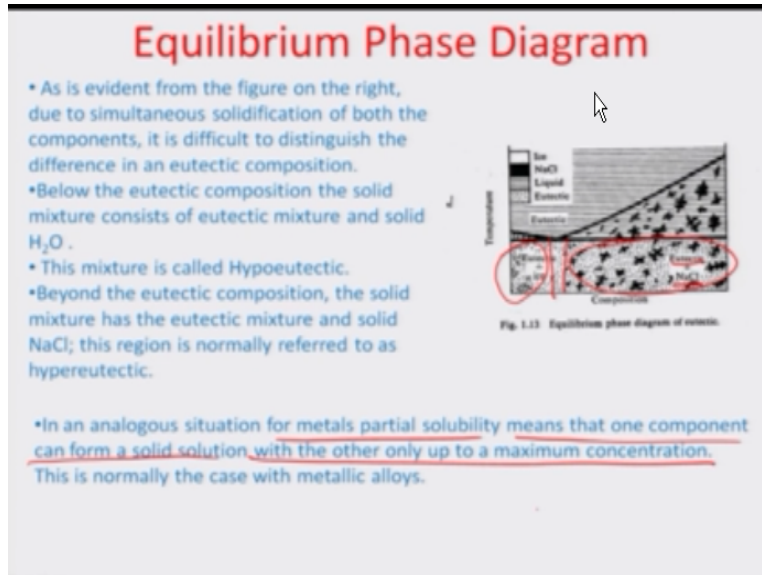
So from this diagram it is obvious that at a particular composition corresponding to let us say 23.5 % NaCl the mixture would like to be like a pure material as a specific freezing point of -22°C okay at which all these states can co-exist that means there is a transition directly from the liquid in to the solid state without any intermediate state as such and whatever is formulated here is a single phase or a single structure you know of the material and this corresponds to only a certain percentage that is about 23.5% of salt beyond which whatever would happen would be an excess salt which will come out you know of the crystal as such.

So this signifies the simultaneous solidification of NaCl at -22°C write about here anything below this line the solid okay. So -22°C is a straight line joining the whole thing where you can assume that anything below this temperature is always solid phase. Now at the point QU in the liquid directly changes to the solid and we cannot distinguish between the different phases of this solid because there are obviously going to be salt and water both but it undistinguishable so this is kind of refer to as the eutectic point which means minimum melting freezing temperature you know beyond the eutectic the solid would I mean the whole mixture would tend to solid almost all it.

So the solid portion let us say add the point x which is towards the left of the eutectic point is again you know going to be solid beyond -22°C right so therefore if this particular liquid here at the point x wants to be completely solid if I did has to come towards the eutectic point or eutectic temperature, so at -22°C the entire solid is ice and the liquid mixture has eutectic composition for example here you can see that you have over you know over concentrated ice in comparison to NaCl or some of the salts or some of the NaCl salt may be in some crystals and some crystals may be completely devoid of the salt and so you have a mixture of the eutectic point here 23.5% which is generally lower but then there are certain other solid water or ice just ice which as no salt as well.

Beyond to the so this region is known as the hypo eutectic region where you have excess ice the eutectic mixture obviously on this other side where the NaCl is more you should have excess NaCl + the eutectic mixture and this is known as the hyper eutectic point.

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So than so you can understand it that you have an excess of salt+ eutectic mixture, the eutectic mixture which is indistinguishable one phase and then other side ice+ eutectic mixture in such partially solvable in solid phase kind of system solutions so in other locus situation for metals again partially solvability means that one component can form a solid solution with the other only up to a maximum concentration beyond which it cannot hold.

So if that kind of a situation happens again like the ice started throwing out the salt beyond the eutectic point similar way in metal solutions then it solids state would also start throwing away the excess component which cannot go into the solid solution and in same manner we have to see or look at what is the equilibrium phase diagram of such a system okay.

So in case of metallic alloys almost always this is the case that two metals are not completely soluble in the solid state but they any be soluble to a higher degree in the liquid state and it ends up into having this ice water kind of a situation as we have just described so in that case a typical equilibrium diagram is shown right here on the right side.

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Equilibrium Phase Diagram

- A typical equilibrium diagram is shown in the figure on the right.
- First of all, let us assume that the maximum solid solubility of A in B is temperature independent and has a % composition X_A .
- The single phase solution have composition at A of 0- X_A is called the α -phase.
- Similarly, the solid solution of B in A having the composition of B from 0 to Y_B is called the β phase.
- The actual maximum solid solubility's vary with temperature, as indicated by the dashed lines.
- Below the eutectic temperature θ_e , the entire material is a mixture of two solid solutions, viz., α and β .
- However, at eutectic composition, it is difficult to distinguish between the α and the β phase and this composition is indicated as $\alpha\beta$ instead of $\alpha + \beta$.

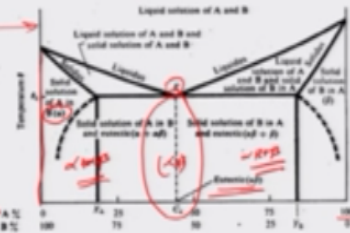


Fig. 1.14 Equilibrium phase diagram of alloy with partial solubility.

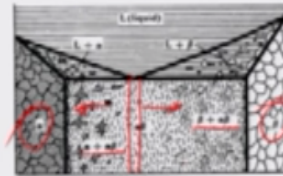


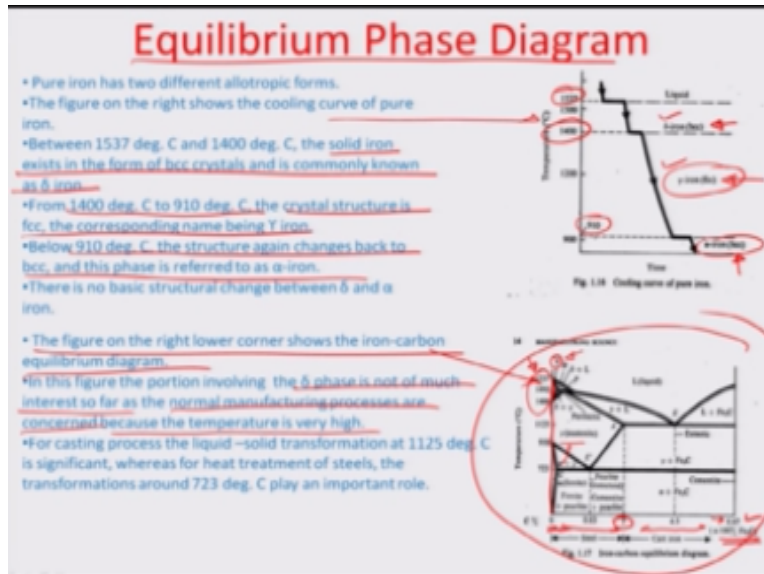
Fig. 1.15 Physical state of various phases in alloy with partial solubility.

You have two components A and B let say whether this is a certain percentage solvability which is allowable within the solid phase so you can see there is a eutectic composition here which is completely you know undistinguishable in divisible phase eutectic at the eutectic point E it is $\alpha\beta$ on the left side you have case where you know you can have complete α which is 100% β you know.

That is crystal state of complete α at this particular concentration and on the right side you have this particular concentration where you complete β which is the you know corresponding to 100% A component so some β phase so you have a indistinguishable phase eutectic at the eutectic point which you call $\alpha\beta$.

And on the left of this $\alpha\beta$ line you have the excess of the α phase and on the right of the $\alpha\beta$ line you have excess of the β phase so that is in the similar manner to the ice system we are trying to generate information from this in the manner. so you can think of it that this is the indistinguishable phase eutectic phase this is the hypo eutectic phase and this is the hyper eutectic phase comprising of $\beta + \alpha\beta$ and $\alpha + \alpha\beta$ respectively so these are the phases were you have complete you know solid solutions of a β structure

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So let us now look into the iron carbon case because that is going to be also very challenging to plot because of the fact iron as allotropic, so it has a FCC and BCC structure both at different temperature ranges. So the figure on the right shows the cooling curve of the pure iron okay. So between 1537⁰c and 1400⁰C, the solid iron exists normally in the form of BCC crystal and it is commonly known as delta iron. Then you know it is between 1400 to 910⁰C it again changes to γ iron, it is known as the FCC face centered cubic structure.

And then beyond the 900 then limit there is α iron which is again the BCC structure which comes at okay. so the solid iron exist in the form BCC crystals commonly known as delta iron from 1400 to 900⁰c, the crystal structure is FCC corresponding to γ iron and below 910⁰c the structure again changes back to BCC and this phase is refer to α iron. So you are adding an additional complexity to this whole paradigm by giving 2 different structures at different temperature ranges.

So the figure on the right lower corner choose the iron carbon equilibrium diagram, so that is how complexity driven it is. So in this fore shone you can see that there is a γ phase, there is a delta phase which is here corresponding to this temperature range and then there is the γ phase for pure iron. Then obviously there is going to be α phase which is the phase or again back to the BCC structure you know in this particular region. So you have 3 different constitutions structurally of the iron and obviously you have the dissolvability of carbon varying between 0 to 6.67% rights here where, in one case it is complete.

In the other case you know this corresponds to 6.67% beyond which the iron cannot like dissolve the carbon. So below this there are different phases in 1 half you know, the strength of the iron increases very highly, upto 2% and beyond 2 and below 6.67 this is actually the cast iron phase. So in this figure the portion involved delta phase is not of much interest, so far the normal manufacturing process are concerned. So normally the manufacturing temperature more or less carried out in a, you know room temperature condition.

And also you know the 1500 to 1400°C this quiet a high temperature range and normally all the material which is used do not get used up in this particular high range of temperature. So therefore considering the delta phase in such a system from an engineering point of view, may not be such significant but obviously the interplay between the γ and α structure would be more or less very critical, the way the material system behave.

You know when we talk about their equilibrium with respect to temperature. So with this I would like to end this module but in the next module we will try to look at some of the interrogates of this iron carbon equilibrium diagrams, in terms of structure extra and there many points which formulate, namely the eutectic toad and the paretic points, so I would tell about those, transition points and what is the physically signify.

It is only the way of representation, you know the % composition is the function of temperature and how they coexist, in one phase and how they coexist, in other phase or maybe there is a solid, liquid combination. So that is a one snapshot explanation that comes out of this one page equilibrium diagram of any constitute. So with this I would like to end this module thank you so much.

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