Surface Engineering for Corrosion and Wear Resistance Application
Prof. Indranil Manna
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Lecture – 20
Diffusive transformation in Steel

So, welcome to the 20th lecture of Surface Engineering. We are still discussing some of the fundamental aspects we did discuss quite a bit of it already about structures, about micro structural evolution, defects and then various forms of engineering properties related to the surface we classified them into mechanical, chemical and physical properties. We also discussed various approaches of surface engineering we classified them into possible 3 possible categories.

And then at the moment we would like to take up discussion on one of the most important engineering solid that is used for various kinds of structural applications meaning where mechanical behaviour and performance under various kinds of loads and rate of loading matter.

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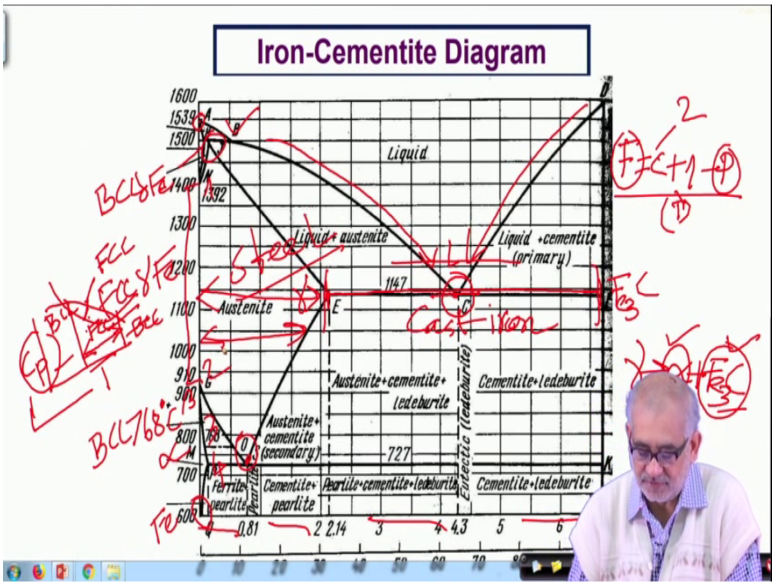

Iron-Cementite Diagram

I am talking about steel and in fact, if you look at the very first view graph, you this is a very well known phase diagram which is essentially an equilibrium diagram, but for a difference to be more precise this is a metastable equilibrium diagram. Because we are dealing with iron cementite where, cementite is not truly an equilibrium product, but for all practical purposes because cementite does not transform at room temperature we consider this to be as good as a phase diagram or an equilibrium phase diagram. Now why is still so important I did allude to that in the last lecture and let me repeat that.

This is the tonnage voice this is the second most important engineering material for all kinds of structural applications starting from construction to various bodies and various tooling and manufacturing applications. The first question is that why is still so, versatile? The main reason lies in the fact that when you talk of steel you actually first have to realize that we are talking about a binary where one part is iron and the other part is cementite.

So, actually the diagram should have ended at a 100 percent, but this is only up to 6.67 percent meaning this is actually a 100 percent of cementite. Now on the other side of course, we have pure iron and we can easily see that after solidification at this melting temperature iron pure iron undergoes three very major allotropic transformations.

So, from delta iron to gamma iron, so, this is the part when steel or iron pure iron exists only in the form of FCC variety which is called gamma iron and then subsequently transforms to beta and then to alpha and the transformation across the curie temperature which is typically about 768 degrees centigrade is only associated with a the paramagnetic to ferromagnetic transformation without any change in crystal structure.

So, BCC FCC then again BCC and this is very unusual because usually for all metallic systems at room temperature you would expect the close packed structure to be stable in that by going by that logic one should have expected FCC to continue until room temperature. But because of a very specific pattern of variation of specific heat as a function of temperature for the two crystallographic varieties or crystal systems variation of two crystal systems which essentially could look like this.

So, it is because of this variation of the two varieties of the crystal lattices of iron pure iron as a function of temperature we see that if this is the BCC phase. If this is the BCC phase and if this is the FCC phase, then sorry if this is the FCC phase then we realize that in this temperature; in this temperature range we see FCC to be stable and in this range and in this range the BCC phase to be stable because C P is lower and accordingly the stability of the phase depends upon the contribution of C P to enthalpy and entropy.

In other words this is the temperature range. So, we see a ; we see a variation of the crystal structure of pure iron going from BCC to FCC and then FCC to BCC. So, this kind of crystallographic transformations of pure iron allows a large number of phase transformations to occur in steel and because of this possibility, we see a very large variation of very large variation of crystallographic forms and hence large variation of properties. We also see that steel will have certain transformations which are called invariant transformations and this invariance transformations are dictated by the Gibbs phase rule.

Which says the degree of freedom is given by a relationship which says the F the degree of freedom is equal to the number of components present plus 1 which represents here only the temperature, but actually it can be 2 if its a non content system where both influences of temperature and pressure are important, but for all condense systems only temperature matters variation of temperature matters. So, C plus 1 minus the number of phases present.

So, since this is the binary. So, since we are talking about binary so; obviously, wherever we have three phases coexisting for example, at this eutectic point or at this peritectic point or at this eutectoid point we have a situation which is called invariant and as a result we see a transformation where for example, here liquid then gamma and F e 3 C should be simultaneously present.

So, these invariant transformations this is not of much use because this is at a high temperature involving a liquid, this certainly has a wide range of applications because it allows the fusion temperature to be drastically decreased from over 1500 or larger to very low temperatures.

So, it makes casting very easy. So, this varieties of iron carbon or iron cementite system is called cast iron and the named cast iron essentially is derived is mainly to signify that casting is very much conducive at this low melting alloys. But the difference between cast iron and steel is not necessarily only in terms of composition, but essentially in terms of this particular horizontal called eutectic isotherm.

So, any composition which intersects this eutectic isotherm is called cast iron and the remaining are essentially called steel, but in plain carbon steel or plain carbon system without much of alloying elements typically this boundaries at about 2 percent of carbon.

Now, coming to the main issue as to why steel is so important as we said that the specific heat is going to be the factor which determines whether we have what form of crystallographic what crystallography form of iron is present and this kind of transformation is called the allotropic transformation which are reversible transformations of pure elements from one particular crystal form to another. So, because of the presence of these kind of allotropic changes 1, 2, 3 and 4, until room temperature for pure iron.

We see a wide variation of property is possible in this steel will elaborate more as we go along. So, what is important is that at room temperature the phase aggregate that we see can be widely varied as we cool from liquid state to lower temperature. So, when the phase aggregates change the microstructure changes and when the microstructure changes the properties change. The for the steel part the most important transformation is this eutectoid change and this eutectoid change essentially means when gamma transforms should keep simultaneously transforms to say ferrite and cementite.

Now this is a solid solution and this is an interstitial compound the combination of this very hard phase with relatively soft and matrix gives you a product solid at the end which can actually be varied in terms of its mechanical properties over a wide range and this is exactly the reason why steel is so versatile. So, here is an alloy which in solid state can give you mechanical strength anywhere from 500 to over 1000 mega Pascal here is an alloy which can give you ductility as low as a 5 percent to close to 100 percent depending on the typical micro structural state we are talking about.

In particular steel also is one of the very rare alloys which apart from showing large variations of mechanical strength can also provide us a very high amount of toughness. So, combination of strength and toughness is what makes steel so, versatile for various kinds of structural applications. So, we need to move on and understand as to what are the possible variations of a steel microstructure that makes it so, versatile.

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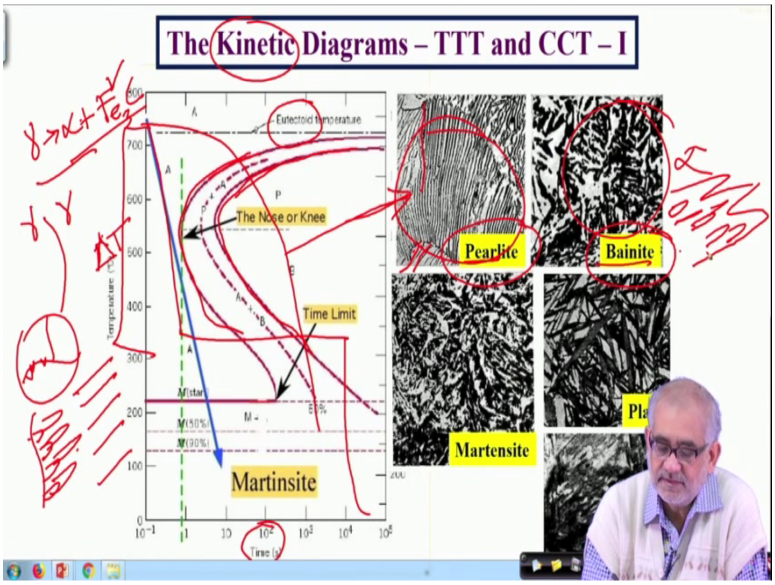

The Kinetic Diagrams – TTT and CCT – I

So, if you look at we first saw the phase diagram and as I mentioned its essentially an equilibrium diagram which only talks about the existence of phases and phase aggregates depending upon the temperature and composition variation or combination. But then when you are talking about a transformation you bring in the kinetic factor which means you now need to invoke the idea of how does the microstructure change with time. So, whenever you bring in the need to disk to bring in time component.

So, you have to now talk about the so, called kinetic diagrams and here is a kinetic diagram which is nothing, but a temperature time. So, variation of essentially variation when you are varying temperature and time independently how does the microstructure change and this is basically explained in terms of certain boundary of transformations. For example, this is one curve which actually shows the beginning of a particular type of transformation this is the other end which is the end of such a transformation. And the transformation that we are talking about is essentially the eutectoid transformation.

Which we just heard as a transformation which involves transformation of austenite which is an FCC solid solution of interstitial carbon in gamma iron in to be a BCC ferrite and cementite. So, this is eutectoid transformation, but this eutectoid transformation depending upon where it is actually intersecting the beginning and the end for example, if the intersection of the time temperature plot is somewhat like this then you end up getting a microstructure which is pearlitic where we have alternate sequence of cementite and this bright regions are ferrite.

So, we have cementite and two cementite and in between the bright regions are ferrite. So, this laminar alternated structure gives us one set of properties which actually is a very nice combination of strength and ductility and this is called pearlite because this morphology resembles the mother of pearl just as you see their shale this morphology is a contour wise very similar to that. So, that is where the name is derived from, but instead of cooling at this rate if you happen to cool for example, in a stepped manner like this then your likely to see another transformation product essentially the same eutectoid transformation same invariant transformation.

But the phase aggregate the mechanism and the sequence of evolution of the phases and their volume fraction distribution is different because the mechanism of transformation is different and that aggregate is called bainite. The interesting fact here is that we are talking about two aggregates pearlite and bainite which are nothing, but the phase aggregates the difference lies primarily in terms of the appearance of the microstructure, but also in the mechanism in case of pearlite usually cementite nucleates first.

So, essentially if you are talking about two grains. So, if this is the prior austronatic microstructure all grains are gamma are austenite. So, on this boundary you would first happen to see certain nucleation of cementite and this kind of a boundary will tend to move when you form such cementite lamely and then they actually grow edgewise simultaneously the portion in between transforms to ferrite. So, nucleation of nucleation of cementite triggering formation of ferrite because of carbon depletion; so, this is how we end up getting such lamellar aggregate where the volume fraction of this aggregate is purely dictated by the phase diagram.

On the other hand when we talk of bainite which essentially forms at a much lower temperature and because of lower temperature now we are talking about a much larger under cooling and hence much greater driving force. So, under this larger driving force when the transformation begins and ends at lower temperature we end up getting a microstructure where for a difference the ferritic sheaves nucleate first.

So, essentially you will see such sheaves like structure of just like leaf. So, these are like palm leaf type of a structure and this in when such a ferritic sheaf nucleates the excess carbon is rejected and those excess carbons nucleate as small stringers or platelets in the form of platelets.

Either between two such consecutive sheaves or embedded within their sheaves. So, accordingly we get sort of upper and lower bainite. So, what is important for us to know is that if the microstructure changes from such pure lamellar alternate sequence of ferrite cementite to a situation where we have broadly for sheaves kind of a structure of ferrite within which cementite is embedded we end up getting a fairly different kind of properties. In fact, we will come to that in a minute. So, from equilibrium diagram what we earlier saw.

So, from this equilibrium diagram where in we saw. So, while talking about this steel part of the diagram what we have seen is that this is the portion which is very very important for us because from a single phase we are going into a two phase aggregate and the way the two phases manifest themselves or present themselves in the microstructure makes it possible to call it perlite or bainite and because of these two aggregates different types of aggregates which arise or emerge because of two different; two different mechanisms of transformations we actually see two different types of microstructures. We will talk about bainite later.

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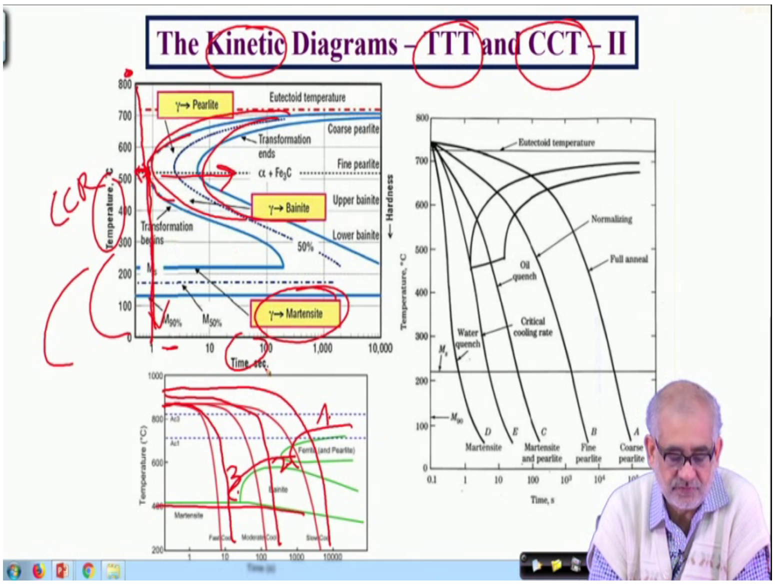
The Kinetic Diagrams – TTT and CCT – II

Now the next question is to be now to make things even more clearer we actually need to follow this micro structural evolution a little bit more, but before we do that I must tell you that this kind of a kinetic diagram that we are seen here. So, this kinetic diagram of essentially time temperature plot its typical of a plain carbon steel and the difference here what is important noting at this point is that this region is the so, called me region. This is where just like our the knee of our leg is a joint between the upper and the lower part of limb and if this is the portion where it bends.

And this is where it comes closest to the temperature axis or in other words this is the limit defined time limit defined which is say which is important if we want to avoid intersecting any of these curves. So, if I need to intersect the start line or the curve which is designating the starting of the pearlitic or bainitic transformations then, I need to employ a cooling rate which is very very fast.

So, our ability to avoid intersecting any of these lines will be determined by the gap between the temperature axis and the tip of this knee and this is called critical cooling rate. For a for various transformations particularly for martensitic transformations we would like to have a situation where this knee portion is actually shifted to the right and if we can shift it way to the right then I can afford to cool fairly slow instead of so, fast and yet be able to avoid this start of these pearlitic or bainitic transformations.

And then intersect the martensitic line which is way below easily and if I cool slow the advantage is that I incur less or least amount of thermal shock because I am cooling all the way from above 800 to room temperature. So, this 800 degree of radiant is large if we need to cool within a few seconds or less than a second.

So, the cooling rate we are talking about is actually a 500 centigrades per second. So, in order to make life easier to be able to not only avoid the intersection with this pearlitic pearlitic or bainitic parts also if we want similar slow cooling somewhat like this where I can take life easy and cool slowly like this and get pearlite. If I cool slightly faster then I actually can get into bainite and make full bainitic microstructure.

And if otherwise if I cool even not as slow as this, but fairly slow and still if I am able to make if I am able to avoid both initiation of pearlitic or bainitic transformation and still end up getting complete martensite that is also possible. So, simply by varying the cooling rates from 1 to 2 to 3, I am able to vary the microstructure over a wide range and this is exactly the reason why steel is the most versatile structural material for all kinds of structural applications.

So, to be able to understand as to why this is happening we must be able to appreciate both the varieties or the information available in the phase diagram and also the application of such kinetic diagrams, but there is one important part which I have talked about and that is how do we change the shape and the contour of such a kinetic diagram from this fairly start and finish. So, exactly from this kind of a manifestation to somewhat a different kind of a shape which is very convenient to me.

So, I have split this curve and this curve into 1 2 and a line. So, instead of having a diagram like this which essentially by the by is called the TTT diagram Time Temperature Transformation diagram, but here the cooling is isothermal, but instead of time temperature transformation if we want to refer to continuous cooling then we have slight variation of these diagrams through some kinetic analysis we can actually transform this TTT into continuous cooling transformation diagram.

And then we can apply this kind of continuous cooling curves and then predict what kind of a microstructure we are going to get. So, the point I am trying to make is that if I want this change in shape of this kind of a TTT or CCT into such split portions.

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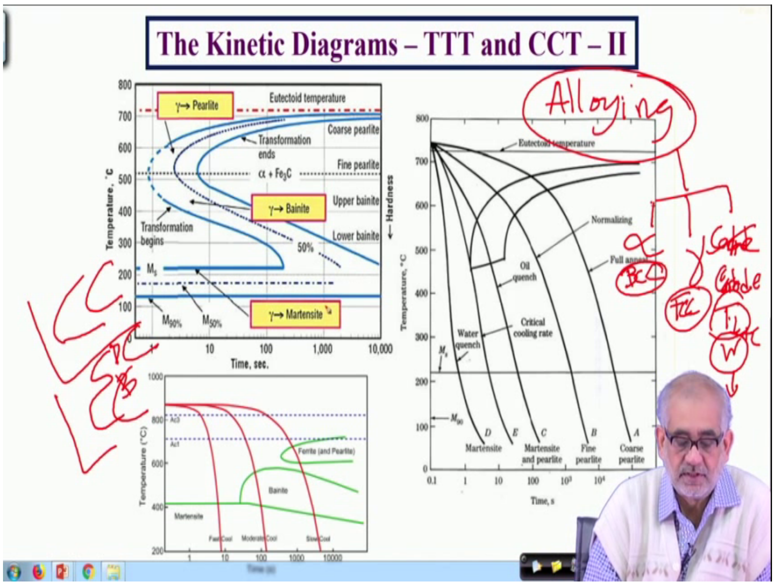

The Kinetic Diagrams – TTT and CCT – II

So, instead of having such a kind of a curve situation if we want to split and split such a way either like this. So, this portion is pearlite and this portion is bainite. So, in order to split the two curves like this or completely have two different curves for pearlite and bainite we need to bring in another influence and that influence is coming from the so, called alloying elements.

So, if I alloy the steel with variants various kinds of alloying elements and in fact, that alloying elements can be of 3 types; one set of elements which stabilize ferrite we call them ferrite stabilizers another form which stabilizes gamma or austenite we call them austenite stabilizers and another form which actually stabilizes or has a large tendency for formation of carbides.

This is proving little difficult for me to write on this board anyway. So, the point I am trying to make is that all elements usually which are BCC in terms of their Bravais lattices they are usually the ferrite stabilizers alloying elements which carry FCC crystal structure or Bravais lattice are usually the austenite stabilizers. And there are elements both coming from BCC and FCC varieties, but usually the BCC ones which have a large tendency for the formation of various kinds of carbides like for example, titanium or tungsten and so on.

Though they this is HCP and this is BCC, but they have a very high affinity for carbon and when they combine with carbon they form these carbides. So, playing with the composition by adding ferrite stabilizer or austenite stabilizers we can shift the contour of not only the kinetic diagram, but actually the phase diagram and from the phase diagram we can also derive the various differences that are possible for such kinetic diagrams.

So, splitting of these curves and giving thems giving space in between. So, that I can cool slowly and then much easily derive the micro structures which are pearlitic or bainitic or martensitic in nature that is quite possible by using such a influence of alloying elements, but even for the same steel if I am not willing to change the composition if I am not actually going to have variations of or addition of various alloying elements.

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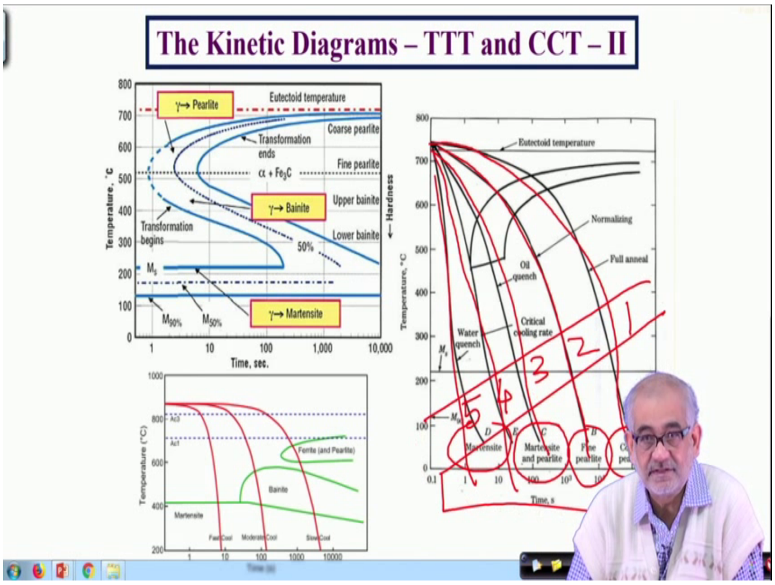

The Kinetic Diagrams – TTT and CCT – II

For the same steel which I alluded right in the beginning I can cool relatively slow slightly faster still faster and much faster and the fastest. So, by way of employing the different kinds of cooling rates I actually can get coarse pearlitic microstructure, fine pearlitic microstructure combination of martensite and pearlite and then finally, full martensitic microstructure.

So, such wide variation of microstructure is possible on the same steel in the in the similar setup, but simply by employing different kinds of cooling rates and this kind of variation of cooling rates essentially our kinetic intervention onto the same alloy giving rise to such differences in micro micro aggregates or phase aggregate and as a result a composition can vary significantly vary.

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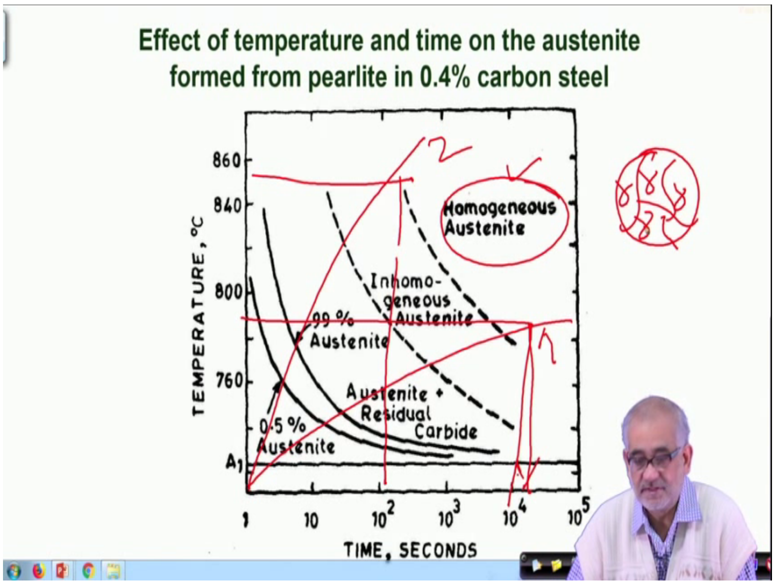
Effect of temperature and time on the austenite formed from pearlite in 0.4% carbon steel

So, one thing which I did not quite mention is the fact that when we talk of all these transformations these are all transformations happening on cooling, but if you look at this phase diagram we must begin from a similar level playing ground and that is austenite. So, in order to create this go into this austenite phase first for any transformation before we actually think of any such transformation.

We must read this or understand this kinetic diagram again very carefully and this is a kinetic diagram with a difference because here what we are saying is that if you start from this point which is essentially the room temperature point and this is the starting point. So, in terms of temperature and time we has this is the starting point. So, if you cool if you sorry heat in these two possible modes then you realize that in order to reach homogeneous austenite state you require much larger time. On the other hand if you are actually willing to heat to higher temperature. So, if the temperature is low then we need to heat for a longer period of time or hold for a longer period of time.

If we are willing to heat to higher temperature then at a much so, if you are willing to heat to higher temperature we are expect we may expect to reach homogenous austenite state at a much lower timeframe. So, it is important for us before we begin any such transformation to make sure that the austenite is single phase. So, the micro structure will be such single phase microstructure all austenite and all exactly of the same composition.

So, homogeneous both in terms of micro structure and composition then only the on cooling whatever microstructure you develop will be reproducible precise and give you the same kind of same set of properties that you want.

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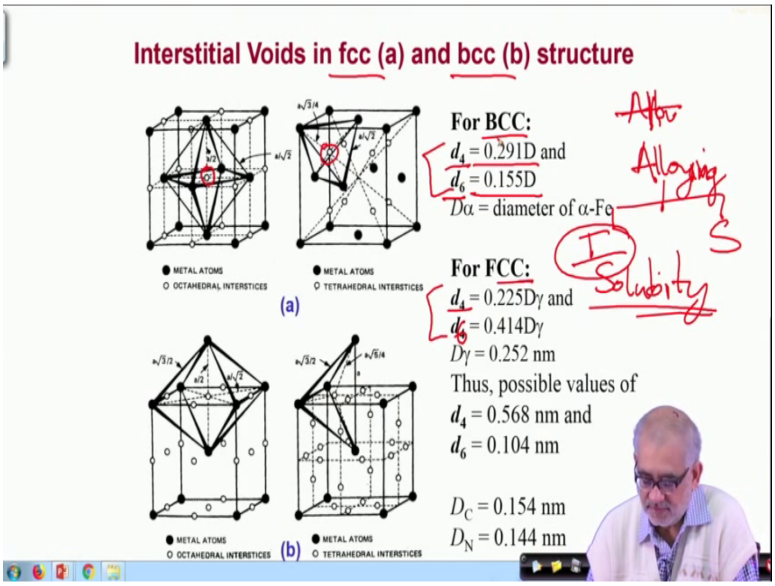

Interstitial Voids in fcc (a) and bcc (b) structure

For BCC:

$d_4 = 0.291D$ and

$d_6 = 0.155D$

$D\alpha$ = diameter of α-Fe

For FCC:

$d_4 = 0.225D\gamma$ and

$d_4 = 0.414D\gamma$

$D\gamma = 0.252$ nm

Thus, possible values of

$d_4 = 0.568$ nm and

$d_6 = 0.104$ nm

$D_C = 0.154$ nm

$D_N = 0.144$ nm

So, this is something which we have discussed earlier, but I thought I would just touch upon it once more to tell you that when we talk of various forms or particularly two major forms of iron pure iron namely the BCC at room temperature and FCC at high temperature. So, in these two varieties the unit cell which is the smallest building block for any Bravais lattice or crystal structure for that pattern allows us to calculate the typical size of the void.

So, in case of FCC this is how we can calculate the size of the void and this if this is the diameter of the iron atom in the BCC form this is how one can calculate the tetrahedral or the octahedral void size for BCC iron. Similarly, for FCC we can calculate the tetrahedral and the octahedral I am sorry this should be the octahedral void size for carbon or any other industrial atom to come and squeeze in.

This is important for us to know because this size relative sizes of these interstitial voids essentially determines what will be the solubility of such interstitial atoms. When we when I was referring to alloying elements I should have mentioned that principally the alloying elements will actually they will be of 2 types; one is the so, called interstitial and the other one is substitutional.

The interstitial ones are the ones which can squeeze into these holes, but these sizes of these holes are actually always smaller than the even the smallest possible atom one can think of. So, whenever we push in such interstitial atom there will be a lot of strained field around that and because of which solubility is limited. So, the solubility part is primarily in particularly in case of with regard to steel is determined by the so, called interstitial void sizes and its because of this reason you can packing always more amount of carbon in FCC variety than in BCC.

But on the other hand the voids in the BCC are interconnected and it is because of this reason that the carbon diffuses faster in the BCC variety than in FCC variety. So, solubility is higher in FCC, but diffusivity is higher in BCC and both these properties are very important in terms of determining whether for various kinds of phase transformations and phase aggregates that we want to bring in.

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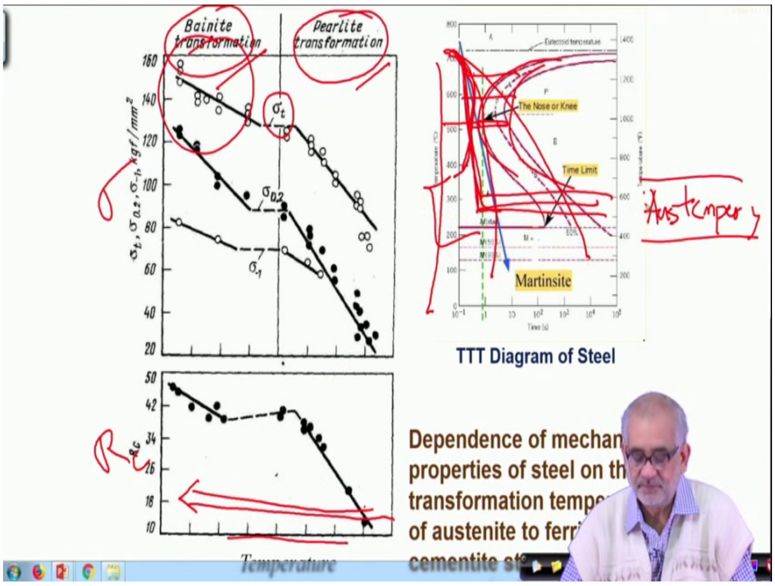

TTT Diagram of Steel

Dependence of mechan
properties of steel on th
transformation tempe
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So, this is what I was trying to say that if you bring in different kinds of phase aggregates for example, when you have pearlitic aggregate or bainitic aggregate. This is the strength properties and this is the hardness properties in terms of the rock well scale. So, the temperature scale here is somewhat similar to the temperature scale that you see in the TTT diagram and what it shows is that if you start from this end; that means, if you actually allow the transformation to take place at relatively higher temperature.

So, somewhere let us say in this region or in this region. So, this is how the temperature is decreasing and as the temperature decreases what we see is that the strength properties both in terms of hardness or yield strength or any other strength representations will always show you higher and higher value.

So, given a choice if you are looking for very high hardness or very high strength for that matter then; obviously, you would prefer to have a bainitic microstructure than pearlitic microstructure, but the problem is that in case of plain carbon steel because of the nature or the curvature of this TTT or the CCT diagram and the cooling rate; obviously, is is going to have slightly just the opposite kind of a curvature.

So, two curves of opposite curvatures can intersect only once and not twice I mean it can be tangential at the most, but you cannot using another kind of a cooling curve with a different curvatures there is no way this curve can actually intersect the other curve with a different opposite curvature at a portion below the knee below the tip of the curvature.

So, you need a stepped quenching in other words if you want bainite then you cannot employ a continuous cooling like you can do for pearlite you have to do a step cooling and this step cooling kind of a transformation is called or austempering and so, its called austempering and this austempering is a heat treatment which requires such stepped cooling.

So, in order to get higher strength properties like here we actually need to allow the transformation to take place at lower temperatures and such transformation is possible not by continuous cooling, but by step cooling.

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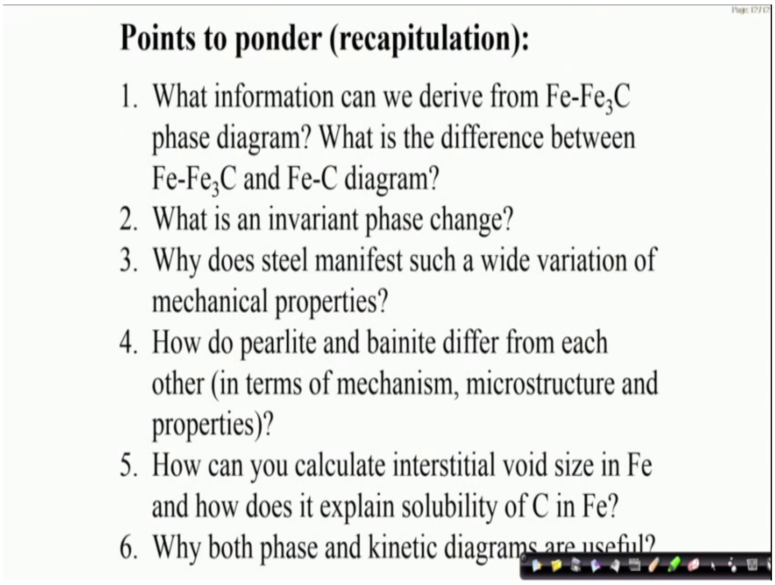

Points to ponder (recapitulation):

1. What information can we derive from Fe-Fe$_3$C phase diagram? What is the difference between Fe-Fe$_3$C and Fe-C diagram?
2. What is an invariant phase change?
3. Why does steel manifest such a wide variation of mechanical properties?
4. How do pearlite and bainite differ from each other (in terms of mechanism, microstructure and properties)?
5. How can you calculate interstitial void size in Fe and how does it explain solubility of C in Fe?
6. Why both phase and kinetic diagrams are useful?

So, so, with this now we actually would like to summarize and as a way of recapitulation what we have understood in this discourse is what is iron cementite diagram and I did not quite mention, but its for you to make out the difference between the so, called precise equilibrium diagram which is called iron carbon or in some cases called iron and graphite diagram because graphite is the stabilized form of carbon in steel. So, the differences will be in terms of the composition of the invariant transformations and the isothermal temperatures where actually this transformations are happening.

So, we talked about various invariant transformations. In fact, all the allotropic changes there are two melting of the two components and then the three invariant transformations peritectic eutectic and eutectoid all these are invariant transformations and they are very important because they determine the microstructure evolution of the alloys not of the pure iron or pure cementite.

We understood that the ability to vary the properties namely the mechanical properties of steel which is what makes it. So, versatile is possible purely because of the ability to vary the microstructure over a very wide range and this is not quite possible in almost all types of other metallic or nonmetallic systems or alloys. We understood the difference between the evolution of pearlite and bainite primarily in terms of the temperature range where it happens that the morphologies of the phases and most importantly the mechanism as to what nucleates and what promotes the formation of the counterpart.

So, in case of pearlite cementite leading to formation of ferrite in case of bainite its actually because of large under cooling its first ferrite and followed by nucleation of cementite. Of course, there is some amount of controversy existing about exact mechanism whether its a diffusional or there is a non diffusional component, but that is a different subject altogether.

We also saw how the interstitial void sizes are different in FCC and BCC form of iron and which is why the solubilities are different in these two forms of iron and alloys. The most important thing is that we need to understand the difference between the phase diagrams or the equilibrium diagrams and kinetic diagrams. For example, when we talk of solubility you certainly refer to thermodynamic diagram when you talk of evolution of phase aggregate or the rate at which they appear you have to refer to a kinetic diagram.

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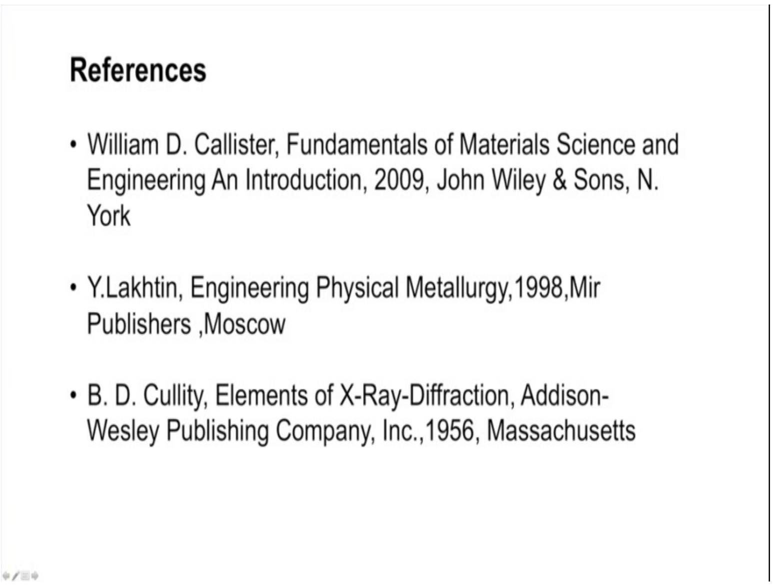

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So, the last thing that I need to mention is that we talked entirely about a bulk of the steel all these discussion are related to the bulk of the steel. And when we go to the next lecture we will realize as to why it is important for us to appreciate, what happens in the bulk of the steel even though this particular entire discussion is related to a course called surface engineering ok.

Thank you very much.