Phase Diagrams in Material Science Engineering

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Lecture – 33
Tempering of Martensite

In the last class, I discussed about the Martensitic transformation. For last two lectures, I have discussed about Martensitic transformations, and I told you about different features of Martensitic transformations. And, I am going to tell you the several points before I discuss. Let me see, whether I have it; just a minute, I may have it. So, most important point is that, Martensite is basically a brittle, and also, it requires certain kind of heat treatment to transform it to a more ductile structure. And, this is what is known as tempering in the literature.

Tempering of Martensite is very important, because, Martensite is so brittle that, even if you, you just have a steel sample quenched in water, it will form a crack. You cannot use it as a kind of material in the (Refer Time: 01:00) real applications. So, this tempering of Martensite is very, is a nothing, but a heat treatment. It is normally done, heat treating these Martensites, which is formed from 100 degrees to about 700 degree Celsius temperature, depending on the requirement in the industry. And, these are not done in one go; these are done in different stages. So, therefore, when I will discuss about the microstructure evolution, and changes in the microstructure, I am going to talk about different stages. Then, I will finally, write down on the board for your information, so that, you do not forget.

As you know, Martensite is what? This is a body centered tetragonal structure, with lot of strength, and lot of, you know, what to say, highly supersaturated solid solution also. Because, if I take a steel, austenite, of suppose, 0.8, or 1.2 percent carbon, what will happen? This austenitic carbon, austenite can take lot of carbon. But, you know, when you transform the austenite to Martensite, it cannot take so much of carbon. So, therefore, whatever extra carbon is remaining inside Martensite, is basically, is beyond a saturation. So, these are all known as super-saturated carbon. So, this super-saturated carbon, along with the defection of Martensites that actually has a role, a strong role in the tempering of Martensites. So, first thing, the first stage of tempering of Martensite is known as stage I. stage I is normally done at, 200 degree Celsius temperature.

That is, if you heat a steel of Martensite, about 100 degree Celsius temperature, 80, 90, or 100 degree Celsius temperature, and what will happen? A few things happen in this. The first which will happen is that, all the extra carbon, super-saturated carbon which is present in the Martensites, they will segregate on the dislocations; that is what you see in this picture.

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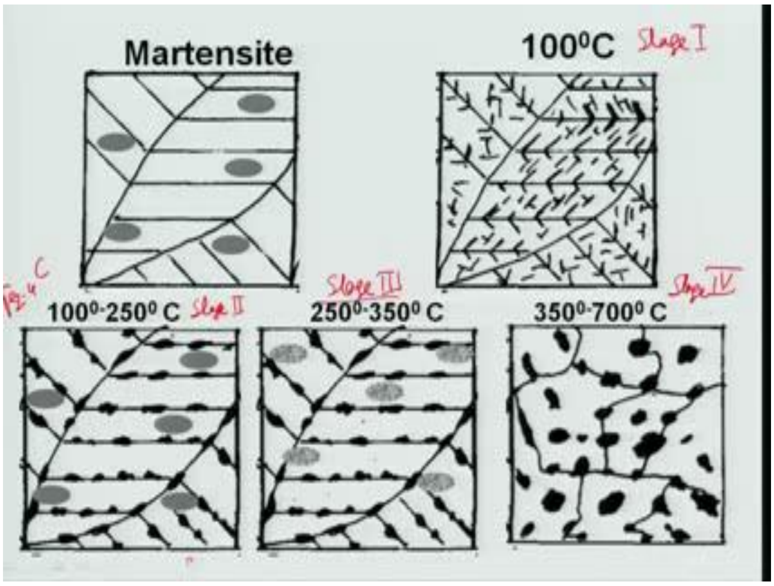

They are, these are the carbon on this, these are the sites, dislocations, and these are twins on which carbon atoms will segregate. Why they will segregate? Well, that is not difficult to understand. You know, a dislocation, if you know as l dislocation, l dislocation has a extra plane of atom, and at, that means what, you have a extra plane of atom is not present below to the dislocation plane, or below the slip end of that.

So, because of that, carbon atom can easily go and sit there, and by sitting there, it can reduce the strain around the structure. That is very routine; you can find in any mechanical metallurgy book, you can understand that. Similarly, if the carbon atom sits on the twin plane, and the distorted twin plane, it can reduce the distortion. So, that is why, at the beginning, (Refer Time: 03:48) simple, at the beginning, it is like a recovery process, in the, in the whole heat treatment, in the, in case of steels, where you deform, and then, heat it at high temperature, it undergoes recovery; same thing, similar things happens here. The Martensite (Refer Time: 04:04) strength by putting this carbon atoms, or segregate the carbon atoms in the dislocation and defects. You know, and, this is how it can actually, its super-saturation can be reduced, because, dislocations, or the defects, if the carbon atom goes out of the unit cell, and then, super-saturation itself can be reduced. This is very simple.

So, first thing, if you want to reduce the strain inside the matrix, inside the Martensites, you heat it up to 100 degree Celsius temperature, most of the strains, residual strains can be relieved. Now, second stage, this is known as stage I, as I have written here; stage I, 100 degree Celsius. Second stage, which normally happens, is from 100 to 250 degree Celsius temperature. This is the stage in which a new phase forms, and (Refer Time: 04:51) the phase is epsilon carbide. As you know, Cementite is also carbide; it is a composition of Fe 3 C; Iron 3 carbon; very strict stoichiometric compound. But, this carbide which forms if you heat this Martensite to 250, up to250 degree Celsius temperature is known as epsilon carbide. It has a composition of Fe 2.4, Fe 2.4.

Sorry, let me write it properly; Fe 2.4 C. This is un-stoichiometric carbide, right. Carbon concentration should have, sorry, the iron concentration should have been more. It should be Fe 3 C, but, instead of that, it is Fe 2.4 C. That is because, the availability of the carbon in the, in this Martensite is so high, then, it easily falls. Well, that is one reason; second reason is that, epsilon carbide is very easy to form; very easy to nucleate. You have lots of defects present, dislocations, and twins, and carbon atoms already segregated onto each of these at, for stage I.

So, next stage, this carbon atom reacts with the iron, and forms this epsilon carbide. And, you know, if carbon concentration is very low, suppose, less that about 0.15 percentage, there will be not much epsilon carbide formation, because, sufficient number of carbon atom is not available to form the epsilon carbide. Only when the carbon atom is beyond 0.2 percentage, epsilon carbide easily forms. Epsilon carbide, as compared to Fe 3 C, has hexagonal crystal structure; it is a h c p structure.

Not only that, it bears a very good orientation relationship with the, with the Martensite alpha prime phase. And here, the Martensites, a close (Refer Time: 06:40) of Martensite, that 0, 1, 1 plane, 1, 1, 0 plane of the Martensites, becomes parallel with the closely packed (Refer Time: 06:46) of the epsilon carbides. Similarly, there are close packed directions. So, that is what actually happens, in the stage II, basically, you are forming the epsilon carbide; by forming epsilon carbide, further super-saturation of carbon is reduced. Not only that, because you are forming a new phase, which is strain free, you reduce the strain of matrix very, very nicely. So, then comes this stage III. Stage III happens at higher temperatures, normally at 250 to 300 degree Celsius temperature; that is what shown in the slide. This is stage III, as you see here. Stage III is very important. Stage III is very, very critical for the most of the Martensitic, most of the Martensite tempering.

And, almost, you know, all the steels you see in the market, at least, they will undergo heat treatment till stage III. Why, because in stage III, retained austenite is transformed into alpha; or, it transforms into Pearlite , depending on what kind of, you know, carbon concentration is there in the, in the retained, austenite. Normally, retained austenites are present, these are the white regions are the retained austenites. So, retained austenite, as I told you, is very, very dangerous. Why, because retained austenite will always have the tensile stress inside it. So, the moment you put into the, component into the actual practice, the cracks will develop and steel will fracture.

So, therefore, you need to transform the retained austenite into something else, which has a lower propensity to crack formation. So, one way of transformation is transforming retained austenite is to form alpha, alpha phase. And, that is what is done by heating up to 350 degree Celsius temperature. So, you have already formed epsilon carbide in stage II. And, in the stage III, you, whatever remaining retained austenite, whatever austenite is retained, that is transformed into the alpha, or Pearlite, depending on the carbon concentration of austenite. Now, stage IV, which happens at high temperature, it can go from 350 to 700 degree Celsius temperature, is optional; is normally not done for all the steels, Martensitic samples. What actually happens in stage IV? Stage IV is categorized by formation of Cementite; it is carbide, basically.

And, you know, not only Cementite forms directly from Martensites. Basically, the moment Cementite form Martensites, whatever is remaining, is nothing, but alpha phase, B C C alpha phase. So, you lose all the strains; correct, it becomes like a Pearlite, but not exactly a Pearlite, but microstructure consisting of alpha and Cementite, both; two separate entities present. So, Martensite completely gets transformed into this Fe 3 C, and alpha; that is what happens there.

Not only that, if you keep this steel at this temperature for long time, long time means, sufficiently long time, I mean to say, if you keep this for sufficiently long time, what is going to happen? This Cementite, which will come as plates at the beginning, will, you know, undergo spheroidisation treatment. What is known as the Cementite, which will form as plates at the beginning, will becomes as ferroids; or, it will become like a circular things, or sphericals of the phase; that is what is shown here. These are all these ferroid Cementites.

And, this is routine in the high temperature tempering treatment of Martensites. So, you have seen that, there are stage I to stage IV on the Martensitic transformation, depending on the temperature you use. I am not talking about time. Time can vary from one day, to about three days; depends on what you actually want to get. But, you know, if you are a industrial, if you are in a industry, and you want to test, temper the Martensites, depending on the strain level, or the ductility level of your component, what, where you are going to use this material, you can actually choose any of this stage. You can actually stop the heat treatment, either in stage II, stage III, or you can go up to stage IV. But, stage IV, as I told you, is not normally done.

So, in a nutshell, you can choose the temperature of the transformations, depending on your need, depending on your stuff, but these are things you should know; you know. As you know, in the stage II, because, stage I is nothing, but stress relieving treatment. So, you do not get completely, you know, out of the, out of the brittleness zone, or brittleness region; you have still a problem of brittleness. But in stage II, after you form the epsilon carbide, and you can relax lot of strain, lot of strain and so, you can bring in ductility into the, into the transformed Martensite. Stage III, obviously, is very critical, as I told you; austenite gets transformed into alpha, or Pearlite, depending on the carbon concentration.

So, stage III is very, very critical to reduce all the brittleness. So, most of the Martensites you find in the plain carbon steel, are actually must be heat treated until stage II to III; that is, up to 350 degree Celsius temperature. But, stage IV is optional, as I told you. So, thus, this is in nutshell, what you should remember in your, you know, in the things. So, now, I am going to write down, what are things happens in the board, and, so that, you do not forget. And, I also do not forget, for the sake of understanding, and then, close this chapter on Martensites. So, tempering of Martensites, (Refer Time: 12:11) at different stages, I told you in the, as a function of temperature, tempering a Martensite.

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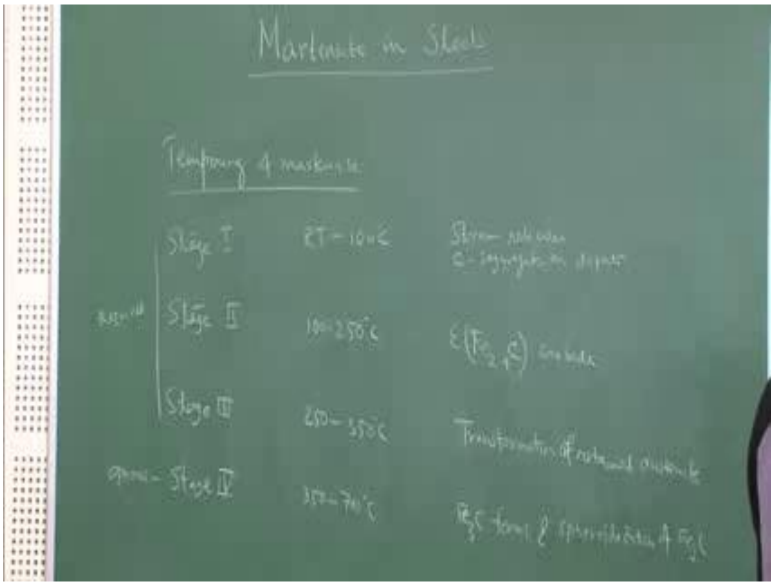

This is to reiterate the fact. First one is, stage I. It happens at temperature, room temperature to 100 degree Celsius temperature. It is nothing, but a strain relieving; strain relieves, and basically, carbon segregates on defects, mean, dislocations and twins. And, stage II is happens from 100 to 250 degree Celsius temperature; will form epsilon carbide. This is known as epsilon carbide; I have given the formula. It is non-stoichiometric carbide, these forms. And, carbon concentrations, super-saturation of carbon is reduced; obviously, because of that. Stage III, very critical; this is happens at 250 to 350 degree Celsius; retained austenite transform; or, rather I write down, transformations of retained austenite; transformations of retained austenite happens, and very critical, because, retained austenite is not good at all for the Martensite.

Our last stage is stage IV, which happens at high temperatures from 350 to 700. This temperature region depends on steel composition. Here, the Cementite forms; that means, whole Martensitic structure is dissolved. Cementite forms and it can actually undergo spheroidisation. Spheroidisation of Cementite, spheroidisation of Cementite can happen. So, these are the, this are the four different stages as I told you, which is, which happens there in the, there in the transformation time. So, stage I and to stage IV; this is optional, as I told in the lecture, but these three stages are required.

Well, in case of alloy steels, you can form other carbides; if you have moly presence, if you have a, suppose, chromium present, then, you can have, form those carbides also, in addition to the epsilon carbides. So, that is the, basically, aspect of the tempering of Martensites which is routinely done.

So, now, I am going to go back to the slides, and whatever time I have, about 10 minutes or so, I am going to start the discussion on the last topic, that is, the last topic on austenitic transformation, that is, on austenite to Bainite transformation. So, I will just show you few microstructures, and try to explain how things happen. You know, Bainite is again, a unique microstructure. The name is give by the scientist Bain, E C Bain, and E C Bain. Bain actually discovered the Bain distortion, and, in the, for the explanation of martensitic transformation. So, to honor that, we have, this name is given to the unit transformation. This is relatively new, and it happens in a unique manner.

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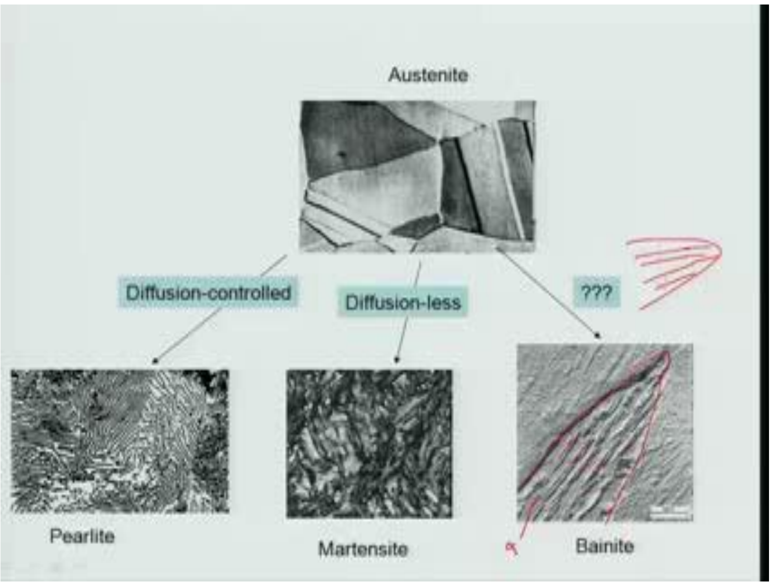

Well, let me first tell you, so, we have discussed a diffusion controlled Pearlite transformation, diffusionless martensitic transformations. Now, we are discussing a transformation for which we do not know how this happens. This can happen both, this can happen in such a way that, both the transformation mechanisms can work. So, this is the Bainite, typical Bainite you see here. It is like a feathery Bainite; it is just like a leaf, and within that leaf, you have Cementite, and alpha iron. The Cementite is the red coloured thing. So, I am putting, and this one is alpha. So, therefore, this actually, like a tree bunch, or as like a tree leaves, in which, if you have a tree leaves like this, in which these are actually Cementite, and remaining parts, this dot things, are actually alpha. So, this is one such of morphology which is observed.

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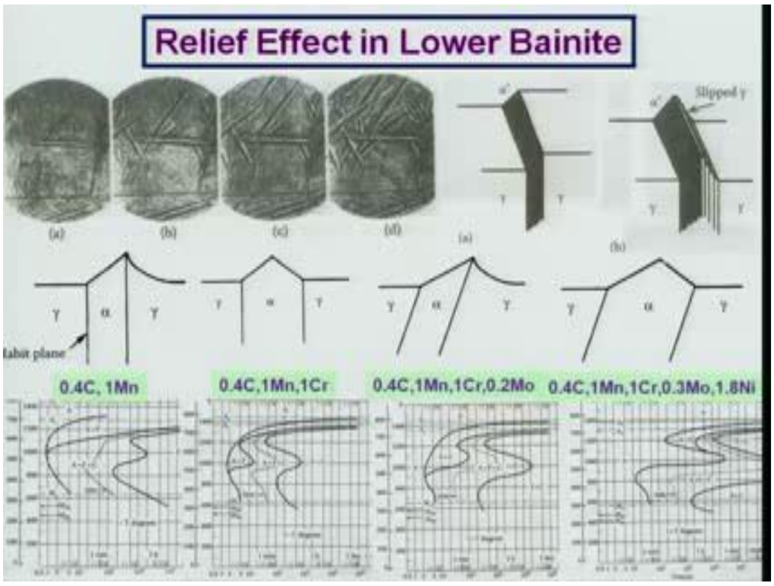
Relief Effect in Lower Bainite

Now, let us, let me just go through it. You know, there are two types of Bainites which forms normally; one is known as the lower Bainite, or upper Bainite.

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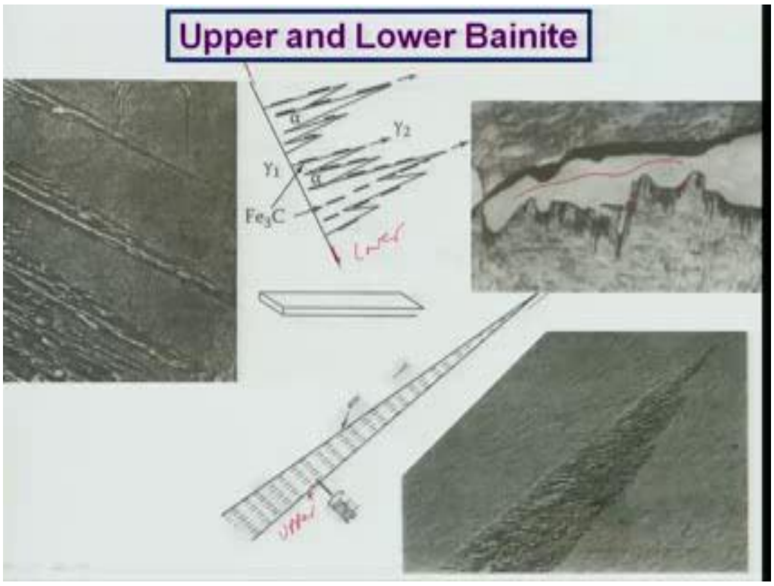
Upper and Lower Bainite

So, what is the difference between lower and upper Bainites? Let me just explain it to it. Very simply, the lower Bainites, sorry, lower Bainites, I will discuss first. Lower Bainites normally forms at temperature, lower temperatures. Well, let me first tell you, the Bainitic transformations happen, you know, in a different way. If I take a steel sample, heat it up to about 950 degree Celsius temperature, and homogenize it; then, I quench the steel to oil bath, which is kept about 350 to 400 degree Celsius temperature; and, if then, I quench it directly from the 950, or 1000 degree Celsius temperature, in which the whole thing was fully austenitic state. See, if I quench it into the oil bath, at about 350, 400 degree Celsius temperature, and keep it for long time, one day, two days, then only, I form the Bainites.

Now, lower means, when the transformation happens at lower temperatures, like about 300, 350; higher means, about higher temperatures, about 450, or 400 degree Celsius temperature. So, there is distinct morphological difference between these two. The one which is shown at the bottom is what is known as the lower Bainite. Here, you see here, on picture it is shown. This looks like a typical laminar structure of Pearlite, but it is not. What we have is a long leaf; that is what I discussed; very long leaf, in which, this leaf is basically alpha phase; whole leaf is basically supersaturated alpha phase; and then, inside leafs, you have Cementite precipitated out.

That is what is the most critical difference of Pearlite, and this most critical difference between Bainite and the Pearlite. So, in Pearlite, you have parallel (Refer Time: 19:14) of Cementite, alpha, Cementite, alpha. But here, you do not have that. What you have is, a leaves of alpha, leaves of alpha; as you see here, leaves of alpha. And, these leaves actually, inside the leaves, you have this carbide precipitated out. That is what is known as the lower Bainite, and so on.

What is upper Bainite? Well, upper Bainite is distinctly different. In upper Bainite, what happens, you have, this is again boundary. This is here; this is again boundary. As you see here, let me take this red colour things, otherwise, it is not visible. This is what is the marking boundary between these transform, and non-transform region; this is gamma. So, as you see here, for upper Bainite, you have this plates of alpha, which is present, and on the, on these sides of this plates, these are the sides of these plates; this, these are actually Cementite.

So, that means, what? That means, suppose, this is what you see here. This is a big plate of, this is a big plate of alpha, and then, this Cementite is precipitated on the sides of the plates. You can see here, all these, these are Cementite plates, or, you can see here much easily. So, therefore, distinctly, these two morphologies are different. In this case, you have alpha plates, inside which Cementite are precipitated out. In this case, large numbers of alpha plates are present, and on the boundary between the two alpha plates, the Cementite is precipitated. So, this, this is the difference between upper and lower Bainites.

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UPPER BAINITE

http://www.msm.cam.ac.uk/phase-trans/2002/bainite.html

So, I am going to show you again. So, this is the upper Bainite; you see here, there are many plates of alpha, and in between the plates, there are Cementite present. Very clearly you can see here. This black things are Cementites. Here, you can see this. This is actually taken from the website of Professor Harry Bhadheshia from Cambridge University.

You can actually go down, because, he worked a lot on this Bainite transformation, and his impact made Bainite useful in the real applications. So, now, question is this, yes, this is what is your, this is the upper; this is the. Sorry, I think, I am making mistake. Upper Bainites will have these things. So, I should go back here; this is what is your upper Bainite; this is upper. Let me write, because whatever I said, you should check; changed now; this is the lower. So, upper Bainites will have this sheath like structure, in which our carbide is precipitated out; lower Bainites will have plates of alpha, and the Cementite is precipitated between the plates.

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So, as you see here, very clearly, this is the t m picture; as you see here, this is the long sheath of this alpha and inside of this cementide is precipitated out. This is what is your upper; and, lower one will have plates of alpha.

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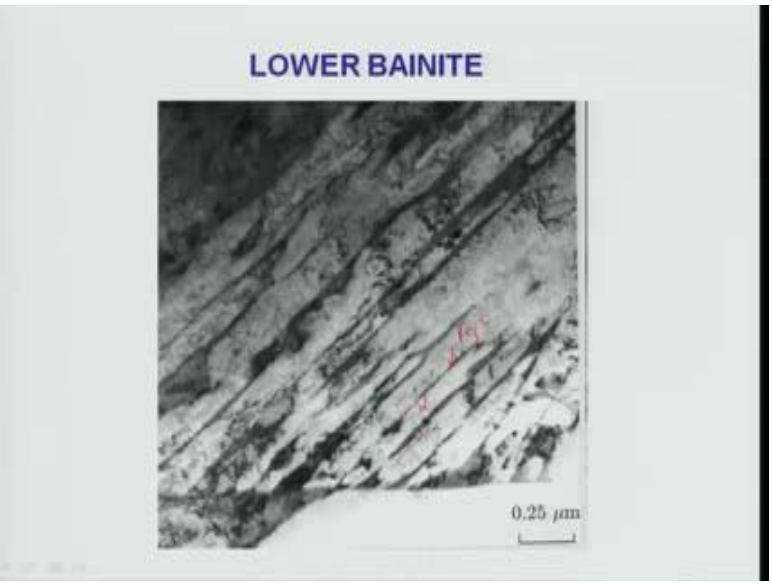
LOWER BAINITE

These are the plates of alpha. These are, each one is alpha, and these things, black color thing, are Cementite. So, Cementite is precipitated at the boundaries of alpha, not inside the alpha; that is a distinct difference. In case of upper Bainite, Cementite precipitated inside the alpha plates or alpha sheaths, but here, this Cementite is precipitated out in between the alpha plates; that is the difference between an upper and lower Bainite.

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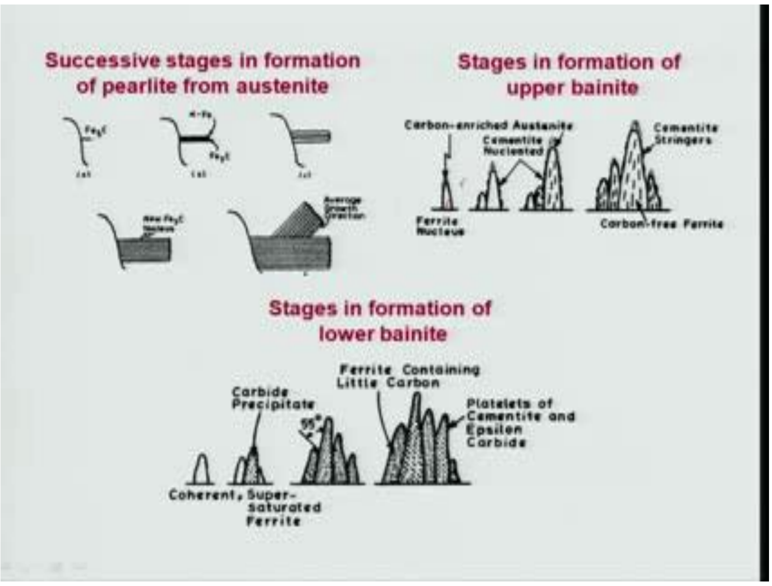

Successive stages in formation of pearlite from austenite

Stages in formation of upper bainite

Stages in formation of lower bainite

There are many pictures to be shown here, and you know, how these things happen. Well, there are many, many theories for this formation of this austenite, formation of this Bainite from austenite. So, I am going to discuss only two things. Well, let me first discuss, let me first tell you that, pearlitic transformation leads to also formation of alpha and Cementite together, and is in a lamellar morphology like this. And, I have shown you, suppose, this is austenite ground boundary, then, Cementite nucleates. As Cementite requires more carbon, nearby region become deplete of carbon. This leads to formation of alpha, on the both sides, and then, you form a lamellar, and then, lamellar grows and becomes Pearlite (Refer Time: 23:12).

Now, in case of upper Bainite, you have a ferrite nucleus, which is carbon enriched from the austenite. And, because it is a carbon enriched from austenite, what will happen? And, this is, and the ferrite grows; as the ferrite grows, this will eject all the carbon. So, all the carbon will be then collected at the boundaries of austenite, and this, and this alpha. This is alpha; this is austenite. So, at the boundaries between the alpha and austenite, all the carbon will be segregated. And, as the carbon concentration will be very high, this will lead to the precipitation of the Cementite.

Similarly, nearby region, there is another lamely of, another, you know, plates of alpha will form. And, then again, the carbon will be segregated at the boundaries of alpha and do that. On the other hand, for the lower Bainite, it does not happen. In lower Bainites, initially, the austenite transforms into alpha, super-saturated alpha. Austenite, which is, which is the high (Refer Time: 24:06) phase, it (Refer Time: 24:08) transforms into super-saturated alpha. And, the alpha phase goes like a sheath, or a tree leaves. And then, at lower temperature, this, because it is a super-saturated phase alpha, this Cementite precipitates on the, inside this, inside this sheaths; that is how the things happens. And, this is what is shown. You know, first you form the coherent alpha from the austenite; and then, it forms large number of coherent alpha phase; and then, the super-saturated alpha will be leading to the formation of precipitation of the carbide phase in the microstructure.

There are many details of this, which I think we can discuss in the next class in details. But, in a nutshell, I would just like to tell you, the Bainite is basically a distinctly different transformation, as, not same as Pearlite transformation, as you might be thinking, but it is not. There are lot of studies have been done for the last 30, 40 years, and it has been conclusively shown that, this is not, you know, completely governed by the diffusion of carbon, or completely governed by the sharing of the, sharing due to formation, leading to formation of Martensites. See, it is in between these two. It looks like, but, still lot of research has to be done, and then only we can find out what is the way things stand.

So, next class, we will discuss remaining part of Bainite, and then, I need to discuss about this TTT diagrams, and subsequently, I need to discuss about the cast irons.