**Aqueous Corrosion and its Control**
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**Lecture – 22**
**Forms of Corrosion: Intergranular corrosion (Part-II)**

We shall continue discussing the chapter on Intergranular Corrosion of metals and alloys. In the previous class, I have highlighted the importance of understanding the intergranular corrosion of metals and alloys.

Because when we use polycrystalline material the grain boundaries they become very active because of high energy areas; and also these high energy grain boundary areas also attract the chemical species to lower the energy. For both these reasons the grain boundaries are selectively attacked. When the grain boundaries are selectively attacked the strength of the material becomes very low leading to loss in load bearing capabilities.

If you have a higher stress applied on the structure, this intergranular corrosion can also lead to intergranular stress corrosion cracking. And we drew the reference to stainless steel; because a stainless steels are very widely used and especially when you weld the stainless steels the weldment on the especially at the heat operated zone becomes prone to intergranular cracking intergranular corrosion we call famously as weld decay.

So, before I also went into discussing the sensitization or the role of heating on the intergranular corrosion we looked at the classification of various types of the stainless steels. And then we went on to say that the normal or conventional 304 stainless steels they have a carbon content much higher than the thermodynamically allowed solubility limit. So, when you are going to do the heating then what happens heat it leads to the precipitation of these carbon.

So, we need to understand the mechanism of the intergranular corrosion in stainless steels. Before I do that I thought I will just introduce a book which I should have done it in the yesterday I introduced this book to you. This is worthwhile to go through this book see this it's a very detailed book on intergranular corrosion of steels and alloys.

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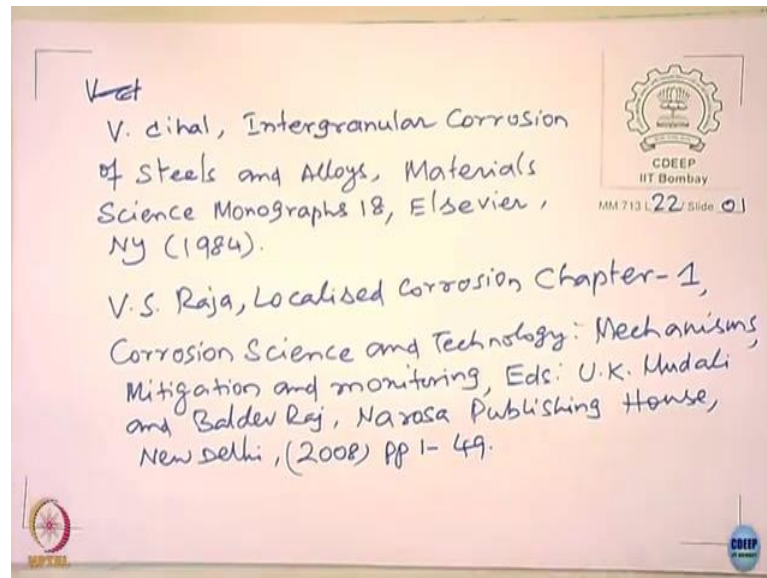


The author is by V. Cihal and he titled intergranular corrosion of steels and alloys, materials science monographs 18, Elsevier Publication, New York. It is it is reasonably old book 1984. And I also have writen a chapter on localized corrosion where I have in reasonable detail discussed the intergranular corrosion of stainless steels and also some reference to aluminum alloys. If you want you can refer this as well.

Mechanisms and mitigation and monitoring. This book is edited by U. K. Mudali and Baldev Raj and it is published by Narosa Publishing House, New Delhi, 2008 the pages 1-49. Actually in this book you will also have a detailed discussion about the other localized forms of corrosion that includes pitting crevice corrosion, selective leaching, et cetera.
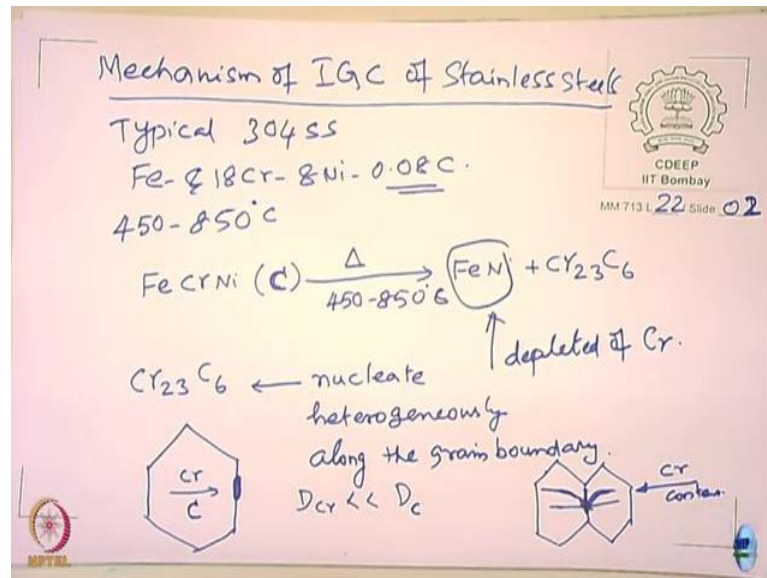
Actually, now you can refer that as well. Let us now discuss about the mechanism of IGC of stainless steels. Please notice that the mechanism of IGC of stainless steels is not same as the mechanism of intergranular corrosion of other kinds of alloys actually. So, you cannot just generalize this mechanism everywhere and we see that as an example for aluminum alloys.

Now, as we have seen that let us say a typical let us say 304 stainless steel and we have seen that it has got iron 18% Cr, 8% Ni and about 0.08% carbon content. And the carbon is super saturated; they are in the solution anneal conditions we also called mill anneal condition, rise temperature of the stainless steel sheet or plate to about 1050°C; where the carbon is highly soluble at that temperature then quench it rapidly so, that the carbon is retained in the solid solution.

Now, if you heat this stainless steel in the range of let us say an about 450°C to 850°C and allow sufficient time then what happens is in the stainless steel you have say in this case you have iron, chromium and nickel and there is carbon.

Please notice I put carbon within the bracket because it is small quantity and in fact it is in the solid solution it is mostly in the interstitial positions. This one is there. Now, what happens when you heat it in the range of 450 to 850 degree Celsius, what happens is you have iron, nickel remains here. So, the carbon combines preferentially with chromium

and forms chromium carbide and why does the chromium carbide form over let us say iron carbide or nickel carbide?

Student: Affinity.

Because affinity is more it is given in terms of the free energy change. So, the chemical potential of this is very negative. So, the free energy change for that is so negative and so it forms preferentially as chromium carbides. And when this forms obviously the matrix is depleted of chromium. Not only this, there is one more important factor here that is $Cr_{23}C_6$ formation you can also have other kind of carbides it can be $M_7C$ carbides can happen most kind of carbides can happen or $M_4C$ can happen.

There are other kinds of carbides can also form. So, these carbides the nucleate heterogeneously. And they nucleate heterogeneously because the nucleation is the most difficult in the phase transformation and the nucleate along the grain boundaries. Why the grain boundary use additional energy? To overcome the nucleation barrier right energy barrier for nucleation.

So, what it means? Suppose I draw as a grain here and the chromium carbides are formed over here preferentially. So, that means, the chromium has to migrate so as the carbon to form the chromium carbide or the grain boundary. If you look at the diffusivity of chromium and the carbon right will they be similar or different?

Yeah.

Student: Different.

Different. So, which will be having a faster diffusivity.

Student: Carbon.

The carbon because of the smaller size carbon diffuses at the fast rate whereas, the chromium diffuses at a lower rate. So, what is the consequence of that? So, that means, the diffusivity of chromium is much smaller than the diffusivity of carbon. Please notice the chemical formula. What is the chemical formula of the carbide?

It is 23 chromium and 4 carbon; that means, approximately 1 carbon takes away 4 chromium; that means, you need to supply more chromium in order to form carbide

chromium carbide, but the diffusivity of chromium is lower compared to the diffusivity of the carbon.

So, what is the consequence then? The consequence of that is if I draw the grain boundary, if I draw the chromium content this is the carbide here. See the chromium content will drop significantly here. Of course, it is not a correct way of writing this here. It should be in fact it goes high here ok.

So, you find that see look at the chromium carbide has got higher chromium right and so there is a huge depletion of chromium along the boundaries because of the fact that the diffusivity of chromium is lower compared to the diffusivity of the carbon here. And the carbon content can go below the required level for a stainless steel.

What is the recovery level for a stainless steel? We talked about yesterday say about 11% something like that and 10.8% something. So, if the carbon, if the chromium content goes below the required level for making it a stainless steel then what happens to passivity is lost. So, that is that is the real problem.

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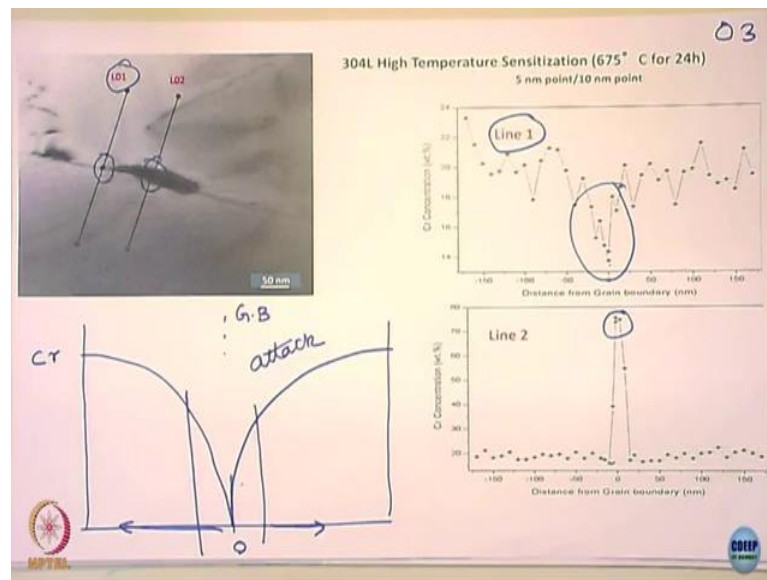


Now, people have examined it. We, in fact, also examined this in our lab. Of course, here please notice it is not a 304SS, it is a 304L actually. The 304L has got low carbon we will talk about the story little later.

But look at this even when the carbon content is very low and you heat it in the range of 675°C for 24 hours long time this is the transmission electron microscope image and you see the carbide chromium carbide formation and in in the grain boundary area this is the grain boundary area I hope you seeing this right. And he has mapped the chromium content next adjacent to the chromium carbide here and around the chromium carbide.

The one what is referred here see here corresponds to this. See that the chromium level see at this magnification there is uncertainty in the composition. You know what is the chromium content here, is supposed to be 18%, but what you report here is about 24%.

So, there are limitation in the experimentation inherently that so do not worry about the absolute values here. But, what you could see is that over here see 0 represent the grain boundary. The grain boundary the chromium content falls very sharply it is about 10%.

Just do not worry about the absolute values, but look at the difference 24 close to that close about 13. So, about 10% reduction in the chromium content occurs the grain boundary because of the chromium depletion taking place you see this here. So, there is a problem of the chromium depletion around these area.

You have also done a scan here along the across the grain boundary where you have a chromium carbon precipitate. Now, you see here the chromium carbide has higher chromium content it is understandable. So, there is more chromium here because of the chromium carbide formation.

The point I am trying to convey here is that when you have chromium carbide formation the depletion of chromium occurs close to the grain boundary area; and it can go to so lower level that the alloy may not be able to passivate. So, loses it is it is stainless steel characteristics completely. So, the chromium is a now what happens suppose I draw this schematically here. This is the grain boundary here. See chromium percentage this is the grain boundary. It moves like this here. You know very well the corrosion rate depends up on the chromium content what will happen.

So, you are going to have somewhere in this region what happens? There is going to be severe attack of the grain boundaries. I showed you some pictures yesterday right where the sensitization has led to deep grain boundary attack. So, the width of this attack what you see here depends upon the extent of depletion that occurs. If the depletion is narrow

what happens, this attack becomes narrow. The depletion is broader the attacks becomes wider actually.

So, essentially it is a chromium depletion that leads to the sensitization of the grain boundaries. So, this theory is called as chromium depletion mechanism. So, the mechanism is fairly simple. It is not very complicated right. Now, we need to understand, what are the governing factors for intergranular corrosion.

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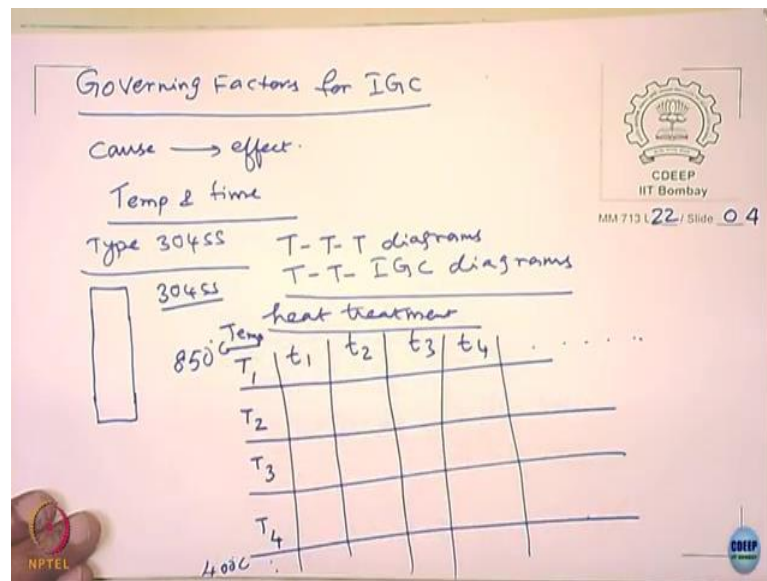


There is a cause and there is an effect here. What is the cause? The cause is subjecting to some heat treatment leading to chromium carbide formation. The effect is corrosion along the grain boundaries. That is what.

So, the primary reason is the chromium carbide formation along the grain boundaries. So, now can you quantify, can we understand the intergranular corrosion in more details. As I told you it is the temperature and the time both are important. Before I go in details how many of you are from the non-metallurgy background? Oh quite a few of them. Have you heard of the time-temperature-transformation, diagrams any of you? So, called the T-T-T diagrams.

So, let me just briefly cover this aspect of this and so that you get a real feel of that. Let me tell you how you get the TTT diagram for sensitization. Suppose you take a stainless steel let us take type 304 stainless steel. I want to establish Time Temperature

Transformation diagrams; they call as TTT diagrams. In this case, I called as time temperature IGC diagrams. How do you establish this diagram? What one does is 304 stainless steel is taken? Maybe say piece.

Let us say about take some long strip of that take long strip of 304 stainless steel; subject them to heat treatment for different temperatures let us say T1, T2, T3, T4 something like that. This is the temperature for different time intervals say t1, t2, t3, t4, et cetera keep doing that actually.

So, you can take this material and subject them to heat treatment in the approximate temperature region. Let us say one can start with maybe about 850°C and be down to this to about 400°C something like that. Different temperature intervals and time intervals do the heat treatment on that. Then you subject them to the intergranular corrosion to like there are various solutions available.

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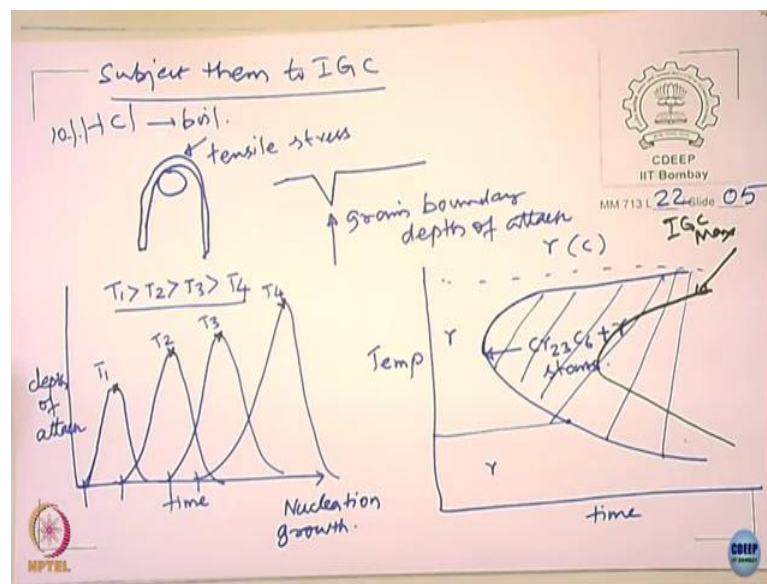


Maybe you can take a hydrochloric acid HCl you can take some maybe you know 10% HCl you can take and boil that, expose the sample. And take the sample out in this case and you can bend the sample over a mandrel you can bend it over mandrel.

When you bend it over mandrel what will happen now there is a tensile stress here. So, what will happen now? When the grain boundaries are attacked very selectively the grain boundaries will open up.

This is the grain boundary and you can measure the depth of attack and the depth of attack is related to the intergranular corrosion. If there is if the grain boundaries are sensitized more and more chromium carbides are formed more chromium depletion has occurred then what happens then the grain boundaries become susceptible to corrosion.

Now, you can have the depth of attack and you have done a big matrix of test, various temperatures and time. In all these cases, what you can do is, you can you can plot depth of attack versus the time.

You can do it for different temperatures and you will notice that so you can have several temperatures and in this case what happen T1 is greater than T2 is greater than T3 greater than T4. What you notice from here? There is time for initiation for intergranular corrosion. So, you can find out this and you can plot you can plot the temperature versus the time for start of IGC this is for the start of IGC.

So, what happens it goes like that. As the temperature is decreased what happens to the time for initiation of IGC? Increases, start increasing like that. Now, if you raise the temperature it was get like this. It is very interesting now. You see when you raise the temperature also again the time for initiation of IGC increases.

This is a little a metallurgical concept. I think those guys who studied phase transformation will understand much easier and above this temperature look at this above this temperature gamma phase stable the gamma has now this is also gamma stable gamma stable here. Here what happens here it is the, what is this this is the initiation of chromium carbide formation starts. Am I right in this?

So, now, you can understand that when low the temperature the time taken is increasing, but again you raise the temperature again the time taken is increasing here. What is the reason for that? Those who have studied metallurgy you should be able to tell this.

Yeah.

Student: Undercooling.

Yeah, you can also say that undercooling well under cooling again this guy should know what undercooling means.

Student: Free energy of change.

Yeah. So, the free energy change the free energy change for that is actually is increasing is increasing like this it is increasing right from here down to this. So, it should go one way only. The reason for that is related to two factors.

If you can recollect any of you it depends upon the nucleation, it also depends upon the growth process and growth process requires higher temperature because the diffusion becomes faster. The nucleation requires more undercooling lower temperatures. So, there is a compromise between these two. So, you find that at high temperature diffusion is faster, but the, nucleation becomes slower.

So, you find that again the time for transformation is increasing actually. So, it goes this is a typical we call as TTT diagram Time Temperature the Transformation diagram. What is transforming here? The gamma is transforming into this one of course, plus the gamma here. Please notice if you look at this diagram what is very clear here. The chromium carbide starts forming only and around these regions there will be no chromium carbide formation. How do I interpret this?

At any given temperature suppose I take this temperature I take this temperature unless you cross this line the alloy will not get sensitized that is true for all cases. You can also plot what you can plot? Please look at you can also plot this is the maximum attack. I can also plot a maximum attack maximum. This is IGC maximum, but again please notice it goes from maximum again falls down here; that means, you heat for longer time what is happening to IGC?

Decrease. Why does it happen? Why should on prolonged annealing the IGCs should drop? Chromium carbide exists there right. That does not dissolve. So, you are allowing enough time for the neutralization of the depleted zone. Now, the chromium earlier the carbon was diffusing faster and chromium could not catch up with that and so there is more depletion along the grain boundary.

So, with the longer interval the depleted region gets neutralized the there will be because there is a concentration in gradient the chromium will start moving towards the depleted regions and get neutralized. So, the IGC decreases, it decreases and decreases and so on please understand that.

So, what does really imply? It implies that what is implication of that in alloy making? What is implication of this alloy making? I will come back to this little later.

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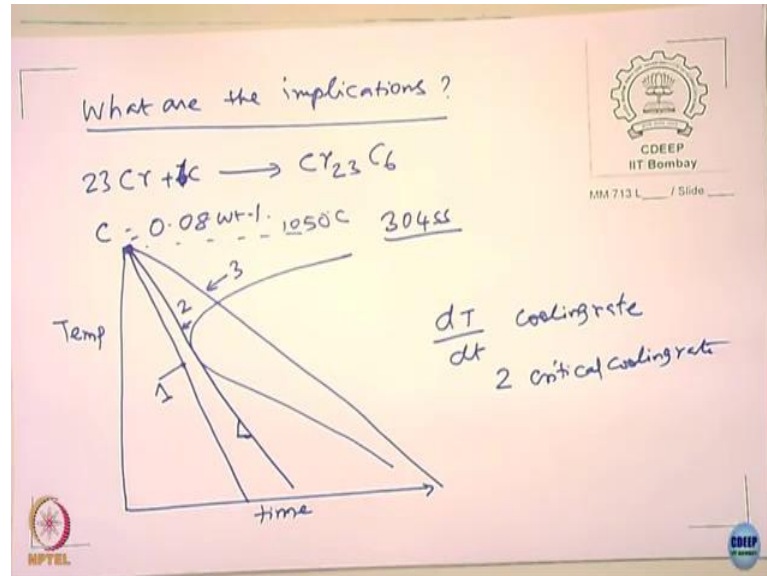


Chromium combines with carbon and forms $Cr_{23}C_6$. What is the carbon content in the alloy? It is about 0.08 wt.%. The carbon takes away the chromium. Can I simply increase the chromium content let us say 40% instead of 18% chromium I added to the alloy 40% chromium. Do you think the sensitization will go away? Because I am compensating with more chromium so.

No, it would not go. Because it is not that we do not have enough chromium to combine with carbon. Even you even if the all the carbon present in the stainless steel combines with chromium the remaining chromium in the overall composition is still higher. The overall composition of chromium in the alloy is still higher to call it as stainless steel.

The problem here is that the chromium depleted around the grain boundary area that is what the concern. That is happening because of the diffusivity difference not because of stoichiometry difference. So, that diffusivity problem still arises and so by just increasing the chromium content of the alloy you cannot simply control the intergranular corrosion. So, that is simply not possible.

So, it is the diffusion kinetics that are responsible for the chromium carbide formation on the grain boundary and the consequent chromium depletion around the grain boundaries.

So, this curve essentially means that I have enough chromium in the material no problem and over a time period the depleted regions they become replenished and so they the grain boundaries become resistance to the intergranular corrosion which of course, this these are the things are not possible in real life situations. We will see later theoretically yes, but practically they are not useful at all actually.

So, the factors that control IGC can be seen from this diagram. If I take say 304 stainless steel I keep it at let us say 1,050 °C I hold it here longer time I quench it fast. In fact, I should quench it faster than this. We quench it little slower. Let us say cooling rate 1, cooling rate 2 and cooling rate 3. The cooling rate 2 is what is the cooling rate? It is dT/dt is the cooling rate.

Now, the 1, 2 is the critical cooling rate. A cooling rate higher than the 2 will avoid sensitization. The cooling rate lower than this will lead to sensitization of the stainless steels. So, this diagram sets a limit for various thermal processes that can lead to either sensitization or that can avoid sensitization.

So, the temperature the time both are important. So, when I said that it is between 450 and 850 please understand that ok. If it is not 450 just like that somebody has a question to you oh can we not be 430, what will be your answer? Will it sensitize at 430? Yes, it could.

860 can it be, yeah possible. Because it is a time and temperature are equally important. So, these numbers are indicative and that also depends upon the alloy. It is not going to be same for all kind of alloys. We will see later actually why it is ok.

So, that means, you need to understand what are the things that govern the time, temperature transformation diagrams. So, you understood this anybody has any question here? This diagram is very relevant because we are going to talk about weld decay and how to avoid weld decay or how do we make new alloys all of them are based on this diagram and so we need to understand this one more clearly. So, it will be no doubt as far as this diagram is concerned.

See, a typical 304 stainless steel, we discussed earlier that it has about 0.08 wt. % carbon or in fact in if you are going to have 18 Cr, 8 Ni, I can go as much as 0.1 wt.% carbon I can go as much of that. Because at the high temperature carbon solubility in the

austenitic matrix increases high temperatures. So, dissolved in single phase gamma phase.

Now, if we quench it very fast then what happens? Now or if you or you cool it very slowly what happens suppose you held it at 1,050 °C and all the carbon is in the soluble state you cool very slowly. So, what will happen now?

The carbon will come out because the solubility of carbon in austenite decreases with temperature because the room temperature solubility of carbon in this alloy is about 0.028%. So, 0.028% is what maximum the alloy can dissolve carbon at ambient temperatures. So, what will happen excess carbon? It is like this is very similar to you know is similar to sodium chloride. You take water and add sodium chloride it dissolves. You keep on adding more what happens after sometime?

Sodium chloride does not dissolves. Raise the temperature what happens to sodium chloride?

Student: Dissolves.

Dissolves a equally down again you start crystallizing from that. So, it is a phase rule nothing different from that. You know in this case when carbon is forced to dissolve at the high temperature when you cool it down thermodynamically it is going to form another phase because it is not soluble. Now, how does the carbon come out? Carbon does not come out as carbon it comes out as chromium carbide precipitate because of this is this gives you the free energy change for that is going to be very negative. So, that what happens here.

Now, if you cool it very fast then what happen you do not allow the carbon to diffuse. It is frozen. And so what at room temperature you may have even 0.1 wt.%, 0.158 wt.% carbon or 0.08 wt.% carbon all of them in the solid state and they are frozen no precipitates. But, you when you heat it again what happens you are giving energy for the carbon atom to move and they move around what happens? It forms chromium carbide because of the phase rule that dictates.

So, in 304 stainless steel when you are the so called mill anneal stainless steel what they have done. They have held this stainless steel or plate whatever at that temperature 1,050

dissolve all the carbon you quench it rapidly and so what you get is a nice 304 you can passivate no chromium carbides.

Now, if you are talking about industry guy what rate you should quench it that is given by this diagram. This diagram tells that this is the lowest cooling rate that is tolerable. If you are going to lower the cooling rate you know below this never happens then you are going to have chromium carbide precipitations. So, that dictates what should be the cooling rate that can avoid the sensitization of 304 stainless steels. So, this is a an important thing that we should be understanding.

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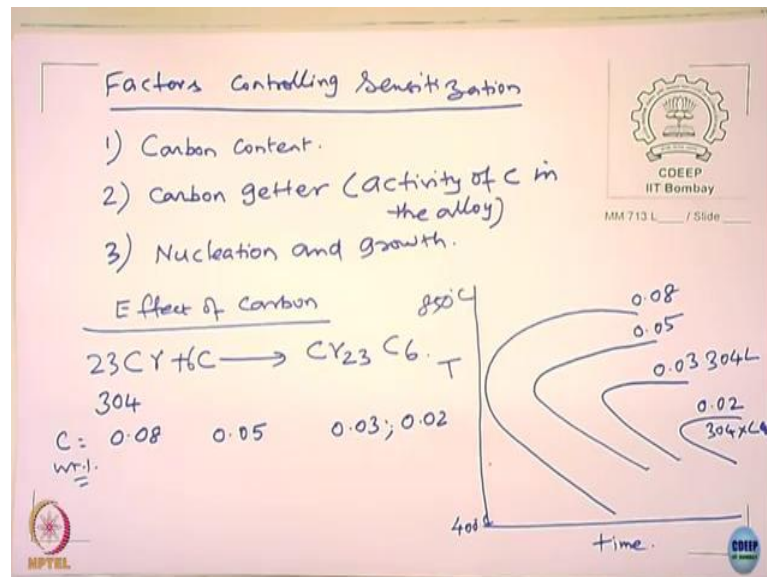


So, let us take this further and see how this the factors controlling sensitization. What is the factor? The first and foremost is the carbon content. You have higher carbon content what will happen to kinetics?

We will have it would be faster right one. Two I use a very crude term carbon getter. If you can remove the carbon activity in the alloy. what happens?

Student: Decreases.

It decreases the kinetics. Carbon getter or which can change the activity of carbon in the alloy. These are all changing the activity of carbon. You can also control this by controlling the nucleation and growth. You can control the nucleation of chromium

carbide formation I can control the sensitization process. So, broadly these are the three ways you can control the sensitization of stainless steels.

Let me take the effect of carbon. It is not rocket science right. If you increase the carbon content you will see the kinetics will increase. Let us take a stainless steel let us say 304 it has got let us say 0.08 the carbon content. So, 0.05, 0.03 and 0.02 wt.% carbon. If I have to draw a TTT diagram for this. So, I am drawing for let us say 304 I am drawing like this. It is about I am keeping here about let us say 400 °C; maybe around about 850 °C. So, what will happen to 0.05, 0.03, 0.02 or you can even have 0.01 for example? It moves towards right fantastic.

Please look at even these like this also coming down, why? Because it is just dissolved, there is no much carbon. So, it dissolves at low temperatures completely. So, you find that this moves towards right side.

The whole lot of stainless steels to avoid sensitization, but developed based on this concept 0.08, 0.03. This is this is called as 304L. This is called as this is called 304 extra low carbon XL extra low carbon. The nuclear industries even 0.03 is not allowed not tolerated. People go for 0.02 or 0.015 something like that people go for that.

So, the development of low carbon stainless steels have a basis. The basis is what? The time, temperature, sensitization diagram so that actually. There is a problem in removing carbon. What is the problem? And of course, making is expensive and what is other one.

Student: Strength.

The strength goes up so ok. So, low carbon stainless steels are a expensive have lower strength.

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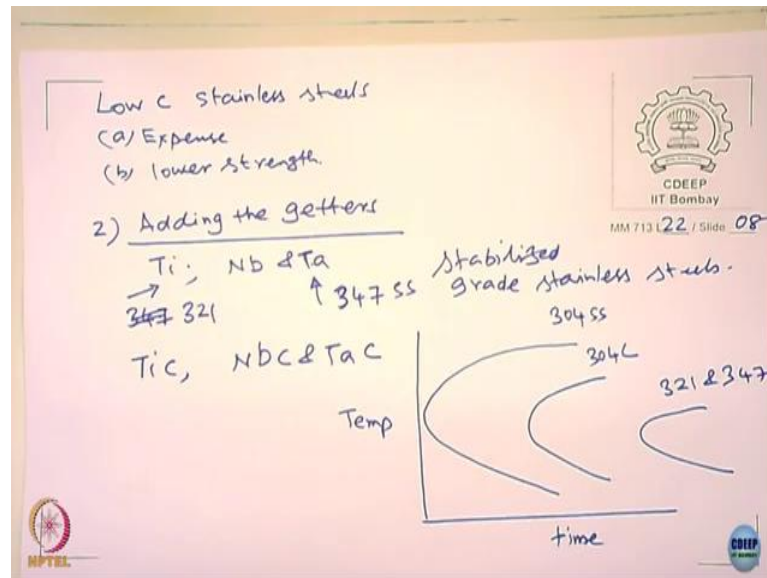


So, somebody is making a pressure vessel automatically the cost goes up on both accounts one related to the expense other one related to the strength levels. So, can we retain the carbon and then prevent sensitization. So, what it will talk about is the second concept adding the getters. What are they? Titanium, niobium, tantalum. The titanium added one this stainless steel is called as 321 and this is called as 347 stainless steel. So, two types of stainless steels have emerged. These are called as stabilized grade stainless steels.

What are the principle here? The principle is very similar to the sensitization. If you take a 304 chromium carbide forms in preference to the iron carbide in preference to that nickel carbide, but you add a third element another element which is forms much stronger carbide then automatically carbon will go to another element.

So, the titanium forms titanium carbide. So, as niobium carbide and tantalum carbides. So, you allow the carbon in the material to interact with them and form this carbide. So, what happens to the activity of carbon in the system? The activity of carbon in the system falls very low and so the sensitization becomes extremely slow.

So, if you can plot this 304, 304L and this is going to be your 321 and 347. In fact, 321 and 347 are much more resistance to sensitization than 304L actually by the carbon content the carbon activity of the stainless steel drops very low because of the

association of titanium carbide, niobium carbide and tantalum carbides into this and they are called as the stabilized grade stainless steels.

Now, there is something which is it will not straight forward little indirect that we need to understand because you will see that some alloys unexpectedly cause sensitization even though the carbon content of these stainless steels are similar. Those who studied metallurgy it will be easier, but some of other people also can try to understand actually.

The activity of an alloying element in an alloy does not depend upon its own concentration. It also depends upon the other elements present in the alloy. For example, carbon activity may depend upon chromium content. It may depend upon the manganese content nitrogen content and so on so forth. And so, when you talk about sensitization it is just not you count only the carbon content in the alloy you have to look at the effective activity of carbon. So, that it does not get sensitized. So, the work has been done actually the R. K. Dayal from IGCAR, Kalpakkam had done some nice work I just make it very brief here.

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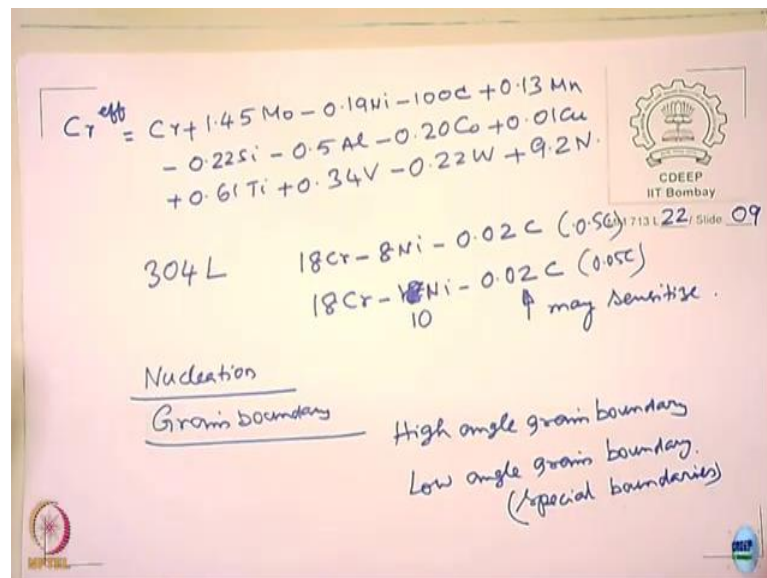


The carbon activity is given in terms of what is called as chromium effective chromium content. Please notice when you add more chromium content the activity of carbon comes down. So, they use a term which is called as chromium effective which is given as Cr + 1.45 Mo - 0.19 Ni - 100 C + 0.13 Mn - 0.22 Si - 0.5 Al - 0.20 Co + 0.01 Cu + 0.61

Ti + 0.34 V - 0.22 W + 9.2 N. It is very difficult for you to remember all of them, but I want you to appreciate this.

There all certain elements. They will favour sensitization. There all certain elements which retard sensitization that is what I want to make the point here. What are the elements that favour sensitization are the ones where you see with minus sign here say nickel obviously, carbon right, silicon, aluminum, cobalt and tungsten.

So, you may have a same carbon content in the alloy, but by chance nickel content is more then what happens? The alloy with higher nickel content will sensitize. The alloy with lower nickel content may not sensitize when you are in the borderline case.

Similarly, if you are going to add let us say manganese in the system molybdenum let us say nitrogen they will suppress sensitization of the alloy here. Where does this problem come? It comes in practice also especially the nuclear industries assume that somebody has got 304L or a XL low carbon. Assume that you have 18 Cr you have let us say 8 Ni and 0.02 C. If the alloy is not controlled is goes what 18 Cr, 10 Ni, 0.02 C what happens. This may sensitize. You may think that the carbon content is similar why not?

So, if there is a 10 Ni by mistake is added or you feel very happy because nickel is expensive ok, but this might sensitize and this guy may not sensitize actually or assume that other way around 0.5 C, 0.05 C this border line this guy does not sensitize here for sure it is going to sensitize. So, you know going into more details about sensitization it is also important to understand what are the associated chemistry of the alloying elements that will affect the intergranular corrosion when you do heat treatment at all.

See please notice that you know if it is all solutionized nicely and they do not have any problem, but when you sensitize it I think some of them may be having some alloys may have faster kinetics some of them may not have sensitize at all actually.

The one more thing that I just want to discuss and then we close for today's discussion. It is about the nucleation. You know about the grain boundaries. We call them as two types high angle grain boundary called as low angle grain boundary.

This also called as special boundaries sometimes. They call special boundaries sigma boundaries they called in metallurgical terms. What is the difference between a high

angle grain boundary and low angle grain boundary? Anybody here have exposure to this? It is a high angle grain boundary you look at the high angle grain boundary if you look at the energy from the point of view.

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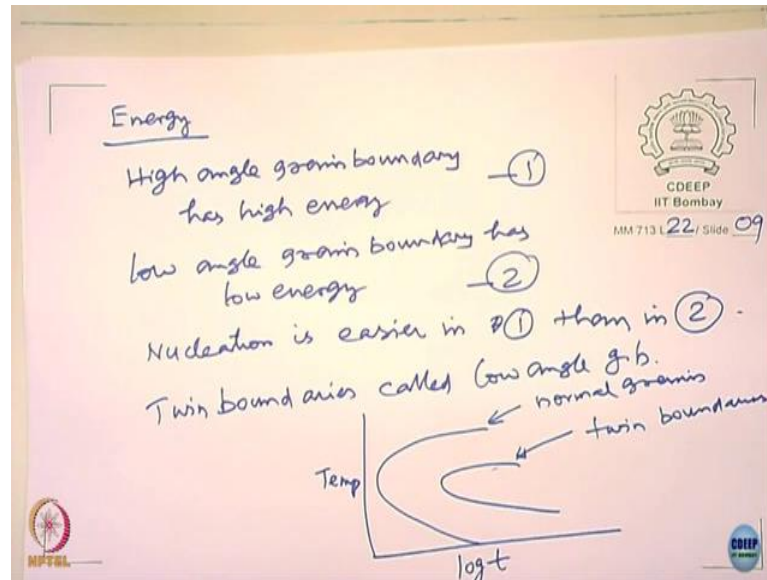


See you have an interface right high angle grain boundary has high energy and low angle grain boundary has low energy. Now, the nucleation occurs heterogeneous nucleation right. Nucleation occurs at the grain boundary because energy of the grain boundary is higher compared to within the grain actually gives interface. Now, what happens? Now, that means, if you look at the nucleation.

So, what happens the nucleation I call this 1 called 2 is easier in 1 than in 2. So, if you are going to now make the alloy with the low angle grain boundaries, then the alloy will not undergo will undergo sensitization, but undergo sensitization at a much lower kinetics.

So, the low angle grain boundary is also called as twin boundaries. Even twin boundaries called low angle grain boundaries. So, if I have to plot time it is these are log actually unfortunately I have not made there properly ok. Time is always log here. Unfortunately, please correct your earlier slides. Normal grains it is all say twin boundaries. So, sensitization. So, you can also change the grains so that you can you can control the sensitization of the alloy actually.

Well, I think we will continue I think it is not over yet. We can talk about it more in the next class. And for the time being we will end discussion related to the grain boundary natures.