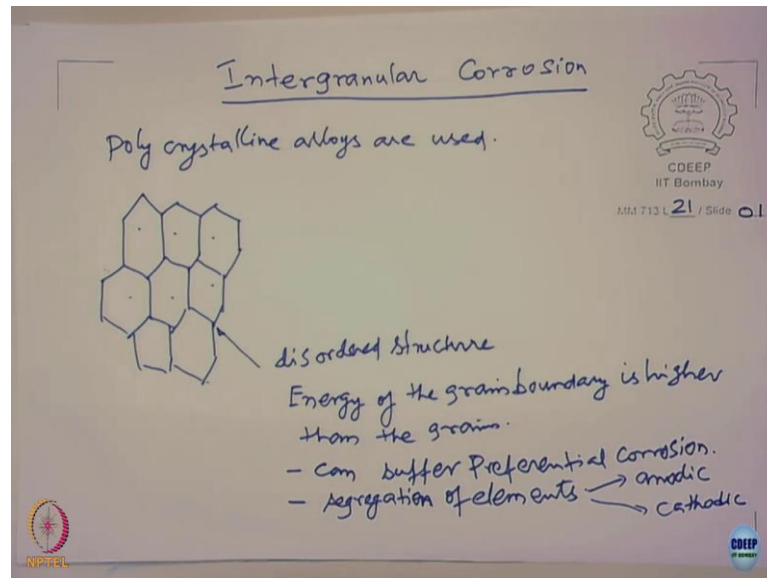


Aqueous Corrosion and its Control
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Lecture – 21
Forms of Corrosion: Intergranular corrosion (Part-I)

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Welcome to the discussion on Intergranular corrosion. This is a very important topic. It relates very strongly to the metallurgy of the metals and alloys that suffer corrosion. Why this topic becomes important? Because, we more often use poly crystalline alloys. The engineering alloys that we deal with they are all poly crystalline in nature right.

So, we use polycrystalline alloys, for many of these structural applications. When I say polycrystalline what do you mean by that? Mean you take this any of these metallic alloys and you grind, polish and etch and look at the surface with the microscope. What will you see? You see nice grain boundaries.

So, schematically if I have to draw and some of you have not seen, the non-metallurgists, what you will see is something like that. You will see polycrystalline. Now each of these grains, it can be considered as a single crystal. They have a similar orientation of atoms and since, these crystals have different orientations at the interface what happens? You will have mismatch between the surrounding crystals.

So, what happens now in that case? You will have a sort of disordered structure, a disordered arrangement of atoms. Which means the energy of the grain boundary is higher than the grains. When I say energy I mean when I say energy of the grain boundary I mean the atoms are at a higher energy state the grain boundary as compared to similar atoms located within the grains.

Now, having a polycrystalline structure is good for many cases, I mean the metallurgists like it, mechanical engineers like them because when you have polycrystalline material, you have higher hardness and higher strength, you have higher toughness. So, you normally want to have very fine grain size. You know Hall-pitch relationship, where you can say that the strength is inversely related to the grain size of that.

But over here, we encounter a different problem. The problem is that these disordered regions have very high energy and so, they can preferentially suffer corrosion so, can suffer preferential corrosion is it is very interesting.

The corrosion of the grain boundary is favored not only because of energy consideration, but also because of the kinetic considerations. If you want to remove an atom from the lattice where the atoms are all well coordinated, is difficult to remove because they are all bonded by so many other neighboring atoms.

But in the grain boundary what happens? The atoms some of them are dangling bonds. They are not really interconnected. So, kinetically it is also easy to remove these atoms that is why removing atom from a grain boundary or removing an atom from the dislocation areas for example, you can etch, you have dislocations you etch it, you get etch pits because when the atoms are loosely held, it is easy to remove. So, the grain boundaries are more favorable sites for corrosion.

The grain boundary is because of high energy, it also leads to segregation of elements. Some elements are intentionally added to improve the property of the material, some of them may be impurities. So, they segregate very heavily. In fact, you know they are in fact, thermodynamic considerations they just segregate.

You know very well right they are surface sensitive. So, they go and go to surfaces actually and sometimes segregation can be as says 10^5 times, 10^6 times, 10^4 times as compared to the bulk. When the elements are segregated, and these elements are going to

be either anodic or they are cathodic. In both the cases, they can induce corrosion of the grain boundary area. If it is anodic, they dissolve. If it is cathodic, what do they do? It induces the dissolution of the grain boundary areas.

So, the grain boundaries are not as corrosion resistant as the grains in a polycrystalline material. Having said that, I also need to caution you that the grain boundaries need not be very highly corrosive if it is a very pure element.

For example if I take let us say tin and aluminum and whose purity is the order of 99.9999 so, 4-5 9's decimals then, you know very well I think as a metallurgist you polish and etch it is not easy to etch the grain boundaries, you cannot see them very easily, but you add a small alloying element it becomes very easy to etch.

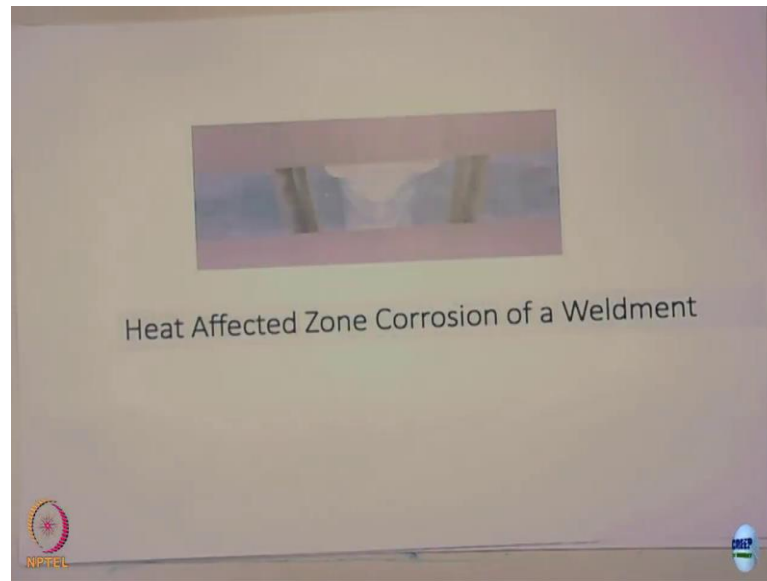
So, the grain boundaries no doubt are high energy sites they corrode, but the extent of corrosion also depends upon the kind of segregating elements present in the material in the grain boundaries especially. So, that has to be very clearly understood. Do not say that all the grain boundaries are going to corrode very heavily and so, you have problems say we have steels for years they do not undergo intergranular corrosion.

The stainless steels, certain conditions they are very prone to intergranular corrosion. Aluminum alloys certain conditions are prone to intergranular corrosion. You can have similar behavior for zinc alloys.

So, this particular discussion, this particular topic brings out what are the mechanisms involved in intergranular corrosion and of course, how do you avoid intergranular corrosion and we give more emphasis to the stainless steels because stainless steels are very widely used in chemical process industries because the stainless steels are primarily developed for corrosion resistance applications, but you build them under certain conditions, they suffer corrosion. We call the term the sensitization.

Similarly, aluminum alloys undergo corrosion at the grain boundaries because of some heat treatments. We call that as exfoliation corrosion. It is one type of intergranular corrosion. So, we will discuss this in details. Now to just give an example, how the weldments can cause selective corrosion.

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Look at this diagram. It is macro photograph of a stainless steel welded and then, exposed to the corrosive medium like sodium chloride solution in this case and you can see that, the corrosions occurred at the both these sides of the fusion zone. You know that this is called the fusion zone, it is a cross section actually, this is the thick plate and it is a cross section, this is the weldment weld fusion zone and this is the heat affected zone, the heat affected zone and you see the corrosion occurs very interesting.

The corrosion does not occur at the fusion zone nor it occurs very close to the weld fusion zone, it occurs away from that. We need to understand why it happens, why not very close to this, why not the fusion zone? It does not happen away from the heat affected zones. This is called the heat affected zone actually. They are more precisely this is called as weld decay zone.

Because stainless steel suffer extensive intergranular corrosion and the term used as weld decay and we will spend quite a bit of time on understanding intergranular corrosion of stainless steels and some time we will spend on aluminum alloys because aluminum alloys also are prone to this type of corrosion not as extensive as stainless steels though.



Now, I do understand that we have people here with a non-metallurgy background I suppose here, for them I just give a brief review of stainless steels so that, you get a clarity when we talk about the intergranular corrosion of weldments of stainless steels.

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Summary of Stainless Steel Alloy Effects

ELEMENTS	PROMOTES	EFFECT ON PROPERTIES
Chromium	Ferrite	Improves general corrosion resistance and resistance to oxidizing environments
Nickel	Austenite	Improves general corrosion resistance and resistance to reducing environments
Carbon	Austenite	Increases strength, decreases corrosion resistance
Nitrogen	Austenite	Increases strength, Improves pitting resistance
Manganese	Austenite or neutral	Improves hot cracking resistance, increases solubility of nitrogen
Molybdenum	Ferrite	Improves pitting and crevice corrosion resistance



I just show some slides here. You might find this in any standard books actually and I just summarized here. We all know that what makes the steel stainless steel is chromium. If chromium is not there, you do not call it stainless steel. All other alloying elements may be there, you can have nickel, you can have molybdenum and you can have all host of elements, but unless you have chromium, we do not call that iron alloy as stainless steel.

They have some properties; I am summarizing here briefly. I can go quickly because most of you would be aware of this. The most alloying element is chromium here. It promotes the ferrite phase I will talk about little later.

The stainless steels are classified based on the crystal structure and one of the class of stainless steels is; a ferritic stainless steel and you have simply only chromium it forms a ferritic based stainless steel and the very purpose is to improve the general corrosion resistance of the iron base alloy.

The nickel is another important constituent which improves the austenite which is essentially is a face centered cubic phase here, it also improves corrosion resistance.

Carbon it is not that you add it, but it is there actually. But it has good properties as well you know we are going to curse all through this the carbon when you talk about intergranular corrosion, but carbon is not in fact, carbon is the real reason why the

intergranular corrosion of tendencies occurs we keep cursing. But then look at this, it increases strength we will see how important it is and if you lower the strength what happen?

The cost of the reactor goes up. If you lower the strength of an alloy, you want to make a pressure vessel, you have to go for a thicker component, thicker thing then means cost goes up. So, carbon is a problem, but then we need to have, we cannot simply ignore the beneficial effect of carbon as well.


Nitrogen is other element, nowadays you come out with a nitrogen containing stainless steels. It increases strength, improves pitting corrosion resistance you have seen before to certain extent, it also improves the weld decay resistance.

The manganese is added. It also reduces the hot cracking when you weld the stainless-steel sheets. The molybdenum again is a ferritic stabilizers you have seen before. Improves pitting corrosion as well as the crevice corrosion resistance.

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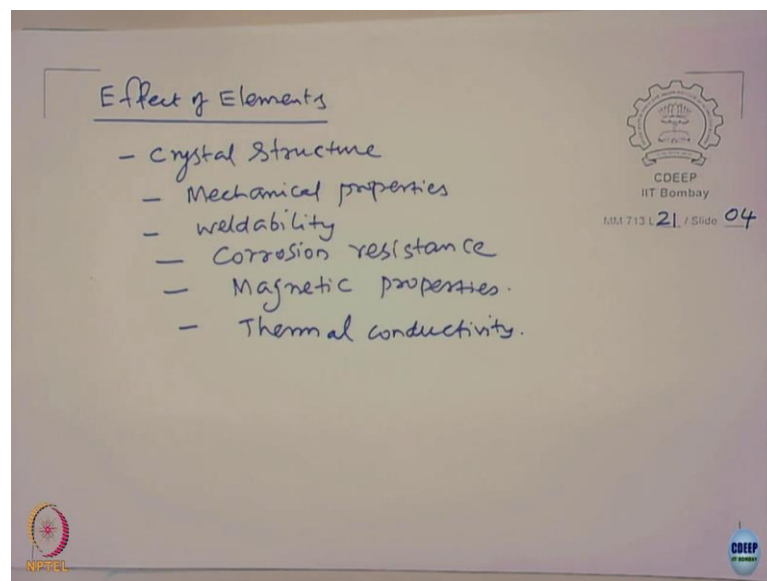
ELEMENT	PROMOTES	EFFECT ON PROPERTIES
Niobium	Ferrite	Forms stable carbonitrides to resist sensitization
Silicon	Ferrite or neutral	Improves wetting and flow, improves high temperature oxidation and carburization resistance
Titanium	Ferrite	Forms stable carbonitrides to resist sensitization
Aluminium	Ferrite	Improves high temperature oxidation temperature oxidation and carburization resistance
Copper	Austenite (weak)	Improves resistance to reducing environments. Can be used for precipitation hardening
Sulfur	Neutral	Improves machinability, promotes hot cracking
Phosphorus	Ferrite	Promotes hot cracking



Niobium is added again we will see later why we add niobium. It is a ferritic stabilizers. It forms stable carbonitrides resist sensitization, can we will see this later. Silicon it improves wetting, flow oxidation resistance all these stuffs. Titanium again has the similar effect as that of the niobium here.

Aluminum improves the high temperature oxidation resistance and the copper in fact, copper is good from the point of view of application sulfuric acids and sulfur is not good at all, but you are going to talk about a stainless steel where you need to do machining, then the sulfur is helps actually as far as promotes hot cracking. So, I given you a brief quick review of the various types of alloying elements that are added to the stainless steels.

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Now, if you look at the stainless steel, when you add these elements what do they do? These elements, effect of elements they may change the crystal structure. It is very important for us. It not only change the other properties like mechanical properties, it can also change the corrosion properties. It can lead to mechanical property changes, can affect weldability of course, it affects the corrosion resistance.

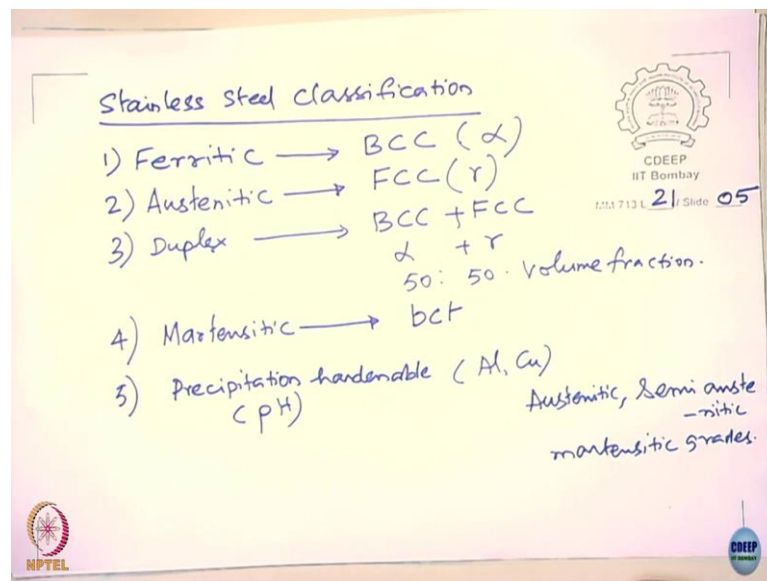
You can also look at it sometimes magnetic properties. You know for body implants what kind of stainless steels people use, you want fracture of the bone for example, what kind of stainless steel people use? People do not use ferritic stainless steels; people do not use duplex stainless steel; people use austenitic, it because it is a diamagnetic.

Otherwise, if it is magnetic then what happens? You will have problems. So, the magnetic properties sometimes may be good, but not always it can affect this. It can also affect the thermal conductivity. This is the property mechanical engineers worry about. Heat exchangers, a carbon steel conducts heat much faster than an austenitic stainless

steels. So, you have a better corrosion resistance, but the designing of heat exchanger has to be taken into account the thermal conductivity of this material.

So, these elements you know have the multiple effect on the properties. When you add these elements, they change the crystal structure and so, you have different classification of the stainless steels.

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Now, just take iron and add chromium to it, you get a stainless steel which is called as a ferritic grade stainless steel. What is the crystal structure of this is BCC body centered cubic structures. Iron at room temperature has a body centered cubic structure, when you add chromium, chromium is a ferrite stabilizers BCC stabilizer so, the crystal structure does not change. So, it remains in the body centered cubic structure.

You are going to add to this required amount of nickel then what happens? Then crystal structure changes and this is called as an austenitic grade stainless steels. The crystal structure is face centered cubic structures. Why? Because the nickel stabilizes an austenite, stabilizes a face centered cubic structure.

Now, you can have a combination of these two I can have. We call them as duplex grade stainless steels. It has got BCC structure plus FCC structures. BCC is also termed as alpha, FCC is termed as a gamma here and this is also called alpha plus gamma

structures. Generally, the volume fraction of these two phases are 50% each is the volume fraction.

Now, if you look at the strength of an austenitic grade stainless steel and the ferritic grade stainless steels and you compare with let us say high strength low alloy steels for example, or you compared with the martensitic steel for example.

You know what is the normal strength of a an austenitic grade stainless steels let us say 304 stainless steel what is the strength levels? Anybody has any idea about it? The UTS can be about 600 MPa something. You can keep increasing more amount of nickel, more chromium, I do not think the strength of the stainless steel increases significantly because they are all substitutional solid solutions.

So, in order to increase the strength of this one, what gives strength in the steel? The carbon. So, you have developed other kind of stainless steels which is called as martensitic grade stainless steel which gives you high strength, high hardness, good wear resistance.

What is the structure here? The bodies centered tetragonal, BCT crystal structure. It is like any other martensitic steel the difference is what? The difference is that it has got chromium.

So, the main purpose of martensitic stainless steel is to have high strength, high mechanical properties, but also have good corrosion resistance, but not as good as ferritic as not as good as austenitic or duplex, but certainly this is better than martensitic steel.

So, it has got reasonable corrosion resistance and good mechanical properties and so, you are not going to apply a martensitic stainless steel where you are going to apply austenitic stainless steel for chemical process industries because corrosion resistance is not that great, but you need to also have good mechanical properties. So, it is a good compromise between an austenitic stainless steel and martensitic steel actually.

You also have other class of stainless steel called as precipitation hardenable stainless steels. It is also called as PH grade stainless steels. In this case, what people do? They add aluminum, they add copper to this. The precipitates formed from the aging treatment ok, they give the strengths.

So, the precipitation hardenable stainless steels, they give you strength equal to or even better than martensitic grade stainless steels, but the corrosion resistance of this PH grade stainless steels are better than martensitic grade stainless steels, but certainly it is not going to be superior compared to austenitic grade or duplex grade stainless steels of course, they are going to very expensive kind of things.

These things they start they may be called as austenitic start from austenitic phase, semi austenitic and martensitic grades. I am not going to discuss more details into this actually. But all I would like to emphasize here is, there are different classes of stainless steels of varying mechanical properties and varying corrosion resistance.

In all these cases, chromium is an important element. The amount of chromium we add to it would change. You guys keep adding chromium, then automatically what happens? Now it is going to change the phase so, you cannot get all this. So, there is going to be a phase balance by adding the other relevant elements.

For example, if I talk about a martensitic stainless steel, I cannot get it unless I have high amount of carbon. In a precipitation hardenable stainless steel, I may not have carbon at all right I would add rather elements like aluminum and copper, then precipitate that give rise to corrosion resistance.

In a martensitic grade stainless steels, you form a martensite, you temper it forms chromium carbide some kind of carbides, the corrosion resistance drops. But that problem does not exist in precipitation hardenable stainless steels because you do not have chromium carbide like as you seen in the previous case, it is the phases related to aluminum and copper and so, the precipitation hardenable stainless steels are superior compared to martensitic grade stainless steels.

But you talk about surgical blades cutleries all these stuffs I think people go for martensitic grade stainless steels. But you talk about aerospace applications and some nuclear applications, people go for precipitation hardenable stainless steels even for because you need to go for good corrosion resistance combined with the mechanical properties.

Student: Sir precipitation hardenable alloys do not contain chromium.

It has chromium.

Student: It has minimum amount of chromium.

No, chromium can be more also. See precipitation hardenable stainless steel 17 PH it has got 17 chromium.

Student: They are also prone to sensitization?

I will come to that point now actually why they are not prone to sensitization? Why for example, a martensitic grade stainless steel is not as prone to sensitization as you find in austenitic grade stainless steels and why the ferritic stainless steels are even more prone to sensitization compared to austenitic grades stainless steels.

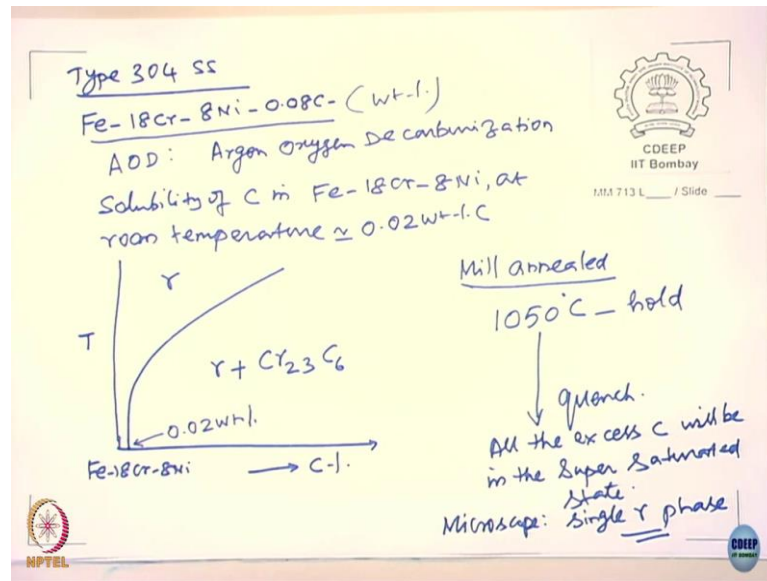
The extent of this is going to change because of crystal structure, because of the precipitation sequence it happens in these stainless steels. So, that we will see during this particular class we can do that.

So, but what I want you to do is you get a clarity because especially when you work on corrosion, you need to know the stainless steels classification and when to use, what kind of combinations are required and that should be well known of course, see I am not claiming that we cannot read, understand completely in this year.

I am only trying to probe you please go and read more details about this material, then only you can be able to; able to be a good corrosion engineer actually otherwise you just get some bare information, it is not possible for you to prevent corrosion effectively.

So, you have any questions here so far? Ok. Let us now discuss one related to the sensitization of stainless steels. Before we discuss this sensitization, we need to understand to some extent the stainless-steel composition especially the austenitic grade stainless steels.

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Let us start with the austenitic grades stainless steel let us say type 304 stainless steel. What is the major alloying element here? Iron. How much is the chromium?

Student: 18.

18 chromium.

Student: 8 nickel.

8 nickel. What is the carbon content?

Student: 0.08.

0.08. Of course, you have manganese and you have some trace alloy element of silicon and sulfur and phosphorus I am not talking about it, but these are major and important elements. As I told you need to add manganese because otherwise there will be weldability problem and see we are not looking at that now.

So, you have 18 chromium, 8 nickel, 0.08 carbon all weight percent (wt.%). You know the 18 chromium is added, it is beyond the minimum required level of chromium required to passivate and you add nickel because nickel is required to make the phase austenite at ambient temperature otherwise, austenite will appear only at the high temperatures.

The carbon; the carbon is present, those days they are found difficult to remove carbon, removal of carbon was very difficult to do that and only the process like AOD what is this called AOD process anybody?

Student: Argon oxygen decarburisation.

Argon Oxygen Decarburization right. When the AOD process was introduced, then they were able to successfully, comfortably remove carbon to large extent otherwise, the removal of carbon was a problem. In fact, you look at the old nuclear reactors and they have formed, the two types of stainless steels are used one, 304 as it is other one was called as stabilized grade stainless steels.

They know about the problem what it is, but they were not knowing how to handle to remove the carbon. But these nuclear reactors suffered the weld decay and it has been real problems you know some of the companies almost become bankrupt because of these kind of corrosion problems.

Now, when you have this, what is the issue here? The issue here is that the solubility of carbon in iron 18 chromium, 8 nickel at room temperature is about 0.02 wt.%. Please notice, I am in all these cases I refer only to the weight percent only. So, only this much only is soluble.

If you look at the phase diagram of this one, I give a part of the phase diagram here, the temperatures and this is the carbon percentages it is iron 18 chromium, 8 nickel if you look at it you will see something it goes, this is the gamma phase and this is your gamma plus and Cr_{23}C_6 phase this is the phase diagram. The phase diagram goes like this only and the carbon level here, approximately 0.2 wt.% carbon.

So, when we use stainless steel, let say type 304 case stainless steel, they use a term called mill annealed. The mill annealed type 304 stainless steel is being used, have been used also. So, when we say mill annealed what does it mean? It means they rise the temperature of this stainless steel to 1050 °C, you hold it, the holding time depends upon the thickness of the sheet or maybe here, maybe a plate or whatever, then what you do? They quench it.

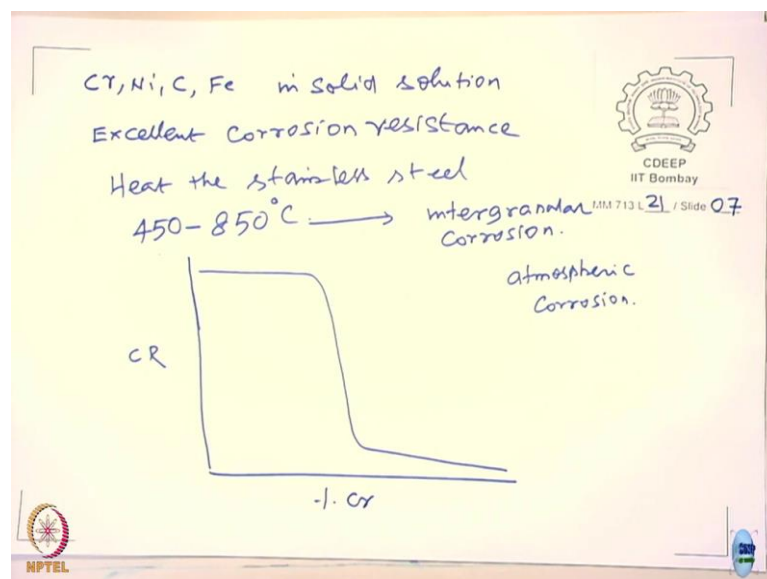
When they quench what happens now? The all the carbon, all the excess carbon will be in the super saturated state that means, they are completely soluble and what you will see? If you see only a single phase. So, look at the microscope this one, you see a single gamma phase, you will see grain boundaries, you see grains all you can see that, but you would not see the presence of chromium carbide phase. It is not going to be there at all.

I am not saying that there are no other phases you know in other sense for example, you may have manganese sulfide inclusions sometimes, sometime you may have some oxide inclusions can be there. I do not mean when I say the gamma phase, this single phase, I do not mean that there are other inclusions, but these inclusions are unwanted one, we have no way of I mean controlling them completely some amount of inclusions are going to be there.

But what I meant was that, it is the phases formed because of iron, chromium, nickel the alloying elements this these are not going to be there at all. It can be single gamma phase are going to be there. So, in this state, chromium is completely in the solid solution and provides an excellent passivity actually.

So, if you look at the microstructure of the stainless steel, I mean especially the austenitic grade stainless steel, it will be chemically homogeneous single phase that is why, the austenitic grade stainless steels are very good materials from the corrosion point of view because chemically they are homogeneous.

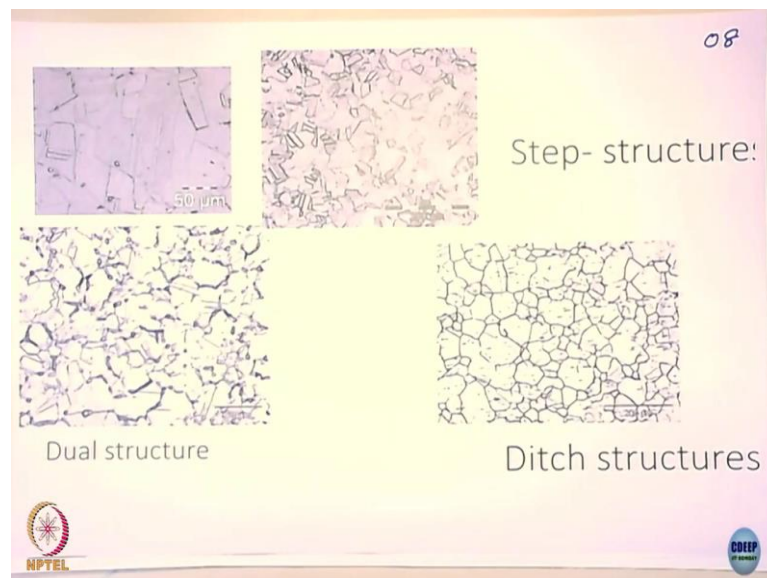
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So, chromium, nickel, carbon and iron of course, are in solid solution. So, provide excellent corrosion resistance. Suppose, now you happen to keep this stainless steel in the range of let say you heat it steel in the temperature regime of 450 to 850 °C, you say that these they suffer intergranular corrosion, they suffer very much intergranular corrosion.

Please see that the temperature has a range here 450 to 850 °C. In fact, you know it can even suffer at 400 °C also I mean it can happen even 400 °C, it can happen even in a nuclear power plant it happens in 300 °C, but it is kept for 40 years, 50 years, 60 years and all. So, you notice that the temperature is one factor, the time is another factor as we go long we will understand the kinetics of sensitization.

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So, it suffers intergranular corrosion. What it is? I have shown you the micrographs of stainless steel under different conditions of treatment. The top one you see here is, see the low magnification of this, this essentially is a mill annealed kind of situation where they heated to 1050 °C and then, quenched in water and then, they carry out a test they called ASTM A262 a test we will see later to reveal the grains here.

And you see that, I hope you will be able to see the difference here for example, you can see this, these are all grain now you can be able to see this slightly ok, you see these grains, it is another grain and in fact, you can see that, this grain is slightly a lowered

compared to this right, slightly elevated lowered probably this is little lowered elevated so, this we call them a step structure.

Please look at this grain what you see here is corroded more as compared to this, the rate of dissolution is more here. But however, look at the interface, the interface is quite clean, neat and very thin kind of grain boundary you seen here in all cases, you can see this very thin boundaries.

Compare that with the one which was held between 450 and 800 °C you do not have to worry about the temperature here, just show the difference and then, you carry out the test, you see this here now you see a clear attack on the grain boundaries, the grain boundaries are thickly corroded actually. I hope you are able to see this attack here and this is called as intergranular corrosion. The corrosion occurred selectively along the grain boundaries are preferentially one of the grain boundaries lead with corrosion here.

If the time is shorter, you see that the grain boundary attack, but the grain boundary attack is not complete now you can see this they are partly attacked here. Please notice this is not the same temperatures, the temperature times are different and so, you see that there are attack, but they are not completely attacked here. This is called as a dual structure. We will see later we called as ditch structures; we call them step structures.

So, in the mill annealed stainless steels would have features microstructure resembling this, the one which is sensitized by heat treatment process will be something like this and this is called as the sensitization. The alloy which is very good having very high resistance to corrosion, now suffering intergranular corrosion.

What is the consequence of that? The consequence of this is very simple and you see this here, it is you know straight forward not simple it is a straight forward because see that, when the grains are getting attacked corroded like that if you have corrosion occurs along with this more and more what happens now? The grains will loosen and come out of the things here.

When the grains loosen, then what will happen to the strength? Strength falls down. So, the strength falls down and if you have applied stress, the cracking occurs along the grain boundaries we call them as intergranular stress corrosion cracking. We will talk about when you deal with stress corrosion cracking subject.

But so, what I am trying to say that these are all prone to corrosion and leading to grain falling and leading to intergranular cracking if you have stresses. If there is no stresses, simply grain falling, the stresses the crack starts moving and then, leading to separation of the component into two parts or many more parts actually. So, that is what will happen. So, it is not a good thing from the structural point of view.

I think we can stop here. We can have the discussion in the next class about the mechanism of sensitization or mechanism of intergranular corrosion of stainless steels. Any questions you have?

Student: Yes sir.

Yeah.

Student: Why 12 wt.% chromium is required in stainless steel to attain passivity?

Why they are adding now this is a good question. See I will tell you what happen. The one we talk about 10% and 12%. How it came? The 12% came by examining the corrosion resistance stainless steels in relation to atmospheric corrosion. They exposed with the atmosphere.

And determine the corrosion rate for example, you see you would have seen this curve, you would have seen this curve corrosion rate versus the chromium content it is something like that it goes. This diagram corresponds to atmospheric corrosion and so that is not a very aggressive environment. So, the definition of stainless steel came from that only.

Of course, you have to start, see you cannot say that you call a stainless steel ah, you cannot designate a stainless steel based on the environment. I cannot say that this is a stainless steel, I call it when I use for atmosphere and I cannot call it as stainless steel when I use for a chemical process industries you cannot do that. So, it is a kind of thumb rule only I say there is no first principle involved in over here first answer.

The second answer is that, the effect of chromium would also depend upon other alloying elements like when you add for example, when I carbon, the corrosion resistance come down right. Similarly, when you add nickel, I would need a little bit

more chromium in order to do that because the enrichment of chromium on the surface. See essentially what happens it has to form a nice passive film protective film.

The passive film formation would depend upon what? Depend upon the environment, it also depend upon other alloying element. When you add other alloying element, then it is possible that the enrichment of chromium on the surface is not that much and so, it depends upon other alloying elements, it depends upon the other environment and so, it is so, that is why you always add to more.

In fact, you look at the stainless steel classification now, ferritic stainless steels lean grade, normal grade, super ferritic, super austenitic all these comes because of this particular reasons. The duplex stainless steels you call it lean grade duplex stainless steels because that bare minimum required some like storage tanks, I do not need huge amount of nickel not required.

So, this is not a very rigid I would say, but you need to have some definition in order to call it as a stainless steel, but that seems reasonable which is atmosphere is a some mild corrosive environment actually ok.

Thank you.