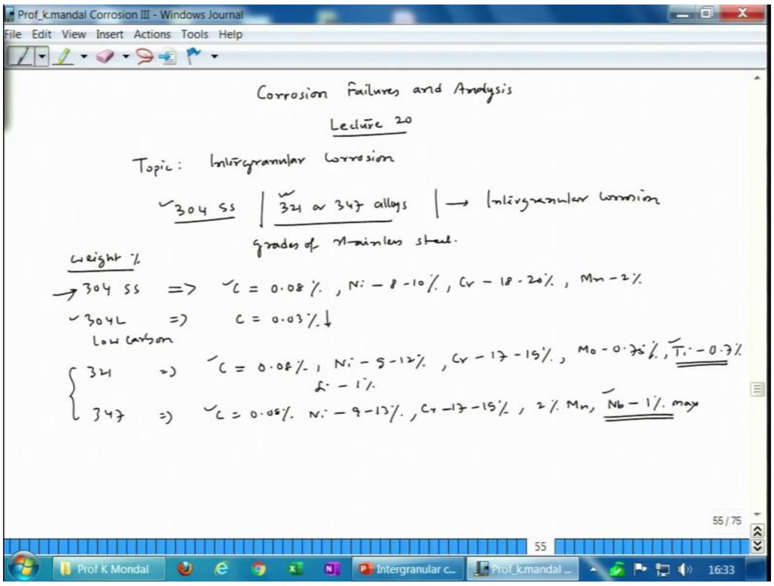
Corrosion Failures and Analysis
Prof. Kallol Mondal
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 20
Intergranular corrosion in case of 304, 321 and 347 stainless steel

Welcome to the course, Corrosion Failures and Analysis. Today we have lecture 20 and our topic will be Intergranular Corrosion.

(Refer Slide Time: 00:30)



Corrosion Failures and Analysis

Lecture 20

Topic: Intergranular Corrosion

✓304 SS | ✓321 or 347 alloys | → Intergranular corrosion

grades of stainless steel.

weight %

→ 304 SS => ✓C = 0.08 %, Ni – 8-10%, Cr – 18-20%, Mn – 2%

✓304L => C = 0.03% ↓

Low carbon

321 => ✓C = 0.08%, Ni – 9-12%, Cr – 17-15%, Mo – 0.75%, Ti – 0.7%

Si – 1%

347 => ✓C = 0.08% Ni – 9-13%, Cr – 17-15%, 2% Mn, Nb – 1% max

So, the course is. If you recall in our last lecture, we started discussing on intergranular corrosion of stainless steel 304, as well as aluminum lithium 8090 series one of the alloys.

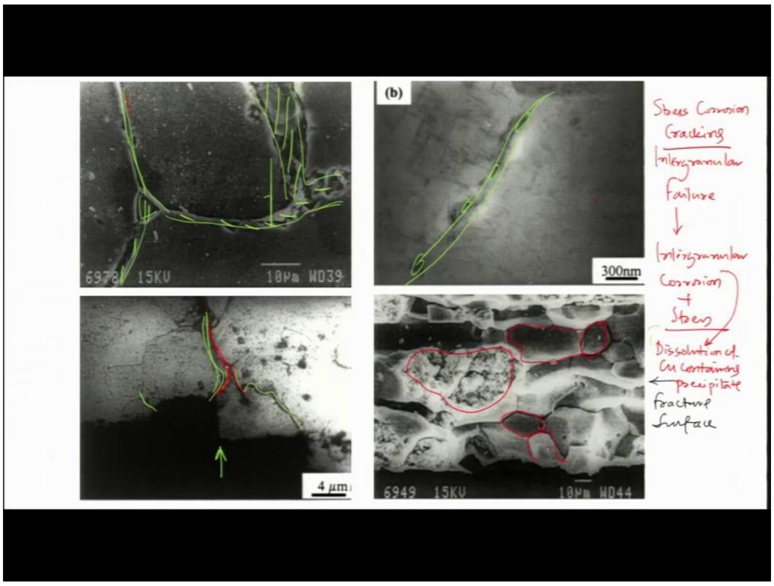
And we saw two instances; one is in case of stainless steel, we have chromium carbide precipitation along the grain boundary and surrounding region of that grain boundary is depleted with chromium and that is what makes it susceptible to intergranular attack. Whereas, in case of 8090 series alloy, where we have precipitation of t 1 or t 2, which are copper containing precipitates is aluminium copper lithium. These three elements are present in those precipitates.

And those precipitates forms along the grain boundary and those dissolve, because those are active precipitates. And there is kind of a de-alloying type situation, copper deposits back on the grain boundary. And we saw that along the grain boundary we have after we had stress corrosion failure of 38090 series aluminum lithium alloy. We examined the grain boundary region and found that it is enriched with copper then, copper content have copper content has reached up to around 70 percent. It is starting from around 1.6 weight percent copper.

So, this is a specific example. This is a kind of typical example of de-alloying and re deposition of copper on the grain boundary. And also, with the help of optical micrograph we saw that yes, the grain boundary attack is taking place. So, in that case, its active dissolution of active precipitates making the grain boundary susceptible to corrosion and that is what it is a severe grain boundary corrosion.

And we have stress which is active and that stress lead to failure in the mode of inter granular fracture ok.

(Refer Slide Time: 03:03)



Stress Corrosion Cracking
Intergranular Failure
↓
Intergranular Corrosion
+
Stress
Dissolution of Cu containing precipitate
← fracture surface

So, if you see this picture so, this is the picture we explain. Along the grain boundary we have. This is the grain boundary attack these are the grain boundary and we saw copper enriched zone and this is the optical micrograph we talked about and you see the dissolution is taking place along the grain boundary ok.

And we have those precipitates forming along the grain boundary and at the same time the fracture surface, because it has lay it has gone under stress corrosion cracking.

Fracture surface also shows a typical inter granular fracture, because it has faceted grains, because those grains have been detached have got detached due to intergranular mode of failure ok.

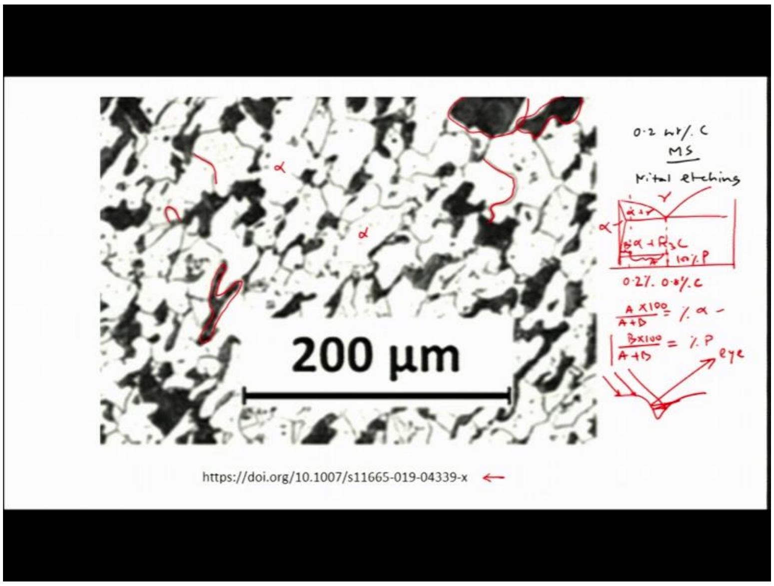
So, this is one typical example where active precipitates dissolve leading to intergranular failure and stress is acting so, that it actually failed in the mode of intergranular failure in the in a and leading to intergranular fracture mold ok. But, in case of in case of stainless steel 304, we have a different situation.

So, we will explain more on that particular aspect, but before I go to that 304. We discussed in the last class that grain boundary evolution of grain you see when you see a multi grain steel, which is let us say mild steel 0.2 percent carbon steel. So, there we saw grain boundaries along with that we have along the corners of the grain we see some amount of pearlite ok.

(Refer Slide Time: 04:51)

https://doi.org/10.1179/174327805X46913

(Refer Slide Time: 04:52)



https://doi.org/10.1007/s11665-019-04339-x

So, that structure let us just have a look at it. So, this is one typical structure point around this is 0.28 percent carbon mild steel MS ok and this is etched Nital; Nital etching and we saw typical grain boundary under optical microscope so, these are the pearlite zone so, these are the zone so, these are the pearlite zone ok. These are the pearlite colonies, because we have certain fraction of pearlite there in mild steel, depending on the depending on the phase diagram.

So, if you see the phase diagram of a steel on the steel part. So, this is the this is 0.8 weight percent carbon. And this is alpha this is alpha plus gamma this is gamma region and this is alpha plus Fe_3C ok. Now, 0.2 if you consider, this will be 0.2 percent and this is your 100 percent pearlite.

So, now if you try to see tie line. So, this amount of so, this there are two arms. So, let us say this is A arm this is B arm so, A divided by A plus B arm would be the fraction of alpha. And if you want to calculate fraction of pearlite so, B arm divided by A plus B arm, would be percentage you just multiply it with 100 you get percentage of pearlite ok.

So, now that is what here you see that is B amount is very small this fraction is small much smaller than this. That is what you have little amount of pearlite present, but rest of the thing will be alpha grain so, these are alpha grains these are all alpha grains and this is optical image.

And you see this grain boundary. So, these are the grain boundaries these are the grain boundaries fine. And these grain boundaries have evolved due to the mechanism I explained in the last lecture, that there is a preferential dissolution along the grain boundary.

And that is what so, thus profile looks like this and there will be light ray is coming falling here and there will be multiple reflection and then finally, the light comes to the eye. And that multiple reflection of the light leads to reduction of the strength of that particular light ray so, that is what it becomes grayish in color or black in color.

So, this happens because there is a small tip, because of the electrochemical dissolution along the grain boundary, but this is not intergranular corrosion. Though it has a typical grain boundary attack, but it cannot be cannot fall under grain boundary corrosion, because for the grain boundary attack or intergranular corrosion, two conditions are to be met.

One is there could be precipitates and forming precipitate free zone, or precipitates are forming that precipitate would lead to dissolution and leading to intergranular failure. So, that is what those two factors are there, but there could be another situation which will be very unusual, but it happens sometimes.

For example, some elements might get entrapped along the grain boundary for example, iron in aluminum ok. So, that might get along the grain boundary so that lead to activity extra activity of that grain boundary could be attack along the grain boundary, but otherwise, it relates to the precipitates formation and that lead to inter precipitate free zone or a depletion of element one of the elements along the grain boundary, or a dissolution of active precipitates ok.

So, these are generally the commonly observed situations we experience, in case of intergranular failure. Sometimes, it happens that those precipitates which are forming, that could be noble and surrounding region could be susceptible to intergranular corrosion or that could itself become active, dissolve and then, leading to intergranular failure.

So, I just wanted to show you the typical picture what we get in case of mild steel, when we have optical microscope, when we metallographically prepare the sample and etch it under in Nital, and that is what the typical structure you get. So, if you want to get want to see this particular structure, you can refer to this particular paper so this is the work at done at IIT, Kanpur ok.

So, now, coming back to our discussion. So, now, today what we will do? We will try to analyze intergranular failure or intergranular corrosion in case of 304 stainless steel ok. Or we can also analyze intergranular corrosion in case of 321 or 347 alloys ok. So, these are some of the grades of stainless steel.

So, if you want to see the general composition range. If you see 304 SS is composition is around its a range let me put a range carbon is about 0.0 weight 8 percentage so, these are all in weight percent. Nickel is around 8 to 10 weight percent or let me not mention all the time weight percent, because these are all in weight percent, fine.

Then, chromium is about 18 to 20 percent fine. And there could be a little bit of manganese 2 percent; so this is a general composition. So, if you try to see 304 L and L means low carbon. So, only carbon changes to 0.03 percent ok so rest of the compositions remain in the same range ok.

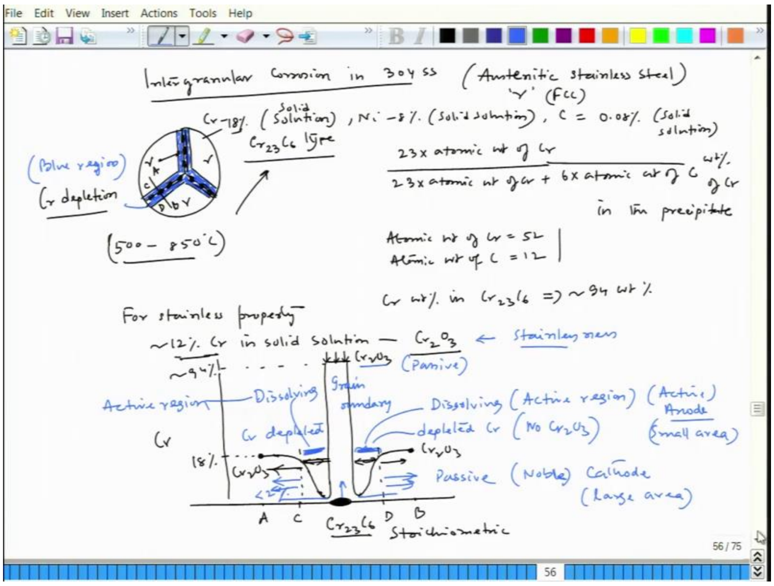
Now, you can have 321, which is if we consider the carbon part carbon is 0.08 percent there and then, nickel is around 9 to 12 percent, chromium about 17 to 19 percent there could be little bit of molybdenum 0.75 percent and then, titanium 0.7 percent, bit of silicon. Silicon also could be present around 1 percent so this is the typical composition of 321. And here, important aspect important thing to note is basically the titanium this is very important.

Now, 347 so I just wanted to mention this composition ranges, because this will come for our discussion when we try to understand the control of intergranular corrosion in stainless steel. Here, carbon is 0.08 percent, nickel of the same level around 9 to 13 percent, chromium 17 to 19 percent. And here we have around 2 percent moly manganese and we can have and here, the most important part what is to be understood is niobium, niobium is about maximum 1 percent ok.

So, here the most important part to mention is this niobium content ok. Now, if you see the composition between these two and this, the only difference is basically here, we have titanium presence here we have the niobium presence. But, here we the difference is between all 4; whatever we have explained, the carbon content is very low compared to this this and this ok. So, these are the typical compositions.

So, there we try to find out and these are all susceptible to intergranular corrosion. But, the mechanism of intergranular corrosion what we experience in this case, is entirely different than the mechanism, what we experience in this particular alloy systems.

(Refer Slide Time: 13:58)



Now, let us look at the intergranular 304. Now, we have shown one typical picture. If you see a grain of this particular alloy, which is typical austenitic austenite austenitic stainless steel here everything is austenite, which is FCC fine face centered cubic. And here the precipitate forms which are basically, forms a kind of network of precipitates along the grain boundaries and this precipitate is basically nothing but $Cr_{23}C_6$ type ok.

Now, if we compare if we try to find out the chromium content and carbon content. So, chromium is about close to 18 percent let us say in the base metal and those are all in solution or we can say solid solution chromium content. And nickel 8 percent, which is also in solid solution and carbon which is 0.08 percent, which is also in solid solution. And if we try to find out this chromium content here so, we can roughly find out the chromium head this is the formula.

So, we can find out 23 into atomic weight chromium divided by 23 into atomic weight of chromium plus 6 into atomic weight of carbon. So, that gives the weight percent of chromium in the precipitate ok. Now, if we try to find out the atomic weight of chromium so, atomic weight of 52 and atomic weight of carbon is 12.

So, from that if we put those values, we can get the chromium weight percent in $Cr_{23}C_6$ is of the order of close to 94 weight percent ok so; that means, that much of chromium it needs for the formation of that chromium that is $Cr_{23}C_6$. Now, chromium being substitutional atoms; substitutional atom mean that particular solid solution. And at room temperature at not room temperature, because it happens at a elevated temperature so, around 450 or 500 that 500 to 850 degree Celsius.

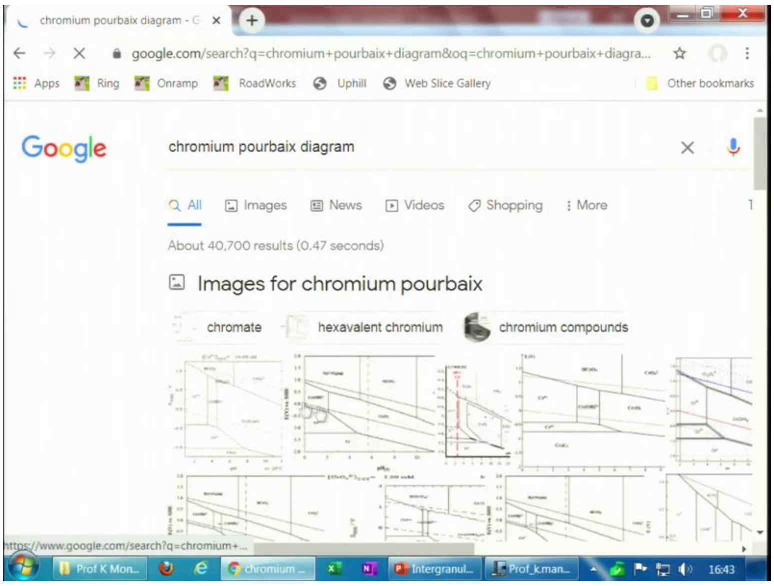
So, this is the temperature range, where this precipitate happens ok it does not happen at room temperature ok. At that temperature since it is a substitutional atom. So, its diffusion is sluggish as compared to the carbon, because carbon is much smaller atom and it is interstitial atom. So, that is what the carbon diffusion is faster than the chromium diffusion. And, because of that particular reason, the chromium cannot come from a large distance to form that particular type of precipitate.

So, chromium cannot come from a bulk to this and then form this kind of precipitate. So, chromium has to come surrounding regions of that particular grain boundary. So, now, if this and you need this much of chromium so, huge amount of chromium is needed to form $Cr_{23}C_6$ type of precipitate. And that happens by supplying chromium adjacent to that particular zone adjacent to that zone and so, in this zone; in this zone chromium gets depleted, because it does not allow long distance diffusion of chromium so, that is what it has to come from adjacent region.

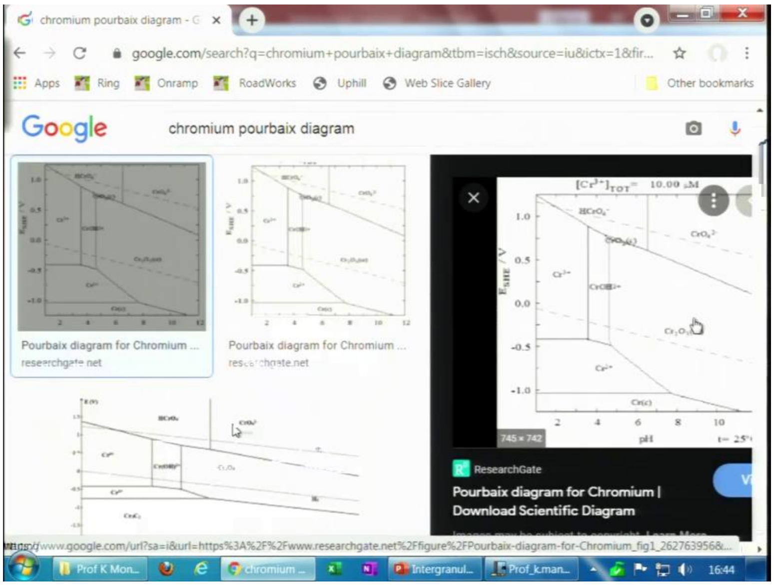
So, this region chromium depletion happens fine, that blue region fine chromium depleted zone Now, because of that chromium depletion now, here we have very high amount of chromium along the grain boundary, because of those precipitates, but surrounding region has a very low chromium and then, rest of the region again we will have 18 percent chromium.

Now, for stainless property, we need around 12 percent chromium in the solid solution and it gives stainless property, because it is passivates quickly and this is usual practice that we say that Cr_2O_3 that precipitate forms. It is not that simple there could be a complex hydroxides also if we see chromium Pourbaix diagram. Let us see that since it is important.

(Refer Slide Time: 20:38)



(Refer Slide Time: 20:47)



So, Chromium Pourbaix diagram you can look at. If you see this particular diagram so, here you can see this, where I my small arm is circulating.

(Refer Slide Time: 20:51)

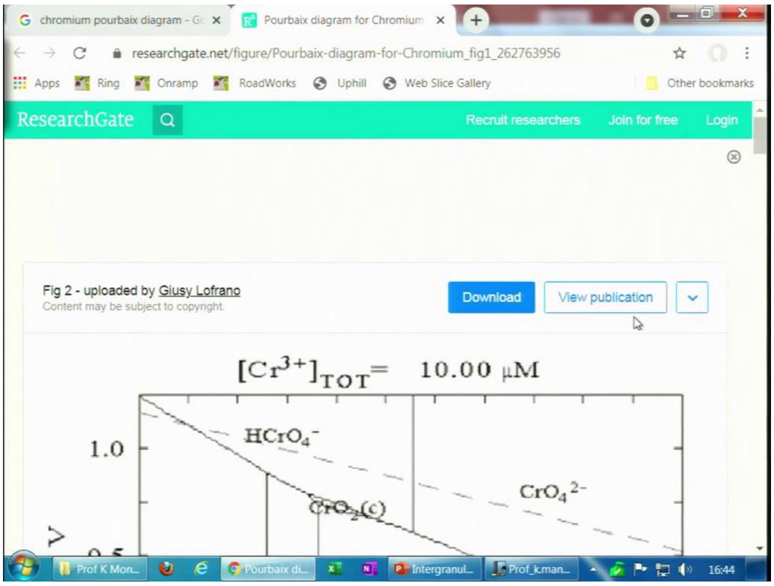
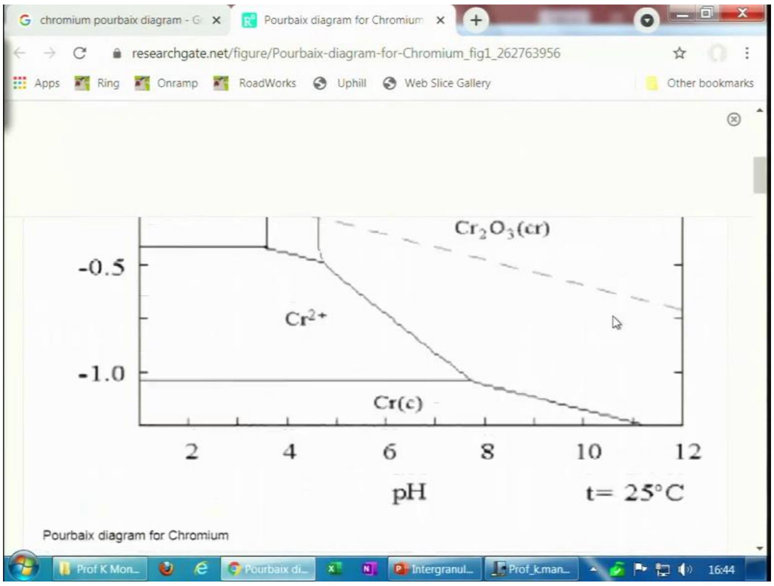


Fig 2 - uploaded by Giusy Lofrano
Content may be subject to copyright.

(Refer Slide Time: 20:53)



Pourbaix diagram for Chromium

So, this region; so this is the wherever my cursor is following so, that is CrO_2 C region. So, that forms on the surface of steel and that gives you stainless property. So, for that you have to have 12 percent chromium ok. So, if you do not have that 12 percent chromium, it does not give you stainless property ok. So, now, question is, because there is a depletion zone.

Now, we can have let us say this is one such precipitate let us say, I want to see composition across this line what we have drawn; that line goes through the bulk of the grain this is austenite grain bulk of the grain then, it comes in contact with the chromium depleted zone. And then, it goes through chromium carbide precipitate and then again depleted zone and then finally, it enters into the bulk ok.

As we have seen that the chromium has been taken from the surrounding region that is what the chromium depletion happens along the grain boundary, because the chromium has lesser diffusivity compared to carbon. So, that is what chromium cannot come cannot migrate long distance so, that was the reason I have given. But now question is we can also plot the composition along that particular line.

Let us say this is the line; this is AB line ok. Along the AB line, if we try to symmetrically if we try to see the composition of chromium. So, this is chromium and let us say, this is A part this is B part. Now, this point let us say C and this point is D ok, the interface between depletion zone and the bulk and then, we have precipitate. So, let us say the precipitate at the center. This is the precipitate, this is the length scale of the precipitate let us say this is Cr_2O_3, sorry.

This is $Cr_{23}C_6$. And let us say this is the interface C and D. Now, this is 12 percent this is 18 percent in the bulk. So, this is 18 percent so, this is the point and here, also 18 percent this is the point. Now, as we go towards the C point, the composition is gradually start falling here; start falling here fine. So, around C region, the composition starts falling. Similarly, here also same situation prevails fine.

Now, as the composition this is the chromium composition I am try trying to plot. Now, once it comes to this particular $Cr_{23}C_6$, the composition again shoots up ok. And since this is compound and if we consider it to be stoichiometric. So, it will be a straight steep rise of chromium content and here, it will be the percentage of chromium what is close to 94 percent right.

So, now you could see that in this zone; in this zone, chromium level can go which is the minimum value here that can go even less than 2 percent ok, because this chromium has been taken surrounding that grain boundary region and this is falling on grain boundary, this is falling on grain boundary so, here it is depleted. Depleted with chromium, chromium depleted.

Now, chromium needs to be more than 12 percent for stainless steel, stainless property or we can say stainlessness. Now, since we have a small region, which does not have chromium which can give the stainless property; that means, chromium oxide cannot form over there if we expose it to the environment.

But chromium oxide will form easily form this onwards this onwards, but in this zone in this zone chromium oxide cannot form again chromium oxide can form here. So, here chromium oxide here chromium oxide here chromium oxide, if we consider passivation, but this zone this part, which is this zone and this zone no chromium oxide ok. So, it does not passivate over there.

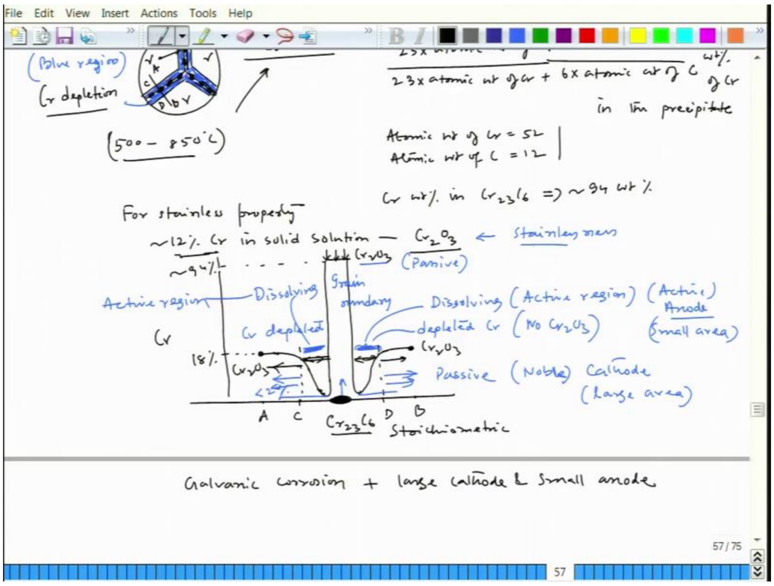
So, if it does not passivate then what happens? It starts dissolving. And here, also chromium oxide would form, because it has sufficient chromium for the passivation ok. So, that is what that particular thin grain boundary region, wherever we have chromium oxide chromium carbide precipitate that would also be passive that would also passivate it.

So, now, this is active region, this is active region and rest of the part; rest of the part. So, we can say this particular sites rest of the part will be passive this is also passive, wherever we have chromium oxide wherever chromium is more than 12 percent. Now, we have a thin region which is active and rest of the things are passive. Now, interesting thing is active region must dissolve.

Now, if you recall in the galvanic series, we talked about passive stainless steel active stainless steel. This is the typical example of active and passive stainless steel, because whenever compare active in the galvanic series, the same stainless steel if it is a passivated mode, it has a very high position in the galvanic series and the same steel if it is in the active mode that has a position much lower in the galvanic series.

So, that is what this will act as noble and this will act as active or anode and this is cathode so; that means, there is a galvanic corrosion here ok. And the small section which has a very small area and that small area and here, we have a large area.

(Refer Slide Time: 29:09)



$23 \times$ atomic wt of Cr + $6 \times$ atomic wt of C — wt.% of Cr in the precipitate

$(500 - 850^\circ C)$

Atomic wt of Cr = 52

Atomic wt of C = 12

Cr wt% in $Cr_{23}C_6 \Rightarrow \sim 94$ wt%

For stainless property

~12% Cr in solid solution — Cr_2O_3 ← Stainlessness

Galvanic corrosion + large cathode & Small anode

So, now, we have two effects; one is galvanic corrosion plus large cathode and small anode. So, now, what happens? These two effect will lead to a huge corrosion along the grain boundary of that chromium depleted zone. So, that is what this blue portion will have huge corrosion attack, the rest of the portion will be protected.

So, that is the mechanism it happens, when we have chromium carbide precipitated along the grain boundary ok. And why grain boundary chromium carbide forms? Because the grain boundary provides heterogeneous sites for the chromium carbide precipitations.

So, let me stop here. We will continue our discussion on topic in our subsequent lectures. This is very important and we have to understand that ok.

Thank you.