Corrosion Failures and Analysis

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Lecture - 21
Intergranular Corrosion: Sensitization and Weld Decay

Welcome back to the course Corrosion Failures and Analysis, today we have lecture 21 and we will continue our discussion on Intergranular Corrosion. And if you see that last lecture we realized that the chromium carbide precipitation along the grain boundary and then subsequent chromium depletion zone along the grain boundary which is adjacent to the grain boundary, that region becomes highly anodic. Because it is chromium content goes down to even less than less than 2 percent which is in weight percent of course.

But rest of the part of the alloy or the soft alloy surface contains 18 percent chromium which is sufficient for passivation to take place, so that become passive stainless steel. At the same time along the grain boundary you have all those network of chromium carbide which is $Cr_{23}C_6$ kind of chromium carbide, so they will also get passivated.

So, that narrow zone which is the depleted in chromium which is the basically depleted in chromium that becomes anode and that anode is highly a narrow region and surrounded by a large cathodic regions because passivated SS or the passivated stainless steel would be noble as compared to the those active stainless steel part.

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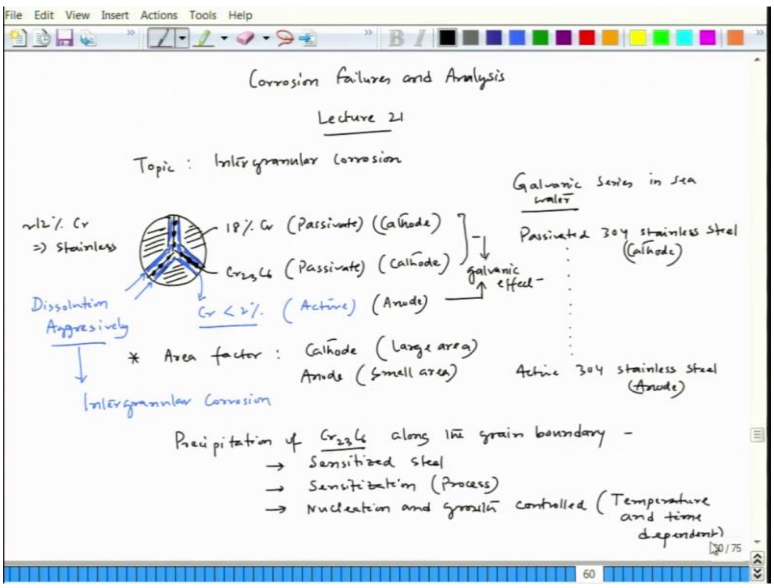

So, the course is lecture 21 topic Intergranular Corrosion. Now, as we have discussed in the last lecture we took one microstructure of austenitic stainless steel which is 18 8 and then we saw along the grain boundary. We have chromium carbide precipitation and it forms a network and this narrow zone this zone basically are actually depleted with chromium and that creates a section which is highly anodic, because 12 percent chromium is needed for sufficient passivation to achieve.

So, the 12 chromium should be required in order to make it stainless steel ok or stainless. Now, around this zone which is huge area of the green that contains the here we contained 18 percent chromium so they will passivate, but even the narrow zone of grain boundary it is $Cr_{23}C_6$. So, passivate sufficient chromium for passivation to take place. But this zone which is the depleted zone where chromium is less than 2 percent will be active it will not passivate.

Now, as per galvanic series if you go back to the galvanic corrosion galvanic series in salt solution NaCl solution or sea water passivated 304 stainless steel is sitting at a very high level in the galvanic series as compared to the active 304 stainless steel. So that means this zone will act as cathode and this zone will also act as cathode and the narrow section which is anode.

So, now there will be galvanic effects. So, this lead to so these 2 and this one they will have strong galvanic effect since these are lying further apart in that galvanic series. So, this is cathode and this is anode that is what it is taking place. Now at the same time there is one more effect that is coming into picture area factor. Since cathode here has large area and anode here which is the depleted zone this blue part is a small area.

And since it cathode area is large so the cathodic reactions have more area and that is what larger number of cathodic reaction would take place which require electron and that electron would be supplied by this narrow anodic region. And that is what the dissolution of this zone will take place aggressively and it leads to intergranular corrosion in stainless steel. Now, coming to this particular phenomena that precipitation of $Cr_{23}C_6$ kind of precipitate along the grain boundary.

So, that process we call it as when this happens then only this depletion happens along the grain boundary adjacent to the grain boundary actually that blue region. So, that time we call that the steel has become sensitized steel and this process is called sensitization.

Now, for this sensitization we need precipitation of this particular phase which is actually a nucleation and growth controlled fine. And whenever it happens that means it is basically temperature and time dependent fine.

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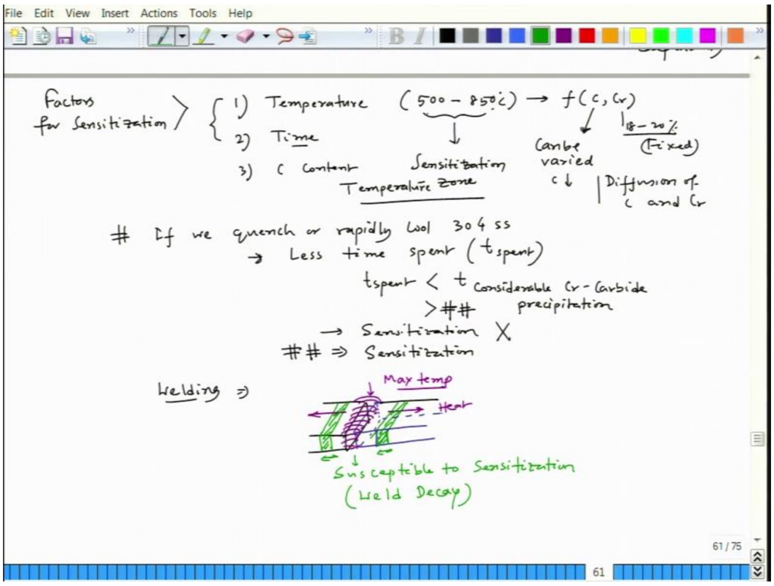

So, if something is temperature and time dependent; that means, for this sensitization to happen we have 2 factors for sensitization 1 temperature and this is more or less universally proven that in case of 18 8 stainless steel which is and rather most of the stainless steels where this 18 8 close to that 18 8 ratio is maintained. So, there we have that particular temperature zone where chromium carbide precipitation is enhanced.

So, that is around 500 to 850 degree Celsius this temperature can vary from either side ok, so it can also reach to around 900 degree Celsius. But this is a kind of a general range where this precipitation happens and this precipitation temperature also depends on function of carbon content as well as chromium content.

Why? Because for this phase to form you need both chromium and carbon but chromium you cannot reduce, because chromium is in the range of 17 to 18 to 20 percent ok, so this is 18 to 20 percent. So, this is essential because that chromium actually gives you the stainless property.

Hence that carbon is becoming important because chromium is fixed this is fixed this is fixed. So, the carbon is can be varied can be varied mainly if we have higher carbon, so then of course chromium carbide precipitation would become easier. Because it has much more solute content for the precipitation to for the accumulation of carbon and get this particular to come out as this particular precipitate. But if carbon content decreases of course that precipitation kinetics slows down ok.

So, that means second part of course this is that means if it is dependent on temperature and it is a nucleation process. And at the same time one more important factor is why it in why it finds a place along the grain boundary, because grain boundary provides heterogeneous nucleation sites that is what it actually tries to form on grain boundary.

So, I will come to that part, but here this is one part and then 2nd part is time, more would be the time within this temperature zone higher would be possibility of formation of chromium carbide, because it is a time dependent. Temperature as well terminal because for that you need diffusion of both carbon and chromium fine, so since it needs diffusion it is a diffusion is a time dependent process. So, that is what time is important.

Now, as I said that more would be the time spent by that particular metal within this temperature zone higher would be the chance of formation of chromium carbide. Now, third factor which actually becomes important in the case of stainless steel. Since we see that the chromium cannot be changed which is the fixed content, if chromium you reduce chromium carbide formation will be reduced, but that we do not want so the carbon can only be controlled.

So, you can say the corollary may be a 3rd factor which control sensitization is the carbon content, provided there is no stabilizing elements. So, just at this moment that there are elements like titanium or niobium they try to stabilize stainless steel. So, we will talk about that addition of niobium on titanium into the stainless steel for making it stabilized. So, that is a falling under control of sensitization. But at this moment we have these 3 factors.

Now, first we will talk about these two part these two part will be important. Now this particular temperature zone we call it sensitization zone sensitization zone or sensitization temperature zone temperature zone. Now this kind of sensitization is possible as you understand from this discussion that, if the steel somehow is taken to the temperature range and we leave it there for some time.

Now, question is if some stainless steel is made and then if it is rapidly quenched to the room temperature. Then of course, the time spent within this temperature would be very small and if that time spent is less than the time required for the sufficient precipitation of chromium carbide along the grain boundary definitely the problem of sensitization would not happen. So that means, if we quench or rapidly cool stainless steel or here the we are talking about 304 SS, so that would allow less time spent.

So, let us say this is t spent ok. So, if this t spent is less than the time required for considerable Cr carbide precipitation chromium carbide precipitation. Of course, due to rapidly cooling when it cools from a higher temperature within this temperature range the time spent is these spent and that is less than the time required for considerable carbon chromium carbide precipitation. And then by the time it drops to room temperature no problem of sensitization will not be absorbed.

But if this time is more than this so that case this is the case, so this is the case where you get sensitization fine. So, this problem is not there but question is if you have to have a component made component made out of stainless steel of this particular grade of stainless steel you need to have welding ok that is joining operation. So, the welding is needed and during welding of course you have two parts this is one part and the another part is this is another part.

So, now here you are doing welding, so the welding is done welding is done. So, that is basically the metal pool and now here we have large heat and the maximum temperature max temperature, because there only we are putting that beam if we do electric arc welding that electric arc is held over there.

So, that is what that will be the highest temperature, now this heat will be dissipated and this dissipation would also happen through conduction. So, the heat is going either side, so the base of that particular both the sides will also be heated up. And interesting observation is if thus this heating is somewhat not very fast we get to see a region which is close to that particular weld pool, but little away from that weld pool in both the sides.

Both the sides we have a zone which is forming say this zone will be susceptible to intergranular corrosion. So, the this green zone this part and this part are basically susceptible sensitization. And since its taking place due to the welding operation we call it weld decay the sensitized part both the sides of that weld 304 SS is called weld decay.

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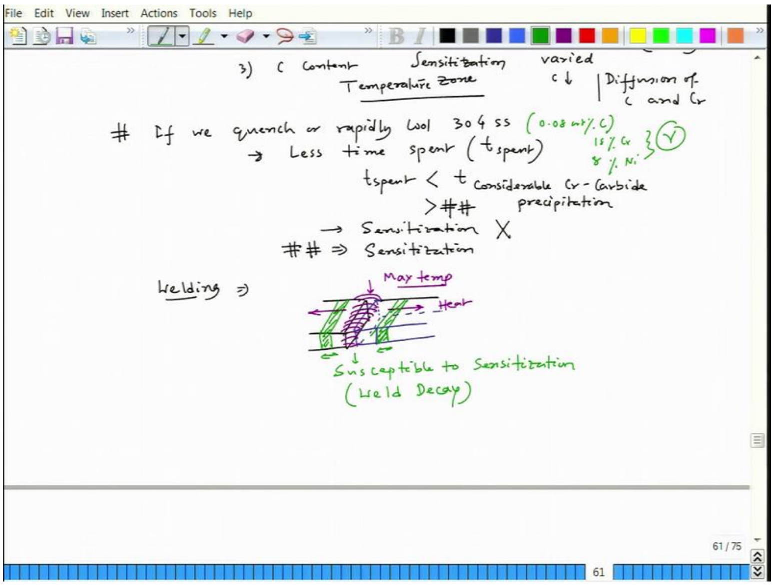

Now, we have to understand why it happens and it is very normal that it can happen if we weld 304 SS which contains this is very important which contains 0.08 weight percent carbon and 18 8 this is still 18 8, 18 percent chromium and 8 percent nickel and this structure is single phase austenitic ok gamma iron is basically a gamma iron ok. Now, why it happens because if we try to see in two dimension how much time I have.

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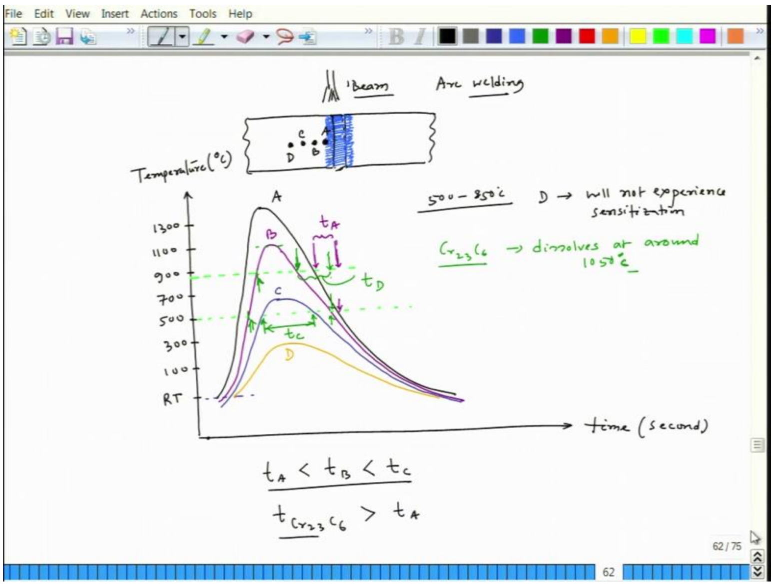

Now if we see it in 2 dimension, so now let us say this is one part this is another part these are the two parts of that same steel component 304 18 8 stainless steel. Now this is the weld zone this is the weld part, so this is the weld pool and now if we put thermocouple here. So that means, this weld pool will spread some distance here both the sides because the base metal needs to be melted also ok. So, then only you can have a very good union.

Now, if we put thermocouple at the junction point of the weld pool and the base metal and then at a particular a regular distance, let us put another thermocouple here another thermocouple here another thermocouple here. So, this thermocouple will try to measure the heat received and that heat received will lead to a temperature. So, actually this thermocouple will measure the temperature at that those points.

Now, this lets name those thermocouple A let us say this is A part this is B this is C this is D and we can have temperature time profile of those thermocouple. And of course, the center part which is actually getting those beam, this is the beam part. So, that center part will be the maximum temperature, but away from it the temperature profile the maximum temperature would definitely decrease, because heat is actually getting dissipated by conduction through the metal.

Now, if we try to look at the time temperature profile let us say this is my temperature axis and this is my time axis and let us say let me just see what happens. And the temperatures are basically let us say this is 1300 let us say this is 1100, 900, 700, 500, 300 like that way it goes up to room temperature. So, let us say this is room temperature fine.

Now, from here heating is done, since the heating stage it will be very steep because you are actually having that beam close to that particular weld pool, so heating stage it will be very steep fine. And since it is away from the melt, so it cannot reach to the and it let us say degree centigrade ok cannot reach to the melting point of that particular metal fine if it is little away from that particular melt zone.

Now, when you cool let us say you remove the beam. So, it will rapidly cool because it was arc welding arc welding is employed. We will discuss why in stainless steel welding we never use gas welding ok. So, the arc welding so the heating, so the cooling would be sluggish because it is a basically in normal air it is left. So, it is a normal the way it actually goes for a normal cooling. So, the cooling curve would be somewhat like this ok.

Now, then at the B point also we can plot fine now the C part C thermocouple also can you can draw fine and the D part D thermocouple can show you and for example this though I have taken it to downwards so actually it is starting here fine. So now D part ok so these are the temperature profile fine. Let us say this is in second now as we see that the sensitization temperature range is around 500 to 900 let us say 850 degree Celsius ok.

So, let us put a boundary there. So, this is let us say 850 this is the 850 and 500 is this one ok. Now let us see how much time a particular thermocouple is staying within that particular magic temperature range, where the sensitization or chromium carbide precipitation would happen. Now if we consider the A part, so this is corresponding to A thermocouple this is corresponding to B thermocouple this is corresponding to C and this is corresponding to D thermocouple fine.

Now in case of D of course, that particular position of that particular metal is not able to reach to 500 even it stops there at around 300 or 250 280. So, since it is not able to reach to that 500 more than 500 it will never experience this particular temperature zone ok in case of D, so D will not experience sensitization. Since this is not reaching to that level of temperature.

Now, in case of C yes if you see that it is entering the that particular temperature at this point and leaving that particular temperature at this point. So, the total time spent within that 500 to 850 degree Celsius temperature is this much. So, I put t c now in case of B if we see how much time it spends when it actually heated and going back to the room temperature due to during cooling.

So, during heating it leaves this magic temperature at this point it leaves it and it reaches around 1100 degree Celsius and interestingly chromium carbide type of precipitate dissolve at around 1050 degree Celsius 50 degree Celsius. So, even if enters this particular magic temperature at this point and leaves at this point during that time the time of spent at this level would be very small, because it is a heating stage and heating is very quick.

So, though the time of residence in that temperature range during heating is less, even if we consider that there is a possibility of little bit of chromium carbide precipitation still it will not stay there along the grain boundary. Because by the time it leaves here and it reaches to around 1100 degree Celsius temperature it will dissolve.

So, again if it dissolves then the chromium and carbon will homogenize again. And remember for getting a very good stainless property all across the mass or the body of that particular stainless steel, we need to have homogenized chromium and homogenized carbon all across it and it will homogenize. So, there will be no problem when we heat it. But when I cool it in the case of B it enters this particular temperature here 850 to 500 and leaves here ok.

So that means, the time of retention during cooling is this much. So, this is the time so if I try to see so this is the time this is the time. So, which is I can say time corresponding to D. Now, during cooling we have a possibility of chromium carbide precipitation again along the grain boundary, because the grain boundary provides heterogeneous sites.

Now, this time we have to analyze ok whether this time is sufficiently large for the chromium carbide precipitation or not. Now if I try to see a point A, A point corresponding to the thermocouple A. So, that point similar analogy during heating is can be given just like we have talked about in case of B, the time of retention and it also time of retention is less during heating in that temperature range at the same time the temperature goes beyond 1300 degree Celsius.

So, even if there is a little bit of formation possibility, but those chromium carbide will dissolve because it dissolves at around 1050 degree Celsius. Now during heating we have again see where it enters. So, during heating it enters here and leaves here ok that A point corresponding to A point.

So, the time of retention in the temperature range is this much so this is tA. Now from this picture it is very clear that you see that tA is less than tB is less than tC. So, here this temperature relation is very important. Now if we consider that the time required for significant chromium carbide precipitation ok.

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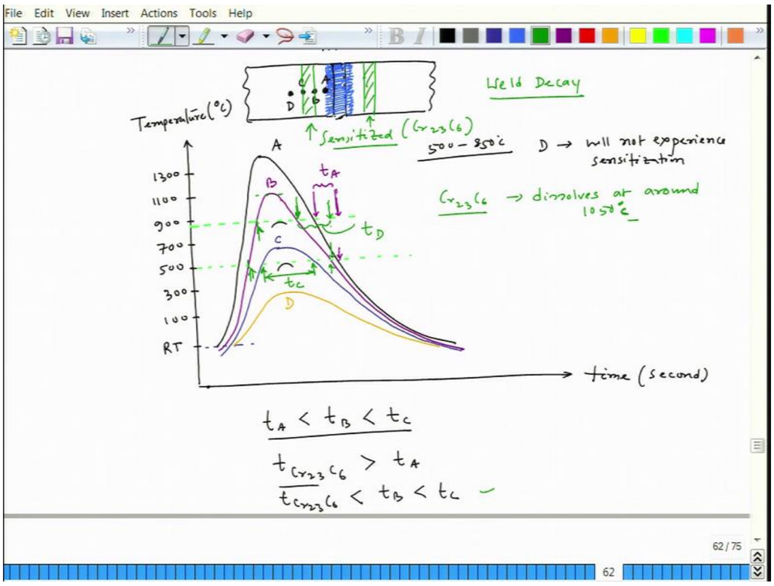

If this time is more than tA but if this time is less than tB and tC, then you can easily make out that when we have at that point of a the time of retention is not able to give sufficient chromium carbide precipitation. Because that time of retention is more less than the time formation for sufficient chromium carbide precipitation.

But in case of B and C we could see that the time required for precipitation of chromium carbide is less than tB and tC. So, we have more time for the formation of chromium carbide in case of B and C. So, in this zone around this zone, so it so you can have to you have to also put close by thermocouple and then see.

So, where is actually just touching this place and where it is just touching this place. So, in that case B will have precipitation C will not have because C it is not going to the that particular temperature range. But the B will have a sufficient time, so that case only that around a B will have precipitation.

So, now in this particular situation whatever diagram we have plotted. So, around this zone around this zone we have chromium carbide precipitation. So, this zone becomes sensitized fine because of this condition. And similarly on the other side you can also do the mirroring experiment ok similar experiment and you will see that the similarly on the other side if the both the stainless steels are same of same 304 normal 304. So, that time this one also will have this temperature profile like this.

So, where chromium carbide precipitation can be possible, so here $Cr_{23}C_6$ forms and it becomes sensitized. So, this is typical phenomena that is observed during welding. So, that is what it is called decay Weld decay ok. So, this is called weld decay fine. So now, let us stop here will take this matter further in our next lecture.

Thank you.