Surface Engineering for Corrosion and Wear Resistance Application
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Lecture – 15
Corrosion – IV

Hello we are in the process of discussions on different modes of Corrosion, particularly the weight corrosion or aqueous corrosion.

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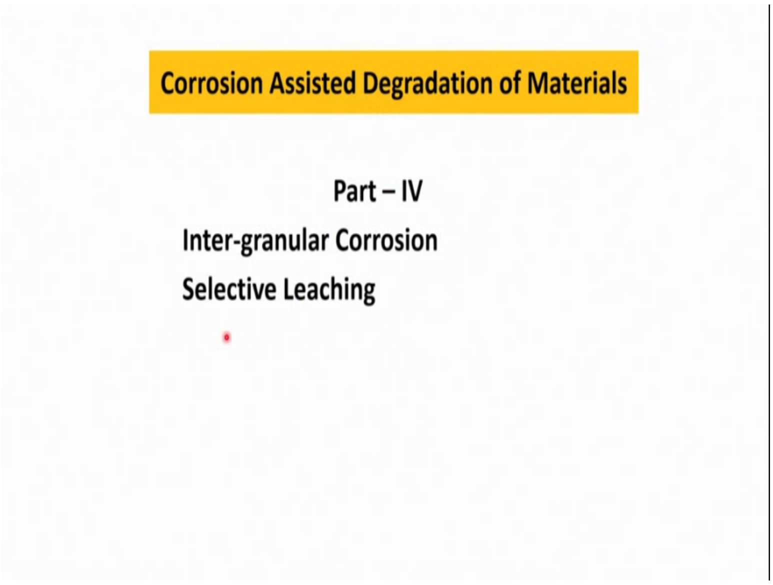

Corrosion Assisted Degradation of Materials

Part – IV

Inter-granular Corrosion

Selective Leaching

So, today in this talk we will discuss about two different modes which are very much dependent and we are very much important as well as dependent on the microstructure of the metals and alloys. So, this is intergranular corrosion and another one is selective leaching.

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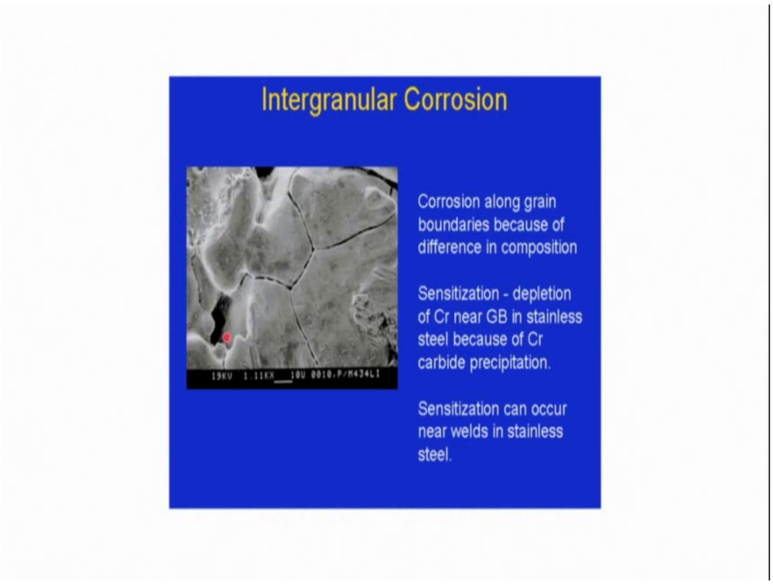

Intergranular Corrosion

Corrosion along grain boundaries because of difference in composition

Sensitization - depletion of Cr near GB in stainless steel because of Cr carbide precipitation.

Sensitization can occur near welds in stainless steel.

So, if you talk about the intergranular corrosion here as the name implies it basically proceeds through the grain boundaries and subsequently leading to failure from the adjacent grain boundary regions of the component. Now, if you just think of the; the basic component of a microstructure you will find that in pure metal, it consists of grains and grain boundaries. On the other hand in alloys also it consist of grain and grain boundaries and different other phases might be there in the microstructure.

So, if you talk about the grain boundaries and grain you will find that grain boundaries are having little bit higher energy than that of grains. So, usually the corrosion rate or maybe attack rate of grain boundaries are much higher than that of the grains of the body, but what happens that is why we see that it is (Refer Time: 01:33) when you see the microstructure of any component.

But you have to understand that in pure metal the area fraction or volume fraction of grain boundaries is much a little low higher than that of grains. But not really so higher, so as to have its effect on the overall corrosion rate of the component. So, when we just expose the pure metal in corrosive environment we will find that, the though the grain boundaries are attacked a little bit higher rate than that of grain bodies, but actually its effect is not so significant. So, even if we just refine the structure it is not this corrosion rate of the refined structure is not really so high as compared to that of annealed structure.

But if we just go on moving to the nano direction nanometer direction naturally when it is we see them a corrosion rate of the nano structured materials you will find that instead of increasing the corrosion rate, its corrosion rate will be even lower than that of annealed structure coarse gains microstructure.

This is a little different defect because there also we find that grain boundaries are attacked a little higher rate than that of grains and hence overall corrosion rate of the grain boundaries are significant in the corrosion behavior. But there what happens is that though the initial kinetics is much higher, but gradually there is formation of a very thin and highly adherent protective film. And that protective film is usually much stronger in nano structured materials than that of annealed coarse grain materials.

So, as a result of which we find that the corrosion rate of nanostructure materials it is usually lower than that of coarse grained micro structured materials. So, this is a case of pure metal, but if we think of alloy system, particularly for that case where grain boundaries consist of lot of different phases which are having completely different electrochemical behavior as that of grains.

Then the kind of corrosion observed in the alloy system is called inter granular corrosion because in that case you will find that because of the presence of the completely different phase along the grain boundaries their electrochemical behavior is widely different from that of grains. So, as a result of which there is a micro galvanic cell formation between grain boundary areas and the grains resulting which you will find that the adjacent grain boundary regions are corroded at a much faster rate than that of rest of the bodies.

So, problem starts from the adjacent grain boundary regions and after a later stage; at a later stage you will find that there is the damage of the component or maybe failure of the component from the near grain boundary regions. This particular effect is more prominent if you see the microstructure of the if you see that case for AISI 304 stainless steel.

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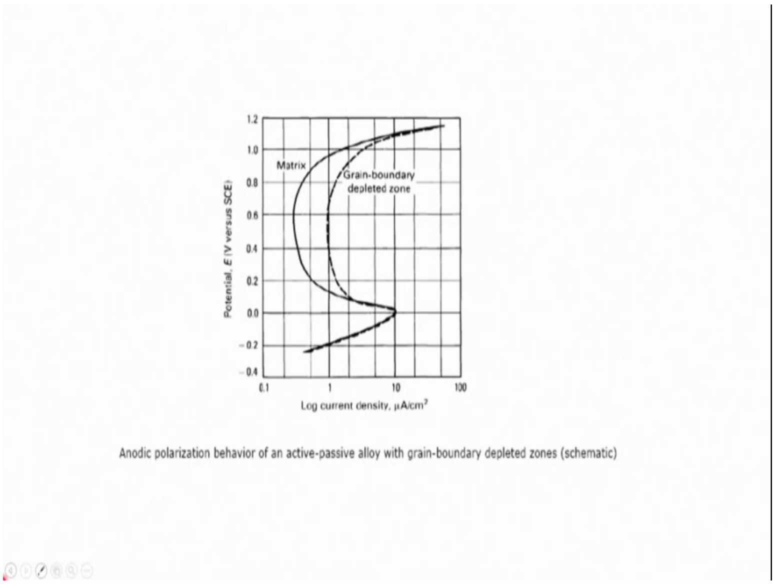

Anodic polarization behavior of an active-passive alloy with grain-boundary depleted zones (schematic)

So, this is the case where the overall grain boundaries contribution on the corrosion rate is so. So, if you just quickly find out the micro corrosion behavior or maybe potential static polarization behavior of the matrix and that of grain boundaries you will find that the particular the passivation threshold current for passivation, for fine grained microstructure or grain boundary regions is much lower than that of overall grains.

So, you will find that the grain boundary regimes are basically passivated or corroded at a much lower current density. And finally, the film breakage current or maybe you can say that transversive regime also starts at a much lower current density as compared to that of matrix. So, this is because of the fact that the grain boundary regions are having higher energy than that of the matrix and as a result of which it happened.

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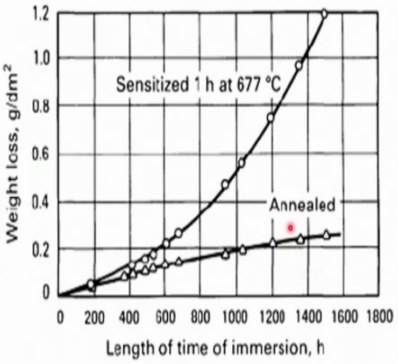

Fig. 3 Corrosion of type 304 steel in inhibited boiling 10% (H_2SO_4). Inhibitor: 0.47 g Fe^{3+}/L of solution added as $Fe_2(SO_4)_3$. Source: Ref 1

On the other hand if you just find AISI 304 stainless steel which is a special kind of stainless steel and which is very prone to inter granular corrosion especially when it is welded by arc welding technique you will find that the grain boundary corrosion behavior or inter granular behavior is very much prominent.

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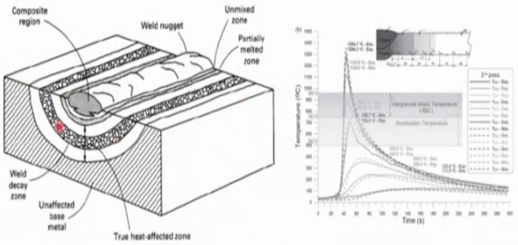

Schematic representation of the microstructure of arc welded AISI 304 stainless steel

So, when the AISI 304 stainless steel is subjected to arc welding you will find that there is a typical in the heat affected zone there is chromium carbide precipitations because the thermal history of the this particular stainless steel which has undergone arc welding is like this.

For example, that along the welded region, the cooling rate is very fast. So, it does not pass through the chromium carbide precipitation region. So, it is having a very good microstructure it does not undergo any kind of inter granular corrosion after the weldings.

But when you think about the heat affected zone microstructure you will find that heat affected zone actually undergoes this particular kind of thermal the history with where the along the heat affected zone that temperature between the 950 to 1450 degree Celsius actually it undergoes the, I mean it passes through the temperature between 950 to 1050 degree Celsius which is the chromium carbide precipitation regime, for a long time. And as a result of which it gets enough time for the chromium carbide to get precipitated along grain boundary region.

So, if you see the microstructure of the grain boundaries of the AISI 304 stainless steel which has been subjected to arc welding, the heat affected zone consists of lot of chromium carbide precipitates along the grain boundary areas. And as a result of which you find that when if the steel after the welding operation is subjected to any kind of corrosive environment or if it encounters corrosive environment you will find corrosion rate of the heat affected zone is much faster than that of rest of the other regions.

So, the steel is called as sensitized steel. So, if you find out the corrosive behavior or corrosion rate of sensitized steel as compared to that of annealed steel you will find that, the corrosion rate is much higher than that of annealed steel. So, this is the typical observation of I mean this is the you can say that this is the major effect because of intergranular corrosion. And this particular kind of corrosion needs to be avoided because when you do arc welding and after that heat affected zone if subjected to that corrosive environment and if heat undergoes corrosion that is not desired.

So, there are various ways by which you can get rid of this kind of inter granular corrosion. So, basic objective is that you have to get rid of this chromium carbide precipitations. So, how can you do that? First of all you can reduce the carbon content of the 304 stainless steel, from 0.2 percent to as low as a 0.2 percent which is 0.2 to 0.3 percent which is 316 varieties of stainless steel you can also make it extra low carbon this is one way. Second way of this particular solving this problem is by solution aging treatment.

So, where you go on heating it above 150, 1100 degree Celsius and then quench it directly from that temperature you find that all chromium carbide they get dissolved in the matrix and they do not really precipitate out. So, if you do this kind of solution ageing treatment after the welding operation naturally chromium carbide would not be there any more in the microstructure and hence you can always use it in corrosive environment. Other way of getting rid of this problem is by addition of some micro alloying elements like columbium, titanium.

So, those elements are I mean they are really prone to form carbides and their free energy of formation of carbide is much lower than that of the chromium carbide and as a result of which when this particular steel is used you will find that there is no possibility of chromium carbide precipitation because there are presence of columbium carbide, titanium carbide those carbides remain in the matrix. And as a result of which you will find that whenever the steel is subjected to arc welding operation there is no free carbon available for the formation of chromium carbide, as a result of which there is no chromium carbide formation.

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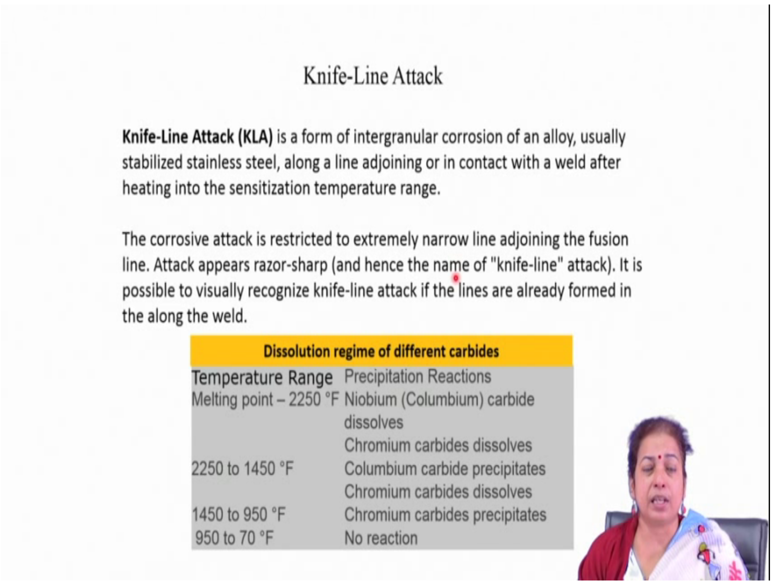

Knife-Line Attack

Knife-Line Attack (KLA) is a form of intergranular corrosion of an alloy, usually stabilized stainless steel, along a line adjoining or in contact with a weld after heating into the sensitization temperature range.

The corrosive attack is restricted to extremely narrow line adjoining the fusion line. Attack appears razor-sharp (and hence the name of "knife-line" attack). It is possible to visually recognize knife-line attack if the lines are already formed in the along the weld.

Dissolution regime of different carbides

Temperature Range	Precipitation Reactions
Melting point – 2250 °F	Niobium (Columbium) carbide dissolves Chromium carbides dissolves
2250 to 1450 °F	Columbium carbide precipitates Chromium carbides dissolves
1450 to 950 °F	Chromium carbides precipitates
950 to 70 °F	No reaction

So, that particular steel is a very much important, so that particular treatment is very much important. So, you can always do this particular treatment or add some micro alloying element. So, that it is there is no chance of formation of any kind of chromium carbide precipitations and this is a desensitized and this is called desensitized steel.

And naturally these particular steel is also very much important, but there is also chance of some kind of attack which you called as knife line attack. And this particular knife line attack is particularly observed in the desensitized steel or you can say that stable stabilized steel where you have addition of chromium columbium carbide and addition of the titanium carbide, niobium carbide addition of titanium, niobium or columbium.

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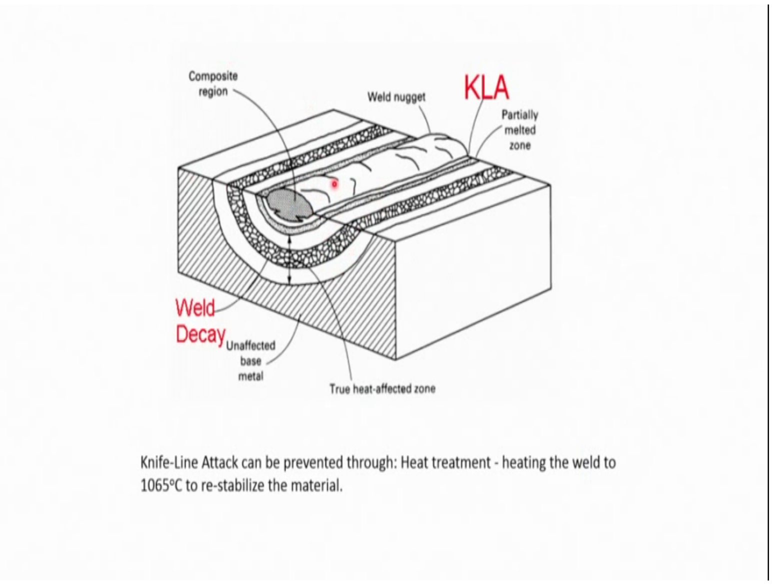

Knife-Line Attack can be prevented through: Heat treatment - heating the weld to 1065°C to re-stabilize the material.

So, what happens is that in knife line attack a little it is a kind of again intergranular attack, but here the zone of the knife line attack is little different from that of zone of this well decayed steel or maybe you could say that intergranular corroded steel that here is a sensitized steel because here knife line attack is usually observed at the interface between the weld zone and that of substrate. So, and it looks like a very thin line, so you call it as knife line.

So, in this particular case what happens is that for stabilized steel where you add columbium, titanium, niobium these all elements for carbide formation, whenever you do welding they go in solution. So, in the weld zone there is no problem, but what happens is that their precipitation temperature it is again a little lower than that of that their melting temperature; melting temperature of the bat metal, but; obviously, a little higher than that of chromium carbide precipitation temperature.

So, the particular zone which is interface between the weld zone and that of base metal along that region there is a temperature which actually undergoes a temperature profile thermal history which is where the temperature is around 225 2250 degree Fahrenheit.

And which is the precipitation temperature of the niobium or columbium carbide. So, at that particular temperature niobium or columbium precipitates along grain boundaries. So, when you subject that steel again it undergoes the intergranular corrosion. So, this is again another kind of very important problem of the stabilize steel where you have added the stabilizing element like niobium, titanium and columbium for getting rid of the intergranular corrosion problem.

So, these kind of corrosions are very important here also again you have to go for the solution as in treatment and then quench. So, that there is no problem of the knife line attack, so these are very important here.

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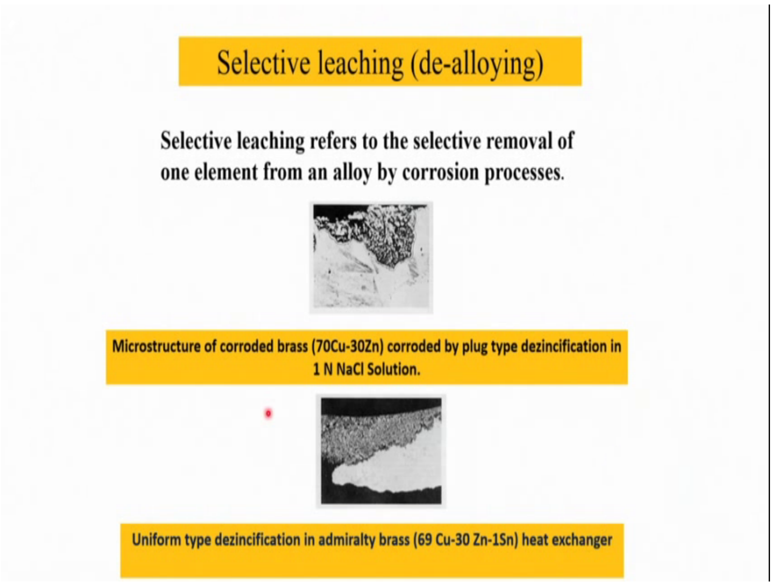

Selective leaching (de-alloying)

Selective leaching refers to the selective removal of one element from an alloy by corrosion processes.

Microstructure of corroded brass (70Cu-30Zn) corroded by plug type dezincification in 1 N NaCl Solution.

Uniform type dezincification in admiralty brass (69 Cu-30 Zn-1Sn) heat exchanger

So, if you talk about the different ways by which we discussed about these all things, but you can one of the important way by which this problem can be solved is by solutionizing operation. So, if you talk about the surface treatment process which might be applied for the mitigation of inter granular corrosion that is may be by surface melting process.

Because otherwise it is very difficult to mitigate this kind of problem, it is done by the typical bulk heat treatment or maybe by addition of micro alloying element in the micro struck in the alloy development problem in the alloy during alloy development. But otherwise if you are interested to take care of this problem by surface treatment you have to go for typical surface melting operation that too by the application of high energy beam like laser or electron beam, where you melt the surface and then quench it very quickly. So, that there is no chance of any kind of chromium carbide precipitates and that particular steel on the surface is highly free from any chromium carbide.

So, whenever this particular problem or inter granular corrosion occurs or observed it is very important that you find out the solution very quickly, so that the particular steel does not undergo any kind of corrosion in service environment. So, another kind of corrosion which again depends on the microstructure and also composition that is selective leaching, again this kind of corrosion is observed in alloy system where there is a wide difference in the electrochemical leaching behavior or corrosion behavior.

Particularly this is observed in particular brass different types of brass where copper and zinc are present. So, if you just find out the position of copper and zinc in EMF series you will find that zinc is more corrodive corrosive as compared to that of copper. So, as a result of which what happens is that, when these alloy is subjected to the corrosive environment, the zinc leaches away leaving aside the copper in the matrix.

So, after the selective leaching of the zinc from the surface you will find that, the alloy gets porous in nature on the surface and again this is not good because this finally, leads to the failure of the component. So, this is called selective leaching, so selective leaching or de alloying.

So, this is nothing, but a selective removal of the material, so of particularly one of the alloying element or two or three alloying elements from the typical alloy because of the differential behavior in the corrosion resistance properties of different alloy different component in the alloy.

So, this is the case for the typical example of the or micro structure or maybe you can say the characteristics of the selectively list brass, here it is a corroded brass corroded by typical intergranular that selective leaching process where the environment was typical sodium chloride solution.

So, you will find that in this particular case the leach because of selective leaching of the brass from the zinc from the alloy you will see there are a lot of porosities in the surface and black region are nothing, but redeposited copper on the selectively leached brass. Now, if you just go quickly go through the kind of selective leaching that are observed in different alloys system you will find that, the typical kind or mode is dependent on though it look how it looks like.

So, for example, in brass it this has been classified into two categories; one is plaque type and another one is uniform type. So, this is typical plaque type the allowing or may be selective leaching where it looks like plaqued, so, where you will find that it is selectively leached and this is usually observed in the acidic solution.

But when there is the pH level is little higher you will find that another kind of selective leaching which is called uniform leaching, here the leaching is more or less same all throughout the surface there is no preferential plaqued like appearance. So, you call it as uniform or uniform dezincification or uniform leaching.

So, this is again observed in admiralty bars brass where which has subject which has been subjected to typical again water environment and pH was a little higher. So, different types of selective leaching behavior is observed in different alloy behavior different alloys. So, depending on the way it looks like or depending on the appearance of the leach surface there are different names which may be applied.

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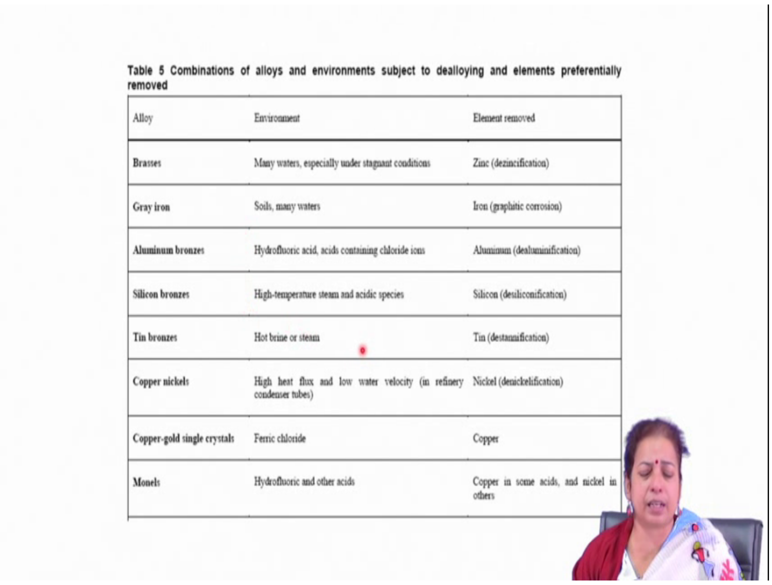

Table 5 Combinations of alloys and environments subject to dealloying and elements preferentially removed

Alloy	Environment	Element removed
Brasses	Many waters, especially under stagnant conditions	Zinc (dezincification)
Gray iron	Soils, many waters	Iron (graphitic corrosion)
Aluminum bronzes	Hydrofluoric acid, acids containing chloride ions	Aluminum (dealuminification)
Silicon bronzes	High-temperature steam and acidic species	Silicon (desiliconification)
Tin bronzes	Hot brine or steam	Tin (destannification)
Copper nickels	High heat flux and low water velocity (in refinery condenser tubes)	Nickel (denickelification)
Copper-gold single crystals	Ferric chloride	Copper
Monels	Hydrofluoric and other acids	Copper in some acids, and nickel in others

Now, if you quickly go through selective leaching you will find that it is not only in brass this is also observed in different other alloys system too. Because naturally this depends on the overall electrochemical behavior of the constituents in the which constitute the alloys. So, for example, in brass there are copper and zinc, so zinc leaches away.

Similarly if you say the case for grey iron where there is graphite and iron here you will find that iron leaches away because of the relative stability electrochemical stability of the graphite is much higher than that of iron. So, you will find that iron leaches away, so you called it as graphitization. So, after the leaching away of the iron from the surface you will find that the surface gets softened and you can nail you can take out the material from the surface by simply nailing, so this is called graphitization.

Similarly, there is also different other forms of different other names are also there in different other alloy system which has undergone that selective leaching like, the siliconization. Then the silicon bronze you will find that silicon desiliconization process where you will find that silicon leaches away, then tin bronze it is again it is called the destannification because tin goes away.

So, like that the element which goes away depending on that the different names are there that copper nickel system you will find it is called denickelification, then copper gold a single crystal in ferric chloride and environment it is, it basically again copper goes away. So, like the different names are there depending on the alloy system and depending on the constituent which basically gets leached away.

So, it is very important that when you choose any alloy for its application in a specific environment you have to know the electrochemical behavior of the constituents which basically which are present in the alloy.

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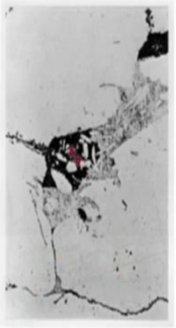

Fig. 12 Dealuminification of a cast aluminum bronze furnace electrode pressure ring exposed to recirculating cooling water (pH = 7.8 to 8.3, conductivity = 1000 to 1100 μS). The preferentially attacked γ phase left behind a residue of copper (darkened regions in eutectoid and along grain boundaries). The α particles within the eutectoid (light-gray areas) are unattacked. Etched with $FeCl_3$. 260×. Courtesy of Robert D. Port. Permission granted by Nalco Chemical Company, 1987

And depending on that you have to choose the typical environment and also use the alloy for that specific purpose. So, this is the at the dealuminification behavior of the aluminium bronze.

So, you find that this particular you will find that there is leaching away of the aluminium from the grain boundaries along the particularly in the grain boundary regions and it looks like black appearance, in addition to that there are a lot of perforations or small pits are there all throughout the region. And as a result of which you will find that after a while there will be crack formation, micro crack formation and then failure of the component which the alloy is made of.

So, these two kinds of corrosion are very important types of corrosion like particularly in this talk we discussed about the two important corrosion process; one is inter granular corrosion and another one is selective leaching. So, both the corrosion are observed in alloy system not really pure metal. So, in one case this is basically this propagates through adjacent grain boundary regions and for this inter granular corrosion it is very important that you find out the grain boundary microstructure prior to its application in actual environment.

If grain boundary possesses any elements which are highly active or highly noble particularly which is highly active that, then the dissolution rate along the grain boundaries will be higher, but on the other hand if it is highly noble in nature like in case of 304 stainless steel after arc welding operation, we get precipitates of chromium carbide along grain boundaries.

So, this is highly noble in nature cathodic as compared to that of surrounding boundary regions. So, you will find that there is micro galvanic cell formation between the grain boundary regions and grade regions and also the adjacent get boundary regions get depleted in chromium. So, that problem starts at the adjacent boundary regions and then actually the after the corrosion is over you will find that failure starts from the adjacent boundary regions rather than red boundaries.

On the other hand if grain boundary possesses lot of active elements your featured electric electro chemically more prone to corrosion as compared to that of grains, there also you will find that grain boundary attack will be more than that of grain bodies. But there you find that the attack is through the grain boundaries. So, you have to understand that which element are or which compound or which what is the composition of the boundaries after the precipitations and if it is engaged with different phases you have to be careful in applying it in the environment.

So, what you have to do? You have to basically homogenize the alloy prior to its application or you can also get rid of this particular problem by typical cathodic protection, anodic protection and also by painting operation this kind of things can be applied whatever are applied in general corrosion in combating the general corrosion problem.

So, similar kind of solutions can be applied, but it is better that you take care of the overall microstructure carefully. So, that there is no grain boundary second phase is present prior to its application in the environment. So, second type is that typical selective leaching for selective leaching also not only micro structure, but composition is very important. So, whenever you have the alloy system where the alloying constituents are having different cell leaching behavior you have to be careful because they may leach away leading to porosities in the matrix.

So, when they leach away leading to porosities in the matrix. So, naturally the alloy the component is no more a continuous in nature. So, there are a lot of there will be lot of defects, those defects might to further problem because if there are porosities on the surface naturally initially those are porosities, but later on it can also lead to some other form of corrosion like through the porosity, there may be pitting corrosion there will be crevice corrosion. So, those problems may be might be invited after this initiation of the corrosion by selective leaching.

And in addition to that, the surface or the component gets weaker because of the selective removal of the some of one element from the surface. So, selective leaching is also very much dependent on the microstructure as well as composition. So, whenever you are interested to use the say alloy which are having different types of elements, having different electrochemical behavior you have to be careful either you get rid of the problem by changing the environment you change the environment completely.

So, that there is no species which can cause corrosion in the environment by the addition of different inhibitors, other way also you can stop the problem by application of coating maybe cathodic protection can be applied and also better would be that you have that alloy see you completely change the alloy system or add some element.

So, that in the alloy system, so that it does not undergo selective leaching and it can take care of your problem very nicely. So, these are very different, these are two different types of corrosions which are very important and need to be addressed prior to the application of the alloy in actual environment.

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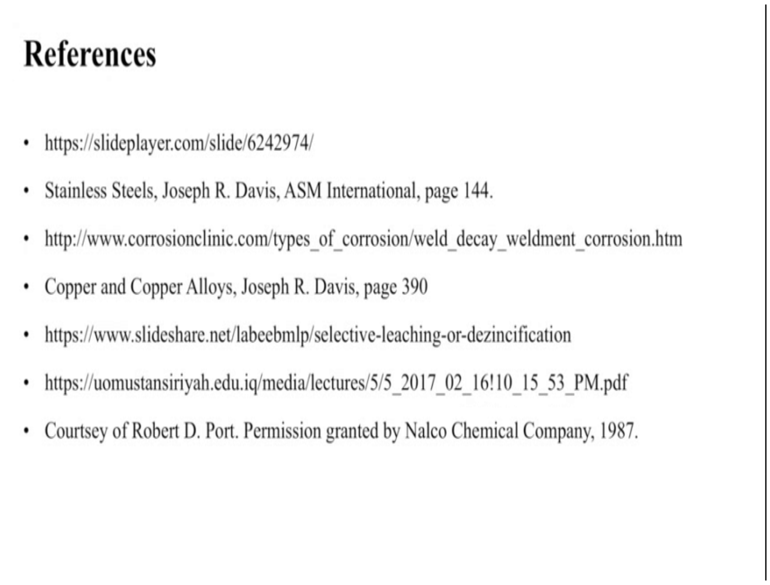

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So, you have to be very much careful in using that those components made of the alloying elements in practice.

So, thank you very much.