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Lecture - 34 High Temperature Degradation

Hello. In this talk we will discuss about two different other modes of corrosion, that is one is high temperature oxidation another one is liquid metal corrosion.

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Corrosion Assisted Degradation of Materials

Part – VI High temperature degradation Liquid metal corrosion

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| High temperature oxid reaction between the me temperatures. | ation of a metal is a corrosion process involving the tal and the atmospheric oxygen at elevated |
|--|--|
| General equation of oxid nM + 1/2kO2 = M _n O _k O ₂ x = Oxide Scale Thicknes | ation reaction of a metal M: F60, F00 F00 F00 F00 F00 F00 F00 F00 F00 F |

So, so far we were discussing about the aqueous corrosion problem, when high temperature the oxidation or dry corrosion is a little bit different from that aqueous corrosion; because in this kind of corrosion there is no aqueous media in the environment. So, if you quickly go through the definition of high temperature oxidation or dry corrosion it is nothing, but it basically occurs in absence of the aqueous media.

So, it is a corrosion where which involve the reaction between the metal and that of atmospheric oxygen or any other species at elevated temperature. So, usually if you just quickly go through the microstructure of the oxidized surface, you will find that there is formation of oxide scale on the surface. And that oxidation is basically diffusion controlled process and as a result of which you will find that you through the external series formation of very thin oxide layer or initiation of the oxidation process are is very fast, but as soon as the oxide layer forms, then subsequent oxidation kinetics will depend on the nature of the oxide film that is forming on the surface.

If the oxide film is highly protective in nature then you will find that kinetics of the oxidation is will be slower, but if it is not protective it if it contains lot of defects on the surface or inside the material, then you will find that the rate of oxidation will be higher with time.

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So, initial initiation of oxidation if you think of you will find that initiation of the oxidation, depends on the free energy of formation of oxide of different alloy system

and, which is actually which is actually documented in the form of in the in the Ellingham. Ellingham diagram where you find that free energy change associated with the oxide formation is plotted as a function of temperature and, different different environment. So, in Ellingham diagram you will find different Ellingham diagrams with different environments, but that Ellingham diagram is basically is very important because it acts as a guideline for the choosing of choice of the material for a specific environment with temperature.

So, this is a kind of guideline for the choice of material, as a function of choice of a material or materials combinations in different environment.

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So, basically this particular, but you have to be careful because the Ellingham diagram gives a information about the initiation probability, but as soon as the oxide layer initiates or initial oxide layer forms the full surface is covered; by the process of like initially there is adsorption then nucleation and growth and then film coverage. So, after that is covered then naturally the subsequent oxidation kinetics will depend on the nature of the oxide film which forms on the surface.

So, particularly for alloy system you have to be careful. In alloy system there are different species in the alloy; so, you will find that there is a formation rate which is different for different species. So, depending on that probability of formation of oxide, that highly probable probable oxide film which forms on this will form on the surface.

And then gradually whether it will continue or not depends on the which elements which oxides are there on the surface and subsequently its nature particularly the kind of defects are there in the oxide scale, whether it is highly protective or not the kind of stretch that stress that is generated after the oxide scale formation. So, those all factors play important role in determining the further kinetics of the oxidation or overall kinetics of the oxidation after the shield formation.

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So, now if you quickly go through the typical parameters, which influence the oxidation kinetics at a later stage. So, initiation is basically controlled by the probability of formation of oxide, but if you take about if you think about propagation first problem, which faces is that that oxide layer is having differential thermal expansion coefficient as compared to that of pure metal.

So, because of the difference in coefficient of thermal expansion between the metal and that of oxide scale, you will find that there is lot of stress generated at the interface. So, there is a parameter which basically is very important and which again is a kind of guideline to do the overall protectiveness of the oxide film which is forms which is formed on the surface that is Pilling Bedworth ratio. So, pilling Bedworth what they say is nothing, but it is a ratio of the volume of the oxide scale to the volume of the metal.

So, this particular volume ratio is very important, because it ultimately controls the overall stress level that is generated at the surface or particularly at the interface because of the oxide formation.

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So, ideally if pilling Bedworth ratio is 1, then the oxide scale is protective highly protective, but if it is much lower than 1 naturally you will find that surface is not fully covered; and if it is much higher than 2 there is there is lot of stress generation in the interface. So, it is not really good it cannot offer the protectiveness on the surface. And if it is much lower than that of 1 and a little bit lower than that of 1 or equal to one or if it is lower than much lower than that of 2 or little bit or near to 2 then the oxide scale is supposed to be protective in nature.

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| Metal | Oxide | PB | Protectiveness |
|------------|------------------|------|----------------|
| Aluminum | Al_2O_3 | 1.28 | Р |
| Calcium | CaO | 0.64 | NP |
| Cadmium | CdO | 1.42 | Р |
| Cobalt | Co_2O_3 | 2.40 | NP |
| Copper | Cu_2O | 1.67 | P |
| Chromium | Cr_2O_3 | 2.02 | NP |
| Iron | FeO | 1.78 | Р |
| Magnesium | MgO | 0.81 | NP |
| Manganese | MnO_2 | 2.37 | NP |
| Molybdenum | MoO ₃ | 3.27 | NP |
| Nickel | NiO | 1.70 | Р |
| Lead | PbO | 1.28 | P |
| Silicon | SiO_2 | 2.15 | NP |
| Tantalum | Ta_2O_3 | 2.47 | NP |
| Titanium | Ti_2O_3 | 1.76 | Р |
| Tungsten | WO3 | 1.87 | Р |
| Uranium | UO_2 | 1.97 | P |
| Zinc | ZnO | 1.58 | P |
| Zirconium | ZrO_2 | 1.57 | P |

So, it is very important to do the pilling Bedworth ratio of the different component of the oxides, which say different components of the different components which are forming oxide in an alloy system for choosing the alloy for a specific environment. So, if you quickly go through the pilling Bedworth ratio of different elements you will find that they vary to a large extent, like in alumina the pilling Bedworth ratio is 1.28.

So, it is highly protective in nature. In calcium it is 0.64 for sure it is not protective in nature. In cadmium it is 1.42, it is again protective. And cobalt it is 2.40. So, it is not protective in nature. So, chromium it is 2.02 2 point o 4. So, it is not protective, but it is also near 2 for sure it is really protective in nature.

Iron it is 1.78 it is protective, magnesium manganese these are not protective because this is much lower than or much higher than a 2. Molybdenum it is not protective, nickel it is a protective. So, lead it is protective. So, you can understand that depending on the element, which are forming it is the protectiveness of the film actually varies.

So, you have to be careful in choosing the element for developing the alloy. So that, the film which is formed on the surface because of the oxidation of the individual ingredient or individual element they are highly protective in nature.



Now, this is a kinetics of the oxygen. So, you will find that you as I mentioned you. So, initially when there is full coverage of the surface with the oxide, usually the oxidation process basically proceeds by the counter ionic diffusion. So, there may be diffusion of metallic ion through the oxide scale at the surface and then reaction of the oxide reaction at the surface and then formation of the oxide film or otherwise it may be like oxygen is migrating through the oxide layer deep inside the metal. So, at the interface between the oxide layer and the metal there is oxide formation.

So, whether this particular thing happens like when the oxygen it greases inside through the oxide scale come to the metal surface and there is formation of oxide scale. So, in that case, the oxidation process in the along the inward direction. On the other hand if the metal ion is basically it gets metal ion just diffuses through the oxide film come at the interface between the oxide and particular interface between the oxide and the environment then at the surface of the oxide there is a oxidation process.

So, that is basically by outward movement of the metallic ion. So, inward movement of the oxygen or outward movement of the metallic ion are responsible for the kinetics of the oxidation at a later stage.

$$W = \frac{M}{A_s} = (K_w t)^n \qquad (10.24)$$
$$\frac{dW}{dt} = nK_w^n t^{n-1} \qquad (10.25)$$
$$K_w = \rho^{1/n}K_z \qquad (10.26)$$

$$K_w = \rho^{1/n} K_x \tag{1}$$

where $K_w = \text{Rate constant } (g.cm^{-2}.time^{-n})$ for weight gain

The above equations are analyzed based on the exponent n for most observable kinetic behavior. Thus, the physical interpretation of n is given below.

- If n = 1, a linear behavior is achieved for a noncontinuous, porous and cracked oxide scale with PB < 1 or PB > 2. In this case, the scale is nonprotective and diffusion of oxygen occurs through the pores, cracks, and vacancies.
- If n = 1/2, a parabolic behavior of nonporous, adherent, and protective scale develops by diffusion mechanism. Thus, $1 \le PB \le 2$ and the mechanism of scale growth is related to metal cations (M^{+z}) diffusing through the oxide scale to react with oxygen at the oxide-gas interface.
- If n = 1/3, a cubic behavior develops for a nonporous, adherent and protective oxide scale. Thus, $1 \le PB \le 2$.

So, if you just quickly go through the different kinetics that follow, when you see the oxidation process you will you will find that they are basically three categories; one is linear behavior then that is another one is parabolic behavior and third one cubic behavior. At the initial stage of oxidation when that component starts oxidizing, very thin layer of oxide forms and at that particular layer that particular stage the oxide scale is basically non continuous porous and cracked in nature. So, you will find that rate of oxidation is very fast.

So, you will get typical linear behavior, but as soon as the surface is covered with the oxide and that oxide is very thick and also non porous. And also that is basically non porous and defect frame in nature defect free in nature, then there is parabolic behavior which is observed.

So, where the mechanism score scale growth is very slow and, you will find like kinetics of the scale growth is very slow and is basically it is a kind of parabolic shows the parabolic behavior. So, here in this case the diffusion of the element or counter ionic diffusion is responsible for the film growth actually. So, but rate of film growth is quite slow the way the field will grow depending on the relative diffusivity of the individual element through the scale.

If the diffusivity of the metal ion through the scale is faster than that of diffusivity the oxygen ion through the oxide scale you will find that the scale is forming at the surface. On the other hand if the diffusivity of the oxide is oxygen ion is much higher than that of diffusivity of the metal ion. You find that film is forming at the interface between the oxide and that of metal.

So, the way film will form in case of the parabolic in case of the oxide oxidation which shows parabolic behavior, that depends on the counter ionic diffusivity of the element relative diffusivities of the element which is participating in the reaction. So, the incase of in that case where the temperature is very high, a cubic behavior is developed for non porous adherent and the thick oxide scale, protective oxide scale.

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So, where it is basically in cubic behavior you will find that this is basically it further reduces to a large extent with time. So, different behaviors are observed basically and depending on the kinetics and also depending on the nature of the film depending on the temperature, depending on the oxygen ion concentration or oxidation oxygen partial pressure.



So, kinetics of oxidation follow different behavior in different stages. So, if you are interested to increase the oxidation or decrease the oxidation tendency of the material, you have to choose proper alloying element so that and. So, that alloying element forms the oxide which is highly protective in nature. You have to think of proper surface alloying that is the one of the remedy for improving the oxidation resistance of the alloy system.

You can also get rid of typical oxidation problem, by typical using it in a temperature which is safer temperature you cannot should not expose that temperature, at which there is very rapid rate of oxidation. So, if you think of the application of the surface engineering, mitigation of the high temperature oxidation, you will find that for oxidation for that oxidation, mechanism in many cases that alloy is responsible.

So, you have to think of surface alloying it with proper alloying element particularly silicon, chromium and aluminum these are three alloying elements which offer very good oxidation resistance property. So, you have to alloy it by any of the existing alloying system like diffusion with surface alloying or maybe laser surface allowing treatment. So, that surface is full of that material that alloy which offers good oxidation resistance property and by that process you can basically minimize the kinetics of oxidation or may be probability of the oxidation phenomena.

So, next type of a corrosion is liquid metal corrosion as I mentioned you that liquid metal corrosion is a difficult kind of corrosion which is called also dissolution. So, so embrittlement because when the component solid metal is in contact with a liquid metal, it gets brittle in nature which is nothing, but degradation where certain metals loss its tensile ductility or undergoes structure when exposed to specific liquid metal.

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So, this is called like liquid metal embrittlement phenomena. So, if you see the surface of the embrittled component you will find that, there are a lot of surfaces full of roughness because there is lot of material removal and on that of that is the loss of it dissolution. Or a dissolution is also there in the right side or in the left side, if you see you will find that there are lot of a micro cracks formation and also the grain boundaries are basically, enriched with the liquid metal.

So, this is the case for the steel 316 stainless steel, 316 stainless steel exposed to liquid sodium at 700 degree Celsius for, you can understand that these liquid metal corrosion because stainless steel is very much used as it can for carrying the liquid sodium.

So, after 8000 hours of exposure this kind of problem may happen, and if you see the surface of the stainless steel you will find that it got (Refer Time: 15:23) fit and (Refer Time: 15:25) and also it a embrittle to a large extent and there is also loss of ductility. So, you have to replace it time and again. So, that this problem is no more there or so, that

new materials come into the carrying purpose. So, you do not have any problem of the overall loss of the component.



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This is the case for corrosion of Inconel alloys 706 exposed to liquid sodium for again 8000 hour at 700 degree Celsius then hot leg circulating system. So, porous sulphur layer has found this porous sulphur layer has formed. So, you will find that this is the basically the cross section, if you see carefully you will find that the porosity content is so high that, many cases it is interconnected in nature. So, this component will fail very I mean at a much faster rate.



When it is subjected to tensile stress so, this is corrosion of nickel in static lithium environment after exposure for 300 hours at 700 degree Celsius. So, you can here also you can say that porosities are basically, interconnected in nature and that on the surface it looks like it is a big holes.

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So, if you quickly go through the tensile ductility tensile strength of that particular liquid metal, embrittled liquid metal embrittled component; you will find that tensile ductility is reduced to a large extent by the process of the liquid metal embrittlement.

So, this is the case for effect this is the graph which shows the effect of environment on the yield stress and, strain hardening rate of various iron aluminum alloys tested in air and mercury indium solution. So, in air if you see you will find that the tensile ductility is much higher, elongation is much higher if you want increasing that and on the other hand it is silver indium solution it is a little high lower.

As you go on increasing the aluminum content you will find that, here in aluminum content in one case it is basically iron another case it is iron aluminide alloys. So, if you go on increasing the aluminum content this formation of iron aluminide that is basically much the actually that particular alloy is much brittle. So, you will find that it is having lower stress and also lower steel strength and also lower u t s and also lower percentage elongation.

So, as you go on adding using the silver indium solution, that their mercury indium solution there you will find that there is further decrease in ductility; and as you go on having a steel with the 17 percent aluminum which is itself which itself is highly brittle in nature, there you will find that there is further decrease in the ductility to such a large extent that it fails very quickly. So, depending on the alloy system the behavior actually changes and, you will find that it gets embrittled to a large extent.

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Sometimes small amount of alloying element such as lead and tellurium, when it added to steel it improve the machinability that leads to the embrittlement phenomena. So, cadmium plated titanium and steel are embrittled due to high temperature service by molten cadmium. So, you can say that different small small amount of the gradients can cause severe trouble by the liquid metal embrittlement problem.

Similarly, indium used as high vacuum seal in steel chamber caused cracking due to breakout operations. Zircolay tubes used in nuclear reactor have been cracked by both solid and liquids the cadmium. So, different again like stress corrosion cracking, liquid metal embrittlement embrittlement process is also minimized environments specific.

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All material does not undergo liquid metal embrittlement in all environments. So, similarly you can say that mechanism also more or less same, as the name implies this is basically liquid metal embrittlement. So, what happens is that naturally here stress has to be there either internal stress or external stress, because embrittlement phenomena is usually observed when it is subjected to stress; otherwise if it is in static condition there is no stress is applied there is no problem.

So, whenever you are applying stress and when there is liquid metal in the environment, it basically there are different ways by which the crack fall initiates and propagates. So, first way or first mechanism of the crack initiation and propagation is dissolution and diffusion. So, whenever the crack tip is subjected to liquid metal or liquid metal faces the crack tip, you will find that it basically it dissolves the stressed part and because of the dissolution and subsequent diffusion you will find that the (Refer Time: 20:27) gets the

inter atomic bond strength in that region decreases as a result of which you will find that crack propagation occurs at a much faster rate.

So, this is one mechanism another mechanism is that adsorption of the liquid metal and adsorption of the liquid metal at the crack tip and, nucleation of dislocation and then, pileup work hardening is all phenomena observed. So, here in this case where there is no liquid metal on the other hand here it is with for liquid metal assisted degradation. So, in that case where there is no liquid metal. So, where the typical phenomena or mechanism of the stress mechanism of the typical frack fracture generation is nucleation and growth of that dislocations.

But in case of here also same mechanism occurs, but here you will find that plastic joint width is much lower. So, small small plastic zone formation is there. So, naturally you can understand that there is inter atomic bond weakening and then say dimples are quite shallow in nature and crack propagates at a much slower rate and also you know by formation of very shallow deeper region and then suddenly it fails.

So, whatever happens in case of normal metal which does not undergo stress corrosion cracking liquid metal embrittlement. If you just think of the same alloy in liquid metal you find that the typical mechanism made event same, but overall ductility because of overall decrease in ductility, you will see that it gets partially embrittled and by that process there is the crack initiation with propagation.

Table 1 Guidelines for materials selection and/or alloy development based on liquid metal corrosion reactions Corrosion reaction Guidelines Example Lower activity of key elements Reduce nickel for lithium, lead, or sodiur Direct dissolution Corrosion product Lower activity of reacting elements. Reduce chromium and nitrogen in lith formation systems. In case of protective oxide, add elements Add aluminum or silicon to steel exp to promote formation. to lead. Increase (or add) elements to decrease Increase chromium content Elemental transfer transfer tendency exposed to sodium or lithium. ent being transferred Reduce oxygen content in metals exp to lithium. Alloying Avoid systems that form stable Do not expose nickel to molten alu compounds. mote formation of corrosion-resistant Add aluminum to lithium to form surface Pro layers by alloying. aluminides. Compound reduction Eliminate solids that can be reduced by Avoid bulk oxide-lithium couples liquid metal.

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So, you will find that there are different reactions which occur one is direct dissolution, in case of lower activity key element like nickel for reduced nickel for lithium lead or sodium system then, corrosion layer formation like low activity reacting element reduce chromium and nitrogen in lithium systems. So, elemental transfer there maybe elemental transfer transferred increase or add element to decrease their transfer tendency. So, as which usually occurs in case of steel by increasing chromium content then alloying phenomena like avoid system that form stable compound that is here do not expose nickel to molten environment.

Then compound reduction is element eliminate through a solids that can be reduced by liquid metal. So, here actually while, you have to take care of this problem by avoiding bulk solid lithium couple.

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Examples of Materials-Combination

- Zn Gallium, Mercury, Indium and Pb-20Zn
- Al Gallium, Cadmium and Mercury
- Copper Mercury, Antimoby, Cadmium, Lead, Thallium
- Steel Aluminium, Antimony, Bismuth, Cadmium, Gallium, Indium, Lead, Lithium, Mercury, Selenium, Silver, Sodium, Tellurium, Thallium



So, you can understand that this problem actually the problem of liquid embrittlement occurs when, there is improper or maybe mismatch in the liquid metal to solid combinations.

This mismatch can be avoided by choosing proper materials for that particular liquid metal environment. So, like zinc if you just use gallium mercury indium and lead 20 percent zinc it will undergo that, liquid metal embrittlement. Aluminum gallium, cadmium and mercury it undergoes liquid metal embrittlement copper, mercury, antimony, Then cadmium and lead thallium this all in undergo and inter metallic that

liquid metal embrittlement; steel in presence of aluminum antimony, bismuth, cadmium, gallium again it undergoes the liquid metal embrittlement.



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So, you have to choose proper environment or for carry where there is chance of the liquid metal exposure which is proper metal proper alloy so that, it does not undergo the nickel metal embrittlement problem. Now if you quickly go through the if you quickly summarize the different modes of corrosion and find out the surface parameters, which are responsible for that kinetics of in controlling the kinetics of different types of corrosion this chart shows a perfect guidelines for that.

For example, now till date we have discussed about three types of corrosion one is the aqueous corrosion, second was high temperature oxidation, third one is the liquid metal corrosion. Now in aqueous corrosion again different modes are there 8 different modes like general corrosion, galvanic corrosion, fatigue corrosion, crevice corrosion, selective leaching, erosion corrosion, stress corrosion, cracking and hydrogen embrittlement.

And if you just quickly go through that surface parameters, which are responsible or which basically controls the corrosion kinetics they are surface roughness, microstructure, composition and phases, hardness toughness and residual stress. So, now, if you think of the effect of these are all parameters which partially influence the general corrosion rate.

So, you can say that that surface roughness surface micro structure composition and phases these three parameters are very important and also residual stress. So, these four parameters are very important which control the general corrosion behavior of the component. If you see the galvanic corrosion behavior again surface composite material composition is very important, roughness is important, microstructure is important. There again residual stress value is important.

If you talk about pitting corrosion again surface roughness, microstructure, composition and residual stress are important crevice corrosion also the same thing. In selective leaching also composition and phases they are very important surface roughness is important to some extent, but not to a large extent if you talk about erosion corrosion, they are basically surface roughness surface composition and phases and your hardness also very much important.

Stress corrosion cracking if you talk about where, basically surface roughness is having very to some extent it is having the influence because it basically controls the initiation rate. So, the surface roughness then composition and phases hardness those all things playing and also toughness play important role.

Hydrogen embrittlement again toughness plays a very important role, toughness composition phases microstructure and surface roughness. If you talk about hydrogen embrittlement if you talk about high temperature oxidation, here two important factors are responsible to cause the high temperature oxidation related damage one is residual stress, second one is typical composition and phases which are present in the microstructure.

So, these and roughness also to some extent and in liquid metal embrittlement phenomena composition and phases are very important. So, you can understand that which are the parameters that, basically influence the different corrosion behavior of the component. So, if you just go on controlling that those parameters you can easily reduce the or minimize the tendency of the corrosion attack by different ways.

Summary

- · Corrosion and its importance
- Classification of Corrosion
- Mechanism of corrosion in different modes
- Characteristics of each form of corrosion
- · Ways to combat them



So, in summary it may be stated that in the last 6 talks we discussed about different types of corrosion and its importance. We also saw different classifications like broadly it may be classified into three types; one is aqueous corrosion, second one is high temperature oxidation and third one is liquid metal corrosion. And aqueous corrosion may further be classified into 8 categories depending on the mode by which it is proceeding and we also discussed about mechanism of corrosion in different modes.

Characteristics of each form of corrosion it is very important that you know the characteristics of different forms of corrosion. If you do not know the characteristics of different form of corrosion it is very difficult to understand in which mode failure has occurred and hence stop it at by taking appropriate measure.

So, finally, we also discussed about ways to combat them in brief extent brief way, but not really in details.

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So, in the next few classes we will discuss about the prevention technique by the corrosion; prevention of corrosion different techniques, which may be applied for prevention of the corrosion.

Thank you very much.

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