Non - Metallic Materials

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Module - 11
Corrosion and degradation of non - metallic materials
Lecture - 56
Oxidation, corrosion of ceramic materials, degradation of polymers: swelling and dissolution, bond rupture, weathering

Welcome to my course Non-Metallic Materials and this is module number 11 Corrosion and degradation of non metallic materials and this is lecture number 56 in continuation to the earlier lecture on corrosion. Here in this particular lecture, we will consider Oxidation, corrosion of ceramic materials, degradation of polymers including swelling and dissolution bond ruptures and weathering.

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CONCEPTS COVERED

- Mechanism of oxidation
- Scale type
- Kinetics of oxidation
- Degradation of polymers

So, first I will introduce the Mechanism of oxidation, then scale type it forms on the metal surface, then the kinetics of oxidation and then finally, different types of degradation behavior of polymeric materials.

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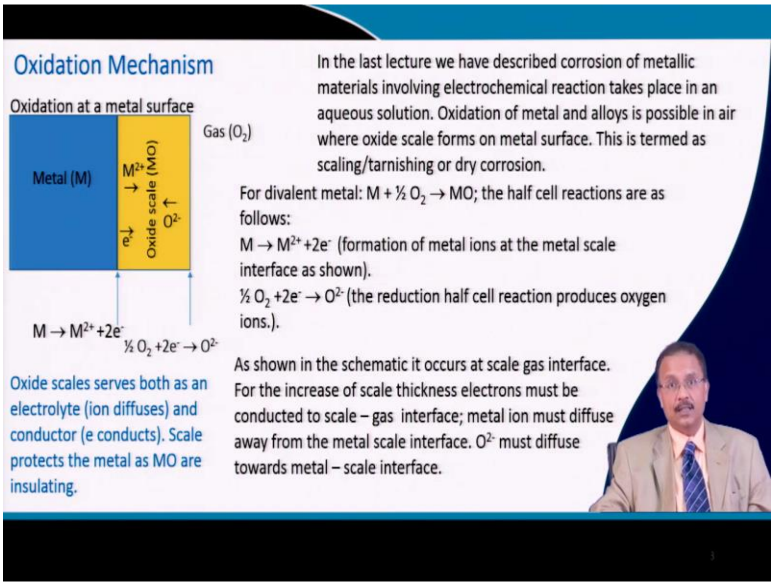

Oxidation Mechanism

Oxidation at a metal surface

Oxide scales serves both as an electrolyte (ion diffuses) and conductor (e conducts). Scale protects the metal as MO are insulating.

In the last lecture we have described corrosion of metallic materials involving electrochemical reaction takes place in an aqueous solution. Oxidation of metal and alloys is possible in air where oxide scale forms on metal surface. This is termed as scaling/tarnishing or dry corrosion.

For divalent metal: $M + \frac{1}{2} O_2 \rightarrow MO$; the half cell reactions are as follows:

$M \rightarrow M^{2+} + 2e^-$ (formation of metal ions at the metal scale interface as shown).

$\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$ (the reduction half cell reaction produces oxygen ions.).

As shown in the schematic it occurs at scale gas interface. For the increase of scale thickness electrons must be conducted to scale – gas interface; metal ion must diffuse away from the metal scale interface. O^{2-} must diffuse towards metal – scale interface.

So, oxidation it protects the metal surface from being corroded. So, in the last lecture I have described the corrosion of this metallic material that basically involve electrochemical reactions that takes place in an aqueous solution. Now, in case of the oxidation of metal or alloys it is possible in air, where eventually it happens at elevated temperature.

So, the metal oxide scales that forms on the metal surface and that is why this type of oxidation that is termed as scaling, sometimes it is called tarnishing and this is in fact dry corrosion, that you can consider as a dry corrosion. So, what is happening? Metal gets oxidized to form metal ion and electron. So, the formation of the metal ion at the metal scale interface that is shown in this figure.

So, this is the metal and the scale is forming, which is denoted by this yellow marked region. So, at this interface metal and scale interface it forms this metal gets oxidized. So, you have metal ion and you have electron that is also generated here. Now, in the other phase where it is under gaseous environment and oxygen is involved, then this oxygen it reacts with this electron to form oxide ions.

So, this reduction half cell reaction it produces oxygen ions. So, it starts from this region, from the scale and gaseous region.

So, this reaction it forms at the scale gas interface. Now, to increase the scale thickness what is required electrons must be conducted to the scale gas interface. So, scale gas interface is here, so electron must be conducted from here to here, metal ions also must diffuse away from the metal scale interface. So, it is also will diffuse from here to here then only this scale will grow, so, metal will get oxidized.

So, oxide scales that serves both as electrolyte, because oxygen ions they are supposed to diffuse in and also conductor of electrons. So, scale protects the metal because, this metal oxide is basically insulating. So, there is a kinetic involved here, it acts like a electrolyte interface and this is not that conducting it is not conducive for electron movement and it is not also very conducive for oxygen ion movement, unless the driving force is high, unless the temperature is high.

So, there is a limitation it forms a limited thickness of the scale, but eventually it protects the metal surface.

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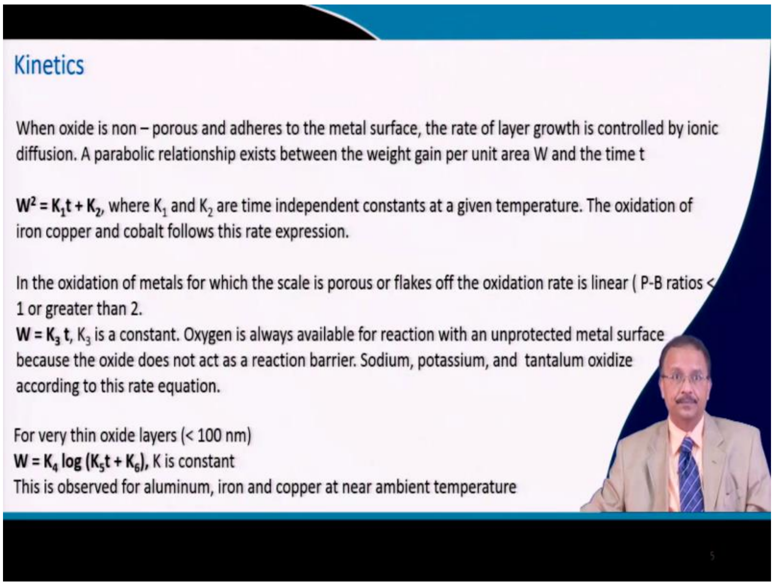

Kinetics

When oxide is non – porous and adheres to the metal surface, the rate of layer growth is controlled by ionic diffusion. A parabolic relationship exists between the weight gain per unit area W and the time t

$W^2 = K_1t + K_2$, where K_1 and K_2 are time independent constants at a given temperature. The oxidation of iron copper and cobalt follows this rate expression.

In the oxidation of metals for which the scale is porous or flakes off the oxidation rate is linear (P-B ratios < 1 or greater than 2.
$W = K_3\ t$, K_3 is a constant. Oxygen is always available for reaction with an unprotected metal surface because the oxide does not act as a reaction barrier. Sodium, potassium, and tantalum oxidize according to this rate equation.

For very thin oxide layers (< 100 nm)
$W = K_4 \log (K_5t + K_6)$, K is constant
This is observed for aluminum, iron and copper at near ambient temperature

So, if I consider the kinetics of this oxide formation. So, this is basically is non porous and adheres to the metal surface and the rate of the growth is controlled by as I said ionic diffusion of oxygen. So, usually a parabolic relationship exists between the weight gain per unit area which is defined as W and time, so the relation is W square.

So, this is the weight gain due to oxide formation is equal to this one is a constant k 1 and k 2 is also a constant and t is the time. So, this k 1 and k 2 are time independent constant at a particular temperature. So, the oxidation of iron, copper, cobalt, etcetera follow this kind of parabolic dependence. In the oxidation of metals for which the scale is not dense, but if it is porous or it flakes off from the metal surface, there it is found that this rate is linear.

So, the rate is linear so the W is equal to k 3 into t, so, k 3 is a constant. So, oxygen is always available for the reaction to take place, because in that case it need not to go through the metallic film, it is porous in nature. So, it always can reach the unprotected metal surface, because this does not act as a reaction barrier. So, in case of highly electro positive material like sodium potassium tantalum oxide, so they follow this kind of linear relationship.

For very thin oxide layer when the thickness is less than 100 nanometer, then a logarithmic equation is usually followed. So, W is a constant k 4 log k 5 t plus k 6. So, this ks are constant and it is observed for aluminum, iron, copper at nearly ambient temperature this is actually observed.

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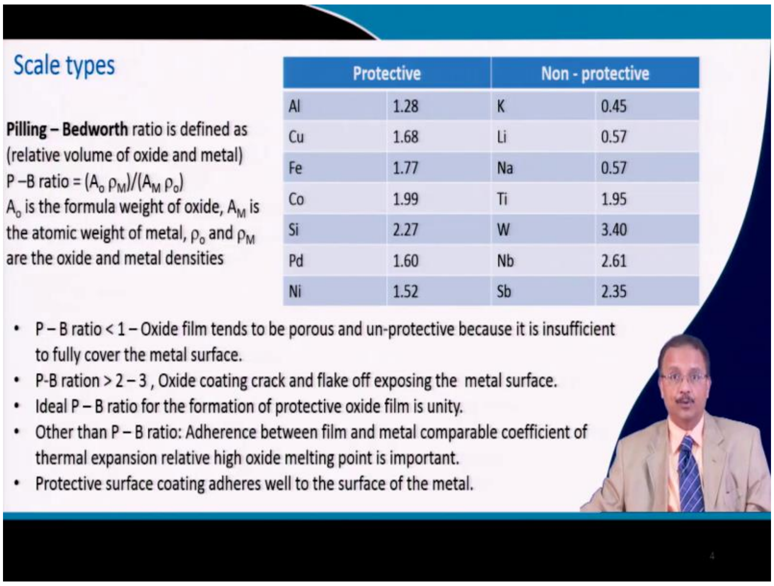

Scale types

Pilling – Bedworth ratio is defined as (relative volume of oxide and metal)
P –B ratio = $(A_o \rho_M)/(A_M \rho_o)$
A_o is the formula weight of oxide, A_M is the atomic weight of metal, ρ_o and ρ_M are the oxide and metal densities

Protective		Non - protective	
Al	1.28	K	0.45
Cu	1.68	Li	0.57
Fe	1.77	Na	0.57
Co	1.99	Ti	1.95
Si	2.27	W	3.40
Pd	1.60	Nb	2.61
Ni	1.52	Sb	2.35

- P – B ratio < 1 – Oxide film tends to be porous and un-protective because it is insufficient to fully cover the metal surface.
- P-B ration > 2 – 3 , Oxide coating crack and flake off exposing the metal surface.
- Ideal P – B ratio for the formation of protective oxide film is unity.
- Other than P – B ratio: Adherence between film and metal comparable coefficient of thermal expansion relative high oxide melting point is important.
- Protective surface coating adheres well to the surface of the metal.

So, scale type that is dependent on the so called pilling bed worth ratio. So, that basically defined as the relative volume of oxide and the metal. So, this abbreviated P-B ratio that is given as A 0 which is the molecular weight of the oxide into the density of the metal divided by atomic weight of the metal and the density of the oxide. So, it is nothing but this is the volumetric ratio of oxide and metal.

So, now, usually it is found that when this pilling bed worth ratio is less than one, then oxide film tends to be porous, of course, it is not fully covered and this is not protective, because insufficient coverage on the middle surface. When this P-B ratio is greater than 2 to 3 then oxide coating basically cracks and flakes off exposing the metal surface. So, that is also not very useful ideally, this P-B ratio to protect the oxide, the metal surface the oxide film the P-B ratio should be nearby to the 2 units.

So, you can see in the table for different types of material, usually it is found for aluminum, copper, iron the protective case where the coverage is fully there then this P-B ratio is something like this which is very close to 1, here it is not very strictly followed But this is semiconductor as well it is not metal, but when the P-B ratio is less than 1 then suddenly this material is not protected by the forming of ah oxide layer.

So, other than this P-B ratio the adherence is important between film and metal and comparable coefficient of their thermal expansion relative high oxide melting point those things are also important to give a good protection. So, protective surface coating adheres well to the surface of the metal ah, so that thing is more important.

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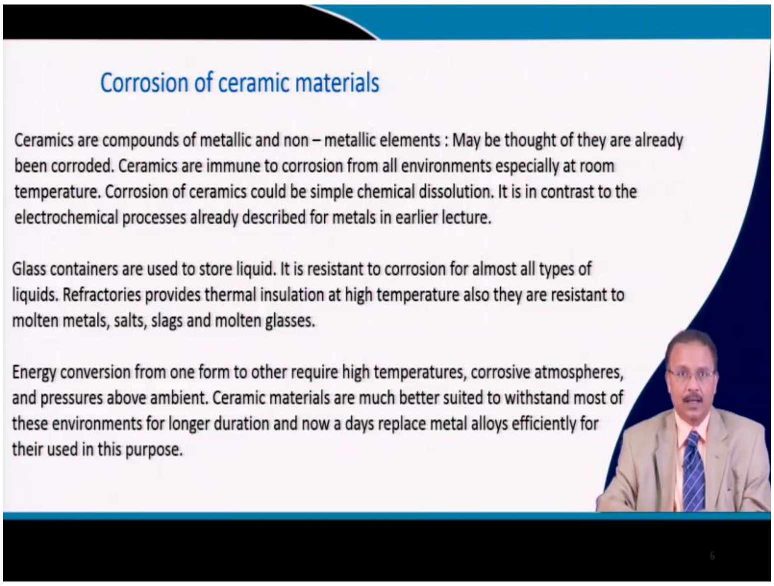

Corrosion of ceramic materials

Ceramics are compounds of metallic and non – metallic elements : May be thought of they are already been corroded. Ceramics are immune to corrosion from all environments especially at room temperature. Corrosion of ceramics could be simple chemical dissolution. It is in contrast to the electrochemical processes already described for metals in earlier lecture.

Glass containers are used to store liquid. It is resistant to corrosion for almost all types of liquids. Refractories provides thermal insulation at high temperature also they are resistant to molten metals, salts, slags and molten glasses.

Energy conversion from one form to other require high temperatures, corrosive atmospheres, and pressures above ambient. Ceramic materials are much better suited to withstand most of these environments for longer duration and now a days replace metal alloys efficiently for their used in this purpose.

In case of the corrosion of metal you can consider that ceramic materials the compound of metal and non metallic elements, they may be thought that they are already corroded, so already oxide is formed. So, they are usually immune for corrosion from all environmental attack, especially, when room temperature is considered. So, usually ceramics are corroded by chemical dissolution in contrast to electrochemical process which we have seen in case of metal.

Glass is one example, one important ceramics almost all liquid it can hold, so it does not corrode, but if you keep hydrofluoric acid then suddenly, it is very rapidly corroded the silica based glass or high alkali that also attack. So, other than that it is quite corrosion less, when exposed to other types of liquid.

But at high temperature particularly the furnace linings that is given by ceramic refractory, so it is important to retard the corrosion, because of the slag attack by molten metal in case of glass tank furnace, also the refractory silica refractory that also does not have enough corrosive effect corrosion attack because of the glass.

So, energy conversion from one form to other required this high temperature. So, nowadays, you know that IC engine or the turbine electric generation more and more temperature is raised to increase the efficiency and corrosive atmosphere is also used. So, in that case the ceramic materials, they are much better suited to withstand most of this environmental corrosion for longer duration.

And nowadays they replace. In fact, the metal alloys which so far people were using by this novel ceramic materials like silicon nitride Sialon etcetera.

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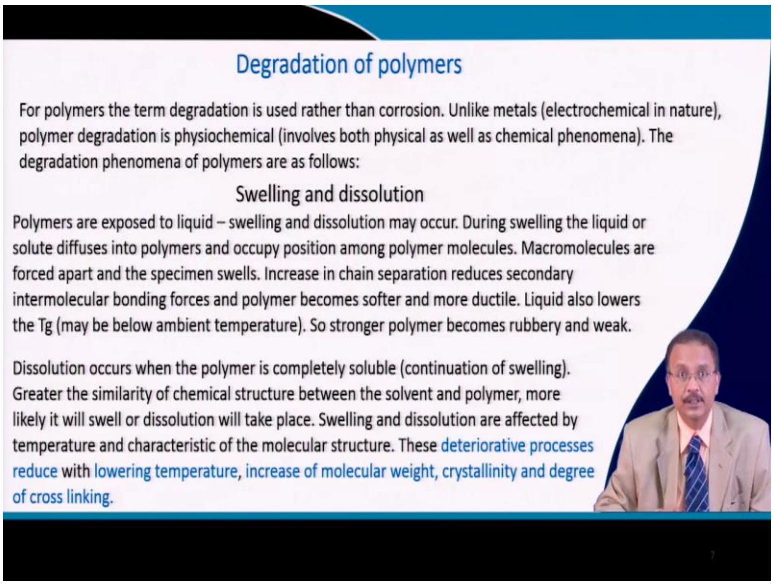

Degradation of polymers

For polymers the term degradation is used rather than corrosion. Unlike metals (electrochemical in nature), polymer degradation is physiochemical (involves both physical as well as chemical phenomena). The degradation phenomena of polymers are as follows:

Swelling and dissolution

Polymers are exposed to liquid – swelling and dissolution may occur. During swelling the liquid or solute diffuses into polymers and occupy position among polymer molecules. Macromolecules are forced apart and the specimen swells. Increase in chain separation reduces secondary intermolecular bonding forces and polymer becomes softer and more ductile. Liquid also lowers the Tg (may be below ambient temperature). So stronger polymer becomes rubbery and weak.

Dissolution occurs when the polymer is completely soluble (continuation of swelling). Greater the similarity of chemical structure between the solvent and polymer, more likely it will swell or dissolution will take place. Swelling and dissolution are affected by temperature and characteristic of the molecular structure. These deteriorative processes reduce with lowering temperature, increase of molecular weight, crystallinity and degree of cross linking.

In case of polymer, we do not term this as corrosion, but we term it as degradation. So, the polymer in case of polymer, this is more appropriate term. So, in metal it is electrochemical in nature, polymer degradation we can think of it is physio chemical in nature. So, it occurs I mean involves both physical as well as chemical phenomena.

The degradation phenomena of polymer could be of swelling type. So, when polymer is exposed to a liquid, then swelling and dissolution both can occur. So, when swelling occurs the liquid solute diffuse into the polymer and occupy the position among the polymer molecules.

So, they are macromolecules, so they are forced apart and the specimen start to swell and when it swells the chain separation reduces secondary intermolecular bonding forces and polymer becomes softer and it becomes also more ductile.

So, the liquid, certain liquid also lowers the glass transition temperature, below the ambient temperature; so stronger polymer becomes rubbery and weak. Dissolution actually occurs when the polymer is completely soluble. So, swelling continues and it turns to be soluble. So, greater the similarity of the chemical structure between the solvent and the polymer more likely it will swell or dissolution will take place.

So, this swelling and dissolution are affected by temperature and characteristics of the molecular structure of the polymer is concerned. So, these are deteriorative processes reduce with lowering the temperature, increase of the molecular weight of the polymer or the crystallinity of the polymer and of course, the degree of cross linking. So, if they are increased then this problem of degradation like swelling and dissolutions are grossly retarded.

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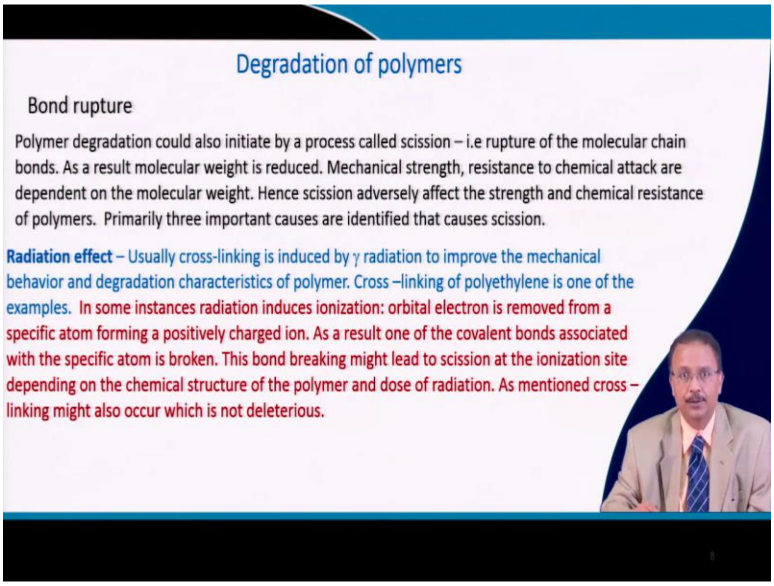

Degradation of polymers

Bond rupture

Polymer degradation could also initiate by a process called scission – i.e rupture of the molecular chain bonds. As a result molecular weight is reduced. Mechanical strength, resistance to chemical attack are dependent on the molecular weight. Hence scission adversely affect the strength and chemical resistance of polymers. Primarily three important causes are identified that causes scission.

Radiation effect – Usually cross-linking is induced by γ radiation to improve the mechanical behavior and degradation characteristics of polymer. Cross –linking of polyethylene is one of the examples. In some instances radiation induces ionization: orbital electron is removed from a specific atom forming a positively charged ion. As a result one of the covalent bonds associated with the specific atom is broken. This bond breaking might lead to scission at the ionization site depending on the chemical structure of the polymer and dose of radiation. As mentioned cross – linking might also occur which is not deleterious.

Degradation of polymer can also occur, because of bond Rupture. So, this kind of degradation can initiate by a process which is called scission, which is a rupture of molecular chain bonds, the rupture of the bonds takes place. So, the molecular weight is reduced as a result mechanical strength, resistance to chemical attack, they are dependent on the molecular weight.

So, the scission is actually adversely affect the strength of the polymer and also the chemical resistance of the polymer. So, primarily 3 important mechanisms of scission is identified. The first one is a radiant effect radiation effect, always not all radiation is bad, usually the cross linking is induced by gamma radiation. So, that is a known standard process to improve the mechanical behavior and degradation characteristics of the polymer.

So, cross linking of polyethylene is one of the examples for that after gamma radiation the mechanical property is involved improved, but in some instances radiation induces ionization. So, orbital electron is removed from the specific atom forming a positively charged ion, as a result one of the covalent bond associated with this particular atom which is ionized that is broken.

So, the breaking might lead to the scission at that particular ionization site. So, depending on the structure of the polymer and dose of the radiation sometimes this radiation like UV radiation that causes a detrimental effect in the polymer. So, cross linking might also occur, but that will improve the strength of the polymer it will not deteriorate the polymer.

So, the effect is mixed sometimes depending on the nature of the polymer radiation effect is good and sometimes it leads to the degradation behavior of the polymer.

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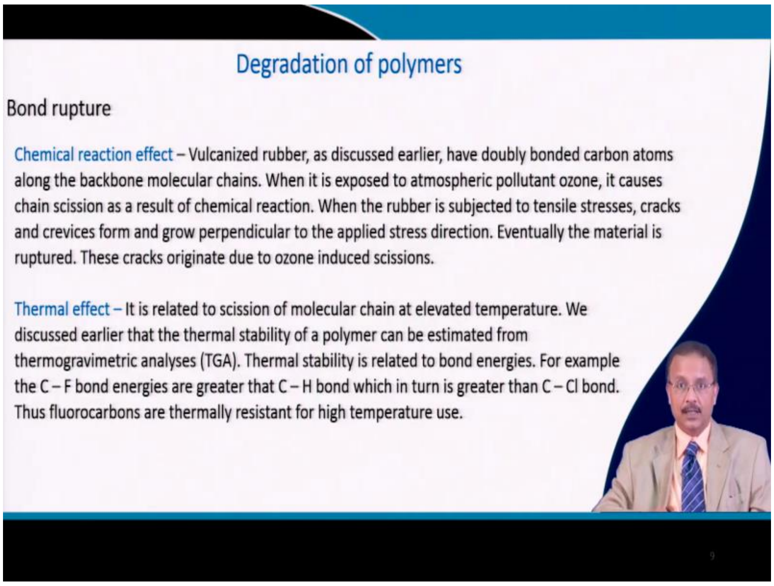

Degradation of polymers

Bond rupture

Chemical reaction effect – Vulcanized rubber, as discussed earlier, have doubly bonded carbon atoms along the backbone molecular chains. When it is exposed to atmospheric pollutant ozone, it causes chain scission as a result of chemical reaction. When the rubber is subjected to tensile stresses, cracks and crevices form and grow perpendicular to the applied stress direction. Eventually the material is ruptured. These cracks originate due to ozone induced scissions.

Thermal effect – It is related to scission of molecular chain at elevated temperature. We discussed earlier that the thermal stability of a polymer can be estimated from thermogravimetric analyses (TGA). Thermal stability is related to bond energies. For example the C – F bond energies are greater that C – H bond which in turn is greater than C – Cl bond. Thus fluorocarbons are thermally resistant for high temperature use.

Bond rapture can also occur by chemical reaction effect and one can cite the example of vulcanized rubber. So, as I have described earlier in the very first module that has this vulcanized rubber has double bonded carbon atoms and that forms the backbone of the molecular chain.

So, when it is exposed to a pollutant in the ambient like ozone, it causes the chain scission and as a result of this chemical reaction. So, when this rubber is exposed to a tensile stress, then cracks are initiated at the surface and that cracks grow perpendicular to the applied stress direction, it is some kind of mode one fracture takes place.

So, eventually the material is ruptured. So, the origin of this micro crack is due to ozone induced scissions in vulcanized rubber. So, this is one another example for chemical reaction effect, there could be thermal effect and while I was teaching the TGA we have shown that this is also related to scission of the molecular chain, but it is at elevated temperature.

So, remember we described about the degradation of the polymer, the stability of the polymer and that actually can be estimated by the thermo gravimetric analyses till that point till that temperature where it is not degraded, the weight loss is not there, but then weight loss is initiated. So, it is getting oxidized the carbonaceous material is getting oxidized with reacting with the ambient oxygen.

So, the thermal stability of the bond energies that is important to avoid this kind of degradation. So, one can cite example, if it is carbon fluorine bond energy that is greater than carbon hydrogen bond energy, which is again greater than carbon chloride bond. So, the fluorocarbons they are thermally resistant to the high temperature use.

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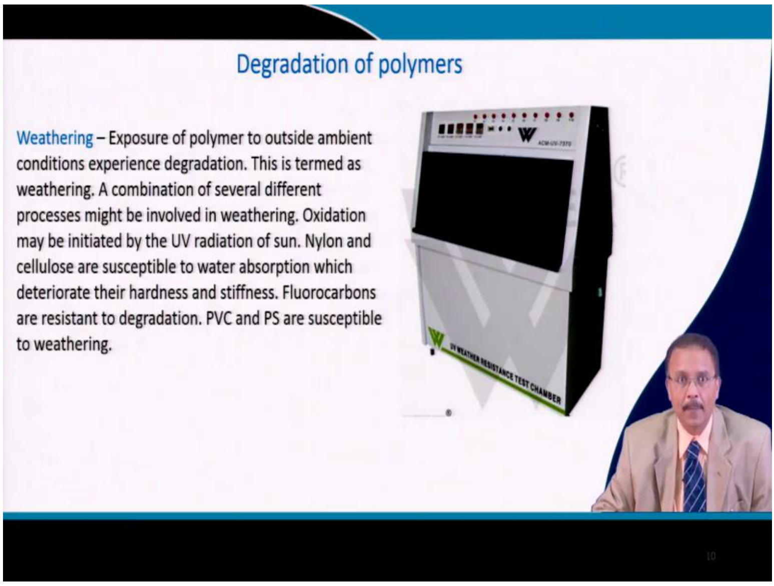

Degradation of polymers

Weathering – Exposure of polymer to outside ambient conditions experience degradation. This is termed as weathering. A combination of several different processes might be involved in weathering. Oxidation may be initiated by the UV radiation of sun. Nylon and cellulose are susceptible to water absorption which deteriorate their hardness and stiffness. Fluorocarbons are resistant to degradation. PVC and PS are susceptible to weathering.

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Weathering of the polymer that is exposure of the polymer to the outside ambient condition so, in outside ambient condition polymer also degrades and this is called weathering. A combination of different types of process might be involved in the weathering. Oxidation that may be initiated by UV radiation of sun and nylon and cellulose they are susceptible to water absorption and which also deteriorates the hardness and stiffness of the polymer.

Fluorocarbons again they are resistive to this kind of degradation and poly vinyl chloride and polystyrene they are susceptible to weathering on the other hand. So, this kind of chambers are commercially available, which will actually you can test in the accelerated condition the weathering effect.

So, UV radiation different doses can be generated they are inside the chamber and raining is also possible, sometimes something equivalent to sun rays at elevated temperature is possible. So, this is good for accelerated test of the polymer degradation.

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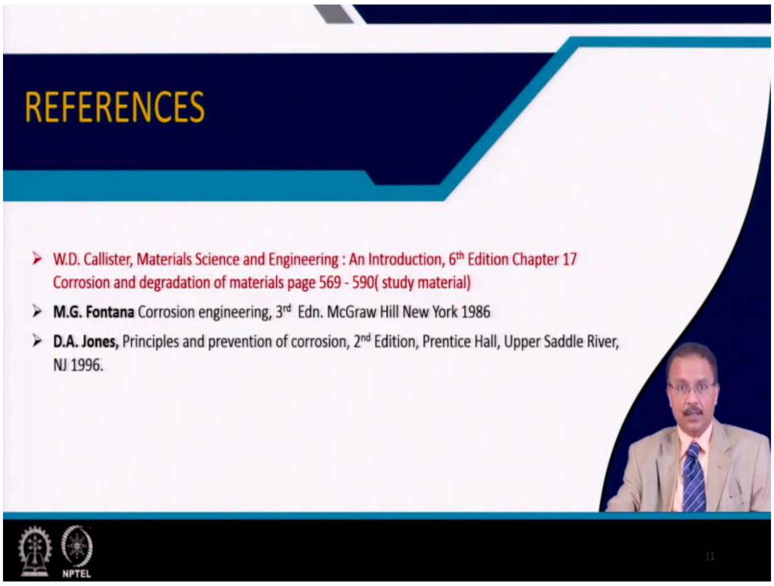

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- W.D. Callister, Materials Science and Engineering : An Introduction, 6th Edition Chapter 17 Corrosion and degradation of materials page 569 - 590(study material)
- **M.G. Fontana** Corrosion engineering, 3rd Edn. McGraw Hill New York 1986
- **D.A. Jones,** Principles and prevention of corrosion, 2nd Edition, Prentice Hall, Upper Saddle River, NJ 1996.

So, this part of the lecture, this is as a study material you can use a book by Callister, the same chapter, chapter number 17 Corrosion and Degradation of material and apart from that the book by M.G Fontana corrosion engineering third edition and also the book by D-A Jones they are helpful.

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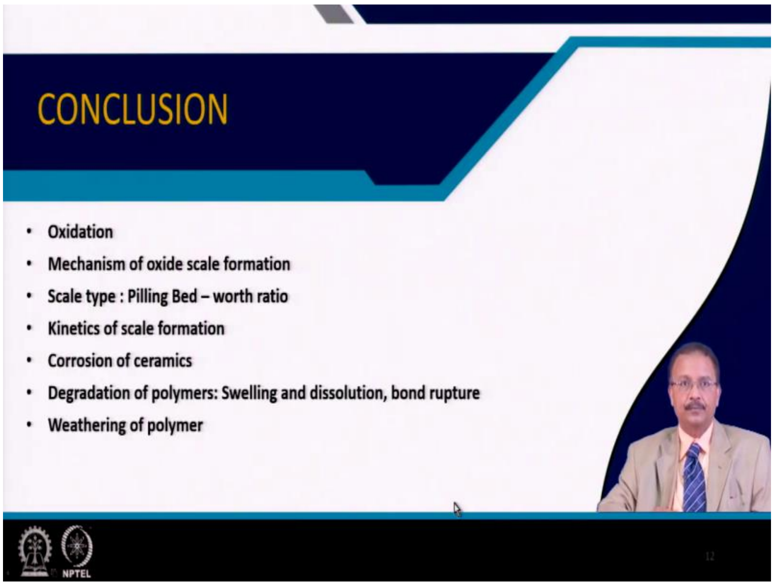

CONCLUSION

- Oxidation
- Mechanism of oxide scale formation
- Scale type : Pilling Bed – worth ratio
- Kinetics of scale formation
- Corrosion of ceramics
- Degradation of polymers: Swelling and dissolution, bond rupture
- Weathering of polymer

So, in this particular lecture, we talked about the oxidation of metal which acts as a protective layer coating on the metal surface to impede the corrosion. Then mechanism of the oxide scale formation, scale type in terms of pilling bed worth ratio that is introduced.

Then kinetics of scale formation, different types of weight gain versus time relation that is introduced, then corrosion of ceramics that is briefly introduced, although ceramics at room temperature they are not corroded, they are already corroded if you consider it is a metal non metallic compound.

Then certain degradation of polymer including swelling and dissolution bond rupture, they have been introduced and finally, weathering of polymer they are described.

Thank you for your attention.