CORROSION ENGINEERING

Subject code: TH4

6th Semester, DIPLOMA

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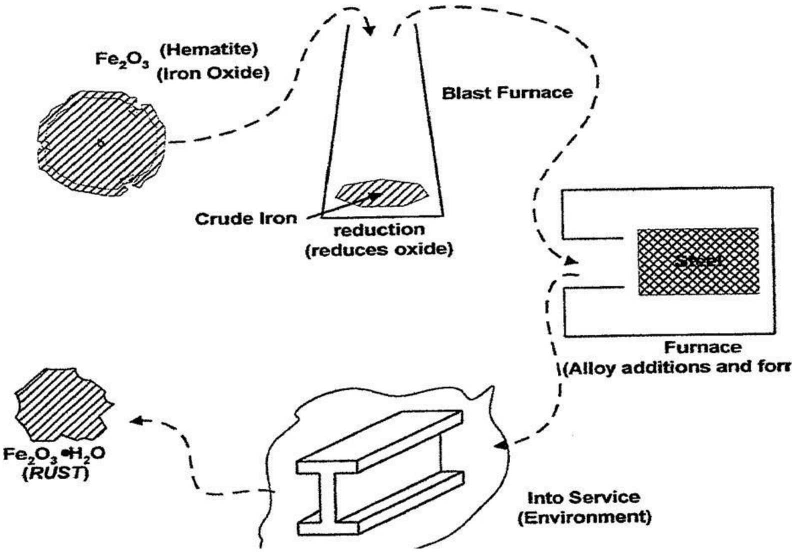
CORROSION AND DEGRADATION OF MATERIAL

LECTURE-1

What is corrosion?

Corrosion is defined as the destruction or deterioration of a material because of reaction with its environment.



Technological importance of corrosion study

Corrosion is the study of degradation is an enormous breadth of engineering systems depend upon corrosion protection for their reliability, performance, and safety

Importance of some engineering systems whose reliable performance and safety depend upon corrosion protection

For example-(i) Nuclear reactors involving high-temperature& high-pressure water

(ii) Ships and oil platforms in oceans and seas

(iii)Transportation vehicles (cars, trucks, and airplanes)

(iv) Electronic circuit boards, communication systems, buried pipelines

(v) Food packaging, home plumbing, tanks for storage of chemicals,

(vi) Carnival rides, vaults for the long-term storage of nuclear waste, water

purification plants, etc.

The best engineering approach is simply to ascertain the expected service life for the use of a cheap material,e.g. steel, and then replace it on a schedule that does not interfere with or endanger the intended functioning of the system. The interdisciplinary nature of corrosion problems and the development of viable solutions have been so important to technological development and safety.

LECTURE-2

Corrosion as non-equilibrium process:-

Corrosion of metal is always accompaniedby dissolution of a metal and reduction of an oxidant such as a proton in acidic solution and dissolved oxygen in a neutral solution.

Metal corrosion is not a single electrode reaction, but a complex reaction composed of the oxidation of metal atoms and the reduction of oxidants.

For example, iron dissolves in acidic solution

$Fe \rightarrow Fe^{2+} (aq) + 2e$ Anodic reaction

$2H^{+} (aq) + 2e \rightarrow H_2$ Cathodic reaction

The dissolution of ironproceeds according to the total reaction

$Fe + 2H^{+} (aq) \rightarrow Fe^{2+} (aq) + H_2$

In a neutral solution, dissolved oxygen attacks iron

Corrosion is complexly affected by the material itself and the environment, producing various kinds of surface films, e.g., oxide or hydroxide film.

In the above reactions, active sites for anodic and cathodic reaction are uniformly distributed over the metal surface,so that corrosion proceeds homogeneously on the surface.

If those reaction sites are localized at particular places, metal dissolution does not take place uniformly, but develops only at specialized places. This is called local corrosion; pitting corrosion through passive-film breakdown on a metal surface is a typical example.

LECTURE-3

Corrosion rate expressions:-

Agood corrosion rate should involve

(i)Familiar units

(ii) Easy calculation with minimum opportunity for error

(iii) Ready conversion to life in years

(iv) Penetration

Other units are (i)in./Yr (ii)in./Month (iii)mg/dm^2/day

$$\text{Mils per year} = 534W/DAT$$

Mils per year is the most commonly used corrosion ratebecause it expresses corrosion rate in terms of penetration using small integers

$$\text{Corrosion penetration rate} = K*(ai/nD)$$

‘a’ is the atomic weight of the metal, ‘i’ is the current density, ‘n’ is the number of electron lost, D is the density, K is a constant.

LECTURE-4

Electrochemical principles of corrosion-cell analogy:-

Two different reactions occur - oxidation and reduction

Electron transfer occurs

Potential (voltage) driving force required

Oxidation occurs at anode

Reduction occurs at cathode

Oxidation - e.g.

$$Fe \rightarrow Fe^{++} + 2e$$

Reduction – e.g.

$$O_2 + 2H_2O \rightarrow 4OH^- - 4e$$

Secondary - e.g.

$$4\,Fe^{++} + O_2 \rightarrow Fe_2O_3 + 8H^+$$

LECTURE-5

Concept of single electrode potential:-

The potential difference across an electrochemical cell is the potential difference measured between two electronic conductors connected to the electrodes.

The electrons will flow from the most negative point to the most positive point and byconvention; the current will flow in the opposite direction.

The electrode potential can be either positive or negative, the electrons in the external circuit can also be said to flow from the least positive electrode to the most positive electrode.

A voltmeter may be used to measure the potential differences across electrochemical cells but cannot measure directly the actual potential of any single electrode.

Part of the cell potential is assigned to one electrode and part to the other. (reference)

LECTURE-6

Reference electrode:-

Reference electrode is called the standard hydrogen electrode (SHE) if a standard solution of acid is used by definition the equilibrium potential of this electrode is zero at any temperature.

The SHE is also called by many normal hydrogen electrodes (NHE) in reference to a solution containing one equivalent of protons.

One must use unit activity rather than concentration of hydrogen ions and unit fugacity rather than unit pressure of hydrogen gas.

Reference electrodes are much preferred for practical considerations

LECTURE-7

E.M.F Series:-

A series in which the reduction electrode potentials of various electrodes have been arranged in the increasing order (downwards) is called Electrochemical Series.

The EMF series is an arrangement of various metals in the order of their electrochemical activities based on their standard oxidation-reduction potentials (E^0).

The standard reduction potential of hydrogen is zero. The electrodes above hydrogen have negative reduction potential while those places below it have positive reduction potential and vice-versa.

The most active metal in the series will be having a high negative standard potentialwhile nobler metals possess relatively less negative (or more positive) standard potential (E^0).

If a couple of two metals in the EMF areconsidered, the one with higher negative E^0 will act as anode (and will corrode) compared to the other with arelatively less negative E^0 value (cathode).

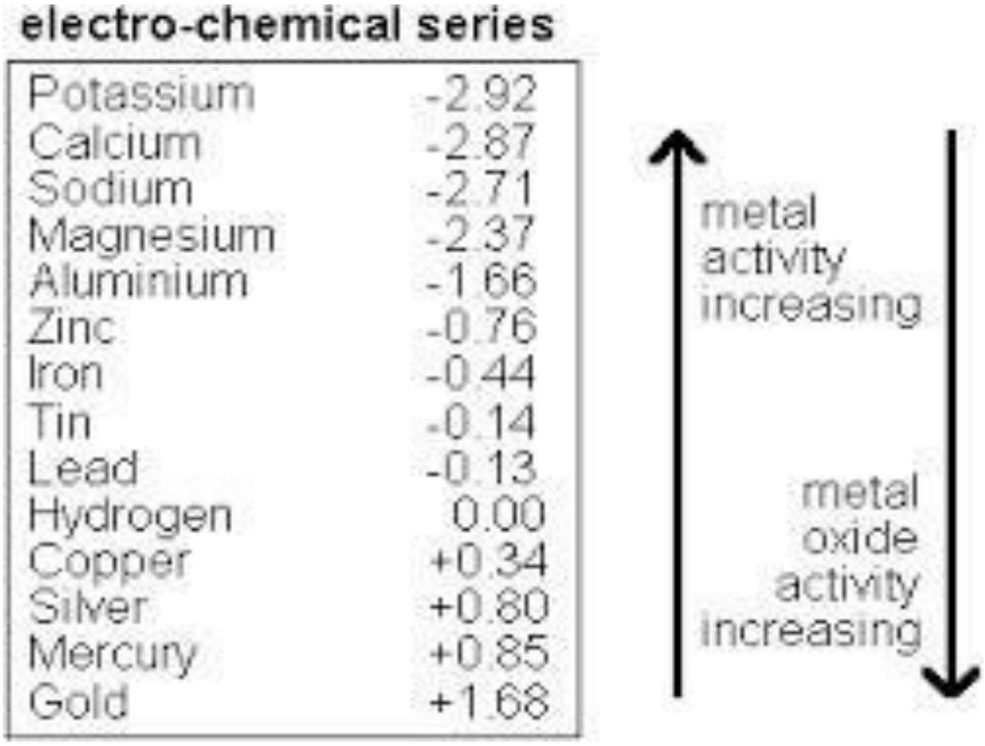
(a)EMF series lists only metals (little engineering application), alloys not included

b) Electrode potentials listed calculated from thermodynamic principles (corrosion potentials are more relevant).

c) Equilibrium potentials with concentrations at unit activity (Exact prediction of galvanic coupling not possible).

d) Predicts only tendency to corrode (Role of passive films and oxidation kinetics not predicted).

e) Effect of environment not predicted (Eg: Sn – Fe couple as in Tin cans)



electro-chemical series

Potassium	-2.92
Calcium	-2.87
Sodium	-2.71
Magnesium	-2.37
Aluminium	-1.66
Zinc	-0.76
Iron	-0.44
Tin	-0.14
Lead	-0.13
Hydrogen	0.00
Copper	+0.34
Silver	+0.80
Mercury	+0.85
Gold	+1.68

LECTURE-8

Galvanic series:-

a) Instead of standard electrode potentials, actually measured rest potentials of metals and alloys in a given environment arranged with respect to nobility and activity.

b) Practically measured potentials vs reference electrode.

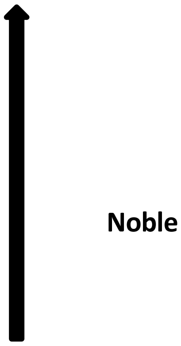
c) Effect of coupling of metals and alloys on corrosion rate can be predicted.

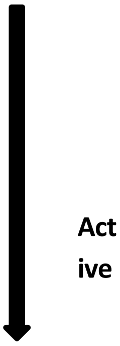
Certain anomalies Eg: Stainless steels (active and passive) galvanic series is generally good for stagnant conditions and not for turbulent conditions.

Galvanising of steels for corrosion protection is a classic example of corrosion protection through proper galvanic (sacrificial) method.

<u>Galvanic series in sea water</u>:-

Platinum
Gold
Graphite
Silver
Hastelloy C
18-8 stainless steel (passive)
Chromium steel > 11% Cr (passive)
Inconel (passive)
Nickel (passive)
Monel
Bronzes
Copper
Brasses
Inconel (active)
Nickel (active)
Tin
Lead
Lead-tin (solder)
18-8 Mo stainless steel (active)
18-8 stainless steel (active)
Chromium steel > 11% Cr (active)
Ni-resist
Cast Iron
Steel or Iron
2024 aluminium
Cadmium
Commercially pure aluminium
Zinc
Magnesium and its alloys





Lecture-9

E.M.F series used in corrosion study for:-

(i) Oxidizing and Reducing Strengths

(ii) Comparison of Reactivities of Metals

(iii) Predicting the Liberation of Hydrogen Gas from Acids by Metals

(iv) Calculation of the EMF of the Cell

(v) Predicting Feasibility of a Redox Reaction

Galvanic series used in corrosion study

Galvanic corrosion is useful for the design engineer in predicting the relative behaviour of adjacent materials in marine applications.

The series shows that alloy composition radically affects the tendency towards corrosion.

Galvanic series gives the accurate result.

It does not indicate the extent of polarisation of electrodes & the rate of corrosion.

It does not predict the effect of Ph.

LECTURE-10

Polarization

Polarization as an electrochemical phenomenon is of importance in the corrosion process. For all metals and alloys in any aqueous environment, cathodic polarization always reduces the corrosion rate. Cathodic protection refers to the application of a cathodic polarization to a corroding system.

Polarization can occur in three ways:

- Concentration polarization
- Resistance polarization
- Activation polarization

Concentration polarization of an electrode is the result of formation of a diffusion layer adjacent to the surface of the electrode where there is a gradient of ion concentration.

Diffusion of the ions through the layers controls the electrochemical reaction and is important for processes such as electroplating and corrosion. Concentration polarization may be reduced by increasing agitation or raising the temperature of the electrolyte.

Resistance polarization describes the potential drop due to the high resistivity of the electrolyte surrounding the electrode. It may also be a result of the insulation effect of the film on the electrode surface formed by the reaction products. Resistance polarization is expressed by the Ohm's law.

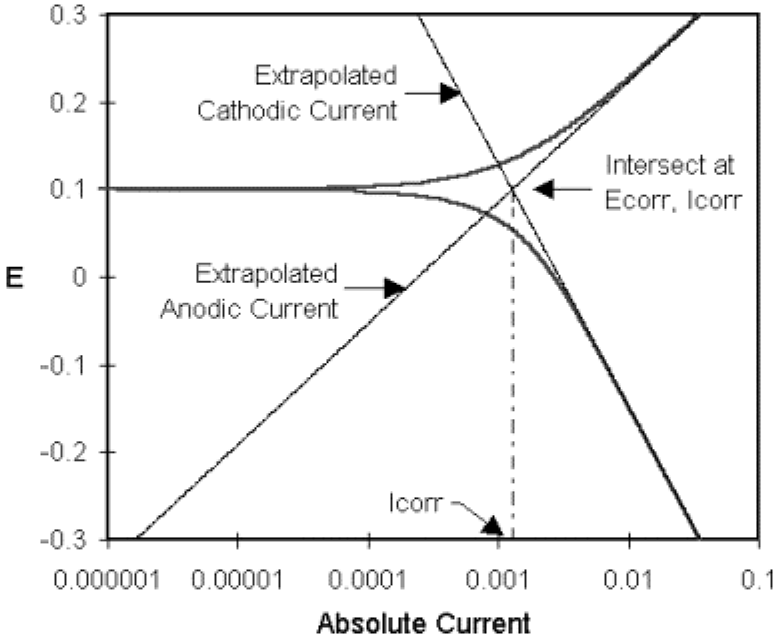
Activation polarization occurs when the electrochemical reaction proceeds through several successive steps. The speed of the overall reaction is determined by the slowest step (known as the rate-determining step) of the process. For example, in a hydrogen reduction reaction, the reaction may proceed as follows:

1. Hydrogen ions are absorbed from the solution onto the anode surface.

2. Electron transfer occurs from the anode to the hydrogen ions to form hydrogen.

3. The hydrogen atoms form hydrogen gas molecules.

4. Hydrogen gas bubbles are formed.



LECTURE-11

Passivity

Passivity means the loss of chemical reactivity experienced by certain metals or alloys under particular environment condition.

Metals that normally fall victim to corrosion will sometimes exhibit passivity to corrosion. Passivity is the characteristic of a metal exhibited when that metal does not become active in thecorrosion reaction.

Passivity is caused by the build-up of a stable, tenacious layer of metal oxideon the surface of the metal.

This oxide layer is formed by corrosion on a clean metal surface, where the corrosion products are insoluble in the particular environment to which the metal isexposed.

Once the layer, or film, is formed, it acts as a barrier separating the metal surface fromthe environment.

For further corrosion to occur, the reactants must diffuse through the oxidefilm. Such diffusion is very slow or non-existent, thus corrosion either decreases markedly or stops.

The behaviour of a metal or alloy can be conveniently divide into three regions

1. Active

2. Passive

3. Trans-passive

Active: - In the active region behaviour of the material is identical to that of a normal metal. Slight increase in the oxidizing power of solution cause a rapid increase in corrosion rate.

Passive:-If more oxidizing agent is added the corrosion rate suddenly decreases. This is the beginning of passive region.

Trans-passive:-At a very high concentration oxidizer or in the presence of powerful oxidizers the corrosion rate increases with increase in oxidizing power. This is known as Trans-passive region.

Pourbaix Diagram

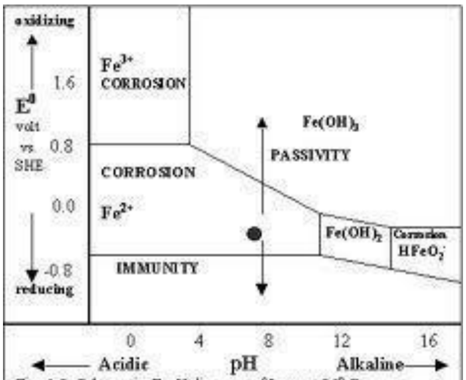


Fig. 1.2 Schematic E-pH diagram of Iron at 25° C
** Not drawn to scale

Pourbaix diagram illustrate the combined effect of the potential and the pH of the aqueous solutions on the products of corrosion in metal water system.

This diagram shows the nature of the stable phase as a function of electrode potential and Ph of the solution.

Different types of behaviour are indicated

1. Immunity to corrosion
2. Corrosion
3. Protection due to formation of a layer of oxide

Horizontal lines, vertical lines, sloping lines are indicated.

Pourbaix diagram predicts the spontaneous direction of reactions,the stability and the composition of the corrosion products and the effects of change in environments to prevent or reduce the corrosion.

Pourbaix diagram are mainly based on thermodynamic data. This diagram give no information on the rate of corrosion.

LECTURE-1

Module-II

Different types of corrosion:-

(i) Uniform attack

(ii) Galvanic corrosion

(iii) Crevice corrosion

(iv) Pitting corrosion

(v) Intergranular corrosion

(vi) Selective leaching

(vii)Erosion corrosion

(viii)Stress corrosion cracking

LECTURE-2

Uniform attack

The whole surface of the metal is corroded to the same degree.

The metal becomes thinner uniformly to eventually fail is called uniform corrosion.

e.g A piece of steel or zinc immersed in dilute sulphuric acid will normally dissolve at a uniform rate over its entire surface.

Characteristic features

It is characterized by a chemical or electrochemical reaction that proceeds uniformly over the entire exposed surface or over a large area.

Causes:-

When a metal is placed in an electrolyte anode and cathode continually shift.

The metal corrode without uniformly without being in contact with a second material.

Remedial Measures:-

(i)Proper material including coatings

(ii)Including coatings

(iii)Cathodic protection

LECTURE-3

Galvanic corrosion

A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution.

Corrosion of the less corrosion resistant metal is usually increased and attack of the more resistant material is decreased when they are not in contact.

Because of electric currents and dissimilar metals involved this form of corrosion is called galvanic or two metal corrosion.

e.g. Dry cell battery.

Characteristic Feature:-

It is electrochemical corrosion in nature. The driving force for current and corrosion is the potential developed between the two metals.

Causes:-

When the metals are placed in contact the potential differences produce electron flow between them.

The less resistant metal becomes anodic and the more resistant metal cathodic.

Cathode or cathodic metal corrodes very little or not at all in this type of couple.

Accelerated corrosion due to galvanic effects is usually greatest near the junction, with attack decreasing with increasing distance from that point.

Another important factor in galvanic corrosion is the area effect or the ratio of cathodic to anodic areas.An unfavourable area ratio consists of a large cathode and a small anode.

Remedial measures

(i) Select combinations of metals as close together as possible in the galvanic series.

(ii) Avoid unfavourable area effect of a small anode and large cathode.

(iii)Insulate dissimilar metals wherever practicable

(iv) Apply coatings with caution

(v) Add inhibitors if to decrease the aggressiveness of the environment.

(vi) Avoid threaded joints for materials far apart in the series.

(vii) Design for the use of readily replaceable anodic parts or make them thicker for longer life.

(viii) Install a third metal that is anodic to both metals in galvanic contact.

LECTURE-4

Crevice corrosion

Corrosion frequently occurs within crevices and other shielded areas on metal surfaces exposed to corrosives.

This type of attack is associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits and crevices under bolt and rivet heads.

Characteristic features

Deposits are produced by crevice corrosion are sand, dirt, corrosion products and other solids.

Deposits act as shield and create a stagnant condition thereafter.

The deposit is also a permeable corrosion product.

This is concentration cell corrosion in nature.

Causes

This consists of four stages. Stage 1: Corrosion occurs as normal both inside and outside the crevice:

Anodic reaction: $M \rightarrow M^{n+} + ne$,

Cathodic reaction: $O_2 + 2H_2O + 4e = 4OH^-$.

The positively charged metallic ions are electrostatically counterbalanced by OH^- .

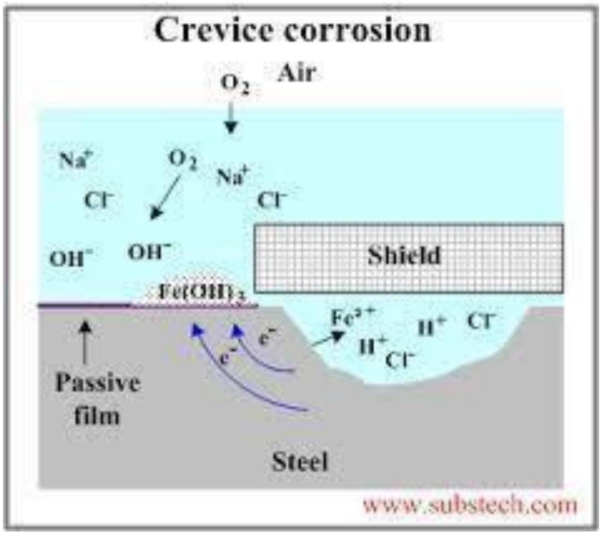
Stage 2: at this stage, the cathodic reaction inside the crevice consumed most of the oxygen available.

Stage 3: Cl^- and OH^- diffuse into the crevice to maintain a minimum potential energy. Metal chloride is formed. Hydrolysis of metal chloride lowers pH and

$MCl_n + nH_2O = M(OH)_n + nHCl$.

Stage 4: More Mn+ ions attack more Cl- leads to lower pH inside crevice, metal dissolution accelerates and more Mn+ ions will be produced that will lower pH. Figure 1 shows mechanism of active and passive corrosion and its corresponding Anodic and Cathodic reactions in crevice corrosion

Corrosion have been developed including cathodic protection and using inhibitors and coatings. Hot wax dip method and sealing crevices with polysulfide are two popular protection methods currently used in automotive and aerospace industries respectively.



Remedial measures

(i) Use welded but joints instead of riveted or bolted joints in new equipment.

(ii)Close crevices in existing lap joints by continuous welding, caulking or soldering.

(iii)Design vessels for complete drainage; avoid sharp corners and stagnant areas.

(iv)Inspect equipment and remove deposits frequently.

(v) Remove solids in suspension early in the process or plant flow sheet, if possible.

(vi) Remove wet packing materials during long shutdown.

(vii) Provide uniform environment, if possible as in the case of back filling a pipeline trench

(viii) Use solids as non-absorbent gaskets such as Teflon wherever possible.

(ix) Weld instead of rolling in tubes in tubes sheets.

LECTURE-5

Pitting corrosion

Pitting corrosion is results in holes in the metal. Holes may be smaller or larger in diameter but in most cases they are relatively smaller.

Pitting corrosion is one the most destructive and insidious forms of corrosion. It causes equipment to fail because of perforation with only small % weight loss of entire structure.

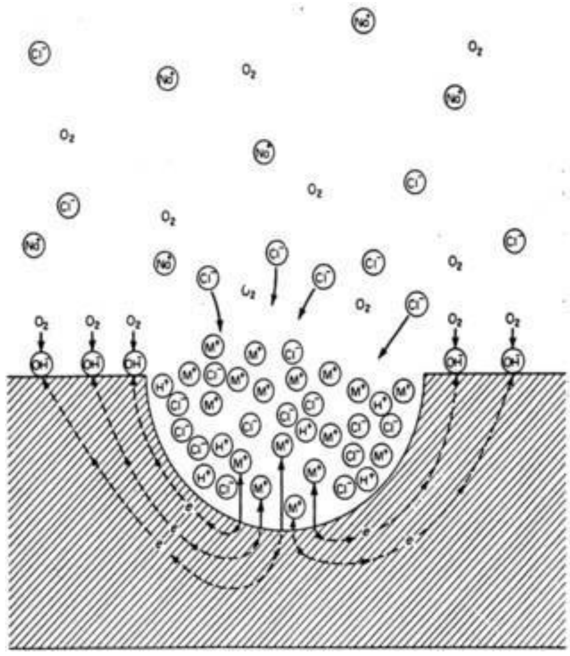
It is very difficult to detect in laboratory test also.

Pitting corrosion is vicious because it is a localized and intense form of corrosion and failures occur with extreme suddenness.

Pits usually grow in the direction of gravity. Pits develop and grow downward from horizontal surface.

Characteristic features

Auto-catalytic nature of pitting



Causes

Solution composition

Most pitting failures caused by chloride and chlorine –containing ions. Much equipment operates in sea water and brackish water.

Hypochlorites are very difficult to handle because of their strong tendencies.

Pitting can be prevented by many instances by the presence of hydroxide, chromate or silicate salts. If these substances tend to accelerate pitting when present in small concentration.

Velocity

Increasing velocity decreases pitting attack.

e.g A stainless steel pump would give good service handling sea water if it were run continuously .

Metallurgical variables

Severe cold working increases pitting attack of 18-8 stainless steel in ferric chlorides.

Holding 304 and 316 stainless steel in the sensitizing temperature range decreases their pitting resistance.

Austenitic stainless steel exhibits the greatest pitting resistance when solution quenched above 1800^0F.

Remedial measures

(i)Use welded but joints instead of riveted or bolted joints in new equipment.

(ii)Close crevices in existing lap joints by continuous welding, caulking or soldering.

(iii)Design vessels for complete drainage; avoid sharp corners and stagnant areas.

(iv)Inspect equipment and remove deposits frequently.

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LECTURE-6

Intergranular corrosion

If a metal corrodes uniform attack results since grain boundaries are usually only slightly more reactive than the matrix.

Grain interfaces are very reactive and intergranular corrosion results.

Localized attack at and adjacent to grain boundaries with relatively little corrosion of the grain is intergranular corrosion.

e.gIntergranular corrosion occurs in 18-8 stainless steel.

Characteristic features

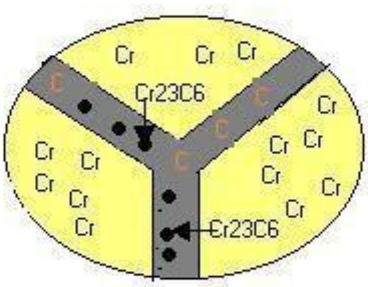
Weld decay-occurs at an appreciable distance from the weld

Knife line Attack-The stabilized austenitic stainless steel is attacked intergranularly under certain condition because of chromium carbide precipitation.

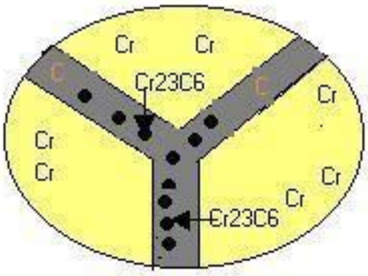
Knife line Attack occurs in a narrow band in the parent metal immediately adjacent to the weld.

Knife Line Attack occurs in stabilized steel.

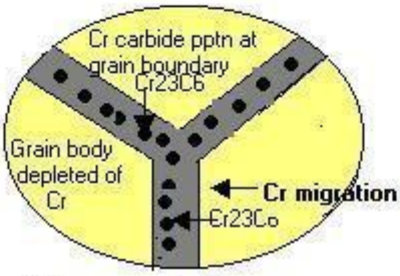
Austenitic stainless steel.



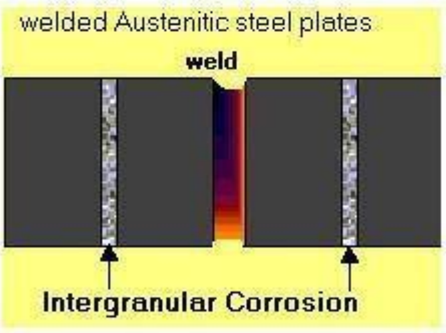
Intergranular Corrosion



Intergranular Corrosion



Intergranular Corrosion



Intergranular Corrosion

Causes

(i)Intergranular corrosion can be caused by impurities at the grain boundaries.

(ii)Enrichment of one of the alloying elements

(iii)Depletion of one of the alloying element in the grain boundary area.

Remedial measures

(i) Employing high-temperature solution heat treatment commonly term quench annealing or solution quenching.

(ii) Adding elements that are strong carbide former

(iii)Lowering the carbon content to below 0.03%.

LECTURE-7

Selective leaching

Selective leaching is the removal of one element from a solid alloy by corrosion processes.

e.g selective removal of zinc in brass alloys

Characteristic feature

Dezincification observed with the naked eye because the alloy assumes a red or copper color that contrasts with the original colour.

There are two types of dezincification layer type or plug type.

Layer type dezincification seems to favour the high brasses and definitely acid environments.

The plug type seems tooccur more often in low brasses and neutral, alkaline or slightly acidic conditions.

Causes

Main mechanism consists of three steps.

(i)The brass dissolves

(ii) The zinc ion stays in solution

(iii) The copper plates back on.

Remedial measures

(i)Reducing the aggressiveness of the environment

(ii)Cathodic protection

LECTURE-8

Erosion corrosion

Erosion corrosion is the acceleration or increase in the rate of deterioration or attack of a metal because of relative movement between a corrosive fluid and the metal surface.

The movement is quite rapid, the mechanical wear effects or abrasion are involved.

Metal is removed from the surface as dissolved ions or it forms solid corrosion products that are mechanically swept from the metal surface.

e.g Pump impeller, heat exchanger tube handling water.

Characteristics feature

Most of the metals or alloys are susceptible to erosion corrosion.

Many of the corrosive medium could cause erosion corrosion.it may be gases, aqueous solution, organic systems, liquid metals.

Erosion corrosion is characterized in appearance by grooves, gullies, waves, roundedholes, valleys and usually exhibit directional pattern.

Failures because of erosion corrosion occur in a relatively short time and they are unexpected.

Causes

(i)The nature and properties of the protective film that forms on some metals or alloys are very important from the stand point of resistance to erosion corrosion.

Velocity strongly influences the mechanisms of the corrosion reaction.

It exhibits mechanical wear effects at high values and particularly when the solution contains solids in suspension.

Increase in velocity result in increased attack if substantial flow rate of flow is involved.

Erosion corrosion can occur on metals and alloys that are completely resistance to a particular environment at low velocities.

Higher velocities also decrease attack in some cases by preventing the deposition of slits or dirt's which cause crevice corrosion.

Velocity can decrease attack and increase the effectiveness of inhibitors by supplying the chemicals to the metal surface at a higher rate.

Erosion corrosion failures occur because turbulence or turbulent flow condition exists.

Galvanic corrosion can influence erosion corrosion when dissimilar metals are in contacts in a flowing system.

Remedial measures

(i)Materials with better resistance to erosion corrosion

(ii)Design

(iii)Alteration of the environment

(iv)Coating

(v) Catholic protection

LECTURE-9

Stress corrosion cracking

Stress corrosion cracking refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium.

There are two types of stress corrosion cracking (i) Season cracking

(ii) Causticembrittlement

Many explosions of riveted boilers occurred in steam driven locomotives. These failures showed crack or brittle failure at the rivet holes.

Characteristic feature

Stress corrosion cracking give the appearance of a brittle mechanical fracture as a result of local corrosion processes.

Both intergranular and trans-granular stress corrosion cracking observed.

Increase the stress decreases the time before cracking occurs. Stress depends on temperature, alloy, composition and environment composition.

The parameter of time in stress corrosion cracking is important since the major damage during SCC occurs during the later stages.

Environmental factor is also the most important factor for SCC.

Causes

1. Dislocation co-planarity

2. Stress aging

3. Adsorption

4. Stress accelerated corrosion

5. Film formation at cracking wall

6. Film rupture

7. Chloride ion migration

8. Hydride formation

9. Hydrogenembrittlement

10. Corrosion products wedging

Remedial measures

(i) Lower the stress

(ii) Eliminating the critical environmental species

(iii) Changing the alloy

(iv) Apply cathodic protection

(v) Adding inhibitors

(vi)Coating

(vii)Shot peening

LECTURE-10

Principle of corrosion prevention

Material selection-Material selection is the most important method of preventing or reducing corrosion damage

Metal purification-The corrosion resistance of a pure metal is better than that of one containing impurities or small amount of other impurities.

Nonmetallics-5types of non-metallic are used for linings or covering of substantial thickness

Plastics

Ceramics

Carbon and graphite

Wood

Lecture-11

Alteration of environment-Altering the environment provides a versatile means for reducing corrosion.

Changing the medium

Lowering the temperature

Decreasing the velocity

Removing oxygen or oxidizers

Changing concentration

Inhibitors-Inhibitors is a substance when added in small concentration to an environment decreases the corrosion rate.

Adsorption type inhibitor-These represent the largest class of inhibiting substances

Vapour phase inhibitor-This possess a high vapour pressure

Design

Design should consider mechanical and strength requirements together with an allowance for corrosion. In all the cases the mechanical design of a component should be based on the material of construction.

This is important to recognize, since materials of construction used for corrosion resistance vary widely in their mechanical characteristics.

Design rules:-

There are many design rules which should be followed for best corrosion resistance. Some of the design rules that should be followed are listed below:-

1. Weld rather than rivet tanks and other conainers.Riveted joints provide sites for crevice corrosion.

2. Design tanks and other containers for easy draining and easy cleaning. Tank bottom should be sloped toward drain holes so that liquid cannot collect after the tank is emptied. Concentrated sulphuric acid is only negligibly corrosive toward steel.

3. Design systems for the easy replacement for components that are expected for fall rapidly in service.

4. Avoid excessive mechanical stresses and stress concentration in components exposed to corrosive mediums.

5. Avoid electrical contact between dissimilar metals to prevent galvanic corrosion.

6. Avoid sharp bends in piping systems when high velocities and/or solid in suspension are involved.

7. Provide thicker structures to take care of impingement effects.

8. Make pure materials are properly selected.

9. Be sure all relevant codes and standards are met.

Lecture-12

<u>Cathodic protection</u>:-

Cathodicprotection is achieved by supplying electrons to the metal structure to be protected.

$$M \rightarrow M^{n+} + ne \text{..................................(1)}$$

$2H^+ + 2e \rightarrow H_2$..(2)

This two equation indicates that the addition of electrons to the structure will tend to suppress metal dissolution and increase the rate of hydrogen evolution.

1. It applicable to all metals.

2. Weak to moderate in corrosive atmosphere.

3. Relative cost of installation is low.

4. Throwing power is low

5. Significance of applied current is very complex-it does not indicate corrosion rate.

Anodic Protection:-

It is based on the formation of a protective film on metals by externally applied anodic currents.

$M \rightarrow M^{n+} + ne$ .... (1)

$2H^{+} + 2e \rightarrow H_2$ ....(2)

Considering the above equation it appears that the application of anodic currents to a structure should tend to increase the dissolution rate of metal and decrease the rate of hydrogen evolution.

1.1.It applicable to active-passive metals only.

2. Weak to aggressive in corrosive atmosphere.

3. Relative cost of installation is high.

4. Throwing power is very high.

5. Significance of applied current is often a direct measure of protected corrosion rate.

Lecture-13

Coatings:-

The main function of coating is to provide an effective barrier. There are two types of coatings

1. Metallic

2. Inorganic

Metallic Coating:-Metal coated articles are automobile bumpers and trim, house hold appliances, galvanised steels and tin cans.

Electro deposition:- It consists of immersing a part to be coated in a solution of the metal to be plated and passing direct current between part and another electrode,e.g. zinc,nickel,tin.

Flame spraying:-It consist of feeding a metal weir or powder throw a melting flame so that the metal is finely divided liquid particles is blown on to the surface protected. This is also called metallising.e.g. Tanks, cars, vessels.

Cladding: - This involves a surface layer of sheet metal usually put on by rolling two sheets of metal together.

Hot-dipping:-These applied to metals by immersing them in a molten metal bath of low melting point metals,e.g. zinc,lead,tin,aluminium.

Vapour-deposition:- This is accomplishment in high vacuum chamber

Diffusion:-Diffusion coating involves heat treatment to cause alloy formation by diffusion of one metal into the other.

Organic Coatings:-This involve relatively thin barrier between substrate material and the environment.e.g. Paints, varnishes, lacquers.

Primers can contain rush inhibitive pigments such as zinc-chromate. Top coat selection is most important.

LECTURE-14

Corrosion testing methods:-

This divided into Four types:-1. Laboratory test

2. Pilot plant test

3. Plan or actual service test

4. Field test

Laboratory test:-This test are characterised by small specimen and small volumes of solutions and actual conditions are simulated.

Pilot plant test-This test are usually the best and more desirable.

Plant or actual service test- It involves tests in particular service or a given palnt.

Field test-This test gives more general information.

Main justification for corrosion testing:-

1. Evolution and selection of material for a specific environment or a given definite application.

2. Evolution of new or old metals or alloys to determine the environments in which they are suitable.

3. Control of corrosion resistance of the material or corrosiveness of the environment

4. Study of the mechanism of corrosion or other research and development purposes.

Corrosion Testing Techniques:-

1. Materials and specimen-

Chemical composition, fabricationhistory, metallurgical history and positive identification of materials are all important

2. Surface Preparation-

Common and widely used surface finish is required for the test

3. Measuring and weighing-

The specimen should be measured and weighed for the calculation of surface area

4. Exposure Techniques-

(i) The corrosive should have easy access to specimen.

(ii) The support should not be failed during the test.

(iii) Specimen should be insulated or isolated electrically for contact with other metal.

(iv)Specimen should be properly positioned.

Duration:-Proper selection of time and number of period of exposure are important

Aeration-The presence of dissolved oxygen in a liquid environment influences the corrosion rate.

Cleaning specimen after exposure-Hold the specimen under a stream of tap water and scrubbing the surface with rubber stopper. Then dry it properly and measured the weight.

Standard expression for corrosion rate:-

Mils/year = 534W/(D*A*T)

Another unit of corrosion is MDD.

MODULE-III

LECTURE-1

Introduction to high temperature corrosion

In caseof gas turbines and rocket engines as a means of air craft propulsion where high temperature corrosion occurs.

There are certain distinguishing features about the morphology of high-temperature corrosion that aid in deciding upon the cause of damage.

Some typical indications include thick scales, grossly thinned metal, burnt (blackened) or charred surfaces, molten phases, deposits of various colors, distortion and cracking, and magnetism in what was first a nonmagnetic (e.g., austenitic) matrix.

Damage varies significantly based upon the environment, and will be most severe when a material’s oxidation limits are exceeded, notably when an alloy sustains breakaway attack by oxygen/sulfur, halogen/oxygen, low-melting fluxing salts, molten glasses, or molten metals, especially.

LECTURE-2

Pilling-Bed worth ratio:-This is the ratio of oxide volume to the volume of metal from which the oxide has formed. If this ratio is less than one there is insufficient oxide to cover the metal.

If this ratio is greater than one an adherent, non-porous oxides protective film forms. If this ratio is greater than two the volume of oxide is greater than that of metal.

LECTURE-3

Oxidation Kinetics:-The rate of oxidation can be expressed as weight gain per unit area or how the thickness of the oxide film increase with time

Linear rate law-Thickness weight gain of the oxide layer increases with time uniformly

$W=At+D$

Logarithm Rate Law-This is usually observed with thin highly protective film at low temperature Fe, Cu,zinc,Ni.

Parabolic Rate law-When diffusion of ion occurs through the different structures of oxide layers the oxidation follow parabolic law

$W^2=At+B$

Cubic Rate Law-Some metal under specific conditions particularly with short exposures periods follow cubic law

$W^3=Kt+C$

LECTURE-4

Oxide defect structure-Metal oxides actually formed on metal surfacedo not have proper crystal lattices. This crystal lattice contains point defects above absolute zero. The defects could be anion vacancies and cation vacancies or interstitial.

When a large concentration of defects are present a change in compositions of the oxide occurs.The deviation could be due to

(i) Excess metal due to anion vacancies

(ii)Excess metal due to interstitial cations

(iii)Excess oxygen due to interstitial anions

(iv)Excess oxygen due to cation vacancies.

1. Metalcation deficient p-type semi conducting oxides such as Nio.

2. Metalcation excess N-type semi conducting oxides such as ZnO, CdO, PbO_2, ZrO_2

LECTURE-5

Wagner-Hauffe valence approach in alloy oxidation:-

1. (a) For N-type oxide-Substitution of cations into the lattice the concentration of interstitialcations or anion vacancies and decreases the concentration of excess electrons a diffusion control oxidation rate would be increased.

(b) Substitution of cations possessing higher valancedecreases the concentration of interstitial cations or anions vacancies and increases of concentration of excess electrons. A diffusion controlled oxidation rate would be increased.

(2) For P type of oxides

(a) The incorporation of lower valencecations decreases the concentration of cation vacancies or interstitial anions and increase of number of electron holes. A diffusion control oxidation rate would be increased

(b) The addition of higher valencecationsincreases the cationvacancies or interstitial anions concentration and decreases the electron hole concentration. A diffusion –controlled oxidation rate would be decreased.

LECTURE-6

Catastrophic Oxidation

Catastrophic oxidation means metal-oxygen reactions that occurs continuously at increasing rates or that break away from protective behaviour & react very rapidly.

Metals which follow linear oxidation kinetics at lower temperatures oxidize catastrophically at high temperatures because of rapid exothermic reaction at their surfaces.

If the rate of heat transfer to the metal and surrounding is less than the rate of heat evolution by the reaction the surface temperature increases.

Metals like Molybdenum, tungsten, osmium, rhenium, vanadium which have volatile oxides oxidize catastrophically but does not result from surface ignition.

Catastrophic oxidation can occur if vanadium oxide or lead oxide compounds are present in the gas phase

Alloys with Cr and Ni retard the effect catastrophic oxidation.

LECTURE-7

Internal Oxidation

Alloy or more dilute components that form more stable oxides than the base metal oxidize preferentially below the external surface of the metal or below the metal scale interface is known as internal oxidation because the oxide precipitate is formed within the metal matrix, rather than the external surface.

Dilute alloys of base metal exhibiting high solubility and diffusivity for atomic oxygen are subject to internal oxidation. Dilute copper and silver base alloys containing Al, Zn, Cd,Be are internal oxidation.

Internal oxidation also occurs in iron, nickel and cobalt alloys used in high temperature applications.

Internal oxidation can be prevented by increasing the less noble alloy content, so that a surface scale is formed with the absence of internal oxidation.

A reduction in the oxidizing activity of the environment for alloy composition favors the formation of a protective scale.

The precipitation of internal oxides is known to harden and strengthen metals; important effect in the applications for high temperature materials is a deleterious increase in notch brittleness.

LECTURE-8

High temperature alloy design

High-temperature alloys are typically iron-, nickel- or cobalt-based alloys containing >20% chromium (or 30% for cobalt), which is sufficient to form a protective oxide against further oxidation.

The basic alloys include various additional elements that aid in corrosion resistance, notably aluminum (typically >4% to develop an alumina scale), silicon (up to 5% to develop an amorphous (glass-like) scale that is complementary to chromia).

Rare earth elements yttrium, cerium, and lanthanum, that improve scale adhesion. Other additions, such as the reactive metals, the refractorymetals, and carbon, primarily improve mechanical properties.

The compositions of high temperature materials used for oxidation resistance and especially in gas turbine application are commonly hardened by precipitation.

LECTURE-9

Prevention of high temperature corrosion use of coating

High-temperature coatings or surface modifications are generally based onchromium, aluminium, or silicon, which, at high temperatures, form protective oxides.

High temperature corrosion prevention coating based on inorganic copolymer with heat-resisting and corrosion resistant pigments. These are used for metal structures such as steel pipes, steam pipes, hot oil pipes, plant facilities etc.

CHARACTERISTICS

Coating can provide

1. Excellent high heat resistance,

2. Dry-hard within 8 hours (25℃), paint film can reach 80% cured in room temperature, when applying temperatures are above 60℃, paintfilm can be cured completely after 3 days.

3. Can be sprayeddirectly to high temperature carbon steel and galvanized steel , stainless facilities when the temperature up to 220℃.

4. Excellent anti-corrosion for thermal shocking structures.

5. Excellent adhesion and corrosion prevention.

6. Good moisture resistance for the condition of hot and cold cycle.

LECTURE-10

Liquid metal embrittlement

Liquid metal penetration along the grain boundaries results cracking and constitutes a real problem. Cu, Al, Ti, stainless steel, Ni alloys are subject to liquid metal cracking.

Zinc is the most common offender because of wide spread use of galvanised steel and zinc pigmented primers in plant but cadmium plated hardware also caused problem.

Contamination of stainless steel by contact with galvanizedwire during heat treatment is an established cause of liquid metal cracking.

Liquid metal cracking does not involve corrosion.

Liquid metal cracking to occur combination of circumstances must exist.

1. A temperature above 400^0C

2. Direct contact with the molten metal

3. A highly stressed alloy.

Remedy of Liquid metal cracking

Liquid metal cracking can be prevented from atmospheric rusting by a zinc free heavy duty coating system such as high build epoxies

Nickel base alloys can suffer intercrystalline cracking during heat treatment or welding due to sulphur contamination.

Sulphur or sulphurous contaminants cause cracking during welding.

Proper cleaning or decontamination before welding or heat treating is an effective remedy.

LECTURE-11

Chemical Degradation of non-metallic material

Rubber:-The outstanding characteristics of rubber are resilience or low modulus of elasticity. Flexibility accounts for most applications such as tubing, belting, automobile tires.

Chemical and abrasion resistance and good insulating qualities result in many corrosion application

A natural rubber has better mechanical properties than the synthetic or natural rubber.

Natural Rubber

Rubber is a long chain molecule of isoprene it comes from tree as liquid latex.it hs coil like structure and high elasticity.

Adding sulphur and heating makes the rubber harder and more brittle. This is known as vulcanization. 50% sulphur makes a hard product known as ebonite.

Semi hard and hard rubber are used for tires, tank linings and other items.

Corrosion resistance usually increases with hardness. In case of lining pipes and tanks rubber is applied soft and then cured in a autoclaves.

Synthetic Rubber

Neoprene and nitrile rubber possess resistance to oils and gasoline.

Butyl rubber exhibits better resistance to oxidizing environments such as air and dilute nitric acid.

An outstanding characteristic of butyl rubber is impermeability to gases. This is used as inner tubes and process equipment such as a seal for floating storage tanks.

Neoprene lined vessels handle strong sodium hydroxide. One of the extensive application is gasoline hoses.

Rubbers can be compounded to produce a wide range of mechanical properties from hard to soft.

Soft rubbers are best abrasion resistance.

Hard rubber is used for erosion corrosion condition.

LECTURE-12

Chemical Degradation of non-metallic material

PLASTICS

Plastics are produced by casting,moulding,extrusion and calendaring .They are available as solid parts,lining coating,foams fibres and films.

A plastic is an essential ingredient an organic substance of large molecular weight is solid in its finished state can be shaped by flow.

Plastics divided into two classes (i) Thermoplastics

(ii) Thermosetting

Plastics do not dissolve like metals. They are degraded and corroded because of swelling, loss in mechanical properties, softening, hardening, spalling and discoloration.

Thermoplastics

Fluorocarbon:-It consists of carbon and fluorine. Its low co-efficient of friction is the basis for a very successful application of Teflon.

A confined Teflon sleeve separates the plug and body of this plug valve and acts as lubricant which prevent freezing or sticking of the metal parts.

Other uses are seals, gaskets, wire insulation, expansion joints, linings for pipes, tape, tubing , valve, coating and heat exchangers.

Corrosion does not occur, corrosion products do not form and stick to the tubing wall.

Acrylics

Methyl methacrylate is the best known of this group.

It is used for brush, purse handles, and transparent displays, working models, airplane canopies and taillights.

Acrylics are soft easily scratched and not very temperature resistant.

Nylon

This material is best for hosiery but finds much use for corrosion resistant applications.Its main application depends on strength, low coefficient of friction and wear resistance.

These are gears, drawer, shelf rollers, fishline, sutures,tennis racket strings, denture, automobile door catches and brush bristles.

It is also used for electrical insulation since it permits high temperature than rubber.

First industrial application of nylon as a bushing for spinning buckets in the manufacture of rayons.

Chlorinated polyther

Penton a chlorinated polyether is one of the newer plastics; it is used for handling corrosives, including aggressive environment.

Solid parts such as valve, pipe, linings, and coating are available. Coatings are applied by the fluidized bed process up to 40 mils thick.

Polyethylene

Alathon,aeroflex,polythene and polyethylene are the largest production of plastics.They are used for packaging film, sheet, squeeze bottles,pans,tumblers,ice trays.

Certain solvent produce stress corrosion cracking of polyethylene. Ultrahigh-molecular weight polyethylene exhibits very good resistance to erosion corrosion.

Polypropylene

It exhibits better heat & corrosion resistance & is stiffer than polyethylene.

It is made into valves, bottles, pipe, fittings and scooter parts.

Polystyrene

This is used for wall tile, battery cases, flow meters, radio cabinets, bottle closures and refrigeration equipment.

It possesses good chemical resistance but is too brittle for many structural applications.

Polystyrene shows good resistance to hydrofluoric acid.

Rigid polyvinyl chloride

This is basically rigid but can be softened by addition of polyvinyl acetate and plasticizers to very mechanical propreties.

PVC is used for pipe and fittings, ducts, fans, sheet, containers and linings.

Vinyls

Tygon,Vinylite,plioflex,saran and other vinyls are well known and versatile group of materials.Most of them are copolymers and vinyl acetate.

Uses are pipe, tubing, packaging film, floor tiles, fibres, phonograph records, raincoats, garden hose and insulation. Laboratory tubing is a common example.

Thermo setters

Epoxies

Epon, durcon, Araldite, and other epoxies represent the best combination of corrosion resistance and mechanical properties.

Epoxies are available as castings, extrusions, sheet, adhesives and coatings. They are used as sinks, bench tops, pipe, valve, pumps, small tanks, potting compound etc,

Phenolics

This is a very good plastics. They are based on phenol formaldehyde.

Applications include radio cabinets, telephones, electrical sockets, plugs, pumps, vlves, trays, auto distributors, rollers and coatings.

Polyesters

These are best known to the general public for their use in the space mirror satellite.

Corrosion resistance of the polyesters compares un favourably with many other plastics.

Main use of polyester involves reinforced material. The body of corvette automobile is made of fiber-glass-reinforced polyester.

Silicones

This offers outstanding heat resistance.Mechanical property changes little with variation of temperatures.This is differ from other is ingredient inorganic silicon.

This is used for moulding compounds, laminating resins, and insulation for electric motors and electronic components.

Resistant to attack is not outstanding.

Ureas

They are based on urea and formaldehyde.

Corrosion resistance is not good.

Used in many kitchen dishware and utensils, electrical fixtures, radio cabinets, closures and adhesives.

Laminates and reinforced plastics

These materials usually consists of thermosetting resins filled or laminated with cloth, mats, paper, chopped fabrics, fiber glass.

Tensile strength can be increased as high as possible.

Another important product is widely used fiber reinforced plastic pump.

LECTURE-13

Chemical Degradation of non-metallic material

Ceramics

Ceramic materials consist of compound of metallic and non-metallicelements.e.gMagnesia. Other ceramics include brick, stone fused silica, stoneware, glass, clay tile, porcelain, concrete abrasives.

Ceramics resist high temperatures and have better corrosion and abrasion resistance including erosion corrosion resistance and are better insulator but are brittle.

Ceramic material exhibit good resistance to chemicals with exception of hydrofluoric acid.

Acid brick

This is made from fire clay with a silica content about 10% greater than ordinary bricks.

Application is linings of tanks and other vessels to resist corrosion by hot acids or erosion corrosion.

Stoneware and porcelain

Both are find many applications because of their good corrosion resistance. porcelain parts are usually smaller in size than stoneware and less porous.

Stoneware sinks, crocks and other vessels pipes valves pumps are available. Porcelain can be made similar equipment & is widely used insulators and spark plugs.

Structural clay

These clay products include building, fire, sewer, and paving brick, terra-cotta, pipe and roofing and wall tiles. Hot acids sometimes attack these materials.

Glass

It is an amorphous inorganic oxide mostly silica cooled to a rigid condition without crystallisation. Pyrex & containers are well known.

Hydrofluoric acid and caustic attack glass and it show slight attack in hot water.

Vitreous silica

This is known as fused quartz has better thermal properties than most ceramics and excellent corrosion resistance at higher temperatures.

It is used for furnace muffles, burners, reaction chambers, absorbers and pipes etc particularly where contamination products are undesirable.

Concrete

Tanks and pipes made of concrete are well known for handling mild corrosives.

If aggressive environment are involved the concrete is protected by coatings or linings.

Alumina is used for pump and valves seats because of its high hardness good wear and corrosion resistance.

LECTURE-14

HYDROGEN DAMAGE

Hydrogen damage which refers to mechanical damage of a metal caused by the presence of or interaction with hydrogen

Hydrogen damage classified into 4 types

(i)Hydrogen blistering

(ii)Hydrogen embrittlement

(iii)Decarburization

(iv)Hydrogen attack

Characteristics

Hydrogen blistering results penetration of hydrogen into a metal.

Hydrogen embrittlement caused by penetration of hydrogen into a metal which results loss of ductility and tensile strength.

Decarburization or removal of carbon from steel is produced by hydrogen at high temperature. Decarburization lowers the strength of steel.

Causes

Hydrogen is produced only by the atomic form of hydrogen.

Hydrogen diffuses through the steel and combines to form hydrogen molecules on the exterior surface.

If hydrogen atoms diffuse into avoid a common defect in rimmed steel they combine into molecular hydrogen.

Molecular hydrogen cannot diffuse the concentration and pressure of hydrogen gas within the void increases.

The equilibrium pressure of molecular hydrogen in contact with atomic hydrogen is several hundred thousand atmospheres which is sufficient to rupture any engineering material.

Hydrogen embrittlement caused by slip inference by dissolved hydrogen.

Prevention

(i) Use clean steel

(ii) Using Coatings

(iii) Use inhibitors

(iii)Removing poisons

(iv)Substituting alloys

(v)Reducing corrosion rate

(vi)Altering plating condition

(vii)Baking

(viii)Substituting alloys

(ix)Practicing proper alloy