CHAPTER 3

CORROSION AND WEAR MECHANISM

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3.A CORROSION AND ITS CONTROL:

3.A .1 Definition of Corrosion

Corrosion is defined as "attack on a material by its reaction with the environment and the resulting deterioration of the materials properties". Most often, it is related to an electrochemical reaction with a liquid or gaseous medium [1]

Corrosion is Greek for "gnawing". An agent gnaws away at a solid material, most often a construction material. This deterioration of the material is undesirable as it may affect strength, surface finish, smoothness rendering the material unsuitable for use. The consequent or indirect losses can be enormous in terms of material, money and safety. The losses worldwide are in terms of billions of dollars. The US is losing more than $276 billion and India Rs. 80,000 crore per annum on account of corrosion. Substantial portion of this can be saved if proper corrosion management system was adopted. [2,3]

3. A. 2 Electro Chemistry of Corrosion:

Ulick R. Evans, the British scientist who is considered the "Father of Corrosion Science", has said that "Corrosion is largely an electrochemical phenomenon, [which] may be defined as destruction by electrochemical or chemical agencies." Corrosion in an aqueous environment and in an atmospheric environment (which also involves thin aqueous layers) is an electrochemical process because corrosion involves the transfer of electrons between a metal surface and an aqueous electrolyte solution. [4]

Metallic corrosion occurs when metal atoms are oxidized and subsequently leave the metal lattice as ions. Valence electrons associated with metal ions (previously atoms) are left behind in the metal, creating an excess of electrons at the metal surface. The oxidation of metal atoms to ions is referred to as an electrochemical reaction because it is a chemical reaction that involves generation and transfer of electrons to electrochemically active species in the electrolyte i.e. ions or molecules (e.g., hydrogen ions or oxygen) that

can be reduced by electrons. The transfer of electrons enables electronic measurement and study of metallic corrosion.
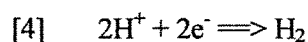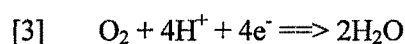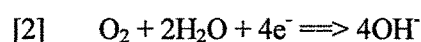
3. A. 3 Corrosion reactions

Some examples of the anodic and cathodic reactions that occur simultaneously on a metal surface in a "corrosion cell" are as follows.

A typical anodic oxidation that produces dissolved ionic product, for example for iron metal is:

[1] $Fe \Longrightarrow Fe^{2+} + 2e^-$

Examples of cathodic reductions involved in corrosion process are:

[2] $O_2 + 2H_2O + 4e^- \Longrightarrow 4OH^-$

[3] $O_2 + 4H^+ + 4e^- \Longrightarrow 2H_2O$

[4] $2H^+ + 2e^- \Longrightarrow H_2$

The cathodic reaction represented by Equation [2] exemplifies corrosion in natural environments where corrosion occurs at nearly neutral pH values. Equations [3] and [4] represent corrosion processes taking place in the acidic environments encountered in industrial processes or for the confined volumes (pits, crevices) where the pH can reach acidic values because of hydrolysis reactions such as:

[5] $Fe^{2+} + 2H_2O \Longrightarrow Fe(OH)_2 + 2H^+$
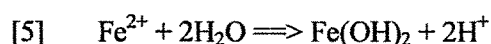
This reaction produces H^+ ions, the concentration of which can, under certain conditions, become large if the H^+ ions cannot readily move out from a confined volume. The overall corrosion reaction is, of course, the sum of the cathodic and anodic partial reactions. For example, for a reaction producing dissolved ions (sum of reactions [1] and [4]):

[6] $Fe + 2H^+ \Longrightarrow Fe^{2+} + H_2$
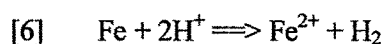
or, for a reaction producing insoluble hydroxide (sum of reactions [1] and [2]):

[7] $2Fe + O_2 + 2H_2O \Longrightarrow 2Fe(OH)_2$

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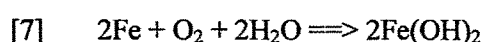
Above equation reads: iron atoms are oxidized to iron ions producing electrons that reduce hydrogen ions (originally from the electrolyte) at the metal surface, forming hydrogen molecules. Examination of the overall corrosion equation and the corresponding anodic and cathodic equations, leads to the hypothesis that corrosion can be halted by preventing one of the half reactions from occurring, and/or removing electrochemically active species from the electrolyte. Unfortunately it is difficult to prevent half reactions from occurring, and there is a long list of electrochemically active species that causes corrosion. [5, 6]

As a result of these reactions, the metal will tend to accumulate a negative or positive charge. The build up of this charge on metal will change its potential in such a way as to inhibit the reaction generating the charge until the potential reaches a value at which the rates of two reactions are equal and opposite. This is known as equilibrium potential, and is the potential the metal will adopt in the solution in the absence of any other reactions.

It is very important to appreciate that when an electrode is immersed in a solution and is at its equilibrium potential, it does not mean that the rates of the two reactions are equal. Since electrochemical reactions invariably involve a transfer of charge, we can define their rates in terms of charge/unit area/unit time or current density. When metal dissolution and reprecipitation reactions are in equilibrium, we refer to the rates of two reactions (equal and opposite) as the EXCHANGE CURRENT DENSITY. The balance between cathodic reactions and metal dissolution reactions results in a rate of reaction given by CORROSION CURRENT DENSITY. One of main applications of electrochemical methods in study of corrosion is estimation of the magnitude of corrosion current density. Electrochemical techniques are also used to study the mechanism of corrosion processes. Current can be converted to a metal corrosion rate such as milligrams per year, using Faraday's Law.

3. A. 4 Polarization of reactions

During the electrochemical corrosion, the anode and the cathode will no longer be at their equilibrium potential. This deviation from equilibrium potential is called polarization. The magnitude of polarization is measured in terms of Over voltage; η. Electrochemical

polarizations are divided into three main types-Activation polarization, Concentration polarization and Resistance polarization.

(a)Activation Polarization:

A system is said to be under activation polarization if the sequence of reaction taking place at metal-electrolyte interface controls the rate of reaction. In other words, activation polarization is caused by a slow electrode reaction because the reaction at the electrode requires activation energy. Both anodic and cathodic reactions can be under activation polarization. This is the change in potential that is required just to make the reaction go faster. A reaction for which activation polarization dominates is referred to as ACTIVATION CONTROLLED.

(b)Concentration Polarization:

Concentration polarization is observed when the reaction rate are controlled by the diffusion species from the bulk of the electrolyte to the metal-electrolyte interface. This occurs when the concentration of the reducible species or the species in the environment is small. An example for this is aerated salt solution. A reaction for which concentration polarization dominates is referred to as DIFFUSION CONTROLLED. Only the cathodic reactions can be under diffusion control during metallic corrosion.

(c)Resistance polarization

If a metal surface is covered by paints or other films of insulating material or if the electrolyte surrounding the electrode has a high electrical resistance it will give rise to potential drop through either portion of electrolyte surrounding the electrode or through the film on metal surface or both, which is known as RESISTANCE OR IR CONTROLLED.

(d)Combined polarization

Both Activation and concentration polarization usually controls, at higher n reaction rates concentration polarization becomes controlling. Total polarization will be the sum of the combination of activation and concentration polarization
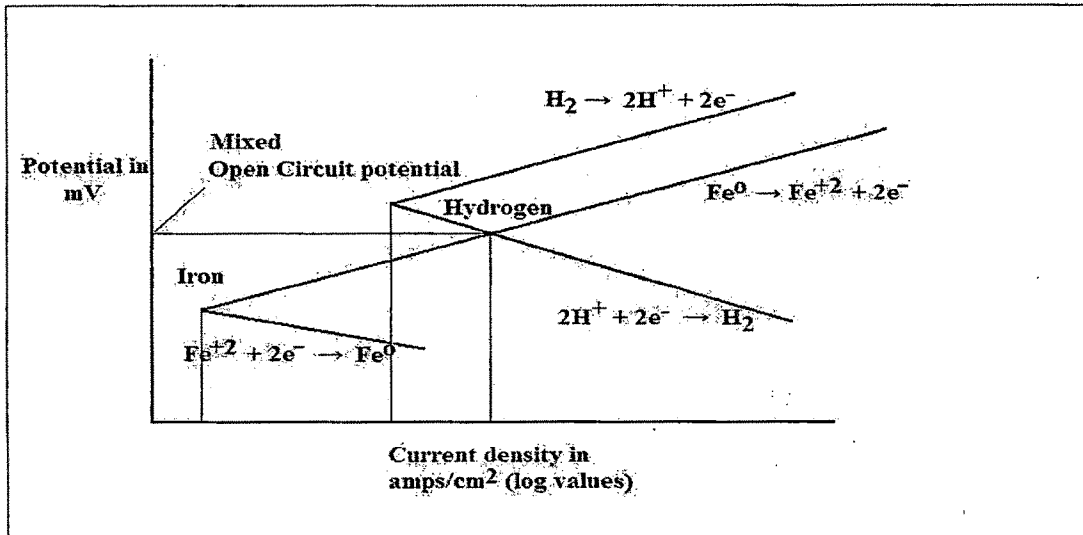
Fig 3.1 E Vs Log I showing mixed open circuit potential for iron in acidic media

The electrochemical characteristics of system (for example, iron in dilute mineral acid solution. HCl) be represented by the modified Evan's diagram as shown in figure 3.1.If an iron piece is immersed in HCl containing some iron ions, the electrode can not remain at either of reversible potential($E_{H2/H+},E_{Fe/Fe2+}$)but lie at some other potential. Iron is metallic and good conductor of electricity and therefore the entire surface will be at constant potential.

The total rate of oxidation and reduction are equal at the intersections of polarization curves for the two processes represented by Ecorr. The rate of H_2 evolution to the rate of iron dissolution will be equal and this is expressed in terms of corrosion current density, icorr. [7]

3. A. 5 Types of Corrosion

In General there are various types of corrosion encountered in a metal/alloy, like:

1. Uniform corrosion
2. Galvanic corrosion
3. Pitting corrosion
4. Crevice corrosion
5. Erosion corrosion
6. Stress corrosion cracking
7. Inter granular corrosion
8. Selective leaching.[8]

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The various types of corrosion are listed in the following table:
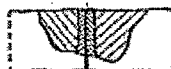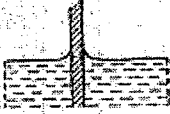
Uniform corrosion The reaction starts at the surface and proceeds uniformly.	**Localized corrosion (pitting corrosion)** The basis metal is eaten away and perforated in places in the manner of holes, the rest of the surface being affected only slightly or not at all.	**Wide pitting corrosion** The corrosion causes localized scarring.
Intergranular corrosion Imperceptible or barely perceptible from outside, since the corrosion proceeds at the grain boundaries.	**Transgranular or intragranular corrosion** The grain boundary material is retained, since the corrosion proceeds preferentially within the grain.	**Galvanic corrosion** Increased corrosion in crevices or cracks or at contact surfaces between two metal articles.
Selective corrosion Corrosive attack on structural constituents	**Exfoliation corrosion** Occurs in deformed articles. Corrosion follows "fiber orientation".	**Interfacial corrosion** Frequently observed at water-air interfaces.

Fig 3.2 Line Diagram of various types of Corrosion [8]
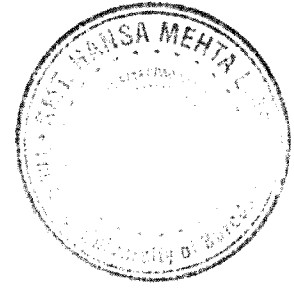
3. A. 6 Common types of corrosion encountered in Ceramic thin films:

(a) Uniform Attack

Uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface or over a large area. The metal becomes thinner and eventually fails. Uniform attack, or general overall corrosion, represents the greatest destruction of metal on a tonnage basis. This form of corrosion, however, is not of too great concern from the technical standpoint, because the life of equipment can be accurately estimated on the basis of comparatively simple tests

(b) Galvanic or Two-Metal Corrosion

A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact (or otherwise electrically connected), this potential difference produces electron flow between them. Corrosion of the less corrosion-resistant metal is usually increased and attack of the more resistant material is decreased, as compared with the behavior of these metals when they are not in contact. The less resistant metal becomes anodic and the more resistant metal cathodic. Usually the- cathode or cathodic metal corrodes very little or not at all in this type of couple. Because of the electric currents and dissimilar metals involved, this form of corrosion is called galvanic, or two-metal, corrosion.

(c) Pitting

Pitting is a form of extremely localized attack that results in holes in the metal. These holes may be small or large in diameter, but in most cases they are relatively small. Pits are sometimes isolated or so close together that they look like a rough surface. Generally a pit may be described as a cavity or hole with the surface diameter about the same as or less than the depth.. Pitting is one of the most destructive and insidious forms of corrosion. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. It is often difficult to detect pits because of their small size and because the pits are often covered with corrosion products. In addition, it is difficult to measure quantitatively and compare the extent of pitting because of the varying depths and numbers of pits that may occur under identical conditions. Pitting is also difficult to predict by laboratory tests. Sometimes the pits require a long time-several

months or a year-to show up in actual service. Pitting is particularly vicious because it is a localized and intense form of corrosion, and failures often occur with extreme suddenness

(d) Intergranular Corrosion

Grain boundary effects are of little or no consequence in most applications or uses of metals. If a metal corrodes, uniform attack results since grain boundaries are usually only slightly more reactive than the matrix. However, under certain conditions, grain interfaces are very reactive and intergranular corrosion results. Localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains, is intergranular corrosion. The alloy disintegrates (grains fall out) and/or loses its strength.

Intergranular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements, or depletion of one of these elements in the grain-boundary areas or higher stresses at grain boundaries. [8]

3. A.7 Corrosion Tests

The corrosion resistance of product or material is evaluated by service history, field testing or laboratory corrosion testing. The most reliable prediction of performance is service experience, followed closely by field testing since they are based on actual environment. When service history is lacking and time and budget constraints prohibit field testing laboratory corrosion tests are used to predict corrosion performance. They are particularly useful for quality control, specification, material selection and materials development. [9,10]

3.A.7.(i) Electronic equipment for corrosion measurements

The sensitivity of modern electronics allows measurement of corrosion long before either metal loss can be detected (by an analytical balance) or enough corrosion products accumulates on a metal surface so that it can be observed by the unaided eye. For example; a 3×10^{-9} Amp/cm^2 current density would cause approximately 1.1×10^{-5} grams of iron loss after 5 months, and would look like a tin reddish pin-point dot on the metal surface. In this case corrosion can be measured with electronic instruments much earlier than it can be seen or weighted.

Electrochemical corrosion measurements utilize the electrochemical nature of metallic corrosion. The equilibrium potential assumed by the metal in the absence of electrical

connections to the metal is called the Open Circuit Potential, Eoc.In most electrochemical corrosion experiments; the first step is the measurement of Eoc. In electrochemical studies, a metal sample with a surface area of a few square centimeters is used to model the metal in a corroding system. The metal sample is immersed in a solution typical of the metal's environment in the system being studied. Both controlled potential (potentiostatic) and controlled current (galvanostatic) polarization is useful. When the polarization is done potentiostatically, current is measured, and when it is done galvanostatically, potential is measured. [11]

3. A.7. (ii) Potentiodynamic Method for evaluation of Corrosion Resistance
(a) Definition of a Potentiostat

A potentiostat is an electronic device that is used to control the potential of a test electrode in an electrolyte. The magnitude of electrode potential change (polarization) is determined by the amount of electrical current supplied by a potentiostat. Electrode potential is measured as the difference between itself and a reference electrode.

(b) Potentiodynamic Testing

ASTM G59 - Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurement

Direct measurement of the corrosion current is usually not possible. Corrosion current is the current between the anodic and cathodic sites and normally both the anodic metal dissolution process and the supporting cathodic process occur at microscopically adjacent points on the metal surface. Inserting an ammeter in this circuit can be difficult. Hence standard test equipment involving reference electrode and counter electrode is used. [12]

These studies were carried out to obtain potential (with respect to SCE) v/s log of current density plot. This plot is commonly known as polarization curve. The potential range was selected in a manner so that sample could be polarized both ways i.e. cathodically and anodically. Though calculations can be performed with the help of this plot by using standard software but these plots have essentially been used for qualitative analysis. The polarization curves of various samples were compared to study and analyze the effects of different bath chemistry.
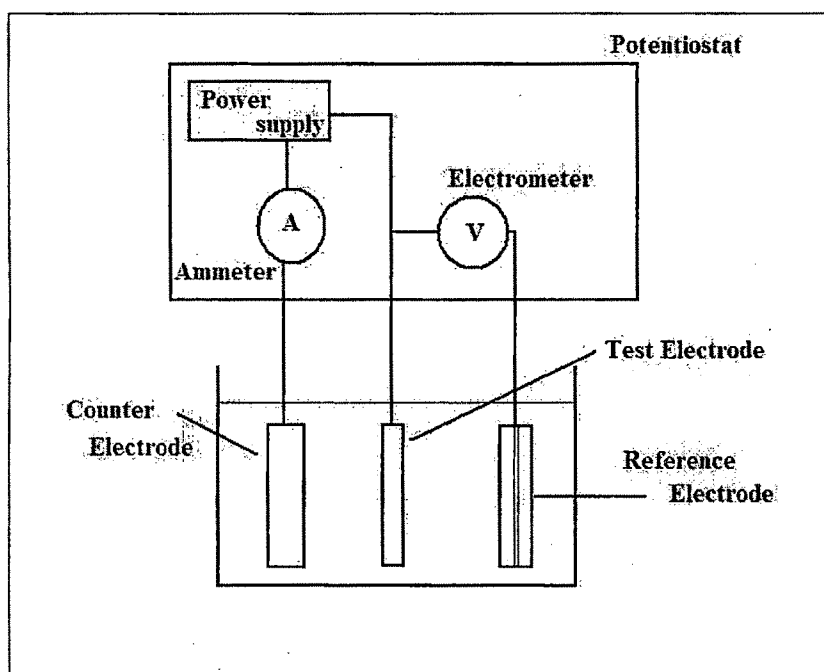
(c) The Electrochemical Experiment

Fig. 3.3 Schematic. Diagram of Three electrode test cell

When current is supplied to a counter electrode, in order to maintain electronic equipment and electrode electrical neutrality (fig 3.3). Electrical current must be concurrently withdrawn from a test electrode Test electrode polarization is measured as a potential difference between reference and test electrodes. No electrical current flows between a potentiostat and reference electrode, so it remains at its OCP and provides a 'fixed' reference point for corrosion measurements. The reference electrode provides feedback to the potentiostat so that test electrode potential can be monitored and adjusted to a desired level.

3. A.7 (iii) Electrochemical Impedence spectroscopy(EIS)
EIS uses a range of low magnitude polarizing voltage. EIS voltages cycle from peak anodic to cathodic magnitudes using spectrum of alternating current (AC) voltage

frequencies instead of single magnitude polarity direct current (DC) voltages .Resistance and capacitance values are obtained from each frequency and this quantity provides information on corrosion behaviour and rates, diffusion and coating properties.

An electrochemical cell can be represented purely by electronic model. For example, an electrode interface during an electrochemical reaction is analogous to an electronic circuit consisting of an array of resistors and capacitors.

In DC theory resistance is defined by Ohm's law (where AC frequency is zero hertz)

$$E = I\,R$$

In DC (E volts) measure resulting current (I amp) computes the resistance (R ohms). For AC, where frequency is non-zero the analogous equation is

$$E = I\,Z$$

'E' and 'I' are the waveform amplitude for potential and the current and 'Z' is defined as 'impedance', the AC equivalent of resistance.

The term resistance and impedance both imply an obstruction to the current or electron flow. When dealing with a direct current (DC), only resistors provide this effect. However, in the case of an alternating current, circuit elements such as capacitors and inductors can also influence electron flow. These elements can affect not only the magnitude of an alternating current in waveform, but also its time-dependent characteristics or phase. Hence Impedance is the AC analogue of DC resistance. Impedance magnitude is equal to AC voltage magnitude divided by the corresponding AC current magnitude..

3. A.8 Graphical Representation of EIS Data.

EIS data can be graphed a number of different ways using component vector magnitudes, total impedance magnitudes, or phase angles. The most common types of EIS graphs are a) complex plane plots or Nyquist plots, and b) Bode's plots.

(a) Nyquist plot

A graph of real and imaginary impedance magnitudes for each frequency is called a complex plane plot. Complex plane plots are also commonly called as Nyquist plots. Figure [3.3] contains a single frequency Nyquist plot. Imaginary impedance magnitudes

are plotted as a function of real impedance magnitudes for each polarization frequency. The semicircle shape in this type of plot is caused by the presence of the capacitor. However, complex plane plots may look more like a straight line than a semicircle when the parallel resistor (corrosion resistance) is very large.
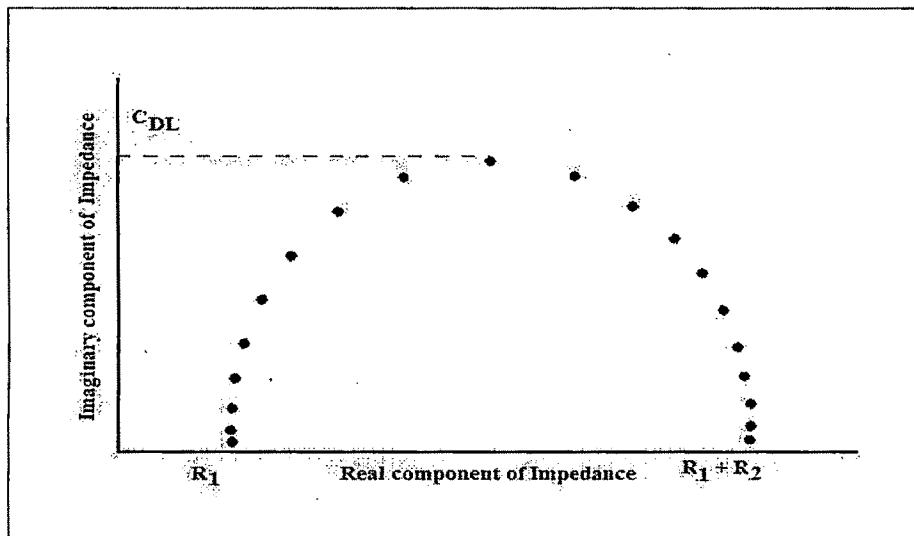

Fig.3.4 Nyquist plot

Uncompensated solution resistance corresponds to R_1 in the figure [3.4] and corrosion resistance corresponds to R_2. The relationship between capacitive reactance magnitude, corrosion resistance and the frequency at the semicircle apex is:

$$C = 1/R_2 \, \omega_{max}$$

Where "C" is capacitor capacitance and

ω_{max} equals 2π times the frequency at the complex plane plot semi circle apex.

(b) Bode's plot

In Bode's plot as shown in figure [3.5] the X axis of a magnitude plot contains log values of frequency. Locations for R_1, R_2 and capacitive reactance are also noted on the magnitude plot. Plot slope is Zero when polarization is "through" resistances, and slope is less than Zero when capacitive reactance becomes part of the circuit response to polarization. Slope magnitude is determined by the ratio of R_2 to R_1 and it approaches -1 as the ratio increases. This plot is generally known as bode magnitude plot.

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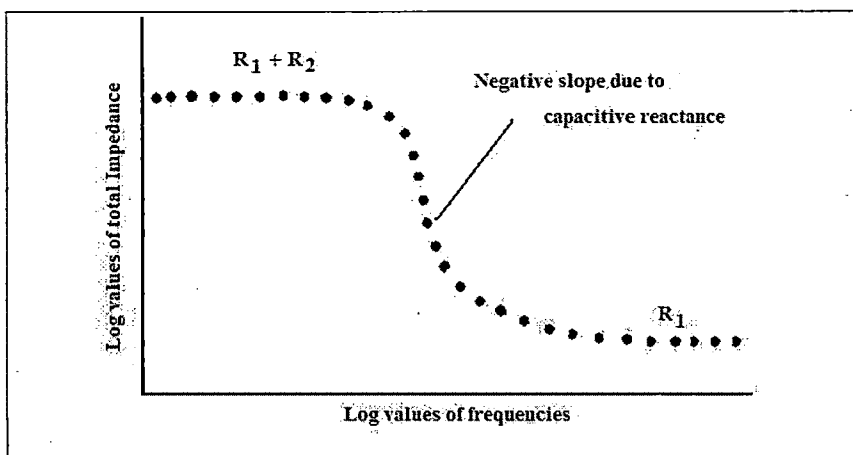
Fig. 3.5 Bode magnitude plot.
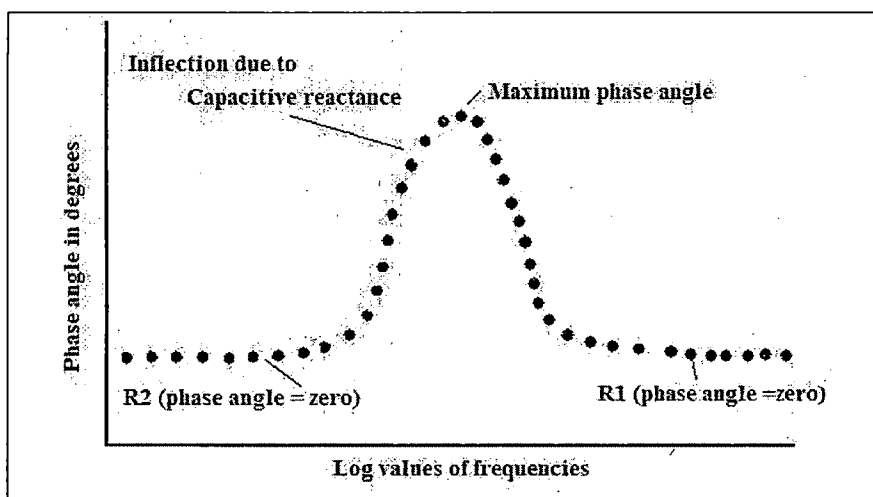
Fig.3.6 Bode phase plot.

Figure [3.5] contains the corresponding Bode phase plot for Resistances R_1 and R_2, and capacitive reactance are also noted in the phase plot. The inflection point frequency in figure [3.6] is equal to:

$$\text{Inflection point frequency} = 1/1.77 \ (R_2) \ C$$

Comparing Bode magnitude and phase plots shows that phase plot inflection corresponds to the area where the Bode magnitude slope is negative. Comparing phase and magnitude plots also illustrates that magnitude plot resistances, R_1 and R_2, correspond to polarizing voltage frequency where phase angle is zero. A variety of processes and surface films can also exhibit capacitive reactance and resistance properties, and produce responses in

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Nyquist plot, Bode magnitude and Bode phase plots. That is, each process or surface film can produce a distinct time constant.

The relationship between a spectrum of electrode potential and their corresponding electrical currents, or a range of voltage frequencies and corresponding impedance values can be used to determine corrosion behavior such as:

- If a metal will passivated or corrode.
- If pitting corrosion will occur.
- If a coating will provide corrosion protection.
- If metallic corrosion occurs under a coating.

Potential-current or frequency-impedance data can also be used to determine corrosion parameters such as:

Electrical double layer capacitance

- Corrosion rates
- Corrosion resistance
- Organic coating capacitance and pore resistance.

The controlled variable in a potentiostat is the cell potential and the measured variable is the cell current. A potentiostat typically functions with an electrochemical cell containing three electrodes and that is true for both field probes and lab cells. [12]

3. A. 9 Corrosion Prevention

Method of counteracting corrosion are many and varied and in general comprise two areas of activity

1. **Indirect protection**: involving creation of conditions for maximum reduction of corrosion hazard for components, products and constructions used in production

> Reduction of pollution of the natural environment by precipitations, wastes, smoke, dusts of industrial, communal or household origin and their utilization, often combined with recycling of components in short supply.

> Replacement of energy consuming technologies used in production by technologies which are energy efficient, including high energy electron beam, glow, plasma and induction technologies which reduces consumption of primary fuels(coal, petroleum ,natural gas).

➢ Maximum degree of elimination of usage of structural materials which are susceptible to corrosion (steel) and their replacement by materials which are more resistant(e.g. Aluminium, synthetic materials)

• Use of structural materials which have low energy recycling after service which implies preference of aluminium over steel.

• Creation of artificial anticorrosive atmosphere by tight packaging of finished products, coupled with the introduction of various inhibitors.

2. Direct protection: It involves design of appropriately resistant materials or protecting of components, products or structures by deposition of protective surface layers, more resistant than the substrate material in working environment. These can be summed up as:

-Application of structural materials which are resistant to the environment in which they work, e.g. use of austenitic stainless steel and special materials in the chemical industry and other nuclear energy. These materials should be so designed that the appropriate material exhibit maximum resistance to corrosion by sulphate,acids,pitting(chemical),welds,cavitations,fatigue,stresses,friction, contact or high energy all this with retention of appropriate strength.[62,63]

- Development on high strength material (usually steel) which are also not highly corrosion resistant, surface layers of high corrosion resistance or coating them with corrosion resistant coatings.

(a) Organic coatings primarily paint play most important role in corrosion protection. Of the approximately 95% of surfaces of steel structures protected against corrosion by protective coatings, as much as 90%are protected by paint.

(b) Electroplated coatings are second most widely used after paint coating. Amongst electroplated coatings greatest significance from the aspect of corrosion protection are zinc coatings.[2]

(c) Hot dip coating comes third in terms of useage. These include, primarily, hot dip galvanizing (zinc) and hot dip aluminizing as well as lead and tin.

(d) Thermally sprayed coating: deposited by flame, induction, arc, plasma or by explosive techniques ,may be generated on the substrate surface or used for the repair of worn substrates or coatings, life of objects regenerated in this was usually being longer than that of original ones.

(e) Cladded coatings: used mainly for enhancing resistance to atmospheric and gas corrosion at elevated temperatures and in chemically aggressive environments.

(f) Overlay Coating: PAD WELDED:(deposited with the application of welding techniques)and melt(deposited with the application of laser, electron or electrode discharge heating) as well as alloy overlays(by laser or electron beam)are widely used now a days predominantly in areas where extreme conditions are expected in service ,e.g. ,high loading forces, high temperature ,corrosion hazards.

(g) Thin and very hard coatings Vacuum deposited by CVD and PVD techniques, mainly to enhance service life of tools, particularly cutting tools (2 to 3 times on the average) and machine components, as well as to achieve significantly favorable decorative properties (hand watches, surgical instruments), also feature high resistance to corrosion in atmosphere, body fluid and some technologically used liquids. From the stand point of tonnage or area of coated surface, they play small role in corrosion protection but their technical significance is big. In future, development in their application is both as single layers(carbides, nitrides, borides or oxides of iron, chromium, titanium, tantalum, aluminium and boron) and as complex layers(e.g. titanium nitride+titanium carbides or TiAlN)especially when combined with diffusion processes(e.g., nitrided layer +TiN or TiAlN layer).From a technical and technological point of view, development is in direction of lowering CVD process temperatures due to the application of auxiliary heating and raising of PVD process temperatures in order to achieve better binding of coating to substrate.[13]

Table 3.1 lists the percentage share of coats of different methods of obtaining surface layers, with special emphasis on coatings in Unite kingdom in 1991[13]

TECHNIQUE	SHARE
Industrial Paint	50
Electroplating	20
Surface Heat treatment	9
Galvanizing	6
Polymer powder coating	4
Phosphating, chromatising	3
Thermal spraying	3
Anodizing	2
Blasting and Peening	2
New Technologies(PVD,CVD,Laser,Plasma ets)	1
Others(enameling,friction,mechanical etc)	1

3. B Tribology in Thin Films:

The tribology in mechanical systems, determined as "a science and technology of interacting surfaces in relative motion", has been widely recognised as a research field embracing the understanding and appropriate appreciation of the relative movement of surfaces in interactive contact accompanied by a resultant transmission and dissipation of energy and material. [14]

The complete tribological process in a contact in relative motion is very complex because it involves simultaneously friction, wear and deformation mechanisms at different scale levels and of different types. [15]
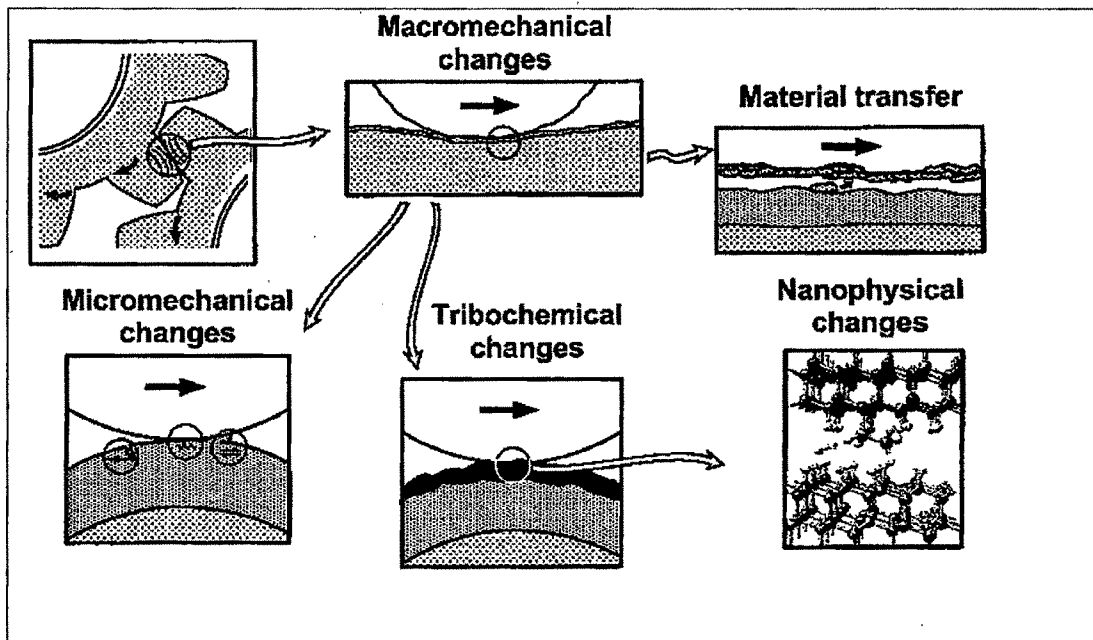

Fig 3.7 Tribological contact mechanisms are related to micromechanical changes, material transfer, micromechanical, tribochemical and nanophysical changes in the contact.

As shown in fig 3.7 the macromechanical changes which is associated with material transfer is result of micromechanical changes(changes in surface morphology),tribochemical changes(changes in surface composition) and nanophysical changes(changes in the bonds structure) on the surface of coating.
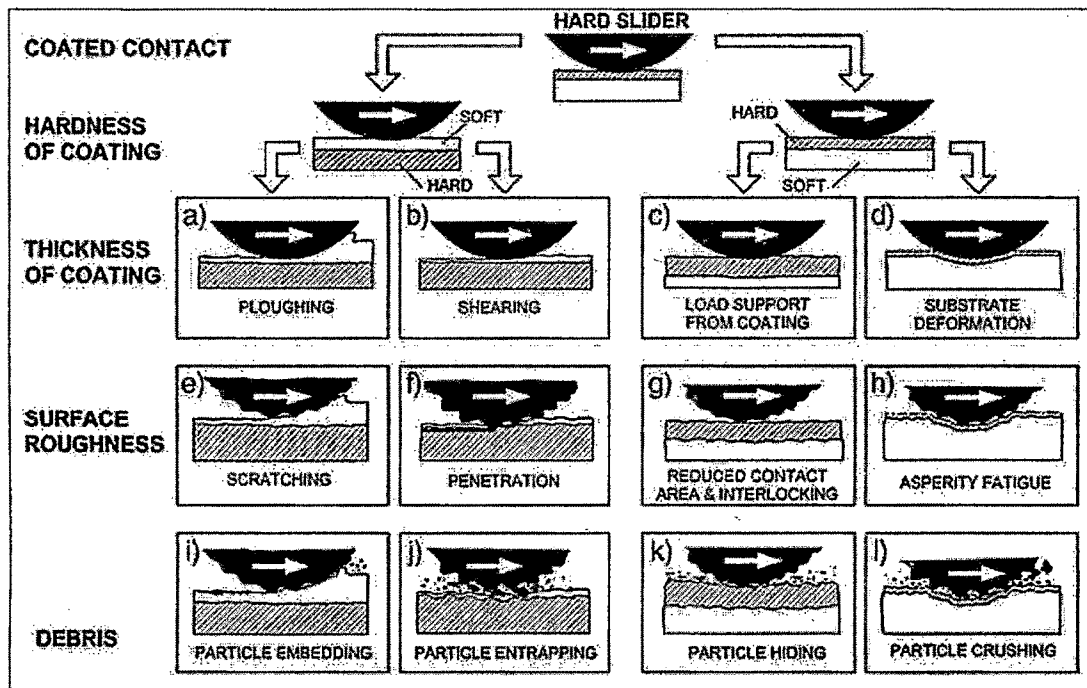
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Fig. 3.8 Interaction mechanism for main parameters influencing friction

The Fig 3.8 shows the main parameters which influence the friction in macro-contact with thin coated surfaces. In contacts between two surfaces of which one or both are coated, four main parameters can be defined which control the tribological contact behaviour. They are the coating-to-substrate hardness relationship, the thickness of the coating, the surface roughness and the size and hardness of any debris in the contact which may originate from external sources or be produced by the surface wear interactions themselves. These parameters result in several different contact conditions, each of which can be modeled in fig 3.8 by a set of dominating parameters and interaction mechanisms as shown in fig 3.8. A hard coating on a softer substrate can decrease friction and wear by preventing ploughing both on a macro scale and a micro scale.

[15,16]

3. B.1 Fundamental of Friction and Wear

3. B. 1 (i) Wear

Wear may be defines as the progressive loss of substance from the operating surface of body occurring as a result of relative motion.

Wear is the surface damage or removal of material from one or both of two solid surfaces in a sliding, rolling, or impact motion relative to one another. In most cases, wear occurs through surface interactions at asperities. During relative motion, first, material on the contacting surface may be displaced so that properties of the solid body, at least at or near the surface, are altered, but little or no material is actually lost. Later, material may be removed from a surface and may result in the transfer to the mating surface or may break loose as a wear particle. In the case of transfer from one surface to another, net volume or mass loss of the interface is zero, although one of the surfaces is worn (with a net volume or mass loss). Wear damage precedes actual loss of material, and it may also occur independently. Definition of wear is generally based on loss or material, but it should be emphasized that damage due to material displacement on a given body (observed using microscopy), with no net change in weight or volume, also constitutes wear. [17]

3. B. 1 (ii) Friction

Friction is the resistance to movement when one object moves relative to another while in contact. There are three basic laws of friction:

> The friction force (f) is proportional to the normal force (F), which leads to the relationship:

$$f = \mu F,$$ where μ is defined as the coefficient of friction,

> The friction force is independent of the apparent area of contact, and

> The friction force is independent of the sliding velocity.

There are some exceptions to these laws, especially in vacuum, but for most situations they are applicable.

There are basically two reasons for friction to occur; the first is due to adhesion that occurs between the molecules of the two surfaces. The second is due to the fact that surfaces are not absolutely flat. When a hard surface slides across a softer surface, small asperities on that hard surface "plow" through the soft surface. This is known as abrasion. For surfaces with contaminant films on them, friction is not a constant. This is because films wear off on repeated sliding which usually causes friction to increase. Also if the

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yield stress of one of the materials is exceeded, friction will increase due to plastic deformation of that surface. Most metals have oxide films on them. When they are slid in air, these oxide films can be reformed as they are worn off. If the same surfaces were slid in vacuum (where there is no oxygen) they would not be reformed and friction would increase significantly.

3. B. 1 (iii) Friction Measurements

Friction should be measured continuously during a test. Usually a test commences with high friction. This is a time where either the lubricant or the materials in contact are plastically rearranged to accommodate the sliding forces. It is called the "running-in" phase. After "running-in", the next phase is a period of time when the friction coefficient is fairly constant and reduced from the initial level. Generally, this is the value reported as the friction coefficient for this lubrication system. The final phase is a period of constantly increasing friction. Increasing friction is an indication that the lubricant is being depleted. [18]

3. B. 2 Classification of Friction and Wear Mechanism:
3. B. 2 (i) Friction Mechanism

In the basic friction mechanisms no material removal is involved. Friction is the motion resisting force at a certain moment in the process of motion between the two surfaces in contact. This may be due to:

(a) Adhesion that is breaking the adhesive bonds between the two surfaces, *Adhesive friction* is dominated by the shear taking place in the surface top layer or the shear in between the two interacting surfaces

(b) Ploughing, that is resistance originating from elastic and possibly plastic deformation when a harder counter surface moves through a softer or more elastic surface and is dominated by the elastic and plastic behaviour of the coating and the substrate. Structural properties, multilayer, gradient, modified and doped structures and structural parameters are important

(c) Hysteresis, that is resistance originating form continuous elastic deformation within one of the surfaces in motion, is mainly dominated by the elastic properties of the substrate but also to some extent by the elastic properties of the coating.
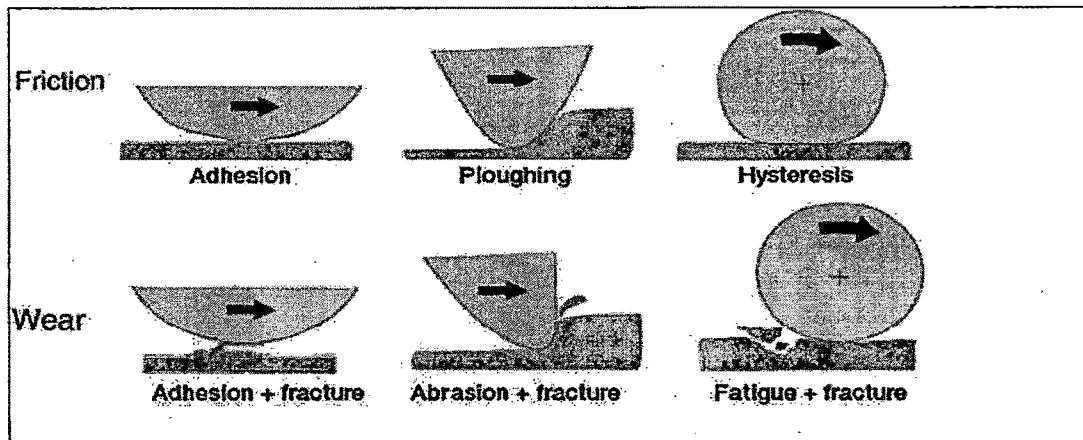
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Fig 3.9 The basic friction and wear mechanisms are related to adhesion, ploughing and hysteresis. In the case of wear these contact mechanisms result in material fracture, detachment and removal. [15]

3. B. 2 (ii)Wear Mechanism:
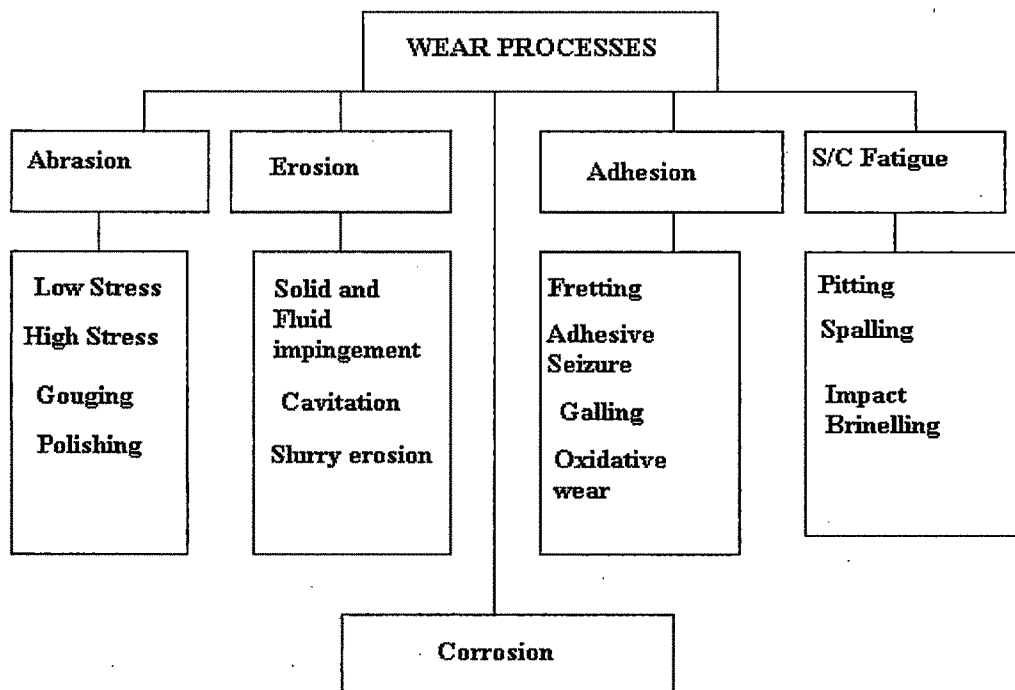
Wear can be classified as given in fig. 3.10.

Fig 3.10 Classification Of Wear Mechanism

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The wear, is not an inherent material property; it depends on the operating conditions and surface conditions. In the case of wear these contact mechanisms result in material fracture, detachment and removal. Wear is the process of detachment of material from one surface the detachment of material may be due to:

1) Adhesion + fracture,(Sliding Wear) that is the adhesive lifting or shearing force is causing such high tension and shear stresses in the surface that they exceed the material strength and a crack is formed, resulting in crack growth and material detachment — a wear debris has been formed, is dominated by the fracture behaviour in the surface top layer, in the coating, at the coating/substrate interface and in the substrate. (Fig 3..11 (a))[20] Adhesive wear is further categorized into mild wear, severe wear and scuffing. Galling and seizure represent severe forms of adhesive metal transfer. [15,19]

2) Abrasion + fracture, that is a hard counter surface moves through a softer surface and deforms it to the extent that such high mainly shear stresses are formed that they exceed the material strength and a crack is formed, resulting in crack growth, fracture and material detachment — a wear debris has been formed.(Fig 3.11 (b))

3) Fatigue + fracture, that is compressive loading of the surface deforms it to the extent that such high, mainly shear, stresses are formed that they exceed the material strength and a crack is formed, resulting in crack growth and material detachment — a wear debris has been formed. The crack growth process may take place during a number of loading cycles. (Fig 3.11 (c)) [20]

4) Tribochemical Wear:

The chemical reactions taking place at the surfaces during sliding contact and also during the periods between repeated contacts, change the composition of the outermost surface layer and its mechanical properties. This has a considerable influence on both friction and wear because they are determined to a great extent by the properties of the surface, where phenomena such as shear, cracking and asperity ploughing take place [21]. The chemical reactions on the surfaces are strongly influenced by the high local pressures and the flash temperatures, which can be over 1000°C, at spots where asperities collide. [15,21-23]
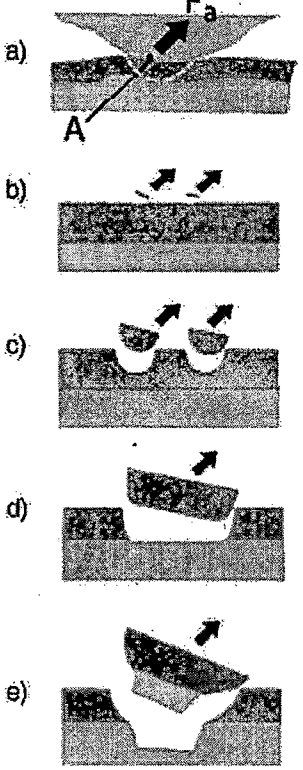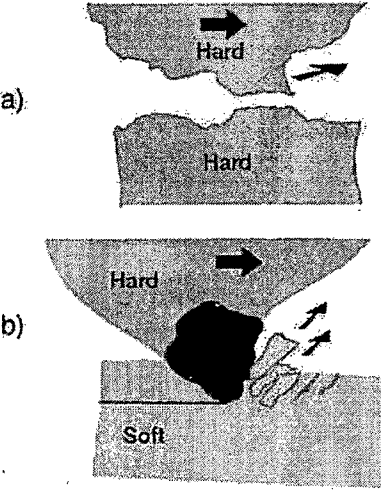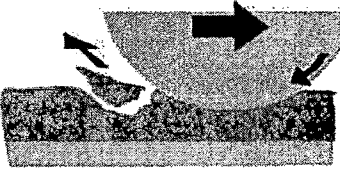
| (a)Two surfaces attach to each other by **adhesion** (a) and the movement of the top surface results in an adhesive force, F_a, that tries to detach material over an area, A, from one of the surfaces. The detachment may take place (b) at the top surface, (c) within the coating, (d) at the coating/substrate interface and (e) in the substrate. | (b)**Abrasive wear** is characterized by a hard asperity (a) or debris (b) that deforms the countersurface in a ductile or brittle way resulting in fracture, cracking and debris generation. | . (c)**Fatigue wear** is characterised by repeated loading of the coated surface resulting in cracking at the surface in the coating, at the interface or in the substrate, followed by fracture, material detachment and debris generation |

Fig 3.11 Schematic diagram of various types of wear(a) adhesive wear,(b) abrasive wear and (c) Fatigue wear.[20]

3. B.3 Friction Transitions during Sliding

During sliding, changes in the conditions of mating surfaces occur which affect friction and wear properties. After some period, the so-called "run-in," "break-in" or "wearing-in" period, the friction force generally stabilizes into what is called steady-state sliding. Typically after sliding for a period of time, friction increases again and reaches another plateau as shown by the S-shaped curve. This process can go on approaching more than two plateaus. After a useful interface lifetime, the interface fails and friction may become very high. During run-in, for example, high asperities may be knocked off, surfaces may mater better, initial surface films may be worn, new steady films may be formed, or structural changes may occur. These changes result in friction either going up or coming down from the initial value. The run-in period is critical for long interface life as incorrect run-in can result in serious damage and early failure. After the first steady-state period, changes in the interface may further occur, such as roughening and trapped particles which lead to an increase in friction to another plateau, a steady-state period. The shape of friction curves can be affected by the interface materials as well as operating conditions.
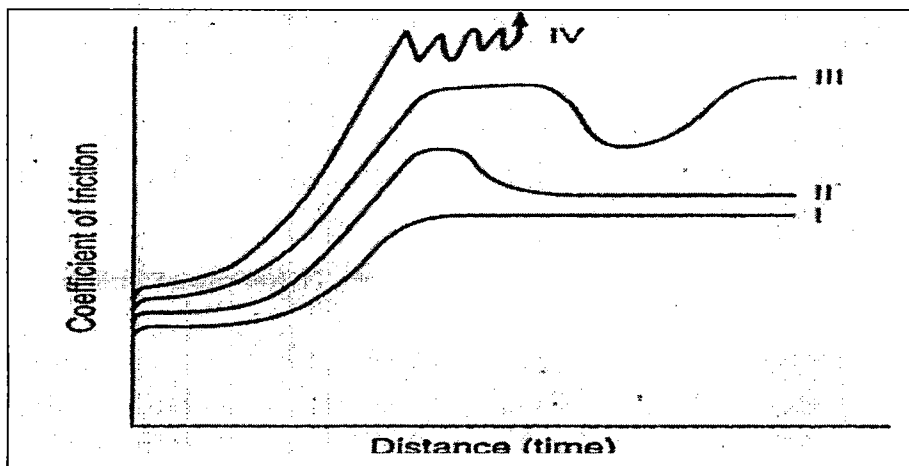

Fig 3.12 Variation of coefficient of friction with Distance/time
Friction may increase in different patterns, such as:

(I)   The friction may remain at its initial value for some time and slowly increase to another steady-state value. Identical metals against each other exhibit the

behavior shown in case I; the increase is associated with ploughing because of roughening and trapped wear particles. In smooth surfaces involving elastic deformation with dominant adhesive component of friction, the increase is associated with smoothing of the surfaces leading to a larger component of adhesive friction

(II)   After being at initial value for some time, it may first increase to a high value then level off at a lower value (but higher than initial value). The drop in the coefficient of friction in case II is associated with smoothing of the two hard surfaces experiencing plastic deformation, which results in a drop in the ploughing component of the friction. For elastic contacts where adhesive component is dominant, roughening and or trapped wear particles reduce the real area of contact, which in turn reduces the adhesive component of the friction

(III)   It may increase to a high value, level off to this value, drop to a lower value, and increase again to a high value; The drop in the friction in case III in plastic contacts is associated with ejection of wear particles, and a subsequent increase is associated with generation and entrapment of wear

(IV)   It may change in a non repeatable manner. In all cases, the coefficient of friction would reach a high value after some period of sliding particles. A significant increase in the friction to an unacceptably high value in a short period in case IV is associated with a poor material pair in which friction is contributed by all sources. [24]

3. B .4 Classification of particles in wear debris

Loose particles or debris are quite often present in sliding contacts. They can either originate from the surrounding environment or be generated by different wear mechanisms. Their influence on friction and wear may be considerable in some contact conditions, depending on the particle diameter, coating thickness and surface roughness relationship and the particle, coating and substrate hardness relationship.

The size and shape of debris may change during sliding in dry and lubricated systems. Mild wear is characterized by finely divided wear debris (typically $0.01 - 1$ μm in particle size). The worn surface is relatively smooth. Severe wear, in contrast, results in

much larger panicles, typically on the order of 20-200 μm in size, which may be visible even with the naked eye; the worn surface is rough.

Particles can be classified based on wear mechanism or their morphology. Particles collected from a wear test may not be in the same state in which these were first produced because of changes in subsequent sliding. Since it is difficult to identify the exact possible wear mechanism, particles are generally classified based on their morphology.

(a) Plate-shaped particles

Thin, plate-shaped or flake-type wear panicles with an aspect ratio of 2-10, are commonly found in wear debris from dry and lubricated interfaces. These particles arc produced as a result or ploughing followed by repeated loading and unloading fatigue, as a result or nucleation and propagation or subsurface cracks or plastic shear in the asperity contacts,

(b) Ribbon-shaped particles

Ribbon-shaped or cutting-type particles are frequently found with aspect ratios, on the order of ten or more; and usually are curved and even curly. These are produced as a result of plastic deformation. They have all the characteristics of machining chips: as a result, the ribbon-shaped particles are referred to as microcutting chips or cutting chips. They are generally produced during run-in, as a result of detachment of fin-like ridges generally present at the edges of the abrasion grooves in machined (e.g. ground) surfaces, These particles are produced with sharp asperities or abrasive particles digging into the mating surface with material flowing up the front face of the asperity or abrasive particles

(c) Spherical particles

Spherical particles are not common. Wear particles of various shapes may not escape from the interface to become loose debris. Some of them remain trapped and are processed further as in the spherical shape. Spherical particles have been observed in sliding , fretting and rolling-contact fatigue ,Spherical particles with 1-5μm diameter are reported to be associated with rolling-contact fatigue just prior to fatigue failure

(d) Irregular shaped particles:

The majority of particles have irregular morphology. Wear debris produced by detachment of transferred fragment in adhesive wear and brittle fracture are irregular shaped [25].

3. B. 5 Wear Testing

Wear is not a material property but instead a system response arising from the conditions at sliding interface. It is affected by number of factors that are relevant to both members of sliding pair and the system as a whole. The variables affecting wear are the materials in contact, the type of relative motion (rolling, sliding or impact) the system configuration(pin on disk, block on ring and so forth),contact stress and stress distribution, sliding speed, surface finish, texture, integrity of surface, type of motion and environment and so forth. Because of these variations different wear rates are commonly reported for same material in literature.

The principle consideration in using a test set up is the sliding configuration that conforms to the practical situation. Sometimes selection is governed by availability of particular set up or of he specimen in particular shape and size. This is much true for ceramic which can be inherently damaged in machining.

Typically in case of ceramics, different wear rates are obtained for same material in different systems. Wear rate strongly depends on

a. The stress state and contact region.

b. Ability of surfaces to cool

c. Kind of motion

d. Method of surface preparation

e. Counterpace material is important as basic component material

f. Sliding speed and normal load. [26]

3. B. 5 (i) Wear Testing with a Pin-on-Disk Apparatus
(ASTM G 99 - Standard Test Method for Wear Testing with a Pin-on-Disk)

There is probably most variation in design, specimen size and operating conditions in pin-on-disc testers than in any other type of wear test. Most pin on disc machines are used for measuring sliding wear and friction properties, but severe adhesive wear or galling is studied as well. For testing coatings, the coating is applied to the end of flat ended or hemispherical pin or to disc or to both (fig 3.13). The test is very versatile since testing conditions can be greatly varied. [27]A laboratory test procedure for determining the wear of materials during sliding using a pin-on-disk apparatus. Materials are tested in

pairs under nominally non-abrasive conditions. During the test extent of wear and coefficient of friction can also be determined.

A Test Pin attached to a gimbaled arm is loaded against a Test Disk mounted on a motor driven turntable. The Friction and Wear characteristics are quantified by measuring frictional forces and material removal and displacement. Precise control and data acquisition provide accurate comparisons of material combinations.
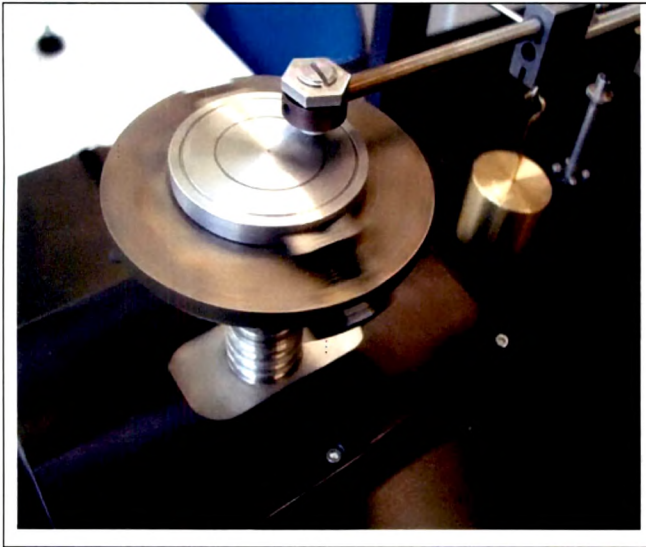

Fig 3.13 Tribometer specimen table [28,29]

A Data Acquisition incorporates a user friendly system for collection and presentation of test data. Operator defined, real time collection of Frictional Data and Coefficient of Friction, Test Temperature, Humidity, Motor Speed, and Test Cycles is displayed on screen and stored in easy to configure files compatible with most Microsoft Windows spreadsheet programs.

The Equipment variables includes optical features allow for temperature control (up to 600°C), controlled humidity environments, lubrication and controlled vacuum environments

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