PROCEEDINGS : COFA-1997
©NML JAMSHEDPUR; pp. 169-211

Localized corrosion and component failures – Causes, mechanism and remedial measures

D. D. N. SINGH
National Metallurgical Laboratory, Jamshedpur 831 007, India.

ABSTRACT

Amongst the various types of failures of the components caused due to corrosion, a majority of them are attributed to localized type of attack of the environments on the surfaces of metals/alloys. The present talk incorporates the discussions on causes, mechanism and remedial measures adopted to control the localized type of corrosion attack. Initially, a brief background about the theoretical aspects of corrosion of metals is given. This includes the various types of cells that cause corrosion of metals and also about the thermodynamical approach to understand the phenomenon of corrosion. The subjects related to five types of localized corrosion, namely pitting, crevice, stress corrosion cracking, corrosion fatigue and intergranular corrosion, who are considered to be the most dangerous type and cause catastrophic failures, are discussed a bit in detail. Their mechanism, causes and remedial measures adopted to control the problems are described. The lecture also touches in brief, the principles involved in failure investigations. This describes the importance of site visit, collection of sample of corrosion products, visual observations, mechanical and chemical tests and fractographic studies. Finally, some examples of case studies of failed components are incorporated to illustrate the application of knowledge in pinpointing the causes of failures and suggest the remedial measures to avoid the recurrences of such failures.

INTRODUCTION

Amongst the various types of failures of components that occur during the service life of an instrument, the majority of them are caused due to corrosion. It is estimated that out of all types of failures caused due to corrosion, about 80% are attributed to localized type of attack (Fig. 1). In general, these type of failures are catastrophic and result in great deal of loss of human lives, components and production. The average thickness of components is found to be unaffected after the failed portion is examined. The types of failures that are encountered due to the

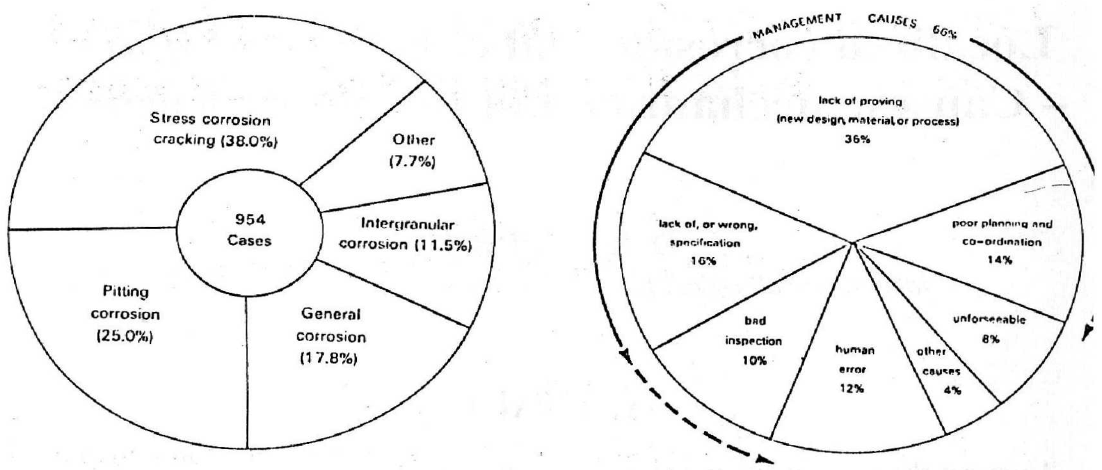


Fig. 1 : Causes of failure and failure types investigated by a large chemical company in USA

localized corrosion are:

a. Pitting corrosion/Crevice corrosion;
b. Stress corrosion cracking;
c. Corrosion fatigue;
d. Intergranular corrosion

In addition to the above mentioned types of failures, the components also fa due to erosion - corrosion, galvanic corrosion and high temperature oxidation. Hov ever, in practice it is observed that the majority of failures, especially catastrophi in nature, occur due to the above mentioned 5 types of corrosion.

Causes of Corrosion

Before we go in more detail on the subject, it is pertinent to discuss in brie about certain fundamental aspects of corrosion and its control. In cases of the mo of the metals and materials (except certain nobler materials), their compounds a thermodynamically more stable than the parent metals. The metals, therefore, ha an inherent tendency to interact with their surroundings to form stable compound "National Association of Corrosion Engineers" define the corrosion as a proce where deterioration of metals and materials occurs due to their interaction wi surrounding environments. In order that a corrosion reaction could proceed, tl necessary and sufficient condition is that the formation of galvanic cells must d velop at the metal/corrodent (electrolyte) interface. These galvanic cells may be ma roscopic or microscopic and involve at least two reactions. One is anodic and the oth is cathodic. The sites at the interface where these reactions take place are known anodic site and cathodic site for anodic and cathodic reactions, respectively.

Anodic reactions

The corrosion of metals and alloys always takes place at the anodic sites of a metal/electrolyte interface. At the anodic sites of a corroding metal, the ionization of metal atoms into metal cations i.e. oxidation takes place.

$$M \rightarrow M^{n+} + ne^{-} \quad \cdots \quad 1$$

Metal cations are released from the metal lattices and the energy required to overcome the activation energy for dislodging the metal cations from the metal lattices is supplied from the potential developed at the metal / electrolyte interface, called potential of double layer. It is to be noted that all the metals do not release their cations from the metal lattices with equal ease. The energy required to release the cations is dependent on (a) the nature of the metal and (b) the nature of the electrolyte. These combined effects are manifested as the standard electrode potential of the metal which is defined as the potential developed at the interface of a metal in contact of its own cations maintained at 1 molar concentration at 25°C. The free energy change in the above reaction (1) i.e. ΔG is given by the equation :

$$\Delta G = -nEF \quad \cdots \quad 2$$

Where n is the number of electrons released as a result of the ionization of metal atom, E is the potential difference developed at the interface i.e. the electrode potential and F is the Faraday constant.

It is evident from the above equation (2) that in order that the free energy change attains a negative value so that the reaction (1) proceeds in right hand side, the E value i.e. the standard electrode potential of the metal should have a positive sign, whereas a metal having least tendency to go into its cation, should attain the negative value of the electrode potential. Based on this principle, the metals have been arranged in a series, called electro motive force (E.M.F.) series. In this series, where metals are arranged in an order of showing their ease with which they can transform into their cations, are placed at the bottom portion of the series (such as Li, K, Na etc. having high positive value of E.M.F.) whereas the metals having least tendency to transform into their cations are at the upper portion of the series (such as Au, Pt, Ag etc. having highly negative E.M.F. values). However, if these metals are placed in the order of ease with which their cations transform into the metals, the order of the series is reversed. The corrosion engineers use the latter convention of the sign and a metal least susceptible to corrosion is placed at the top (exhibit more positive potential) and a metal having highest susceptibility to corrosion is placed in the bottom (exhibit more negative potential) of the EMF series.

Cathodic reactions

In order that the spontaneity of the reaction as shown in (1) is maintained, th electrons liberated as a result of transformation of metal atoms into the metal cations, should be removed from the interface. This is achieved by the cathodic reactions i.e. the reduction of some species present in the solution/electrolyte interface The most probable cathodic reactions that occur during the corrosion process are

(i) Reduction of a higher valence metal cations into lower one:
$M^{n+} + e^{-} \rightarrow M^{(n-1)+}$
(ii) Hydrogen evolution (generally in acidic environment)
$2H^{+} + 2e^{-} \rightarrow H_2$
(iii) Water/moisture decomposition in anaerobic media:
$2H_2O + 2e^{-} \rightarrow H_2 + 2(OH)^{-}$
(iv) Oxygen reduction in alkaline or neutral media
$O_2 + 2H_2O + 4e^{-} \rightarrow 4(OH)^{-}$
(v) Oxygen reduction in acidic environment:
$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$

Thus from the above reactions, we find that for a spontaneous corrosion process, the anodic and the cathodic reactions must take place simultaneously. If any o the above reaction is hindered, we observe **polarization** (control) of the corrosio reactions. If cathodic reaction is hindered, we call it as cathodic polarization, wherea the hindrance in anodic reaction, is termed as the anodic polarization of the corrosion process.

Another prerequisite for the corrosion reaction to proceed is the existence o anodic and cathodic sites at the metal/electrolyte interface. Both the sites must b spatially separated but electrically connected and also should be in contact of conducting electrolyte. As per the convention of sign of potential, as discussed previously, the anode (getting corroded) will have a more negative potential than th cathodic site (where reduction occurs). This will form a galvanic couple and th flow of current will commence. The direction of the current in a galvanic couple i from cathode to anode. The most common example of a galvanic couple is th galvanic cell comprising of Zn and Cu electrodes dipped in their respective salt and externally connected with a copper wire. The reaction proceeds at 1.1 V till som hindrance (polarization effects) are generated during the progress of the reaction.

Different types of Galvanic Cells

It is clear from the above discussions that the existence of anodic and cathodi sites, reacting and conducting electrolytes are prerequisite for the onset and progres of the corrosion reactions. In other words, for a metal to corrode, the formation of galvanic cells at the metal/electrolyte interface is a prerequisite. The possible galvanic cells that cause corrosion reactions can be classified in three categories :

(a) Composition Cells
(b) Concentration Cells, and
(c) Stress Cells

Composition Cells

This type of cells are developed when two or more metals having different standard electrode potential, come in contact with each other in conducting electrolyte. Two very popular examples are galvanized and tinned Steel surfaces. If some scratch develops in these coatings, the Steel (Eo = -0.44V) in galvanized metal behaves as a cathode and Zinc (Eo = -0.76V) as anode. As a result, zinc corrodes in the electrolyte (humid air, water, or other conducting environments) at the cost of steel which is protected. In case of tinned steel, on the other hand, Steel (Eo = –0.44V) behaves as an anode and tin (Eo = -0.14V) as cathode. A localized type of attack takes place on the steel surface resulting in a perforation of the structure. The other examples where onset of corrosion takes place due to the formation of composition galvanic cells are; steel screws in brass in marine environments, propeller shafts made of steel in bronze bearings, solder of Pb-Sn on copper surface, steel pipes connected with copper plumber etc.

It is to be noted here that the galvanic cells not only form in macro level but also in micro level. Micro galvanic cells formed in two phase alloys systems are popular examples of microcells. A steel having >0.02% of carbon, for example, has two phases i.e. cementite (Fe_3C) and ferrite. When the polished specimen of the steel is exposed to a *nital* solution, the carbide behaves as an anode where as ferrite as a cathode. When polished and nital etched sample is observed microscopically, we see the darker structures of cementite (as corrosion products left on the etched cementite do not allow to reflect the light from the cementite zone.

Concentration Cells

Concentration cells are formed due to the presence of two phases of electrolyte (electrolytically connected) present at the corroding interface. Formation of this type of cell can be explained by arranging a cell of a copper metal exposed in dilute solution of copper sulphate (behaves as anode) and a similar metal exposed in a concentrated solution which acts as cathode. This is obviously due to the imbalance of equilibrium existing in the solution and thus each side of copper electrode attaining different values of electrode potential. In concentrations cells, therefore, a site having lower concentration of species (ions, oxygen or any other specy) behaves as anode in comparison to the site having higher concentration of the species. This aspect will be discussed in more detail in subsequent parts of the lecture.

Stress Cells

The arrangement of atoms in a metal or alloy is such that they can attain the lowest energy state. However, due to certain external factors or some times due to the inherent characteristics of the metals and alloys, the atoms attain different states of energy levels and galvanic cells are developed due to the existence of potentia difference. The atoms having higher energy behave as an anode whereas those in lower states behave as cathode. One example is the grain boundaries in a metal or alloy, one grain has different unit and all the grains are arranged in same orientation and pattern and have same energy levels. However, at the grain boundaries, between two adjacent grains, there is a transition zone which is not aligned with other grains. If we want to see the grains structure of a metals, we can not observe i directly with microscope. The surface has to be mirror polished and then etched with a suitable etchant. These etchants attack the grain boundaries as the atoms a the grains are not at their lowest energy state and thus acquire higher negative potential (more active) and become anode. The rest of the grain, however, behaves as the cathode. This is obviously due to the stress developed at the grain boundaries during the crystallization of metals and alloys from their molten state. The other examples of stress cell formation is cold working of metals. An annealed wire for example when bent at a portion, due to strain hardening this portion becomes anode in comparison to the other portions of the wire and rusting of the bent portion takes place during its exposure to an electrolyte.

LOCALIZED CORROSION

As discussed earlier, for a corrosion reaction to proceed, the existence of anodic and cathodic reactions and respective sites are essential. The corrosion rate can be expressed in terms of corrosion current flowing between the anode and the cathode It is important to note here that although, the total anodic and the cathodic currents are same but current densities (current per unit area) at the anode and the cathode may differ to a significant extent. The current density depends upon the area of anode and cathode. If area ratio between cathode and anode of a metal undergoing corrosion is very high, a localized type of attack takes place at the anode. This is owing to the fact that the total anodic current which is equal to the reduction of larger amount of species available at comparatively larger cathodic area, is produced from the smaller area of anode. Thus the current density at the anode is extremely high and causes a localized penetrating type of attack on the metal surface This is the main cause of localized attack. Some examples of localized attack are:

Grain boundary attack : Due to small anodic area of grain boundary in comparison to grains.

Propagation of cracks : Due to very small area of crack tip (anode) in comparison to adjacent surface (cathode).

Pitting attack at the inclusions: The inclusions in metals especially sulphide types, have high electronic conductivity and encourage the adsorption of chloride or other aggressive ions on them. These inclusions dissolve as anode whereas the metal matrix behaves as cathode (higher surface area). As a result, a localized type of attack takes place at the sites of these inclusions.

Pitting Corrosion

Pitting is a form of localized corrosion and is encountered most often in technologically important metallic materials. It has been established that almost all catastrophic corrosion failures of components take place due to the onset of pit nucleation followed by the other forms of failures. Ironically, Pitting is a detrimental side effect of the beneficial phenomenon of passivity.

Causes for on set of Pitting

As stated earlier, pitting is a form of localized corrosion and takes place due to higher area ratio of cathode to anode. Therefore, a necessary condition for onset of pitting is the existence of considerably higher value of cathode to anode area ratio. More the value of area ratio greater is the probability and severity of pitting corrosion reaction. A material developed to exhibit high degree of corrosion resistance for a system, is extremely prone to pitting attack if some flaws or defects exist in passive film. One of the characteristic features of this type of localized attack is the existence of a threshold value of the anodic potential below which the pitting does not occur. If active–passive behaviour of a metal/alloy in an environment is expressed in the form of anodic polarization curves (change in current density of a corroding metal/alloy with impressed anodic potential from an external source), we get the curves as shown in Fig. 2. This curve incorporates all the changes in surface film of metal/alloy exposed in an aqueous environment [2]. The metal/alloy initially corrodes actively upto a certain anodic potential Ecp (Critical passivation potential). Above this potential, a sudden drop in current density takes place and then attains a minimum value of current which is stable upto a fairly high value of anodic potential. This zone depicts the porosity of the passive film framed on the surface. Lesser value of current in this zone indicates compact and flawless passive film on the surface. The potential at which the passivation starts, is known as the passivation potential (Epp). Above a critical value of potential of passive zone, a sudden increase in current takes place. This is known as the pit nucleation potential (Enp). This pit nucleation potential is very important for a particular metal /alloys-electro-

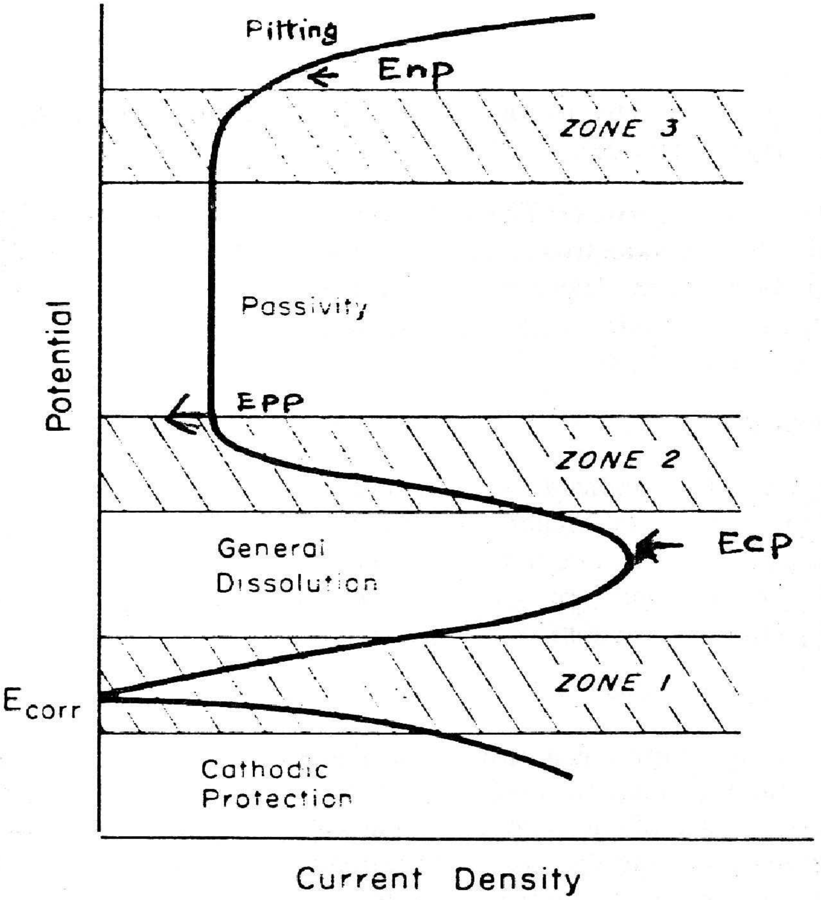


Fig. 2 : Schematic diagram illustrating positions of zones of critical passivation potential Ecp and break down potential, Enp

lyte system. More the positive value of this potential, more is the tolerance of tl alloy against pitting attack.

Passive films and pitting

As mentioned earlier, pitting is a side effect of making an alloy/metal mo resistant to corrosion. If passive film is not formed on the surface of a metal, it w: suffer a uniform type of corrosion. The nature of the passive film formed on tl metals/alloys surfaces during their corrosion, is therefore, very important for ons of pitting and its propagation. The passive films formed on the surface of a meta alloy can be classified as : (1) Continuous films, which cover the metal surfa completely and (2) Non-continuous films which do not entirely separate the met from its surrounding medium/electrolyte. It is second type of passive film who hel in onset and propagation of pits on the surface.

Potential sites for pit nucleation

It has been mentioned earlier that, an in homogeneity must exist at the metal/electrolyte interface for a corrosion reaction to proceed. Some nonmetallic inclusions e.g. sulphides and complex sulphide-oxide inclusions and second phase precipitates, are the most commonly observed inhomogeneities in the iron based alloys where pits are nucleated. These chemical inhomogeneities form weaker spots in the passive film. The type of inhomogeneities formed in cases of inclusions are [3]:

1. Boundaries between the metal matrix and non metallic inclusions where difference in the coefficients of thermal expansions exist. Here, the following possibilities exist:
    a) If a non metallic inclusion has a higher value of coefficient of expansion the metal matrix (e.g. MnS in ferrite or martensitic matrix), a crevice may form between them on cooling.
    b) In case of smaller expansion coefficients of inclusions than that of matrix (e.g. SiO_2 or Al_2O_3 in various steels), a field of textural stresses can occur around the inclusion which also creates the inhomogeneity.
2. Boundaries between the metal matrix and second phase precipitates often have the ability to impoverish the elements from the alloy who are responsible for the passivation (Cr impoverishment of Cr-Ni Stainless Steels due to the formation of chromium carbide). This results in homogeneities.
3. Inclusions having greater chemical reactivity compared to that of the metal or alloy itself.
4. Mechanically damaged spots of the films are also a potent site for the nucleation of the pits.

Sulphide inclusions as potent sites for pit nucleations

Sulphide inclusions in iron based alloys play very important role in determining the suitability of the components in a particular media. Sulphur is present as an impurity in all commercial steels and in pure metals such as iron and nickel. Due to the low solubility of sulphur in iron and iron based alloys, precipitates in forms of sulphides of Mn, Fe, Ca, Cr, Mn or Al, Cr, Mn, Ti etc., appear in these alloys. Potential–pH diagram for the above types of sulphides indicate that they are unstable in aqueous phases at relatively low anodic potentials. This results in a weak point in the passive layer of the metals and a preferential attack on the surface takes place.

It is to be noted here that amongst the above type of sulphide inclusions normally present in the Steel, MnS is the most vulnerable to attack by the aqueous environments. Of course, the susceptibility of attack is governed by the Fe:Mn ratio in the steel. Sulphides rich in Mn are easily attacked by the corrosive media wher as the sulphides rich in iron are not. It is important to mention here that not all typ of inclusions in the form of sulphides cause pitting corrosion. In case, the steel i having MnS inclusions, it corrodes preferentially in comparison to the matrix. pitting type of attack, therefore, commences which is due to the high cathode (meta matrix) to anode (MnS inclusion) area ratio. Other sulphides such as (Mn, Cu)S an (Mn,Fe)S, on the other hand, exhibit lesser tendency towards the pitting. The various types of inclusions and heterogeneities observed on the steel surfaces can b arranged as follows in the increasing order of pitting aids [4]:

$$\text{Oxides} <<< \text{Grain boundaries} < (Mn,Cu)S < (Mn,Fe)S < MnS + Al_2O_3 < MnS + Cr_2S_3 < (Mn,Cr)S$$

The above sequence of pitting indicates that the steels containing sulphide inclusions of Cr, Al and Mn are more prone to pitting than steels having inclusions o Cu and Ni. In case of Stainless Steel also, the above order holds good. MnS i reported to be the most vulnerable spot for the onset of the pitting reactions.

Mechanism of Pit Nucleation at Sulphide inclusions [3]

The following are the sequences of steps involved in onset of pitting reaction a inclusions :

1. Because of higher coefficient of thermal expansion of Mn S than the metal matrix, sulphides contract more during cooling than the metal does. This results i crevice formation.
2. Because of high electronic conductivity of sulphide inclusions compared wit that of the surrounding oxide film, chloride ions (a potent culprit in initiation o pits) are selectively adsorbed on the surface of sulphide particles. These chloride ions complex with the sulphide inclusion to form soluble corrosion product: $MnS + 2Cl^- + 2H_2O \rightarrow MnCl_2 + H_2S + 2OH^-$
3. Since corrosion pits have a solution of acidic nature, hydrogen sulphide i.e. H_2S which is quite stable in acidic solution combines with iron/metal (Me) as follows:

   $Me + H_2S \rightarrow Me(H_2S)_{ads}$

   $2Me(H_2S)_{ads} \rightarrow 2(MeH_2S)^{2+} + 2e^-$

   $(MeH_2S)^{2+} \rightarrow Me^{2+} + H_2S$
4. The above reaction is autocatalytic in nature and a spontaneous generation o H_2S in pits causes the propagation of pits with passage of time.

Controls of Pits Nucleation

As discussed above, the susceptibility of a material towards pitting can be reduced if (a) Inhomogeneity at the metal/electrolyte interface can be minimized, and (b) the metal is kept below the critical pitting potential (Fig. 2). In order to achieve the above conditions, following techniques are employed:

a) Controlling the composition of the alloy: In low alloy steels, sulphide inclusions, especially MnS or complex sulphide inclusions should be kept minimum.

b) The pitting tendency of Cr-Ni alloyed steels can be reduced by adding carbide-forming elements. These include Mo, Nb, Ti etc.

c) Stainless steels having Cr and Ni get sensitized during heat-treatments and onset of pitting starts due to the impoverishment of Cr at the grain boundaries. Precautions should be taken to avoid sensitization of Cr-Ni alloyed steels.

d) Severe cold working also causes an increase in susceptibility of metals towards pitting.

e) Welded zone and heat affected zones are more prone to pitting attack than the parent metal. A proper protective device should be used to protect these zones. Autogenous welding has a deleterious effect on the pitting resistance. It is observed that in an austenitic stainless steel, the welded metal having 7 to 10% ferrite has considerably higher pitting resistance that the purely austenitic steel.

f) Wherever possible, pitting corrosion inhibitors should be used to control pitting. The following thumb rules can be adopted for controlling pitting in chloride containing media:

   o Iron & Carbon steels : Sulphates, nitrates, carbonates, mixture of carbonate & phosphates, nitrites, ammonia, gelatin, starch and quinoline perform well.

   o Stainless Steel : Chromates, chlorates, sulphates, molybdates, phosphates, nitrates and sulphates are good inhibitors for pitting attack.

   o Zinc : Phosphates and chromates.

   o Al and Alloys : Acetates, benzoates, citrates, phosphates, chromates, and tartarates.

   o Nickel: Sulphates, nitrates and aromatic sulphides.

g) Application of cathodic protection to a system is also helpful in reducing the pitting reactions.

Crevice Corrosion

Crevice corrosion (CC) occurs due to the limited accessibility of the environment on a particular spot of a metal/alloy in comparison to the accessibility of the environment on the major portions of the component. Due to the limited accessibility, a concentration cell (as discussed in different forms of cells) develops and the part of the component having poor accessibility behaves as anode whereas the other part acts as cathode. The concentration ratio is very high (cathode/anode) and thus an ideal situation for the onset of localized corrosion develops. This results in CC of the metal.

Mechanism of Crevice Corrosion

The following sequences of steps are invloved in CC attacks :

- Initially, the corrosion all over the surface is uniform and progresses with the following reactions:

  Anodic : $M \rightarrow M^{z+} + Ze^{-}$
  Cathodi : $ZH_2O + ZO_2 + Ze^{-} \rightarrow Z(OH)^{-}$
  Overall : $M + ZH_2O + ZO_2 \rightarrow M(OH)_z$

where Z is the valency of the metal undergoing corrosion reaction.

- The dissolved oxygen inside the solution of crevice decreases with exposure time as a result of restricted mass transfer and system behaves as the differential concentration cell.
- Metal inside the crevice acts as anode and the rest part as the cathode.
- Slow anodic dissolution of metal inside of the crevice causes local agglomeration of the metal cation (M^{z+}). To maintain charge neutrality, the anions (mainly Cl^{-}) from the bulk solution migrate to the crevice site.
- Hydrolysis of corrosion product (MCl_2) inside the crevice takes place, resulting in an increase in acidity of the solution traped inside of the crevice.
- At a critical pH value, the passivity of the metal is destroyed and localized attack sets in.
- This reaction covers whole crevice area and the attack is extremely fast.

Differences between pitting and crevice corrosions [3]*:*

- Pitting occurs mainly at the surface having inhomogeneity, whereas CC may take place even when surface has no inhomogeneities.
- Onset of pitting corrosion takes place due to the localized attack whereas in CC, the initiation is as uniform attack.
- Pitting can take place even in moving solution but for CC, a stagnant solution is essential.
- The CC nucleation potential (Cnp) is more active than the pitting nucleation potential.

- The pH change inside the crevice is more faster (acidic) than the pits.
- Above a critical width of a crevice, the propagation of corrosion and deepening of the crevice ceases. However, no such relationship exists for pitting corrosion.

Factors affecting CC

- The meta alloy determines the susceptibility of pitting attack. In Cl^- containing acid media, CC susceptibility of AISI Stainless Steel decreases as 304>302>321>316. However, in acidic Cl^- free media, the susceptibility decreases as : 302>304>316>321.
- Crevice geometry decides the propagation of CC. For 13% Cr SS e.g., the propagation of CC ceases if width of crevice is >0.25mm. In case of Al also, it is reported that CC does not occur in crevices wider than ~0.25mm.
- CC initiation is also affected by the type of material forming the second wall of a crevice. For CC of stainless steel, the effectiveness of second material is found to decrease in the order [3]:

  Elastic >> Glass or Teflon > Metal > Nylon or Wood.

Avoiding/Controlling of CC

- Joints of metal/nonmetal should be avoided.
- The butt joints between two metal parts or between metal and another nonmetal,, riveted seams, badly executed welds etc. should be coated with an adherent defect free coating.
- As far as possible, the stagnancy of the corrosive fluid should be avoided.
- In boiler tubes or other components where the possibilities of formation of thicker oxide exists, a frequent cleaning operation of the oxide should be performed.
- If system permits, suitable inhibitors may also be used.

STRESS CORROSION CRACKING (SCC)

Stress corrosion cracking is defined by the ASTM Committee on the corrosion of metals as " a cracking process requiring the simultaneous action of a corrodent and sustained tensile stress". A metal can fail by SCC only if a protective passive film is formed on its surface under the influence of an environment and sustained tensile stress. Graphically, the synergistic effect of the three factors may be represented as follows [5]:

Thus, a material exposed to an environment and undergoing a severe corrosion may not fail under the influence of tensile stress due to SCC. Similarly a materi having foolproof passive film will not fail due to SCC. Simultaneous action of thre factors are necessary to fail a material through SCC mechanism which takes plac well below to normal fracture stress of the material.

Historical Background : Discoveries of occurences of SCC

The first phenomenon of SCC was reported in late 19th Century for brass cartridge cases in ammonia liberated from stables. The following table incorporate the history of SCC problems:

Table IA : Discoveries of SCC problems [6]

Period		Metal/Electrolyte
Late 19th Century	:	Brass in Ammonia
End 19th Century	:	Caustic Cracking of boilers
Early 20th Century	:	Mild Steels in nitrates
-do -	:	Al alloys in moist air
1930's	:	Stainless steels in chlorides
-do-	:	Mg alloys in moist atmosphere
1950's	:	Martensitic steels in aerospace environments
1950-60	:	Titanium hot salts, N_2O_4, Methanol
Recent years	:	Composite materials in suitable environments.

Mechanism of Stress Corrosion Cracking [7]

At one time, it was believed that there existed an universal mechanism that applied to all systems where SCC were found. However, it is now established that SCC may occur due to a number of mechanisms. Three mechanisms which are able to explain a majority of SCC failures, will be discussed in brief here.

Stress Sorption Mechanism[8]

According to this mechanism, the specific species adsorb and interact with strained bonds at the crack tip which causes in a reduction of the bond strength or in thermodynamic term, the reduction in surface energy (γ). Theoretical stress to produce brittle fracture (T_f) is given by the relation :

$$Tf = \left(\frac{E\gamma}{d}\right)^{1/2}$$

where E is the elastic modulus and d is the atomic spacing. Due to decreasing, in γ, Tf decreases squirely and thus causing the failure of the material well below its normal fracture stress.

This mechanism, however, failed to explain many observations in SCC. For example, it is observed in all processes of SCC failures, that a thin protective film exists on metals in SCC environments. These film reform rapidly. The proposed model does not take into account the film present on the crack tip as these protective films will strongly influence or prevent the adsorption of anions at the bond of the bare metal.

Film rupture - metal dissolution mechanism

According to this mechanism, the protective film present at the crack tip is ruptured by continued plastic deformation and thus exposing the metal to environment at a very small area (crack tip). This area behaves as anode and rest of the walls of the crack behaves as cathode. The cathode to anode area ratio is very high and a localized type of attack takes place. A schematic representation [9] of the steps involved in failure of components due to this mechanis are shown in Figs. 3 and 4. According to this mechanism, the following steps are involved in initiation and propagation of SCC.

- Film rupture
- A time t is required for repassivation of crack tip
- During this time, the dissolution takes place for a distance of L.
- A strain transient just ahead of the newly created crack tip takes place (Fig. 5)
- In time t a critical strain builds up (Ec) which is sufficient to cause rupture of the newly reformed film at the base of the new crack
- Above processes repeat and propagation of crack takes place.

The above mechanism, although, is capable of explaining the majority of SCC failures but it fails in certain cases such as transgranular cracking in some alloys. These types of failures indicate that a brittle material must exist at the crack tip instead of simple anodic dissolution. Moreover, the current measured during the straining of electrode shows a discrepancy with the current calculated on the basis of crack growth rate.

Hydrogen embrittlement (HE) mechanism

This phenomenon is considered by many authorities different than SCC. However, this mechanism is capable of explaining the transgranular cracking, and therefore, is considered a form of SCC. According to this mechanism, the fracture results due to the production of a brittle region just ahead of the crack tip, because of

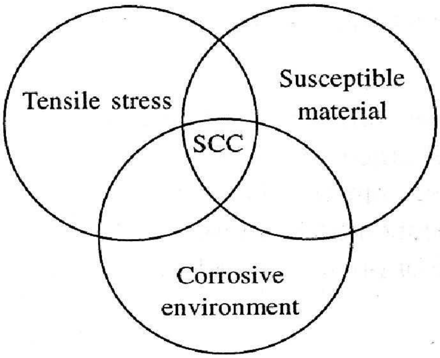
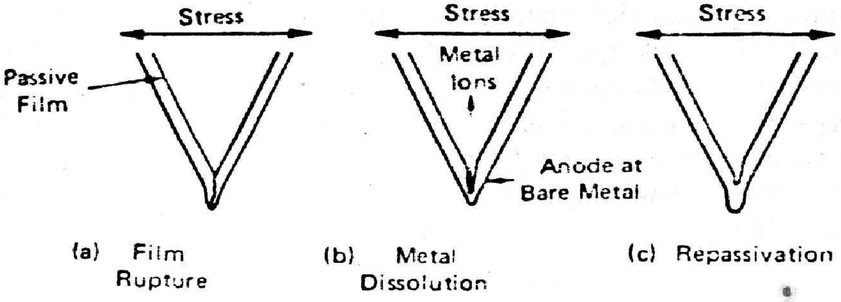


Fig. 3 : Simultaneous tensile stress, susceptible metallurgical condition, and critical corrosive solution required for stress corrosion cracking



(a) Film Rupture (b) Metal Dissolution (c) Repassivation

Fig. 4 : Film rupture-metal dissolution mechanism for SCC, (a) Rupture of the protective film at tip of a crack by the application of a tensile stress, (b) Dissolution of the metal exposed when film is ruptured. Tip of crack is an anode and film covered walls of the crack is a cathode, (c) Repassivation of the exposed metal at the tip of the crack

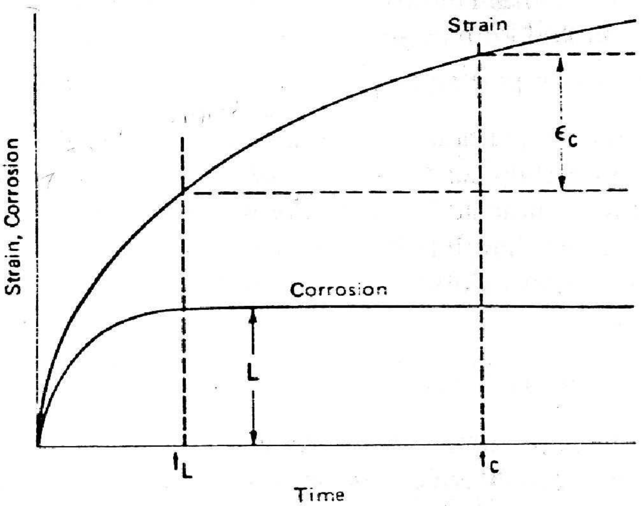


Fig. 5: Time dependence of events occurring after film rupture. Repassivation time is t_L. The time to produce the critical strain, E_C, necessary to cause film rupture is t_C (From Vermilyea)

introduction of hydrogen into the alloy via cathodic reactions. A schematic representation of production of brittle region at the crack tip is presented in Fig. 6a.

The above mechanism, if accepted to occur in all the cases of SCC, as has been suggested by many authors, then an application of cathodic protection to cracking material should enhance crack growth rate (due to production of more hydrogen). This is indeed true in many cases but in certain other cases, it retards SCC propagation rate. In the latter cases, HE mechanism is inapplicable and the causes of failure is attributed to the other reasons. A summary of different proposed mechanisms are schematically shown in Fig. 6.

Techniques employed lo study the SCC

Three approaches are made to study SCC susceptibilities of materials. These include:

a) *Techniques dealing with corrodent aspects*

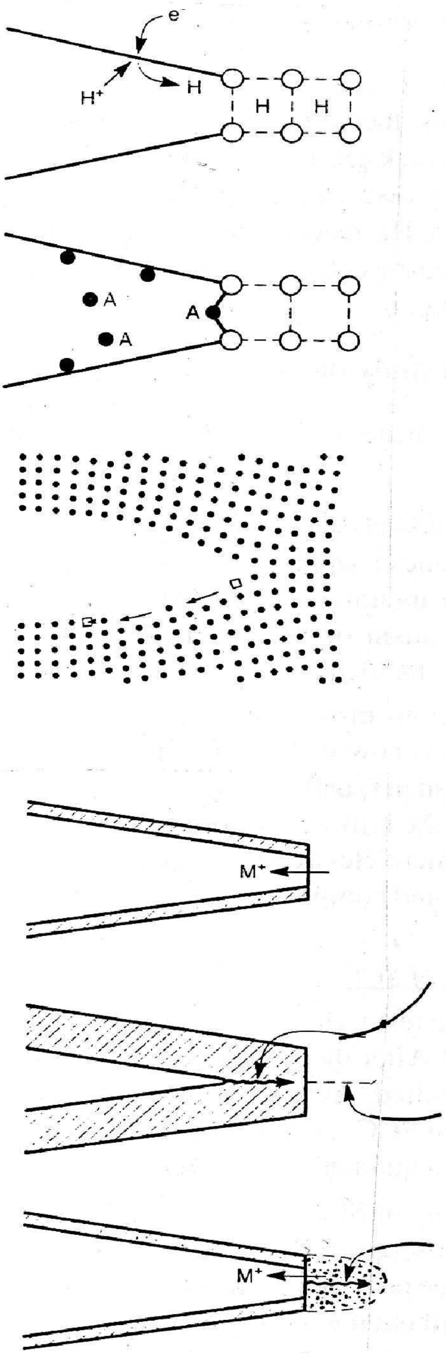
   i) Repassivation kinetics : In this technique, a bare surface either by straining or by scratching or abrading is produced. This represents the film rupture/repassivation mechanism of SCC and provides clues about the nature of corrodent fowards the metal.

   ii) Chemistry of solutions inside the crack : Here one studies the environment inside the crack. It is now well established that the solution inside the crack (its composition and pH) and the potential at the crack tip, differ to a considerable extent than the bulk of the solution. Some techniques are now developed such as the micro electrodes which are introduced at the crack tip having wet lens tissue and composition and pH of the solution in side the pits are directly measured.

b) *Metallurgical aspects of SCC*

   i) Constant strain rate test : Here, the material is subjected to a slow strain rate in an environment. After the material fractures, the morphology of the fractured surface is studied. Although, this technique does not provide exactly actual conditions of SCC, yet it is very popular due to severity of test conditions and providing quicker positive results.

   ii) Electron microscopy of SCC : High voltage electron microscopy and scanning electron microscopy of the structure of the material and morphology of the fractured surface provide important informations about diagnosis of SCC failures as well as about the prediction of the likelihood of the failures. It has been established that metallurgical substructure plays an important role in the formation of corrosion tunnels leading to SCC. This has been possible by the use of electron microscope. Scanning electron microscopy helps in diagnoising the SCC failures. This helps the engineers to know the exact



a) Hydrogen embrittlement

Dissolved H-atoms dilate lattice and weake atomic bonds

b) Absorption induced cleavage

Adsorption of A weakens crack tip bonds

c) Surface mobility

Atoms migrate out o crack tip

d) Film rupture

Crack grows by anodi dissolution at crack ti where film is ruptured

e) Film induced cleavage

Brittle crack initiates i brittle film

Propagates in ductil crack tip metal

f) Localized surface pasticity

Brittle crack propagates into crack ti metal weakened by anodic dissolution resulting from film rupture

Fig. 6 : Schematic summary of some proposed mechanisms of stress corrosion[10]

cause of the failure and also to adopt proper remedial measures to avoid such failures in future.

c) Mechanics of SCC

In order to predict susceptibility of a material towards SCC, two mechanical approaches are adopted:

i) *Evaluation of smooth specimen:* In this technique, smooth specimen are exposed to testing environment under the influence of a stress, and time to failure for the specimen are recorded. The detail about the testing procedures and types of specimen are discussed in detail by Logan. This technique, although very simple and convenient for testing of materials, suffers from a number of drawbacks. The first drawback is associated with geometry of the stress field around the crack tip, which is very poorly defined. The second drawback, which gives entirely misleading result about the nature of a material, is the fact that total time to failure incorporates the period required for initiation of crack and time taken for its propagation to cause the failure. For example, Ti alloys which are highly resistant to pitting, do not exhibit SCC in normal environments. However, the same material can fail with faster speed if initiation sites can be introduced in the specimen.

ii) *Linear elastic fracture mechanics:* To over come the above problems associated with the smooth specimen, liner elastic fracture mechanics (LEFM) approach is adopted. This technique envisages that no material is free of flaws and defines the stress field around already existing cracks in the materials and its propagation. In LEFM approach, the stress intensity factor, K, is an important parameter and incorporates the load, configuration of the specimen and crack length. For a crack of length of 2a in an infinite plate where the crack is normal to the tensile stress field of value σ, the value of K is given by,

$$K= \sigma (\pi \alpha)^{1/2}$$

In LEFM approach a crack is introduced intentionally in the specimen and its propagation is monitored with increase in stress intensity factor. A plot of the type as shown in Fig. 7 is observed [6]. In this plot, KISCC, i.e. the threshold stress intensity factor is very important, as below KISCC, no SCC is expected to take place in the medium. Also using KISCC, the critical flaw depth (a_{cr}) can be calculated which will indicate the critical value of crack length below which a component can survive without any failure.

Prediction, Diagnosis and Control of SCC

Before deciding the preventive measures, one must know the geometry of the crack and hence stress intensity factor around an existing crack, chemistry of the

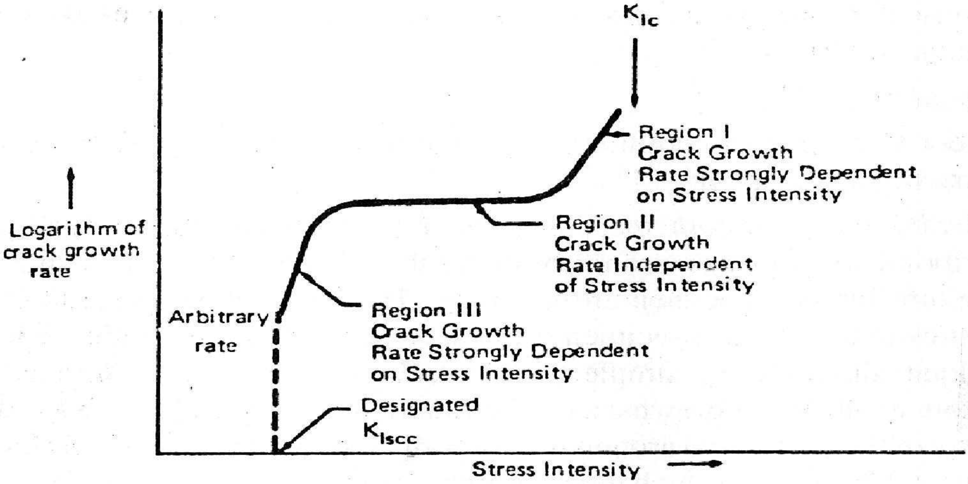


Fig. 7: Schematic diagram of the data obtained from fracture mechanics techniques applied to stress corrosion cracking after Smith and Piper

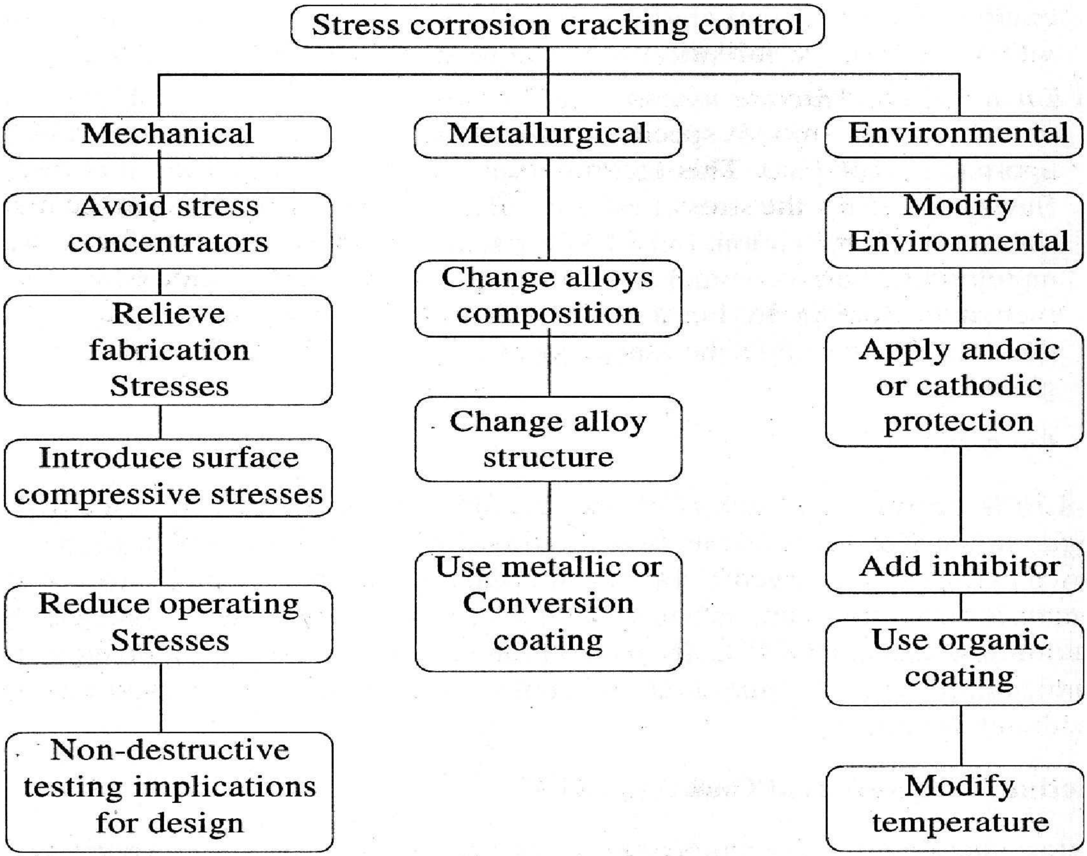


Table 1B : Possible techniques to control SCC solution inside the crack and type of mechanisms involved in SCC. Thus, to suggest a remedial measure, the knowledge of chemistry, metallurgy and mechanics are essential. Various techniques employed to control SCC are tabulated in Table 1.

Mechanical Approaches to control SCC

Most practical instance of SCC results from the presence of residual stress in structures, remnant of the fabrication process used. In case of SCC causing due to the presence of residual stresses, thermal stress relief, especially with welded fabrication is beneficial. Limitations, related to the availability of bigger furnaces required for treating of larger components, however, restrict the application of residual stress relieving of materials. In some cases, the components distort at the relatively high temperatures involved (about 650°C for mild steels and 800°C for austenitic stainless steels). A partial stress relief at lower temperatures than that required for full stress relief can be adequate in these cases where the residual and operating stresses can be reduced below the threshold stress. A locally applied heating on large structures can also be beneficial. The following example illustrates the beneficial effect of stress relieving for 1h on mild steel into boiling nitrate solution.

Table 2: Effect of low temperature annealing on SCC of mild steel (0.09%C) in boiling nitrate solution [12]. (Materials Performance, August, 1985)

Annealing temp. (°C)	Time for appearance of first crack (h)	No. of cracks after 500 h	% stress relief
As welded	5	12	0
250	15	7	15
300	60	5	27
350	200	1	40
400	-	0 (1600h)	47
600	-	0 (1600 h)	95

Another means to control SCC through mechanical route is to provide surface compressive stress. In this method, shot peening and grit blasting are frequently employed to reduce the onset of environmental assisted cracking. Following example illustrates the beneficial effect of peening and shot blasting of mild steel exposed in boiling nitrate cracking solution.

It is to be noted here that the compressive stresses introduced by such mechanical means do not penetrate to the depths. The cold working effect on the surface is less than 0.01 mm. If this layer is removed either mechanically or through pitting, SCC occurrence tendency will return. This technique is quite useful in removing high residual tensile stresses to site welds where other methods are not applicable.

Table 3 : Effect of shot peening and grit blasting of surface on SCC[11]

Type of plate	No. of cracks	Time tested (h)	Min. time of cracking (h)
Butt weld (as welded)	7	210	48
Butt weld (shot peening)	0	840	-
Patch weld (shot peened)	0	1320	-

Metallurgical control of SCC

Cracking susceptibility of an ally can be greatly influenced by slight manipulation of compositions of an alloy. The intergranular cracking of stainless steels as piping in boiling water reactors is due to sensitization in the weld heat affected zone due to the precipitation of grain boundary chromium carbide followed by its corrosion due to the loss of passivity. Alternate pipe materials such as AISI 304 and 316SS having restricted carbon to a maximum of 0.02% are used to avoid failure due to SCC. To compensate the loss of necessary mechanical properties, 0.1% N is added in the alloys. Similarly, structural variations also play important role. In 70/30 brass, for example, the threshold for SCC in sodium nitrite solution greatly improves with decrease in grain size. Heat treatments may be effective in redistributing electrochemical heterogeneities at the grain boundaries and thus avoiding/minimising of intergranular SCC. Thus solution treatment of stainless steels to redissolve the carbides and eliminate chromium depletion at previously sensitized grain boundaries is reported to provide beneficial effect in boiling water reactor environment. Redistribution of grain boundary segregates on precipitates may also be reason why 18 Ni maraging steel can be made appreciably more resistant to SCC in chloride environments by minimising the austenitizing temperatures prior to aging. Cold working, is also reported to have beneficial effect. However, the cold work should be more than 15%. At lower degree of cold working, a deleterious effect have been reported.

Environmental control of SCC

It is well established that there exists a restricted range of potential between which SCC failure takes place for a metal/alloy environment system. These sensitive ranges are shown in Fig. 8. These potential ranges, if avoided by any means such as by application of direct potential/current to the system or by the use of suitable inhibitors, SCC may be controlled to a considerable extent. If SCC is associated with the ingress of hydrogen into the metal, attempts should be made to avoid the occurrence of potential below which hydrogen evolution reaction takes place.

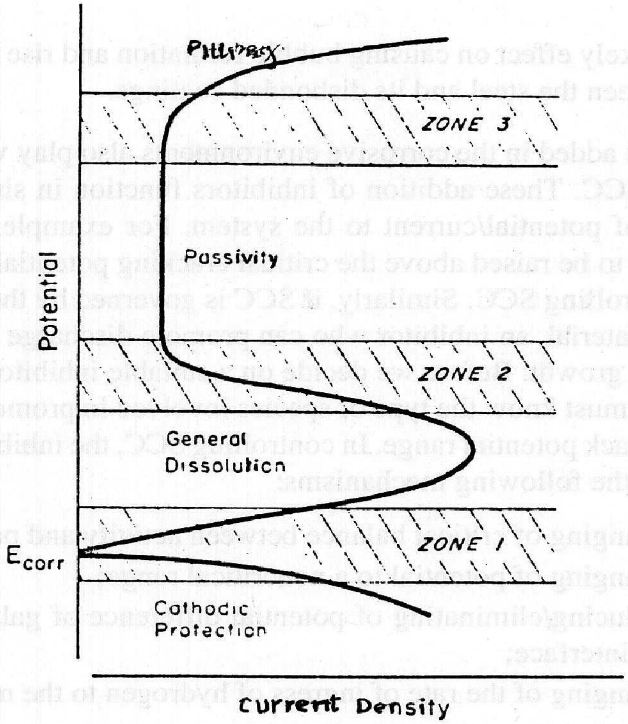


Fig. 8 : Schematic diagram illustrating positions of zones 1, 2 and 3 for stress corrosion cracking or polarization curve

The cases frequently observed with the cracking of high pressure gas/oil transmission lines, are excellent examples of occurrence of SCC due to poor control of cathodic protection system applied from the outside [11]. These pipeline materials are prone to SCC in carbonate/bicarbonate medium. This medium is generated where steel and coating (generally coaltar based coatings) are disbonded and ingress of water occurs. Due to the presence cathodic potential, applied from the cathodic protection device, hydrogen evolution reaction or combination of H with oxygen will take place and a rise in pH occurs. Very small amount of hydrogen evolution is required to rise the pH from 6 (typical of many ground waters) to about 10. At this pH, the solubility of CO_2 from environment is extremely high and a carbonate/bicarbonate type of electrolyte is formed at these disbonded sites. The critical potential for the SCC to take place for this system is between -0.55 to -0.75V (measured against saturated calomel electrode, SCE). A potential drop occurs as a result of flow of current (from the cathodic protection source) through the crevices formed and potential increases in the order of -0.15 to -0.2 V. This makes the system highly prone to SCC and failure occurs. Thus cathodic protection, which is applied to control pitting and other types of corrosion, starts helping in SCC. A proper care should, therefore, be taken to maintain the potential in the range of -0.85 to -1.0V where problems of SCC will not arise. An overprotection, however, should be avoided in view of its likely effect on causing bubble formation and rise of potential along th crevice between the steel and its disbonded coatings.

Inhibitors added in the corrosive environments also play very beneficial role i controlling SCC. These addition of inhibitors function in similar way as that th application of potential/current to the system. For example, for a system wher potential has to be raised above the critical cracking potential, bubbling of oxyge helps in controlling SCC. Similarly, if SCC is governed by the ingress of hydroge in side the material, an inhibitor who can promote discharge of hydrogen, may ir fluence SCC growth. Before we decide on a suitable inhibitor addition to an envi ronment, we must know the type of species involved in promotion of SCC and als the critical crack potential range. In controlling SCC, the inhibitors may function b any or all of the following mechanisms:

i) Changing of critical balance between activity and passivity;
ii) Changing of potential to a noncritical range;
iii) Reducing/eliminating of potential difference of galvanic cells formed the interface;
iv) Changing of the rate of ingress of hydrogen to the metal.

Corrosion Fatigue

As mentioned earlier, SCC can not take place in all metal/environment system For a metal or alloy, certain specific environments are required for SCC to occur. I SCC, the critical balance between stress, corrosion and passivity is essential. How ever, in corrosion fatigue, which is caused due to the simultaneous action of fluctu ating stress and corrosion, presence of a specific environment is not necessary fc the initiation or propagation of crack. Corrosion fatigue cracking (CFC) of a met or alloy may occur in any environment which is corrosive to the metal. Corrosio fatigue crack growth rate $(da/dN)_{CF}$ may be expressed as the combination of a fatigue rate $(da/dN)_{Fatigue}$ and stress corrosion crack growth rate $(da/dN)_{SCC}$ for metal/alloy, provided the system exhibits SCC[13]. During corrosion fatigue, a fluc tuating load $(\Delta\sigma)$ causes in initiation and propagation of crack.

Factors Affecting CF

The corrosion fatigue crack initiation and growth of a metal/alloy, depends o the following factors:

- Amplitude of cyclic load $(\Delta\sigma)$ or stress intensity factor range(ΔK)
- Ratio of stress intensity factor (R)
- Frequency of fluctuating load (f)
- Corrosiveness of environment,
- Geometry of crack tip or stress concentration.

Amplitude of Cyclic load

This is the difference between the maximum stress and minimum stress during the one cycle of loading. As described in SCC discussion, the stress can be represented as the stress intensity factor K and accordingly, the fluctuating stress can be written as amplitude of stress intensity factor i.e. ΔK.

Δk takes into account the factors associated with crack length (2a) and geometry of the specimen. It is in general, reported, that the corrosion fatigue susceptibility of a material increases with increase in Δk provided the other parameters especially K_{max} and R are kept constant.

Stress Value or R value

This is the ratio of K_{min}/K_{max} in a given cycle of loading. There is no definite relationship between the corrosion fatigue susceptibility of a material and R. It mainly depends upon the value of K_{max} and K_{min}.

Frequency of Cycle

The frequency of the fluctuating load plays very important role in determining the initiation and propagation of CFC. If frequency is too high, the corrosion fatigue behaviour of the material shows similarity with its behaviour in air as the time required for corrosion reaction to take place at the crack tip during one cycle is too short.

Geometry of the crack tip

As discussed in SCC part of the discussion, the stress concentration at the crack tip should be very high so that propagation of the crack may take place. Similar is the case with corrosion fatigue also. A specimen having very sharp crack tip will fail more quickly than the other specimen having same parameters of test but with blunt crack tip.

Corrosion intensity of the environment

An environment showing too high aggressiveness towards a material will not have much influence on CF crack initiation or propagation. This is due to the reason that the crack tip gets blunted due to very rapid attack of the environment at the crack tip. Similarly, an environment which is completely in occurs towards the metal, has least effect on corrosion fatigue.

Mechanisms of Corrosion fatigue

Three steps are involved in initiation and propagation of corrosion fatigue cracks[14]

i) In first step, cyclic plastic deformation is localized onto a favourable o ented slip plane. Any oxidation or adsorption process may prevent sl step reversal and continuing slip on adjacent planes leads to closely spac groups of slip planes known as persistent slip bands. Schematically the steps are shown in Figs. 9 and 10. These slip processes can be intrusio and extrusions of the material at the slip band with incipient cracks for ing at the intrusions. The strain localization takes place at grain boun aries, metallic precipitates or simply a mechanical stress concentration su as a notch or a pit.

ii) The first stage of initiation takes the form of propagation after visible crac are formed. This is stage II and propagation of crack is perpendicular the imposed principle tensile stress. This process continues till the mat rial fails due to plastic collapse or brittle fracture of remaining segment

Corrosion Fatigue (CF) Control

All most all the techniques used in SCC control can be used for fatigue cra initiation and growth. There is an old rule of thumb about fatigue tests which sa that 10% of damage occurs in 90% of time and 90% of the damage in the last 10 of the time. This means that more importance should be given in controlling initi tion than the propagation of corrosion fatigue. The following consideration shou be taken into account to reduce the possibilities of fatigue failures:

i) Materials choice: Strong alloys exhibit poor resistance to C.F.

ii) Design aspects: Stress concentrations such as flaws, grooves, pits notch etc. are potent sites for CF initiation

iii) Cold working: Shot peerning or grit blasting provide compressional stress and control C.F.

iv) Nitriding : Certain special steels containing elements like Cr and Mo po ses affinity towards nitrogen. When they are heated in ammonia, the su face is converted into nitrides and the product is volumnous than the ba alloy surface. This provides compressive stress and raises fatigue streng of the material.

Intergranular Corrosion

Grain boundaries are favoured sites for precipitation and segregation which r sult in formation of inhomogeneities on the surface of a metals alloys. This create a favourable condition for corrosion in specific environments. Most metals allo are prone to intergranular corrosion when exposed to a specific environment. In th part of the discussion, intergranular corrosion of stainless steels caused due to th sensitization will be discussed.

Sensitization of austenitic grades of Stainless Steel

When austenitic grades of stainless steels are heated in the range of 427 to 816°C, the materials become susceptible to intergranular corrosion (IGC) primarily due to the precipitation of chromium rich carabides ($Cr_{23}C_6$) at the grain boundaries. Time and temperature of sensitization govern the degree of susceptibility of the alloy towards IGC. If material is exposed for a shorter duration in higher range of temperature of sensitization, the degree of IGC susceptibility may be of the same order as that of the material exposed at lower range of sensitization temperature for longer duration of time susceptibility to IGC of the steel results usually from one of the following reasons:

- Welding is one of the most common cause of IGC. During welding, metal on both sides of weld attains the temperature of the sensitization zone for several seconds or minutes. The material when exposed to a specific environment suffers from corrosion on these heat affected zones. This is termed as weld decay.
- During stress relieving: When alloys are stress relieved for several hours in the sensitization range, they suffer from sensitization attack.
- Slow cooling from an annealing treatment: In larger products (during forging or casting), the cooling is slower in sensitization range and makes the materials sensitive to IGC. Sensitization process is schematically illustrated in Fig. 11 [5].

Mechanisms of IGC four mechanisms of IGC attack are suggested. These are

Chromium depletion mechanism: At the annealing temperature of austenitic stainless steels, the solubility of carbon is of the order of 0.07%. However, at lower temperatures, the solubility is very limited, for example less than 0.01% by weight at ambient temperature. A rapid cooling of the components from the annealing temperature to ambient temperature results in super saturation of carbon in solution. Subsequent holding in the sensitization range enables the carbide to precipitate out as chromium rich carbides such as $(CrFe)_{23}C_3$, where chromium content is as high as 70%. This extra chromium is drawn out from the adjacent area of high chromium grain boundary carbides. These adjacent areas, therefore, become more susceptible to corrosion due to the loss of passivity.

Strain mechanism: According to this mechanism, the lattices adjacent to the precipitates are distorted. This may cause a preferential attack.

Electrochemical mechanism: According to this theory, IGC attack is due to the galvanic corrosion between the more noble chromium carbides and the adjacent

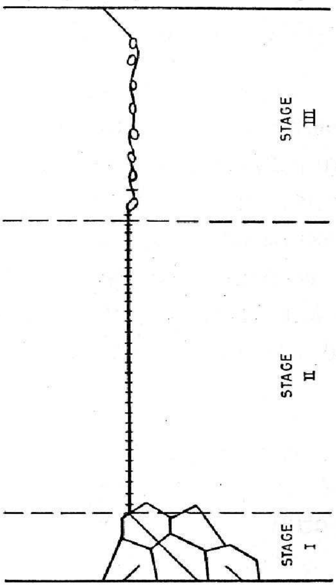


Fig. 9 : Fatigue crack propagation across specimen section (after Tomkins and Wareing)

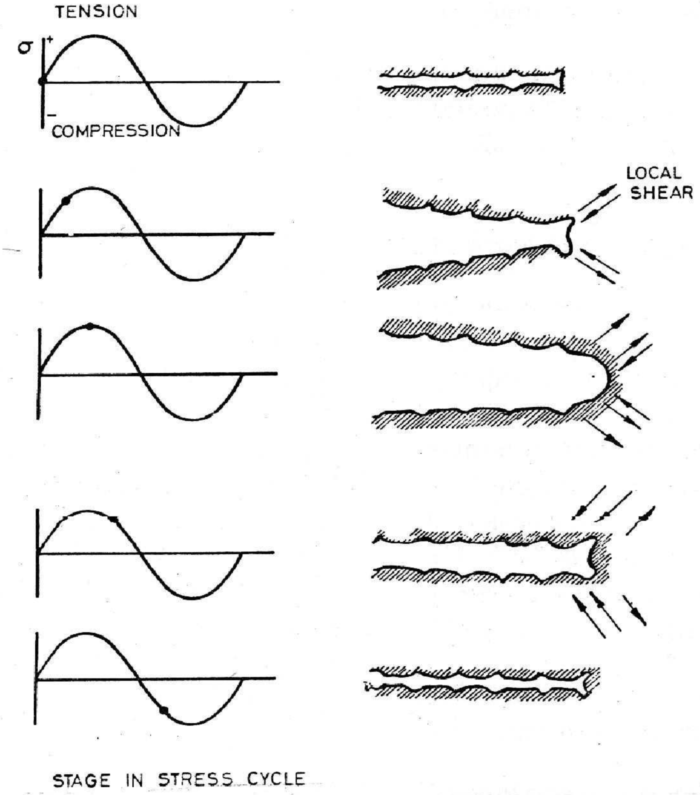


Fig. 10 : Crack-blunting model of stage II crack propagation (after Laird)

matrix. It is established that the chromium carbides are nobler than the adjacent matrix and anodic dissolution takes place at the matrix.

Electrochemical more active chromium depleted region: According to this theory, the chromium depleted zone adjacent to the grain boundaries having high chromium rich carbides, is more active than the grain boundaries. This chromium depleted zone is preferably attacked by the corrosive environment.

Amongst all the four theories described for IGC, the last one i.e. the electrochemical-active chromium depleted zone mechanism is more convincing and is capable of explaining most of the IGC attacks.

<u>Avoiding IGC in austeniti Stainless Steels</u>

Following methods are employed to avoid IGC attack -

i) *Quenching to avoid carbon precipitation:* In this method, the annealed material is quenched and cooled rapidly, through the sensitization range to avoid the precipitation of chromium carbide. However, if service condition requires temperature to be maintained in the precipitation zone this technique should not be used.

ii) *Longer duration of annealing in the carbide separation zone:* Some improvement in IGC is observed due to the longer period of annealing. This is due to the agglomeration of the carbides and the homogenization of the chromium content in the grain boundaries due to slow migration of Cr from the adjacent areas.

iii) *Use of low carbon steel:* The steels with < 0.03% C are less sensitive to IGC in most of the environments. However, they are not immune to IGC attack. These steels such as 304L grades, although, quite expensive due to the difficulty in removing C to such a low level, can be safely used in welded or stress relieved conditions.

iv) *Use of steels with strong carbide formers:* Strong carbide formers, such as Ti in type 321 and columbium in type 347, are added in steels to tie up carbon before the chromium gets a chance to do so. Steels are, however, unsafe to be used where welding, forming etc. is to be performed. Titanium or Columbium carbide goes into solid solution at the high temperature associated with welding. In corroding solution, they form knife line attack.

v) *Higher chromium in the steel:* Use of higher chromium (>18%) and Ni makes the alloy more resistant to IGC attack

vi) *Cold working:* It is observed that short peenring or grit blasting makes the alloy more resistant to IGC attack. In welded zone, this technique can be

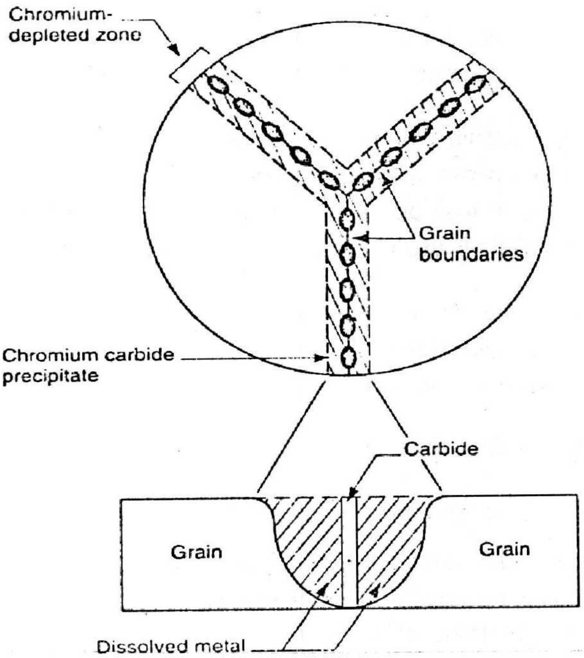


Fig. 11: Schematic representation of sensitization of austenitic stainless steels

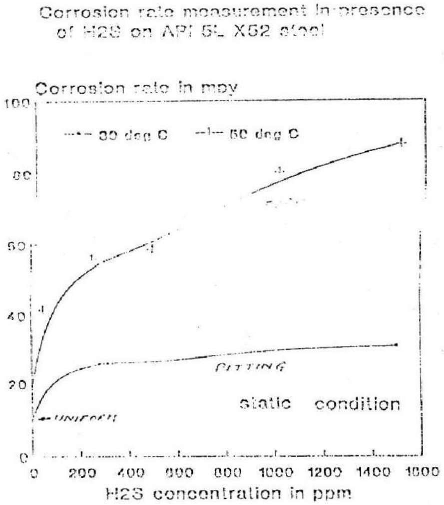


Fig. 12: Variation in corrosion rate with concentration of H_2S

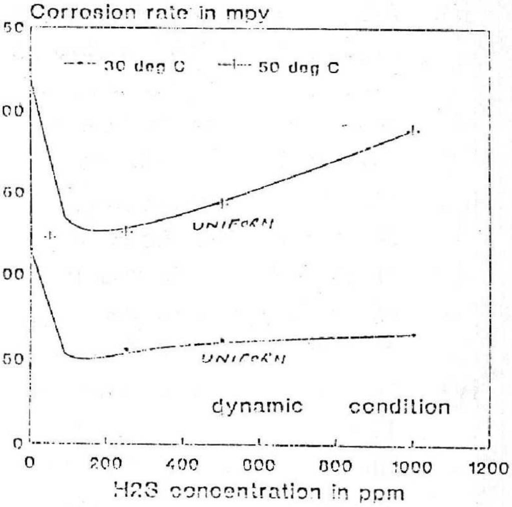


Fig. 13: Variation in corrosion rate with concentration of H_2S

employed. The beneficial effect is attributed to the introduction of carbid nucleation sites within the cold worked matrix so minimizing continuou grain boundary network.

vii) *Grain size effect:* Although not established beyound doubt, it is reporte that the materials with smaller grain size behave better than bigger grai size materials. This is attributed to the fact that a material with smaller grains, has more grain surface area and therefore, less chance of continuous network of precipitate.

IGC attack in non sensitized austentitc stainless steels

IGC attack also takes place in nonsensitized SS. Here, the solution causing IGC is commonly oxidizing media such as nitric acid having sodium dichromate. The cause of IGC is attributed to the raising of potential in the presence of NO_3^- and Cr_6^+ which depolarizes the cathodic reaction and thus anodic reaction at the grain boundaries (these are the higher energy areas) are also enhanced. This solution is used to test unsensitized austentic stainless steel, against their vulnerability towards IGC.

IGC attacks are also observed in ferritic stainless steels. The cause of their sensitivity towards IGC is however, different from austenitic grades. This aspect is beyond the scope of the present falk.

Duplex stainless steels (austenitic-ferritic) containing about 5% or more delta ferrite show improved IGC resistance. This improvement is attributed to :

i) The quantity of carbide precipitates per unit area is less due to an increase in grain boundaries area and phase interfaces.

ii) Chromium in ferrite is significantly higher than in austenite. During carbide precipitation, the chromium depletion from ferrite, therefore, has not much effect on passivity.

iii) The diffusion rate of chromium is more in ferrite than in austenite. Its depletion adjacent to grain boundaries is therefore, less.

iv) The islands of ferrite present minimize the formation of continuous grain boundary precipitates in the austenite grain boundaries.

PRINCIPLES OF CORROSION FAILURE ANALYSIS[16]

Failure analysis provides very important informations which are quite useful in adopting the future strategies in running the plants without relapse of similar type of failures. A careful examination of failures causes and if possible, simulation of the similar conditions at the lab scale, to test the material and achieving similar failures, gives confidence to the plant management to implement the suggestions of the failure analyst. Following initial steps are necessary in taking up any failure analysis for detail investigation:

1) *Sampling:* Representative samples should be collected. For example, the bolts failure of a pump may occur due to CF of only one bolt and others may fail due to overload. The representative sample will not be that of the other bolts but one which failed due to CF.

2) *Corrosion product:* Many times, vital evidences are destroyed before exper reaches at the site to collect corrosion product. As far as possible, the exper should be called immediately to investigate the failure on the spot.
3) *Background about the failure:* The expert should be given free hand to interact with the operators and collect past history about the performance of th component.
4) *Visual examination:* An expert is capable of gathering very vital informations by just visual observations of the failed component. For example, an dimensional changes such as swelling or thinning may provide enough information to the expert which is not possible if small samples are sent in th laboratory for investigation. Discoloration or rusting on stainless surface ma signal iron contamination. Effect of overheating is manifested by heavy tub deposits. Sketches and photographs are quite helpful in interpretation of th findings.
5) *Microscopic examination*:This is the second step in failure analysis and provides some clues on causes of failure. Optical microscopes can be used fo this purpose. However, SEM with more depth of field, is preferred as it doe not require any special preparation of samples.
6) *Chemical analysis*: This provides the information on corroding agent. Th corrosion products deposited on the failed surface provides important clue about the corrodent.
7) *Mechanical testing*: These tests help in reaching to the conclusion whethe the strength characteristics were suitable for service conditions. Hardnes tests help in to determine whether correct or uniform heat-treatment wa applied.
8) Fractography: Fractography identifies the mode of failure for the sampl under study. It helps in locating the origin of crack, knowing of the stages o crack growth and also provide clues about the quality of the material.

FAILURE ANALYSIS OF SOME FAILED COMPONENTS/EQUIPMENT

Failure of offshore pipeline carrying crude oil and gases [17]

Frequent leakages of offshore pipelines carrying crude oil and gases were observed in a section of pipelines of ONGC. The problem was referred to NML t know the exact causes of failures and also to sugggest the their remedial measures Failure history of the pipeline is given in Table 4.

Type of failures: Surface observations indicated pitting type of failures.

Material : The material was API 5L x 52 grade of steel having the compositio as follows (in Wt.%) : 0.2C, 1.12Mn, 0.2Si, 0.01S, 0.01P, 0.04V and 0.04Nb. The composition having very small amount of S (≃ 0.01%) indicates that MnS inclusion (a potent site for pitting attack) should be negligible in the steel.

Metallographic examinations: Irrespective of the locations, the microstructure consisted of fine ferrite and pearlitic regions. % pearlite was 20 - 25% as expected in 0.20% C Steel.

Sites of failures :Failures took place at 6 O'clock position.

EDAX analysis :Cl^- were found at the pits sites at 6 O'clock position. This indicates that Cl^- were the main culprit for pits initiation.

Crude analysis : No sulphide was present. SO_4^{--} observed.

Details about the investigations

The study revealed that the failure of the pipeline was due to localised corrosion. Chemical analysis of the corrosion product would no doubt have helped in identifying the exact mechanism of corrosion. However, no such products could be collected as the areas were apparently clean. Nevertheless, EDX analysis carried out on the inner surface and on the entire cross section showed (Table 5) that S concentration at the surface is undoubtedly higher. Although the existence of sulphide was not reported either in the crude or in the water, the presence of sulphate ion in water collected from similar wells indicates possibility of S^{2+} and HS^- being produced by sulphate reducing bacteria. It is reported that these bacteria become extremely active, especially in the conditions of stagnant fluids having poor access to oxygen and their action is essentially localized.

In order to confirm the above, a set of experiments were performed where the artificial pits were created on the surface of the specimen cut from the pipeline. These were then exposed to the solution having water, chloride and sulphate ions and also 50 and 100 ppm of sulphide iron along with chloride and sulphate. The concentration of the latter two ions were maintained to the same level as reported in the water flowing with the crude. 50 and 100 ppm of sulphide was taken with a supposition that bacteria could have converted sulphate to sulphide to this extent. After 100 hrs of exposure, the specimens were taken out and after removal of corrosion product, were examined for their surface conditions. It was noted that pits in the presence of sulphide had expended to a considerable extent, in their diameter as well in the depth. Not much difference was noted in the conditions of pits exposed to 50 and 100 ppm of sulphide ion. In case of the solution where no sulphide was present, the pits were, however, not much affected during this period of exposure. All the above experiments were performed under stagnant conditions of fluid as the flow of fluid in actual condition is not expected to affect the condensate trapped inside the preexisting pits.

The above observations clearly indicated that for a quick failure of the material, the presence of sulphide ion in the fluid was essential. The surface in its absence was no doubt affected due to corrosion, but the dimension of the pit was hardly affected. It is pertinent to mention here that the corrosion rate is expected to increase and pitting tendency to decrease if the velocity of the fluid flowing in the pipe is very high. This is owing to the possibilities of washing out of the entrapped corrodent inside the preexisting pits at higher velocities of the fluid.

In order to confirm this, two sets of experiments were performed where all the parameters were kept constant except that one was performed in the dynamic condition whereas the other was carried out in the stagnant condition. The specimen in both the cases were prepared by grinding them on very rough grade of emery paper (1/0). This was done intentionally to create uneven surface which could be considered as the preexisting surface defects as is presumed to be in the case of failed pipeline. The r.p.m. of the fluid was maintained at 40. After taking the specimen off from the corrodents, the surface conditions and the corrosion rates were measured for the two types of the specimen. The results are recorded in Figs. 12, 13. It is evident from these results that under dynamic conditions, although the corrosion rate was higher compared to that under static conditions, the surface did not show pits.

The Figs. 12, 13 further bring out the fact that the temperature plays a very decisive role on the corrosion rate of the material. A 20°C rise in temperature from 30°C to 50°C has been found to accelerate the corrosion rate to the order of two fold in the absence of H_2S, whereas in its presence, a higher order of dissolution has been noted. A similar trend has also been noted for the tests carried out under the stagnant conditions.

Another interesting observation which has been noted under the dynamic condition test is that the presence of hydrogen sulphide in the corrodent drastically reduces the corrosion rate (Fig. 13). Under the static condition, however, the corrosion rate is found to be accelerated in the presence of the hydrogen sulphide (Fig. 11). This behaviour has been noted at lower (30°C), as well as at elevated temperature (50°C). Although there is no satisfactory explanation for this behaviour, it appears that this was probably due to the reason that the surface remains free from H_2S attack for a fraction of time, during the exposure and also perhaps due to the setting up of another cathodic reaction (e.g. oxygen reduction) having higher activation over voltage.

Mechanism of Corrosion

Amongst the different impurities present in the crude, chloride and sulphide ions are considered to be the most injurious to the lines. Chloride ion, due to its smaller ionic size and being associated with very high electron density, quickly combines with cations produced at the anode and thus strongly depolarizes the anodic reactions. Moreover, the surface activity of the chloride ions is extremely high and thus forms metal complex species due to the overlapping of the electron of chloride ion and the metal orbitals. These effects make the materials in contact with chlorides to corrode very vigorously. Since the major portions of the pipelines are covered with oil phase, these reactions take place at the locations where aqueous phase becomes stagnant owing to certain reasons.

Sulphide ions, on the other hand poison the cathodic reactions but have strong depolarizing actions on the anodic reactions. It is believed that due to the stronger surface adsorption tendency of sulphide ions, they quickly get adsorbed on to the steel surface and form a complex of the type:

$$M + HS \rightarrow M\ldots\ldots\ldots S\ldots\ldots\ldots\ldots H$$

The formation of the above type of intermediate complex gets discharged at lower overvoltage and facilitates the anodic reaction.

In the presence of H_2S, the hydrogen absorption reaction in the steel is drastically increased. This is primarily due to the reason that the recombination step in the hydrogen evolution reaction i.e. :

$$M\ldots\ldots H + M\ldots\ldots\ldots H \rightarrow 2M + H_2$$

is poisoned in the presence of hydrogen sulphide and provides ample opportunity for the H atom to penetrate inside the steel. For the materials having higher mechanical strenth, this diffusion causes the embrittlement resulting in the failure of the structures. For lower strength steels, however, this problem is not accute and generally uniform type of attacks are noted.

Effect of Inhibitors

It was noted that no protective measures were taken to prevent the corrosion of the inner wall of the pipelines. Generally, corrosion inhibitors are injected along with the flowing fluid to control corrosion caused due to the condensate carrying different types of aggressive corrodents. However, this practice is not adopted in this branch of the pipeline where the failure had take place. It was probably due to the reason that the used materials of the pipeline is considered to be quite resistant to the attack of normal condensates having no hydrogen sulphide which is indeed observed in our present study (Figure 11) where corrosion rate in the absence of H_2S is found to be of the order of only 10 mpy which is considered to be acceptable limit for the most of the structures exposed to corrosive conditions. The surface has also been found to be free of pits which clearly demonstrates the excellent corrosio resistance of the material.

In order to explore the possibilities of using of inhibitors to combat the corrosion in the pipeline carrying crude, a test was performed by using 100 and 200 ppn of an NML developed inhibitor suitable for such purposes and the results are summarized in the Table 7.

It can be seen from this table that on the addition of 200 ppm of this inhibito even under the conditions of the extreme aggressiveness (1500 ppm H_2S was take which is the highest limit of H_2S solubility in such condensates) 80% of the corrosion taking place in its absence can be prevented. Another very interesting observation of this study is that the surface after exposure was found to be completely fre of any pits.

In order to study the effect of this inhibitor on the growing tendency of alread existing pits on the surface, another set of experiments under stagnant conditio was performed where the surface of the specimen having intentionally created pit was exposed to the aggressive solution (as stated in Figs. 12 and 13). It was note after the test that these pits were found not to have grown in size in the presence o the inhibitor. In the absence of the inhibitor, however, the pits had grown to a considerable extent. These observations suggest that a suitably designed inhibitor ca be fed into the flowing fluid at a suitable place to combat such type of failures Before adopting this practice, however, other factors pertaining to the productio shall have to be taken into account.

Conclusions/Recommendations

On the basis of the above investigations the following conclusions/recommendations were made:

1. The pipe correspond to API 5L x 52 seamless and cold expanded grade.
2. The material properties have not undergone any degradation as a result o service exposure.
3. Under normal operating conditions the pipe design meets leak before rupture criteria.
4. The material as such has excellent resistance to pitting in absence of H_2S and HS^- ions.
5. In presence of H_2S the material is susceptible to pitting in a stagnant environment.
6. Water in the crude in similar gather line of ONGC contains 300 ppm o SO_4^{-2}, which could be reduced by bacteria to produce S^- and HS^- ions

responsible for pitting.

7. Under dynamic conditions the steel resists pitting even though uniform corrosion rate increases.
8. Preexisting pits grow in size only in presence of H_2S.
9. The time a pit takes to develop into a leak is around 3 years.
10. Presence of S^- has been detected on the inner wall of pipe by EDAX.
11. Pitting due to presence of S^- ion in the environment is the main cause of failure.
12. Use of inhibitor can suppress both nucleation and growth of pits.
13. A code of practice to mark 6 O'clock position during prolonged storage can ensure that during laying of pipeline the vulnerable area containing pits is kept at 12 O'clock position. This ensures longer life.
14. Increased flow rate beyond 0.9 m/sec may reduce pitting corrosion significantly.

Table 4 : Failure History of 12" No-N3 pipeline commissioned in March 11, 1986.

Date	Location w.r.t. clock position	Distance in meters from	No. end
1st leak 8.10.89	6	5	(1)*
2nd leak 12.8.89	5	8.2	
3rd leak 21.9.89	6	8	
4th leak 4.11.90	6	5.5	(2)*
Section 14.11.90 replacement			
5th leak 15.11.90	6	50	

* Portions investigated at NML. Numbers within bracket are used for identification.

Table 2 : Chemical composition (%) of the failed pie and Std.

Standard	C	Mn	Si	S	P	V	Nb
5L x 52 (Max. allowable)	0.29	1.25	Not specified	0.05	0.04	By agreement	
Failed pipe	0.2	1.12	0.2	0.01	0.01	0.04	0.04

Table 5: Summary of EDS chemical analysis of major elements responsible for corrosion attack

Location	Major elements analysed		
	Cl	Ca	S
Inner wall at 6 O'clock position	3.23	0.16	0.31
Inner wall at 12 O'clock position	0.27	4.03	0.20
Cross section	0.10	0.09	0.06

Table 6: Effect of the presence of inhibitor on corrosion rate and surface condition of the specimen exposed to simulated corrosive environments having Cl, SO_4 and sulphide ion

Temperature: 50°C	Condition of test : Static	
Concentration of inhibitor (ppm)	%Efficiency of inhition	Surface conditions
Blank	-	Highly pitted
100	70.9	Slightly pitted
200	80.0	Completely pit free and bright surface

Failure of 5000 lit. reactor [18]

Background : A new reactor of 304 SS having wall thickness of 7 - 8 mm wa installed in a chemical plant handling organic chemicals (high molecular weig alcohol and aliphatic hydrocarbon). The material is considered to be ideal for suc mixture of the organic chemicals especially at lower temperatures (50°C was th temperature of reactants). However, the material failed within one year. The cause of this failure were investigated and findings were as follows :

<u>*Failure investigations*</u>

Material : 304 SS (7 - 8 mm thick plate)

Pressure : About 5 kg/mm^2

Inspection of failed component revealed that at the bottom of the reactor, lot o tarry masses were accumulated. These masses were collected and analyzed for thei chemical constituents. Besides this, the chemical composition of the failed portio was also determined. The failed part was metallographically examined. Followin results were observed.

Chemical composition of the tardy mass

Cl^- = 3 - 5 % (varied from place to place)
Zn^{++} = Appreciably higher concentrations present
Fe^{++} = Appreciably present
pH = 3 - 4 (tarry mass dissolved in water)

Metal composition : Conformed to usual 304 SS composition with 0.02% Carbon

Metallographic observations : Transgranular stress corrosion cracking noted.

Causes of failure

Although, 304 SS is quite resistant to attack of nonacidic i.e., organic chemicals, it is, however, extremely prone to be attacked in the presence of halogen derivatives in contact with moisture. This complexity is further enhanced if water content inside the solution is very small. This is due to the fact that the passivation of the surface film is not proper in the absence of appropriate amount of water. These halogen derivatives form organic halogen acids and quickly attack the metal surface.

The microstructural observations as shown in Figs. 14(a) - (c) clearly indicate that the material has failed due to transgranular stress corrosion cracking (TGSCC). All the conditions for TGSCC i.e. the existence of tensile stress, highly passive surface and aggressive media (zinc chloride which is highly acidic and corrosive) and limited supply of water to the solution (the solution has no intentional addition of water), were present. This was further aggravated with the non-uniformity of the environment (tarry mass did not have uniform composition of Cl^- and Zn^{++}). All these factors caused the material to be cracked transgranularly.

Recommendations

Recommendations were as follows :

1) Use of Ni based alloys/innercasing of nonmetals;
2) Regular cleaning of the reactor; and
3) Use of purer chemicals in the reaction

Failure Investigations of Autoclave [18]

Autoclave failure, made of SS-316, took place during the operation in a chemical plant. Following were the background about the material, corrodent and history of the failure:

Material : Made of 316 SS (Wall thickness: 15.5 mm and Bottom thickness: 35 mm)

Equipment in operations : Since last about 5 years.

Electrolyte being handled: (1) Chloroaromatics + NaOH + methanol + sodium chl ride + water, (2) Aromatic hydrocarbon + nitric acid (fuming) + chloride ions

Duration of each batch of operations : About 10 hours
Pressure : 25 Kg/cm^2
Temperature : 205°C

Cracking zone : At the sharp edges of bend as shown in the following figure

Fig. 15 : Schematic presentation of the sharp edges of autoclave

<u>*Investigations of the failure*</u>

Cracked segment of the equipment was analyzed for material and any residu corrosion product left. The material composition conformed to 316 SS. No corr sion product could be traced out. Microscopic examinations revealed intergranul stress corrosion cracking of the material. The main cause of IGC assisted by stre corrosion is attributed to the presence of highly oxidizing media (HNO_3). It is r ported by many investigators that in oxidizing media, IGC of even nonsensitiz austenitic stainless steel takes place. The causes for this is the depolarizing actio of oxidizers (here NO_3^- and NO_2^-). On cathodic reactions which enhances anod dissolution of grains also. The edges are affected preferentially due to the presen of stress concentration at the sharp edges. Grain boundaries are attacked. They a high energy area than the matrix.

<u>*Recommendations*</u>

To avoid such failures in futures, following recommendations were made.

1) It was suggested to provide larger radius at the edges, during fabricati stage of the antoclaves (as illustrated in Fig. 15).
2) Ni based alloys, in the above environment, are expected to behave bett However, before implementing this type of alloys, thorough investigatio are necessary.
3) Nonmetallic lining may also be used especially at the edges.

Failure of 304 SS in boiling zinc chloride solution[18]

Zinc chloride is highly corrosive towards most of the ordinary metals used f the construction of vessels for the manufacture of $ZnCl_2$ or other chemicals bas on $ZnCl_2$. Mild steels, coated with enamel coating in the interior side of vessels, a used, for reaction and evaporation purpose of $ZnCl_2$ based chemicals. Due to gre

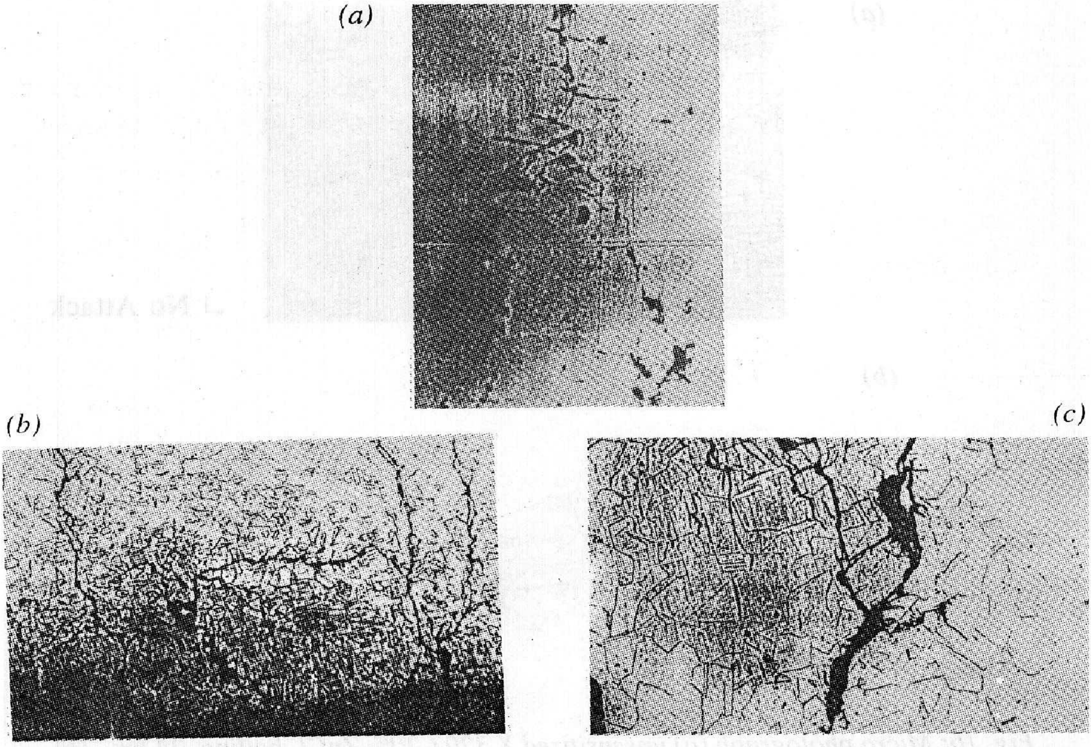


Fig. 14: (a) Cross sectional view of crack at X 200 magnification, (b) Cross sectional view of micrsotructure of failed metal (near surface) at X 50 magnification and (c) Microstructure of failed metal at X 200 magnification (cross sectional view)

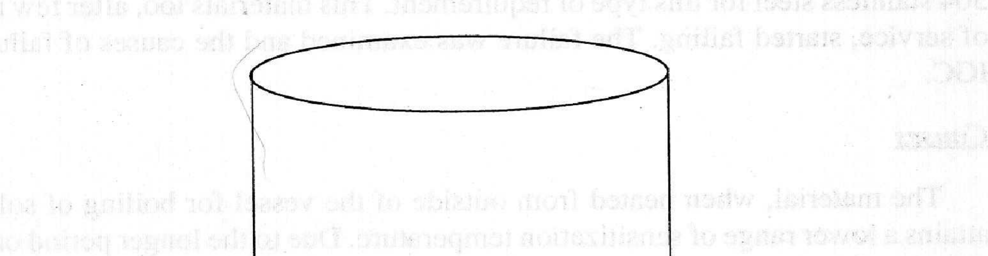


Fig. 15 : Schematic presentation of the sharp edges of autoclave

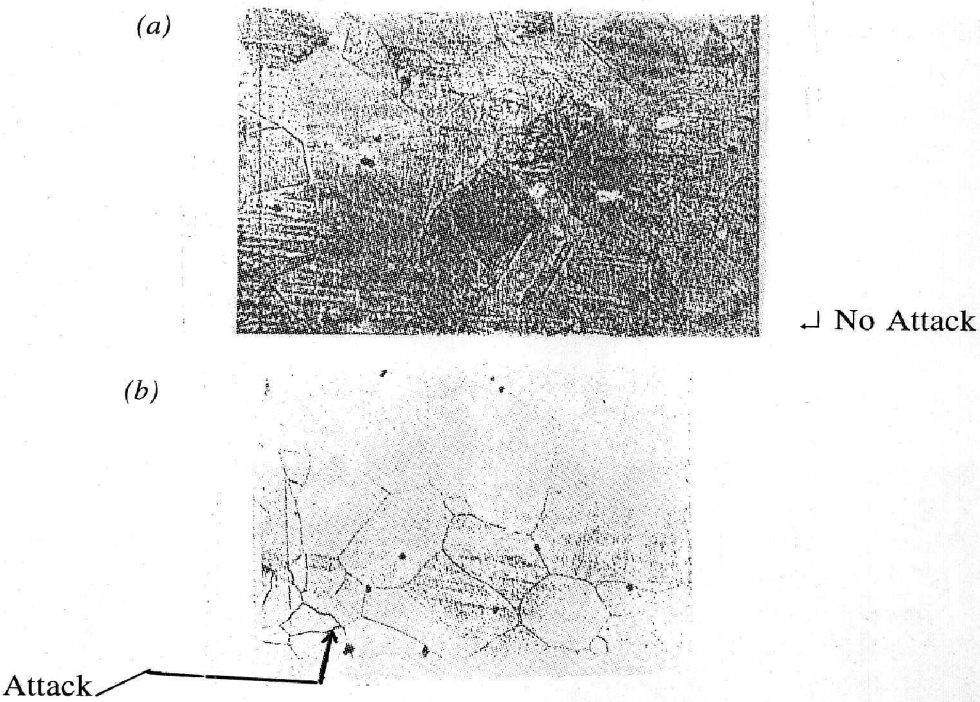


Fig. 16: Micro photograph (a) unsensitized X 320 (20% $ZnCl_2$ *boiling, 24 hrs., (b) Sensitized X 320 and exposed in 0.5%* $ZnCl_2$

difference in the thermal coefficient of expansion of these materials i.e., steel an ceramic coatings, frequent failures of the vessels take place. It was suggested to us 304 stainless steel for this type of requirement. This materials too, after few month of service, started failing. The failure was examined and the causes of failure wa IGC.

<u>Causes</u>

The material, when heated from outside of the vessel for boiling of solutions attains a lower range of sensitization temperature. Due to the longer period of maintenance of this temperature, the degree of sensitization in the material increases The pH of the boiling solution is about 2 - 3 and concentration of chloride is quit high. This crates an ideal condition for IGC attack on 304 SS. Some microphotographs are shown in Figs. 16(a-b).

<u>Remedial Measures</u>

Use of 316 L stainless steel was recommended. Based on this suggestion, plant manufacturing $ZnCl_2$ based chemical, has been using reaction vessel of 316 L steel since last two years, without any failure.

REFERENCES

[1] G. G. Page, Mateials Performacne, 28(7),1989, p. 58.

[2] R. W. Stachle, et. al., NACE-5, NACE, Houston, 1977, p. 193.

[3] Pitting corrosion of emtals by Z. Szrlarska-Kmialowaska, NACE, Houston, Texas, USA, 1986, p. 69.

[4] L. I. Gainer and G. R. Wallwork, Corrosion, Vol. 36 (7), 1980, p. 348.

[5] Principles and Prevention of Corrosion, by D. A. Jones, Maxweld MacMillan Interantional Editors, New York, 1992, p. 237.

[6] B. F. Brown, ed., Naval Research Laboratory, U.S. Govt. Printing Office, Washington, 1972, p. 2, also cited in "Stree Corrosion Cracking", by J. Yanalam and A. Aladjem, Paper of J. Kruger, p. 7.

[7] J. KJruger, in Stress Corrosion Cracking, by J. Yahalam and A. Aladjem, Prefered Publising House, Israil.

[8] H. H. Uhlig in 'Proc. Conf. fundamental Aspects of Stress Corrosion Cracking, NACE, Houston, 1969.

[9] D. A. Verunilyea in 'Proc. Conf. fundamental Aspects of Stress Corrosion Cracking, NACE, Houston, 1969.

[10] Principles and Prevention of Corrosion, by D. A. Jones, Maxweld MacMillan Interantional Editors, New York, 1992, p. 279.

[11] R. N. Parkins, An overview – prevention and control of stress corrosion cracking, Materials Performance, August, 1985, p. 9.

[12] J. Yu, N. J. H. Holroyd, R. N. Parkins, ASTM Conference at national Bureau of Standards, 1982.

[13] R. N. Parkins, Metal Science, July, 1979, p. 381.

[14] B. Tomkins and J. Wareing, Metal Science, 11, 1977, p. 414.

[15] Michael Henthorne, Intergranular corrosion in iron and nickel base alloys, I localized corrosion – causes of metal failure, ASTM STP - 516, ASTM, 1972, p. 6.

[16] Corrosion and its control, by J. T. N. Atkinson and H. VanDroftelaar, Houston, Texas, NACE, 1982.

[17] R. N. Ghosh et. al., Investigation report on offshore pipeline failure of ONGC pipe carrying crude and gases, NML Report, 1990.

[18] NML's preexploratory project report, 1994.