Training Module
on
Stainless Steel vs Corrosion
(Effects and Resistances to Corrosion by Stainless Steel)

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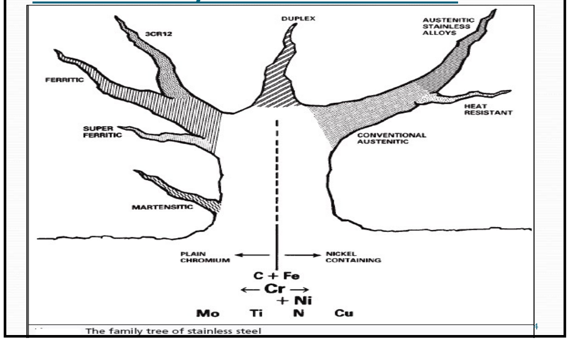
What is STAINLESS STEEL?

- In nature Iron is found in most natural stable form as ferrous oxide.
- Man made Steel is an unnatural form of iron, which is widely used as construction material.
- Stainless Steel is advanced ferrous (iron based) material, which possesses the prime property of corrosion resistance. It can be used in severly harsh, adverse & aggressive conditions, which many of the materials simply can not withstand.

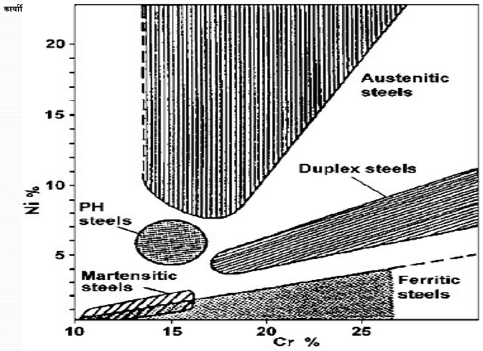
What is STAINLESS STEEL?

- Stainless steels are basically iron-based (Fe) alloys
- containing a maximum alloy content of approximately 50% (the balance being iron).
- Stainless steel consists of the family of chromium-containing (Cr) alloys.
- The chromium (Cr) content is usually between 10.5-30%. Other alloying elements which increase the corrosion resistance of stainless steel - that may also be added are Nickel (Ni)
- Molybdenum (Mo)
- Copper (Cu)
- Tititanium (Ti)
- Niobium (Nb).
- Stainless steels are classified according to their internal crystal structures which result from their different chemical compositions (alloy content)

The family tree of stainless steel



The family tree of stainless steel

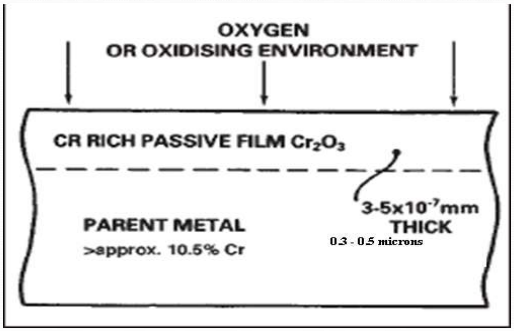


Effect of Ni on SS structure

- The plain Cr stainless steels (Nickle free) are martensitic or ferritic types.
- Stainless steels containing ≥ 8% Ni are austenitic, which have an alloy content of more than 50%.
- Lower Ni levels do not result in a fully-austenitic crystal structure and, instead, the duplex stainless steels, which have a mixed ferritic/austenitic crystal structure.

PASSIVITY & INERTNESS due to Cr content

- Passivity is the built-in natural resistance which stainless steels possess to fight corrosion. It is defined as a state in which a metal or alloy loses its chemical reactivity and becomes inert.
- A Cr content of more than approximately 10.5% gives stainless steel this passivity, due to the formation of an extremely thin (0.3 - 0.5 microns) & uniform, continuous, and stable Cr rich oxide film on the surface.



Passiveness Enhancement

- The properties of the passive film are further enhanced by higher Cr content and additions of other alloying elements, e.g. Ni and Mo.
- The resulting improved passivity extends the use of stainless steel into applications of higher corrosiveness and concentrations. The Cr oxide passive film forms spontaneously in air, but chemical oxidation (e.g. use of 15% nitric acid HNO_3 for 20-30 minutes at 60°C followed by a thorough water wash) improves its integrity and results in a higher resistance to corrosion.
- The nitric acid application should be done after removing all traces of oils and other contaminants. This is particularly necessary if the components are for use as critical components in aggressive environments.

THE PROCESS OF CORROSION

Usually there are two forms of corrosion in existance:

- **Wet (Aqueous) Corrosion**
- **Dry (Gaseous) Corrosion**

This presentation covers the more common forms of wet (aqueous) corrosion of stainless steel:

1. **General Corrosion**
2. **Galvanic Corrosion**
3. **Erosion/Abrasion Corrosion**
4. **InterGranular Corrosion**
5. **Pitting Corrosion**
6. **Crevice (shielded) Corrosion**
7. **Microbiologically-induced Corrosion (MIC)**
8. **Stress Corrosion Cracking (SCC)**

Carbon steels, low alloy steels and other metals and alloys also undergo similar forms of corrosive attack. Some forms of corrosion are easily visible or readily identifiable (e.g. general and pitting corrosion), whereas others are not always easily detectable nor apparent (e.g. stress corrosion cracking – SCC).

Wet (Aqueous) Corrosion

Wet (aqueous) corrosion is an attack on the metal by aggressive substances, generally dissolved in water to give a corrosive solution (electrolyte).

A damp film or dust containing dissolved aggressive substances also results in a corrosive electrolyte.

The severity and extent of the corrosion depends on the following:

- • The concentration of the aggressive substances in the corrosive solution;
- • The temperature of the corrosive solution;
- • The presence and nature of contaminants and trace elements within the solution.

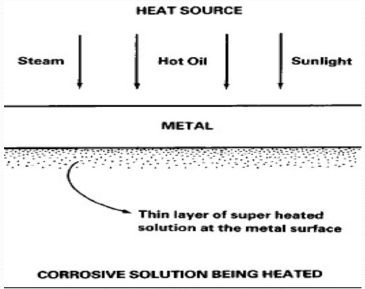
Factors controlling severity and extent of corrosion

1. The concentration is generally both known and controlled. It is desirable to avoid conditions where the concentration can vary, such as condensation, evaporation and concentration in crevices. This may result in unexpected, severe or localised corrosion attack.

Factors controlling severity and extent of corrosion

2. The **temperature** is usually known and uniform. It is desirable not to have higher localised temperatures, e.g. during heat transfer in solar heaters or heating coils.

A thin film of super-heated corrosive solution coats the metal surface through which the heat is transferred. The temperature of this film must be taken into account, as it gives rise to far more aggressive conditions than those related to the average bulk temperature.



Schematic illustration of superheated layer occuring at the metal surface under conditions of heat transfer

Factors controlling severity and extent of corrosion

3. All aqueous corrosion is electrochemical, so there is always an equilibrium between the reactions at the metal surface and those within the corrosive solution. Consequently even small / trace amounts of **contaminants** can affect this balance and either aggravate or lower the severity of the corrosion.

CORROSION TYPES

1. **General Corrosion**
2. **Galvanic Corrosion**
3. **Erosion/Abrasion Corrosion**
4. **InterGranular Corrosion**
5. **Pitting Corrosion**
6. **Crevice (shielded) Corrosion**
7. **Microbiologically-induced Corrosion (MIC)**
8. **Stress Corrosion Cracking (SCC)**

1. GENERAL CORROSION

- **General corrosion occurs uniformly over the entire surface of the stainless steel. It is the least dangerous form of corrosion because the rate of corrosion is measurable and predictable and can, therefore, be allowed for when designing for a required life or safety factor.**

- **General corrosion rates are measured and reported in different units:**
- • **Loss of Mass:** **grams/square metre/hour ($g/m^2/hr$)**
- • **Loss of Thickness:** **millimetres/year (mm/yr) or**
- **mils per year (mpy) [FPS system]**
    - **The approximate interrelationship of these units is**
    - **1 $g/m^2/hr$ = 1.1 mm/yr = 43 mpy. [0.254 mm= 1 mil]**

- **The severity of attack or suitability of material is indicated in different ways as shown in tables 1 & 2.**

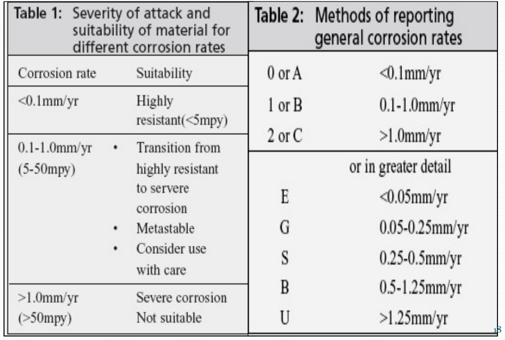
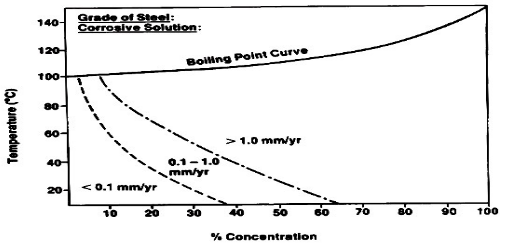


Table 1: Severity of attack and suitability of material for different corrosion rates

Corrosion rate	Suitability
<0.1mm/yr	Highly resistant(<5mpy)
0.1-1.0mm/yr (5-50mpy)	• Transition from highly resistant to servere corrosion • Metastable • Consider use with care
>1.0mm/yr (>50mpy)	Severe corrosion Not suitable

Table 2: Methods of reporting general corrosion rates

0 or A	<0.1mm/yr
1 or B	0.1-1.0mm/yr
2 or C	>1.0mm/yr
	or in greater detail
E	<0.05mm/yr
G	0.05-0.25mm/yr
S	0.25-0.5mm/yr
B	0.5-1.25mm/yr
U	>1.25mm/yr



eg 10% up to 60°C < 0.1 mm/yr

30% up to 20°C < 0.1 mm/yr

20% between 35°C – 70°C, 0.1 – 1.0 mm/year

Schematic illustration of an ISO-Corrosion Chart showing corrosion rates over range of temperature/concentration

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Low Corrosion rate of SS

- General corrosion rates for stainless steels are often very low.
- For example, in a particular solution, grade 316 may corrode at 0.03mm/yr and grade 304 at 0.07mm/yr. This does not mean that 316 is twice as corrosion-resistant as 304, but that both are suitably resistant to corrosion because each corrodes at less than 0.1mm/year.
- Stainless Steels undergo very low general corrosion rates in many highly aggressive, corrosive environments. They are not totally immune or impervious, but are versatile construction materials offering attractive and viable life-cycle costs.

Staining or Visible Rusting

- Under some conditions, the SS surface may exhibit signs of staining, i.e. visible rusting.
- It is seldom occurrence but such staining indicates corrosion rates equivalent to those of plain carbon (mild) steel and, even if left untreated, minimal metal loss will occur in SS.
- A simple cleaning process will usually remove the staining and restore the surface appearance. However, the cause should be investigated, especially if severe dark staining is evident, as it is an indication that passivity has broken down.

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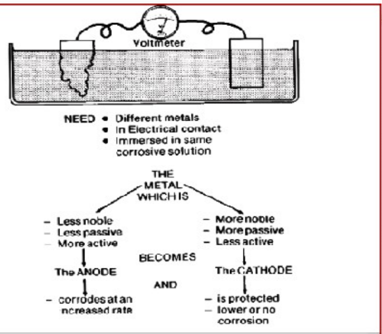
2. GALVANIC CORROSION

- Galvanic Corrosion occurs when two different metals are in electrical contact and immersed in the same electrolyte (corrosive solution)
- The less noble, less passive, more active metal of the two becomes the anode and corrodes at a faster rate.
- The more noble, more passive, less active metal of the two becomes the cathode and is protected, corroding at a slower than normal corrosion rate.
- An electric current will flow between the different metals and through the corrosive solution. This can be detected by a voltmeter in the circuit.



Schematic illustration of Galvanic Corrosion and the conditions which are required and result

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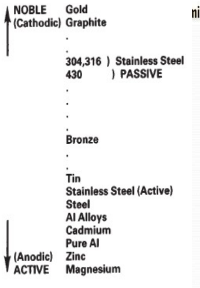
Metals and alloys may be ranked according to how active (anodic) or noble (cathodic) they are in any specific electrolyte. This is known as Galvanic Series. The most common is the galvanic series in sea water.

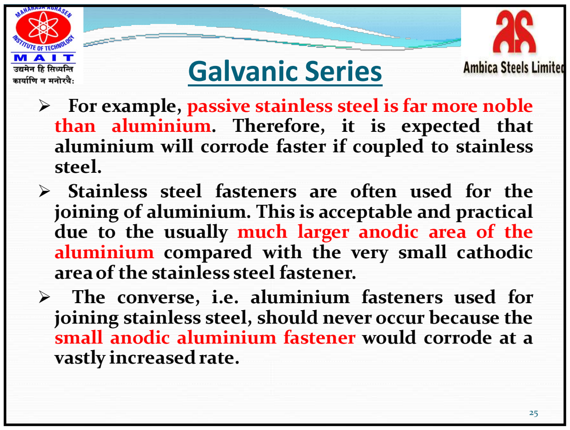
The rate at which the anodic member corrodes depends on the following:

- The difference in the corrosion potentials, i.e. how far apart they are in the galvanic series;
- The ratio of the surface areas of Anodic (active) metal to cathodic (noble) metal; and
- to a lesser degree, the physical Distances between the metals.



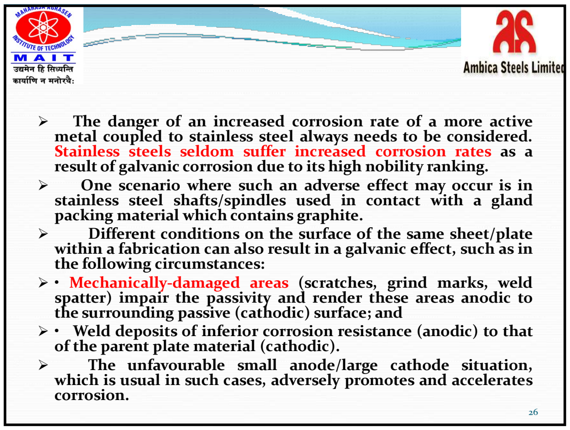
NOBLE (Cathodic)	Gold Graphite
	. .
	304,316) Stainless Steel 430) PASSIVE
	. . . .
	Bronze
	. .
	Tin Stainless Steel (Active) Steel Al Alloys Cadmium Pure Al
(Anodic) ACTIVE	Zinc Magnesium

Galvanic series of commercial metals and alloys in sea water (reduced)

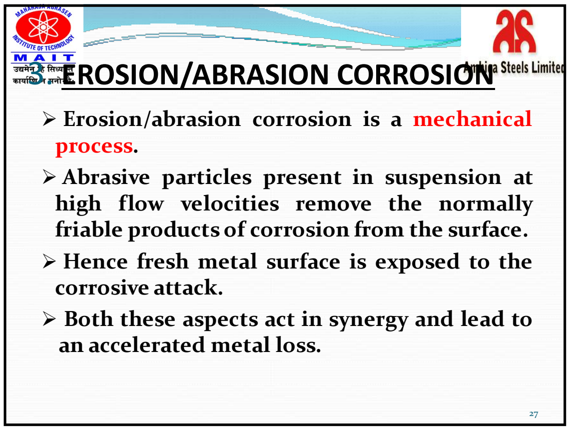


Galvanic Series

- For example, passive stainless steel is far more noble than aluminium. Therefore, it is expected that aluminium will corrode faster if coupled to stainless steel.
- Stainless steel fasteners are often used for the joining of aluminium. This is acceptable and practical due to the usually much larger anodic area of the aluminium compared with the very small cathodic area of the stainless steel fastener.
- The converse, i.e. aluminium fasteners used for joining stainless steel, should never occur because the small anodic aluminium fastener would corrode at a vastly increased rate.

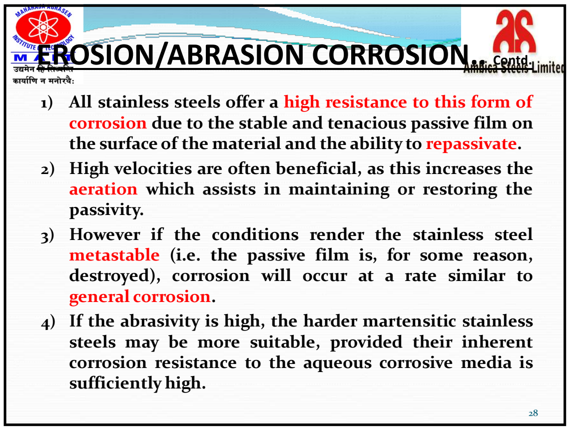


- The danger of an increased corrosion rate of a more active metal coupled to stainless steel always needs to be considered. Stainless steels seldom suffer increased corrosion rates as a result of galvanic corrosion due to its high nobility ranking.
- One scenario where such an adverse effect may occur is in stainless steel shafts/spindles used in contact with a gland packing material which contains graphite.
- Different conditions on the surface of the same sheet/plate within a fabrication can also result in a galvanic effect, such as in the following circumstances:
- • Mechanically-damaged areas (scratches, grind marks, weld spatter) impair the passivity and render these areas anodic to the surrounding passive (cathodic) surface; and
- • Weld deposits of inferior corrosion resistance (anodic) to that of the parent plate material (cathodic).
- The unfavourable small anode/large cathode situation, which is usual in such cases, adversely promotes and accelerates corrosion.



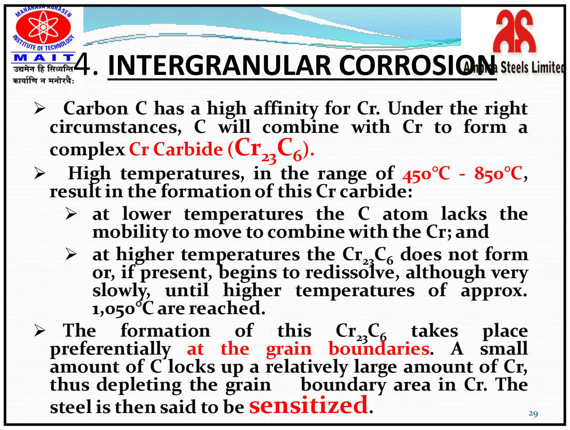
3. EROSION/ABRASION CORROSION

- Erosion/abrasion corrosion is a mechanical process.
- Abrasive particles present in suspension at high flow velocities remove the normally friable products of corrosion from the surface.
- Hence fresh metal surface is exposed to the corrosive attack.
- Both these aspects act in synergy and lead to an accelerated metal loss.



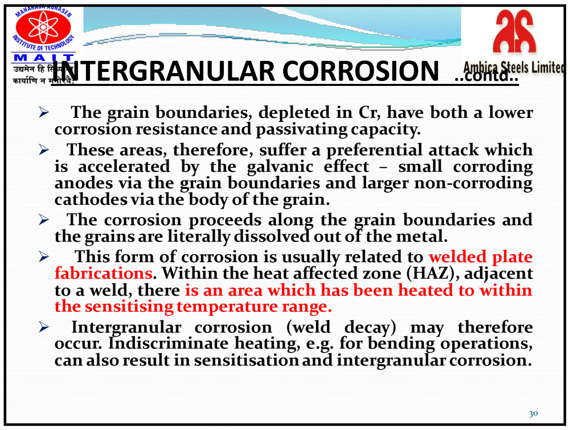
EROSION/ABRASION CORROSION … Contd.

1) All stainless steels offer a high resistance to this form of corrosion due to the stable and tenacious passive film on the surface of the material and the ability to repassivate.
2) High velocities are often beneficial, as this increases the aeration which assists in maintaining or restoring the passivity.
3) However if the conditions render the stainless steel metastable (i.e. the passive film is, for some reason, destroyed), corrosion will occur at a rate similar to general corrosion.
4) If the abrasivity is high, the harder martensitic stainless steels may be more suitable, provided their inherent corrosion resistance to the aqueous corrosive media is sufficiently high.



4. INTERGRANULAR CORROSION

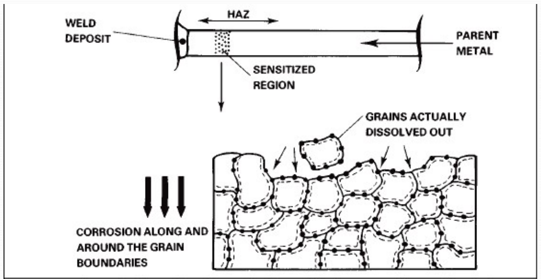
- Carbon C has a high affinity for Cr. Under the right circumstances, C will combine with Cr to form a complex Cr Carbide ($Cr_{23}C_6$).
- High temperatures, in the range of 450°C - 850°C, result in the formation of this Cr carbide:
  - at lower temperatures the C atom lacks the mobility to move to combine with the Cr; and
  - at higher temperatures the $Cr_{23}C_6$ does not form or, if present, begins to redissolve, although very slowly, until higher temperatures of approx. 1,050°C are reached.
- The formation of this $Cr_{23}C_6$ takes place preferentially at the grain boundaries. A small amount of C locks up a relatively large amount of Cr, thus depleting the grain boundary area in Cr. The steel is then said to be sensitized.



INTERGRANULAR CORROSION ..contd..

- The grain boundaries, depleted in Cr, have both a lower corrosion resistance and passivating capacity.
- These areas, therefore, suffer a preferential attack which is accelerated by the galvanic effect – small corroding anodes via the grain boundaries and larger non-corroding cathodes via the body of the grain.
- The corrosion proceeds along the grain boundaries and the grains are literally dissolved out of the metal.
- This form of corrosion is usually related to welded plate fabrications. Within the heat affected zone (HAZ), adjacent to a weld, there is an area which has been heated to within the sensitising temperature range.
- Intergranular corrosion (weld decay) may therefore occur. Indiscriminate heating, e.g. for bending operations, can also result in sensitisation and intergranular corrosion.

INTERGRANULAR CORROSION



Schematic illustration of sensitization within the NAZ; with associated chrome carbide precipitation and chromium depletion at the grain boundaries.

The Cure to INTERGRANULAR CORROSION

- **Solution Annealing** de-sensitizes the steel because it dissolves the $Cr_{23}C_6$ at the high temperatures used, i.e. the Cr23C6 is taken back into solution within the metal.
-
- The metal is uniformly heated to **1,050°C- 1,060°C and rapidly cooled** to prevent the reformation of any Cr23C6 during the cooling cycle.
-
- This process is easy to apply to individual sheets, plates or small components, but is difficult to apply to a completed fabrication because of the following reasons:
  - • distortion can occur at high temperatures;
  - • uneven heating and cooling can induce thermal stresses; and
  - • the surface will be scaled (oxidised) at these high temperatures, necessitating the repickling and repassivation of the entire surface.

Preventing interGranular corrosion

1. Fabrication of the material should be done in the **fully annealed state**, if possible.
2. **Stabilised grades** of stainless steel should be used. These stabilised grades contain the alloying elements of titanium(Ti) or niobium (Nb). These elements have a higher affinity than Cr for C. Therefore, they lock up the C as Ti or Nb carbides, leaving insufficient free C to combine with and deplete the Cr.
3. If possible **'L' grade stainless steels** should be used. The lower C content of 'L' grades significantly increases the time necessary for sensitization to occur, therefore providing adequate protection against sensitization during welding.

5. PITTING CORROSION

This is a dangerous, very **localised form of corrosion** which results in small holes or perforations. There is little measurable general metal loss.

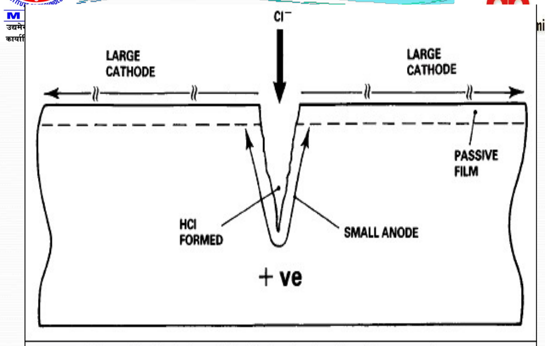
The chloride ion (Cl-) is the usual cause of pitting corrosion. It is very aggressive, mobile and, unfortunately, very common.

Under suitable conditions, a pit may form, say through the dissolution of a surface inclusion, perhaps accelerated by a layer of dirt that limits oxygen entry. Once formed, the pit will have a lower oxygen concentration at the base compared with the surface and corrosion will continue at an increasing rate.

This corrosion is accelerated by the migration of chloride ions into the pit due to their electrostatic attraction to the dissolving metal ions. The M+Cl- formed will hydrolyse, generating free hydrochloric acid that helps continue the corrosion:

$$M + Cl^- + H_2O \rightarrow MOH + HCl$$

The large surrounding cathodic area will also assist in maintaining a high corrosion rate at the base of the pit.



Schematic illustration of the factors involved in pitting corrosion

PITTING CORROSION

Pitting corrosion occurs in both acidic and basic aqueous solutions. It is **more severe in acid solution** (pH< 7) and is less likely to occur at high pH (solutions of high basicity).

Elevated temperatures increase the danger of and accelerate the attack.

Pitting corrosion is also more severe in **stagnant or de-oxygenated solutions**.

Pitting corrosion in a free machining stainless steel plug from a line containing a high chloride food pulp.

Pitting corrosion in an agitator shaft and housing made from 316 material left in contact with stagnant saturated calcium chloride. Corrosion was accelerated in the mini-crevices formed from deposits that settled on the surface from the stagnant liquid.

Preventing Pitting Corrosion

Let us first understand the Pitting Resistance Equivalent (PRE) .

The **PRE = %Cr + (3.3 x %Mo) + (16 x %N).**

An alloy with a PRE less than 32 may be susceptible to pitting (and/or crevice corrosion), whereas a PRE greater than 32 indicates the alloy is resistant to these forms of corrosion.

Pitting can be prevented by increasing the Pitting Resistance Equivalent (PRE) in the following ways:

- Increase flow rates:
- improve oxygenation of the corrosive solution;
- remove Cl from incipient pits; and
- prevent stagnant areas, sedimentation and possible local areas of higher temperature or concentration.

Preventing Pitting Corrosion ..contd..

- • Good design to prevent stagnant areas and crevices where the Cl can concentrate.
- • A chemically-produced passive film.
- • Non-impairment, damage or contamination of the passive film.
- • Use of cathodic protection, i.e. intentionally connecting an active, sacrificial anode (e.g. zinc anode) to the stainless steel, thereby chemically protecting (instead of accelerating) the corroding areas (the pits).
- • Using stainless steels of higher alloy content to raise the corrosion resistance/passivity.

6. CREVICE (SHIELDED) CORROSION

This type of corrosion attacks the metal surface where it is shielded or occluded or hidden, e.g.

- under washers or bolt heads,
- in the threads of bolts or pipe fittings,
- in contact with loose or absorbent gaskets,
- under sediments or settled solids,
- under marine growth.

Such areas promote localised concentration effects and stagnant solutions and, particularly, the lack of free access/availability of oxygen.

CREVICE (SHIELDED) CORROSION .contd..

Many aqueous solutions cause crevice corrosion. Those containing Cl are the more common because the very mobile Cl enters the crevice and builds up in concentration.

Crevice corrosion is similar to pitting corrosion in that limited areas are attacked, which gives rise to the unfavourable galvanic effects of small anodes and large cathodes.

Preventing the CREVICE (SHIELDED) CORROSION

The following precautions will help prevent crevice corrosion:

- • Avoid flat bottomed tanks where solids can settle out (sediments);
- • Have tanks on legs (skirt), rather than resting on the floor;
- • In the design avoid stagnant areas where sedimentation can occur;
- • Outlets should be able to drain the tank completely;
- • Rounded corners are better than square corners;
- • Avoid porosity and undercuts in welds;
- • Use butt welds rather than lap welds;

Preventing the CREVICE (SHIELDED) CORROSION

The following precautions will help prevent crevice corrosion:

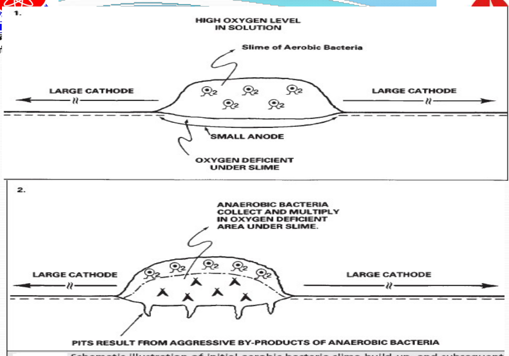
- Use continuous rather than spaced welds;
- Use impervious gasket material tightened to ensure no ingress of corrosive solution;
- Seal threads and other occluded areas with sealing compounds;
- Use materials of higher alloy content to increase passivity; and
- Clean the surface of settled dust and spillage.

7. MICROBIOLOGICALLY INDUCED CORROSION (MIC)

This form of corrosion results from the microbiological activity of bacteria. It has many similarities to both crevice and pitting corrosion. Many aqueous solutions, especially untreated natural dam, river mine water, contain an abundance of bacteria.

The bacteria are of two types:

- aerobic, i.e. requiring an environment containing oxygen (O_2), where the bacteria are active in the aqueous solution; and
- anaerobic, i.e. requiring an environment free of oxygen, where the bacteria are dormant in the aqueous solution.



Schematic illustration of initial aerobic bacteria slime build-up, and subsequent effects of anaerobic bacteria in the resultant oxygen deficient area

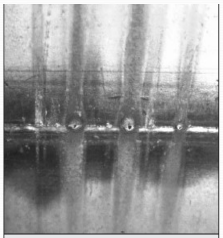
MIC

- If any area on the metal surface attract and anchor the active aerobic bacteria, slime will build up. This can become thick enough to lower the oxygen level under the slime, resulting in a situation equivalent to a crevice.
- The oxygen-deficient area under the slime then leads to the anaerobic bacteria collecting and multiplying in this area. These anaerobic bacteria have the property of producing aggressive metabolic products which attack the passive film on stainless steel. Due to the lack of oxygen, repassivation is inhibited and pitting attack results.
- The corrosion attack is typified by a shallow corroded depression which contains a few deep pits.

Preventing MIC

MIC can be prevented if the following precautions are taken:

- drain and flush the equipment immediately after stoppages or plant shut down;
- Employ higher flow rates to prevent sedimentation and slime build up where anaerobes can collect and multiply; and
- treat (sterilise) the water to kill the bacteria.



Microbial corrosion associated with a weld. The streaking is a common feature of this type of corrosion.

8. STRESS CORROSION CRACKING (SCC)

Stainless steels are unjustifiably often not considered for applications due to fear of stress corrosion cracking. Three co-existing and inter-relating factors are necessary for SCC to occur:

1. Tensile stress (either applied or residual SCC will not occur under compressive stress conditions) – the higher the stress the more dangerous the condition.
2. Temperature – the higher the temperature the higher the risk (SCC seldom occurs under 60°C).
3. The presence of an insidious ion (usually a halide ion - the chloride ion (Cl) being the most common). Hydroxides, e.g. caustic soda (NaOH) and hydrogen sulphide (H_2S), can cause SCC under conditions of high temperatures and concentrations.

Stress corrosion cracking from a plate type 316 stainless steel heat exchanger in a chloride environment. Cracking originated from the process fluid side and some metal around the opening has fallen away. Other cracks can be seen associated with the stressed areas formed during the cold pressing of the ridges.

Stress corrosion in a 316 filter made from punched sheet. The filter was in a hot chloride line in a food processing plant.

SCC

SCC can be induced by highly aggressive laboratory tests in all stainless steels, but the common austenitic grades (304 and 316) are particularly prone to this form of corrosion.

Duplex steels and the super austenitic grades are usually specified when chloride SCC is probable.

Ferritic stainless steel can also suffer from SCC but, in this case, the offending chemical is more usually H_2S. This can be a particular problem with sour gas oil wells.

The initiation of SCC is equivalent to that of pitting corrosion. Once a pit is formed, the tensile strength is concentrated at the base of the pit. The finer the pit, the higher the stress concentration factor. This leads to mechanical rupture of the metal at the base of the pit, exposing fresh, unpassivated (active) metal.

The result is accelerated corrosive attack at the pit base, re-concentration of stress, and further mechanical failure. SCC may take considerable time to initiate but, once it has begun, there is usually rapid transcrystalline crack propagation which results in final failure.

Preventing SCC

Design is critical to the prevention of SCC. The design should avoid the following:

- highly-stressed components;
- areas of stress concentration;
- fabrication requirements which result in residual stress; and
- factors which may contribute to the initiation of pitting.

Avoid conditions which may introduce Cl:

- Cl-contaminated insulation;
- leakage into the insulation jacket (evaporation of such leakage concentrates any Cl which it contains within the insulation); and
- spillage containing Cl which will concentrate the Cl on evaporation.

THANK YOU.

Any Query?

Feel free to ask.