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Pitting corrosion evaluation and inhibition of stainless steels: A review

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Abstract

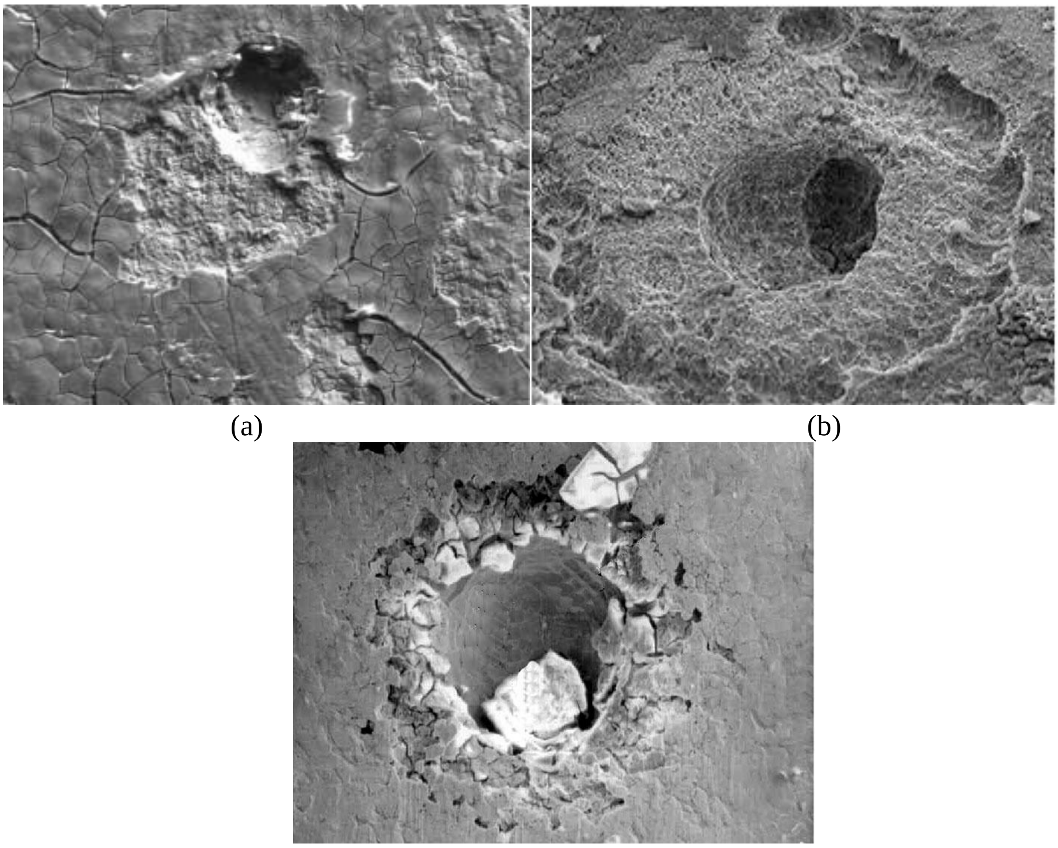
The effects of corrosion on the metallurgical characteristics and structural rigidity of metallic alloys has been a subject of interest for decades. This paper delineates the various researches on pitting corrosion. It reviews the techniques used to study pitting corrosion resistance, susceptibility and inhibition of stainless steel alloys. An extensive discourse can be found on pitting corrosion addressing the initiation and propagation of pits from the work of different authors due to localized corrosion in the presence of chlorides and other halogens and its effects on the electrochemical and metallurgical properties of the steel. Review of various research shows pitting corrosion is excercebated with increase in majorly chloride ion concentration leading to rapid deterioration of the steel alloys. Research also shows pitting corrosion can be controlled through conventional electrochemical techniques and changes substrate metal. The effect of changes in environment on the mechanism and rate of pitting corrosion is discussed.

Keywords: corrosion; pitting; passivity; stainless steel

1. Introduction

Pitting corrosion is a localized corrosion process that results in the formation of microscopic holes in metallic alloys. Corrosion pits forms at microscopic sizes and below, resulting from flaws, scratches, breakages and cracks on the passive film lead to pit formation on the metal surface especially in regions or sites of inclusions or impurities [1, 2]. There are some metals and alloys that show preferential sites for pit formation with metallurgical microstructural and micro-compositional features defining the susceptibility. These sites become anodic while an unknown but potentially vast area becomes cathodic. The corrosion propagates autocatalytically penetrating the metal insidiously [3]. The self-activating reaction mechanisms associated with pitting starts at the surface in different forms and sizes depending on the metallurgical property of the alloy, the electrolyte and other electrochemical factors [4]. Pitting is more deleterious and dangerous than general corrosion because it's difficult to ascertain, foreknow and design against [5]. An insignificant small pit with infinitesimal metal loss as shown in Figures 1 can progress leading to collapse of a complete mechanical system. The failure is due to microscopic breaches while general corrosion determined through weight loss can possibly be minimised. The metal loss is minimal even though the deep metal substrate is severely damaged. Occlusion (corrosion products) often prevents observation of the pits on the metal surface.

In cases where pit depths increase rapidly, the environment is usually such that no repair or repassivation of the protective layer can be accomplished. For other instances where many shallow pits form, the environment is usually one where repassivation of the damaged film can be made, but initiation of new sites is occurring on a regular basis. The localized nature of pitting attack can be associated with component geometry, the mechanics of the corrosion process, or with imperfections in the material itself. Use of corrosion control methods has been based on trial and error initiative with mixed or satisfactory results. Understanding of the pitting corrosion mechanism and its control is an ongoing research and the work of various authors has given differential facets of knowledge on this destructive phenomenon. This paper reviews progress from previous research to date concerning the study of pitting corrosion in aqueous solutions and its inhibition.



(a) (b)

(c)

Figure 1 (a) Pit formation, (b) Growth of pit and (c) Pitted steel

2. Mechanism of Pitting Corrosion

Generally there are two steps to the mechanism of pitting corrosion i.e. pit initiation and pit propagation. The initiation of pitting corrosion is often linked to the presence of local defects at the metal surface such as flaws in the oxide or segregates of alloy elements, and the presence of aggressive anions such as chlorides in the environment. The chlorides are believed to locally disrupt the oxide, preferably at pre-existing weak spots, resulting in micro fissures of several *nm* in diameter. Amongst the many initiated pits only a few will propagate [6]. The corrosion mechanism first occurs with the dissolution of the passivating layer and gradual acidification of the electrolyte caused by depleted oxygen supply.

Pit initiation occurs on the alloy surface passivated by an oxide film due to the following reasons;

- Damage to the protective film caused by scratches resulting in anodic reaction on the metal surface disclosed to the electrolyte. The unexposed protective surrounding becomes the cathode.
- Non-metallic inclusions, intermetallic inclusions, micro-segregations and other particles of the second phase on the metal surface exposed to the electrolyte selectively precipitates along grain boundaries and cracks or flaws, thereby becoming local anodes leading to localized galvanic corrosion and formation of initial pits.
- Stress points and regions due to dislocations and fatigue emerging on the surface are likely to become anodes and initiate pits.
- Non-homogeneous environment may dissolve the passive film at certain locations where initial pits form.

Adsorbed oxygen rather than metal oxide is considered to make up the passive film on stainless steels [7]. Oxygen normally has higher affinity than Cl^- for adsorption sites on the stainless steel surface, but as the potential of the alloy is shifted in the positive [noble] direction, more Cl^- ions move into the double layer. Prior to the adsorption of Cl^- on the film, Cl^- should be transported through the diffuse layer to the film [8, 9]. At a sufficient concentration corresponding to the critical potential, Cl^- ions succeed at favored sites in destroying passivity by displacing adsorbed oxygen ions [10 - 15].

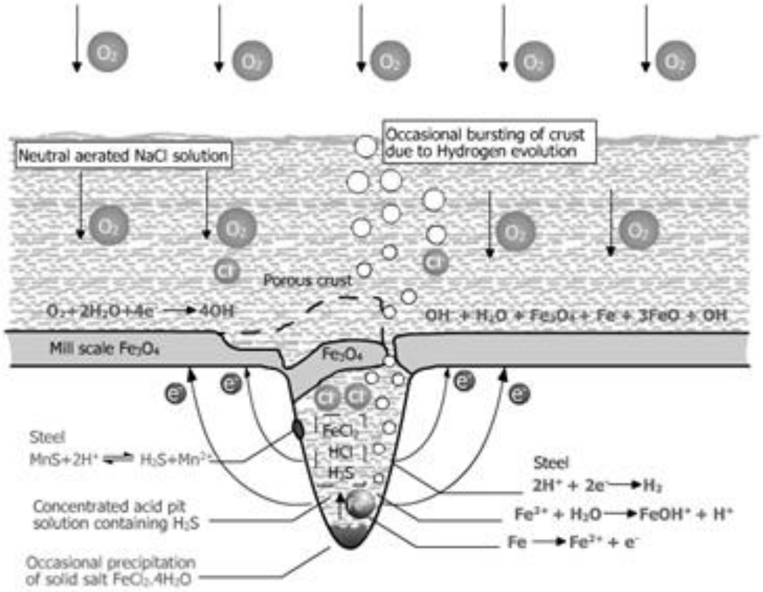


Figure 2 Electrochemical reactions that occur when a pit is initiated at sulphide inclusions in a carbon steel [16].

Pit propagation occurs in chloride and sulphate containing solutions where pits formation progresses autocatalytically in Figure 2 according to the illustration.

Anodic reactions inside the pit:
$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^+ + 8e$ (1)
$Fe \rightarrow Fe^{2+} + 2e^-$ (dissolution of iron) (2)
$Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+$ (3)
$3Fe(OH)^+ + H_2O \rightarrow Fe_3O_4 + 5H^+ + 2e$ (4)

In the presence of Cl^-, the hydrolysis of Fe^{2+} is accelerated, as shown in the reactions below;
$Fe^{2+} + Cl^{2-} \rightarrow FeCl_2$ (5)
$FeCl_2 + H_2O \rightarrow Fe(OH)^+ + H^+ + 2Cl^-$ (6)
$Fe^{2+} + H_2O \rightarrow Fe(OH)^+ + H^+$ (7)

The electrons given up by the anode flow to the cathode (passivated surface) where they are discharged in the cathodic reaction:
$\frac{1}{2} O_2 + H_2O + 2e- \leftrightarrow 2(OH^-)$ (8)
$H^+ + e \rightarrow H$ (9)
$2H^+ + 2e \rightarrow H_2$ (10)

The corrosion process within a pit is a unique type of anodic reaction and produces conditions which are both stimulating to, and indeed necessary for, continuing activity of the pit. In the pit there is a high concentration of metal and chloride ions and as a result of hydrolysis, a high concentration of hydrogen ions [17].

Electrochemical diffusion of chloride ions within the pit activates the redox reactions. This increases the entropy of the ions and electrolytic reactions in the pit, including hydrogen evolution reactions (equations 9 & 10) thereby accelerating the confined corrosion process on the steel. Increase in $_{\text{P}}$H of the electrolyte within the pit decreases (acidity increases) which further accelerates the corrosion reaction mechanism favored by large ratio between the anode and cathode. Corrosion products [Fe(OH) $_3$] form around the pit resulting in further separation of its electrolyte [18].

The corrosion products have a high ionic conductivity, resulting in a higher corrosion rate in the pits in contrast to the remaining areas that are passive. When chlorides are sufficiently concentrated the pits may become so numerous and so large that an overall anodic brightening of the whole surface occurs [19 – 25]. This results in metal dissolution leading to cation production within the growing pits. The chloride ions in solution electromigrates to the pits due to electrostatic attraction and encourages the formation of the metal ions accelerating the corrosion process, being autocatalytic [5]. It has been previously postulated that gravitational effect causes downward concentration gradient of the released ions in the pit hole caused by the corrosion, as the concentrated solution is denser, but more conventionally the acidity within the pit is sustained by the redox electrochemical process [26].

3. Metastable and Stable Pitting

Metastable pits are pits that forms and later dissapears due to the reformation of the passive film due to several factors. These pits are considered microscopic in size with a very short lifespan. They form at very low potentiostatic potentials well below the potentials at which pitting corrosion occurs. The importance of metastable pits lies in the fact that the capacity of a metal to quickly repassivate is a good measure of its capacity to withstand pit formation and subsequent growth depending on the strenght of the passive film. The lower the potential at which an alloy repassivates the greater the resistance of the alloy to pitting. Metastable pits precede stable pits [27-29]. The size and the geometry of active impurities as well as the presence of fatigue stress are important parameters for metastable pitting and transition to stable pitting [30]. During potentiostatic test the current increases below the pitting potential which results in breakdown and repassivation of the passive film as indicated by the decrease in current. Such transients have been reported in stainless steels [31-33] for many years. Individual metastable pit current transients can be analyzed for pit current density, and stochastic approaches can be applied to groups of metastable pits. The occurrence and disappearance of metastable pits is usually within seconds [34-35].

The growth of corrosion pits is systematically dependent on the composition of the alloy, electrolytic composition and acidity (pH) and potential within the pit. The electrolytic diffusion phenomena within the pit is strongly associated with the kinetics of the growth process. Electrolytes with aggresive anions especially halogens, sulphates and sulphides results in accelerated anodic dissolution. The electrolyte at these critical concentrations within the pit, if stable pit growth continues. The conditions at minimum must be aggressive enough to prevent repassivation.

4. Pitting corrosion evaluation

Numerous researches have been done to understand the pitting corrosion paradox. Efforts have been directed toward the characterization of pitting corrosion assessment of two known potential of pitting, namely i.e. pitting potential, and passivation potential. Theoretically the pitting potential is the potential at which pitting corrosion occurs, but below which pits do not nucleate. The passivation potential is the potential value at which potentials greater or equal to this potential, pit do propagate, but below which the metal retains its passivity. Pitting corrosion of Type 304 stainless steel under drops of $MgCl_2$ solution was studied to clarify the rusting mechanism in marine atmospheres under the droplets with various combinations of the diameter and thickness (height) by exposure to a constant relative humidity. The probability of occurrence of pitting corrosion decreased with decrease in diameter and thickness, however pitting corrosion progressed only when the Cl^- exceeded 6 M (relative humidity < 65%). In almost cases, there was a small hole (~10 μm diameter) in the center of a single pit, which may be the trace of an inclusion particle like MnS dissolved out [36].

Asaduzzaman et al [37] investigated the pitting corrosion behavior of austenitic stainless steel in aqueous chloride solution using potentiodynamic technique. Corrosion potential measurements along with microscopic examinations suggest that within or above 3.5 % NaCl solution at a pH value of 2, pitting corrosion took place on the surface in the absence of applied potential after 6 hours immersion. Test results revealed that the corrosion potential and pitting potential decreased and current density in the passive region increased with increase in chloride ion concentration. Similar results were obtained from the pitting corrosion study of austenitic stainless steel ($Cr_{18}Mn_{12}N$) in dilute solutions of sulphuric acid contaminated with chloride ions with the aid of cyclic potentiodynamic method to analyze the effects of chloride ions and agitation rate on the pitting and repassivation potentials. The results obtained with chromium–manganese– nitrogen steel were compared with those of austenitic $Cr_{18}Ni_9$ stainless steel. Similarity in pit initiation was established, while steel composition exhibits no significant effect. $Cr_{18}Mn_{12}N$ steel was observed to be less prone to repassivation as compared with $Cr_{18}Ni_9$ steel [38]. The research work of Dong et al [39] involved the use of scanning electrochemical microscopy equipment to study experimentally the metastable and stable pitting corrosion reaction on stainless steel within the chloride media. Observation showed that metastable pitting occurs on the steel at the corrosion and passive potential and the change in potential increases the metastable pitting current. Use of a potential exceeding the pitting potential causes stabilization resulting in a continuous pit growth.

Results for in situ monitoring of localized corrosion processes of reinforcing steel in NaCl containing solution indicates that the chloride ions selectively precipitates, adsorbs and accumulates at the regions with flaws leading to the formation and progress of pitting corrosion on the reinforcing steel surface. Observation of the on and off site visuals show that manganese sulphide impurities in reinforcing steel are the most susceptible defects to pitting corrosion in chloride-containing solution [40]. Pitting corrosion of type 430 stainless steels under drops of $MgCl_2$ solutions were investigated at specific relative humidity's under droplets with differential dimensions. The tendency for pitting to occur reduced as the dimensions reduces. Pit propagation occurred when the chloride concentration increased above a critical amount i.e. the steady concentration at 80% relative humidity; accordingly, pitting of Type 430 initiated when the relative humidity was less than 80% [41]. The pitting corrosion behavior of type 304 austenitic stainless steel was investigated by Maier, et al [42] under electrolyte droplet with a layer of silica particles on the surface with a Kelvin probe. The chloride concentration increased and pitting corrosion initiated which was detected by a sudden drop in open-circuit potential. Metastable pits repassivates slower under the silica particle layer than on bare stainless steel. Pits on silica-coated stainless steel initiated within a narrow chloride concentration and time range unlike pits on bare steels.

Singh [43] studied the pitting characteristics of two nickel-based alloys, Alloy 600 (UNS N06600) and Alloy 601 (UNS N06601) in aggressive acidic environments using potentiodynamic anodic polarization in the presence of various concentrations of sodium chloride (NaCl) in 0. 1M of sulphuric acid. Results show that the addition of NaCl increased the corrosion rate and critical current density for the passivation of both alloys significantly. Potential- related parameters such as open-circuit potential and pitting potential shifted in the active direction with the increase of NaCl concentration. The pitting potential for Alloy 601 was almost 200 mV more positive than that for Alloy 600 in the presence of a particular concentration of NaCl. Increase of temperature from 30 ^{o}C to 90 ^{o}C excercebated the pitting attack on the alloys. The effect of surface finish of type 304L stainless steels to its corrosion and pitting potential in 3.5% NaCl aqueous solution was investigated by Neusa, et al [44]. Observation shows the corrosion potential and its standard deviation is significantly influenced by the nature of surface finish. Metastable pitting of ferritic (FeCr type) and austenitic (FeCrNi type) stainless steels in chloride containing oxidizing electrolytes was investigated at rest potential using experimental technique that allows for recording of the potential and corrosion current variations on BA and 2B industrial surface conditions. Observations showed that the number of pitting events decreased with the exposure time and BA condition provides better resistance to pitting than 2B [45]. Passivation and breakdown reactions of type 304 stainless steel studied by El-Egamy et al [46] in acidic sodium sulfate solutions confirmed the formation of a bilayer as a primary passive film based on results from potential and impedance measurements under open circuit conditions. The results from cyclic polarization curves showed that pitting and protection potentials increases with increasing chloride ion concentration indicating failure of the steel sample due to pitting.

Impedance spectra recorded at different passivation potentials showed a maximum at 0.4 V due to film thickening above which film breakdown occurs.

Pitting corrosion behavior of stainless steel 304 under droplets of chloride solution was investigated by Bastian et al [47] using a Kelvin probe (KP). Pit initiation was detected by a sudden decrease in open circuit potential under small droplets than under large drops. The chloride concentration at initiation was between 3.0 and 8.4 M for droplets with a starting concentration of 0.88 M Cl^-. The initiation concentration increased when the initial concentration of the droplet was higher. The anodic current demand of pits growing at the open circuit potential decreased with time as did the available cathodic current. When the current demand exceeded the available cathodic current, the active pit area decreased. The experimental studies show that chloride ions strongly influence the pitting corrosion resistance and susceptibility of ferrous alloys. Cl^- ions are aggressive on steel and initiate pitting. The small size of Cl^- ions enables penetration through the passive oxide film. Migration of Cl^- ions into pits is enhanced to maintain electrical neutrality and hydrolysis of the corrosion products inside pits causing acidification, and hence prevents repassivation. This mechanism is autocatalytic because the increased acidity accelerates the dissolution rate within pits. Cl^- ion concentration has a strong influence on potentiodynamic polarization curves of stainless steel chloride media, the values of the electrochemical parameters: corrosion current density, corrosion potential, and pitting potential are strongly influenced in the presence of chloride concentrations. The value of Icorr tends to increase with increase in NaCl concentration. Moreover, an increase in NaCl concentration shifts pitting potential towards anodic direction with increase in corrosion current due to pitting corrosion while the steel electrode is passive over a short range indicating a decrease of pitting corrosion resistance. In the absence of NaCl the steel electrode is passive over a wide potential range. Chloride ion incorporation can be strongly detected within the passive film, especially when the critical pitting potential is reached. The activity of Cl^- ions determines the stability of the passive film

Some researchers focussed on the effect of other corrosive media without chloride ions, alloying elements and the use of non-electrochemical techniques to study pitting corrosion. Potentiodynamic cyclic anodic polarization, scanning electron microscopy, and energy dispersive x-ray techniques were used to study pitting corrosion behaviour of type 904L stainless steel in aerated and argon deaerated 0.6 M sodium bromide (NaBr) solutions at 25^{o}C by Abd El Meguid [48]. The steel underwent pitting corrosion despite the high molybdenum content (4.596 Mo). The critical pitting potential decreased with increase in temperature and CBr^- . The influence of Cu and Sn on the pitting corrosion resistance of AISI 304 and 316 stainless steels in chloride-containing media was evaluated by cyclic polarization, potentiostatic CPT measurements and electrochemical impedance spectroscopy in 3.5 wt% NaCl. Data shows that the presence of Cu promoted pit nucleation but prevents the propagation, in contrast Sn caused the opposite effect reaction of Cu. Studies by SEM, X-ray mapping and EDS analysis showed Cu-, Cl- and O-rich corrosion products reduce the extent of corrosion damage [49]. In situ observations of pitting corrosion as it spreads across the surface of stainless steel were carried out by Dornhege et al [50] who applied ellipsomicroscopy for visualizing changes of surface film properties and contrast-enhanced microscopy for monitoring nucleation and reactivation of metastable corrosion pits. A correlation between oxide film weakening caused by individual pits and the nucleation of subsequent pits was found. The presence of front propagation depicts that the properties of the process are consistent with the behavior of stochastic reaction diffusion systems and that the onset of corrosion is a cooperative critical effect.

The uptake of chloride (Cl^-) by the passive oxide film on 316L austenitic stainless steel polarized at potentials below the pitting potential in 0.6 M NaCl solutions was studied using X-ray photoelectron spectroscopy (XPS). The XPS spectra for the stainless steel showed that chloride was not adsorbed or present in the passive oxide film [51]. Jose [52] developed pit model on the assumption that the metal ions hydrolyzes inside the pits and that the corrosion products are transported by diffusion. He found that the main reason for passivity breakdown at the initial stages of pit growth is the localized acidification due to metal ions hydrolysis. Through analysis of the transport processes inside a pit it was also concluded that the pitting potential of a metal changes with CI^- ion concentration. Equilibrium calculations on some sulfide systems in commercial stainless steel have shown that the sulfides cannot thermodynamically exist at the potential of the passive steel. The ions released by the dissolution of the sulfides give rise to an acid solution in micro-areas. The sulfides are polarized to the potential of the passive steel surface and tend to dissolve. During the dissolution a virgin metal surface is exposed to the environment. When the solution in the micro-area thus developed has reached a certain composition, the contacting metal can no longer passivate and the metal starts to dissolve [53]. Potentiostatic scratch technique was methodically used to grade the pitting corrosion resistance of market grade and laboratory austenitic, super austenitic and extra low interstitial ferritic stainless steels in chloride environment depicting the condition of the human body and seawater. The method produced satisfactory results especially with the pits in the vicinity of the scratched regions. It was established that martensitic transformation resulting from deformation is insignificant on the pitting corrosion behavior of the metastable austenitic stainless steels. It was suggested that the nonmetallic inclusions aggregated at the critical regions for pitting corrosion progression than the bare scratched sites [54].

Okada [55] studied the repassivation of pits responsible for the formation of pitting corrosion within astringent conditions from the dynamic aspect of observation. Understanding of the unchangeable thermodynamic equilibrium shows that repassivation process initiates when the monolayer accumulation of the metal oxide attains stability within the pit depth. Observation reveals that the repassivation potential is significantly near the critical pitting potential; in contrast pit formation potential varies and aligns only when the passive film is very thin. The pitting behavior of a range of sulfide free iron-chromium thin film alloys was studied by electrochemical methods coupled with in situ optical microscopy. David et al [56] expounds the electrolytic processes responsible for accelerated deterioration of sulfide impurities leading to pit initiation to be as a result of changes impressed within the sulfides due to decline in temperature of the substrate specimen from the melting point temperature to the solidification temperature of the inclusions. Under this temperature condition as temperature declines, on cooling significant chromium depletion of the steel probably takes place within the environment of the sulfide resulting in precipitation of metallic phases within the sulfides. The chromium depleted regions are responsible for the accelerated dissolution causing pitting corrosion.

Initiation of pitting corrosion on type (304) stainless steel in dilute sodium chloride solution was studied at about 200 sites. Pit growth occurred locally at manganese sulphide inclusions and inclusions of mixed manganese sulphide /oxide. At the early periods of pit growth the earlier mentioned impurities caused high surface concentrations within the cavity and the surrounding vicinity. Smaller inclusions were unable to initiate pits due to repassivation of the steel [57]. Break-through-potential data and confirmatory immersion-corrosion data showed that no passivation treatment confers lasting protection to stainless steel immersed in media which corrode the unpassivated metal. Equally effective results were obtained with stainless steel which was cleanly pickled, thoroughly rinsed, and air dried. Although no definite evidence of the existence of passive films was found by reflection electron diffraction studies, bulk oxides produced by chemical or air oxidation on 18/8 stainless steel were found to consist chiefly of Cr_2O_3 with no nickel oxide and little iron oxide present. The bulk oxides formed by air oxidation on straight chromium-iron alloys consisted of FeO, Fe_2O_3, Fe_3O_4, and mixtures of these oxides [58].

Szklarska-Smialowska [59] described the mechanism of the breakdown of passive film of transition metals in a chloride solution based on the similarity between the electrical breakdown of insulators and the pitting breakdown. He is proposed that nucleation of pits occurs by electrical breakdown most probably by the Zener mechanism. Results show that the creation of a very high current locally destroys the passive film and causes the dissolution of the metal forming metastable or stable pits. Mattin et al [60] expounds the initiation of corrosion pits on stainless steel in chloride containing conditions based on time transient currents conducted under high resolution. Results reveal the formation mechanism to be quick, the rise time was less than 1 ms, due to collapse of the protective oxide as a result of the initiation of microscopic patches of metal chloride at the metal-oxide interface. The pitting corrosion resistances of cast stainless steels grades 1A and 3A from ASTM A890 standard were studied in 3.5% sodium chloride solution with the steels depicting critical pitting temperatures (CPT) in the 45–50 °C range, although steel 3A has a pitting resistance equivalent (PRE = 36) higher than steel 1A (PRE = 32). Steel 3A, in fact proved to be slightly more pitting resistant due to higher pitting potentials values than steel 1A [61].

DC and AC electrochemical methods were investigated as a means of elucidating the pitting susceptibility of austenitic and duplex stainless steels in acid chloride environments containing hydrochloric acid mixed with either perchloric acid or sodium chloride for a constant hydrogen ion or a constant chloride ion concentration of 1M. Results were correlated with pitting resistance equivalence (PRE) values based on the molybdenum, chromium, and nitrogen contents of the steels. Test results for austenitic stainless steels based on 18Cr-15Ni-0·2Mo and 25Cr-24·5Ni-2·5Mo (wt-%) with PRE numbers of approximately 20 and 35·6 respectively revealed generally low resistance to pitting for hydrochloric acid concentrations of 0·1, 0·5, and 0·9M. Greatly improved resistance to pitting in these environments was indicated for a 20·5Cr-25Ni- 6·4Mo alloy, for which the PRE number was 45·5. The two duplex stainless steels based on 26·5Cr-4·8Ni-1·5Mo and 25·5Cr-5·7Ni-3·1Mo with PRE numbers of 34·8 and 38·8 respectively performed well in the electrochemical tests in 0·1M hydrochloric acid, but less so within hydrochloric acid concentrations of 0·5M and 0·9M respectively [62]. The pitting potential of the $Cr_{12}Ni_2W_1Mo_1V$ steel specimens, hardened and tempered at different temperatures was measured under different corrosion environments and stress levels. Test results showed that external stresses have great influence on the pitting initiation of the $Cr_{12}Ni_2W_1Mo_1V$ steel besides the material processing, microstructure and corrosion environments. Pitting potentials increased with decrease in concentration of chloride ion. Pitting potentials decrease dramatically with the increasing of the stress when the stress is lower than 50 MPa. Pitting potentials decrease little with the increase of the stress in the region of 50–400 MPa, pitting potentials tend to be stable when the stress is higher than 400 MPa [63].

Besides chlorides, other anions implicated in pitting include thiosulfates ($S_2O_3^{2-}$), fluorides and iodides. Stagnant water conditions favor pitting. Thiosulfates are particularly aggressive species and are formed by partial oxidation of pyrite, or partial reduction of sulfate. Thiosulfates are a concern for corrosion in many industries: sulfide ores processing, oil wells and pipelines transporting soured oils, Kraft paper production plants, and photographic industry, methionine and lysine factories. Comparative analysis on the pitting corrosion behavior of type 304 and 316 stainless steel alloys in 3.5% NaCl solution with 100 ppm thiosulfate ion to initiate the pitting corrosion process through potentiodynamic polarization and potentiostatic techniques was done at room temperature. The morphology and dimension of the pits was approximated with metallurgical light microscope while the fatigue strength and fracture surface were determined using plain-bending fatigue test machine and the scanning electron microscope. Results show that the 304 stainless steel is more prone pitting compared to the 316 stainless steel coupled with its lower fatigue strength than the 316 stainless steel [64].

The effect of thiosulfate concentration on the corrosion behavior of duplex stainless steels S32101 and S31803 was investigated in thiosulfate- and chloride-containing environments through cyclic potentiodynamic polarization and potentiostatic scratch test to study their localized corrosion behavior and the results compared with results from austenitic stainless steels S30403 and S31603. Cyclic polarization results indicated that the presence of thiosulfate ions considerably lowered the repassivation potential of the stainless steels tested. S31803, with the highest molybdenum and chromium content, was the most resistant to pitting corrosion among the four grades of stainless steels tested [65]. Naghizadeh et al [66] studied the effect of thiosulfate ion on pitting corrosion behavior of 316 stainless steel with emphasis on the influence of thiosulfate on the critical pitting temperature of the steel in 0.1M chloride solution, and its effect on the pit chemistry. Results from electrochemical experiments with and without 0.01 M thiosulfate ion showed that thiosulfate deteriorates the critical pitting potential. According to Burstein et al [67-75], the pitting potential only represents the transition from metastable pit formation to stable pitting corrosion which are all part of the pit enlargement process. He states that the pitting potential is not the familiar breakdown potential of the alloy surface; neither does it mark the boundary between pitting corrosion and its absence, but that pits can and do form, and increases in size at potentials below the pitting potential.

5. Pitting corrosion inhibition

Pitting corrosion can be inhibited with the same technique used to control general corrosion, such as modification of the environment through the use of chemical compounds commonly known as inhibitors [76-

81]. Studies have shown that inhibitor adsorption on metallic surface depends on the physicochemical characteristics of inhibitor molecule such as functional groups, steric factors, aromacity, electron density of the donor atoms, π-orbital character of donating electrons, polymerization resulting in formation of protective film and the electronic structure of the molecules [82-84]. Most of the well-known corrosion inhibitors are organic compounds [85-91]. Organic compounds containing functional groups with heteroatoms such as oxygen, nitrogen and sulphur capable of donating valence electrons, has been observed to perform excellently against metallic corrosion in a significant number of industrial conditions [92-94]. A number of nontoxic organic compounds containing polar functions with nitrogen, oxygen, and/or sulphur in conjugated systems in their molecules have been effectively used as inhibitors in many corrosion systems [95-100]. The inhibiting action of such compounds is attributed to the adsorption of the additives to the metal/solution interface.

Alloying elements within the matrix of the base metal has a profound influence on the microstructural properties of the alloy hence its tendency to pit. Elements such as nickel, chromium are responsible for the passivation effect on stainless steels mainly through formation of chromium oxide layer [101-103]. Increase in chromium contents significantly increases the potentiostatic potential at which pitting occurs on the potentiodynamic scale [59, 104]. Alloying elements such as molydbdenum, manganese, nitrogen etc in limited amounts influences the pitting resistance characteristics of stainless steel. Molybdenum improves the high-temperature creep and rupture strength by promoting stabilization of carbides. In some instances, it also increases high-temperature corrosion resistance [105-107]. The presence of sufficient nickel in iron improves resistance to pitting as it stabilises the austenite phase and limits the ferrite content which if too high may result in lower rust resistance and ductility. In 0.5 M hydrochloric acid solution; iron-chromium alloys with less than 16% did not pit at any potential, whereas alloys with atomic content greater than 16% chromium pit at approximately +500 mV standard calomel electrodes. The sharp transition is believed to be associated with the existence of a critical size of iron cluster which act as pit nucleation sites. The pits propagate under remnants of the passive film as two-dimensional disks, with current densities up to 80 A cm^2 and simultaneous hydrogen evolution [108].

Wei et al [109] observed that the volume of surfactant and surface charge exerted significant influence on the pitting corrosion inhibition of type 304 stainless steel by N-lauroylsarcosine sodium salt (NLS) in dilute sodium chloride media. Observation shows NLS enhances the pitting corrosion resistance of the steel with total inhibition at higher NLS concentrations. Adsorption of the compound occurs strongly on the steel with the possibility of bilayer coverage. Results from electrophoretic mobility for the steel particles show that the surface of 304 the steel is negative in sodium chloride media at neutral pH. Pardo et al [110] introduced Mn and Mo in AISI 304 and 316 stainless steel composition to modify their pitting corrosion resistance in chloride-containing media and investigated the corrosion behavior using gravimetric tests in 6 wt.% FeCl3, as well as potentiodynamic and potentiostatic polarization measurements in 3.5 wt.% NaCl. Observation showed that addition of Mo made the steel more resistant to deterioration caused by the corrosive species and causes the formation of Mo insoluble compounds in the aggressive pit environment thus facilitating the pit repassivation. Conversely, Mn additions exerted an opposite effect, mainly due to the presence of MnS inclusions which acted as pit initiators. Bond, et al [111] performed potentiodynamic polarization experiments in 0.1M hydrochloric acid and in 1M sodium chloride with austenitic alloys containing 18 to 20% Cr, 13 to 39% Ni and 0 to 5% Mo. The pitting potentials varied consistently with alloy content and correlated well with the results of exposure tests in 0.33M ferric chloride. Increasing the molybdenum and nickel contents increased the resistance to pitting; however, decreasing the carbon and nitrogen contents also increased the resistance to pitting. Critical current densities for passivity decreased sharply at all nickel levels with increase in molybdenum content.

Zhenqiang et al [112] assessed the inhibiting properties of anionic sodium dodecylsulfate (SDS), cationic dodecyltrimethylammonium chloride (DTAC), and nonionic Triton-X-100 (Triton) as pitting corrosion inhibitors of type 304 stainless steel in neutral sodium solutions. SDS was found to increase the pitting resistance of the stainless steel, while neither DTAC nor Triton showed any inhibition effect, indicating that the negative headgroup is preferred in pitting inhibition of stainless steels. The three surfactants tested adsorbed significantly on the stainless steel, suggesting that the adsorption alone is not sufficient for pitting inhibition. Results obtained for the electrophoretic mobility of the particles in surfactant solutions showed that only SDS made the surface of the stainless steel more negative. Gluconate anion was investigated for its corrosion inhibition potentials on chloride induced pitting corrosion of delta vanadium steel. Observation of the results revealed total coverage of the steel at low concentration of the inhibiting compound in weak alkaline media while increase in sodium gluconate concentrations results in aggravation of the pitting corrosion on the steel samples as a result of the unstable iron–G complex [113]. Heikki et al [114] examined the role of composition, inclusions, and precipitates on the pitting corrosion resistance of Mn-alloyed austenitic stainless steels sea water (3.56 wt% NaCl), sulfuric acid (0.5M H_2SO_4), and sulfuric acid + salt (0.5 M H_2SO_4 + 0.4 M NaCl) solutions. Observation showed that manganese sulfides act as corrosion pit initiators. Decrease in Cr content coupled with partial replacement of Ni by Mn resulted in decrease in the pitting corrosion resistance in seawater and H_2SO_4 + NaCl solutions. The amount of inclusions was not found to have a clear correlation to the potential at which corrosion pits initiate.

Surface conditions also affects the pitting corrosion behaviour of alloys. Impurities and non-metallic inclusions serve as initiation sites for localised electrochemical corrosion reactions leading to anodic dissolution of the alloy substrates. The more exposed they are on the surface, the greater the tendency of the metal to pit. Polished surfaces reduces alloy susceptibility to pitting and resulting in a higher pitting potential on the potentiodynamic curve. The effect of electropolishing on pitting corrosion of 304 stainless steel (SS) was investigated through polarization technique in conjunction with the scanning electron microcopy examination. A significant decrease on passive current density and also shift of pitting potential towards noble value was recorded on electropolished specimen revealing a pronounce effect of this technique on surface modification. Results revealed the reduction on the number and magnitude of metastable pitting transients prior to occurrence of stable pitting on electropolished specimen. Modification in surface roughness during electropolishing was the main reason of pitting corrosion improvement [115]. Heptamolybdate ions was used by Albrimi et al to inhibit pitting corrosion of 304 stainless steel in dilute hydrochloric acid solution at 298 K was investigated using gravimetric, electrochemical and optical microscopy methods. Increase in inhibitor concentration led to significant reduction in the corrosion rate of stainless steel, with inhibitor efficiency values well above 90% [116]

Conclusion

Pitting corrosion is a complex problem responsible for a significant number of corrosion failures. The phenomenon as observed from study through a variety of techniques over the years has resulted in ground breaking conclusions which generally agree that improvement in the metallurgical structure of metal alloys through increase in the percentage content of alloying elements such as chromium, molybdenum improves pitting corrosion resistance. The application of conventional corrosion inhibition method especially with the use of film forming compounds proves to be highly effective, however there's need for an agglomeration of the differential facets of knowledge acquired through the use of various techniques the reviewed investigations presented to combat the phenomenon with respect to factors such as the environmental, metallurgical and material properties and surface characteristics of stainless steel alloys which are critical to the pitting process. Most of the review on pitting corrosion evaluation shows that pitting corrosion is generally characterized by the breakdown potential of the metallic surface and sometimes the repassivation potential; they have form an integral part of research on pitting corrosion

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