Pitting studies of plain carbon steel in chloride containing borate buffer solution

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requirements for the degree of

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Submitted
by

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CERTIFICATE

This is to certify that the thesis entitled “Pitting studies of plain carbon steel in chloride containing borate buffer solution” submitted by M.Dilip kumar (111MM0486) and Himanshu chouhan (111mm0456) in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Metallurgical and Materials Engineering at the National Institute of Technology, Rourkela, is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge the matter embodied in this thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

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Abstract

Passivation is the process of temporary or permanent halt in degradation or corrosion rate of a metal due to the formation of different types of surface layers or films that protects the underlying metal. Pitting corrosion is the breakdown of the surface film due to presence of aggressive ions such as chloride ions. The breakdown of the passivity film is characterized by breakdown potential (Vc) which is dependent on the pH of the solution, concentration of the aggressive ions and the potential sweep rate. This study used the Point Defect Model to characterize the breakdown potential with respect to varying pH and concentration. The pH of the solution was kept a constant at 10.4. The breakdown potential is found to decrease with increasing chloride concentration and decrease with increasing pH. The cumulative distribution of the breakdown potential was found to be in well agreement with the experimentally obtained data. Optical micrographs showed stable and Meta stable pitting. The parameters from point defect model was found to be in well agreement with the experimental data

Keywords: Passivation, steel, breakdown potential, borate buffer, point defect model

Contents

Chapter 1: Introduction

Corrosion is a process through which metals in created states return to their normal oxidation states. This method is a reduction oxidation reaction in which the metal is being oxidized by its surroundings, routinely the oxygen in air. This reaction is both unconstrained and electrochemically upheld. Corrosion is essentially the creation of voltaic, or galvanic, cells where the metal being alluded to goes about as an anode and generally crumbles or loses its quality.

A buffer solution is an aqueous solution consisting of a mixture of a weak acid and its conjugate base,or vice versa.Its PH changes very little when a small amount of stronge acid or base is added to it and thus it is used to prevent changes in the PH of a solution. Buffer solutions are used as a means of keeping PH at a nearly constant value in a wide variety of chemical applications.

Passivation is the process of formation of a protective layer of metal compound on the surface of the metal which protects it from corrosion and helps reduce the degradation rate.

Depending on the microscopic structure of the corroded metal corrosion can be divided into eight different forms namely [1]:

(1)uniform, or general assault, (2) galvanic, or two-metal consumption, (3)intergranular corrosion, (4) Erosion corrosion, (5) Crevice corrsion, (6) Selective leaching, (7) stress corrosion cracking, and (8) Pitting corrosion.

Three Generations of PDM have been produced, with every advancing to address basic issues of the past era that got to be evident upon correlation with test information. This common movement, which is in keeping with the "exploratory technique", has brought about a model that now has no known clashes with trial and which has brought about the expectation of a few phenomena that were beforehand obscure or not completely perceived in the field. These incorporate the photograph hindrance of latency breakdown, the gratefulness that lack of involvement is a meta-stable, not a thermodynamically stable, state, and depassivation (demolition of the boundary layer) by the vicinity of the external layer. Moreover, the PDM has prompted the improvement of the deterministic convention, Damage Function Analysis that is presently being utilized to foresee general and limited erosion harm in an assortment of handy frameworks, including abnormal state atomic waste stores, gathering warmth exchangers, oil and gas transmission lines, and low weight steam turbines.

As the chloride ion concentration increases the breakdown potential of the film decreases rapidly at very low values of pH the passive zone seems to decrease substantially at very low values passive zone does not exist [2].

Passivation plays an important role in electro chemistry, the objective of this experiment is to study the passivation behaviour of steels at different electrode potentials and varying amounts of chloride ions and its effects on the break down potentials of passive films.

And we calculated the cumulative probability distribution of the above samples at different break down potentials.

Chapter 2: Literature review

2.1. Corrosion

Corrosion is a characteristic process, which converts refined metal to their more steady oxide. It is the progressive annihilation of materials (normally metals) chemical reaction with their surroundings.

In the most widely recognized utilization corrosion implies electrochemical oxidation of metals in response with an oxidant, for example, oxygen. Rusting, the arrangement of iron oxides, is a no doubt understood case of electrochemical erosion. This kind of harm commonly delivers oxide(s) or salt(s) of the first metal. Erosion can likewise happen in materials other than metals, for example, earthenware production or polymers, albeit in this connection, the term corruption is more normal. Erosion debases the valuable properties of materials and structures including quality, appearance and penetrability to fluids and gasses.

2.1.1. Why Study Corrosion?

Corosion is a typical event, similar to the rusting and chipping of an old iron yard piece. Here we will investigate the procedure by which consumption happens and the diverse ways undesirable Corosion can be controlled. Vitality, frequently vast sums, are filled winning the craved metals from their common minerals; fabricating some metal items can be unreasonable. Consumption causes decay of made items, harming their structure and eventually rendering the item pointless. Permitting erosion is not cost effective and can hinder profitability; understanding and avoiding consumption is critical for keeping up foundations and apparatus or any items that face corrosion.

2.2. Environmental effects

On the off chance that iron or steel was presented to air and water, rust would be relied upon to grow inside a matter of minutes then again hours. Indeed, it would be astonishing if the uncovered iron did not consume or rust. Obviously, if copper, metal, aluminum, or stainless steel was substituted for iron, a given level of consumption may take longer, however some corrosion would even now be expected. As opposed to framing rust (a manifestation of iron oxide), a few oxides of copper, aluminum, or chromium may frame a defensive covering on the uncovered metal. This oxide covering, regardless of the fact that amazingly thin, may give an halfway hindrance to proceeded with assault and ease off the rate of consumption.

A surface layer arrangement, whether it is oxide, carbonate, sulfate, or some other compound, is a central point in corrosion resistance, especially if the layer viably divides the hidden metal from its surroundings. Such a characteristically shaped covering must be dispersion and dampness impervious to be powerful. Standard iron does not characteristically frame an powerful obstruction; regularly happening rust is permeable and does not avoid oxygen and dampness to infiltrate and proceed rusting. In this manner, unless insurances are taken, disappointment will inevitably happen.

Different metals and amalgams, for example, stainless steel, titanium, or aluminum, are often left unpainted. This is definitely not since these metals are inactive, but since oxygen noticeable all around aides build up a defensive oxide layer on the metallic surface. In spite of the fact that these oxide layers are so thin as to be imperceptible to the eye, they can be distinguished and their vicinity checked.

Precautionary measures to keep iron and its compounds from consuming constitute a real exertion in corrosion control. It is here that we regularly turn to the utilization of defensive coatings over the metallic surface to draw out its valuable life. Different methods for example, anodic and cathodic security can give extremely effective corrosion control in the most requesting situations. A fewsituations are more destructive than others. While there are special cases, the accompanying articulations are by and large acknowledged as truths.

1. Damp air is more destructive than dry air

2. Hot air is more destructive than chilly air

3. Heated water is more destructive than icy water

4. Contaminated air is more destructive than clean air

5. Acids are more destructive than bases (alkalies) to steels

6. Salt water is more destructive than new water

7. Stainless steel will outlive standard steel

8. No erosion will happen in a vacuum, even at high temperatures

2.2.1 Atmospheric corrosion

It is confined to temperatures and conditions resulting from exposure to the natural ambient environment. Dissolved oxygen is more readily transported through a thin layer surface of water than through bulk water during complete immersion. Humidity is necessary for atmospheric corrosion. A thin layer of water deposited acts as an electrolyte. Pollutants and other contaminants stabilize the water films and enhance electrolytic properties. Sulphur dioxide forms sulphuric acid when dissolved in surface films, even 0.001% of sulphur dioxide can increase the corrosion rate rapidly.

High temperature dries the surface and reduces the corrosion. Sometimes ambient temperature may enhance the condensation of aqueous surface film to increase corrosion.

2.2.2 Effect of PH

- In intermediate PH range 4 to 10 a loose, porous, ferrous oxide deposit shelters the surface and maintains the PH to about 9.5 beneath the deposit. The corrosion rate is nearly constant and is determined by the uniform diffusion of dissolved oxygen through the deposit in this intermediate range [3].

- In more acidic solutions below PH 4 the oxide is soluble and corrosion increases due to availability of hydrogen ions for reduction [3]. The absence of the surface deposit also enhances access of dissolved oxygen which enhances corrosion rate.

- At PH 5 corrosion rate is low due to formation of passive ferric oxide film in the presence of dissolved oxygen [4].

- At PH above 14 corrosion rate may increase when soluble ferrite ion forms.

2.2.3. Effect of dissolved oxygen

Corrosion of iron and steel at near ambient temperature requires dissolved oxygen in neutral and alkaline solutions. A protective magnetite film is stable in the absence of dissolved oxygen. Factors affecting dissolved oxygen thus affect the corrosion of steel proportionally. Solution agitiation on stirring increases transport of dissolved oxygen increases corrosion rate.

2.3. Eight Forms of Corrosion

It is worthwhile to request corrosion by the structures in which it shows itself, the reason for this game plan being the vicinity of the expended metal. Each structure can be perceived by immaterial visual recognition. Huge information for the plan of an utilization issue can every now and again be obtained through careful view of the expended test cases or failed equipment. Examination before cleaning is particularly appealing. A part of the eight appearances of utilization are exceptional, yet every one of them are essentially interrelated.

The eight structures are:

(1) uniform, or general assault, (2) galvanic, or two-metal consumption, (3) intergranular corrosion, (4) Erosion corrosion, (5) Crevice corrosion, (6) Selective leaching, (7) stress corrosion cracking, and (8) Pitting corrosion.

2.3.1. Uniform Attack

Uniform attack is the most broadly perceived indication of corrosion. It is normally depicted by a compound or electrochemical reaction which proceeds reliably over the entire uncovered surface or over a sweeping region. The metal gets the opportunity to be more slim and at last misses the mark. A valid example, a touch of steel or zinc splashed in debilitate sulfuric destructive will routinely separate at a uniform rate over its entire surface. A sheet iron housetop will show essentially the same level of rusting over its entire outside surface.

2.3.2. Galvanic or Two-Metal Corrosion

A potential distinction ordinarily exists between two unique metals when they are drenched in a destructive or conductive arrangement. In the event that these metals are put in contact (or generally electrically associated), this potential contrast produces electron stream between them. Corrosion of the less consumption safe metal is generally expanded and assault of the more safe material is diminished, as contrasted and the conduct of these metals when they are not in contact. The less safe metal gets to be anodic and the more safe metal cathodic[5].

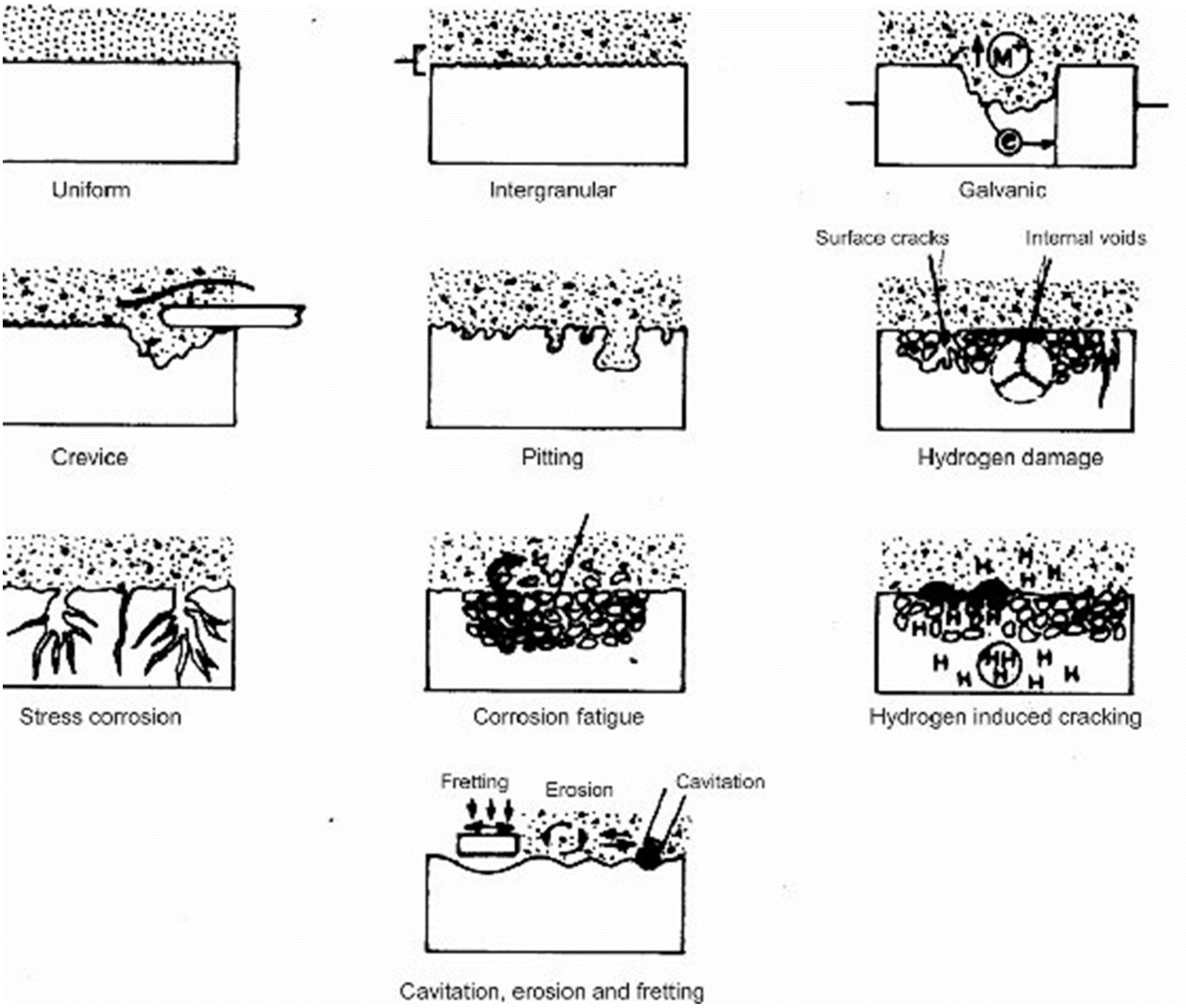


Fig 1. Different types of corrosion

2.3.3. Intergranular Corrosion

Grain limit impacts are of next to zero result in many applications or employments of metals. On the off chance that a metal erodes, uniform assault results since grain limits are normally just somewhat more responsive than the framework. Nonetheless, under specific conditions, grain interfaces are extremely responsive and intergranular consumption results. Restricted assault at and nearby grain limits, with moderately little consumption of the grains, is intergranular erosion. The combination crumbles (grains drop out) and/or loses its quality**.**

2.3.4. Selective leaching

Selective leaching is the removal of one element from a solid alloy by corrosion processes. The most well-known sample is the specific evacuation of zinc in metal combinations (dezincification). Comparable courses of action happen in other compound frameworks in which aluminum; iron, cobalt, chromium, and different components are evacuated**.**

2.3.5. Erosion Corrosion

Erosion corrosion is the speeding up or increment in rate of weakening or assault on a metal in light of relative development between a destructive liquid and the metal surface. By and large, this development is very fast, and mechanical wear impacts or scraped spot are included. Metal is expelled from the surface as broken up particles, or it frames strong erosion items which are mechanically cleared from the metal surface. In some cases, development of nature declines erosion, especially when restricted assault happens under stagnant conditions, yet this is not disintegration consumption on the grounds that decay is not expanded.

2.3.6. Stress-corrosion cracking

Stress-corrosion cracking alludes to splitting brought about by the synchronous vicinity of tractable anxiety and a particular destructive medium [6]. Numerous agents have grouped every single breaking disappointment happening in destructive mediums as anxiety erosion splitting, including disappointments because of hydrogen embrittlement. Then again, these two sorts of splitting disappointments react diversely to ecological variables. To delineate, cathodic assurance is a powerful technique for counteracting anxiety erosion splitting while it quickly quickens hydrogen-embrittlement impacts. Subsequently, the significance of considering anxiety erosion breaking and hydrogen embrittlement as particular phenomena is self-evident. Consequently, the two splitting phenomena are examined independently in this section.

2.3.7. Pitting corrosion

Certain conditions, for instance, low convergences of oxygen or high concentration of foreign species, for instance, chloride which complete as anions, can intrude with a given amalgam's ability to re-outline a passivation film [7]. In the most cynical situation, most of the surface will stay secured, however little close-by fluctuations will corrupt the oxide film in several separating core interests. Corrosion at these centers will be fantastically increased, and can realize disintegration pits of a couple of sorts, dependent upon conditions. While the disintegration pits simply nucleate under really convincing circumstances, they can continue growing despite when conditions return to run of the mill, following within a pit is typically prevented from securing oxygen and essentially the pH decreases to low values and the utilization rate increases due to an autocatalytic system. In astonishing cases, the sharp tips of extraordinarily long and confined utilization pits can achieve tension obsession to the point that for the most part serious mixes can break; a wobbly film infiltrated by an impalpably small opening can hide a thumb assessed pit from viewpoint. These issues are especially risky in light of the fact that they are difficult to recognize before a part or structure misses the mark. Setting stays among the most generally perceived and hurting sorts of utilization in passivized alloys [8], be that as it may it can be hindered by control of the composite's surroundings.

Setting results when a touch of opening, or gap, outlines in the metal, generally as an eventual outcome of de-passivation of a little zone. This area gets the opportunity to be anodic, while some bit of the staying metal gets the chance to be cathodic, conveying a constrained galvanic reaction. The debilitating of this little zone invades the metal and can provoke dissatisfaction. This indication of utilization is frequently difficult to perceive on account of the way that it is regularly by and large little and may be secured and concealed by disintegration.

Fig. 2 Pitting corrosion

2.4. Passivity

To ensure having the maximum corrosion resistance the steel must be in a passive state [9]. The passive condition on the surface of the stainless steel is obtained by formation of a chromium oxide film on the metal‘s surface. This is accomplished by passivizing the metal. Chemical passivation procedures using alkalines, wetting agents, chelants, and organic or inorganic acids are used to clean the metal surface thoroughly and in conjunction with an oxygen rich atmosphere, a uniform chromium oxide film forms. The key is to have a uniform chromium oxide film with an acceptable chrome to iron ratio (typically>1) and thickness (20-50) angstroms. Passivation is required to restore or enhance the chromium oxide film on the stainless steel surface when it has been manipulated by surface finishing, welding, grinding, external contamination, etc.The term passive refers to steel being unreactive. Normally in steels with the increase of solution oxidizing power the corrosion rate increases and then it transforms from cathodic corrosion to anodic corrosion at the OCP(open circuit potential). If we further increase the oxidizing potential the the steel enters into a passive state from active state this is due to the formation of a surface film usually oxides of the alloying elements such as chromium. On further increase of oxidizing potential the surface film breaks down and the steel again undergoes corrosion. This region is termed as transpassive region [8].

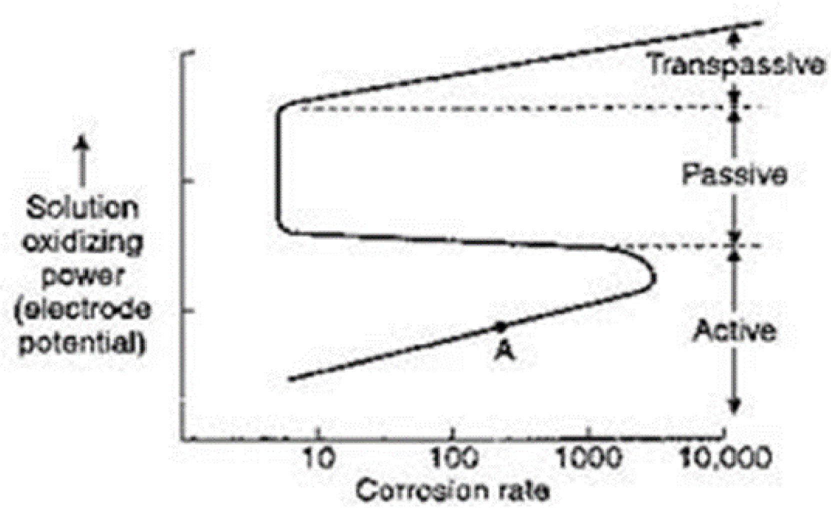


Fig 3. Electrode potential vs corrosion rate

2.4.1. Why Passivation?

The passivation procedure gives back the stainless steel or different metals back to its unique details by expelling undesirable trash and oils from the surface and afterward submerging the part into a passivating shower. At the point when a part is machined, different particles can saturate the surface of the base metal, debilitating its imperviousness to consumption and making the part more helpless to ecological variables. Soil and different particles and deposit, for example, free iron, oil and machining oils all influence the quality of the common surface and can get to be implanted in the surface amid the machining methodology. These regularly go concealed to the human eye and are frequently the reason for the weakening.

As expressed above, "uninvolved" is characterized as being less influenced by natural components. The methodology enhances and sanitizes the surface of the part. The restored surface acts like a defensive covering to ecological variables, for example, air, water and other great situations. It is essential to note that passivation does not change the outward appearance of the base metal.

2.4.2. Passivation of Stainless steel

The passivation of stainless steel is a methodology performed to make a surface detached, i.e., a surface film is made that causes the surface to lose its synthetic reactivity [8]. Stainless steel is as of now known as being consumption safe, however the passivation process further fortifies its regular covering by enhancing the outside surface of the general part. Stainless steel passivation uni potentializes the stainless steel with the oxygen consumed by the metal surface, making a monomolecular oxide film. Passivation can bring about the all that much sought low consumption rate of the metal. Passivation likewise is expert

Stainless steels are consumption safe by nature, which may propose that passivating them would be pointless. Be that as it may, stainless steels are not totally impenetrable to rusting. One regular method of corrosion in consumption safe steels is when little spots at first glance start to rust in light of the fact that grain limits or installed bits of outside matter permit water particles to oxidize a portion of the iron in those spots in spite of the alloying chromium. This is called rouging. A few evaluations of stainless steel are particularly impervious to rouging.

A two-stage strategy - keeping in mind the end goal to make a surface on stainless steel that would be impervious to corrosion. It is two different courses of action. Pickling (or Chemical Descaling) is done to uproot scale and to clean the part before the passivation procedure happens. The passivating of stainless steel is a post creation process with the final objective of making the surface more detached and erosion safe by restoring the surface to the first attributes with defensive oxide filmby stainless steel electropolishing.

2.4.3. Metal pickling

Pickling or compound descaling is however one of a few pretreatment steps accessible for setting up an article for further handling, for example, passivation or electro-polishing, or to perform a prevalent cleaning operation of welded structures [10].

Before pickling, the substantial surface soils, for example, oil, oil, buffing mixes, drawing aggravates, some scale, overwhelming rust, color and paint markings, tape, glue deposit and other remote substances must be uprooted. This step may be fulfilled by the utilization of soluble cleaners, dissolvable cleaning, vapor degreasing, ultrasonic cleaning, steam cleaning, water-flying, or other mechanical cleaning. Pre-cleaning is not obliged if oxide or scale is the main soil at first glance

2.4.4. Advantages of Passivation

1. Enhanced Corrosion Resistance
2. Uniform, Smooth Appearance and Finish
3. Cleanliness
4. Enhanced and Extended Life of Product

2.5. Buffer solution

A buffer solution is an aqueous solution consisting of a mixture of a weak acid and its conjugate base,or vice versa [11].Its PH changes very little when a small amount of strong acid or base is added to it and thus it is used to prevent changes in the PH of a solution. Buffer solutions are used as a means of keeping PH at a nearly constant value in a wide variety of chemical applications.

Saturated borax is a solution of borax in water.It is a white crystalline powder.The protective nature of a layer which forms upon the surface of metal under particular form of oxidation is supposed to be connected with the crystal structure of passive films. Thus anodic passivity of metal is resulted from the formation of oxide or hydroxide films in the reactions of metals in electrolytic solution [12].

EIS is a very much used for characterization of the electronic properties of passive films on metals and alloys. The electrical properties of their passive films are expected to be of crucial importance in the understanding of their passivity and their protective character against corrosion.

2.6. Point defect model

Point defect model (PDM) for the development and breakdown of passive films on metal and combination surfaces in contact with fluid arrangements [13]. The model gives a sensible record of the steady-state properties of cation-conducting and anion-conducting boundary layers on nickel and tungsten, individually, in phosphate cradle arrangements [14]; of the impedance qualities of barrier layer on nickel; of the breakdown of latent movies on an extensive variety of metals and composites; of the disseminations in the breakdown parameters (breakdown voltage and affectation time); of the part of alloying components in upgrading the resistance of amalgams to lack of involvement breakdown [13]; of transpassive disintegration and electro-polishing; of erosion-corrosion; and of photo-inhibition of pit nucleation. Furthermore, the PDM has permitted us to detail an arrangement of standards for outlining new combinations and has prompted the advancement of a deterministic strategy for foreseeing restricted corrosion damage function.

2.6.1. Generation I PDM

The Generation I (PDM-I) was basically an endeavor to exchange the thoughts of Wagner [14] for the development of oxide movies on metal surfaces under dry oxidation conditions to the development of oxide film on metals in contact with dense media, remarkably fluid arrangements. . PDM-I imagined that the latent film embodied a solitary deficient oxide layer that hindered the stream of current over the metal/arrangement interface**.**

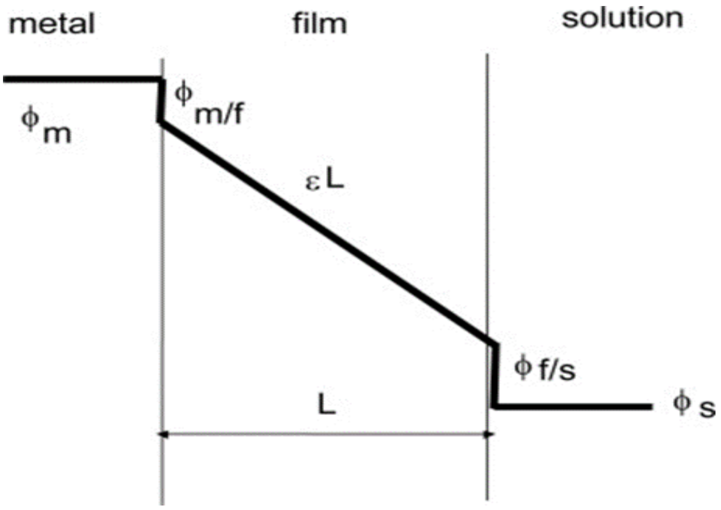


Fig 4. Schematic potential distribution across the metal/barrier layer/solution interphase

Equations governing generation 1 PDM :

Metal | Barrier Layer | Solution

$$(1)\ m + V_M^{\chi'} = M_M + v_m + \chi e^- \qquad (3)\ M_M = M^{\delta+} + V_M^{\chi'} + (\delta - \chi)e^-$$

$$(2)\ m = M_M + \frac{\chi}{2} V_O^{\cdot\cdot} + \chi e^- \qquad (4)\ V_O^{\cdot\cdot} + H_2O = O_O + 2H^+$$

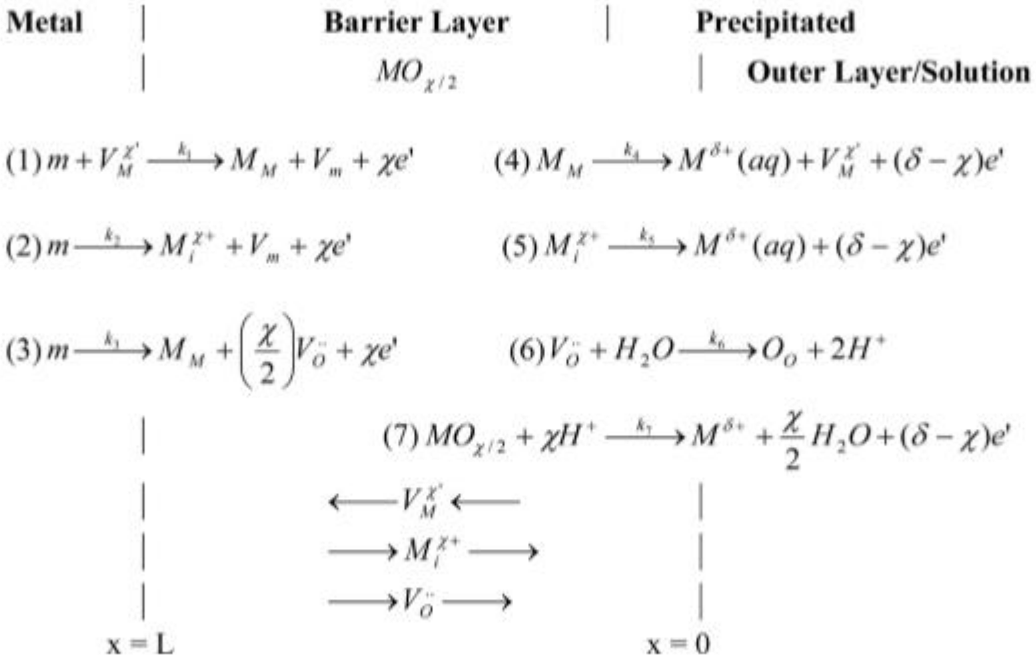
$$x = 0 \qquad x = L$$

2.6.2. Generation II PDM

The Generation II PDM was developed to address the shortcomings in the Generation I model noted above. Specific features and assumptions of PDM-II, in addition to those invoked in the development of PDM-I [14].

Perceives the pretended by obstruction layer dissolution – permits the film to accomplish unfaltering states in thickness and current. The boundary layer breaks down at the obstruction layer/arrangement (external layer) interface by either compound or electrochemical courses of action.Acquaints interstitials furthermore with cation opening and oxygen opportunities as the deformities in the hindrance layer [13]. Demonstrated that, much of the time, the interstitials are the prevailing deformities (Fe, Zn, Pt, stainless steel,Al).

Equations governing generation 2 PDM :



$$(1)\, m + V_M^{\chi'} \xrightarrow{k_1} M_M + V_m + \chi e'$$

$$(2)\, m \xrightarrow{k_2} M_i^{\chi+} + V_m + \chi e'$$

$$(3)\, m \xrightarrow{k_3} M_M + \left(\frac{\chi}{2}\right) V_O^{\cdot\cdot} + \chi e'$$

$$(4)\, M_M \xrightarrow{k_4} M^{\delta+}(aq) + V_M^{\chi'} + (\delta - \chi) e'$$

$$(5)\, M_i^{\chi+} \xrightarrow{k_5} M^{\delta+}(aq) + (\delta - \chi) e'$$

$$(6)\, V_O^{\cdot\cdot} + H_2O \xrightarrow{k_6} O_O + 2H^+$$

$$(7)\, MO_{\chi/2} + \chi H^+ \xrightarrow{k_7} M^{\delta+} + \frac{\chi}{2} H_2O + (\delta - \chi) e'$$

CHAPTER 3: Experimental Procedure

3.1. Specimen Preparation

The metallographic specimen preparation process for microstructural investigations of steels specimens usually consists of five stages: sampling, cold or hot mounting, grinding, polishing, and etching with a suitable etchant to reveal the microstructure.

3.1.1. Grinding and Polishing

To ensure proper microstructure of the sample the use of an automated grinding-polishing machine is recommended over manual preparation. The automated equipment makes it possible, in comparison to manual specimen preparation, to properly control the orientation of the specimen surface relative to the grinding or polishing surface, to maintain constantly the desired load on the specimens, touniformly rotate the specimens relative to the work surface, and to control the time for eachpreparation step. Proper control of these factorsinfluences graphite retention, although other factorshare also important.A good, general principle is to minimize the number of grinding and polishing stages. Also,the load on each specimen, or on all specimens in the holder, must be chosen to obtain a correctly polished surface in the shortest possible time.

3.2. Experiment

1) Firstly the prepared electrode was cold mounted on a pmma (poly-methyl methacrylate)

2) The electrode surface was polished on a polish paper of respective grid sizes 200, 400, 600, 800.

3) Then diamond polishing of the electrode was done.

4) Then etching was done using a nital solution**.**

5) The microstructure of the electrode was revealed with the help of a electron microscope at a magnification of 100x**.**

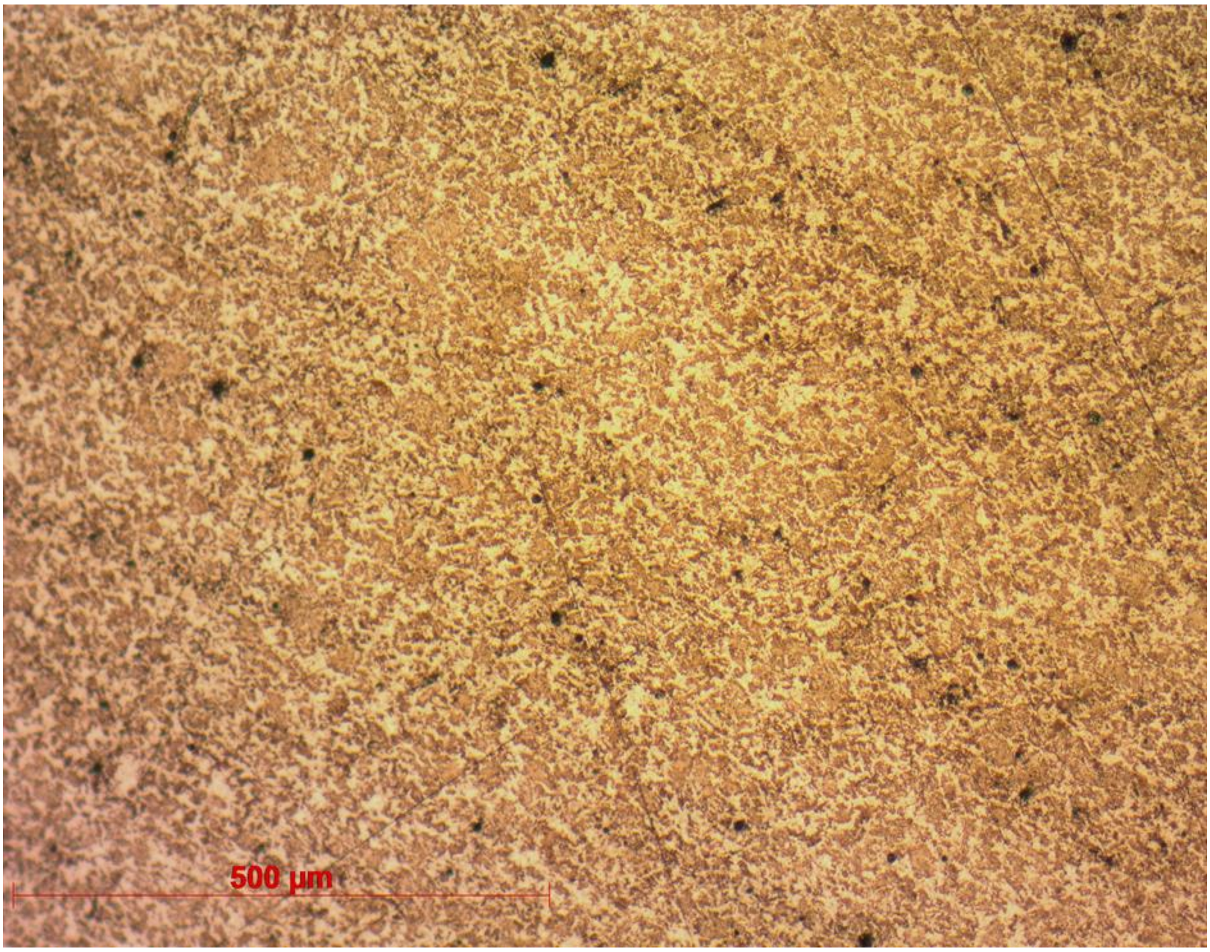


Fig.5 Microstucture of steel after polishing at 500x

6) A borate buffer solution of pH 10.4 has been prepared using 0.5M boric acid, 0.5M NaOH and 1M NaCl.

7) The plain carbon steel electrode is connected in a three electrode system where a SCE electrode acts as reference electrode and a platinum electrode acts as a counter electrode.

8)The break down potential is measured for varying pH and chloride ion concentration.

Chapter 4: Results and Discussion

Figure 1 shows the experimental potentiodynamic polarization curve for carbon steel run in borate buffer solutions at pH 10. The scan has been performed from cathodic to anodic region to estimate the corrosion potential and the passivity behavior. The equilibrium corrosion potential was found be around - 850 mV which indicates that corrosion is almost negligible in borate buffer solution at equilibrium condition. Then after the anodic scan indicates a very short active region and a relatively long passive region, signifying that the steel is well pasivating in the said solution. After the passive region there is a sharp increase in current as pitting was observed in the steel.

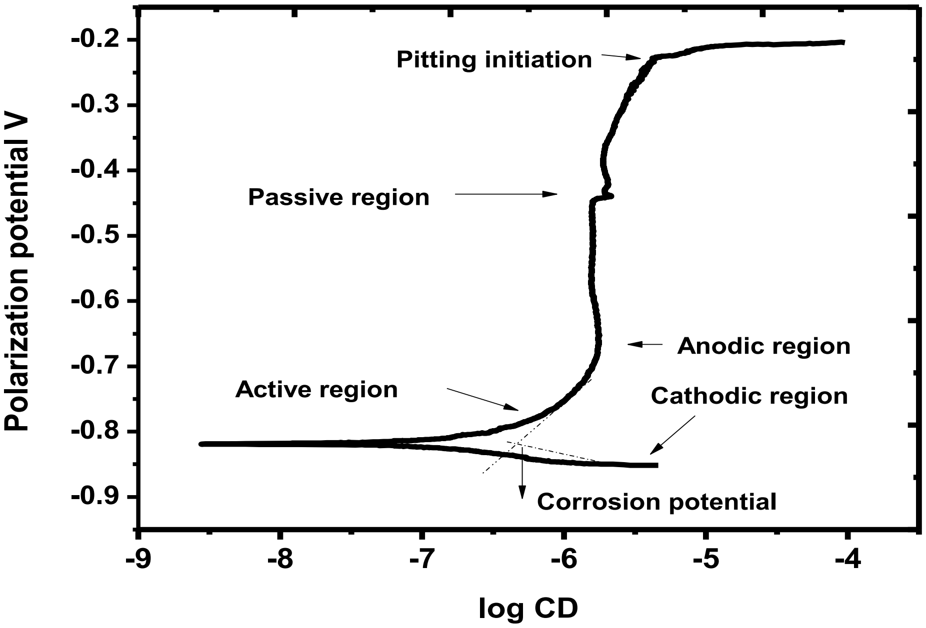


Figure 6. Potentiodynamic polarization scan of plain carbon steel in borate buffer solution at pH 10.4

To study the pitting behavior and validate the point defect model 20 such scans have been performed along with potentiodynamic scans at varying scan rates and Cl ion concentrations to generate the kinetic parameters for modeling. Figure 7 shows the five scans for he pitting potential. It can be observed that there is almost good reproducability with the pitting potential.

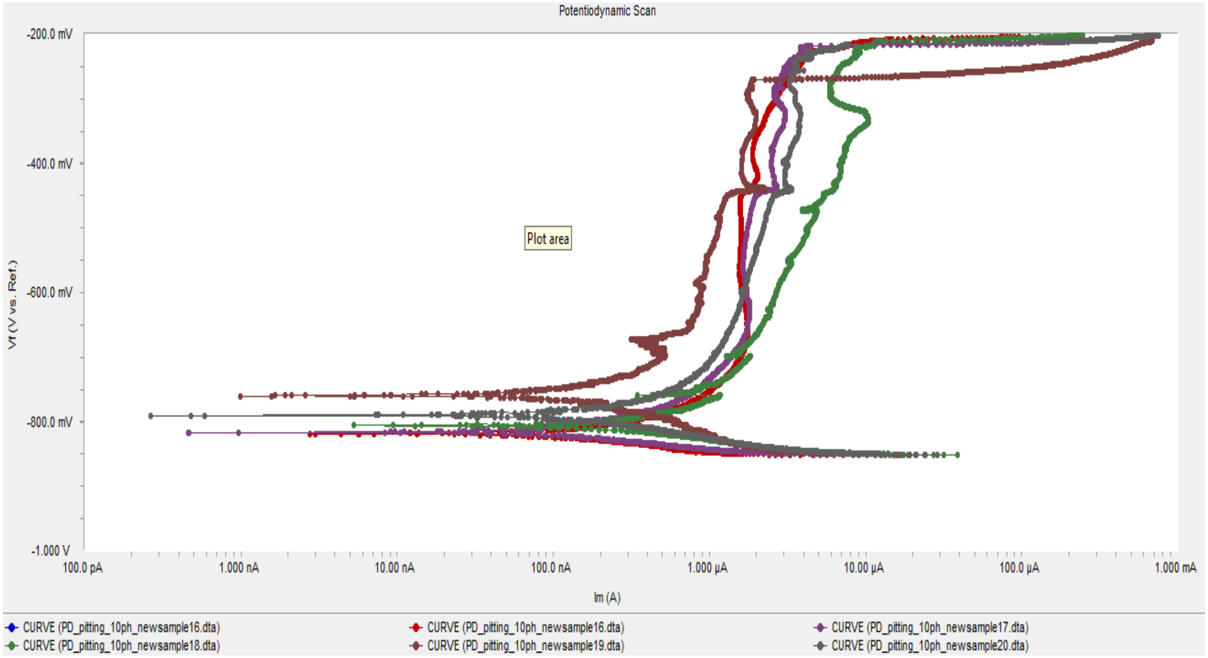


Figure 7. Breakdown potentials for carbon steel at pH=10.4 in borate buffer solution

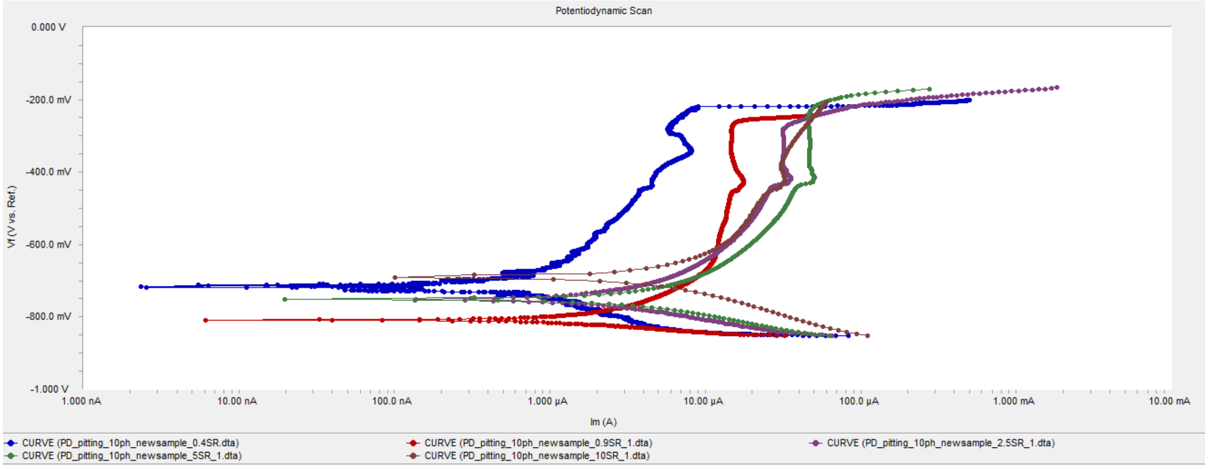


Figure 8. Breakdown potentials for carbon steel at pH=10.4 in borate buffer solution at different scan rates

According to the PDM, taking into account only chloride anion adsorption/ Schottky-pair vacancy generation, the following relationship for the critical breakdown potential (V_c) can be derived:

$$V_c = \frac{4.606RT}{\chi\alpha F}\log\left(\frac{b}{D}\right) - \frac{2.303RT}{\alpha F}\log\left(a_{Cl^-}\right)$$

Where

$$b = \frac{RTJ_m\Omega}{F\chi\varepsilon N_V}\times\exp\left(\frac{\Delta G_s^0 + \frac{\chi}{2}\Delta G_A^0 - \frac{\chi}{2}\beta FpH - \frac{\chi}{2}F\phi_{f/s}^0}{RT}\right)$$

V_c is predicted to follow a near normal distribution, as has been observed experimentally and mentioned by the following equation:

$$\frac{dN}{dV_c} = \frac{-b\gamma'}{\sqrt{2\pi}.\sigma_D.a_{Cl^-}^{\chi/2}}\exp\left[\frac{-\left(e^{-\gamma' V_c} - e^{-\gamma'\bar{V}_c}\right)^2 b^2}{2\sigma_D^2 a_{Cl^-}^{\chi}}\right]\exp\left(-\gamma' V_c\right)$$

Where

$$\gamma' = \frac{\chi\alpha F}{2RT} \qquad \bar{V}_c = \frac{1}{\gamma'}Ln\left(\frac{b}{\bar{D}}\times a_{Cl^-}^{-\chi/2}\right)$$

The cumulative probability in breakdown potential is defined as

$$P(V_c) = 100\times\frac{\int_{-\infty}^{V_c}\left(\frac{dN}{dV_c}\right)dV_c}{\int_{-\infty}^{\infty}\left(\frac{dN}{dV_c}\right)dV_c}$$

As per the above hypothesis the modelling has been done and shown in figure 9.

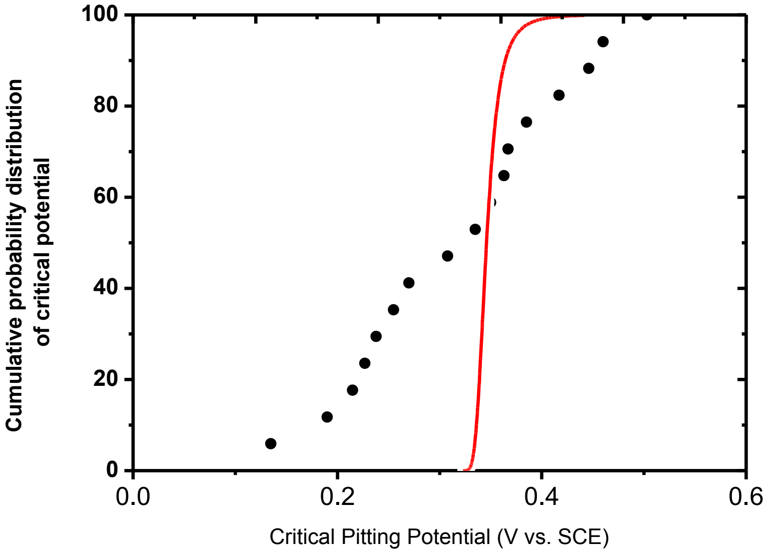


Figure 9 Calculated cumulative probabilities in apparent breakdown potential, for Carbon steel in deaerated borate buffer solutions containing 1M NaCl at pH 10.4

Figure 9 shows the experimental and theoretical modeling data, the points are for experimental and solid is calculated. The values used to do the modeling are presented in Table 1. The cumulative break down voltage of twenty different samples were calculated and plotted they were not that well agreement with the experimental data. The curve was plotted between cumulative probability and the critical breakdown potential. Hence the cauculation may need futher optimization for better matching of the experimental and simulated data.

Table 1. Parameter values used in calculating cumulative probabilities in the breakdown potential for carbon steel in deaerated borate buffer solutions containing 1M NaCl at room temperature

Parameters	Value	Unit
F, Faraday constant	96487	C mol^{-1}
R, the gas constant	8.314	J $(mol\ K)^{-1}$
T, the absolute temperature	295	K
N_v, Avogadro's number	6.023×10^{23}	mol^{-1}
χ, the barrier layer stoichiometry (Fe_2O_3)	3	
Ω, molar volume of Fe_2O_3 per cation	15.23	$cm^3\ mol^{-1}$
, the mean cation vacancy diffusivity	2×10^{-17}	$cm^2\ s^{-1}$
σ_D, the standard deviation for *D*	1×10^{-17}	$cm^2\ s^{-1}$
α, potential dependence of $\varphi_{f/s}$	0.83	
ε, the electric field strength	3×10^6	$V\ cm^{-1}$
ξ, the critical vacancy concentration	4.9×10^{14}	cm^{-2}
J_m, the critical vacancy flux	2.7×10^{13}	$cm^{-2}s^{-1}$
β, pH dependence of $\varphi_{f/s}$	-0.01	V
	-35.148	kJ mol^{-1}

The surface of the steel corrodes heavily as soon as the protective passive film breaks down due to agitation, disturbance due to halide ions or due to variation pH. As soon as the material reaches the breakdown potential the steel material corrodes in a highly localized manner at multiple sites by the formation of pits which eventually grow in size and penetrate deep inside the metal body this is an example of pitting corrosion. Figure 10 shows the micrographs of the pitted samples. The figure shows both metastable and fully grown pits on the surface

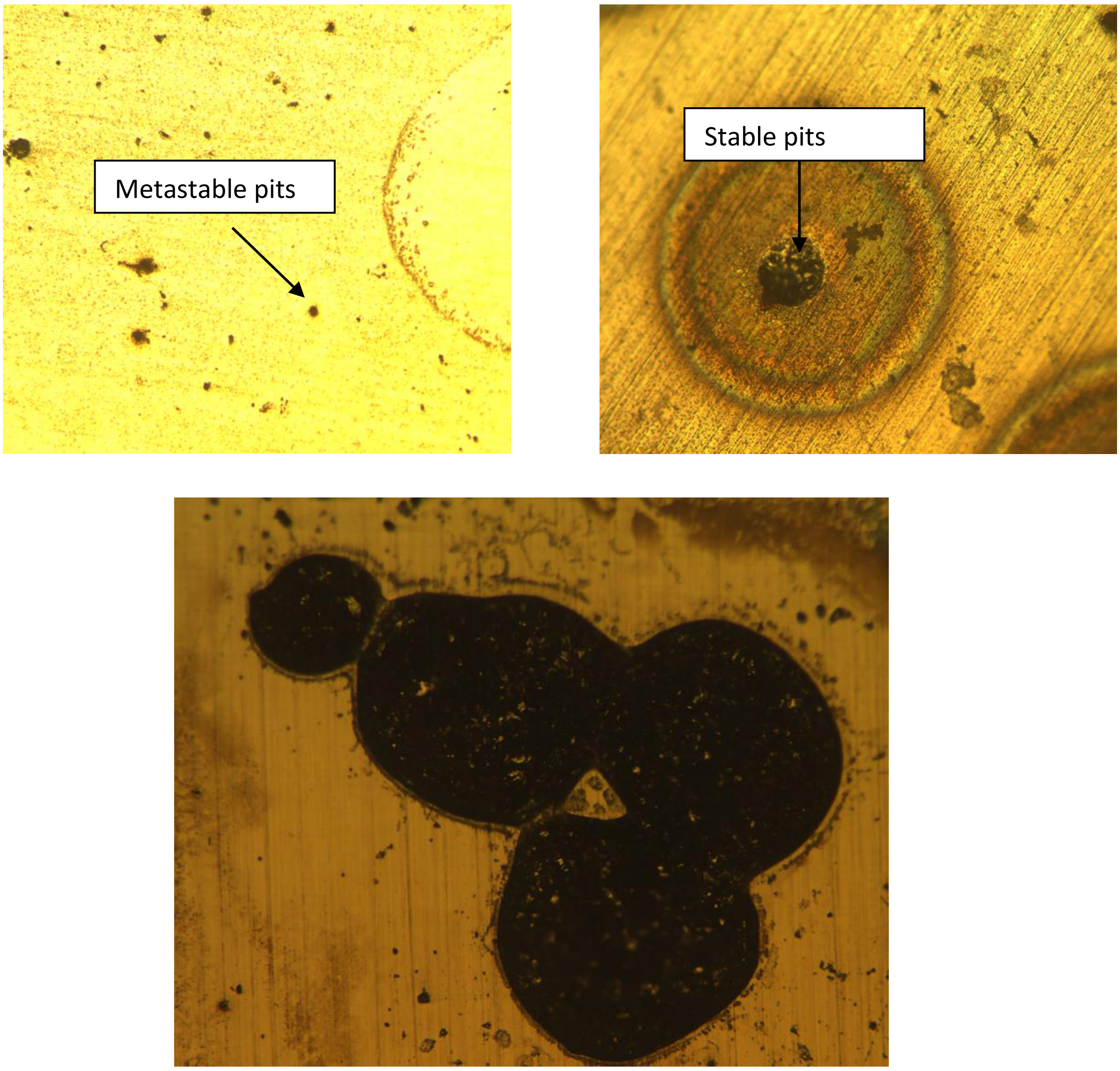


Figure 11. Optical micrographs of pitted carbon steel (a) metastable pit, (b) stable pit and (c) fully grown pits

Chapter 5: Conclusions

Conclusions

The experiments and studies performed above lead to the following conclusions:

1. The above data is found to be consistent with the PDM (point defect model) in terms of relation between breakdown voltage and the chloride ion concentration
2. The breakdown of the passivity film is characterized by breakdown potential (Vc) which is dependent on the pH of the solution, concentration of the aggressive ions and the potential sweep rate.
3. The thickness, composition as well as the breakdown potential of the passive film depends largely on the applied potential and surroundings of the film such as pH and concentration of anions.
4. The cumulative distribution of the breakdown potential was found to be in well agreement with the experimentally obtained data.
5. Optical micrographs showed stable and Meta stable pitting**.**

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