

Pitting corrosion of type 304 stainless steel and sulfate inhibition effect in chloride containing environments

Raul Davalos Monteiro^a, Satria Dwi Ananda^b

^a Corrosion and Protection Centre, The University of Manchester, Manchester, Reino Unido
raul.davalosmonteiro@postgrad.manchester.ac.uk

^b Wilson Walton International, Jakarta, Indonesia
satria@wilsonwalton.co.id

Abstract. A detailed experiment of pitting corrosion phenomena of type 304 stainless steel in chloride environments was performed; two experimental methods potentiodynamic and galvanostatic testing were carried out in samples of type 304 stainless steel in order to understand the effect of pit depth and the stable pitting behavior. For both tests, the environment was a solution of 0.1 M NaCl, and the potential values were measured in a reference to a Saturated Calomel Electrode (SCE) and a platinum counter electrode. The results shown that the repassivation potential in the deeper pit is lower, in simple terms, the deeper the pit the lower the re-passivation potential therefore deeper pits are more stable and those type of pits are more difficult to repassivate. The effect of sulfate ions was tested by performing a potentiodynamic polarization test in 0.1 M NaCl + 0.1 M Na₂SO₄ solution. the sulfate in the solution has an inhibiting effect by increasing the pitting potential which indicate a longer time for pit to be stable and reduce the pit nucleation on the sample surface hence it has less metastable pits. In the galvanostatic experiment the metastable and stable pitting behaviors are elucidated, between 0 to 350 seconds the sample had a metastable pitting behavior, since the potential rises and falls in rapid intervals of time which shows the creation and repassivation of metastable pits. After 350 seconds the potential dropped and the stable pitting behavior started, it means that the process reached a steady state in which the pit will have a stable growth. These results and conclusions have significant meaning in understanding the pitting corrosion of stainless steel 304, and finally it is noteworthy to conclude that type 304 is very susceptible to pitting corrosion in chloride environments and the presence of sulfate ions in the a chloride effect has a positive impact on the pitting corrosion resistance of type 304.

Key Words: Pitting; Stainless Steel; Chloride; Sulphate; Pit Depth; Inhibition.

1 Introduction

Type 304 Stainless steel is widely used for many applications because of its good mechanical properties and high corrosion resistance. Type 304 Stainless steel could limit electrochemical reactions on its surface by forming stable passive oxide film composed by chromium hydroxide Cr(OH)₃ outer layer and mixed chromium-iron oxides inner layer [1]. However, presence of aggressive ions could lead to breakdown of its passive film and initiate localized pitting corrosion on stainless steel.

The term pit is used to describe any localized corrosion spot that forms a cavity, pitting causes a kind of unexpected corrosion than any other form of corrosion attack.

It is particularly dangerous because the total amount of metal lost is small but the perforation is rapid. [2]

Pitting corrosion commonly takes place in corrosion cells with clearly separated anode and cathode surfaces. The anode is situated in the pit and the cathode usually on the surrounding surface. [3]

Pitting initiates as a localized breakdown of a protective film (generally passive films) on the metal surface, the breakdown may occur at a weak spot in the film, such as at a defect or impurity on the surface, or at a scratch [4]. The active corrosion pit is surrounded by passive metal and also the metal starts to oxidized into metal ions, the production of metal ions (Fe^{2+} , Cr^{3+} for stainless steel 304) inside the pit will attract Cl^- from the solution to migrate inside the pit (pitting most commonly occurs in chloride solutions). The migration of chloride ions into the pit permits metal salts to form and hydrolyze, making the environment inside the pit vey acidic. In figure 1 is shown a schematic diagram of pitting in stainless steel.

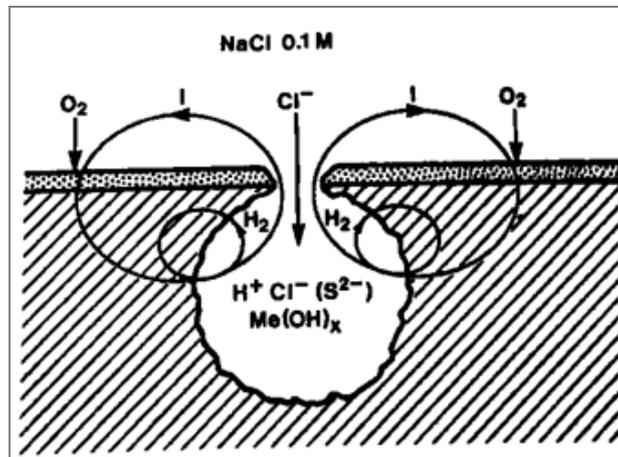
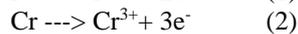
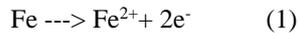
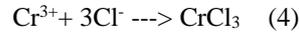
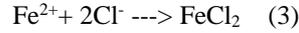


Figure 1. Pitting on the metal surface in chloride environment. [2]

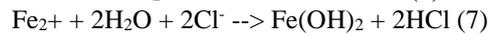
Pitting corrosion caused by loss or damage of passive film at a particular location due to electrochemical reaction by aggressive ion, such as chloride (Cl^-) which is the most common pitting agent, in the electrolyte if it presents in sufficient concentration [5]. The passive film breakdown starts in the location where there is defect (which always exist) on the oxide film. At that defect location, metal atoms start to oxidized into metal cations (pit initiation) because it is in contact with the electrolyte and will act as local anode in respect to its surrounding passive film.



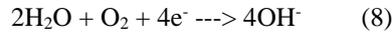
Production of metal ions inside the pit will attract Cl^- from the bulk solution to migrate inside the pit. This Cl^- migration could lead into its reaction with oxidized metal cations to form salts that prevent repassivation of the oxide layer because of the competition between Cl^- and OH^- to react with Fe^{2+} or Cr^{2+} .



Furthermore, excess of cations could be followed with hydrolysis inside the pit and produce a lot of H^+ ions leading to localized acidification by this following reaction.



While on the adjacent passive film surface, cathodic reaction of oxygen reduction must take place in order to counter the electrochemical reaction inside the pit.



While Cl^- is considered as aggressive ion that could break the passivity of the film, there are also many anionic species such as SO_4^{2-} , ClO_4^{2-} , and NO_3^- that could play role as pitting corrosion inhibitors if they are exist at particular concentration in the solution. In the case of SO_4^{2-} , absorption of this anion will be relatively greater than chloride [6]. SO_4^{2-} has an inhibitory effect in the initial stage of pitting by decreasing the numbers of metastable pit before they become stable pit [7].

The use of instrumentation such as potentiostat allows further investigation of pitting characteristics. Some of important things to study about are pitting potential (E_p) and repassivation potential (E_r), which could be determined by polarization technique in the laboratory. Theoretically, pitting potential is the point where there is a sharp inflexion after the passive region which indicates passive film breakdown occurrence [8] while repassivation potential is the point where the curve will intersect the passive region in the potential-current density polarization curve as illustrated in Figure 2.

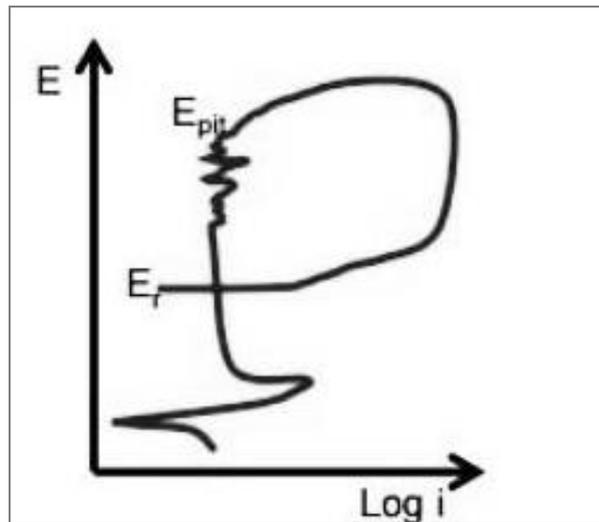


Figure 2. Potentiodynamic polarization curve showing pitting corrosion

2 Experimental Procedure

2.1 Potentiodynamic Pitting depth experiment

In order to perform a potentiodynamic pitting test in 304 stainless steels in 0.1 M NaCl solution and look for the effect of Pit Depth the following procedure has been done.

The electrochemical cell as shown in figure 3 was prepared with immersed SCE and Pt electrodes and it was filled with 0.1 M NaCl Solution – non de-aeration of the solution was required- and finally the cell was connected to the potentiostat.

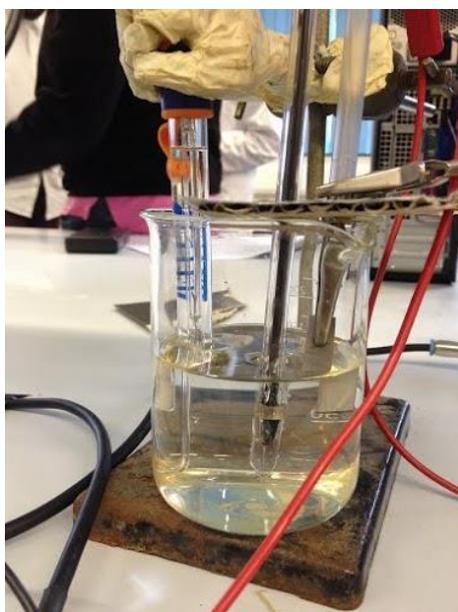


Figure 3. Electrochemical Cell set up

The sample of stainless steel 304 electrode was immersed in the solution with a waterline below the electrical contact. It is very important to keep the immersed area about the same for all the experiments in order to have accurately data to compare.

Leave the stainless steel 304 electrode for a few minutes to stabilize its open circuit potential.

A potentiodynamic sweep test (cyclic voltammetry program) anodically from 500 mV below the OCP was performed. When the current reaches a value of 1 mA manually reverse the scan. The experiment was stopped after the current became cathodic.

In order to understand the effect of pit depth, another potentiodynamic sweep test (cyclic voltammetry program) was performed in the same way, but in this case when the current started to reach a constant value we reversed the scan. Finally the experiment was stopped when current became cathodic.

2.2. Potentiodynamic Pitting inhibition experiment

The samples used for this experiment are Stainless Steel 304 with dimension of 20mm x 10mm x 1mm. These samples will be immersed in 0.1 M NaCl solution and 0.1 M NaCl + 0.1 M Na₂SO₄ solution without de-aeration to compare the pitting behaviour between solutions containing Cl⁻ with the other one with addition of dissolved SO₄²⁻.

The potentials recorded in this experiment were measured refer to Saturated Calomel Electrode (SCE) and platinum counter electrode. The measurement is done by potentiodynamic sweep (cyclic voltammetry program) using PalmSens3 Potentiostat that started anodically from 500mV below OCP (which is measured before cyclic voltammetry) with 5 mV/s scan rate. Scanning process is reversed when the current reached a value of 1mA. The experiment will be stopped when the current becomes cathodic (300mV below the new E_{corr}).

2.3. Galvanostatic Pitting Test

A polarization experiment was performed on the sample of stainless steel 304 in 0.1 M NaCl with a current value that was around 50mV near the pitting potential, the test was performed for 900 seconds. The aim of this galvanostatic pitting test is to look at the pitting stability on the material.

Finally, the sample has been observed under the optical microscope to know whether there is any pit exists on the sample surface.

3 Results

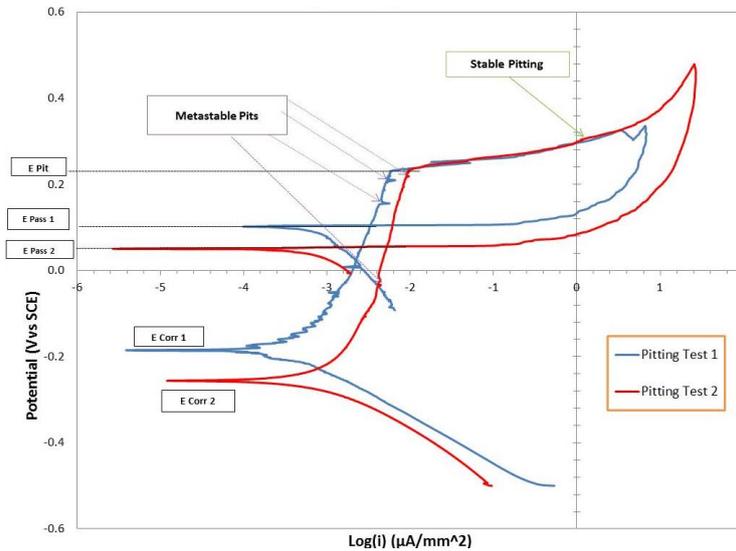


Figure 4. Effect of pit depth in a pitting test on 304 SS in 0.1 M NaCl.

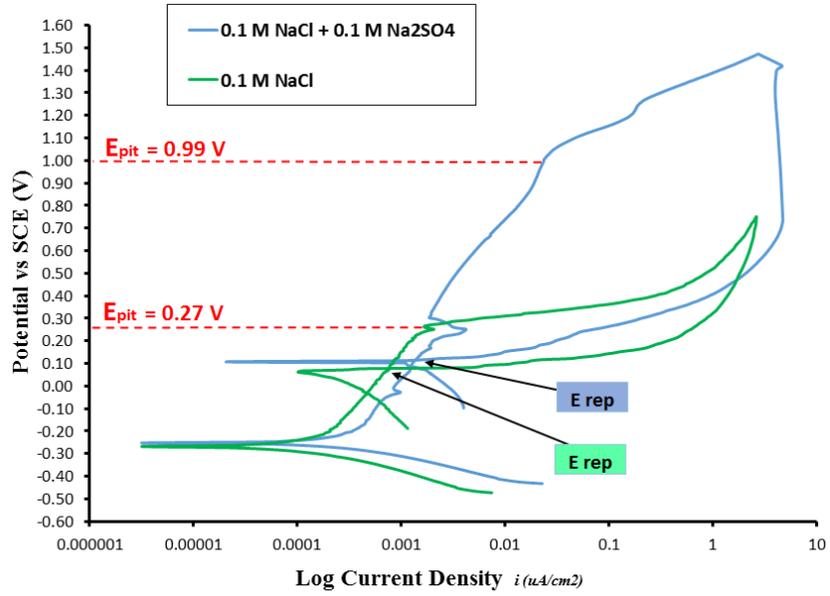


Figure 5. Polarization curve of type 304 stainless steel in 0.1M NaCl solution and 0.1M NaCl + 0.1M Na₂SO₄ solution.

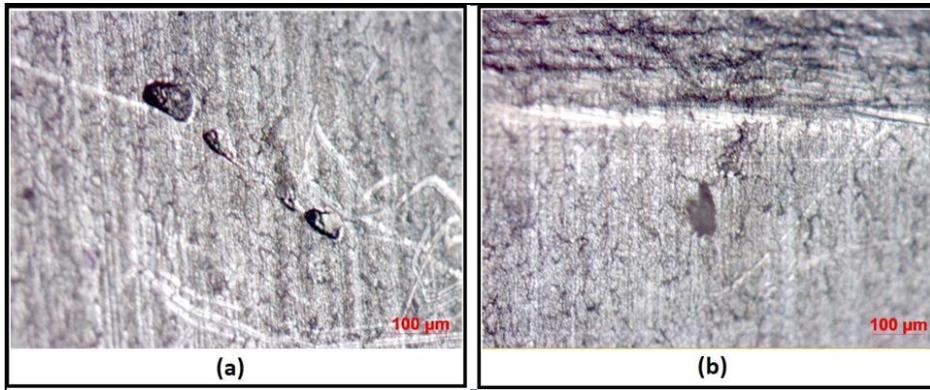


Figure 6. Pits nucleation on 304 Stainless Steel in (a) 0.1M NaCl solution and (b) 0.1M NaCl + 0.1M Na₂SO₄ solution.

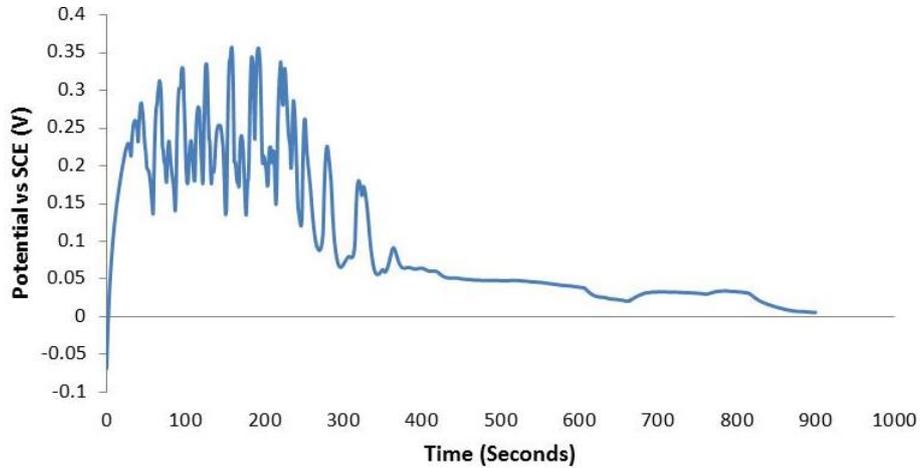


Figure 7. Galvanostatic test in type 304 stainless steel at 0.1 M NaCl.

4 Discussion

4.1. Main Features

Figure 4 shows the polarization curves of two pitting tests for 304 stainless steel in 0.1 M NaCl solution, the key features that can be seen from the graph are: The pitting potential, the two samples have the same pitting potential this is a logical result that we expected from the same material, but also from the graph we can see a slightly difference in the corrosion potential, this variation in the corrosion potential could have been produced due to changing the potentiostat between tests.

Both samples present a passive region in which some metastable pits appear, a metastable pit is a kind of pit that would initiate and vanish after a short time (repassivate), it happens because the concentration of chloride in the bottom of the metastable pit is lower than the critical concentration of chloride in order to produce a stable pit.

4.2. Effect of pit depth

As it can be appreciated in Pitting test 2 (red line) of figure 4, when the pitting has been initiated (E Pit) the stable pitting processes started, and the growth has reached steady state conditions with the following characteristics.

- a. The pH value in the pit is lower than in the environment of the solution, because anodically dissolved metal ions, such as Fe^{2+} and Cr^{3+} (in 304 SS) have been hydrolyzed with the formation of oxides, hydroxides or hydroxide salts thus releasing hydrogen ions.

- b. The solution inside the pit has a higher chloride concentration than the environment in the solution. This is because chloride ions migrate inside the pit against the electric current.

One of the most important in the effect of pit growth is the repassivation potential of the pit, the deeper the pit the lower the repassivation potential (more negative) as it can be proved from the graph E-pass 1 is higher than E-pass2 since the pit in test 2 is deeper than pit in test 1. In other words, is more difficult to repassivate a pit when it reached a considerable depth. In addition a salt film can be produced in a deeper pit due to the high concentration of anions(Cl^-) an cations (Fe^{2+}) this kind of salt films increase the resistance to form a passive film.

4.3. Sulfate Inhibition Effect in pitting corrosion

Figure 5 shows the polarization curve of 304 Stainless Steel in both solutions. For the sample immersed in 0.1M NaCl solution, there were some noises in the passive region of the curve which mean during the passivation of the metal, the Cl^- ions already initiate to attack the oxide film on the surface and start the rupture of the film hence make metastable pits up until the potential is about 0.27 V (vs SCE) and the pit growth rate become stable.

Meanwhile for the sample immersed in 0.1M NaCl + 0.1M Na_2SO_4 solution, the passive region looks smoother indicating that there are less amount of metastable pits on the surface of the metal compared to the one without Na_2SO_4 .

It could be caused by the presence of dissolved SO_4^{2-} ions in the solution that will propagate at the surface of the metal so it will be more difficult for the chloride to initiate metastable pit. Sulfate ions also play role in repassivation of the oxide film. When eventually there is a pit formation, the sulphate anions will reduce the penetration of Cl^- attacks to the metal because the presence of SO_4^{2-} in the pit will decrease the concentration of migrating Cl^- into the pit so the accumulation of critical concentration of Cl^- needed to grow the pit being prevented and it is easier for the oxide film to repassivate. This occurrence could be observed from the polarization curve at Figure 5 that the E-Rep of sample in the presence of SO_4^{2-} is higher than E-Rep in the absence of SO_4^{2-} .

Because the availability of pit sites are lowered, the E_{pit} in this solution, which is 0.99 V (vs SCE), is higher than E_{pit} of the sample in sulphate-free solution, which is 0.27 V (vs SCE). It indicates that sample in the sulphate-containing solution is less susceptible to pitting than the one in the sulphate-free solution. Figure 6 shows that in 0.1M NaCl solution there are more pits nucleate than in 0.1M NaCl + 0.1M Na_2SO_4 solution when the samples were observed under the optical microscope.

4.4. Pitting stability: Galvanostatic Test.

From the figure 7 it can be seen the result for a galvanostatic test with a constant anodic current of 5 μA in a sample of Stainless Steel 304 type in 0.1M NaCl solution. Between 0 to 350 seconds the sample has a metastable pitting behavior, since the potential rises and falls in very quick intervals of time which shows the creation and repassivation of metastable pits. After 350 seconds the potential falls and the stable

pitting behavior starts, it means that the process reaches a steady state in which the pit will have a stable growth.

The reason that the potential decreases when the metastable pitting becomes a stable pitting is on the ohm law, the current that is applied is constant it means that the only thing that will change the potential is the resistance, when the stable pit is created the concentration of ions inside the pit rises therefore the conductivity increases and the resistance falls, so according to ohms law when the resistances decrease and the current is constant the potential decrease. The difference between with the potentiodynamic test is that the current is not constant and then the potential increases when the pitting is stable.

4 Conclusions

The effect of pit depth directly influences the repassivation potential, the deeper the pit the lower the repassivation potential (more negative).

In order to have a stable pitting behavior the concentration of Cl^- on the surface of the pit should be higher than the critical concentration of Cl^- .

The pH value in the pit is lower than in the environment of the solution.

The solution inside the pit has a higher chloride concentration than the environment in the solution.

Salt films can be produced in a deeper pit due to the high concentration of anions (Cl^-) cations (Fe^{2+}). Salt films will increase the resistance to repassivate the pit.

A sulphate addition in the solution has inhibitory effect to stainless steel by making competition with Cl^- to adsorb to the surface/defect of the oxide film hence increasing the E-pit of type 304 stainless steel. SO_4^{2-} also decreasing the availability of sites for metastable pits to be nucleated.

The water chemistry of pit is stable at lower potential.

References

1. El-Egamy, S.S. and Badaway, W.A. (2004) "Passivity and passivity breakdown of 304 Stainless Steel in alkaline sodium sulphate solutions", *Journal of Applied Electrochemistry*, 34 (2004), p. 1153.
2. Bradford, A., Samuel. (1993) *Corrosion Control*, (Vol. 16), New York: Van Nostrand Reinhold.
3. Dillon, C. (1995) *Corrosion resistance of stainless steels*, (Vol. 2), New York, Basel, Hong Kong: Marcel Dekker Inc.
4. Marcus, P., Oudar, J. (1995) *Corrosion Mechanisms in Theory and Practice*, (Vol. 10), Paris: Marcel Dekker Inc.
5. Cottis, B. et al (2010) *Shreir's Corrosion Volume 2*. 4th edn. Elsevier Ltd., p 748.
6. Kolics, A., Polkinghorne, J.C., and Wieckowski, A. (1997) "Adsorption of sulfate and chloride ions on aluminium", *Electrochimica Acta*, 43 (18), p. 2608.

7. Hong, T. and Nagumo, M. (1997) "The effect of SO₄²⁻ concentration in NaCl Solution on early stages of pitting corrosion of type 430 Stainless Steel", *Corrosion Science*, 39 (5), pp. 965-966.
8. Man, H.C. and Gabe, D.R. (1980) "The determination of pitting potentials", *Corrosion Science*, 21 (4), p. 323.
9. Mattson, E. (1996) *Basic Corrosion Technology for scientists and Engineers*, (Vol. 2), Bournemouth: The Institute of Materials.
10. Sastri, V., Ghali, E. and Elboujdaini, M. (2006) *Corrosion prevention and protection: practical solutions*, 1st edition, London: Wiley.
11. Schweitzer, P. A. (2004). *Encyclopedia of corrosion technology* (Vol. 20). New York: CRC Press.
12. Brossia, C.S. and Kelly, R.G. (1997) "Influence of alloy sulfur content and bulk electrolyte composition on crevice corrosion initiation of Austenitic Stainless Steel", *Corrosion : The Journal of Science and Engineering*, 54 (2), p. 152.
13. Drogowska, M. and Menard, H. (1997) "Pitting of AISI 304 Stainless Steel in bicarbonate and chloride solutions", *Journal of Applied Electrochemistry*, 27 (1997), p. 172.