In-situ Electrochemical Investigations for Monitoring Pitting Corrosion Potential of Passivated Steel under Diverse Cl⁻ Anion Stress and its Micro Structural Evaluation

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Abstract

Pitting corrosion is very menacing and fatal type of localized attack on metallic structures. Customarily pitting corrosion is monitored by pitting potential which could be readily measured by the galvanostatic anodic polarization technique. In current communication, potentiodynamic scan graphs were acquired to find out pitting potential, corrosion potential and passivating potential for stainless steel type 304 sample electrodes while immersed in the 0M, 2M, 3M, 4M and 5M HCl solutions. Comparison of results have concluded that as chloride ion stress increased, it more aggressively attacked on passive layer and induced pitting corrosion at lower threshold potentials thus decreased Pitting potential (E_{pit}) of subject stainless steel type 304 sample electrodes. Moreover pH of electrolyte decreased inside the pit due to hydrolysis of $FeCl_2$ which furnished strong acid (HCl) and weak base ($Fe(OH)_2$) thus further accelerate corrosion process and promote pits penetration. A large ratio between the anode and cathode areas have also favoured propagation of pits depth. In summary, stainless steel type 304 is vulnerable to pitting corrosion attack under chloride ion stress.

Keywords: Pitting Corrosion, Stainless Steel, Passivation Potential, Pitting Potential, Cyclic Polarization Curve.

1. Introduction

Pitting corrosion is very menacing and fatal type of localized attack on metallic constructions. Stainless steels irrespective of their passive ability, are also vulnerable to pitting corrosion in chloride ion solutions [1]. Customarily pitting corrosion is monitored by pitting potential which could be readily measured by the galvanostatic anodic polarization technique [2]. Particularly cyclic slow potentiodynamic anodic polarization method is worth mentioning to apply on Fe, Ni and Co alloys for quality control and material selections as depicted in ASTM G-61

standard [3]. Corrosion is associated with number of structural engineering problems subject to service conditions of fabricating alloy materials. Steel usually undergoes electrochemical corrosion mechanism which induced by various ions in the propinquity of the steel surface. Usually Stainless steels perform well under most of service environment owning to their good corrosion resistance which in turn depends upon constituent alloying elements. However under certain harsh conditions exposure stainless steel undergo corrosion attack because of passive film cracking. These defective small area points activate associated metal surface while large metal area remains passivated. This difference in relative areas promotes the corrosion, causing the pits to penetrate deeper. Aggressiveness of this phenomenon is determined by pH, nature of electrolyte and metal composition [4]. Several researchers have worked on stainless steel to find the extent of pitting corrosion in various electrolytes [5, 6, 7]. In current communication, potentiodynamic polarization attributes of stainless steel was studied in various chloride ions concentration and were reported in terms of passivation potential, pitting potential and corrosion potential of stainless steel.

2. Experimental

Five austenitic stainless steel type 304 sample coupons in rectangular shape of size 1×1 cm and of composition C 0.08%, S 0.03%, Mn 1.33%, Ni 9.88%, Mo 2.44% and Cr 16.72% were employed for subject study. Electrodes preparation were involved epoxy mounting of sample metals and their subsequent drying for 24 Hrs. Afterward electrodes were grinded on MOPAO 260 E Grinder Machine by employing emery papers of range 180, 220, 800 and 1000 mesh size. In order to remove all kinds of grinding marks, Benetec Polishing Machine were used. Afterward samples were washed with de-ionized water, rinsed with acetone before drying and stored in desiccators. Copper wire was soldered onto the sample surface and the soldered sample then cold mounted in epoxy (Figure 1).

Figure 1: Mounted soldered Sample for Potentiostat experiment

After mounting the sample, thermal conductivity of sample was measured to check the continuity of electrical connection with the sample through digital multi meter. After the working electrodes preparation, sample area was measured by using stereo microscope. The prepared samples were then analysed for cyclic polarization in the Computerized Potentiostat G750-350 series. Corrosion cell was comprised of three electrodes (i) working electrode i.e. Stainless Steel sample electrode (ii) counter electrode (Graphite) and (iii) the reference electrode (Saturated calomel electrode). Potentiodynamic scans were run with these three electrodes immersed in the 0M, 2M, 3M, 4M and 5M HCl solution. Micrograph analysis was carried out via Olympus GX51 for the determination of pit formation on these samples in chloride ion containing electrolyte.

3.   Results and Discussion

Potentiodynamic scan graphs were acquired for stainless steel type 304 sample electrodes while immersed in the 0M, 2M, 3M, 4M and 5M HCl solutions and were depicted in figures. Figure 2 showed the variation of potential (E) with Current (I) for stainless steel 304 in dilute hydrochloric acid. The line AB represents the cathodic behaviour of the sample while line BC located in active zone i.e. anodic dissolution reaction. At potentials more positive than B, corrosion rate increases, and reaches maximum at the point C, which is passivation potential (E_{ps}). The transition from active dissolution occurs in the region C to D. A protective film begins to form and causes a sudden drop in corrosion current density. At point D breakdown of the protective film begins which correspond to pitting potential (E_{pit}) and promotes pitting consequently specimen failure.
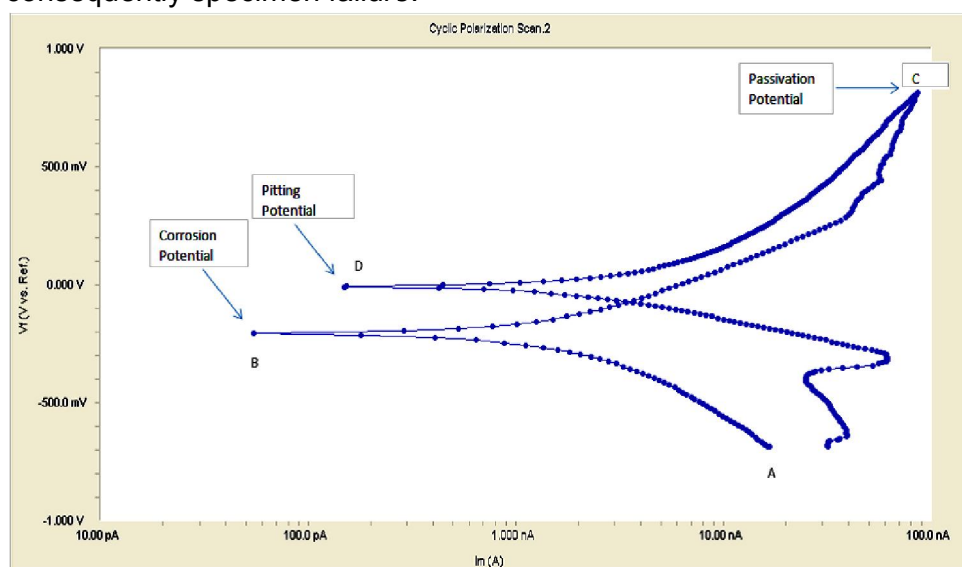

Figure 2: Cyclic Polarization curve (E vs I) of stainless steel in dilute HCl solution

Figures 3 to 7 had represented polarization curve relationships between current (I) and Potential (E) for stainless steel type 304 sample electrodes in the 0M, 2M, 3M, 4M and 5M HCl solutions respectively. In figure 3 (0M HCl/ deionized water) corrosion potential (E_{corr}) was -217.5 mV, passivation potential (E_p) was 856 mV & the pitting potential (E_{pitt}) was found to be 7.141 mV. Figure 4 (2M HCl) had exhibited the corrosion potential (E_{corr}) at -205.6 mV, passivation potential (E_p) at 808 mV and the pitting potential (E_{pit}) was at -10.87 mV. In figure 5 (3M HCl) the corrosion potential (E_{corr}) was found to be -194 mV, passivation potential (E_p) was 760 mV & the pitting potential (E_{pitt}) was -84 mV. Whereas figure 6 (4M HCl) had displayed corrosion potential (E_{corr}) at -165 mV, passivation potential (E_p) at 689 mV & the pitting potential (E_{pitt}) at-145 mV. In figure 7 (5M HCl) the corrosion potential (E_{corr}) was found to be -151.8 mV, passivation potential (E_p) was 600 mV & the pitting potential (E_{pitt}) was -161.8 mV.
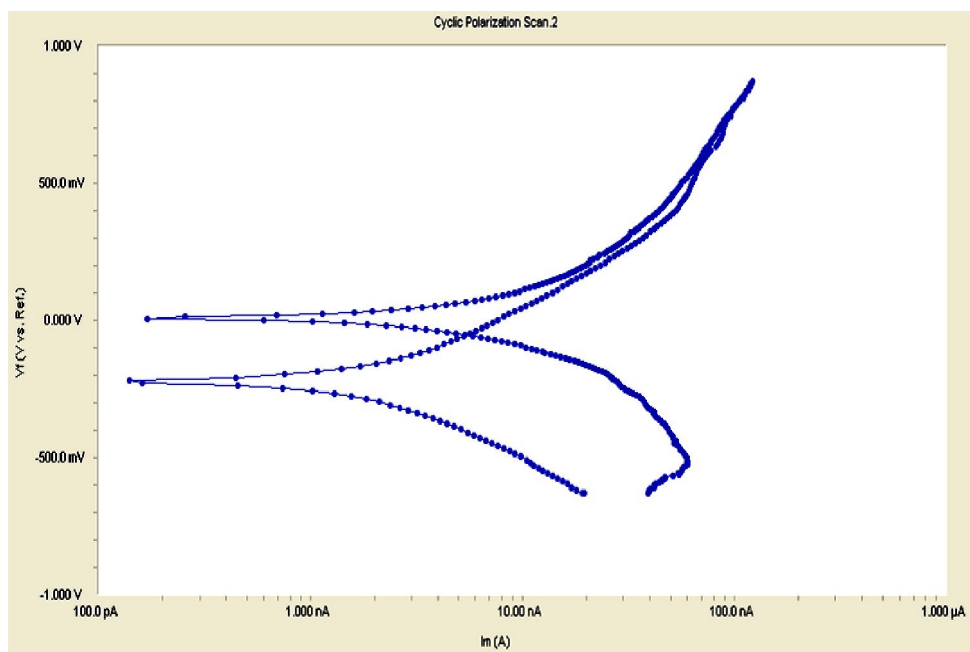

Figure 3. Cyclic Polarization Curve of Stainless Steel Sample 1 in deionized water (0 M HCl)
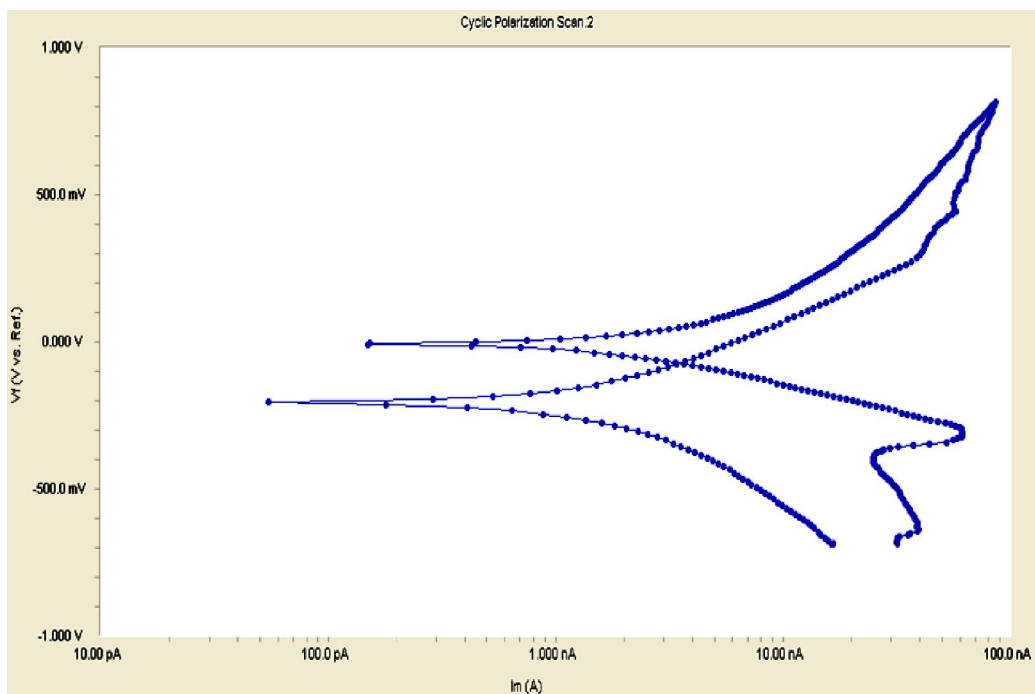
Figure 4: Cyclic Polarization Curve of Stainless Steel Sample 2 in 2M HCl Solution
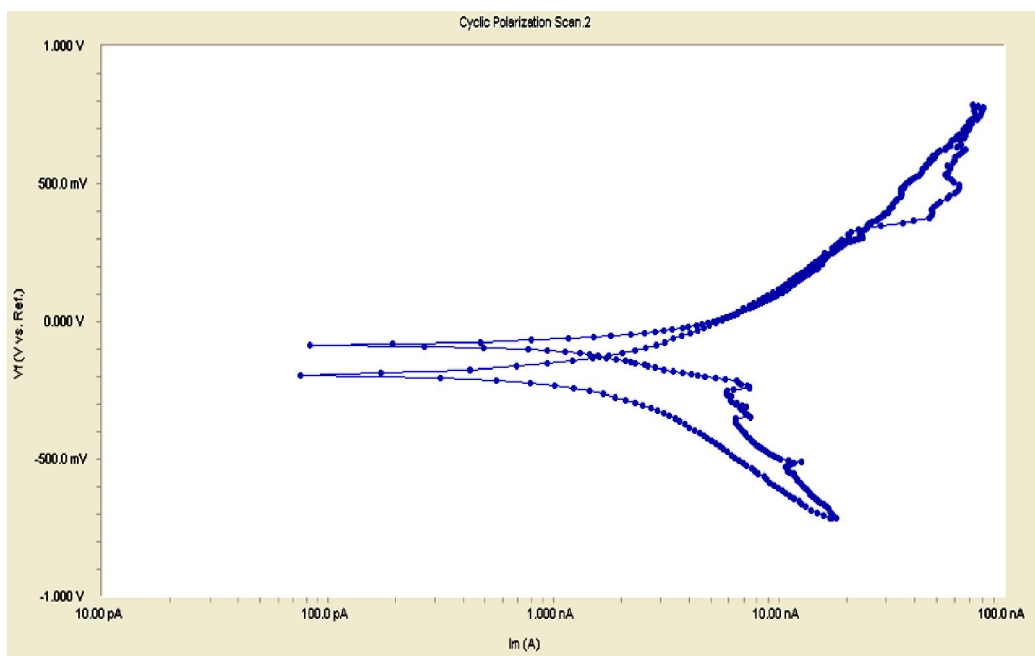

Figure 5: Cyclic Polarization Curve of Stainless Steel Sample 3 in 3M HCl Solution.
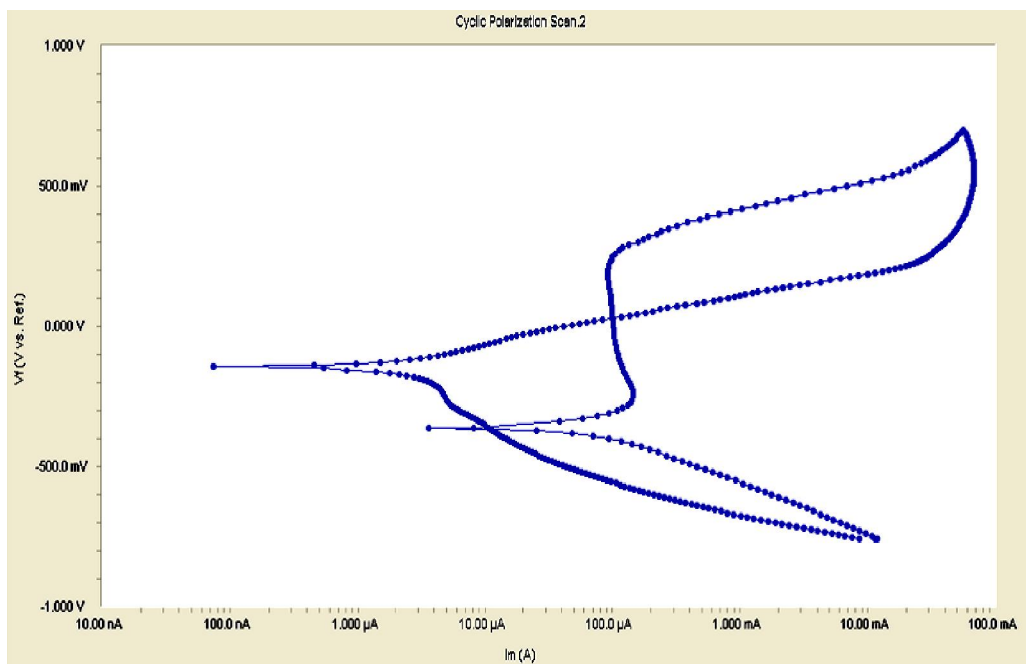
Figure 6: Cyclic Polarization Curve of Stainless Steel Sample 4 in 4M HCl Solution.
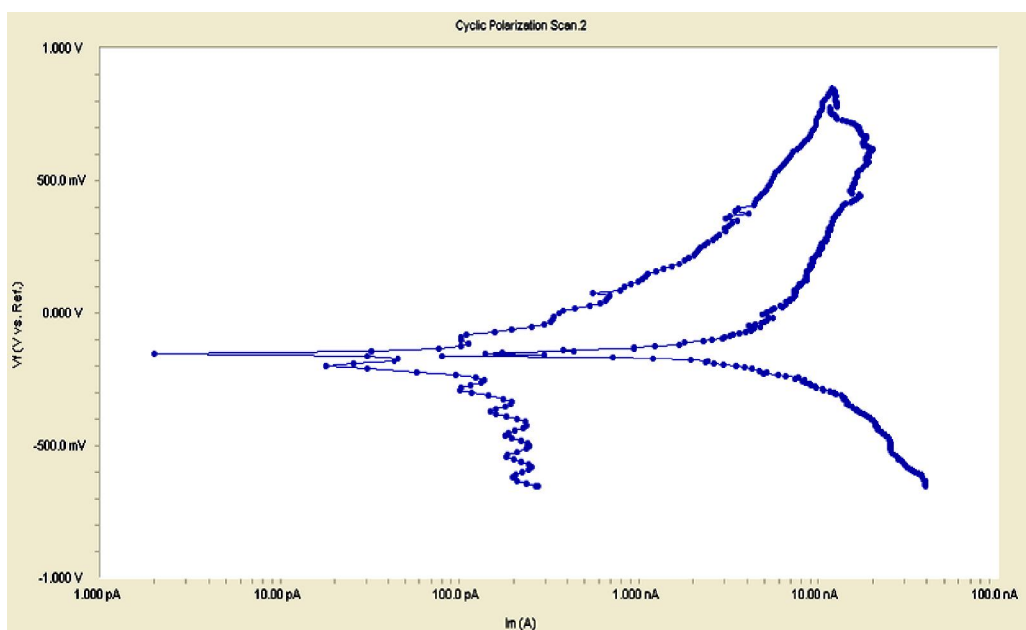

Figure 7: Cyclic Polarization Curve of Stainless Steel Sample 5 in 5M HCl Solution.

Figure 8 depicted variation trend of Passivation Potentials of stainless steel in different chlorine concentrations and data values were also tabulated in table 1. It showed that as the molar concentration of the chloride electrolyte increased the passivation potential decreased i.e. potential required to passivate the material

decreased. Figure 9 displayed relationships established between measured pitting potential (mV) of stainless steel sample electrode and HCl solution concentration while data values were also tabulated in table 2. It has showed that as the molar strength of chloride ion solution increased the pitting potential of stainless steel sample electrode decreased that is sample steel electrodes were more prone to pitting corrosion under high chloride ion stress.
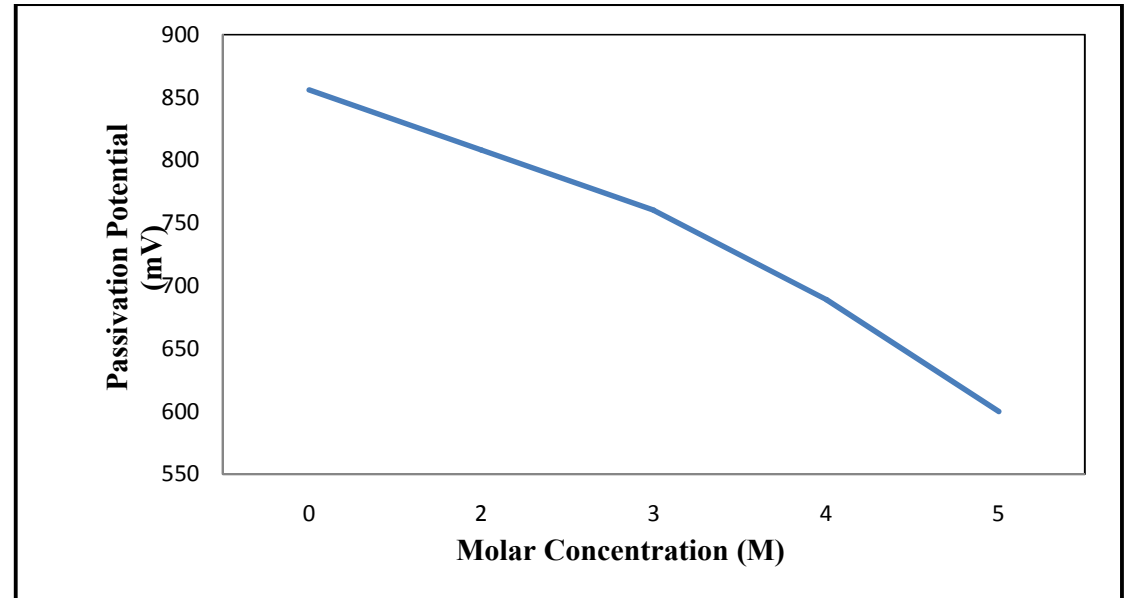

Figure 8: Variation of Passivation Potentials with Chloride Concentrations
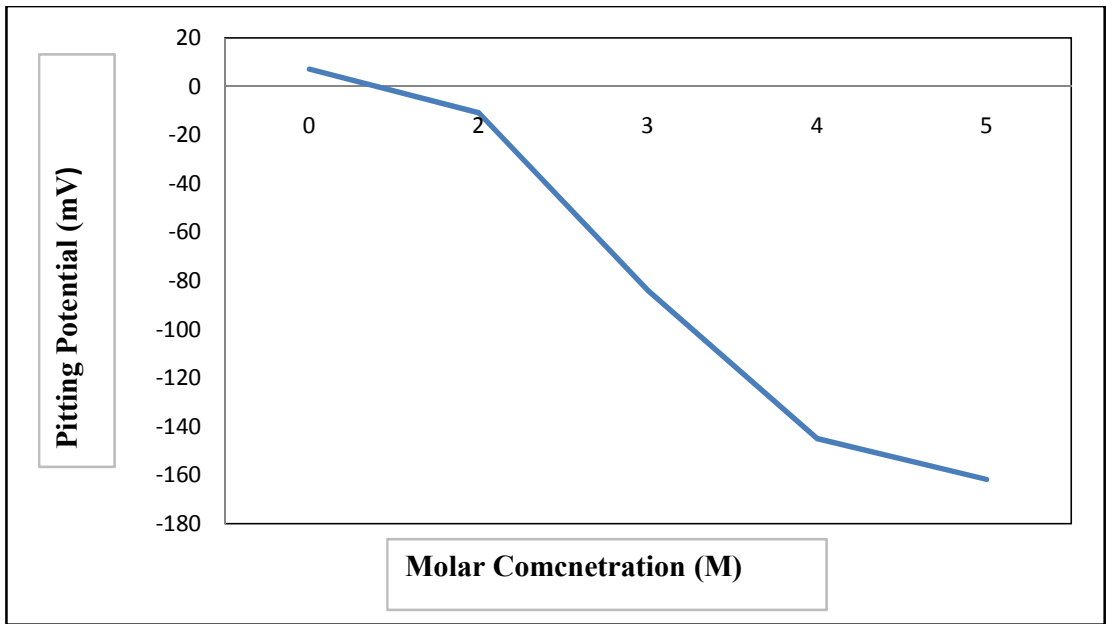

Figure 9: Variation of Pitting Potentials with Chloride Concentration

Figure 10 has illustrated the micrographs (at 500× & 1000× magnification) of stainless steel sample electrode after acquiring anticipated pitting potential state during potentiodynamic scan with immersion in 5 M HCl solution. By analysis of micrograph it was revealed that significant pitting attack occurred on the surface of Stainless Steel in chloride ion solution which confirmed that pits were forming at computed pitting potentials. Pits were formed at defective points of passive layer by oxidation of metal which accumulated positive charges in the form of Fe^{2+}. It would then attract negatively charged chloride ions. The resulting ferrous chloride has hydrolysed to produce an insoluble ferrous hydroxide plus excess hydrogen and chloride ions. These ions have further promote the corrosion to propagate depth of pit as described by Loto [2].
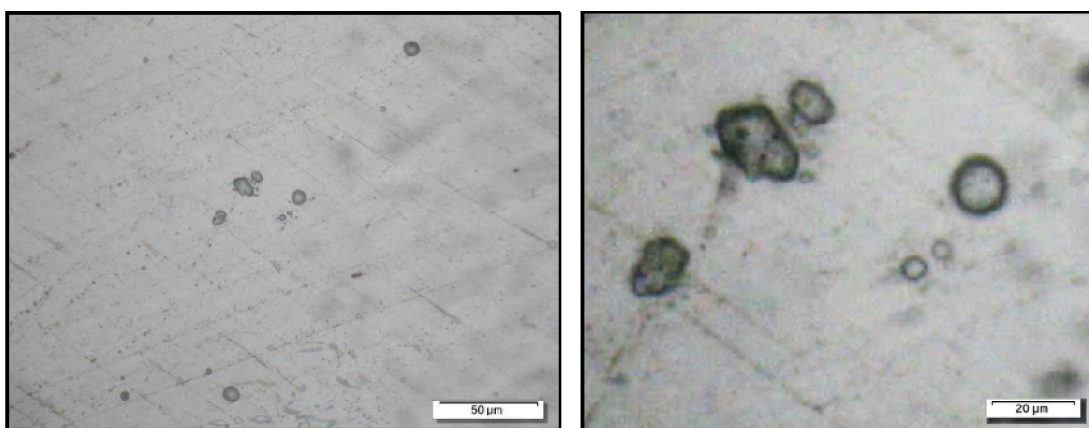

Figure 10: Micrograph of a Pitted Sample in Chloride Ion Solution.

4. Conclusion

Potential state at which pitting of metal initiated is called Pitting potential (E_{pit}). It was recognized by sudden sharp rise of anodic current in polarization curve of figures 4-8 under various chloride ion stresses. Comparison of graphs concluded that as chloride ion stress increased, it more aggressively attacked on passive layer and induced pitting corrosion at lower threshold potentials thus decreased Pitting potential (E_{pit}) of subject stainless steel type 304 sample electrodes. Moreover pH of electrolyte decreased inside the pit due to hydrolysis of $FeCl_2$ which furnished strong acid (HCl) and weak base ($Fe(OH)_2$) thus further accelerate corrosion process and promote pits penetration. A large ratio between the anode and cathode areas also favoured propagation of pits depth.

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