INVESTIGATION INTO TUBULAR STRUCTURE FORMED BY PITTING CORROSION ON THE SURFACE OF CARBON STEEL

Tawfeeq A. Alkanhal\textsuperscript{1}, M.Osman\textsuperscript{2}, and S. M. Ahmed\textsuperscript{3}, *

\textsuperscript{1} Research Center director of Engineering and Applied Science, Faculty of Engineering, Majmaah University, Saudi Arabia, E-mail: t.alkanhal@mu.edu.sa
\textsuperscript{2, 3} Mechanical Engineering Department, Faculty of Engineering, Majmaah University, Saudi Arabia

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ABSTRACT

The formation and development of pitting corrosion on carbon steel surface during the initial stage of immersion test in tap water have been studied by scanning electron microscopy. The pitting was analyzed for static and rotating specimens during immersion. The results showed that the features of the pits formed on the surfaces of samples that are rotating are different from those on the surfaces of static samples. Since the rotating-pit samples were followed by a tubular structure of corrosion products in the reverse direction of rotation. The results showed also that this tubular structure depends on the size of the pit and test time. Moreover, this tubular structure plays an important role in the development of damage to the surface. This shows that the corrosion products have a hostile influence. Interactions localized corrosion pits occurred between large and small pits in its configuration, as well as between the tubular structures. The features of formed pits were a cavity at the center of the pit and a rough circular band or ring of products around the cavity.

Keywords: corrosion, pitting corrosion, tubular structure, pit interactions, immersion test, carbon steel, tap water

1. Introduction

In general, it is considered that pitting corrosion is the most disastrous form of corrosion as its occurrence can be extremely difficult to predict. Pitting is regarded as one of the most insidious forms of corrosion, since it often leads to perforation and to a consequent corrosion failure [1-4]. Predictors are less accurate as the complexity of the corrosive environment increases. The pitting process occurs as the result of a series of stages. In some cases, the most important such step is the initiation stage, which is still the subject of a great number of studies and various assumptions.

Pitting is a highly localized form of corrosion that produces sharply defined holes. These holes may be small or large in diameter, but in most cases, they are relatively small. Pits may be isolated from each other on the surface or so close together that they resemble a roughened surface.

Many metals and their alloys are susceptible to pitting. Pitting occurs when one area of a metal becomes anodic with respect to the rest of the surface or when highly localized changes in the corrodent in contact with the metal, as in crevices, cause accelerated localized attack. Understanding pit initiation will lead to an increased accuracy in lifetime predictions and reliability. Such an understanding could lead to new corrosion monitoring
schemes as well as corrosion inhibition schemes, including new alloy chemistries with microstructures resistant to pitting corrosion. Overall, an understanding of the pit initiation process will make an impact on many of the existing efforts in metal corrosion studies.

Carbon steel, the most widely used engineering material, accounts for approximately 85%, of the annual steel production worldwide. Despite its relatively limited corrosion resistance, carbon steel is used in large tonnages in marine applications, nuclear power and fossil fuel power plants, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction and metal-processing equipment [5].

The objective of this study is to investigate the pitting corrosion of carbon steel immersed in tap water with the test time for two cases namely; stationary and rotated specimens.

2. Pitting initiation

The pitting process occurs as the result of a sequence of stages that includes: (1) pitting initiation or nucleation, (2) meta-stable pitting, (3) stable pitting and (4) repassivation or stable pit death [6]. In some cases, the most important such stage is the initiation stage, which is still the subject of a great number of studies and various assumptions [7-12]. The initiation of pits can be considered as an event that results from conjunction of various phenomena. These phenomena are related to several factors that are mainly properties of the solution and those of the metal, which exert themselves through a broad range scale.

It is well known that the inclusions and their concentrations play a vital role in pitting initiation [13-16]. Manganese sulphide inclusions (MnS) are known to be often precursor sites for pitting corrosion [17-19]. It must be also emphasized that the size [20] and geometry [13] of a MnS inclusion seem to be relevant to the propagation or repassivation of a pit embryo. In addition, the presence of mechanical stresses reduces pitting potential appreciably in the presence of MnS inclusions [13].

In addition to the inclusions, the phase structure of the material seems to play an important part in the pitting initiation. Grain boundaries are sites of structural discontinuity, and they can also have microstructural and chemical differences with respect to the bulk grains. These discontinuities and differences can affect the corrosion behavior of the metal. The important consideration within the context of corrosion pitting is that many alloys are not homogeneous, pure materials, but rather are a mixture of multiple phases. Each phase has its characteristic crystallographic structure and chemical composition. When these structures are then exposed to a corrosive environment, it is not surprising that the different phases exhibit different corrosion behaviors. This leads to preferential corrosion of specific constituents of the alloy. Krawiec et al. [21] has shown that ADI (Austempered ductile iron) austempered at 430oC has upper ausferritic microstructure and reveals a better corrosion resistance in sodium chloride solution than ADI austempered at 280oC. Moreover, the corrosion resistance increases as the volume fracture of ferrite increases and the carbon content of austenite decreases. The good corrosion behaviour of ADI austempered at 430oC was also related to the good coarsening of the austenite grains and broad ferrite needles (less ferrite/austenite interfaces). It has
been demonstrated that silicon is the alloying element hindering the anodic dissolution of the alloy. Boucherit et al. [12] studied the behavior of four steels: Fe.06C, Fe.18C, Fe.22C and Fe.43C in basic pitting solutions. Their results showed that in a solution with a low chlorine concentration, the performance of the steels according to pitting corrosion resistance decreased with the increase in carbon content. Using potentiodynamic polarization and immersion test, Bhagavathi et al.[22] evaluated corrosion properties of dual-phase steels with different volume fractions of martensite. They found that the corrosion rate and the pitting for dual-phase steels is found to be lower than that for subcritically heat treated ferrite–pearlite steel. They added that the higher corrosion resistance of dual-phase steels is explained on the basis of microstructural features.

Another key factor in pit initiation is the presence of hydrogen in hydro-electrolytes, which may diffuse to metal, when the metal is not covered with an oxide layer. The resulting dissolved hydrogen can thereafter influence the electrochemical behavior of the metals and alloys. It has been found that hydrogen increases the corrosion rate and decreases the pitting resistance of some metals. The decrease in the stability of the passive film by the presence of hydrogen has been reported for some time [23]. Recently, however, Yuan [24] investigated the effects of hydrogen on the pitting processes of X70 carbon steel in neutral chloride ions containing solution by using the scanning electrochemical microscope (SECM) technique. Pitting is much more easily observed after the specimen has been pre-charged with hydrogen, for the oxidation of the hydrogen in the X70 decreases the pH value at the X70/solution interface, which retards the formation of an oxide film and subsequently promotes the pitting processes. The observed behaviour is further verified by the decrease of the solution's pH.

Although it has been well known for many decades that Cl– gives rise to local pitting corrosion of metals and alloys, the precise role of Cl– in achieving pitting is not well understood [25]. Cheng et al. [26] studied the role of chloride ions in metastable pitting of A516-70 carbon steel based on the statistical analysis of recorded current and potential noise. An analysis of the probability distribution of pit repassivation time vs. chloride concentration shows that the main role of chloride ions in pitting is to increase the chance of the breakdown of passive film, rather than to inhibit the surface repassivation.

3. Experimental procedure

A rotating corrosion-test equipment was used for studying pitting corrosion behavior. The specimen was immersed in 1200 ml open pot having 700 ml of tap water. The pot was fitted with four vertical baffles to break up the rotational flow pattern. The pot and the baffles were made from plastic material. Because of the rotational speed, turbulence was generated in the test water, together with a tendency for a rise in water temperature. Since the test water temperature markedly affects the corrosion rate [27], the test water was changed every one hour. The temperatures at the beginning and the end of test were 23 °C and 24 °C, respectively. Table 1 shows the composition of test water determined by chemical analysis.

Coupon specimens with dimensions of 50x30x1 mm were cut from a single sheet of carbon steel to ensure metallurgical uniformity. Since the surface roughness plays an
important role in developing the corrosion [28,29]. Therefore the specimen's working faces were polished with grade 800 silicon carbide paper. A typical polished surface is shown in Fig.1. The inclined vertical lines shown in the figure are the traces of polishing. Each specimen was attached to a rotating shaft with pvc washer and a plastic screw to avoid the galvanic corrosion. Specimens were rotated at 160 rpm (linear velocity of 0.5 m/s) for test periods of 1, 3, 5, and 7 h. An immersion tests were carried out with zero specimen's velocity for 1 h to explore the effect of velocity. At the end of test period the rotating shaft with specimen was withdrawn, and air dried. The corroded surfaces were examined by a Scanning electron microscope (SEM).

Table 1
Chemical analysis of test water

<table>
<thead>
<tr>
<th>Element</th>
<th>Na⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>K⁺</th>
<th>HCO₃⁻</th>
<th>Cl⁻</th>
<th>F⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>pH</th>
<th>TDS</th>
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<tbody>
<tr>
<td></td>
<td>3</td>
<td>75</td>
<td>6.8</td>
<td>2</td>
<td>70.</td>
<td>7</td>
<td>0</td>
<td>2</td>
<td>10</td>
<td>7</td>
<td>3</td>
</tr>
</tbody>
</table>

Note: all values except pH are in mg/l

4. Results and discussion

At the first the photographs were taken at four positions to thoroughly highlight the pitting corrosion formation and to investigate the effect of velocity in case of specimen rotation at different times.
4.1. Static immersion tests

The typical corrosion pits formed on the polished surfaces after 1 h immersed in tap water are shown in Fig. 2. Pits showed similar characteristics for all positions on the test surfaces. The characteristic features of these pits are the presence of two parts: a cavity at the pit centre and a rough circular band around the cavity, which is labeled 1, as well as circular rings, labeled 2. The same shape for these pits has been observed before in the literature on corrosion tests (e.g. Budiansky et al. [30] and Wang et al. [31], Karrab et al. [32, 33]). With respect to the size of these pits, they have different sizes ranged from few micrometers to the order of one hundred micrometers. The number of pits was calculated from three micrographs (each micrograph has an area of 4.051 mm²) and the average number of pits was 912 pits/cm².

To elucidate the pit formation, a slightly high magnification for the areas bounded by box in Fig. 2 is presented in Fig. 3. In this figure, we can distinguish three areas: A1 area in the centre of the pit and which is the inclusion; A2 area is the ring area of product corrosion formed around the inclusion and the A3 area is the dissolution of the oxide film around the ring area. The mechanism of formation will be explained in the next paragraph.

![Fig.2. Corrosion pits formed after 1 h immersion and at stationary conditions](image)

The thing worth noting in these photographs is the interaction amongst the localized corrosion sites. These interactions are illustrated by arrows in Fig 2(a). For more clarity some of these interactions are magnified as shown in Fig. 4. The spatial interactions have been seen visually in the form of satellite pits, labeled Ps ,that tend to form patterns around larger primary pits, labeled PL as shown in Fig. 4. This is in agreement with that reported in the literature [30, 34]. It can also be observed from this figure and Fig. 3 the dissolution
of oxide film around the pits. This can be explained [34], when a pit begins to form, the local environment changes. Concentration changes in solution occur when metal cations enter solution and hydrolyze, bringing about an increase in both the local chloride concentration and local acidity. The environment in this way becomes more aggressive. Solution concentration and potential gradients develop that can affect pitting susceptibility on adjacent surfaces. These factors can also affect nearby oxide film and non-metallic inclusions to produce more permanent interactions. Taking into account these local changes, pitting can have a significant influence on the susceptibility of adjacent surfaces to localized corrosion. However, the time constant associated with each of these interactive processes differs.

Fig. 2. Continued

Fig. 3. SEM photos representing a slightly high magnification for the pit bounded by boxes in Fig. 2(b)
Fig. 4. Showing the interaction amongst the localized corrosion sites.

4.2. Rotation tests

Figure 5 presents a pitting corrosion formed at the different positions on surface of rotated specimens for 1 h. At first glance, the pit formed during rotation test differed from that formed during static tests. The photos in Fig. 5 show that each pit formed has a track accompanied it which appears as black in photos and which looks like a comet streak tail. These comet tails were formed in opposite direction to the rotation of the specimen. The comet tails take the form of cone tubular structure. The circular base of cone is the ring that formed around the inclusion and which referred to it in the static immersion test. This phenomenon has been observed in the literature [35-37]. The geometric dimensions of these tubular depend upon the pit sizes, the tubular corrosion products, conjoint of nearly tubular and the local velocity at which pit formed. The conjoint of the tubular longitudinally or transversely will be more developed for the lager test time. The number of pits was calculated from four photos (each photo has an area of 4.051 mm²) it was 600 pits/cm². By comparing the number of pits for the two tests, static and rotation tests, i.e. 912 versus 600 pits/cm², it is seen that the number of pits are less when the specimen is rotated. This can be attributed that many pits in the static tests are metastable, while for rotation tests all the pits are often stable.

The pit's rings formed around inclusions and the material dissolution around the ring as well as the tubular structure formed due specimen rotation can be explained by the tube growth mechanisms. Schematic representation of the proposed corrosion mechanism, and which is called corrosion tube growth mechanism is shown in Fig.6 [38]. The carbon steel is oxidized in the anodic region inside the pit and oxygen reduction occurs in the cathodic region.
Further oxidation of ferrous hydroxides leads to the formation of a semi-permeable solid membrane of various iron oxide layers which form around the pits. The hydrolysis of ferrous ions results in a lower pH inside the pits and the negatively charged chloride anions diffuse into the pits to maintain the charge neutrality. The buildup of a highly acidic chloride environment inside the pits accelerates the corrosion process. This SEM study revealed formation of unique corrosion product structures on pitted carbon steel surfaces which are consistent with the tubular growth corrosion mechanism in a pit. For more clarity about this phenomenon, the tube structure can be revealed from Fig. 7.

Fig. 5. Pitting corrosion formed at different positions on the surface of specimen immersed for 1 h and rotated at 160 rpm
Fig. 5. Continued

Fig. 6. Schematic representation of tubular growth of corrosion products on carbon steel [38]
4.3. Pit developing with the test time

The effect of time on the pitting corrosion development for rotation test is illustrated in Fig. 8. The striking feature is the remarkable increase in the track length with time. It was noted that the track length was 2200 µm, equivalent 15 times the size of pit that formed that tubular structure. Another feature for the tracks is the joined of tubular structure transversely or longitudinally as illustrated in Figs 9 and 10, respectively. The role of interaction of the tubular structure is not clear and will be investigated in the future. The role of tracks in developing the corrosion damage can be revealed from Fig. 11. It can be seen that many pits formed and material removed along the track direction. This gives evidence that the corrosion products are aggressive.

For the same test time the pit size for the rotation test was larger than that for the static test. As the test time of rotation increases the pit size increases. However, for the rotation test, the pit interactions which was discussed for static test became more pronounced as shown in Fig. 12 for different exposure times. The photos illustrate that many satellite pits, labelled Ps, formed around the large pit, labelled PL. These visual patterns give evidence of spatial interactions amongst the localized corrosion sites.
Fig. 8. Pitting corrosion development with time for the rotated specimens;

(a) 1 h, (b) 3 h, (c) 5 h, (d) 7 h
Fig. 8. Continued
Fig. 9. Transversely Joint of tubular corrosion structures

Fig. 10. Longitudinally joint of tubular corrosion structures
Fig. 11. Showing the damage effect of tubular corrosion structures
Fig. 12. The interaction amongst the localized corrosion sites for rotation test

For different test times: (a) 3h, (b) 5h, (c) 7h

Fig. 12. Continued
5. Conclusions

From the results and discussions presented above, the following conclusions can be drawn.
1. A tubular corrosion product structure developed with corrosion pit in reverse direction of rotation. The size of tubular structure depends on the test time of rotation and the pit size.
2. Along the tubular structure track, surface damage was observed. This gives evidence that the corrosion products are aggressive in-nature.
3. Interactions of localized corrosion sites amongst the pits were observed. Along with this interaction between tubular structure was also observed.
4. All the pits formed for static and rotated immersion-tests have similar features, in which ring areas formed around micropits and rough circular bands around micropits were developed on the surface.

References

T. A. Alkanhal et al, Investigation into tubular structure formed by pitting corrosion on the surface of carbon steel, pp. 483 - 500


دراسة الهيكل الأنبوبية المتكون نتيجة تنقر التآكل على سطح الصلب الكربوني

ملخص:

في هذا البحث تم دراسة تنقر وتطور تنقر التآكل على سطح الصلب الكربوني خلال المرحلة الأولى بواسطة المجهر الإلكتروني وذلك باختبار الغمر في مياه الصنبور. تم تحليل النتائج على العينات الثابتة في حالة الحركة الدورية على سطح العينات الثابتة، وذلك بأن النقر المتكون على العينات المتحركة أتبعت مسارًا من غمر النقر المتكون على العينات الثابتة، وذلك بأن النقر المتكون على العينات المتحركة أتبعت مسارًا من غمر النقر المتكون على العينات الثابتة. أظهرت النتائج أيضا أن هذا الهيكل الأنبوبية يعتمد على حجم الحفرة وزمان الانتشار. وعلاوة على ذلك هذا الهيكل الأنبوبية يلعب دورا هاما في تطور الأضرار التي لحقت السطح وله تأثيرات محورية. كما أنه حدثت تفاعلات بين النقر التآكل وبين النقر الكبيرة والصغيرة في كونها، وكذلك بين الهيكل الأنبوبية. ملامح النقر المتكونة هي تجويف في مركز النقر وشريط داري خشن أو حلقية من المنتجات حول التجويف.

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