Effect of Thiosulfate on Pitting Corrosion of 316SS

II. Metastable Pitting and Transition to Stability

D. Nakhaie, M. Zakeri, M. Naghizadeh, and M. H. Moayed
Metallurgical and Material Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran

In the present part of study, the effect of thiosulfate ion on pitting corrosion of AISI 316 stainless steel in 0.1 M NaCl solution was investigated. In order to elucidate the effect of thiosulfate on pitting corrosion, the metastable pitting has been studied in more details. The results showed that the thiosulfate addition increased susceptibility to pit initiation and increased the dissolution kinetics of metastable growing pits in a fashion that facilitates the transition from metastability to stability. Consequently, the pitting potential of the stainless steel was decreased in the presence of thiosulfate ion.

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Experimental

The chemical composition of the AISI 316 stainless steel was shown in part I of this study. The alloy was received as round rod with diameter of 10 mm. Two sets of specimens were prepared for electrochemical experiments, i.e. specimens with surface area of 0.785 cm² for potentiodynamic polarization and specimens with surface area of 0.2 cm² for potentiostatic polarization. Electrodes were separately mounted in epoxy resin with a copper wire connection at the end. Using samples with small surface area in potentiostatic polarizations allows better management of the number of metastable pits developed on the specimen. Prior to each test, electrodes were prepared by wet grinding up to 1200 grit SiC paper. All electrochemical experiments were carried out in 0.1 M NaCl solution and 0.1 M NaCl + 0.01 M Na₂S₂O₃ solution. The chloride and the thiosulfate concentrations were chosen based on the results reported by Ke and Alkire, to ensure that the alloy was in the active region. For each test, fresh solution was prepared from analytical grade chemicals and distilled water, and all tests were conducted at 25 ± 1 °C.

A conventional three electrode cell incorporating a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the counter electrode was used. The electrochemical cell was a 200 mL open to air beaker. Before each electrochemical test, the open circuit potential was monitored for 60 min, which was sufficient to approach the steady state condition. Potentiodynamic polarization was performed at potential scan rate of 30 mV min⁻¹. In the present study, the pitting potential was defined as the potential at which the current density progressively began to increase. In order to study the influence of the thiosulfate ion on metastable pitting of AISI 316 stainless steel, the potentiostatic polarizations conducted at the constant potential of 250 mV (SCE) for 1800 s. During the polarization at this potential if stable pitting took place the record was discarded. Another set of potentiostatic experiments were carried out to determine the role of thiosulfate ion on survival probability. For this purpose, specimens were polarized at two distinct potentials of 280 mV (SCE) and 300 mV (SCE) until the current density reached to 0.5 mA cm⁻² and continued to increase. Corresponding time was considered as a criterion for the induction time of stable pitting. Repeat experiments were carried out for each potential/solution combination to evaluate the survival probability.

Results

Pitting potential.— Figure 1 shows typical potentiodynamic polarization curves of AISI 316 stainless steel obtained in 0.1 M NaCl solution and 0.1 M NaCl + 0.01 M Na₂S₂O₃ solution. As can be seen, by addition of thiosulfate ion, the corrosion potential decreased and the passive current density increased. Moreover, the pitting potential of the stainless steel decreased in the presence of thiosulfate ion. On both curves some current fluctuations can be seen, which are representative of the occurrence of metastable pits.

As the potential at which stable pits form has a probabilistic nature, it would give broader perspective to study the effect of thiosulfate ion considering the probability distribution. The probability of stable pitting as a function of applied potential in the presence and
the absence of thiosulfate ion is shown in Figure 2. The probability distribution function is defined as follow.

\[ P(E) = \frac{n}{1 + N} \]  

where \( N \) is the total number of experiments, and \( n \) is the number of the pitted specimen. It has been shown that the distribution of pitting potential obtained from potentiodynamic polarization is strongly dependent on the threshold current at which stable pits are assumed to form.\(^{19} \) Different current thresholds have been proposed to determine the pitting potential of stainless steels.\(^{10, 19} \) One way to compare the pitting distribution obtained in both test solutions is to consider the median of the probability distribution, i.e. \( P(E) = 0.5.^{15, 20} \) While the median of the pitting probability obtained in 0.1 M NaCl solution was 430 mV (SCE), half of the specimens tested in the presence of 0.01 M \( \text{S}_2\text{O}_3^{2-} \) were pitted at potentials less than 344 mV (SCE). The deleterious influence of thiosulfate on pitting potential is in agreement with those reported for type 304 stainless steel,\(^{21} \) highly alloyed stainless steel\(^{22} \) and alloy 800.\(^{23} \)

**Figure 1.** Typical potentiodynamic polarization curves of AISI 316 stainless steel obtained at potential scan rate of 0.5 mV s\(^{-1} \) in 0.1 M NaCl and 0.1 M NaCl + 0.01 M Na\(_2\text{S}_2\text{O}_3\) solutions at 25°C.

**Figure 2.** Cumulative probability of stable pitting as a function of potential obtained from potentiodynamic polarization conducted in 0.1 M NaCl and 0.1 M NaCl + 0.01 M Na\(_2\text{S}_2\text{O}_3\) solutions at 25°C.

**Figure 3.** Current transients obtained from metastable pitting of 316 stainless steel potentiostatically polarized at 250 mV (SCE) at 25°C in: a) 0.1 M NaCl solution, b) 0.1 M NaCl + 0.01 M Na\(_2\text{S}_2\text{O}_3\) solution.

**Metastable pitting.**—Metastable pit growth, which has been well-documented by Frankel et al.,\(^{24} \) is the early stage in the pitting corrosion of stainless steels in chloride containing solution. Metastable pitting can be observed as negative events in potential at the open-circuit condition or anodic galvanostatic polarization, or as anodic current excursions during potentiostatic polarization below the pitting potential.\(^{25} \) It has been shown that metastable pitting plays an important role in the resistance to pitting corrosion of stainless steels.\(^{17} \) In order to study the effect of thiosulfate ion on metastable pitting of AISI 316 stainless steel, potentiostatic polarization experiments were conducted at 250 mV (SCE). Figure 3 illustrates typical current transient obtained from the potentiostatic polarization of 316 stainless steel in 0.1 M NaCl and 0.1 M NaCl + 0.01 M Na\(_2\text{S}_2\text{O}_3\) solutions. As can be seen, the background current with time. Moreover, there are many current spikes superimposed on the background passive current. These events are characterized by increasing the current from the passivity background as the pit nucleates and begins to grow and sharp decrease in the current by repassivation of the metastable pit.\(^{24} \) The frequency of metastable pitting (\( \lambda \)) was calculated by counting the number of current spikes in successive 100 s time intervals divided by the electrode surface area (0.2 cm\(^2\)). Based on instrumentation limits, all events were greater than 3 nA were counted as metastable pits. Note that the background noise of current records was well below the considered threshold. Figure 4 depicts the change in \( \lambda \) with time.
for both test solutions. Each data point in Figure 4 represents the average frequency of events calculated from 5 separate experiments. The error bars give the 95% confidence limit. As can be seen from Figure 4, during the first 500 s of experiments the rate of metastable pitting of 316 SS showed similar behavior in both 0.1 M NaCl and 0.1 M NaCl + 0.01 M S2O32− solutions. After this period, the frequency of events for NaCl solution was slightly increased. On the other hand, the rate of metastable pit formation for thiosulfate containing solution was dramatically increased. However, λ remained almost constant for the rest of the test. Although it has been shown that the frequency of metastable pitting decays with time,14,17 no meaningful decrease in λ was observed in the present study. Such behavior in metastable pitting is in agreement with that reported by other researchers.26–28

The exhaustion of available site capable of metastable pitting with time on 50 μm diameter electrode was shown to take place with first order kinetics.17 However, in the present study, the electrode surface area was not small enough that such a decay in the frequency of metastable pitting could be detected.

Figure 5 depicts the current transients of two metastable pits developed on AISI 316 SS obtained from potentiostatic polarization at 250 mV (SCE) in 0.1 M NaCl + 0.01 M Na2S2O3 solution. Also, the key characteristics of these transients, i.e. the pit peak current (Ipeak), the pit growth time (tg), the pit repassivation time (tr), and the background current noise were graphically presented. It is evident from Figure 5 that the metastable pits could be easily distinguished from one another. However, in the case that the transients overlap, it was considered as a separate metastable pit if during the repassivation of a metastable pit the corresponding current were decreased more than 50% of the peak current. Otherwise, i.e. the current decreased but less than 50% of the peak current, the overlapped events were considered as a metastable pit. In the present study, the overlapped transients were less than 10% of the all events, regardless of test solutions.

The results of potentiostatic experiments showed that the peak current of metastable pits was increased by addition of S2O32−. The cumulative distribution plots of the Ipeak of metastable pits for both test solutions are depicted in Figure 6. The Ipeak was taken as the difference between the maximum current measured in a transient and the background current noise.29 The median distribution of Ipeak increased from 19 nA in the absence of thiosulfate to 482 nA in the presence of 0.01 M thiosulfate ion. Such an enormous increase in the metastable pit peak current shows the deteriorative influence of the thiosulfate on metastable pitting of the investigated stainless steel.

Figure 7 and Figure 8 show the cumulative distribution plots of metastable pit growth time, tg, and metastable pit repassivation time, tr, respectively. The pit growth time was defined as the difference between the moment at which the current starts to increase (pit birth) and the moment at which the current reaches its peak (pit death). The tg obtained in 0.1 M NaCl solution ranged between 0.1 s and 7.8 s, while growth time of the metastable pits formed in the presence of 0.01 M thiosulfate ion was ranged from 0.15 s to 33.8 s. Moreover, the median distribution of tg was 0.8 s and 3 s for Cl− and Cl− + S2O32− containing solutions, respectively. Similarly, the presence of thiosulfate ion increased the repassivation time of metastable pits, since the median distribution of tr increased from 0.25 s to 0.4 s by addition of 0.01 M S2O32−. Therefore, one may conclude that the thiosulfate ion hindered the repassivation of metastable pits.

It has been shown that metastable pits formed on stainless steels can be assumed to be hemispheres.37 This assumption, the apparent radii of metastable pits can be calculated using Faraday’s second law.
Figure 7. Cumulative probability of metastable pit growth time obtained from potentiostatic polarization at applied potential of 250 mV (SCE) in 0.1 M NaCl and 0.1 M NaCl + 0.01 M Na₂S₂O₃ solutions at 25°C.

as follow.

\[ r = \left( \frac{3QM_w}{2\pi F n \rho} \right)^{\frac{1}{3}} \]  \[2\]

where \( r \) is the metastable pit radius, \( Q \) is the anodic charge calculated by integration of the current-time transient during the pit growth, \( M_w \) is the atomic weight of the alloy, \( F \) is the Faraday’s constant, \( n \) is the dissolution valence of the alloy, and \( \rho \) is the density of the alloy. The apparent metastable pit radii were calculated using equation 2 and their cumulative distribution is plotted in Figure 9. As can be seen, the metastable pits formed in the thiosulfate containing solution were bigger than those formed in pure chloride solution.

Transition to stable pitting.— For a unidirectional pit with current density of \( i \) and depth of \( a \), the product of \( i.a \) must exceed a critical value to pit grow stably.\(^{30}\) The product of \( i.a \), which is known as the pit stability product, can be considered to evaluate the tendency of transition from metastability to stability.\(^{8,15,16}\) During the pit growth, when the current increases proportionally to \( t^2 \), the current density is approximately constant with time.\(^{24}\) For most of the metastable pits developed during potentiostatic polarization in both solutions, the current was proportional to \( t^2 \) Therefore, it is reasonable to calculate the stability product of metastable pits by multiplying the current density of a metastable pit to its radius just before the repassivation. The cumulative distribution of pit stability products for both test solutions is shown in Figure 10. The median distribution of \( i.a \) was increased from 0.079 mA cm\(^{-1}\) to 0.442 mA cm\(^{-1}\) when the composition of the solution was altered from 0.1 M NaCl to 0.1 M NaCl + 0.01 M S\(_2\)O\(_3\)^{2-}. As can be seen, the stability product of the metastable pits for thiosulfate containing solution is significantly greater than that of 0.1 M NaCl solution.

Plots of the survival probability against the induction time at constant potentials for both Cl\(^-\) and Cl\(^- + \) S\(_2\)O\(_3\)^{2-} solutions are presented in Figure 11. The plots were obtained from the results of potentiostatic polarizations at constant potentials of 280 mV (SCE) and 300...
mV (SCE). The induction time was considered as the moment at which stable pits were formed on the surface. In other words, during polarization at the mentioned potentials, reaching the current density to 0.5 mA cm$^{-2}$ was considered as the criterion for induction time of stable pitting. Once the distribution of induction time is obtained at each applied potential, the survival probability versus induction time as a function of applied potential can be plotted.\(^1\) The survival probability is expressed as:

$$P(t) = 1 - P(E) = 1 - \frac{n}{1 + N} \hspace{1cm} [3]$$

where \(P(t)\), which is known as the survival probability, is the quantity of non-pitted specimens at the time \(t\), \(n\) is the \(n_b\) specimen pitted at time \(t\) and \(N\) is the total number of the specimens examined.

It has been shown that the pit initiation rate (\(\lambda\)) is proportional to the applied potential.\(^1\) The pit initiation rate, or the frequency of pit initiation per unit time, is given by the following equation.

$$\lambda(t) = -\frac{d \ln P(t)}{dt} \hspace{1cm} [4]$$

According to equation 4, the pit generation rate can be determined from the negative tangent of the log \(P(t)\) versus the induction time. As can be seen from Figure 11, for both test solutions the log \(P(t)\) decreased linearly with time. All specimens polarized at 280 mV (SCE) in the presence of 0.01 M thiosulfate were failed in less than 796 s, while at the same potential in pure chloride solution there were specimens that survived up to 6000 s. By increasing the potential to 300 mV (SCE) the induction time was also decreased for those developed in pure chloride solution (Figure 9). Increasing the pits diameter in the presence of thiosulfate implies that, not only the dissolution process took place at a higher rate, but also achieving the critical stability product was more feasible. Although the mean value of the current density within a single metastably growing pit is independent of potential, the distribution of current densities depends on the solution composition.\(^3\) Higher current density indicates higher anodic dissolution of the metal. In the case of the present study, it can be inferred that the dissolution rate from pits formed in \(S_2O_3^{2-}\) containing solution should be higher. Therefore, the higher current density from these pits facilitates reaching the critical value of \(I_a\) necessary for stability.

The frequency of metastable pitting of a stainless steel depends on important features of the solution, such as pH and chloride concentration. The rate of metastable pitting decreases with a decrease in chloride concentration, a phenomenon which is believed to be associated with the decrease of the total number of surface sites available for metastable pitting.\(^3\) Moreover, a decrease in the frequency of metastable pitting occurrence on 304 and 316 stainless steels has been observed in the presence of chromate and molybdate ions.\(^6\) The beneficial influence of these anions on pitting corrosion is believed to be a deactivation of the potential sites for metastable pitting, and hence decreasing the probability of developing stable pits. Similar results have been reported for the role of alloyed molybdenum in reduction of metastable pitting frequency.\(^4\) On the contrary, as Figure 4 shows, addition of 0.01 M thiosulfate ion has a deteriorative effect on the metastable pitting events. In other words, in the presence of thiosulfate ion, the probability of metastable pitting occurrence on unit surface area increased. This implies that thiosulfate promoted the initiation of metastable pitting. This could happen either by decreasing the metastable pitting potential, or by generating more sites for developing metastable pits. The former can be discussed as the thiosulfate decreases the pit initiation potential of stainless steels.\(^6\) Moreover, increasing the aggressive species in solution decreases the metastable pitting potential.\(^3\) The latter could be explained as follow. Some electrochemically active sites, likely sulfide inclusions, are preferable sites for metastable pitting nucleation.\(^1\) Additionally, metastable pit initiation rate strongly depends on the number of the sulfide inclusions in the stainless steels surface.\(^2\) Furthermore, the role of thiosulfate is favored on surfaces containing heterogeneities, i.e. MnS inclusions.\(^8\) Therefore, the presence of thiosulfate increases the rate of metastable pit generation, as Figure 3 shows. In addition, Mott-Schottky analysis has revealed that in the presence of thiosulfate ion the density of defects in the passive layer increases, which according to point defect model, increases the probability of breakdown in the passive layer, and hence, increases the metastable pit initiation.\(^3\)

Based on XPS investigations, the following equation has been proposed for thiosulfate reduction into absorbed sulfur and sulfides on a metallic bare surface.\(^6\)

$$M + S_2O_3^{2-} + H_2O \leftrightarrow M - S_{ad} + SO_4^{2-} + 2H^+ + 2e^- \hspace{1cm} [5]$$

And the growth of the absorbed sulfate with immersion time has been expressed by:

$$M - S_{ad} \rightarrow S_{MxSy} \hspace{1cm} [6]$$

Besides the increase in the number of events, the thiosulfate ion changed the dissolution behavior of pits. In the presence of thiosulfate, the metastable pits possess higher radii (Figure 9). Since the growth of the metastable pit is a measure of the rate at which the metal dissolution takes place, dissolution occurred faster in the presence of thiosulfate ion.

As Figure 8 shows, by addition of thiosulfate, the repassivation time of the metastable pits increased. It has been proposed that the reduced sulfur on the surface of the dissolving metal increases the dissolution rate and prevents repassivation of the growing pit.\(^7\) This is in agreement with XPS analysis that the thiosulfate ion influences in a reduced form.\(^6\) The reduced sulfur can be either a combined sulfide in

**Figure 11.** Survival probability of AISI 316 stainless steel plotted as a function of induction time obtained in 0.1 M NaCl solution with and without 0.01 M thiosulfate ion at applied potentials of 280 mV (SCE) and 300 mV (SCE).
the oxide layer or absorbed sulfur at the oxide/metal interface. Moreover, formation of sulfide islands at the bare alloy surface prevents repassivation. The life time of the metastable pits increases in the presence of thiosulfate. On the other hand, in pure chloride solution the metastable pits repassivate spontaneously after a short period of growth.

As the dissolution of metal takes place within a growing pit, the local pH decreases by hydrolysis of dissolving cations. The concentration of metal cations within the pit anolyte can be used to evaluate the aggressiveness of the pit chemistry. It has been shown that the concentration of metal cations have to be more than ca. 75% of the saturation of the chloride salt to prevent the repassivation of a propagating pit. Below this concentration the anolyte is not aggressive enough, which makes the repassivation inevitable. Additionally, a diffusion barrier for dissolving metal cations is required to maintain the dissolution process. Such diffusion barrier is either perforated cover over the pits mouth, or the pit depth itself. At the early stages of the pit growth, the existence of a perforated cover is necessary to preserve the required aggressiveness of the anolyte to prevent the repassivation of the pit. As the dissolution proceeds, the pit depth becomes large enough to act as a barrier for metal cations to migrate outward from the pit. Metastable pit death takes place when the lacy cover over the pit mouth breaks down before the stable growth stage is reached. Accordingly, the anolyte dilutes and the pit repassivates. As discussed previously, the product of the current density (i) and the radius (a) of a hemispherical pit must exceed a critical value to pit remain stable. Considering the minimum concentration of metal cations required for pit growth, the critical value of the pit stability product can be determined using equation 7.

\[ i.a = \frac{3nF}{2\pi} DC \]  

where \( i \) is the pit current density, \( a \) is the pit radius, \( DC \) is the gradient of cations between the pit interior and the bulk solution, and \( D \) is the diffusion coefficient of metal cations. If the metal cation concentration in the bulk solution assumed to be zero, \( DC \) is the concentration at the base of the pit \( (C_b) \). The value of \( D \) has been estimated to be equal to \( 10^{-5} \) cm\(^2\) s\(^{-1}\). In part I of the present study, by using 50 \( \mu \)m diameter electrodes the values of \( DC \) have been accurately assessed for 316 SS in both pure chloride and chloride + thiosulfate solutions and are summarized in Table I. Comparing the critical pit stability products for test solutions and the distribution of stability product of the metastable pits presented in Figure 10, it is quite clear that the thiosulfate ion facilitated the transition from metastability to stability, not only by increasing the product of pit current density to its depth, but also by decreasing the critical value of \( i.a \) necessary for pit stability. In other words, in the presence of 0.01 M thiosulfate ion, the metastable pits underwent stable pitting because their currents and sizes were high enough, which allowed them to attain the pit stability product easier than in the absence of this ion.

**Pitting potential.**— It has been shown that the early stage of the growth of a stable pit is identical to the growth of metastable pits. The metastable pits that survive beyond some critical age would achieve the state of stable propagation. This phenomenon can be expanded upon the stochastic model as follow:

\[ \Lambda = \lambda \exp(-\mu \tau_i) \]  

where \( \Lambda \) is the nucleation frequency of the stable pits, \( \mu \) is the probability of repassivation, and \( \tau_i \) is the critical age beyond which the pit growth stably. According to this model, the likelihood of stable pitting depends on the probability of activating sites capable of metastable pit growth and the probability of the growing metastable pit to attain stability. From the results presented above, both these probabilities are higher in the presence of thiosulfate ion compared with pure chloride solution.

As discussed previously, the rate of pit generation can be determined from the slope of \( \log P(t) \) vs. the induction time. Decrease in the survival probability in high sulfur stainless steel has been reported. The pit generation rate depends on both the applied potential and the solution composition (Figure 11). Regardless of the solution composition, it is evident that \( \Lambda \) was increased by increasing the applied potential. Also, in the presence of \( \text{S}_2\text{O}_3^{2-} \), the frequency of formation of the metastable pits was increased. In addition, as a result of the acceleration in the dissolution kinetics in the presence of thiosulfate, the current density, radii, and therefore, stability product of the metastable pits were increased. Consequently, the probability of formation of the stable pits was increased.

The increase of the rate of metastable pitting increased the chance of formation of pits capable of attaining the critical pit stability product. On the other hand, metastable pits formed in the thiosulfate containing solution experience higher rates of anodic dissolution, so that the achievement of the minimum metal cation concentration required for the stable growth would be more feasible in the thiosulfate containing solution. Accordingly, the product of these two probabilities resulted in a decrease of the pitting potential of 316 stainless steel in the solution containing 0.01 M thiosulfate ion.

## Conclusions

The effect of addition of 0.01 M Na\(_2\)S\(_2\)O\(_3\) on pitting corrosion of AISI 316 stainless steel in 0.1 M NaCl solution at 25 ± 1°C was studied. In order to elucidate the influence of thiosulfate ion on the pitting corrosion resistance, statistic/stochastic approach was employed. The following conclusions can be summarized according to the presented results:

1. Potentiodynamic polarizations revealed that the pitting potential of AISI 316 stainless steel was decreased in the presence of thiosulfate ion. The median distribution of pitting potential was decreased from 430 mV (SCE) to 344 mV (SCE) by addition of 0.01 M thiosulfate.

2. Potentiostatic experiments showed that the frequency of metastable pitting was increased by addition of thiosulfate. Also, the dissolution kinetics of metastable pits were increased with addition of thiosulfate ion. The pit peak current and the pit growth time were increased in the presence of this ion. In thiosulfate containing solution, compared with a pure chloride solution, the metastable pit radii and the pit stability product were increased, therefore, the achievement of the critical value of stability product required to prevent the repassivation of metastable pits was more feasible. In addition, the survival probability was decreased in the presence of thiosulfate ion, and hence, the rate of stable pit generation was increased.

3. The probability of formation of stable pits was increased in thiosulfate containing solution. The presence of thiosulfate increased the frequency of metastable pitting occurrence and the probability of transition from metastability to stability. As a result, by addition of 0.01 M S\(_2\)O\(_3^{2-}\) the likelihood of generation of stable pits was increased and the pitting corrosion potential was decreased.

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