



Effect of Thiosulfate on Pitting Corrosion of 316SS

I. Critical Pitting Temperature and Pit Chemistry

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In this research, the effect of thiosulfate ion on pitting corrosion behavior of 316 stainless steel was studied. Part I of this work deals with the influence of thiosulfate on the critical pitting temperature of 316 SS in 0.1 M chloride solution and studies the effect of this ion on the pit chemistry. Electrochemical experiments performed in absence and presence of 0.01 M thiosulfate ion revealed that thiosulfate deteriorates the CPT. Pencil electrode studies showed that thiosulfate addition decreases both saturation concentration of metal cations necessary to metal salt precipitate at the pit bottom (C_S) (the value of diffusion controlled limiting current density (i_{Lim}) was decreased) and the ratio of C^*/C_S (where C^* is the critical concentration of metal cations in pit solution essential for a pit to remain stable) while it increases the anodic dissolution rate in a simulated pit solution. Furthermore, scanning electron microscopy showed that the lacy cover formed over the pits mouth has coarser pore structure in the presence of thiosulfate ion.
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Manuscript submitted September 12, 2014; revised manuscript received November 18, 2014. Published November 26, 2014.

The effect of thiosulfate in industrial environments, in particular, in the pulp and paper industries and in refinery equipment, is of importance. Moreover, the role of thiosulfate is not necessarily limited to the cases where thiosulfate exists in the media, but also formed by electrochemical dissolution of sulfide inclusions, where it might be considered as the way that pitting corrosion initiates.^{1,2} However, it is well known that pits in stainless steels would not be stable in pure thiosulfate solutions,³ but it has been proven that thiosulfate and chloride have a synergistic effect in inducing localized corrosion. In other words, small thiosulfate additions are known to enhance localized corrosion in chloride solutions,^{4,5} although the effect of thiosulfate ions does not exist until the chloride ion leads to breakdown of the passive layer.⁵ Using X-ray photoelectron spectroscopy, Duret-Thual et al.⁶ showed that no reduced sulfur could be produced when a well-developed passive film was exposed to thiosulfate containing solution. They also showed that thiosulfate ions or their products of decomposition do not penetrate into the passive film. It is recognized that the internal surfaces of pits are at the pH of around zero.⁷ Thiosulfate ion is quite stable in neutral solutions.⁸ However, under low pH conditions, thiosulfate has thermodynamic tendency for chemical disproportionation and is reduced into adsorbed sulfur and sulfide on the bare metallic surface.⁶ Marcus et al.⁹ showed that formation of adsorbed sulfur (S_{ads}) layer on the dissolving surface of pure nickel leads to a catalytic process that lowers the metal-metal bond energy and reduces the activation energy for metal dissolution. The catalytic effect of adsorbed sulfur was demonstrated later for stainless steels.^{3,9,10} In addition, it is suggested that when molybdenum is present in alloy, the sulfur is unstable as S^0 and is reduced to aqueous H_2S .¹¹ Besides, reduction of $S_2O_3^{2-}$ to SO_4^{2-} may also give hydrogen sulfide (H_2S or HS^-).¹² Iofa et al.¹³ have demonstrated that aqueous hydrogen sulfide is a catalyst for the dissolution of iron.

Most studies of the influence of thiosulfate on the pitting corrosion of stainless steels have used surfaces with many pits. It was suggested that pit propagation stability can be evaluated by one-dimensional analysis.¹⁴ Newman and Franz measured growth rates of single neutral pits in 304SS in a thiosulfate containing solution.¹⁵ Techniques for providing a single corrosion pit have been found to be advantageous for the study of the pit chemistry of stainless steels.^{1,16-19} Moayed and Newman¹⁸ used the pencil electrode method to investigate the effect of sulfate on the critical pitting temperature (CPT) of 904L SS. Using the same approaches, the influence of nitrate ion on the CPT of DSS 2205 has been recently investigated.¹⁹ Regardless of the potential, the transition to stability never happens at temperatures below the CPT.²⁰⁻²² Based on the view that the CPT is associated with the ability to precipitate a salt film, comparing the maximum current density for passivation within the pit solution (i_{max}) and anodic current

density required to maintain acidity via metal ion concentration at the pit solution (C_S) provides a valuable interpretation of the transition from metastable to stable pitting.¹⁴ This theory relates the CPT to the temperature at which the maximum current density is equal to the limiting current density.¹⁴ Further refinement of this CPT theory suggests that sustaining the pit as an open cavity is impossible and this is the undercutting process which makes a pit stable.¹⁶ If surface undercutting at the necessary rate is impossible, continual widening of a pit would lead to repassivation. Temperature influences the kinetics of undercutting process and the rate of diffusion-controlled dissolution. However, in comparison, the former is more affected. At temperatures below a certain temperature (i.e. the CPT), the active dissolution rate at undercutting sites is not sufficient because it would exceed the maximum current density for passivation. Undercutting of surface produces a lacy metal cover,^{16,17} which provides a diffusion barrier, stabilizing pit growth in the early stage.²³ This process is influenced by the addition of anions. On this basis, Moayed explained the influence of sulfate on pit stability.¹⁸

The effect of thiosulfate ion on corrosion resistance of 316 SS is evaluated in related work (part II). In this part of study, the effect of thiosulfate ion on the CPT of 316 SS is explored utilizing electrochemical evaluations. Further studies were performed on the effect of thiosulfate ion on pit chemistry and the correlation between CPT and pit chemistry in presence of dichromate ion using pencil electrode. The role of thiosulfate anions on pit propagation stage is of particular interest.

Experimental

Materials and specimens preparation.— CPT experiments were performed on AISI 316 stainless steel cylindrical samples. Specimens were wet ground to 1200 silicon carbide paper. The exposed surface area was 4 cm². Precise inspections were performed with a stereo microscope after each test to confirm that only definite pitting was occurring. For artificial electrode studies, 50 μm diameter 316 stainless steel wire was used. The composition of the materials used in this study are listed in Table I. Pencil electrodes were prepared by mounting the wire in epoxy resin with one cross-sectional surface exposed to the test solution. The exposed surface was ground to 60 grit. The

Table I. Chemical composition of alloy 316 SS (wt%) for (a) material used for CPT measurements (b) 50 μm dia. wire used for pencil electrode studies.

Metal	C	S	P	Si	Mn	Ni	Cr	Mo	Fe
Bulk alloy	0.05	0.012	0.02	0.4	1.9	10.5	18.1	2.1	Bal.
50 μm dia. wire	0.045	0.015	0.019	0.5	2.1	10.8	18.7	2.05	Bal.

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base solution was 0.1 M NaCl. To study the effect of thiosulfate ion, 0.01 M and 0.03 M thiosulfate in the form of $\text{Na}_2\text{S}_2\text{O}_3$ was added. All solutions were made from analytical grade reagents and distilled water and before each test, the test solution was renewed.

Electrochemical procedures.— All electrochemical polarization experiments were conducted by using a Gill AC automated potentiostat (ACM Instruments). Electrochemical cells were composed of platinum counter electrode and a saturated calomel electrode (SCE) as reference electrode. All potentials quoted in this work refer to SCE. Prior to each test the exposed surface of specimen was washed with deionized water and dried with warm air.

Potentiodynamic polarization measurements were conducted at temperatures between 0°C and 40°C with 5°C intervals by sweeping the potential from 50 mV below the rest potential, at a given scan rate (0.5 mV s^{-1}) until the current density exceeded $300 \mu\text{A cm}^{-2}$. The potential at which the current density abruptly started to increase was considered as the breakdown potential (E_b)²⁴ and the temperature at which the value of E_b decreased dramatically, considered as the CPT.^{18,19}

To employ potentiostatic polarization in CPT determination, the specimens were polarized at 750 mV (SCE) and the solution temperature was increased at the rate of $0.6^\circ\text{C min}^{-1}$ until the current density reached to $300 \mu\text{A cm}^{-2}$. The CPT value was considered as the temperature at which current density began to increase gradually.²⁴

For creating a single corrosion pit, pencil electrodes were exposed to the medium facing upward to avoid venting of the precipitated salt and convection within the pit.²⁵ To study the effect of thiosulfate ion on the pit chemistry at a given temperature, the electrodes were potentiostatically polarized at 750 mV (vs. SCE) in 0.1 M chloride solution containing 0, 0.01, and 0.03 M thiosulfate at 25°C. Subsequently, the potential was reversely swept to the passive region potentiodynamically at a sweep rate of 1 mV s^{-1} . Each test was repeated at least 7 times. In addition, this test was also carried out for 0.1 M NaCl and 0.1 M NaCl + 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ solutions at different temperatures (from 20°C to 40°C at 5°C intervals) to investigate the effect of temperature on C_s (metal cations saturation concentration essential for metal salt precipitation at the pit bottom) and C^* (metal cations critical saturation crucial for a pit to remain stable). Each test was repeated 3 times.

The maximum current density at various temperatures was assessed by potentiodynamic polarization tests using pencil electrode in 5 M HCl as the simulated pit solution^{26,27} at temperatures between -5°C and 15°C at 5°C intervals to study the effect of thiosulfate ion. The specimens were placed in an electrochemical cell facing upwards. After obtaining stable condition polarization curves were recorded at a sweep rate of 5 mV s^{-1} . The aim of selecting electrodes with very small diameter was single pit dissolution establishment.

Pit morphology study.— For SEM investigation, grinding was performed with silicon carbide papers of 60 to 2500 grit size and polishing with $0.3 \mu\text{m}$ alumina paste. After performing potentiodynamic polarization (at the scan rate of 0.5 mV s^{-1}), sample surfaces were rinsed with alcohol and dried. The morphology of lacy cover of pits formed in solutions with and without thiosulfate addition was studied using scanning electron microscopy. Then, the lacy cover was removed ultrasonically and morphology of pits was explored.

Experimental

CPT measurements.— The critical pitting temperature of 316 SS was assessed in chloride solution with and without thiosulfate addition by potentiostatic and potentiodynamic polarization methods.

An example of potentiostatic CPT determination in the presence of various concentrations of $\text{S}_2\text{O}_3^{2-}$ is shown in Figure 1. Considering the CPT as a temperature at which the gradual increase in current density is observed, alloy CPT in 0.1 M NaCl is ca. 7°C . This value seems quite low for CPT of 316 SS, which could be due to relatively high sulfur content of the alloy. The CPT decreases to ca. 3°C and

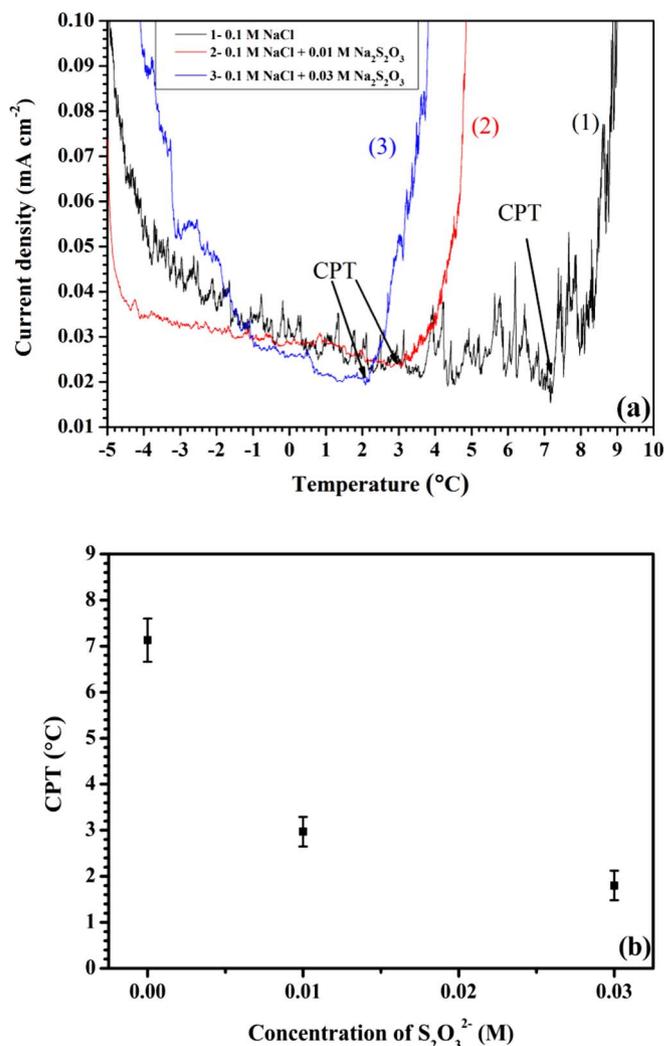


Figure 1. (a) Current density-time response for 316 SS, Evaluation of the CPT by potentiostatic measurement at 750 mV (SCE) in various solutions, temperature increasing rate was 0.6°C s^{-1} . (b) CPT values as function of thiosulfate concentration, obtained from potentiostatic measurement at 750 mV (SCE). Error bars represent 95% confidence limits measured from five experimental tests under identical conditions.

2°C in the presence of 0.01 M and 0.03 M thiosulfate, respectively which indicates the deleterious effect of thiosulfate ion on the CPT of this alloy.

Additionally, potentiodynamic polarization of alloy in pure NaCl and solution containing 0.01 M thiosulfate was performed to determine the CPT. Figure 2a illustrates the anodic polarization curves of 316 SS in 0.1 M NaCl and 0.1 M NaCl + 0.01 $\text{Na}_2\text{S}_2\text{O}_3$ at different temperatures. Apparently, in pure chloride solution, pitting corrosion does not occur at 5°C and current density increment is due to transpassivity. In thiosulfate containing system, an abrupt increase in current density happens at potential well below transpassivity region indicating pitting corrosion at 0°C .

The breakdown potentials obtained from polarization curves are plotted vs. temperature in Figure 2b. It can be seen that the breakdown potential in both solutions decreases with test temperature. The results of potentiodynamic tests show that pitting corrosion occurs in both solutions at temperatures above 5°C . In comparison to 0.1 M NaCl solution, decreased values of E_b were observed from the results of tests performed in 0.1 M NaCl + 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$ solution at any given temperature. At 0°C , the value of E_b was ca. 1265 mV (SCE) and ca. 760 mV (SCE) in the absence and the presence of 0.01 M $\text{S}_2\text{O}_3^{2-}$ ions,

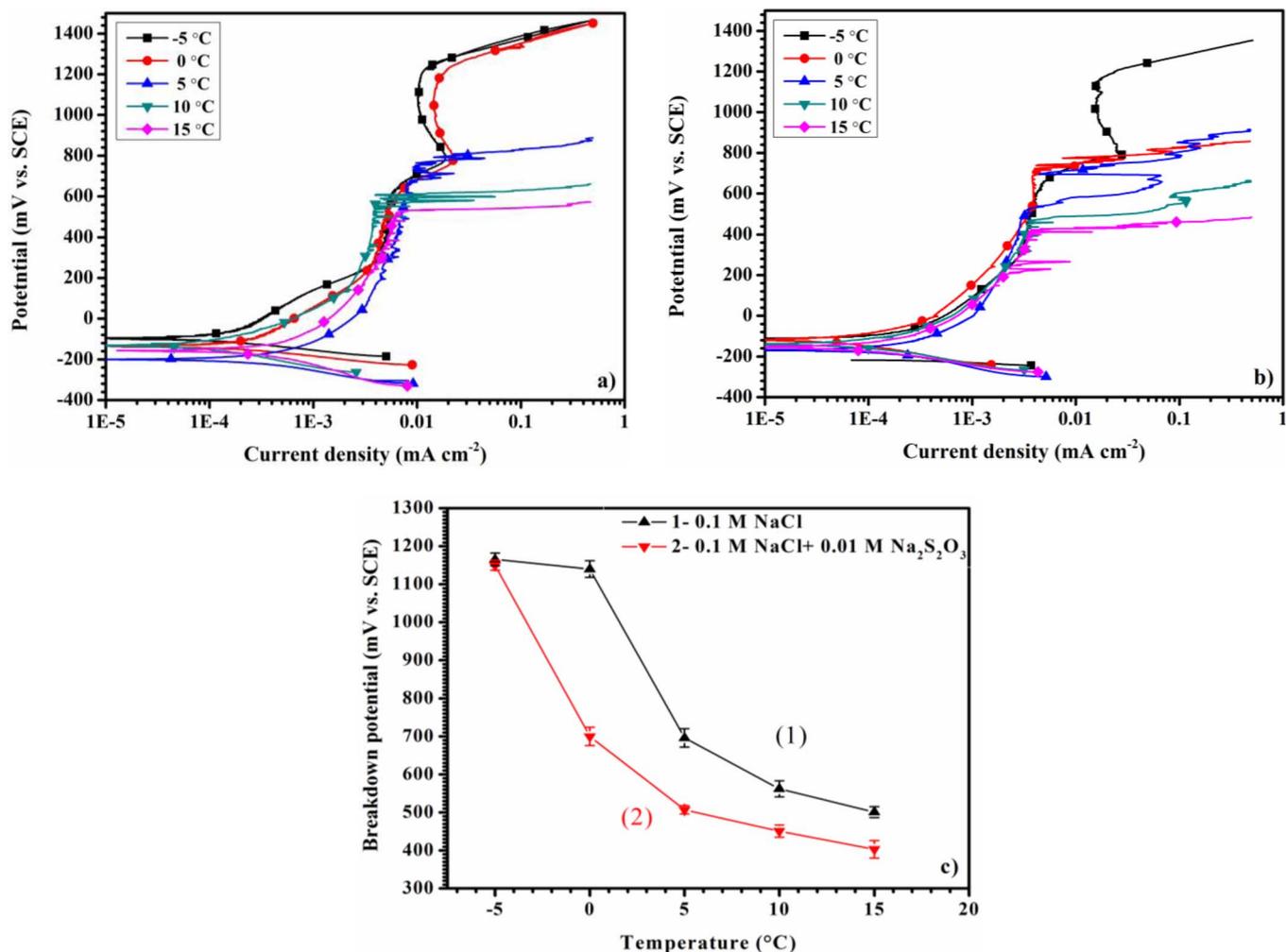


Figure 2. The results of potentiodynamic CPT measurements at various temperatures in chloride solution with and without 0.01 M thiosulfate ion. (a) Potentiodynamic polarization curves in 0.1 M NaCl solution without thiosulfate ion. (b) Potentiodynamic polarization curves in 0.1 M NaCl solution with 0.01 M thiosulfate ion (c) values of the breakdown potential. Error bars represent 95% confidence limits measured from at least five experimental tests under identical conditions.

respectively. The alloy in pure NaCl solution shows passivity behavior in this temperature, whereas pitting corrosion occurs in thiosulfate containing solution. Therefore, we can conclude that CPT of 316 SS in 0.1 M NaCl lies between 0 °C and 5 °C, while in the presence of 0.01 M S₂O₃²⁻ ions the alloy CPT is less than 0 °C. The CPT determined by the potentiodynamic test method yielded slightly higher values in all solutions, possibly because the heating rate was not sufficiently low to allow for the incubation of pits.¹⁴

Influence of thiosulfate on anodic dissolution rate.— The hydrolysis of metal cations decreases the solution pH to a value low enough to sustain the very high rate of anodic dissolution.²⁸ Electrochemical tests in 5 M HCl solution with and without thiosulfate addition could provide valuable information about anodic dissolution kinetics in the solution within the pit. Figure 3 gives the anodic polarization curves in simulated pit solution (5 M HCl solution with and without 0.01 M thiosulfate addition) at various temperatures. The overall behaviour observed in both solutions was the same. It is evident that thiosulfate ion is not influential on the passivity behavior in simulated pit solution. In both solutions, passivation occurs when temperature is below 15 °C. At a temperature of 15 °C passivation under the salt film is likely to occur in both solutions. Fluctuations in current density observed in the plateau region at temperatures above 5 °C is an indicative of alternative activation and repassivation under the salt film.²⁹ Furthermore,

the potentials at which passivity occurs in each temperatures are the same in both solutions.

However, the kinetics of anodic dissolution at all temperatures are affected by thiosulfate addition. The average values of maximum current density (i_{\max}) of the alloy in 5 M HCl at various temperatures are shown in Figure 4. As observed, the maximum current densities in both solutions are increased almost linearly with increasing temperature. The slope of increasing trend of i_{\max} values does not change with temperature and this slope is approximately the same for both solutions. The maximum current density is significantly higher in the presence of thiosulfate at any given temperature.

Influence of thiosulfate on pit chemistry.— Artificial pit experiments were done to make a direct connection with the pit chemistry and the CPT of type 316 stainless steel as a function of thiosulfate concentration.

The current density vs. time behavior obtained from both potentiostatic and potentiodynamic polarization stages was same as that reported before.¹⁷⁻¹⁹ Precipitation of a salt layer was likely to occur at a very early stage in this test. The variation of current density with time in all curves were square root dependent and thus suggests a diffusion limited growth mechanism.³⁰ When metal salt films are present at the bottom of a stable pit, mass transport of products out of the pit controls the corrosion current.^{31,32}

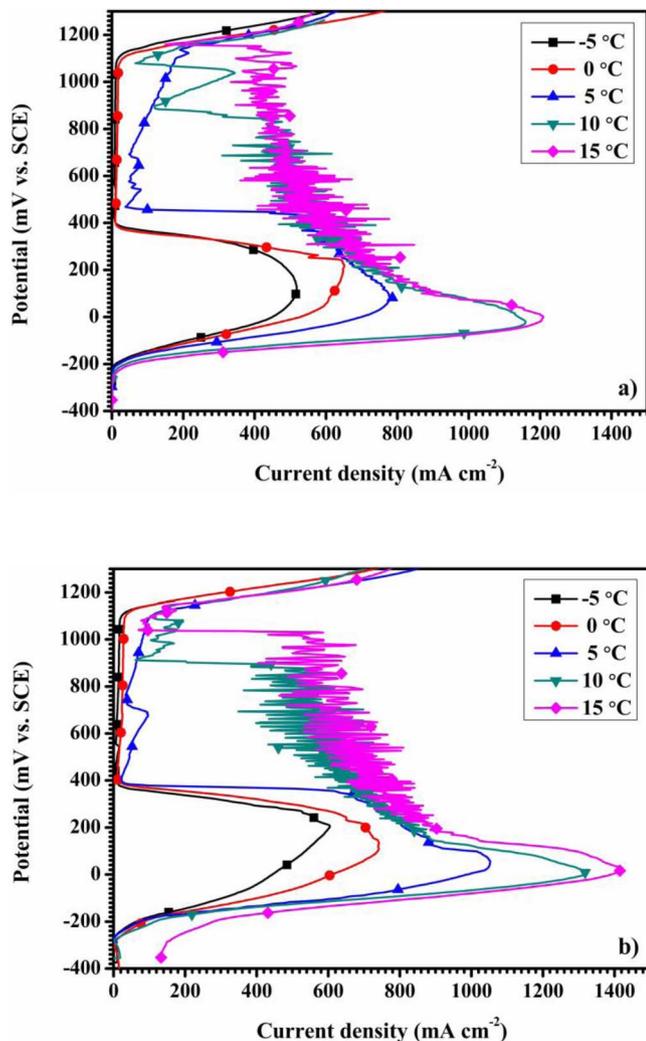


Figure 3. Typical potentiodynamic polarization curves for 316 SS pencil electrode in 5 M HCl media in 0.1 M NaCl after addition of a) 0 M and b) 0.01 M $\text{Na}_2\text{S}_2\text{O}_3$. Scan rate was 5 mV s^{-1} .

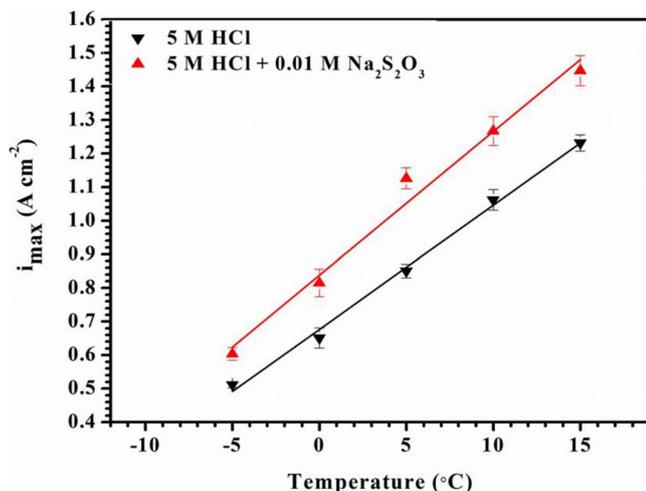


Figure 4. Maximum current densities as function of temperature obtained from potentiodynamic polarization curves of 316 SS pencil electrode in 5 M HCl media. Error bars represent 95% confidence limits measured from at least five experimental tests under identical conditions.

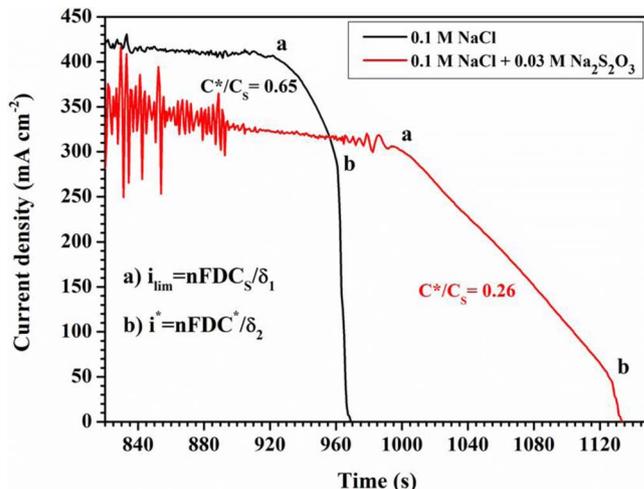


Figure 5. Current density vs. time obtained from potentiodynamic polarization performed in 0.1 M NaCl and 0.1 M NaCl + 0.03 M $\text{Na}_2\text{S}_2\text{O}_3$ solutions using $50 \mu\text{m}$ dia. 316 SS stainless steel. Backscan rate was 1 mV s^{-1} .

For each single pit, the pit depth was calculated by current integration and using Faraday's second law. All evaluations were performed for pits with depth of approximately $200 \mu\text{m}$. On the basis of the assumption that iron, chromium, and nickel dissolve into pit solution as Fe(II), Cr(III), and Ni(II) according to their stoichiometric proportion participated in the bulk alloy,²⁵ a mean atomic weight of ($M_w = 56.2 \text{ gr.mol}^{-1}$), density of ($\rho = 7.9 \text{ gr.cm}^{-3}$), and the valence ($n = 2.16$) were used to calculate the pit depth (δ) using Faraday's second law (equation 1).

$$\delta = \frac{M_w}{nF\rho} \int i dt \quad [1]$$

As shown in Figure 5, the measured current density vs. pit depth (i - t) relations confirmed the effect of $\text{S}_2\text{O}_3^{2-}$ on lowering the limiting current density. Note too, current fluctuation observed during diffusion controlled growth can be explained by local passivation and activation under the salt layer.²⁹ Figure 5 compares the current density-time curves from the backscanning step of artificial pit experiment in 0.1 M NaCl and 0.1 M NaCl + 0.03 M $\text{Na}_2\text{S}_2\text{O}_3$ solutions. As observed, the limiting current density in thiosulfate containing solution is lower than for pure chloride solution.

By comparison of current densities in a given pit depth in diffusion controlled region and based on equation 2, we can conclude that thiosulfate decreases the value of DC_S in the pit solution.

$$i_{\text{Lim}} = \frac{nFDC_S}{\delta} \quad [2]$$

where D represents the diffusion coefficient, and C_S is the saturation concentration.

Figure 6 shows the values of DC_S in the artificial pit as determined from the pencil electrode experiments calculated from equation 2. Because the metal cations diffusivity may be influenced by the thiosulfate concentration, the values of DC_S were presented instead of just the C_S values. Ignoring the effect of thiosulfate ion on the diffusion coefficient, the saturation concentration of metal cations decreases as the thiosulfate concentration increases. Under the assumption that metal diffusivity has a constant value equal to $10^{-5} \text{ cm}^2 \text{ s}^{-1}$,^{17,19,33} the average value of saturation concentration of cations for 0.1 M NaCl solution containing 0 M, 0.01 M, and 0.03 M $\text{Na}_2\text{S}_2\text{O}_3$ is 3.35×10^{-3} , 2.75×10^{-3} , and $2.38 \times 10^{-3} \text{ mol.cm}^{-3}$, respectively.

Moreover, an extended activation/ohmic controlled region is the observed in the curve attributed to 0.1 M NaCl + 0.03 M $\text{Na}_2\text{S}_2\text{O}_3$ (see Figure 5). The critical chemistry, C^* , or the critical ion concentration buildup in the pit electrolyte corresponding to the critical condition for growing pits in the absence and the presence of thiosulfate ion in

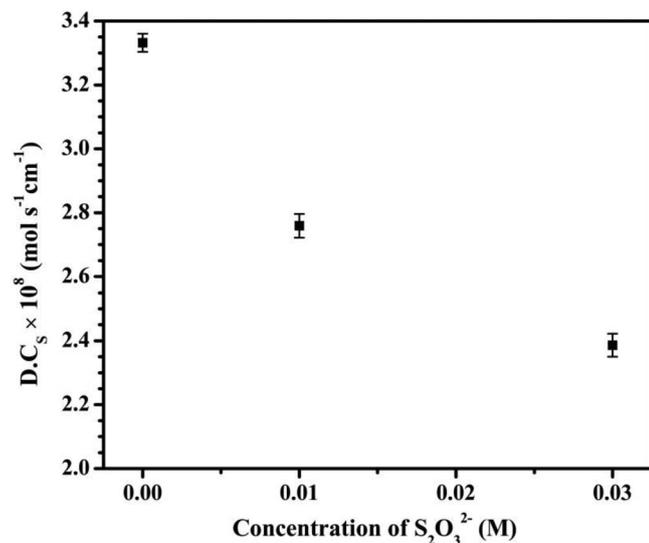


Figure 6. $D.C_s$ values as function of thiosulfate concentration in bulk solution, from pencil electrode studies on 316 SS at 25°C. Error bars represent 95% confidence limits measured from at least five experimental tests under identical conditions.

chloride solution, was determined from the pencil electrode experiment results. When $C < C^*$, immediate activation of pit was impossible during upward scanning. The value of DC^* decreases from ca. $2.62 \times 10^{-8} \text{ mol s}^{-1} \text{ cm}^{-1}$ in pure chloride solution to a value approximately $6.64 \times 10^{-9} \text{ mol s}^{-1} \text{ cm}^{-1}$ in the presence of 0.01 M thiosulfate ion. Addition of higher concentration of $S_2O_3^{2-}$ (i.e. 0.03 M) slightly decreases the determined critical chemistry (to $6.27 \times 10^{-9} \text{ mol s}^{-1} \text{ cm}^{-1}$).

The values of C^*/C_s were calculated in solution with various concentrations of $S_2O_3^{2-}$. As can be seen in Figure 6, the difference between limiting current density and the maximum current density is higher. For pure chloride system, C^*/C_s was ca. 0.65 and dropped to 0.26 in the presence of 0.03 M thiosulfate.

Variation of the pit chemistry with temperature was also evaluated. Figure 7 shows DC_s and DC^* values obtained in both solutions. At a given temperature, values obtained in both solutions are increased, as expected, with the temperature. However, in comparison to critical

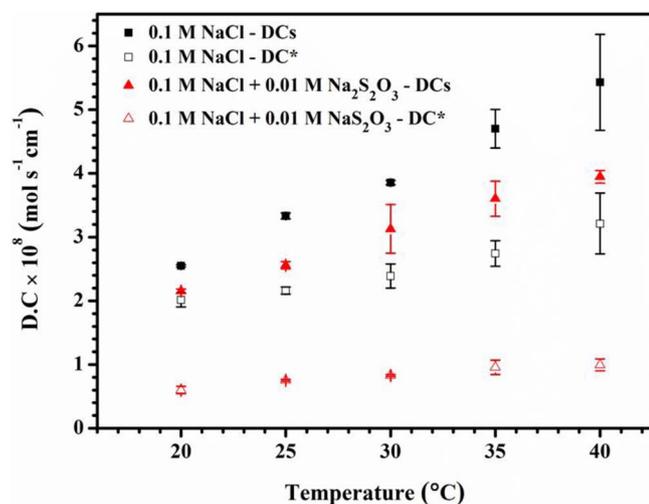


Figure 7. $D.C_s$ and DC^* values as function of temperature, from pencil electrode studies on 316 SS in various solution. Error bars represent 95% confidence limits measured from at least five experimental tests under identical conditions.

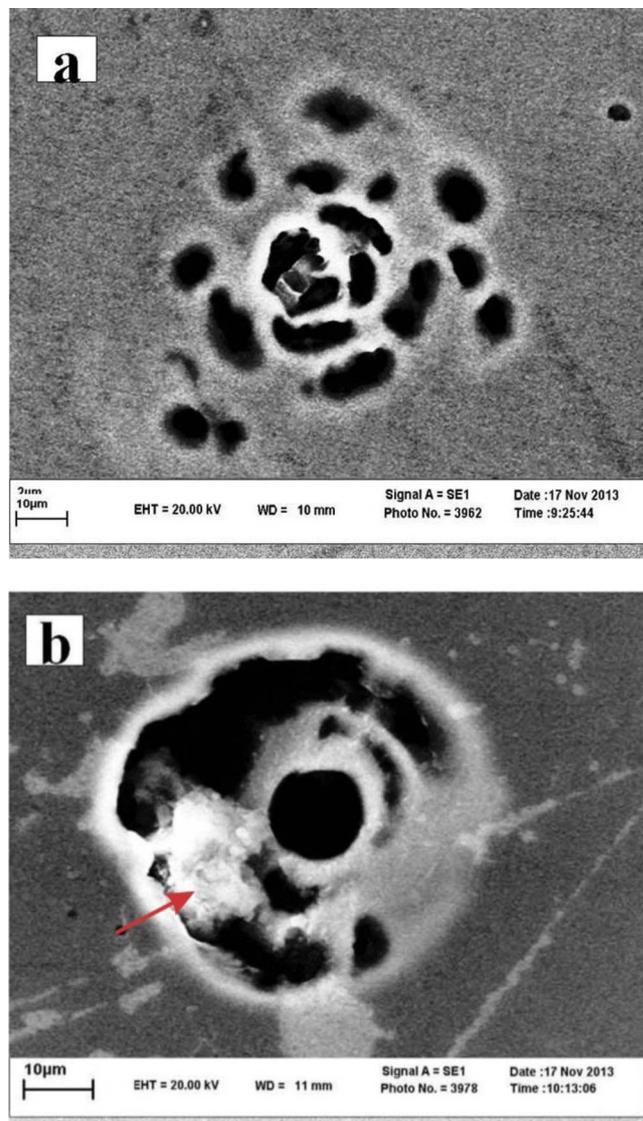


Figure 8. SEM images of a stable pit on 316 SS after potentiostatic test at 750 mV (SCE) at 25°C: (a) in 0.1 M NaCl, (b) in 0.1 M NaCl + 0.01 M $Na_2S_2O_3$ (before ultrasonic cleaning). The arrow indicates iron sulfide deposit, identified by EDS analysis.

concentration of metal ions, the saturation concentration of metal cations is more strongly influenced by temperature. As a result, the value of DC_s at a given temperature is higher than that of DC^* . In addition, as can be seen, at a constant temperature the presence of thiosulfate ion leads to a decrease in the values of both DC_s and DC^* .

Observation of pit cover morphology.— Some samples were prepared for SEM observations by potentiostatic polarization at 750 mV (SCE) at 25°C. The mature pits with the same size were selected to evaluate the pit cover morphology. In the presence of thiosulfate, there was some black material on the pit rims, which could be easily distinguished by naked eye. Newman and Franz identified these black deposits as iron sulfide.¹⁵ SEM examination of the pits revealed the presence of a lacy perforated cover over the pits (as shown in Figure 8a and Figure 8b). It is apparent that the pits formed on the 316 SS surface in 0.1 M NaCl solution were small with constricted openings in lacy cover (see Figure 8a), but those observed in the presence of thiosulfate ion were larger and more open (see Figure 8b). Comparison of SEM images shows that the structure of lacy cover in thiosulfate system is coarser in comparison to pure chloride system.

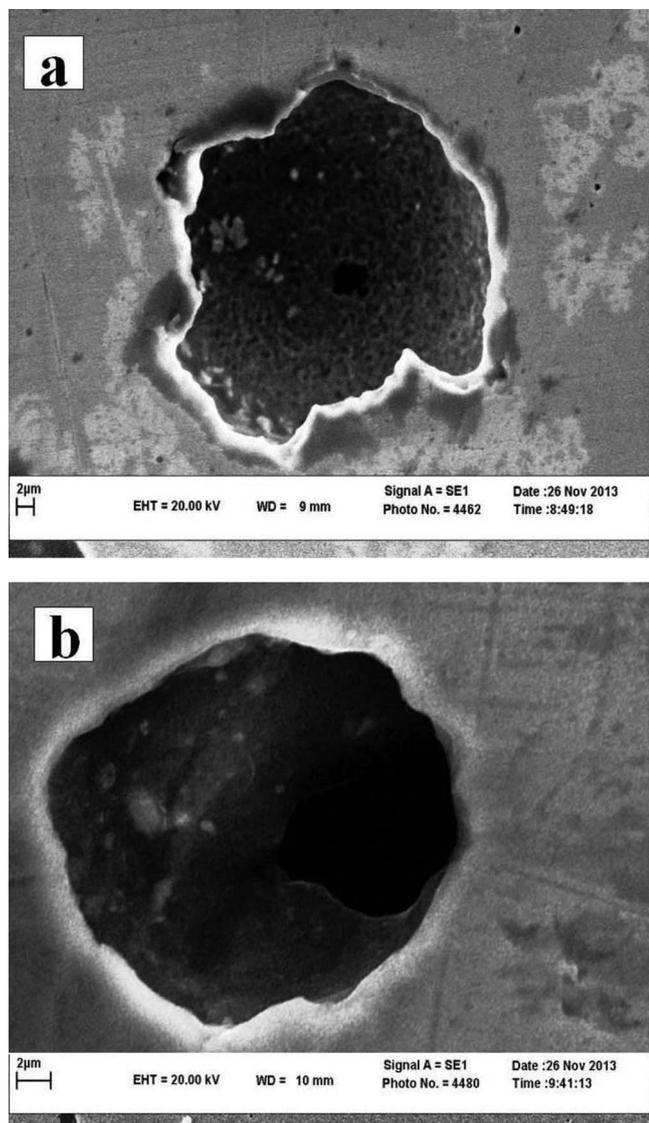


Figure 9. SEM images of a stable pit on 316 SS after potentiostatic test at 750 mV (SCE) at 25°C: (a) in 0.1 M NaCl, (b) in 0.1 M NaCl + 0.01 M Na₂S₂O₃ (after ultrasonic cleaning).

Figure 9a and Figure 9b show the morphology of stable pits after removal of lacy metal cover.

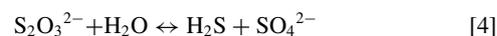
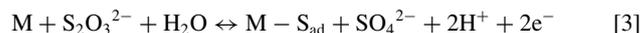
Discussion

Enhanced pitting corrosion by thiosulfate ions in the presence of Cl⁻ has been reported for austenitic stainless steels.^{4,5} A similar behavior was observed for 316 SS in this work. The addition of 0.01 M sodium thiosulfate to chloride solution caused a detrimental effect on the pitting resistance of alloy as revealed in Figure 1. It is believed that thiosulfate ion is reduced to S_(ads) and H₂S_(aq), which eventually reacted with nickel ions (Ni²⁺) produced by metal dissolution. As a result, precipitation of an insoluble sulfide would occur.³⁴ Additionally, the possibility of the reaction of pre-existing metal oxide with H₂S, which leads to formation of sulfide, has been reported. Marcus demonstrated that sulfide causes the retardation of passivity in the environments containing sulfur species.³⁵ The formation of thick sulfide with loose structure sulfide could promote the occurrence of pitting corrosion in the potentials range of 0.15 V to 0.35 V.⁴

Comparison of potentiodynamic curves in simulated pit solution showed that thiosulfate has a significant influence on the anodic polar-

ization behavior of 316 SS alloy in 5 M HCl. Based on the observation of the corrosion behavior in acidic concentrated chloride solution, at all temperatures, thiosulfate enhances the dissolution rate in the active region but does not affect the corrosion potential and the passivation ability of steel.

The enhanced anodic activity of the alloy is not unexpected. The measured current densities in the simulated pit solution (Figure 3 and Figure 4) confirm the catalytic effect of thiosulfate disproportionation products.^{8,34}



When S₂O₃²⁻ is present, the formation of sulfur due to the reduction of S₂O₃²⁻ occurred, which is subsequently reduced to form H₂S. The adsorbed H₂S on the metal surface could cause an increase in metal dissolution. Thus, the higher values of maximum current density in solution containing thiosulfate was consistent with an increase in the anodic dissolution kinetics via catalysis of the anodic reaction¹³ and H₂S could be considered as the most likely catalytic species in this work.

Thiosulfate addition increases the *i*_{max} at any given temperatures. At temperatures below the CPT, because of salt precipitation, enough anodic current density cannot be generated on the alloy surface to maintain pit stability. Therefore, increasing the temperature may compensate for the lack of anodic current density within the pit cavity.³⁶ Since in the presence of thiosulfate ion, the value of *i*_{max} increases, the required current density for pit stability can be reached at lower temperatures. This means that alloy shows lower CPT in the presence of thiosulfate ion.

The results of pencil electrode studies showed that thiosulfate decreases the saturation concentration of metal salts in the pit. This result is consistent with the observations by Park et al.³⁷ who showed that small addition of thiosulfate ion promotes stability of pits via the formation of a salt film. The metal ions solubility and the associated current depend on the pit chemistry within the pit cavity.³² It is shown that pit stability is enhanced by thiosulfate addition. It was mentioned above that the environment inside the pit is too acidic and too reducing to keep thiosulfate stable.³⁸ Thus, formation of metal thiosulfate salts is not expected. The sulfate ions formed according to equation 3 are dissolved in the electrolyte. Pistorius and Burstein³⁹ proposed that the composition of the salt layer precipitated at the pit bottom changed from FeCl₂ in pure NaCl solution to FeCl₂+FeSO₄ in the presence of sulfate. Considering the solubility of FeCl₂ and FeSO₄ salts at 23°C as 4.2 M and 1.8 M, they estimated the solubility of the salt film in a solution containing a mixture of sulfate and chloride ions. Based on the relative solubility of various cations in mixed chloride-sulfate electrolytes given by Silcock,⁴⁰ it has been approximated that the ratio of metal cations solubility in chloride solution containing 0.1 M sulfate to that in the sulfate-free solution is 2:3. Therefore, it is reasonable that sulfate ions formed in the thiosulfate decomposition reaction, which will occur in highly acidic solution of pits, play an important role in lowering the saturation concentration of metal salt in the presence of thiosulfate. A decrease in C_S value facilitates salt precipitation at the pit bottom in the presence of thiosulfate ion. This means that the temperature at which a stable pit could be formed (CPT), is decreased in the presence of thiosulfate ion. The value of C_S is directly related to the value of diffusion limiting current density (*i*_{Lim}) (equation 2), and the value of *i*_{Lim} decreases in the presence of thiosulfate ion.

As mentioned, Salinas-Bravo and Newman,¹⁴ have related the CPT to the pit chemistry. Based on this CPT definition (i.e. the temperature at which *i*_{Lim} = *i*_{max}), the reasons for the deleterious effect of thiosulfate on CPT of 316 stainless steel are the lower limiting current density and also higher maximum current density in presence of thiosulfate ion. These changes leads to a decrease in the temperature at which these two items are equal.

In addition, based on the pit chemistry, another definition of CPT was proposed by Ernst and Newman¹⁶ who calculated the DC_S and DC^* vs. temperature for SS 304 in 1 M NaCl. They showed that, by extrapolating of DC_S and DC^* data to lower temperatures, the CPT could be predicted as the temperature at which $C_S = C^*$. The results of this study indicated that, in comparison to the values obtained in pure NaCl solution, in solution containing thiosulfate the values of DC_S as well as DC^* is lower at any given temperatures (Figure 7). Thus, the decrease in CPT value of 316 stainless steel in the presence of thiosulfate ion could be explained.

Scanning electron microscopy showed that the lacy cover formed over the pits in 0.1 M NaCl solution have constricted openings, but those observed in the presence of thiosulfate ion were more open. It has been shown that the cover over the pits is the residue of the passive film^{23,41} or metal.^{42,43} It is known that the formation of a lacy metal cover on the pit mouth provides a diffusion barrier and maintains the solution at a sufficiently aggressive concentration in small pits.²³ The lacy cover forms by passivation and undercutting processes at the pit rim. The less covered morphology of pits in the presence of thiosulfate ion can be explained by the lower ratio of C^*/C_S in the presence of thiosulfate ion. The rim passivation is reduced at lower C^*/C_S .^{16-18,44} The holes in the cover grow until the cation concentration is close to the critical concentration necessary to attain pit growth. Further dilution of the pit solution leads C to drop below the critical value and passivation occurs in the region near the pit mouth.¹⁶ When thiosulfate is present, dilution of the pit would continue to very much lower concentration of metal cations and therefore coarser holes in pit cover are expected.

Conclusions

1. Polarization results revealed that addition of thiosulfate ion to sodium chloride solution shifts the CPT value of 316 stainless steel to lower temperatures. Potentiodynamic polarization experiments showed that addition of 0.01 M thiosulfate to 0.1 M sodium chloride solution shifts the CPT of alloy from values between 0°C and 5°C to values less than 0°C. Potentiostatic evaluations revealed that the CPT value in 0.1 M NaCl solution is ca. 7°C and addition of 0.01 M and 0.03 M thiosulfate ion to the solution, leads to decrease in the CPT to 3°C and 2°C, respectively.
2. Anodic dissolution in simulated pit solution was found to be increased in the presence of 0.01 M thiosulfate, and higher maximum current densities were detected in thiosulfate containing solution.
3. Determination of pit anolyte by the pencil electrode method revealed that thiosulfate causes a decrease in both saturation and critical concentration of metal salt within the pit solution. A decreased diffusion limiting current density, which is a consequence of decreased C_S , was observed in the presence of thiosulfate.
4. Considering the CPT as the temperature at which i_{Lim} equals i_{max} , the observed decrease in limiting current density and increase in maximum current density in the presence of thiosulfate ion, leads to a decrease the intersection point of these to variations and consequently a deterioration in the CPT.

5. Increased size of the holes in the lacy cover pore size in the presence of thiosulfate can be explained on the basis of the observed decrease in C^*/C_S . In the presence of thiosulfate, pit rim repassivation may become inferior and dilution of the pit would continue to very much lower concentration of metal cations and therefore coarser holes in pit cover are expected.

Acknowledgments

This investigation was supported by the Department of Metallurgical and Material Engineering under grant No. 2/28111 through the Materials Research Laboratory at the Ferdowsi University of Mashhad/Iran.

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