

Pitting corrosion of a Ni-Cr-Fe alloy in chloride and thiosulfate solutions: one-dimensional artificial pit electrode studies

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ABSTRACT

Ni-Cr-Fe alloys such as UNS N08800 (alloy 800) suffer pitting corrosion in chloride (Cl^-) plus thiosulfate ($\text{S}_2\text{O}_3^{2-}$) solutions. This occurs due to a synergistic effect between both ions in a certain range of solution concentration and electrochemical potential. Potentiodynamic tests in 1 M NaCl + 10^{-3} M $\text{S}_2\text{O}_3^{2-}$ solutions evidenced thiosulfate pitting by a peak in anodic current centered near $-0.15 \text{ V}_{\text{SCE}}$. The maximum anodic current of this peak increased with a decrease in potential scanning rate, reflecting the autocatalytic nature of the pitting process and the increased available time for pit growth. A wire of alloy UNS N08800 was embedded in epoxy to study the kinetics of anodic dissolution using the one-dimensional artificial pit electrode. Pits were grown at $-0.16 \text{ V}_{\text{SCE}}$, near the anodic peak observed in potentiodynamic tests, and at $0.4 \text{ V}_{\text{SCE}}$, i.e. above the conventional chloride pitting potential. At $-0.16 \text{ V}_{\text{SCE}}$, the one-dimensional pit was under ohmic drop control. When the wire was polarized to $0.4 \text{ V}_{\text{SCE}}$, the usual transitions from activation, ohmic drop and diffusion control regimes were observed. Thiosulfate increased the rate of anodic dissolution during the activation-controlled regime of pit growth and decreased the transition potential (E_T), the potential where pit growth shifts from activation/ohmic drop control to diffusion control.

Keywords: UNS N08800, artificial one-dimensional pit, localized corrosion, thiosulfate, chloride

INTRODUCTION

Thiosulfate ion ($\text{S}_2\text{O}_3^{2-}$) promotes pitting corrosion in stainless steels and nickel-based alloys, in solutions where an anion of a strong acid is also present.¹ Thiosulfate pitting was mostly studied in chloride (Cl^-) or sulfate (SO_4^{2-}) solutions.¹ One of the main effects of $\text{S}_2\text{O}_3^{2-}$ is the inhibition of pit repassivation. It is thought that this is related to $\text{S}_2\text{O}_3^{2-}$ reduction to adsorbed sulfur (S_{ads}) or sulfide at the pit bottom.² In accord with the first pioneering studies of Newman et al. in 1982³, several investigations⁴⁻⁷ showed that $\text{S}_2\text{O}_3^{2-}$ maximum aggressiveness occurs in certain intermediate ranges of potentials and $\text{S}_2\text{O}_3^{2-}$ to Cl^- (or SO_4^{2-}) concentration ratios.

Ni-Cr-Fe alloys, like UNS N08800 (alloy 800), UNS N06690 (alloy 690) and UNS N06600 (alloy 600) are extensively used in steam generator tubing of nuclear power plants. Localized corrosion of those alloys is related to heat transfer crevices, like those present in the top of the tube sheet and tube supports.⁸ On those zones, the restricted access of refrigerating secondary water causes a local superheating, which favors concentration of impurities in the secondary water. Sulfate ions are a common impurity in the secondary water, and in the reducing environment of the steam generator they can react yielding thiosulfate and other reduced sulfur species.⁹ During refueling or other plant outages, oxygen may ingress into the steam generator, increasing the corrosion potential and favoring localized corrosion processes. Thiosulfate is aggressive for Ni-Cr-Fe alloys even near room temperature, which has motivated recent investigations on this topic.⁴⁻⁷

UNS N08800 can suffer pitting corrosion assisted by $\text{S}_2\text{O}_3^{2-}$ in $\text{S}_2\text{O}_3^{2-} + \text{Cl}^-$ solutions,^{4, 10} even at the open circuit potential (OCP) in deaerated solutions at room temperature.¹¹ In 1 M $\text{Cl}^- + 10^{-3}$ M $\text{S}_2\text{O}_3^{2-}$ solutions at room temperature, Alloy UNS N08800 suffers a pitting corrosion submode close to E_{CORR} , caused by a synergistic effect between $\text{S}_2\text{O}_3^{2-}$ and Cl^- . This submode was named low potential pitting corrosion (LPPC) to differentiate it from conventional chloride pitting or high potential pitting corrosion (HPPC), observed at higher electrochemical potentials.^{10, 11} LPPC is restricted to a narrow zone of electrochemical potential because it requires reduction of $\text{S}_2\text{O}_3^{2-}$ to S_{ads} and also oxidation of metal at pit bottoms to sustain acidification.¹² LPPC has a slower pit growth kinetics than HPPC and it generates hemispherical pits with sulfur-rich corrosion products at pit bottoms.¹⁰ In potentiodynamic curves, LPPC is evidenced by an anodic peak, related to pitting corrosion in this narrow range of potential. HPPC exhibits a conventional breakdown potential, and both submodes are separated by a zone where the alloy exhibits passivity with increasing intensity of metastable pitting as potential is increased. At a higher concentration of thiosulfate, namely 10^{-2} M $\text{S}_2\text{O}_3^{2-}$, the two submodes merge into a single submode and a single breakdown potential is measured in potentiodynamic experiments, similarly to what was previously reported for stainless steels or lower chromium nickel alloys such as UNS N06600 (alloy 600).^{3, 13, 14}

Pit growth experiments with the one-dimensional artificial pit electrode give valuable information about the rate of anodic reactions occurring at pit bottoms.¹⁵⁻¹⁹ Those experiments are useful to determine the critical conditions for pit repassivation and pit stability. Previous studies addressed the effect of thiosulfate on the rate of anodic reactions in UNS S31600 (AISI 316)^{7, 17, 20} and UNS S30400 (AISI 304)²⁰ stainless steels,²¹ but there are no studies reported in the literature for UNS N08800 in $\text{S}_2\text{O}_3^{2-} + \text{Cl}^-$ solutions. Thiosulfate can favor pit growth by the acceleration of the rate of the anodic reaction, by stabilizing the salt film at lower electrochemical potentials^{1,2,13} or by a cathodic-side reaction that yields a layer of sulfur.²⁰ Therefore, the aim of this work is to gain insight into the effect of $\text{S}_2\text{O}_3^{2-}$ on the repassivation behavior and the stability of pits grown at low and high potentials in UNS N08800 using the artificial pit electrode in 1 M Cl^- plus $\text{S}_2\text{O}_3^{2-}$ solutions. Also, the influence of potential scanning rate on the LPPC anodic peak in potentiodynamic curves was studied.

EXPERIMENTAL PROCEDURE

Specimens of UNS N08800 were prepared from a 1 mm diameter wire. The chemical composition of the alloy was obtained by X-ray fluorescence analysis, Table 1. All tested wire specimens were cold mounted in epoxy resin, prepared with 120 grit silicon carbide emery paper and finally washed in high-purity water and ethanol.

Table 1.
Chemical composition of the UNS N08800 wire (in weight percent)

Ni	Cr	Fe	C	Mn	Si	Al	Si	Ti
30.7	20.1	41.8	0.10	1.50	0.64	0.60	0.64	0.64

A conventional three-electrode cell was filled with 100 cm³ of solution and the working electrode was placed face up. The electrochemical potential was measured and is reported against a saturated calomel reference electrode ($E_{SCE} = 0.242 V_{NHE}$). The counter electrode was a platinum wire with an area around 50 cm². Tests were performed at room temperature and atmospheric pressure. Three repetitions were performed for each testing condition. Testing solutions were 1 M NaCl with and without Na₂S₂O₃ additions (10⁻³ and 10⁻² M). Solutions were prepared with analytical grade reagents and ultrapure water (resistivity of 18.2 MΩ.cm at 25°C). Prior to all tests, OCP was measured for 5 minutes.

Cyclic Potentiodynamic Polarization (CPP) tests were performed to characterize the electrochemical behavior of UNS N08800 wire in 1 M NaCl solutions with and without Na₂S₂O₃ additions. The CPP tests started after a conditioning step at E_{CORR} for 5 minutes. The scan started 50 mV below OCP, and it was reversed from anodic to cathodic when the current density reached 0.05 A/cm². The repassivation potential, E_{RP} , was estimated as the potential where the backward scan intersected with the forward scan. Additionally, the potential zone where the anodic peak associated with LPPC was observed was scanned at a rate that was varied from 0.00167 to 10 mV/s.

Specimens of N08800 wire were used to produce artificial one-dimensional (1D) pits of different depths in 1 M NaCl solutions with and without Na₂S₂O₃ additions. Mounted specimens had an exposed area of 0.00785 cm². These tests consisted of several concatenated cycles that started with a pit growth step and ended with a pit repassivation step. The pit growth step consisted of a potentiostatic polarization at -0.16 (LPPC) or 0.4 V_{SCE} (HPPC), for a certain amount of time required to achieve a given dissolution charge (Q). Once the desired Q was reached, the potential was scanned in the active direction at 10 mV/s up to -0.4 V_{SCE}, thus repassivating the artificial pit. During this potentiodynamic scan, the diffusion-limited dissolution current density (i_{lim}), the transition potential (E_T) and the corrosion potential (E_{CORR}) were measured for each Q. The transition potential is defined as the potential where pit growth shifts from diffusion to activation/ohmic control.¹⁹ The pit depth x was related to Q by Faraday's law:

$$x = M_{\text{alloy}} Q / (\pi r_{1D}^2 \rho_{\text{alloy}} n F) \quad (1)$$

where r_{1D} is the radius of the wire, 0.05 cm in this work; ρ_{alloy} is the density of UNS N08800, 7.79 g cm⁻³; n is the average valence of the dissolved metal cations, 2.15 equiv. mol⁻¹ (considering that the main alloying elements are dissolved as Fe²⁺, Ni²⁺ and Cr³⁺); M_{alloy} is the average atomic weight of the alloy, 55.84 g mol⁻¹; and F is the Faraday constant, 96489 C equiv⁻¹. For example, to dissolve 1 mm of UNS N08800 wire ($x = 0.1$ cm), a charge of 23.7 C is required. Once the pit was repassivated, the process was started again by an anodic polarization and the required charge was calculated considering the final depth reached in the previous step.

RESULTS AND DISCUSSION

Figure 1 shows the typical CPP curves obtained for specimens of UNS N08800, in 1 M Cl⁻ and 1 M Cl⁻ plus 10⁻³ M S₂O₃²⁻ naturally aerated solutions. Considering the amount of charge that circulated during the whole potential range of CPP curve (ca. 2 C of total charge) and the dimensions of the wire, the working electrode behaved as a conventional two-dimensional planar electrode, i.e. not as a one-dimensional artificial pit. In 1 M Cl⁻ solutions passive behavior and some metastable events were recorded at potentials between -0.20 and 0.40 V_{SCE}. When 10⁻³ M S₂O₃²⁻ was added, an anodic peak centered at -0.16 V_{SCE} and of approximately 0.15 V in width appeared in the polarization curve. Despite the curve has a similar shape to that observed during the active to passive transition of stainless steel, previous work showed that the anodic peak is associated with LPPC occurrence.¹⁰ Hemispherical pits nucleate and grow in this potential range, and they are special in the sense that they can be repassivated by shifting the potential either in the active or noble direction.¹⁰ Both curves showed similar characteristics at potentials nobler than -0.10 V_{SCE}: a hysteresis cycle and frequent metastable pitting events. These events were associated with conventional Cl⁻-pitting corrosion, called HPPC when the solution contains Cl⁻ + S₂O₃²⁻ to distinguish it from LPPC.¹⁰ The E_{RP} values associated with HPPC estimated from the CPP curves were similar independently of the presence of S₂O₃²⁻ and close to 0 V_{SCE}, Figure 1.

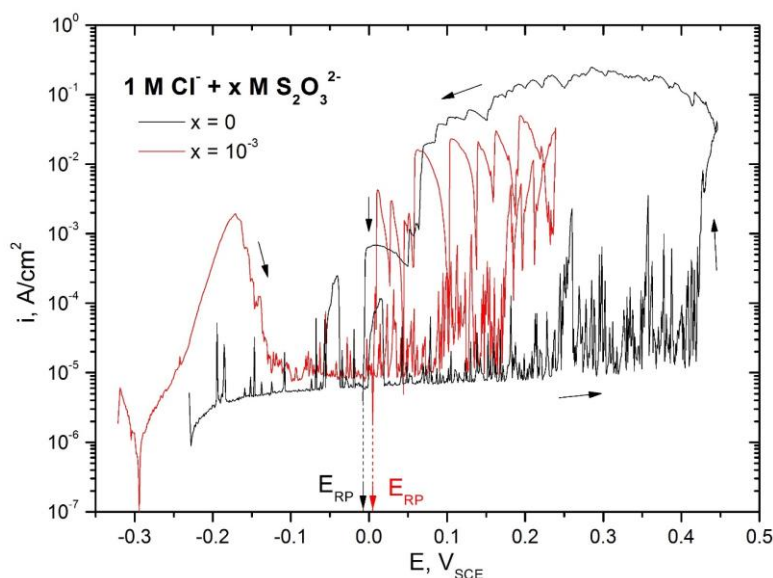


Figure 1: Cyclic potentiodynamic polarization curves obtained in 1 M Cl⁻ and 1 M Cl⁻ + 10⁻³ M S₂O₃²⁻ at room temperature, at a potential scan rate equal to 0.167 mV/s. Naturally aerated solutions.

Figure 2 shows the effect of different potential scanning rates on details of the potentiodynamic curves in the region of the anodic peak observed in 1 M Cl⁻ + 10⁻³ M S₂O₃²⁻ solution (Figure 1). The anodic peak was only observed at 0.00167 mV/s and 0.167 mV/s. The height of the anodic peak increased by an order of magnitude with a two-order-of-magnitude decrease in potential scan rate. This could be related to longer available time in the LPPC growth region and the autocatalytic nature of this pitting process, as shown in potentiostatic transients reported in a previous publication.¹⁰ LPPC requires thiosulfate reduction at pit bottoms that yields a sulfur layer that prevents repassivation. It is expected that the rate of this cathodic reaction will decrease as potential is increased; hence, those pits present the unusual ability to repassivate by an increase in electrochemical potential.^{10, 11, 13} When the scan rate decreased, the repassivation potential of LPPC pits increased, from -0.13 V_{SCE} at 0.167 mV/s to -0.09 V_{SCE} at 0.00167 mV/s. The electrochemical potential at the bottom of the pit is $E = E_{app} - \Phi_{IR}$, where Φ_{IR} is the ohmic drop and E_{app} is the applied potential. It is likely that due to the longer time for pit growth deeper pits were obtained after scanning the potential at a slower rate. Those deeper pits will have an

associated larger ohmic drop, and E_{app} for repassivation must be larger, as shown in Figure 2. At a scan rate of 1.67 mV/s or higher, the anodic peak observed at lower potential scan rates was not observed, rather, a monotonic increase in current density was observed as the potential increased. This is in accord with an increase in passive current density as the potential scan rate increases, as it has been previously reported in other systems.²² The absence of LPPC could be related to long induction times for pit initiation and an insufficient time in the potential region of occurrence of the process.

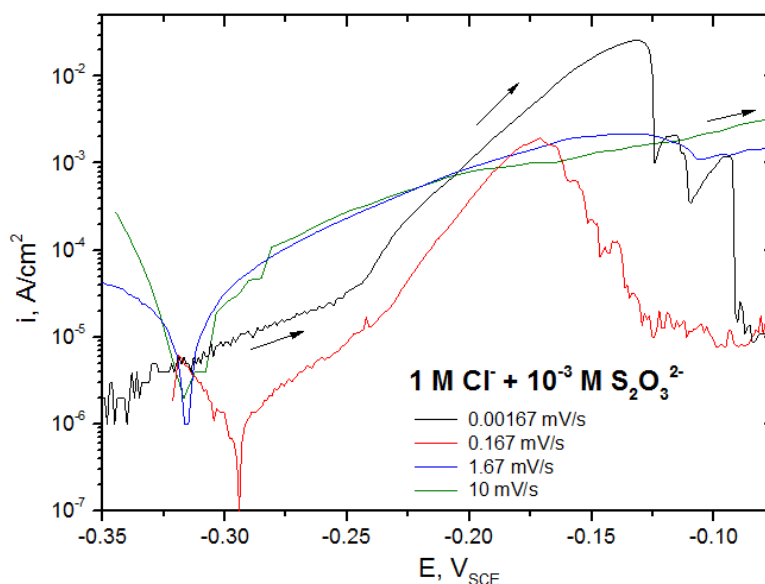


Figure 2: Effect of potential scan rate on polarization curves measured in 1 M Cl⁻ + 10⁻³ M S₂O₃²⁻ solutions, in the potential region of LPPC.

Figure 3 shows the current transients measured during the potentiostatic steps at 0.40 V_{SCE} and -0.16 V_{SCE}, using 1 M Cl⁻ solutions with or without S₂O₃²⁻ additions. The current transients associated with the growth of the one-dimensional pit at 0.4 V_{SCE} showed a maximum in current density followed by a monotonic decrease in current, Figure 3a. This maximum increased when S₂O₃²⁻ was added. For pits grown at 0.40 V_{SCE}, the decrease in current after this maximum is related to pit growth under diffusion control.^{7, 11, 12, 15, 19} During diffusion control, a salt film precipitates at the bottom of the pit and the current density is limited by the rate at which metal cations can diffuse out of the pit.¹⁹ Assuming that the concentration of metal cations in the bulk of the solution is negligible, i_{lim} can be estimated by the following equation:^{15, 16, 19}

$$i_{lim} = n F D C_{sat} / x \quad (2)$$

where D is the diffusion coefficient of metal cations, C_{sat} is the saturation concentration of metal ions and x is the artificial pit depth. In the diffusion control stage, as time increases, x increases and hence i_{lim} decreases, as predicted by equation 2. Figure 3 [a] shows the slow decrease of i_{lim} with time after the current density peak was reached. In 1 M Cl⁻ plus 10⁻³ M S₂O₃²⁻ solutions, higher current density values were measured at 0.4 V_{SCE} than at -0.16 V_{SCE} in the activation/ohmic drop control regions, Figure 3 [a]. The one-dimensional pits grown at 0.4 V_{SCE} were associated to HPPC, whereas those grown at -0.16 V_{SCE} were associated to LPPC, Figure 1. The slower kinetics of pit growth at -0.16 V_{SCE} vs. 0.4 V_{SCE} can be related to a slower increase in current measured in potentiostatic experiments of planar electrodes, reported in a previous publication¹⁰. For 1D pits grown at -0.16 V_{SCE}, there was a modest increase in current density up to ca. 0.1 A/cm², and then it remained almost constant, Figure 3a. A magnified plot shown in Figure 3b shows that current decreases at a slow rate after ~7000 s. As will be discussed below, it is likely that 1D pits grew ohmically controlled at this potential.