

Influence of Temperature, Roughness and Washer Shape on Crevice Corrosion for 254 SMO Alloy

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Abstract. Effect of temperature, roughness and washer shape on 254 SMO alloy was applied to study the susceptibility of alloy's crevice corrosion. XPS measurements have been carried out to detect and define the products which formed on the surface of 254 SMO in 22% NaCl at 30°C at applied potential 600 mVSCE. The formation of Fe, Cr and Mo compounds which play a great role to protect the alloy was found.

1. Introduction

254 SMO is considered to be a very high austenitic stainless steel. It was originally developed for use in seawater and other aggressive chloride-bearing environments. Many parameters, such as temperature and crevice geometry, were used to obtain their effect on crevice corrosion.

An increase in temperature tends to stimulate corrosive attack by increasing the rate of electrochemical reactions [1]. For stainless steels and other alloys that are prone to pitting and crevice corrosion, an increase in temperature tends to facilitate initiation of these types of attack [1]. Many parameters that influence corrosion can vary with temperature: dissolved oxygen solubility, solution properties (e.g. viscosity and ion mobility), ferrous oxidation rate and thermodynamic properties of iron scale (leading to formation of different phases or compounds) [2].

Crevice geometry is one of the important factors in crevice corrosion susceptibility. The two dimensions that characterize a crevice, the gap and the depth or length exert a great deal of control on the initiation and propagation of crevice corrosion, in agreement with that in the other studies [3]. The current flow from the crevice to the outer surface is partially supported by the inward migration on anions such as Cl⁻, which further lowers the pH. In these respects, the mechanisms of the crevice and pitting corrosion are similar. In view of this sequence, the crevice geometry parameters of gap width and depth become important [4]. The corrosion rate within the crevice increased as the crevice dimension decreases [5].



2. Experimental

In this study, the effect temperature, roughness and washer shape on the crevice corrosion of 254 SMO alloy was tested. XPS technique was used to identifying constituent species of corrosion products.

Table 1. Chemical compositions (%wt) of 254 SMO

C	Cr	Cu	Mn	Mo	Ni	N	P	Si	S	Fe
≤0.020	20	0.7	≤1.00	6.1	18	0.20	≤0.030	≤0.80	≤0.010	53.14

A multiple crevice test assembly made of Teflon from Metal Samples Co. Each washer has 20 teeth. A circular disc of 25 mm diameter was cleaned and degreased by ultrasound using double distilled water. The multiple crevice washers were bolted to both sides of each specimen using screw and nuts (made of Titanium). The screw bolt was inserted in a plastic tube, Fig. 1, to protect it from the solution.

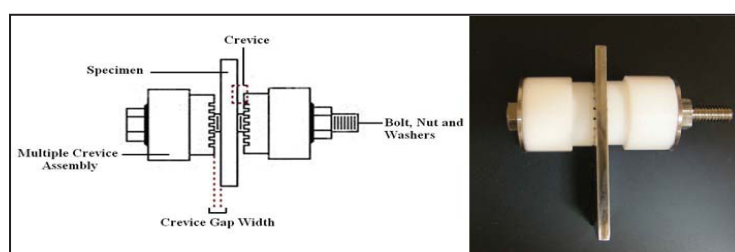


Figure 1. Schematic and photograph of the crevice assembly used in the study.

The corrosion cell contains 1000 ml of aerated 22% NaCl solution. A carbon electrode and a saturated calomel electrode (SCE) were used as a counter and a reference electrodes respectively. Salt bridge with Luggin capillary was used to connect the reference electrode to the corrosion cell. Test solution was used in the salt bridge. The cell was connected to PC14/750 Gamrypotentiostat for the potentiostatic study. Effect of temperature was tested at $E_{\text{apply}} = 600 \text{ mV}_{\text{SCE}}$ at room temperature, 30°C, 40°C and 55°C. SCE was put in the Luggin capillary, not in the direct solution and the value of SCE potential doesn't change in the studied range of temperature. After experiments, SCE impedance was tested using Gamry EIS. Effect of roughness was tested at $E_{\text{apply}} = 400 \text{ mV}_{\text{SCE}}$ at final polishing 600 and 1200 SiC. Effect of washers shape was tested using grooved and flat washers at $E_{\text{apply}} = 400 \text{ mV}_{\text{SCE}}$.

Chemical compositions on 254 SMO surface after the study were noticed by XPS using a multi-technique surface analysis system (MAX200, Leybold).

3. Results and Discussion

3.1 Effect of Temperature

The effect of temperature on crevice corrosion behavior for 254 SMO alloy was studied at four temperatures in 22% NaCl at applied potential $600 \text{ mV}_{\text{SCE}}$ as shown in Table 2. The sample that was tested at room temperature (25°C) did not show any signs of crevice corrosion after three days. Also, it did not show any corrosion activity through current measurements with time (Figs. 2 and 3). The samples tested at 30, 40 and 55°C showed crevice corrosion attacks as shown in Fig.2. It is appeared that the crevice corrosion sets increased with temperature increasing.

Table 2. Crevice Corrosion Susceptibility Results for 254 SMO at Different Temperatures in 22% NaCl at $E_{\text{appl}} = 600 \text{ mV}_{\text{SCE}}$ at Torque Value = 2.5 in lbf

Temp. ($^{\circ}\text{C}$)	Time (ks)	Corrosion attack	Induction period(ks)
Room temp.(25°C)	259.2	No	-
30	259.2	Yes (12/40)	72.13
40	259.2	Yes (34/40)	5.345
55	0.420	Yes (40/40)	0.040

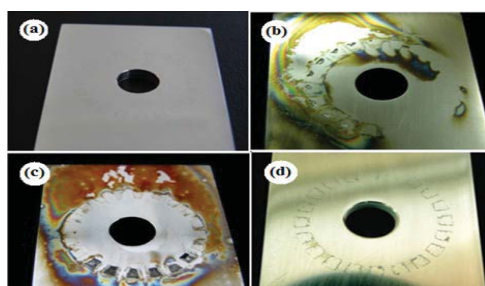


Figure 4. Effect of temperature on crevice corrosion for 254 SMO sample in 22% NaCl at $E_{\text{appl}} = 600 \text{ mV}_{\text{SCE}}$ at torque value = 2.5 in lbf

(a) at room temperature(25°C), (b) at 30°C , (c) at 40°C , (d) at 50°C

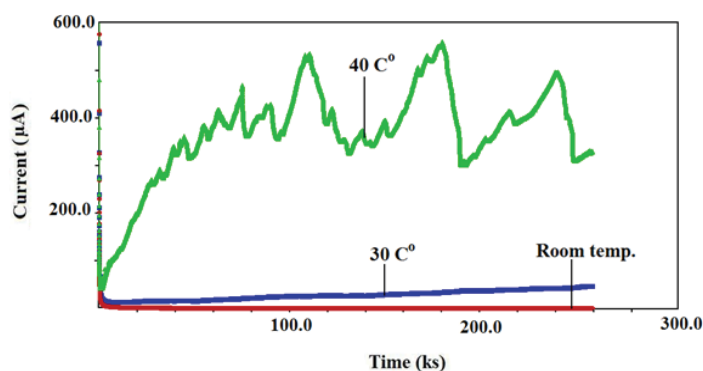


Figure 3. Measured current with time for 254 SMO sample at different temperatures in 22% NaCl at $E_{\text{appl}} = 600 \text{ mV}_{\text{SCE}}$ at torque value = 2.5 in lbf

In the test at 30°C , the current continued to increase gradually in very low rate ($0.1080 \mu\text{A}/\text{ks}$) with time (Fig.3). While at 40°C , the current increased significantly with time at the beginning of the experiment then a noticeable fluctuation in current value is found which is suggested to be due to a competition between formation and deformation of oxide passive film. Dissolution and re-built of the protective films were continued until the end of the experiment. The fluctuation in current value may be due to the competitive mechanism between passivating species $[\text{MOOH}]_{\text{ads}}$, $[\text{MOMOH}]_{\text{ads}}$ and non-passivating species $[\text{MOH}]_{\text{ads}}$, $[\text{MOMCl}]_{\text{ads}}$, $[\text{MOMOHCl}]_{\text{ads}}$ as suggested by [6].

Figure 4 shows the current resulted from 254 SMO corrosion at 55°C . The current increased sharply to $\sim 20.5 \text{ mA}$ in 7 minutes only. Comparing test at temperatures 30°C , 40°C and 55°C , the induction period decreased with the temperature increasing as shown in Table 2.

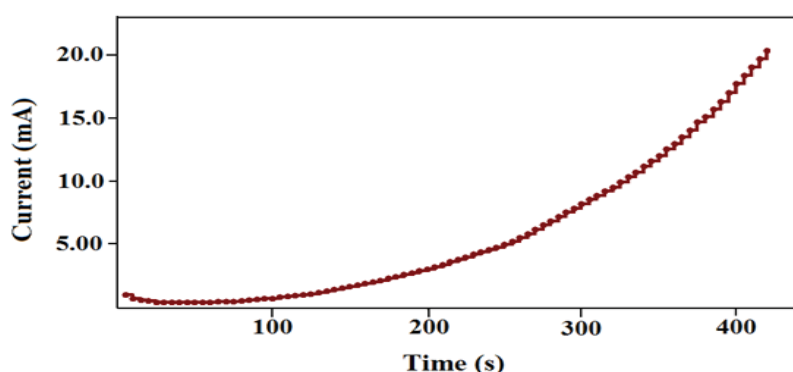


Figure 4. Measured current with time for 254 SMO sample in 22% NaCl at $E_{\text{appl}} = 600 \text{ mV}_{\text{SCE}}$ at 55°C at torque value = 2.5 in lbf

The possibility of a temperature induced change in the protective properties of the passive film on alloy surface, resulting in a reduction in its resistance to breakdown as temperature is increased. This change can be rationalized by taking two possibilities into consideration. First, the porosity of the passive film often assumed to increase with temperature [7]. The increase in porosity with temperature is supported by the fact that Cl^- ions have been found to incorporate into the passive film on stainless steel at high temperatures, but not at lower temperatures Wang et al.[8] have proved that at higher temperatures, the passive film on stainless steel becomes thicker but more porous, leading it to be much less protected. So, at higher temperatures, weaker the protective property of the passive film is found. Second, the passive film may undergo an intrinsic modification of its chemical composition and/or physical structure resulting, for example, in a variation of the density of vacancies or voids in the oxide film [9].

In NaCl solution, 254 SMO can form the passive film. Once a film is formed, the reaction rate between a metal and its surrounding environment will be lower several orders of magnitude. The passive film, probably with a bilayer structure: an inner layer rich in Cr_2O_3 and an outer porous layer abundant with $\text{Cr}(\text{OH})_3$ [10-12]. According to Qvarfort [13], the two steps that a passive film formed in a solution will be, as follows: first chromium-rich passive film dissolves in the solution, and second the chromium inside the stainless steel diffuses to the metal surface and then forms new passive layers. As the temperature rises, the first step is quicker than the second step. So with the temperature increasing, the passive film becomes thinner and leads the film easier to be ruptured. Both possibilities should be considered [7,14].

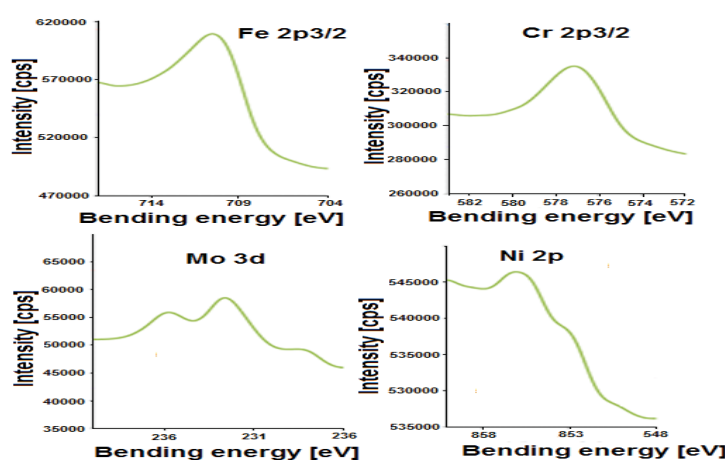


Figure 5. XPS measurement for Cr, Fe, Mo and Ni on 254 SMO alloy surface after corrosion in 22% NaCl at 30°C at $600 \text{ mV}_{\text{SCE}}$.

To define the products of the corrosion, XPS has been carried out to 254 SMO surface after corrosion in 22% NaCl at applied potential = $600 \text{ mV}_{\text{SCE}}$ as shown in Fig. 5. Iron compounds (Fe_2O_3 and FeCl_2),

Chromium compounds (CrCl_3 , Cr_2O_3 and CrOOH), Molybdenum oxide (MoO_3) and Nickel chloride have been detected by XPS measurement. The nature of passive film of stainless steels is a mixture of metal oxides and oxyhydroxides. It has been suggested that Mo^{6+} ions are present in the outer layer. They may act as cation selective species in the outer layer producing a bipolar passive film, with the inner layer which contains Cr_2O_3 being anion selective. Thus, the inward passage of cations produced by metallic dissolution at the metal/oxide interface is not favoured [15,16].

3.2 Effect of Surface Roughness

To study the effect of surface roughness, two tests were performed at same experiment conditions, in 22% NaCl at $E_{\text{appl}} = 400 \text{ mV}_{\text{SCE}}$, but they have different final polishing (600 and 1200 SiC). It was found that the number of crevice corrosion sets with final polishing 600 SiC (17/40) is more than the number of crevice corrosion sets with final polishing 1200 SiC (14/40) as shown in Table 3 and Fig. 6.

Table 3. Crevice Corrosion Susceptibility Results for 254 SMO at Different Surface Roughness in 22% NaCl at $E_{\text{appl}} = 400 \text{ mV}_{\text{SCE}}$ at 30°C at Torque Value = 10 in lbf.

Time (ks)	Final polishing	Corrosion attack	Induction period (ks)
172.8	1200	Yes (14/40)	2.681
86.40	600	Yes (17/40)	3.888

The current for 254 SMO corrosion at final polishing 600 SiC takes more time to increase than it at final polishing 1200SiC, Table 4, and it increased slightly to values more than it at final polishing 1200SiC as shown in Fig. 7. The corrosion rates for 254 SMO corrosion in the two tests were almost the same ($2.8 \mu\text{A/ks}$) but the current in test at final polishing 600SiC continue to increase for longer time.

Table 4. Crevice Corrosion Susceptibility Results for 254 SMO at Different Washer Shape in 22% NaCl at $E_{\text{appl}} = 400 \text{ mV}_{\text{SCE}}$ at 30°C at Torque Value = 10.5 in lbf

Time (s)	washers	Corrosion attack
172.8	Grooved washers	Yes (14/40)
86.40	Flat washers	Yes

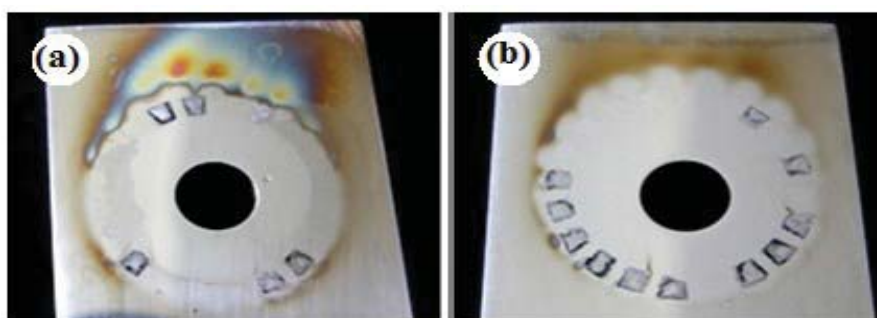


Figure 6. Effect of roughness (final polishing) on crevice corrosion for 254 SMO sample in 22% NaCl at $E_{\text{appl}} = 400 \text{ mV}_{\text{SCE}}$ at 30°C at torque value = 10 in lbf. (a) 1200 SiC paper, (b) 600 SiC paper

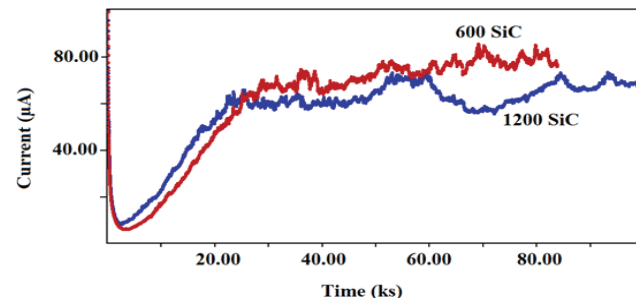


Figure 7. Measured current with time for 254 SMO sample at different final polishing in 22% NaCl at $E_{\text{appl}} = 400 \text{ mV}_{\text{SCE}}$ at 30°C at torque value = 10 in lbf

3.3 Effect of Washers Shape

Flat and grooved washers were used for 254 SMO alloy in 22% NaCl at $E_{\text{appl}} = 400 \text{ mV}_{\text{SCE}}$ as shown in Table 4 and Fig. 8. By comparing the results between the test using flat washers and the test using grooved washers, the sample using flat takes more time to start corrosion. The value of current with time, Fig. 9, for 254 SMO sample corrosion in the test using flat washers is lower than it in the test using grooved washers.

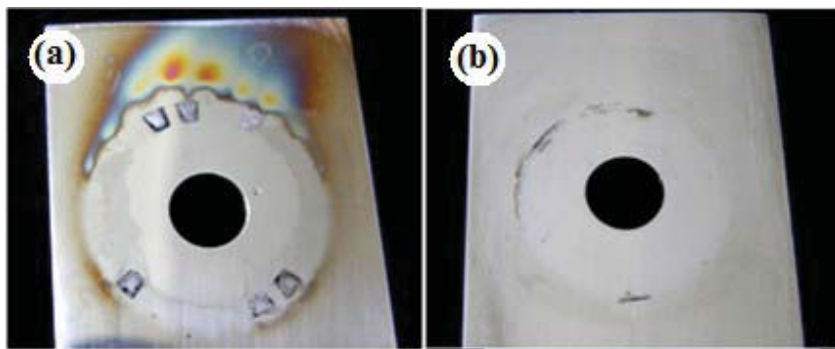


Figure 8. Effect of washers shape on crevice corrosion for 254 SMO sample in 22% NaCl at $E_{\text{appl}} = 400 \text{ mV}_{\text{SCE}}$ at 30°C at torque value = 10 in lbf. (a) grooved washers, (b) flat washers

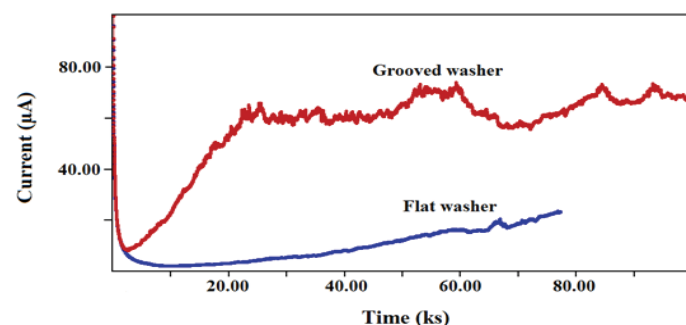


Figure 9. Measured current with time for 254 SMO sample at different washer shapes in 22% NaCl at $E_{\text{appl}} = 400 \text{ mV}_{\text{SCE}}$ at 30°C at torque value = 10 in lbf

In the test using grooved washers, there are 40 locations (40 crevices) where crevice corrosion can initiate during the exposure time in the test. Each crevice may separately initiate crevice corrosion at different times during the study. If crevice corrosion initiated at one location, then stifled may appear in another location, this behavior may give the zigzag shape in the current-time curve. While in the

test using flat washers, a gradual increase and smooth shape are found due to the presence of only one crevice.

The grooved washers have smaller crevice than the flat washers which means that the oxygen depletion and chloride-ion influx increased in grooved washer leading to accelerate the crevice corrosion initiation. Oldfield et al. [17], have shown that the gap dimension of the crevice has a major influence on the development of a critical crevice solution within the crevice and initiation/no initiation in any given crevice.

4. Conclusion

1. Increasing temperature leads to increase the number of corrosion sets and decrease the induction period.
2. The effect of polishing on the corrosion results for the sample (from 600 SiC to 1200 SiC) did not show significant differences in current values but the number of corrosion sets decreases with final polishing increasing.
3. Flat washer has delayed the corrosion initiation comparing with grooved washer.

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