Comparison of the Corrosion Resistance of ATI 2003® Alloy and 316L Stainless Steel

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Abstract

The corrosion resistance of a lean duplex stainless steel, ATI 2003® alloy (UNS S32003), and a common austenitic stainless steel, Type 316L (UNS S31603), were compared in the base and welded conditions. Pitting corrosion resistance was investigated by ASTM G48 Method C in acidified ferric chloride and by cyclic polarization in a 3.5% NaCl solution and an acidified 17.5% NaCl solution. Additionally, general corrosion was examined in boiling 2% sulfuric acid (H_2SO_4). Consistent with previously reported data, the tests show the superior corrosion resistance of ATI 2003 alloy over Type 316L stainless steel. The CCT of ATI 2003 alloy was greater than Type 316L (15-20 vs 0 ºC) and the CPT of ATI 2003 alloy was greater than Type 316L (30 vs. 5 ºC). Welded ATI 2003 alloy, although somewhat less resistance to pitting corrosion than the unwelded material, demonstrated better resistance than Type 316L base metal. Additionally, the pitting corrosion propagation rate of ATI 2003 alloy was two orders of magnitude less than that of 316L stainless steel.

Introduction

ATI 2003® alloy (UNS S32003) is a lean duplex stainless steel with a nominal composition of 21 Cr, 3.7 Ni, and 1.8 Mo (wt. %). This composition was selected to create a duplex alloy with strength similar to 2205 stainless steel (UNS S32205) and a corrosion resistance superior to 316L (UNS S31603) stainless steel. The reduced Cr and Mo contents of ATI 2003 alloy as compared to 2205, provides increased resistance to sigma phase. ATI 2003 alloy is an economical alternative to 316L stainless steel with greater strength and corrosion resistance.

Previous work has documented many of the desirable characteristics of ATI 2003 alloy and will be briefly mentioned here. The development of this alloy has been detailed by Dunn and Bergstrom [1]. Weldability characteristics have been presented by Dunn, Schott, and Bergstrom [2]. In this paper, sulfide stress cracking and stress corrosion cracking testing was performed. Under conditions simulating North Sea formation water, no cracking was observed. The ASME code case (#2503) for ATI 2003 alloy was presented by Grubb along with corrosion test results [3]. The alloy was shown to have a higher maximum design temperature than UNS S31803 duplex stainless steel based on

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superior resistance to embrittlement at high temperatures. Resistance to stress corrosion cracking was shown in boiling 26% NaCl. While 316L cracked during a 1000 hour exposure test, ATI 2003 alloy remained crack-free. In another study, plate samples of ATI 2003 alloy were subjected to the ASTM G48 Method C critical pitting temperature (CPT) tests [4]. The results showed that ATI 2003 alloy passed this test at 5°C while Type 316L failed the same test at 0°C. Woollin and Holmes measured the electrochemical CPT per ASTM G150 for unwelded and welded conditions of the lean duplex and saw a decrease from 40 to 30°C upon welding [5]. Additionally, using an ASTM G48 Method E test modified with an inhibitor, they measured a CPT of 35°C and 10°C for the base and welded conditions, respectively. Ozturk et al. also compared the corrosion resistance of ATI 2003 alloy to 316L stainless steel [6]. ATI 2003 alloy was shown to be far superior in crevice corrosion resistance as measured by ASTM G48 Method B. The same study also demonstrated the resistance of ATI 2003 alloy to general corrosion to be equal to or better than 316L in a wide range of boiling acids including 1% HCl, 10% oxalic, 20% acetic, 20% phosphoric, 10% sulfuric, 10% sulfamic, and 45% formic.

The current paper builds upon previous efforts to compare ATI 2003 alloy with 316L stainless steel by examining both localized corrosion and general corrosion resistance. Repassivation characteristics of the alloys in the welded condition will also be considered.

Experimental

Corrosion testing was performed on ATI 2003 sheet (UNS S32003) and Type 316L sheet (UNS S31603) of a thickness of 2.54 mm (0.100") in the welded and unwelded condition. The compositions are listed in Table 1. Welding was performed by autogenous Gas Tungsten Arc Welding. A nitrogen addition to the purge gas is recommended with autogenous welding of ATI 2003 alloy. To demonstrate a worst case scenario, nitrogen was not used in this study.

Table 1. Alloy compositions

Alloy	Heat	Cr	Ni	Mo	N	C	Mn	P	S	Si	PREN
ATI2003®	826612	21.9	3.7	1.71	0.17	0.017	1.73	0.028	0.001	0.24	30.3
316L	837928	16.73	10.05	2.03	0.04	0.016	1.67	0.031	0.0001	0.37	24.1

PREN = Cr + 3.3Mo + 16N

General Corrosion - Immersion in Sulfuric Acid

The welded sheets were cut into 2.1x5.1 cm (1.0x2.0 inch) test samples with the weld in the longitudinal direction (along the 5.1 cm dimension, through the middle of the width). After cutting, the edges were ground with 240 grit SiC paper. Pickling was performed to remove weld oxide in 8% nitric acid (HNO_3) and 4% hydrofluoric acid (HF) at 65 °C for 5 min. Unwelded samples were pickled as well for equal comparison. An abrasive-impregnated rubber eraser was also used to remove the heat tint along the weld. Following pickling, samples were dried and rinsed with acetone. Two samples were used for each condition (welded and base metal). Testing was based on ASTM G157 [9] using a boiling solution of 2% H_2SO_4. Exposure consisted of three 48 hr periods. An attempt was made to activate the sample at the beginning of each exposure period by scratching the surface with a steel rod. Mass loss was determined after each period. The final mass loss was the average of the three periods.

Crevice Corrosion - Immersion in Ferric Chloride Solution - ASTM G48 Method F

For ferric chloride immersion, samples were prepared as described above for sulfuric acid testing with the exception that some of the samples were 3.8 cm wide to accommodate a large single crevice assembly as described below (nitric acid cleaning).   Per ASTM G48 Method F [7], the samples were immersed in a 6% $FeCl_3$, 1% HCl solution at a given temperature for 24 hours. Three samples were tested for each temperature. The Critical Crevice Temperature (CCT) was determined. In addition to the multiple crevice assembly (MCA) described in ASTM G48, testing was also performed with a single crevice assembly. The single crevice was formed by applying the flat face of a 2.5 cm diameter PTFE cylinder against the metal sample (Figure 1). The crevice was attached using the same bolt assembly and torque as defined in ASTM G48 Method F. The crevice wall surface area of the single crevice was much greater than that of the MCA and therefore provided a more severe test (4.7 mm^2 and 0.7 cm^2, respectively).
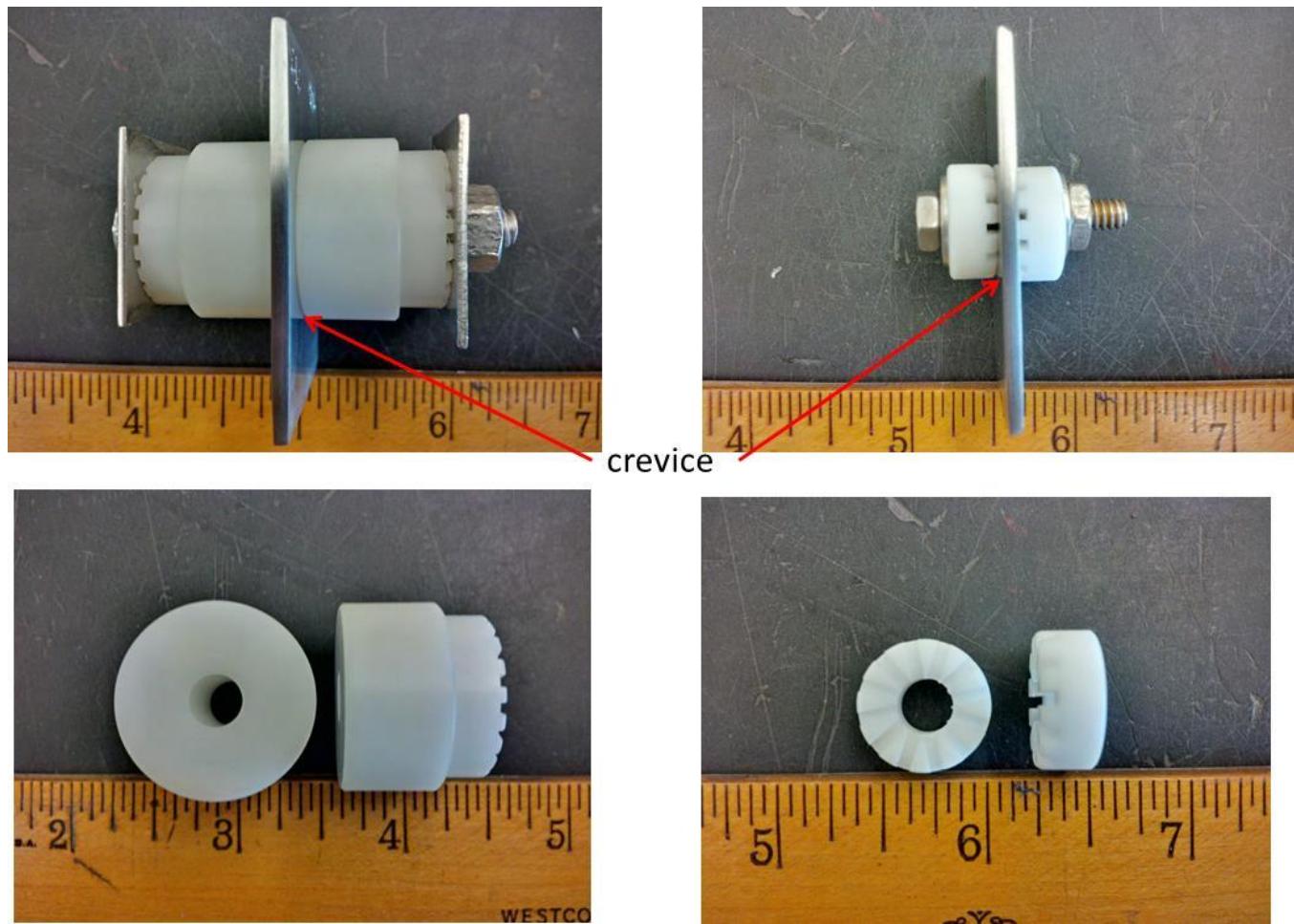

Figure 1 – Crevice assemblies and crevice formers: Single crevice former (left), MCA (right).

Pitting Corrosion - Immersion in Ferric Chloride Solution - ASTM G48 Method C

For ferric chloride immersion, samples were prepared as described above for sulfuric acid testing(nitric acid cleaning).   Per ASTM G48 Method C [7], the samples were immersed in a 6% $FeCl_3$, 1% HCl solution at a given temperature for 72 hours. Three samples were tested for each temperature. The Critical Pitting Temperature (CPT) was determined.

Pitting Corrosion - Cyclic Polarization

Cyclic polarization was used to determine pitting potential and repassivation potential in two sodium chloride (NaCl) solutions. The first solution was neutral 3.5% (0.6M) NaCl, selected to approximate

the chloride concentration of seawater. The second was an acidified solution representative of aggressive conditions that can develop within a crevice: 17.5% (3 M) NaCl acidified to pH 1 with hydrochloric acid (HCl). All testing was performed at ambient temperature.

The test material was cut in 5.1x5.1 cm (2.0x2.0 inch) squares. Following cutting, the edges and faces were ground with 240 grit SiC paper. Welds were ground flat to provide a level surface for proper sealing of the test cell. Because the weld oxide was mechanically removed, a hydrofluoric-based pickling treatment was not required to remove the Cr-depleted oxide. However, the samples were cleaned in 20% HNO_3 for 10 min at 55 °C. After cleaning the samples were rinse in deionized water, dried, and degreased with acetone. The test cell used was the flooded gasket test cell as described in ASTM G150 [8]. This set up was selected to prevent unintended crevice corrosion and to allow a large surface area for adequate representation of the material. The exposed surface area was 5 cm^2. After placing the sample in the test cell, the solution was purged with nitrogen (99.999%) for 30 min. A potentiostat was used to perform a potentiodynamic polarization in the noble direction starting at a potential of -200 mV vs. open circuit. Once the current density exceeded 100 µA/cm^2, the scan reversed direction until the starting potential was reached. The pitting potential was defined as the potential at which the current reached 100 µA/cm^2. The repassivation potential was defined as the potential at which the current decreased to the passive rate (intersection of the reverse and forward scan plots). The occurrence of pitting was confirmed by *ex situ* visual inspection of the sample under 20x magnification. Three samples were used for each condition.

To accurately compare repassivation characteristics of two alloys, it is critical that pitting is initiated under similar conditions. With this point in mind, a modified procedure was used to investigate repassivation. Pitting was initiated pH 1, 17.5% NaCl by a 800 mV potentiostatic hold. This potential was selected from polarization curves as exceeding E_p for both alloys. Following the initiation of pitting (i.e., current density exceeding 100 µA/cm^2), a reverse polarization scan starting at 800 mV was performed to determine E_{rp}.

Results and Discussion

Immersion in Sulfuric Acid

For immersion in boiling 2% sulfuric acid, the corrosion resistance of ATI 2003 alloy was greater than 316L stainless steel. Type 316L showed a corrosion rate of 2.11 mm/yr (83.30 mpy) while the rate for ATI 2003 alloy was only 0.111 mm/yr (4.37 mpy) (Figure 1). Welding produced no decrease in the corrosion resistance of ATI 2003 alloy. Welded 316L stainless steel was not tested in boiling sulfuric acid, but based on previous work, no detrimental impact is expected.
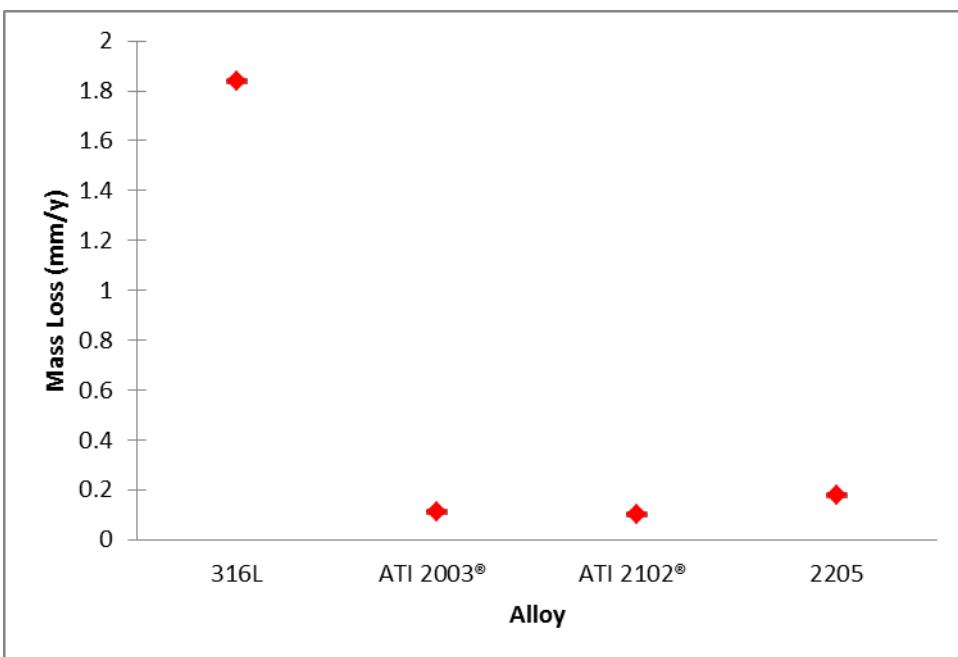
Figure 1. Mass loss of ATI 2003® alloy and 316L stainless steel after exposure to boiling 2% H_2SO_4. Minimum and maximum markers are masked by data points. Duplex alloys ATI 2102® alloy and 2205 shown for comparison.

Crevice Corrosion - Immersion in Ferric Chloride Solution - ASTM G48 Method F

The CCT per ASTM G48 Method F using the specified MCA was determined to be 15-20 °C for ATI 2003 alloy. The exact CCT of Type 316L was not measured due to cooling limitations but was determined to be ≤ 0 °C. A comparison of the mass loss during ferric chloride exposure is show in Table 2. The significant difference in crevice corrosion resistance of these alloys is evident by the 15 °C difference in CCT. The difference is also apparent from visual inspect of the test samples (Figures 3-5). For example, in figure 3, it is apparent that at 10 °C, significant attack of Type 316L has occurred while no corrosion is evident on the ATI 2003 alloy. Surface etching of ATI 2003 does not appear until the solution temperature is 20 °C. A similar trend holds for the single crevice assembly (Figure 4). At 10 °C, deep grooves have formed on Type 316L at the edge of the crevice whereas, only slight etching is apparent on one of the ATI 2003 alloy samples.

The greater severity of the single crevice former is shown in figure 5. At 15 °C, the ATI 2003 alloy samples with the MCA are unattacked with the exception of one small area on one sample. Use of the larger, single crevice former at 15 °C results in crevice corrosion on all three samples. Although the torque, and consequently, the crevice gap, on both assemblies was the same, the larger crevice former has a greater crevice depth. The greater crevice depth promotes more rapid crevice solution acidification and a larger IR voltage drop, both of which drive the crevice corrosion process. The roles of acidification and voltage (potential) drop on the mechanism of crevice corrosion have been discussed in detail previously [10].

Table 2. Mass loss for ferric chloride immersion crevice corrosion tests: Single crevice and MCA

Single Crevice	ATI 2003	316L
Temperature (C)	**Mass loss (mg/cm^2)**	
10	<0.01	3.18
15	0.48	-

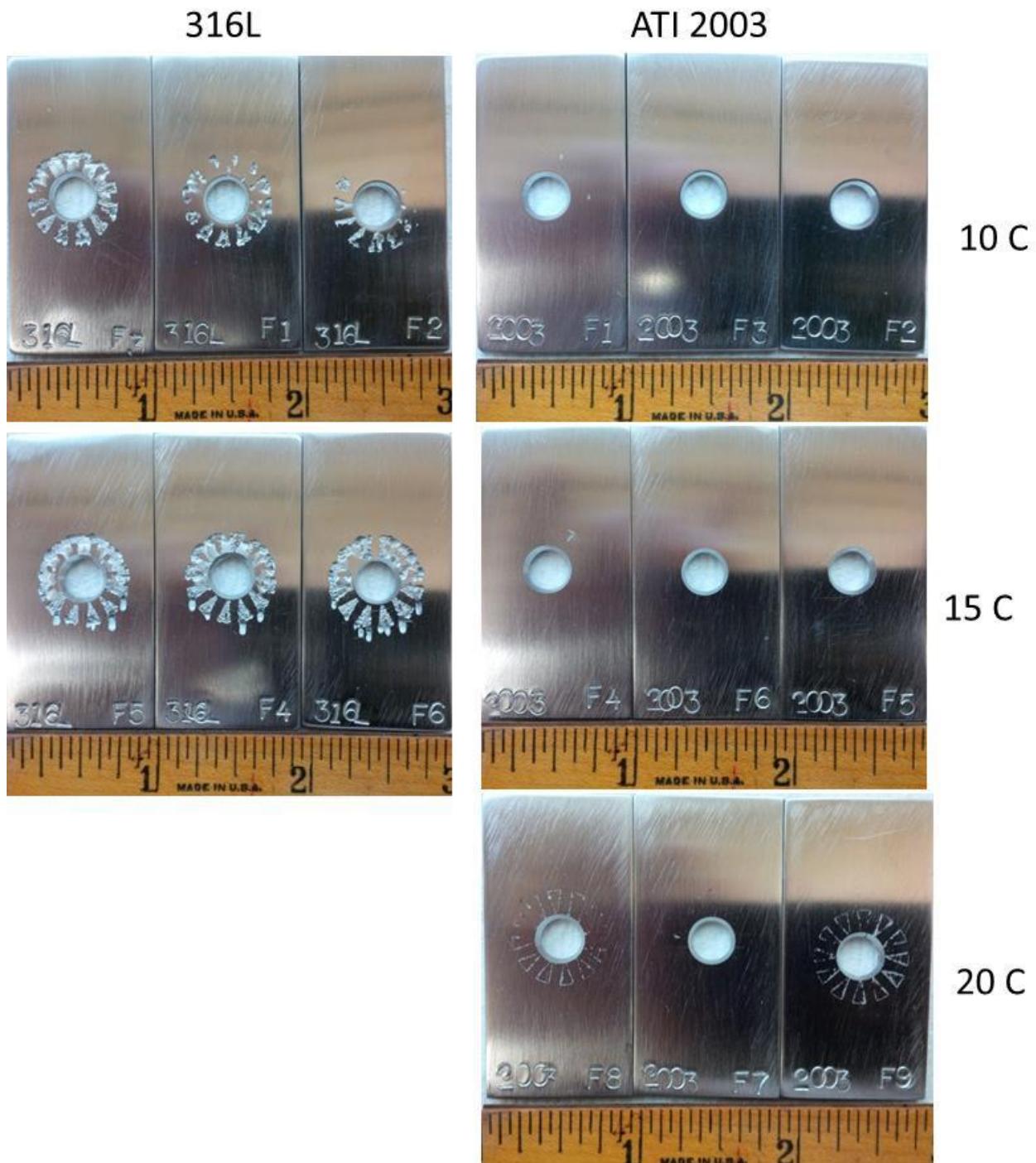| MCA	ATI 2003	316L
Temperature (C)	**Mass loss (mg/cm^2)**	
10	<.01	5.60
15	0.01	11.75
20	0.11	-

Figure 3. ATI 2003® alloy and 316L stainless steel after crevice corrosion testing in acidified ferric chloride using the MCA.
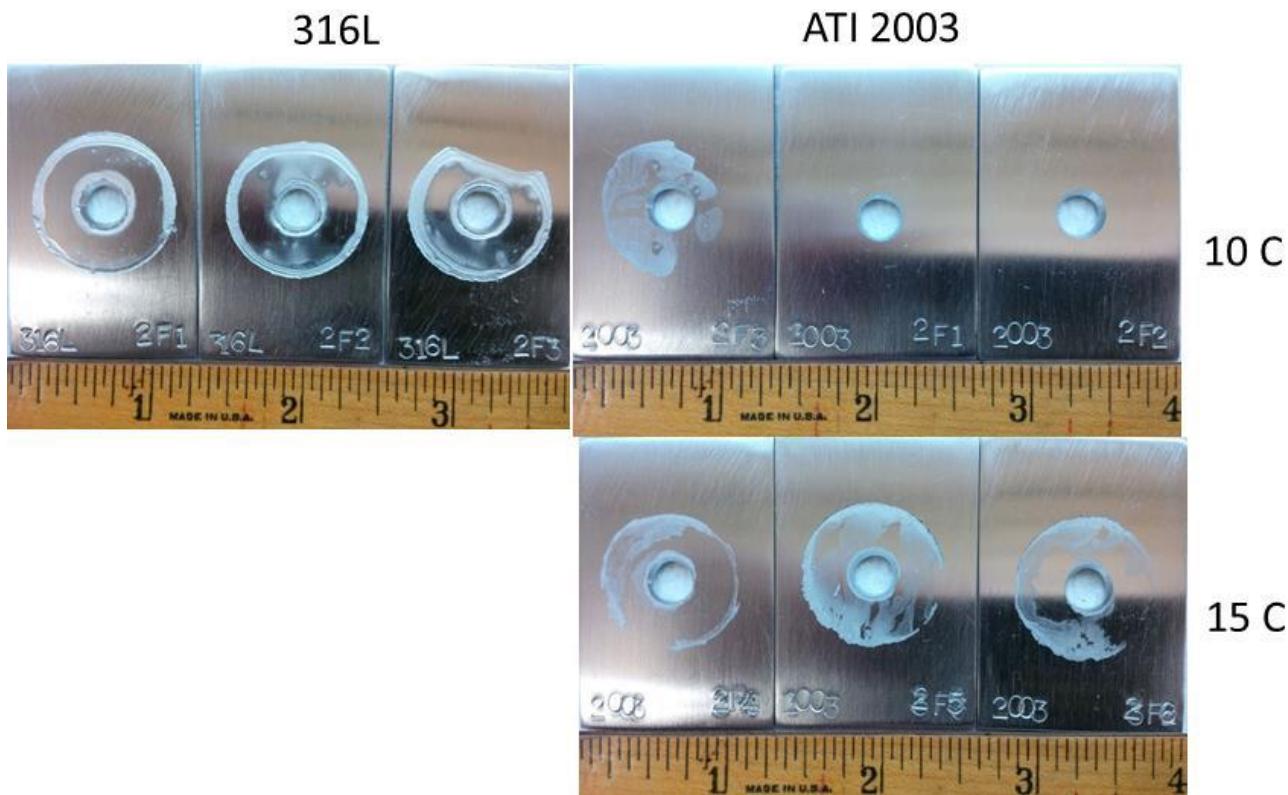
Figure 4. ATI 2003® alloy and 316L stainless steel after crevice corrosion testing in acidified ferric chloride using a single crevice assembly.

Figure 5. ATI 2003® alloy after crevice corrosion testing in acidified ferric chloride showing the difference in attack of the MCA (left) and the single crevice assembly (right) at 15 °C.

Pitting Corrosion - Immersion in Ferric Chloride Solution - ASTM G48 Method C

For all samples tested, the CPT of 316L stainless steel was 5 °C in the unwelded condition and ≤0 °C for the autogenously welded sample (0 °C was the lowest temperature evaluated). ATI 2003 alloy demonstrated a CPT of 30 °C for the base metal and 15 °C for the as-welded condition. The results, summarized in Figure 2, show the superior corrosion resistance of ATI 2003 alloy over 316L stainless steel. The CPT of ATI 2003 alloy is significantly higher than that of 316L. Although the results show a decrease in corrosion resistance when ATI 2003 alloy is welded, the welded condition has a higher CPT than unwelded 316L stainless steel. This is a general observation for as-welded versus base

metal corrosion resistance for the duplex family of alloys. In the case of lean duplex grades which are highly resistance to sigma formation, the lower corrosion resistance in the as-welded condition is mainly due to nitride formation in the HAZ. (For welded pipe and tube that are annealed after welding, duplex grades should perform similarly to base metal in corrosion testing.) Therefore, it is important to note that the negative effect of weld heat input on corrosion resistance is expected to be more significant for thicker material with multipass, unannealed welds. However, previous testing has shown that even in 20 mm thick plate material, the CPT of 2209 filler-welded ATI 2003 alloy without post weld heat treatment is still greater than as-welded 316L stainless steel [4].
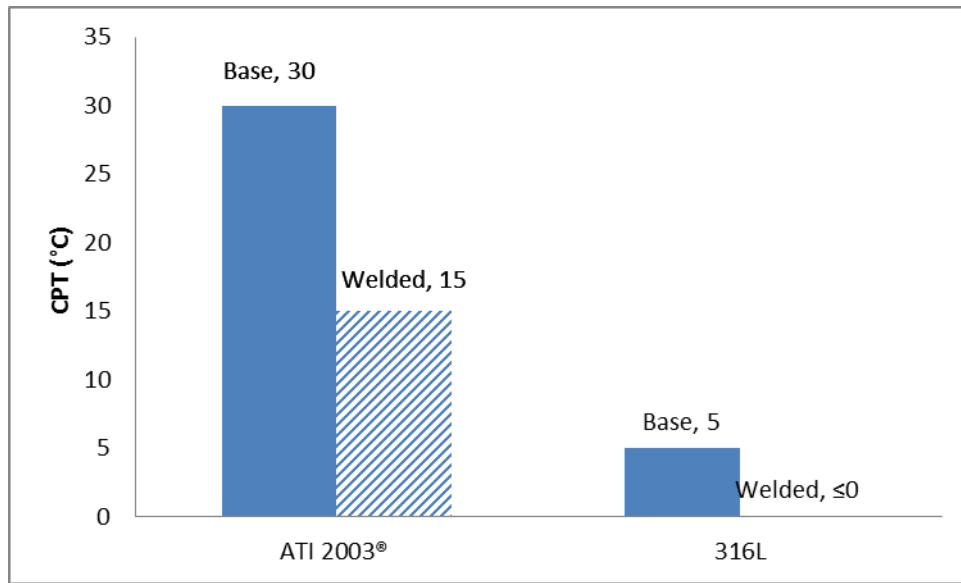

Figure 2. CPT of ATI 2003® alloy and 316L stainless steel per ASTM G48C in the base (unwelded) and welded conditions. Each bar represents three equal results.

Pitting Corrosion - Cyclic Polarization in NaCl Solution

The cyclic polarization tests demonstrate the superior resistance to chloride-induced pitting corrosion of ATI 2003 alloy as compared to 316L material. Representative polarization curves are shown in Figure 3 and 4. In 3.5% NaCl, 316L has a pitting potential, E_p, of 600 mV and a repassivation potential, E_{rp} (the potential at which the high current returns to the passive current value), of 200 mV, whereas ATI 2003 alloy showed no pitting up to a potential of 1300 mV at which onset of transpassive dissolution occurs (Figure 5). In the aggressive simulated crevice solution (17.5% NaCl, pH 1), a similar trend was observed. Pitting occurred on 316L at 220 mV followed by repassivation at -23 mV. No pitting was observed with ATI 2003 alloy up to a potential of 960 mV (onset of transpassive dissolution) (Figure 6).
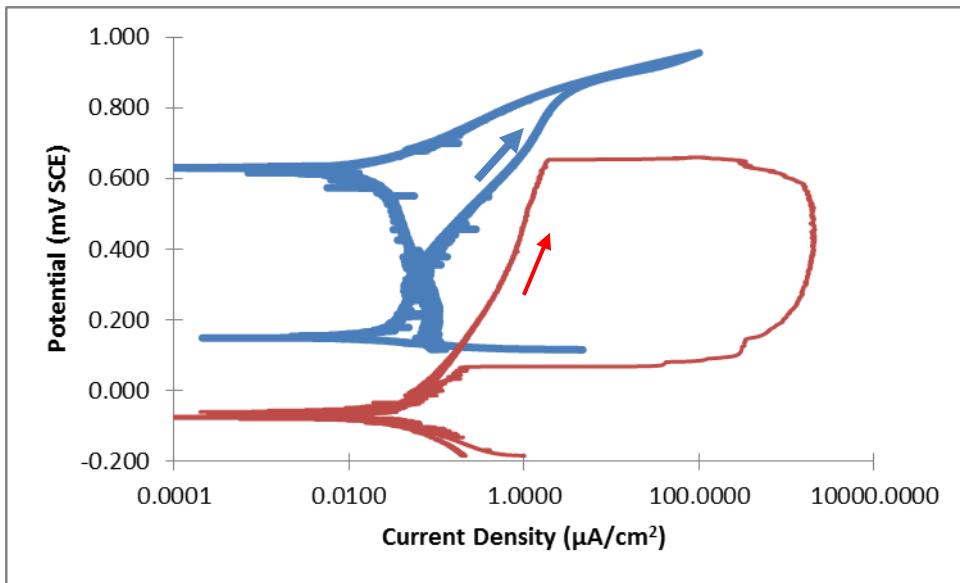
Figure 3. Cyclic polarization curves for ATI 2003$^®$ alloy and 316L stainless steel in 3.5% NaCl. ATI 2003 alloy showed no pitting up to the onset of transpassive dissolution at 1300 mV. Blue, bold line is ATI 2003 alloy. Arrows indicate forward scan direction.
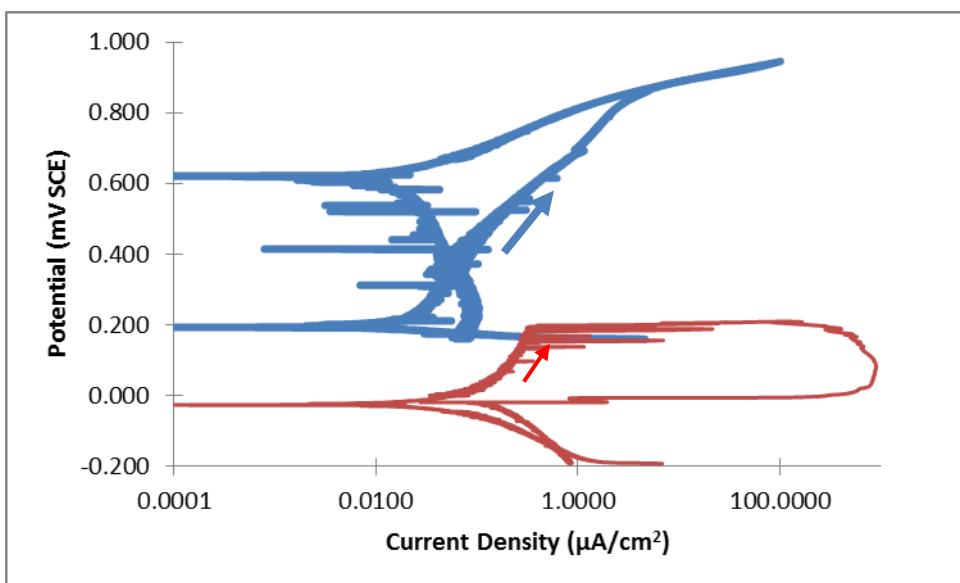

Figure 4. Cyclic polarization curve of ATI 2003$^®$ alloy and 316L stainless steel in 17.5% NaCl acidified to pH 1. ATI 2003 alloy showed no pitting up to the onset of transpassive dissolution at 960 mV. Blue, bold line is ATI 2003 alloy. Arrows indicate forward scan direction.
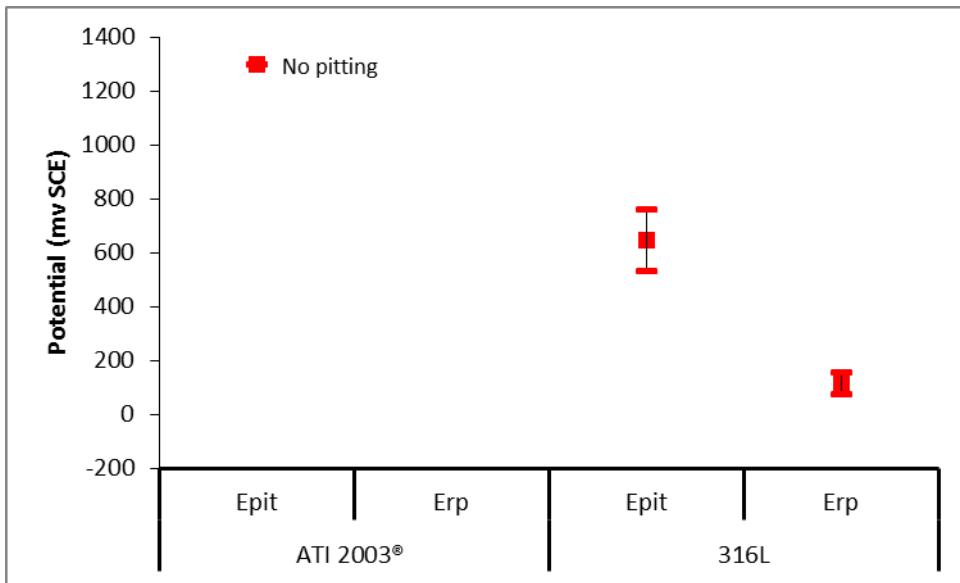
Figure 5. Pitting and repassivation potentials of ATI 2003® alloy and 316L stainless steel in 3.5% NaCl. ATI 2003 alloy showed no pitting up to the onset of transpassive dissolution at 1300 mV.
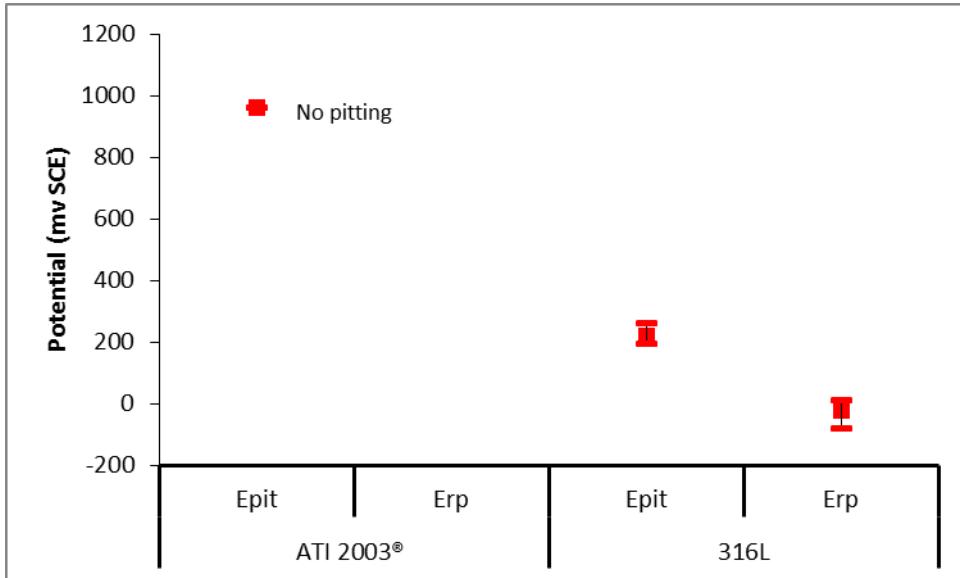

Figure 6. Pitting and repassivation potentials of ATI 2003® alloy and 316L stainless steel in 17.5% NaCl acidified to pH 1. ATI 2003 alloy showed no pitting up to the onset of transpassive dissolution at 960 mV.

For the as-welded samples, ATI 2003 alloy demonstrates superior corrosion resistance over 316L stainless steel. Although a decrease in pitting corrosion resistance is observed for the lean duplex alloy, the reduced resistance is still greater than 316L unwelded. In pH 1, 17.5% NaCl, ATI 2003 alloy has a E_p = 750 mV and repassivation does not occur until the potential is decrease to the open circuit potential (Figure 7). For 316L stainless steel, the welded samples show pitting and repassivation potentials similar to the base material (E_p = 25 mv, E_{rp} = -25 mV). By comparing the two alloys, it is obvious that in the welded condition, ATI 2003 alloy is much more resistant to the initiation of pitting corrosion with E_p = 750 mV, versus 200 mV for 316L. During the reverse polarization scan, after the onset of pitting, in pH 1, 17.5% NaCl, ATI 2003 alloy shows more resistance to pitting propagation and reaches a maximum current of 200 µA/cm^2, versus 1500 µA/cm^2 for 316L. From the cyclic polarization curves, the E_{rp} of ATI 2003 alloy and 316L stainless steel could be defined as -200 mV and -25 mV, respectively. By only considering the repassivation potential ($E_{rp,}$), one could mistakenly

conclude that 316L stainless steel, with a more noble E_{rp}, repassivates more readily than ATI 2003 alloy. However, it is important to recognize that the ATI 2003 alloy shows a wide range of passivity over a potential range that results in pitting of 316L stainless steel (from 200 to 750 mV).

To accurately compare repassivation characteristics of two alloys, it is critical that pitting is initiated under similar conditions. With this point in mind, a modified procedure was used to investigate repassivation. Pitting was initiated pH 1, 17.5% NaCl by a 800 mV potentiostatic hold. This potential was selected from polarization curves (Figure 7) as exceeding E_p for both alloys. Following the initiation of pitting (i.e., current density exceeding 100 µA/cm^2), a reverse polarization scan starting at 800 mV was performed to determine E_{rp}. The results of the reverse cyclic scans are presented in Figure 8. Under these test conditions, 361L stainless steel does not repassivate during the reverse scan. The current remains active until the corrosion potential is reached at which point the current becomes cathodic. For ATI 2003 alloy, there was a wide range of repassivation behavior observed among the tested samples. Generally speaking, as the potential was decreased, some degree of repassivation occurred, with currents ranging from ~ 5 to 500 µA/cm^2. In one case, no pitting occurred during the potentiostatic hold (up to one hour) and passivity was observed during the entire reverse scan. All of the measure curves for ATI 2003 alloy demonstrate a greater resistance to pitting corrosion and greater tendency for repassivation as compared to 316L stainless steel.

An important difference between the curves is the magnitude of the active current. The peak current of 316L stainless steel exceeds that of ATI 2003 alloy by two orders of magnitude. In other words, although the dependence on potential for repassivation is the same for the two alloys, the propagation rate during the pitting process is much greater for 316L stainless steel in the environment evaluated. Examination of the test samples following the polarization scan confirms the large difference in propagation rate (Figure 9).
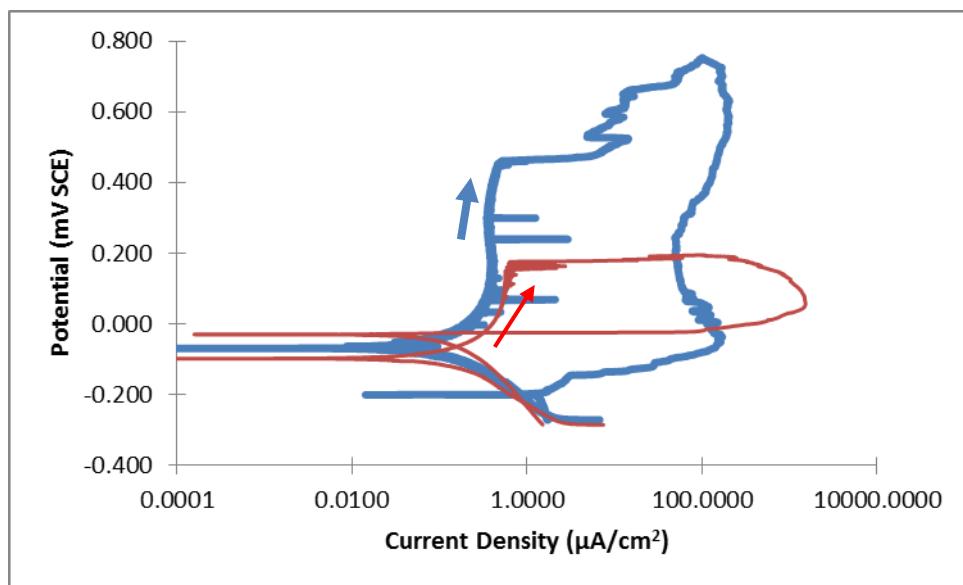

Figure 7. Cyclic polarization curve of welded ATI 2003$^®$ alloy and 316L stainless steel in 17.5% NaCl acidified to pH 1. Bold blue line is ATI 2003 alloy. Arrows indicate forward scan direction.
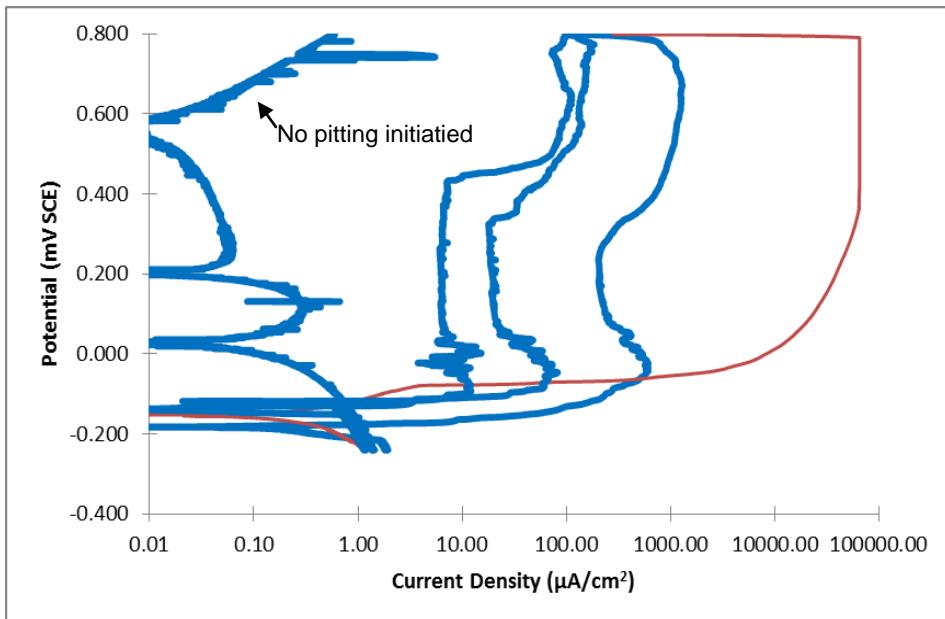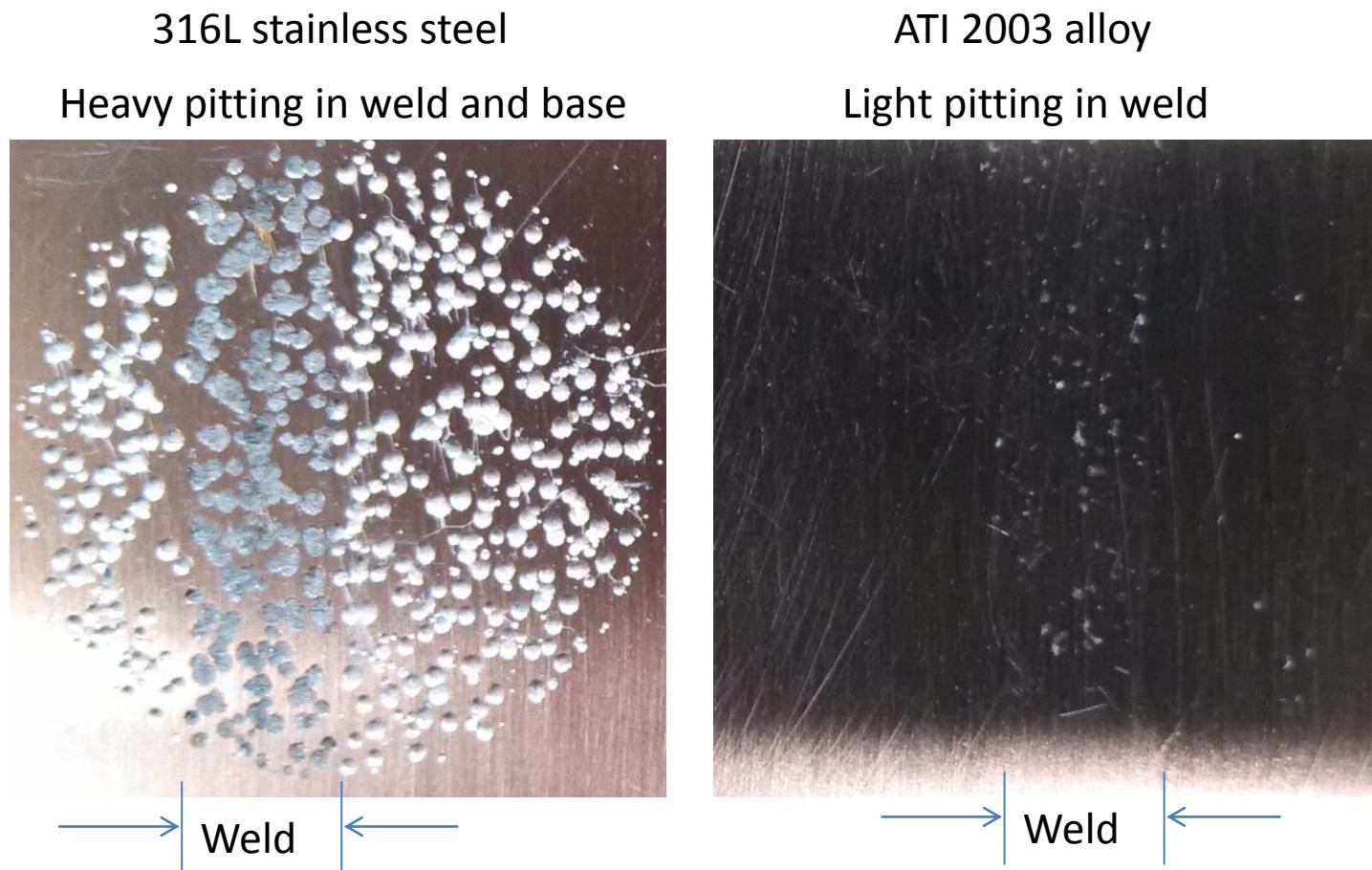
Figure 8. Reverse polarization scan of welded ATI 2003® alloy and 316L stainless steel following a potentiostatic hold at 800 mV to initiate pitting in 17.5% NaCl acidified to pH 1. Bold blue lines are ATI 2003 alloy. Vertical line for 316L reflects the current exceeding the current limit (300 µA) of the potentiostat.

316L stainless steel
Heavy pitting in weld and base

ATI 2003 alloy
Light pitting in weld

Figure 9. Comparision of pitting propagation of welded ATI 2003® alloy and 316L stainless steel following a reverse polarization scan in 17.5% NaCl acidified to pH 1 starting at 800 mV.

Conclusions

The corrosion resistance of ATI 2003® alloy was demonstrated to be superior to 316L stainless steel in tests of localized and general corrosion. This conclusion, which is consistent with previous work, is based on the following observations.

In the unwelded condition:

1. The resistance of ATI 2003 alloy to corrosion in boiling 2% H_2SO_4 is significantly greater than that of 316L stainless steel (0.111 vs. 2.11 mm/yr).

2. The CCT of ATI 2003 alloy is greater than that of 316L stainless steel (15-20 vs. 0 °C).

3. The CPT of ATI 2003 alloy is greater than that of 316L stainless steel (30 vs. 5 °C).

4. In 3.5% NaCl at room temperature, ATI 2003 alloy does not pit, while 316L stainless steel has a pitting potential of 600 mV.

5. In pH 1, 17.5% NaCl at room temperature, ATI 2003 alloy does not pit, while 316L stainless steel has a pitting potential of 220 mV.

In the welded condition:

1. The CPT of ATI 2003 alloy is greater than that of 316L stainless steel (15 vs. 0 °C).

2. In pH 1, 17.5% NaCl, ATI 2003 alloy has a pitting potential of 750 mV, while 316L stainless steel has a pitting potential of 200 mV.

3. Under conditions selected to initiate pitting in ATI 2003 alloy, 316L does not repassivate during cyclic polarization. ATI 2003 alloy shows varying degrees of passivation. The pitting propagation rate of 316L stainless steel is two orders of magnitude greater than that of ATI 2003 alloy.

Noteworthy aspects of the experimental method of this study are:

1. Based on ASTM G48 Method F, a single crevice former with a greater surface area and crevice depth was demonstrated to be more aggressive than the specified multiple crevice assembly (MCA).

2. A flooded-gasket test cell was used to avoid unintended crevice corrosion while determining pitting characteristics.

3. Repassivation characteristics of the two alloys were determined under identical pitting initiation conditions.

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4. Non-ideal weld parameters were used for production of the ATI 2003 alloy weld samples in order to simulate worst case field weld practices.

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