

Evaluation of Girth-Welded 22Cr Duplex Stainless Steel Piping for Susceptibility to Environmentally Assisted Cracking (EAC), Pitting, and General Corrosion in a Sour Environment

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ABSTRACT

The results of a stress corrosion cracking (SCC) qualification study of twenty-four heats of girth-welded 22Cr duplex stainless steel (DSS) piping are reported. This study evaluated the performance of either triplicate welded ANSI/NACE TM0177-2016 Method A tensile specimens or triplicate welded NACE TM0316-2016-compliant four-point-bend-beam (FPBB) specimens per heat exposed to a sour environment at 90 °C. All environmentally assisted cracking (EAC) specimens were stressed to an equivalent of 90% of their respective 0.2%-offset yield strengths at 90 °C to assess SCC susceptibility. In addition, duplicate welded corrosion coupons were machined per heat for determination of pitting susceptibility and weight loss corrosion rates. All EAC specimens and corrosion coupons were machined in the longitudinal direction with the weld metal transecting the specimens at mid-length so that each specimen contained a portion of parent metal, the heat-affected zone (HAZ) and weld metal.

Tensile specimens were installed in proprietary Window-Box Sustained-Load (WBSL) fixtures and loaded to 90% of the actual uniaxial 0.2% offset yield strength at 90°C ($AYS_{90^{\circ}C}$), of the heat-specific parent material per ANSI/NACE MR0175/ISO 15156-3:2015. Alternately, FPBB specimens were assembled in four-point bending fixtures and deflected at room temperature to the strain corresponding to 90% $AYS_{90^{\circ}C}$ of the heat-specific parent material. The stressed EAC specimens and corrosion coupons were exposed to a simulated sour service environment containing up to 0.18 bar H_2S and 33,000 mg/L Cl^- at 90 °C for 720 hours. All EAC specimens passed and weight-loss corrosion rates were ≤ 0.036 mpy.

In addition, Annex A.7.3, ANSI/NACE MR0175/ISO 15156-3:2015 specifies hardness requirements. Hardness surveys of a girth-weld sample per heat were performed using Vickers hardness tester in accordance with this Standard for butt welds. Hardness survey of each heat demonstrated that hardness of base metal, HAZs and weld did not exceed the maximum hardness specified in the Standard.

Keywords: *Sour Service Qualification, Environmentally Assisted Cracking, EAC, Duplex Stainless Steel, DSS, Girth-weld, Tensile, four-point-bend-beam, FPBB, ANSI/NACE MR0175/ISO 15156-3*

INTRODUCTION

Applications of UNS S31803 (22Cr duplex stainless steel [DSS]) for sour service are limited by its susceptibility to stress corrosion cracking (SCC) at high temperature and sulfide stress cracking (SSC) at low temperature along with pitting corrosion caused by factors such as pH_2S , chloride, temperature and pH. In compliance with ANSI/NACE MR0175/ISO 15156-3:2015 (herein referred to as the Standard), the sour service limit for UNS S31803 22Cr DSS is 0.1 bar pH_2S and 232 °C for any combination of chloride and pH [1]. While several studies [2 - 6] have been performed to extend the safe use sour service limit of UNS S31803 of the parent material beyond the threshold defined by the Standard, there is scarce testing data regarding applications of welded 22Cr DSS for sour service.

Both the Standard and the European Federation of Corrosion (EFC) Publications Number 17 [7] allow testing piping girth welds, using four-point bend beam (FPBB) and smooth tensile specimens. Per B.3.4 of the Standard, testing a material at 90% of actual yield strength (AYS) for a tensile specimen or at 100% AYS for a FPBB to qualify welding procedure for sour service is recommended. A lower stress threshold can be applied if agreed by all parties for specific applications.

To qualify the girth welds of small-diameter DSS tubing for sour service, according to the Standard, Annex B, laboratory qualification of given DSS for a particular set of service conditions requires that triplicate specimens of three heats of the same alloy must be tested for susceptibility to:

- **SCC**, a high-temperature anodically-controlled phenomenon in which cracking under stress results from an active path dissolution mechanism, at the maximum anticipated service temperature.
- **SCC at 90°C** (intermediate temperature), and
- **SSC**, a low-temperature cathodically-controlled phenomenon in which cracking under stress occurs due to the introduction of corrosion-product atomic hydrogen into the metal lattice due to the presence of hydrogen sulfide, at the lowest anticipated service temperature.

This testing program for qualification of girth welded DSS (UNS S31803) was undertaken to determine its suitability as an External Turret material for a mooring system. Given the relatively high pH_2S , high chloride and high CO_2 content very likely to be encountered in the service life of the External Turret, along with operating at the temperature of 90°C, it was deemed critical to confirm the resistance to SCC of the girth welded alloy. A lack of literature data to support the use of welded UNS S31803 grade compelled undertaking this study. Qualification testing was performed per ANSI/NACE TM0177-2016 Method A and NACE TM0316-2016 standards to determine susceptibility of UNS S31803 welds to SSC/SCC for the given operating conditions listed elsewhere in this paper. As part of the sour qualification program, evaluation of SCC susceptibility of twenty-four heats of girth-welded 22Cr DSS piping in a specific sour environment containing up to 0.18 bara pH_2S and 33,000 mg/L Cl^- , shown in Table 1, was performed. Figure 1 shows a flow chart describing the qualification program. This paper will present the qualification procedure and results for welded 22Cr DSS piping, and discuss the opportunities for welded 22Cr DSS applications.

EXPERIMENTAL

Materials and Welding

Table 2 shows a total of twenty-four (24) heats of girth-welded UNS S31803 22Cr DSS piping as source materials for testing in this study. Chemical composition of the 24 heats of parent 22Cr DSS piping are listed in Table 3.

Girth-welded pipes were prepared according to the welding procedure specification (WPS) by three third party welding service vendors as listed in Table 2. Welding was performed by gas tungsten arc welding (GTAW) with 99.999% Argon shielding gas and 98% Argon + 2% Nitrogen purging gas. 25.10.4.L (AWS ER2594) welding wire was used as consumable filler metal. The filler material contains max. 0.02% C, 0.3 % Si, 0.4% Mn, max. 0.020% P, max. 0.015% S, 25% Cr, 9.5% Ni, 4% Mo and 0.24% N.

Specimens Machining

A 6-inch long ring-shaped girth-welded pipe segment, with the weld in the center from each girth-welded pipe, was cut off for machining EAC specimens and corrosion coupons. All EAC specimens and corrosion coupons were machined with their length axes along the longitudinal direction of the pipe with the girth weld metal at mid-span of the specimen.

Piping wall thickness ≥ 0.375 -inch:

Four NACE TM0177-compliant tensile specimens were machined from each heat of ring with adequate wall thickness (0.375-inch minimum): Three for exposure and one extra tensile specimen. All welded tensile specimens were machined per Figure 2, with the girth weld metal centered in the narrow gage section of the specimens.

Piping wall thickness < 0.375 -inch:

Five NACE TM0316-2016 FPBB specimens with dimensions 3" long x 0.18" wide x 0.06" thick were machined from each heat of girth-welded rings too thin (< 0.375 -inch) for machining NACE TM0177 Method A tensile specimens: Three for exposure, one for strain-deflection calibration and one spare. All welded FPBB specimens were machined per Figure 3, with the girth weld metal centered in the middle of the FPBB specimen.

In addition, two corrosion coupons per each heat were machined.

Mechanical Properties Testing

An 8-inch length strip from the pipe parent metal on each heat of girth-welded pipe was cut for triplicate determinations of the actual uniaxial 0.2% offset yield strength (AYS) at room temperature (AYS_{RT}) and at the test temperature 90 °C (AYS_{90°C}), as well as the μ -strain at 90% AYS_{90°C} for FPBB specimens testing.

The mechanical properties were determined per ASTM E8/E8M-16a at room temperature and ASTM E21-17 at the elevated temperature 90 °C. Table 4 summarizes the mechanical properties testing results of these 24 heats of 22Cr DSS parent materials. Table 4 lists the average AYS values of each heat of 22Cr DSS at room temperature AYS_{RT} and at 90 °C AYS_{90°C}. 90% of AYS_{90°C} values were used for stressing tensile specimens. In addition, Table 4 also lists the average μ -strain at 90% of AYS_{90°C} of each heat of 22Cr DSS piping used for machining FPBB specimens.

Hardness Testing

A 6-inch long by 0.5-inch wide weld hardness test strip from each of these 24 girth-welded pipes was cut, with the girth-weld in the center of each strip. These hardness test specimens contained the weld metal plus at least 3 inches of parent metal to either side of the weld bead metal.

Hardness surveys (shown in Figure 4) were performed in accordance with ANSI/NACE MR0175/ISO 15156-2:2015 for butt welds, in a third-party laboratory using Vickers 10 HV hardness tester. A longitudinal metallographic mount of each strip sample was prepared in the third-party laboratory. After polishing, each mount was etched, revealing the weld metal, heat affected zones (HAZs), and the parent metal to either side of the weld. Per ANSI/NACE MR0175/ISO 15156-2:2015, 19 micro-hardness measurements were taken by Vickers 10 HV tester on each metallographic mount at the locations shown in Figure 4.

Per Annex A.7.3 of the Standard, the hardness of the HAZ after welding shall not exceed the maximum hardness allowed for the base metal and the hardness of the weld metal shall not exceed the maximum hardness limit of the respective alloy used for the welding consumable. Applications of DSS requiring compliance with Table A.24 (Environmental and materials limits for duplex stainless steels used for any equipment or component) and Table A.25 (Environmental and materials limits for duplex stainless steels used as downhole tubular components and as packers and other subsurface equipment) from the Standard. Table A.24 is silent on hardness requirement for DSS and Table A.25 requires a maximum hardness of 36 HRC (342 Vickers HV).

ANSI/NACE TM0177-2016 Method A Tensile Specimens Preparation

“Window-Box” sustained load apparatus and methodology [8], a derivative of the spring-loaded rigid frame described in ANSI/NACE TM0177-2016 [9] Method A tensile specimens, was adopted in this work for testing tensile specimens.

After visual inspection to verify that the gage sections were free of visible flaws, triplicate measurements of the tensile gage diameter were made to the nearest 0.0001 inch using a calibrated caliper, and the loads required to impart a stress of 90% of $AYS_{90^{\circ}\text{C}}$ were calculated as shown in Table 5. The tensile specimens were then cleaned with toluene and rinsed with acetone to remove any oil or grease residues, and stressed to respective 90% $AYS_{90^{\circ}\text{C}}$. The loading procedures followed the requirements described in the Standard Section 3, Appendix B using in-house Window-Box Sustained Load (WBSL) Fixtures [8].

Triplicate welded tensile specimens per each of the nine (9) heats, were installed in a proprietary WBSL Fixtures as shown in Figure 5. These fixtures were inserted one by one into a loading frame, shown in Figure 6, on an MTS Tensile Test Machine. Downward load was applied to each tensile specimen until the applied stress equaled 90% of $AYS_{90^{\circ}\text{C}}$ and the bottom nut was tightened against the W-B frame, locking in and sustaining the applied stress.

NACE TM0316-2016 Four-Point Bent-Beam Specimens Preparation

In compliance with the Standard, qualification at a lower applied stress is acceptable if agreed to by all parties for specific applications. As agreed to by all parties, a stress level of 90% of respective parent metal's $AYS_{90^{\circ}\text{C}}$ was applied to all FPBB specimens for testing in this work. The FPBB EAC testing was performed following NACE TM0316-2016 [10]. Prior to exposure, a FPBB calibration specimen of each heat was used for strain-deflection calibration to determine the required deflection at room temperature to attain the required strain corresponding to 90% $AYS_{90^{\circ}\text{C}}$ at test temperature, as shown in the last column in Table 4.

Two strain gauges were glued to the base metal on either side of the weld on each FPBB specimen used for calibration, and then these FPBB specimens were assembled into fixtures. The metallic components of the stressing fixtures are made of alloy C-276 coated with a fusion-bonded fluoropolymer. The two points of contact between the upper surface of the beam and the fixture were electrically insulated with ceramic sleeves over C-276 bolts, while the two points of contact on the underside of the beam were electrically insulated with borosilicate glass beads. A thermally resistant epoxy was used as an adhesive.

The strain gauge leads were connected to a four-channel micro-strain meter. Each fixture was then tightened incrementally at room temperature to the target μ -strain equivalent to 90% of $AYS_{90^{\circ}\text{C}}$ based on mechanical testing. Table 4 summarizes the 90% AYS at both room temperature, 90 °C, and the equivalent μ -strain per heat. The deflection obtained once either side base metal adjacent to the weld first reached target strain is recorded in the second column in Table 6. The resulting room-temperature strain-deflection plot was curve-fitted to obtain the strain-deflection correlation equation of that heat.

Subsequently, each FPBB specimen stressed to its respective 90% $AYS_{90^{\circ}\text{C}}$ was placed in a nitrogen-purged oven and heat-soaked overnight at 90 ± 3 °C to monitor any strain relaxation arising from differential thermal expansions in the specimens and their corresponding stressing hardware. The FPBB

specimen installed in the fixture was still connected to the micro-strain meter to monitor the change in strain during thermal aging, $\Delta \text{Strain}_{90\text{-RT}}(\%)$, as shown in the third column in Table 6. The change in strain during thermal aging was added to the original target strain to obtain the adjusted target strain of each heat. The adjusted target strains were then inserted into the strain-deflection correlation equation to obtain the needed deflections at room temperature of each heat. Hence, the room temperature deflection to be applied was adjusted to compensate for this relaxation for each heat. The final room temperature deflections required for stressing the FPBB specimens of each heat to 90% of their $\text{AYS}_{90^\circ\text{C}}$ were thus obtained, as shown in the last column in Table 6. Even though not required by the Standard, cold creep of strained FPBB specimens 30 days after straining was studied and found to be negligible ($< 1\%$).

Corrosion Coupons Preparation

Duplicate (2) corrosion coupons per each heat were used for evaluation of weight-loss corrosion rate and pitting corrosion. The corrosion coupons were nominally 1-inch wide by 2.00-inch long by 0.125-inch thick with a single 0.28-inch diameter mounting hole near one end of each coupon. The faces of the coupons were wet-round with 120-grit SiC paper in compliance with ASTM G1 [11].

Sour Exposure Tests in Batch-Loaded Autoclaves

Three exposure tests were performed in this work, as shown in Table 1. For each test, the cavity of the autoclave was lined with thin Teflon sheet, and the tensile specimens stressed at 90% $\text{AYS}_{90^\circ\text{C}}$, FPBB specimens installed in the fixtures and stressed at 90% $\text{AYS}_{90^\circ\text{C}}$ or corrosion coupons were then inserted into the autoclave.

The autoclave was sealed and leak-tested with ultra-high purity (UHP) nitrogen, then the pressure was vented from the dry autoclave which was triple-flushed with UHP nitrogen. The deaerated solution prepared from reagent-grade chemicals and distilled water, in accordance with the composition shown in Table 1, was transferred into the autoclave under a continuously replenished UHP nitrogen blanket to prevent contamination by contact with air. During the solution transfer, dissolved oxygen (DO) in the solution was monitored by connecting a HACH Model 3100 Orbisphere meter between the solution flask and the autoclave.

After solution transfer was complete, the solution in the autoclave was purged *in-situ* overnight with UHP nitrogen, saturating the solution and flushing the headspace with the UHP nitrogen. The autoclave was then shut in and heated to target test temperature $90^\circ\text{C} \pm 3^\circ\text{C}$. The ionic-equation of state (EOS) framework, OLI 9.6.2 MSE-SRK software module, was used for simulating acid gases loading to reach the specified partial pressures in the headspace gas at equilibrium. Accordingly, upon stabilization of the temperature at $90^\circ\text{C} \pm 3^\circ\text{C}$, the autoclave was pressurized with $\text{H}_2\text{S}/\text{N}_2$ certified mixed gas (CMG), and then with Research Purity 99.999% CO_2 gas. Finally, the autoclave was pressurized up with UHP nitrogen gas.

A gas sample was collected from the autoclave headspace 24-hr after the test started, once every week, and at the end of the 720-hr exposure. H_2S and CO_2 concentrations in the gas sample were measured using glass detector tube. Solution sample was taken for pH measurement as well after 24-hr, midpoint and at the end of exposure. During the test, the acid gases H_2S and CO_2 were periodically replenished to maintain stable targeted acid gases partial pressures throughout each test of 720 ± 12 hours.

Temperature and pressure was continuously recorded and monitored both during the heat-up process and throughout the 720 ± 12 hours' test exposure. Timing of the test exposures started upon stabilization of the targeted temperature and pressure. Upon test completion, heater was shut down and then the solution from autoclave was expelled to a spent solution drum when temperature cooled to 60°C . The autoclave was backfilled with clean tap water which was also expelled to the spent solution drum using UHP nitrogen. The autoclave was then opened and the specimens were retrieved for post-test analysis.